

PATENT SPECIFICATION

Application Date : March 21, 1935. No. 8918 / 35.

458,664

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 photographic 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.

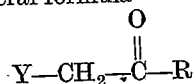
When a silver halide emulsion containing a latent photographic image is developed, the silver halide is reduced to metallic silver and the developing agent is oxidised. The aromatic diamino compounds which have been used as developers form, on oxidation, products which will react with coupling compounds 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

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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 washed 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, nitrophenylacetone nitriles and acetoacetic esters. Benzoyl acetone in conjunction with diethyl-*p*-phenylene diamine hydrochloride is suggested in our patent application No. 26084/33 (Serial Number 427,472).

According to the present invention the substances employed as colour couplers have the general formula



where

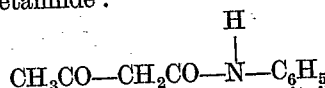
Y = an aceto or cyano group and

R = an aryl-substituted amino group.

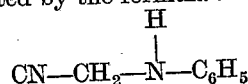
The group represented by Y is such that the methylene group to which it is attached is reactive in the dye-forming reaction.

The compounds employed include acetoacetanilide and substituted acetoacetanilides, such as the halogen and alkyl-substituted compounds. Among these are para-bromo-aceto-acetanilide, dichloro-acetoacetanilide, and 4-nitro-acetoacetanilide.

When Y = aceto and R = aryl-substituted amino, a typical compound is acetoacetanilide :



A compound in which Y is a nitrile group is represented by the formula :



The aromatic amino compounds which may be used as developers in the present invention include the mono-, di-, and tri-amino aryl compounds formed therefrom by substitution in the amino group as well as in the ring, such as alkyl phenylene diamines and alkyl toluylene diamines. These compounds are usually used in the salt form, such as the hydrochloride or the sulphate which are more stable than the amines themselves. Examples are diethylparaphenylene diamine hydrochloride, monomethylparaphenylene diamine hydrochloride, and dimethylparaphenylene diamine sulphate.

The following are examples of developer solutions which may be used according to the present invention.

EXAMPLE I.

20	A. Diethyl <i>p</i> . phenylenedi- amine HCl	-	-	2 g.
	Sodium Sulphite	-	-	5 g.
	Sodium carbonate	-	-	30 g.
	Water to	-	-	1000 ccs.
25	B. <i>p</i> -bromo acetoacetanilide	-	-	2 g.
	Acetone	-	-	100 cc.

Add B to A.

EXAMPLE II.

A. Dimethyl <i>p</i> - phenylenedi- amine sulphate	-	-	1 g.	30
Sodium Sulphite	-	-	2 g.	
Sodium carbonate	-	-	30 g.	
Water to	-	-	1000 cc.	
B. 4-nitro acetoacetanilide	-	-	2.5 g.	
Iso-propyl alcohol	-	-	100 cc.	35

Add B to A.

The present invention may be utilised in the formation of coloured photographic images in films as well as in plates, and the dyes formed will attach to gelatin or other carriers for the silver halide, such as collodion. The emulsion treated may be on one side or on both sides of a film support and may be in one layer or a plurality of differently sensitised layers. The dyes formed may be decolourised 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 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 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.

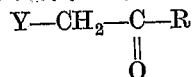
The invention also includes a photographic element having at least one layer containing a clear transparent image composed essentially of the product resulting from the coupling in situ, during development of a developable silver salt, of a colour coupler as hereinafter defined with the oxidation product 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, 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. 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 organic compounds with a reactive methylene group, having the general formula



where

Y = one of the electro-negative groups CN— or X.CO— (where X is an alkyl or aryl group, substituted or unsubstituted).

R = an aryl- or heterocyclo-substituted amino group.

Such compounds may be termed cyanacetyl and aceto-acetyl derivatives of aryl or heterocyclo amines.

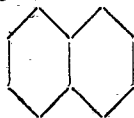
Examples of such colour couplers are the following:—

1. $\text{CN}.\text{CH}_2.\text{CO}.\text{NH}$



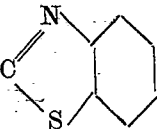
Cyanacetanilide

2. $\text{CN}.\text{CH}_2.\text{CO}.\text{NH}$



Cyanaceto - β - naphthalide

3. $\text{CN}.\text{CH}_2.\text{CO}.\text{NH} : \text{C}$



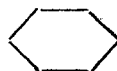
1-Cyanacetaminobenzothiazole.

