

ALIEN PROPERTY CUSTODIAN

COLOUR COUPLERS FOR PHOTOGRAPHIC COLOUR DEVELOPMENT

Honore Verkinderen, Mortsel, and Norbert Vankiersbillek, Leuven, Belgium; vested in the Alien Property Custodian

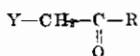
No Drawing. Application filed April 18, 1941

This invention relates to photographic color development and to processes of color development for use in connection with color photography.

It is known that color photographic images may be formed by using a developer which forms a colored and insoluble oxidation product during development, the colored product thus formed coloring the gelatine adjacent to the silver grains of the silver image. It is also known that a colored 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 coloring substance which is deposited adjacent to the developed silver grains.

Fischer in United States Specification No. 1,102,028 described the production of colored photographic images by means of coupler compounds of the above-mentioned kind.

Further, in U. S. Patent No. 2,108,662 is described a process of color development by means of compounds of the general formula:

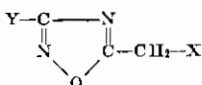


where:

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

It is an object of the present invention to provide a new class of color couplers which produce color images having higher color density and better transparency than the hitherto known compounds. The color couplers of the new class present the following further advantages over the hitherto known color couplers: they can be used in developing solutions containing a fair amount of sulphite; they resist the action of bisulphite and acetic acid; they produce colored images, which have sharp absorption curves.

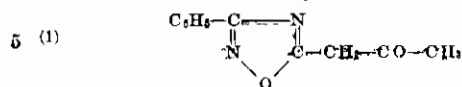
The new class of color couplers according to the invention are compounds having the general formula:



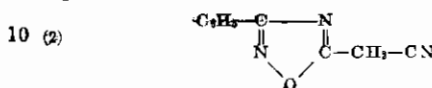
wherein X is an electro-negative organic radical such as acyl-, cyano-etc., and Y is an organic rad-

ical such as hydrogen, alkyl or aryl, the last two may be substituted or unsubstituted.

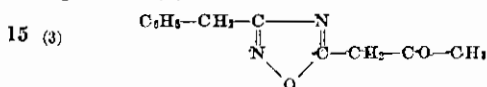
Examples of such couplers are:



3 phenyl-5 acetyl-1,2,4-oxadiazole.



3 phenyl-1,2,4-oxadiazolyl (5) acetonitrile.



3 benzyl-5 acetyl-1,2,4-oxadiazole.

20 These color couplers, on coupling with the oxidation product of an aromatic-amino-developer during the development of the latent image, form a yellow color when belonging to the class as illustrated by Example 1, and an orange color when belonging to the class as illustrated by Example 2.

25 These compounds are prepared by the method described in "Berichte der Deutschen Chemischen Gesellschaft" 22 (1889), page 2414. The compound of Example 2 is prepared by reacting cuprous cyanide with 3-phenyl-5 chloroacetyl-1,2,4 oxadiazole which can be obtained by the process described in "Berichte" 18 (1885), page 1082.

The present invention consists, broadly, in the process of producing color photographic images by the use of color couplers as above defined.

35 Thus the invention comprises the process of forming color photographic images by the incorporation, in the photographic emulsion, before or after coating, of a color coupler as above defined and, further, the process of developing a latent photographic image by means of a color developer comprising in addition to an aromatic amino developing agent a color coupler as above defined.

40 Thus the invention includes the method of color development which comprises developing a latent photographic image by means of an aromatic amino developer in the presence of color couplers as above defined, and eliminating the silver image which is formed during development so that a clear and transparent color image remains.

The invention also consists in new or improved color forming developers comprising, in addition to an aromatic amino developing agent, color couplers as above defined.

The present invention further includes photographic elements having at least one layer containing a clear and transparent image composed essentially of the product resulting from the coupling in situ during development of color couplers as above defined, with the oxidation product of an aromatic amino developing agent.

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 mono-amino developing agents may be mentioned amino-phenols and amino-cresols and their halogen derivatives and amino-naphthols.

The developing agents preferably used and having hitherto given the best results in connection with the present invention are the aromatic ortho- and para- diamines, such as para-phenylenediamine and its substitution products. These developing agents may be substituted in one amino group or in the ring or in both, forming compounds such as:

NN' Diethyl-para-phenylenediamine.
Monoethyl - para - phenylenediamine, dimethyl-para-phenylenediamine, and
3-amino-6 dimethylamino-toluene.

These compounds are usually kept in the salt form such as hydrochloride or sulphate.

