

UNITED STATES PATENT OFFICE

2,113,330

COLOR-FORMING DEVELOPERS

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Serial No. 8,519

4 Claims. (Cl. 95—88)

This invention relates to dyes and more particularly to dyes formed by coupling during photographic development.

It is known that colored photographic images may be formed by using a developer which forms a colored compound on development. The colored compound thus formed is deposited adjacent the silver image during the development. It is also known that a colored image may be formed by adding to the developer solution a compound which combines with the oxidation product of the developer and forms a coloring substance.

It is an object of the present invention to provide a developer which produces a dye simultaneously and in situ with photographic development. It is a further object to produce novel dyes in color-forming photographic development.

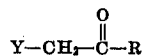
These objects are accomplished by the present invention by the use of aromatic diamino developers together with certain specific coupling compounds hereinafter disclosed.

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-soluble 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.

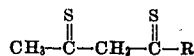
The aromatic amino compounds which may be used as developers in our process include the mono-, di-, and tri-amino aryl compounds and compounds formed therefrom by substitution in the amino group as well as in the ring, such as alkyl phenylene diamines and alkyl toluylene diamines. These compounds are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

The coupling or color-forming compounds which are used according to our invention are certain compounds containing a substituted acetyl group which includes a reactive methylene group. These include acetoacetanilide and substituted

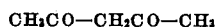
acetoacetanilides, such as the halogen and alkyl-substituted compounds. Among these are parabromo - acetoacetanilide, dichloro - acetoacetanilide, and 4-nitro acetoacetanilide. Other compounds containing this group are benzoyl acetone and acetyl acetone. In these compounds the acetyl group is substituted with an aceto group, $\text{CH}_3\text{CO}-$, but it may also be substituted with a cyano, $\text{CN}-$, or with any substituent group which will produce a reactive methylene group. The compounds which we contemplate using as color-formers have the general formula



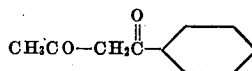
where Y=an aceto, cyano, sulfonyl, carbonyl, or equivalent group, and R=an alkyl or an aryl group. The group represented by Y must be such that the methylene group to which it is attached is reactive in the dye-forming reaction. The acetyl group may contain sulfur instead of oxygen atoms, thus forming thioacetyl groups of the formula



Among the color-forming compounds used, where Y=aceto and R=alkyl, a typical compound is acetyl acetone:



When Y=aceto and R=aryl, a typical compound is benzoyl acetone:



The following are examples of developer solutions which may be used according to our process:

Example I

A. Diethyl p.phenylenediamine HCl	g--	2	40
Sodium sulfite	g--	5	
Sodium carbonate	g--	30	
Water to	cc--	1,000	
B. Benzoyl acetone	g--	2	
Acetone	cc--	100	45
Add B to A.			

Example II

A. Dimethyl p.phenylenediamine sulphate	g--	1	50
Sodium sulfite	g--	2	
Sodium carbonate	g--	30	
Water to	cc--	1,000	
B. Acetyl acetone	g--	2.5	
Iso-propyl alcohol	cc--	100	55
Add B to A.			

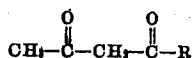
Our process may be used to form colored photographic images in films as well as in plates, and the dyes formed will attach to gelatin or other

carrier 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 sensitized layers.

- 5 The dyes formed may be bleached by an oxidizing agent, such as chromic acid, and colorless soluble compounds thereby formed. The bleaching of the dye in this manner does not destroy the silver image and a silver image may be colored, 10 bleached, and recolored a number of times. Such a process is disclosed in our application, Serial No. 8,516, filed February 27, 1935.

What we claim is:

1. A color-forming photographic developer 15 comprising an aromatic amino developing compound and a coupler compound having the formula

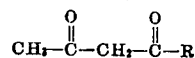


where R is a group selected from the group consisting of alkyl and aryl groups.

2. A color-forming photographic developer comprising an aromatic amino developing compound and acetyl acetone.

3. A color-forming photographic developer comprising an aromatic amino developing compound and benzoyl acetone.

4. A color-forming photographic developer comprising a paraphenylenediamine developing compound and a coupler compound having the formula 10



where R is a group selected from the group consisting of alkyl and aryl groups. 15

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