

## PATENT SPECIFICATION



Application Date: April 23, 1936. No. 14350/37.

478,989

(Divided out of No. 478,942.)

Complete Specification Left: May 24, 1937.

Complete Specification Accepted: Jan. 24, 1938.

### PROVISIONAL SPECIFICATION

#### 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, nitrophenylacetone nitriles 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

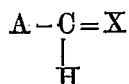
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the processing. Many of the colour couplers employed according to the present invention are suitable in carrying out the processing described in our prior patents Nos. 427,472, 427,516, 427,518, 427,520, 440,032, 440,089, and Application No. 16012/35.

According to the present invention the substances employed as colour couplers are compounds of the general formula



where A = a benzene nucleus containing at least one hydroxyl group, with or without other substituents  
 X = a divalent group or a closed ring

Examples of such colour couplers are:—

*o*-styrylphenol  
 disalicylalicyclohexanone  
 1-(*o*-hydroxystyryl)-benzthiazole  
 2-(*o*-hydroxystyryl)-pyridine  
 2-(*o*-hydroxystyryl)-thiazoline  
 3-phenyl-5-(*o*-hydroxybenzol)-2:4-thiazolidione.

The colours given by the colour couplers named above when used in conjunction with *p*-aminodiethylaniline, for example, as developing agent are shades of green.

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 monamino compounds may be mentioned the aminophenols and aminocresols

and their halogen substituted derivations as well as the aminonaphthols. 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 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 orthoamino-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.

## COMPLETE SPECIFICATION

### 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, 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 developing agent.

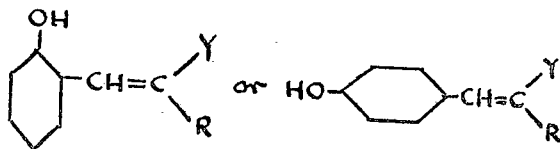
When a silver halide emulsion containing a latent photographic image is developed, the silver halide is reduced to metallic silver and the developing agent is oxidized. The aromatic diamino compounds which have been used as developing agents form, on oxidation, products which will couple with colour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

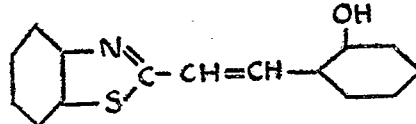
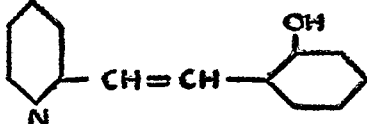
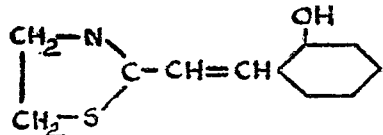
Many of the colour couplers employed according to the present invention are suitable in carrying out the processing described in our prior patents Nos. 427,472, 427,516, 427,518, 427,520, 440,032, 440,089 and 447,092.

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

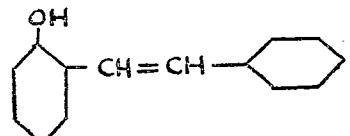


in which Y is hydrogen atom and R is a heterocyclic ring or a carbocyclic ring or Y and R together form a heterocyclic ring or a carbocyclic ring.

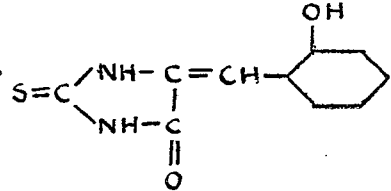
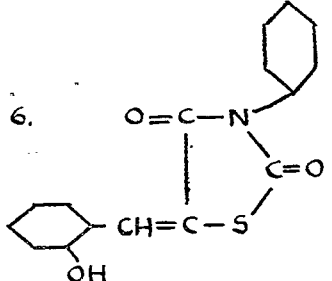
Examples of such compounds in which Y is a hydrogen atom and R is a heterocyclic ring are:—

1.  1-(*o*-Hydroxystyryl)  
benzthiazole
2.  2-(*o*-Hydroxystyryl)  
pyridine
3.  2-(*o*-Hydroxystyryl)  
thiazoline

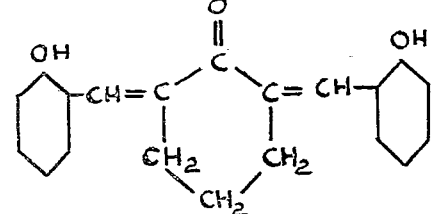
An example of a compound in which Y is a hydrogen atom and R is an aromatic nucleus is:—

4.  *o*-Styrylphenol

In the following compounds Y and R together represent a heterocyclic ring:—

5.  5-(*o*-Hydroxybenzal)-  
2-thiohydantoin
6.  3-Phenyl-5-  
(*o*-hydroxybenzal)-  
2:4-thiazolidione

In the following compound Y and R together represent an aromatic ring:—

7.  -(*o*-hydroxybenzal)-  
Dicyclohexanone

These compounds may be substituted in the aromatic ring with groups including halogen, nitro, amino, substituted amino, alkyl, aryl, and carboxyl groups. These groups may be substituted in the ring at any position except in most cases the position para with respect to the hydroxyl group. In certain cases, however, the substituted groups may occur both ortho and para to the hydroxyl group and in this case the coupling with the developer will occur in the position ortho with respect to the hydroxyl group.