4. $\text{CH}_3.\text{CO}.\text{CH}_2.\text{CO}.\text{NH}$

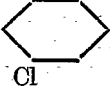
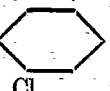

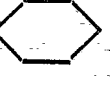
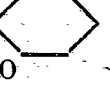
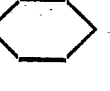
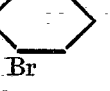
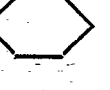
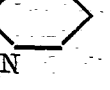
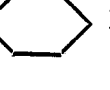
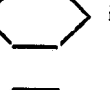
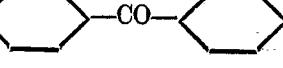




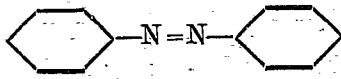
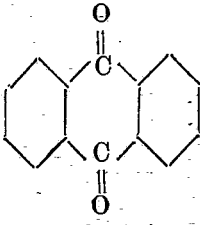
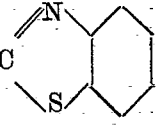
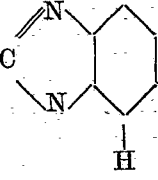
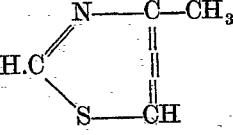
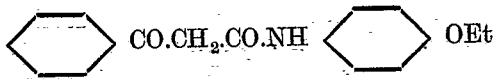
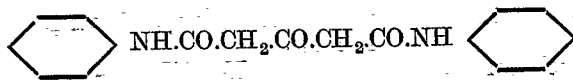
Acetoacetanilide.

5. $\text{CH}_3.\text{CO}.\text{CH}_2.\text{CO}.\text{NH}$



Acetoacet-*p*-bromanilide
(*p*-bromoacetoacetanilide)

	6.	$\text{CH}_3\text{CO.CH}_2\text{CO.NH}$		Cl	Acetoacet-2 : 4-dichloro-anilide.
	7.	$\text{CH}_3\text{CO.CH}_2\text{CO.NH}$		Cl	Acetoacet-2 : 5-dichloro-anilide.
	8.	$\text{CH}_3\text{CO.CH}_2\text{CO.NH}$		NO_2	Acetoacet- <i>m</i> -nitro-anilide
	9.	$\text{CH}_3\text{CO.CH}_2\text{CO.NH}$		NO_2	Acetoacet- <i>p</i> -nitro-anilide (4-nitroacetoacet-anilide)
5	10.	$\text{CH}_3\text{CO.CH}_2\text{CO.NH}$		MeO	<i>o</i> -methoxyacetoacet-anilide (acetoacet- <i>o</i> -anisidine)
	11.	$\text{CH}_3\text{CO.CH}_2\text{CO.NH}$		OMe	Acetoacet- <i>p</i> -anisidine
	12.	$\text{CH}_3\text{CO.CH}_2\text{CO.NH}$		OEt Br	Acetoacet-2-bromo- <i>p</i> -phenetidide
	13.	$\text{CH}_3\text{CO.CH}_2\text{CO.NH}$		NH_2	Acetoacet- <i>p</i> -amino-anilide.
	14.	$\text{CH}_3\text{CO.CH}_2\text{CO.NH}$		$(\text{Me})_2\text{N}$	Acetoacet- <i>o</i> -dimethyl-aminoanilide
10	15.	$\text{CH}_3\text{CO.CH}_2\text{CO.NH}$		$\text{N}(\text{Me})_2$	Acetoacet- <i>p</i> -dimethyl-aminoanilide
	16.	$\text{CH}_3\text{CO.CH}_2\text{CO.NH}$		SO_3Na	Sodium acetoacet-anilide- <i>p</i> -sulphonate
	17.	$\text{CH}_3\text{CO.CH}_2\text{CO.NH}$		CO	<i>p</i> -benzoylacetoacet-anilide
	18.	$\text{CH}_3\text{CO.CH}_2\text{CO.NH}$			Acetoacetyl- β -naphthylamine (Acetoacet- β -naphthalide)
	19.	$\text{CH}_3\text{CO.CH}_2\text{CO.NH}$		SO_3Na	Sodium acetoacet-2-naphthalide-7-sulphonate