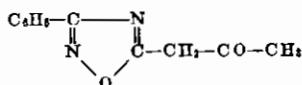
The following developer solutions may be used to give a color image according to the present invention:

FORMULA 1

A

NN' Diethyl-para-phenylenediamine	
HCl	g-- 2
Sodium sulphite (cryst.)	g-- 25
Sodium carbonate (cryst.)	g-- 60
Sodium hydroxide	g-- 2
Water	ccm-- 1000

B



	g-- 3
Methanol	ccm-- 100

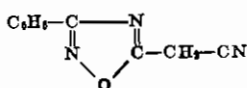
For use B is added to A.

FORMULA 2

A

3-amino-6 dimethylamino-toluene hydrochloride	g-- 4
Sodium sulphite (cryst.)	g-- 10
Potassium carbonate	g-- 50
Sodium hydroxide	g-- 3
Water	ccm-- 1000

B



	g-- 5
Methanol	ccm-- 100

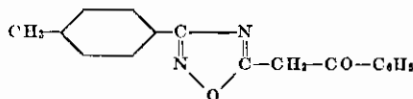
For use B is added to A.

FORMULA 3

A

N—N' diethyl-para-phenylenediamine	
HCl	g-- 2
Sodium sulphite (cryst.)	g-- 25
Sodium carbonate (cryst.)	g-- 60
Sodium hydroxide	g-- 2
Water	ccm-- 1000

B



	g-- 3
Methanol	ccm-- 100

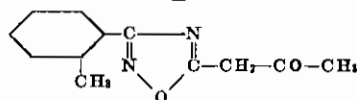
For use B is added to A.

FORMULA 4

A

N—N' diethyl-para-phenylenediamine	
HCl	g-- 2
Sodium sulphite (cryst.)	g-- 25
Sodium carbonate (cryst.)	g-- 60
Sodium hydroxide	g-- 2
Water	ccm-- 1000

B



	g-- 3
Methanol	ccm-- 100

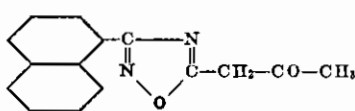
For use B is added to A.

FORMULA 5

A

N—N' diethyl-para-phenylenediamine HCl	
	g-- 2
Sodium sulphite (cryst.)	g-- 25
Sodium carbonate (cryst.)	g-- 60
Sodium hydroxide	g-- 2
Water	ccm-- 1000

B



	g-- 3
Methanol	ccm-- 100

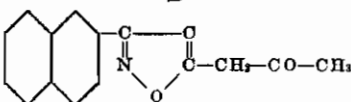
For use B is added to A.

FORMULA 6

A

N—N' diethyl-para-phenylenediamine HCl	
	g-- 2
Sodium sulphite (cryst.)	g-- 25
Sodium carbonate (cryst.)	g-- 60
Sodium hydroxide	g-- 2
Water	ccm-- 1000

B



	g-- 3
Methanol	ccm-- 100

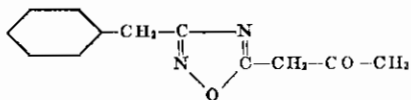
For use B is added to A.

FORMULA 7

A

N--N' diethyl-para-phenylenediamine HCl	g--	2
Sodium sulphite (cryst.)	g--	25
Sodium carbonate (cryst.)	g--	60
Sodium hydroxide	g--	2
Water	ccm--	1000

B



Methanol	g--	3
	ccm--	100

For use B is added to A.

Organic solvents, for instance acetone, alcohols or the like, may be used to dissolve the color couplers.

The invention is in no way limited to the use of the color couplers in the developing solution itself.

Thus as above stated, one of the essential products, the color coupler, which during the development forms the dye, can also be added to the photographic emulsion (for instance by adsorp-

tion upon the silver salts), before or after coating. The other ingredients of the color forming baths, containing chiefly the aromatic amino developer, may be applied later, during the developing process, as a bath.

The present invention may be utilised in the formation of colored photographic images on plates or papers as well as on films, employing gelatine or some other carrier substance for the silver halide.

The developing process may be used for developing photographic material, provided with one or more sensitive layers, which are applied on one side or on both sides of the support.

The silver formed during the developing process may be eliminated. For this purpose a bath should be used, however, which does not destroy the dye. Thus, a bath consisting of a solution in water of potassium ferricyanide and sodium thiosulphate easily eliminates the silver without destroying the dye, leaving a pure dye image.

We do not wish to be limited to the exact details of the invention as described in the foregoing specification as various modifications will occur to a person skilled in the art.

HONORE VERKINDEREN.
NORBERT VANKEIRSBILCK.