

UNITED STATES PATENT OFFICE

2,206,142

DIKETONE COUPLER COMPOUNDS

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No Drawing. Application March 11, 1939, Serial No. 261,304

15 Claims. (Cl. 95-6)

This invention relates to photographic color-forming compounds and more particularly to coupler compounds of the diketone type which react with the oxidation product of certain photographic developers to form a colored image in a photographic layer.

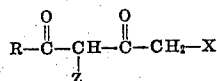
The formation of colored photographic images by using a primary aromatic amino developing agent which couples with a color-forming compound on development has been the subject of numerous prior patents. In Mannes and Godowsky U. S. Patent No. 2,113,330, April 5, 1938, color forming compounds of the diketone type are described such as acetyl acetone and benzoyl-acetone. These compounds coupled with the oxidation product of primary aromatic amino developing compounds such as p-phenylene diamine or its alkyl substitution products and salts such as di-ethyl-p-phenylenediamine-hydrochloride to form colored photographic images on development. The dyes thus formed are insoluble in water and are stable to ordinary photographic developing and fixing baths, although the silver images formed simultaneously with them may be removed from the photographic layer.

An objection to the coupler compounds of the type of Mannes and Godowsky Patent 2,113,330 is that they have some tendency to be decomposed by heat or light. The photographic images formed from them, therefore, tend to fade, and in a multilayer film the colored images lose their color balance and after a time appear weaker and incorrectly colored.

It is, therefore, an object of the present invention to provide a novel photographic developer which produces a stable colored image simultaneously with photographic development. A further object is to provide novel coupler compounds which form photographic images stable to heat and light. A still further object is to provide a method of photographic development resulting in the formation of dye images which are not readily decomposed by heat and light.

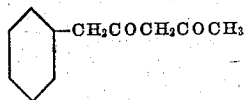
These objects are accomplished by the use of aromatic amino developing agents in conjunction with certain diketone coupling compounds hereinafter described.

The diketone couplers forming the subject of the present invention are those having the general formula:

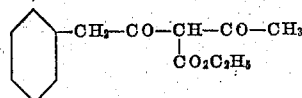


propyl or isopropyl or an aryl group such as a phenyl group; X is an aryl radical such as a phenyl radical, a benzyl group, an aralkyl group, or a phenoxyalkyl group such as phenoxyethyl; and Z is a hydrogen atom or a carbalkoxy radical such as an ethyl ester radical.

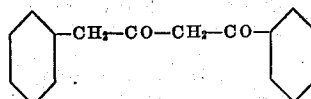
The following specific compounds falling in this group are suitable for use as couplers according to our invention:



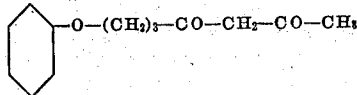
ω-Phenylacetylacetone



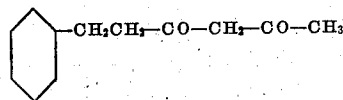
Ethyl α-acetyl-γ-phenyl acetoacetate



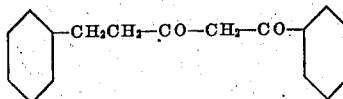
Phenacetylbenzoylmethane



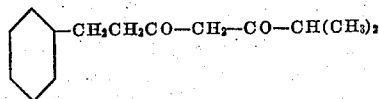
γ-Phenoxybutyrylacetone



6-phenylhexanedione-2,4



1,5-diphenylpentanedione-1,3



1-phenyl-6-methylheptane-dione-3,5

The following examples, which are illustrative

where R is an alkyl radical such as methyl, ethyl,

only, indicate typical developing solutions made according to our invention.

Example 1

5	A. Diethyl - p - phenylenediaminehydrochloride	grams	2
	Sodium sulfite	do	5
	Sodium carbonate	do	30
	Water to	cc	1000
10	B. 6-phenylhexanedione-2,4	grams	2
	acetone	cc	50
	Add B to A.		

Example 2

15	A. Dimethyl - p - phenylene diamine sulfate	gram	1
	Sodium sulfite	do	2
	Sodium carbonate	do	30
	Water to	cc	1000
20	B. Phenacetylbenzoylmethane	grams	2.5
	Isopropyl alcohol	cc	100
	Add B to A.		

In the foregoing examples, we have described adding the coupler compound to the developing solution itself. However, the coupler compound may be incorporated in the photographic layer prior to exposure and the colored image formed by development in the primary aromatic amino developing solution. Special dispersing agents may be used for incorporating the coupler compound in the emulsion and in certain cases the coupler compound may be absorbed or adsorbed to the sensitive salt or may be combined with the sensitive silver salt as a chemical combination. In the case of a multi-layer photographic film in which the color forming compounds may be incorporated in one or more layers of the film, it may be necessary to take special precautions to prevent wandering of the coupler compound from the sensitive layer in which it is incorporated. The aromatic amino developing agents used with the coupler compounds of our invention include the mono, di and tri-aminoaryl compounds and their derivatives formed by substitution in the amino group as well as in the ring, such as alkylphenylenediamines and alkyltoluylenediamines. These compounds are usually used in the salt form such as the hydrochloride or the sulfate which are more stable than the amines themselves. Suitable compounds are diethyl-p-phenylenediamine hydrochloride monomethyl-p-phenylenediamine hydrochloride and dimethyl-p-phenylenediamine sulfate. The p-aminophenols and their substitution products may also be used where the amino group is unsubstituted. All of these compounds have an unsubstituted amino group at which the oxidation products of the developer couple with the color forming compounds to form a dye image.