Di-(*o*-hydroxybenzal) cyclohexanone was prepared in a manner similar to that described by Decker and Felser, Ber. 41, 3001, for the preparation of disalicylacetone. The product melted at 159°—161° C.

2-(*o*-hydroxystyryl) pyridine was synthesised by heating a mixture of equimolecular quantities of *a*-picoline and salicylaldehyde with a half molecular quantity of zinc chloride at 150°—155° C. for two and a half hours. The product was washed well with water followed by recrystallisation from alcohol, whereupon it melted at 158°—161° C.

2-(*o*-hydroxystyryl) thiazoline was prepared in a similar manner and melted at 139°—141° C.

1-(*o*-hydroxystyryl) benzthiazole was prepared in a similar manner and melted at 235°—236° C.

3-Phenyl-2:4-thiazolidione was prepared in accordance with the directions given in J.A.C.S. 52, 2137, (1930) and melted at 131°—132° C.

The method for preparing 3-phenyl-5-(*o*-hydroxybenzal)-2:4-thiazolidione was by heating equimolecular amounts of salicylaldehyde with the 3-phenyl-2:4-thiazolidione at 135°—150° C. for three hours in the presence of zinc chloride. The purified product melted at 175°—177° C.

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 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.

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		
Diethyl para phenylene-		
diamine hydrochloride	- - -	1 gram
Sodium sulphite	- - -	0.5 gram
Sodium carbonate	- - -	20 grams
Water to	- - -	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 named above on coupling with the oxidization product of the developer in general range from blue to green. The colours given by the specific couplers referred to above when used in the above example, as indicated by visual tests, are as follows:—

Blue-green	-	1-( <i>o</i> -Hydroxystyryl)-benzthiazole	
Blue-green	-	2-( <i>o</i> -Hydroxystyryl)pyridine	
Blue-green	-	2-( <i>o</i> -Hydroxystyryl)thiazoline	110
Dark green	-	<i>o</i> -Styrylphenol	
Yellow green	-	5-( <i>o</i> -Hydroxybenzal)-2-thiohydantoin	
Light green	-	3-Phenyl-5-( <i>o</i> -hydroxybenzal) - 2:4 - thiazolidione	115
Green	-	Di - ( <i>o</i> - hydroxybenzal)-cyclo-hexanone.	

The colour of dyes formed from couplers having substituent groups in the ring may vary according to the type of substituent group employed.

Although we have described our inven-

tion 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 development. It may be absorbed upon the sensitive silver halide grains.

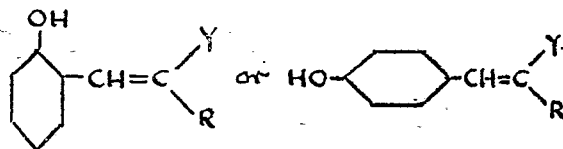
The present invention may be utilised in the formation of coloured photographic images on plates or papers as well as on films employing gelatine or other carrier for the silver halide. The plates, films or papers may have differently sensitized emulsions of the mixed grain type or superimposed on one 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.

The accompanying drawing shows the absorption characteristics of the dye formed when di-(*o*-hydroxybenzal)-cyclohexanone is used as the coupler. This drawing is a graph in which the density of the coloured image is represented on the ordinate and wave lengths on the abscissa.

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 having the formula,



in which Y is a hydrogen atom and R is a heterocyclic ring or a carbocyclic ring or Y and R together form a heterocyclic ring or a carbocyclic ring.

2. A colour forming developer as claimed in claim 1 in which R or R and Y are constituted by a ring of the thiazolo type.

3. A colour forming developer as claimed in claim 1 or 2 in which the developing agent is an aromatic diamino compound.

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

5. 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.

6. 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 4.

7. 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 or 2 with the oxidation product of an aromatic amino developing agent and subsequent removal of metallic silver.

8. A sensitive photographic element having a colour coupler as defined in claim 1 or 2 incorporated in one or more emulsion layers.

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

10. 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 21st day of May, 1937.

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

[This Drawing is a reproduction of the Original on a reduced scale.]