20. $\text{CH}_3\text{CO.CH}_2\text{CO.NH}$  *p*-phenylazoacetoacetanilide
21. $\text{CH}_3\text{CO.CH}_2\text{CO.NH}$  2-acetoacetaminoanthraquinone.
22. $\text{CH}_3\text{CO.CH}_2\text{CO.NH.C}$  1-acetoacetaminobenzothiazole.
23. $\text{CH}_3\text{CO.CH}_2\text{CO.NH.C}$  1-acetoacetaminobenzimidazole.
24. $\text{CH}_3\text{CO.CH}_2\text{CO.NH.C}$  2-acetoacetamino-4-methylthiazole
25.  *N*-Benzoylacetyl-*p*-phenetidine
26.  Acetone di-(carboxanilide)

The above colour couplers, when used in conjunction with *p*-aminodiethyl-aniline, for example, as the developing agent, give the following colours :—

10	Nos. 1, 2 and 3	— — — — —	Orange-red to magenta
	Nos. 4 to 22 inclusive, 24 and 25	— — — — —	Yellow
	No. 23	— — — — —	Green
	No. 26	— — — — —	Purple

15 The colours vary as between one compound and another and offer a useful choice of shades for two and three colour photography. Nos. 1 and 2 are particularly suitable for a two colour process. in general, the colour is minus blue-violet to minus blue where Y is aceto, but in the minus green class where Y is cyano. As the molecular weight increases the absorption shifts towards the longer wave region. This shift is greater when R is a hetero-cyclo-substituted amino group.

25 The compounds mentioned above, by way of example, do not all give colours equal quality or value and in general it is advisable to make preliminary tests

before selecting a compound for any particular process. For example, it may be mentioned that Nos. 13, 19, 20, 21, 23 and 26 are, in general, inferior to the other compounds mentioned. Nos. 4 to 12 give a very good minus blue for a three colour process as does No. 22 although the latter is rather more orange.

The colours mentioned above are all given with *p*-amino diethyl-aniline as the developing agent.

40 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 men-

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tioned the aminophenols, aminocresols and their halogen substituted derivatives, as well as the aminonaphthols. The developing agents usually used are the diamino compounds such as paraphenylenediamine 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 alkylphenylenediamines, toluenylenediamines, 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-methylpara-phenylenediamine, 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.

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

FORMULA I.	
A. Diethyl <i>p</i> -phenylenediamine hydrochloride -	2 g.
Sodium Sulphite - - -	5 g.
Sodium carbonate - - -	30 g.
Water to - - - - -	1000 cc.
B. <i>p</i> -bromo acetoacetanilide	2 g.
Acetone - - - - -	100 cc.

For use, add solution B to solution A.

FORMULA II.	
A. Dimethyl <i>p</i> -phenylenediamine sulphate - - -	1 g.
Sodium Sulphite - - -	2 g.
Sodium carbonate - - -	30 g.
Water to - - - - -	1000 cc.
B. 4-nitro acetoacetanilide -	2.5 g.
Iso-propyl alcohol - - -	100 cc.

For use, add solution B to solution A.

Other solvents for the colour coupler, particularly alcohols, may be used in bath B.

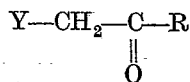
The present invention may be utilised in the formation of coloured photographic images on plates or papers as well as on films and the dyes will be formed when gelatine or other carrier for the silver halide is used. The emulsion treated may be in one layer or a plurality of differently

sensitized layers on one side or on both sides of the support. The dyes formed may be decolorized 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 colour couplers of the present invention possess advantages over many of the colour couplers heretofore known and used among which may be mentioned an increased insolubility in water of the dyes formed by coupling with the oxidation product of the aromatic amino developing agent and a decreased sensitivity of the couplers themselves towards sodium sulphite in the developer. A tolerance of the coupler towards larger amounts of sodium sulphite than have heretofore been practicable in colour-forming developers is of particular importance since the presence of sodium sulphite in the developer is required to give stability upon exposure to air.

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 an organic compound with a reactive methylene group, having the general formula



where

Y = one of the electro-negative groups CN-- or X.CO-- (where X is an alkyl or aryl group, substituted or unsubstituted)

R = an aryl- or heterocyclo-substituted amino group.

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 colour forming developer as claimed in any of the preceding claims in which R is a phenylamino group with or without substituents in the phenyl ring.

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.

5 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 colour coupler as defined in Claim 1 with the oxidation product of an aromatic amino developing agent.

10 7. A sensitive photographic element having a silver halide emulsion layer in

which is incorporated a colour coupler as defined in claim 1 or claim 4. 15

8. The colour forming developers and methods of colour development employing cyanoacetyl or acyloacetyl derivatives of aryl or heterocycloamines as colour couplers in conjunction with aromatic amino developing agents, substantially as herein described. 20

Dated this 21st day of March, 1936.

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