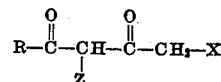
Our development process may be employed for the production of colored photographic images in layers of gelatin or other carrier such as collodion, organic esters of cellulose, or synthetic resins. The carrier may be supported by a transparent medium such as glass, a cellulose ester, or a non-transparent reflecting medium such as paper or an opaque cellulose ester. The emulsion may be coated as a single layer or as multiple layers on the support or, in the case of a transparent support, as superposed layers on both sides of the support. The superposed layers may be differentially sensitized and the dyes formed therein by coupling may be bleached by an oxidizing agent such as chromic acid to colorless soluble compounds. The destruction of the dye in

this way does not destroy the silver image and the silver may be resensitized and developed to color a number of times, thus permitting the formation of natural color images in superposed layers as described, for example, in Mannes and Gadowsky U. S. Patent No. 2,113,329.

The examples and compounds set forth in the present specification are illustrative only and it is to be understood that our invention is to be taken as limited only by the scope of the appended claims.

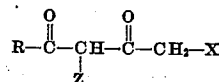
We claim:

1. A color-forming photographic developer comprising an aromatic amino developing agent and a coupler compound having the formula:



where R is selected from the class consisting of alkyl and aryl groups, X is selected from the class consisting of aryl, aralkyl, benzyl, and phenoxy alkyl groups, and Z is selected from the class consisting of hydrogen and carbalkoxy radicals.

2. A color-forming photographic developer comprising a dialkyl paraphenylenediamine salt and a coupler compound having the formula:



where R is selected from the class consisting of alkyl and aryl groups, X is selected from the class consisting of aryl, aralkyl, benzyl, and phenoxy alkyl groups, and Z is selected from the class consisting of hydrogen and carbalkoxy radicals.

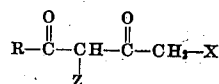
3. A color-forming photographic developer comprising an aromatic amino developing agent and a coupler compound comprising an acetyl acetone in which one hydrogen atom on at least one of the ω -carbon atoms is replaced with an aryl-containing group.

4. A color-forming photographic developer comprising an aromatic amino developing agent and ω -phenylacetylacetone as a coupler.

5. A color-forming photographic developer comprising an aromatic amino developing agent and phenacetylbenzoylmethane as a coupler.

6. A color-forming photographic developer comprising an aromatic amino developing agent and 1:5-diphenylpentanedione-1:3 as a coupler.

7. The method of producing a colored photographic image in a gelatino-silver halide emulsion layer, which comprises exposing and developing it, and, simultaneously with the development, coupling the development product of an aromatic amino developing agent containing a primary amino group, in the presence of the developed image, with a compound having the formula:

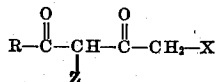


where R is selected from the class consisting of alkyl and aryl groups, X is selected from the class consisting of aryl, aralkyl, benzyl, and phenoxy alkyl groups, and Z is selected from the class consisting of hydrogen and carbalkoxy radicals.

8. The method of producing a colored photographic image in a gelatino-silver halide emulsion layer, which comprises exposing and devel-

opening it, and, simultaneously with the development, coupling the development product of an aromatic amino developing agent containing a primary amino group, in the presence of the developed image, with an acetyl acetone in which one hydrogen atom on at least one of the ω -carbon atoms is replaced with an aryl containing group.

9. A photographic emulsion for forming colored images comprising a carrier containing a sensitive silver halide and a compound having the formula:

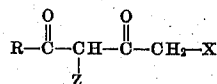


- where R is selected from the class consisting of alkyl and aryl groups, X is selected from the class consisting of aryl, aralkyl, benzyl, and phenoxy alkyl groups, and Z is selected from the class consisting of hydrogen and carbalkoxy radicals.

10. A photographic emulsion for forming colored images comprising a carrier containing a sensitive silver halide and an acetyl acetone in which one hydrogen atom on at least one of the ω -carbon atoms is replaced with an aryl-containing group.

11. A color-forming photographic layer com-

prising a gelatino-silver halide emulsion containing a coupler compound having the formula:



where R is selected from the class consisting of alkyl and aryl groups, X is selected from the class consisting of aryl, aralkyl, benzyl, and phenoxy alkyl groups, and Z is selected from the class consisting of hydrogen and carbalkoxy radicals.

12. A color-forming photographic layer comprising a gelatino-silver halide emulsion containing as a coupler compound an acetyl acetone in which one hydrogen atom on at least one of the ω -carbon atoms is replaced with an aryl-containing group.

13. A color-forming photographic layer comprising a gelatino-silver halide emulsion containing ω -phenylacetylacetone as a coupler.

14. A color-forming photographic layer comprising a gelatino-silver halide emulsion containing phenacetylbenzoylmethane as a coupler.

15. A color-forming photographic layer comprising a gelatino-silver halide emulsion containing 1:5-diphenylpentanedione-1:3 as a coupler.

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