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PHOTOGRAPHIC COLOR FORMING COMPOUND

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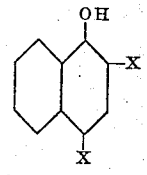
11 Claims. (Cl. 95—6)

This invention relates to color photography and more particularly to compounds which form dyes by coupling with the developing compound on photographic development.

The method of forming colored photographic images by depositing a colored compound in the photographic layer adjacent the silver image on development has been described in numerous prior patents. Dyes formed in this way are insoluble in water and in the ordinary photographic developing and fixing baths, although the silver images formed simultaneously with them during photographic development may be removed from the photographic layer to leave pure dye images in the layer. Compounds employed in conjunction with the developing agent for the silver and which couple with the development product of the developer during photographic development are referred to herein as coupling components or couplers. Depending upon their solubility or diffusion characteristics, these compounds may be incorporated in the emulsion layer prior to exposure or may be dissolved in the developing solution. When these coupling components are incorporated in the photographic layer prior to exposure, they do not affect the exposure and development of the layer in the usual way, but when the development is carried out with a suitable developing agent, they combine with the oxidation product of the developer to form a colored image in situ with the silver image.

The developing agents used in color forming development of the type contemplated by our invention comprise aromatic amino developers including the mono-, di- and triaminoaryl compounds and their derivatives formed by substitution in the amino group as well as in the ring, such as alkylphenylenediamines, alkyltoluenendiamines and p-aminophenols. These compounds are ordinarily 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-phenylene-diamine 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 which enables the oxidation products of the developer to couple with the color-forming compounds to form a dye image.

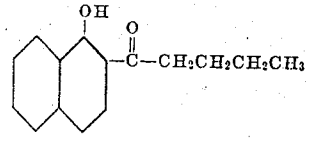
We have found that α-naphthols having valeryl or cinnamoyl substituent groups in the 2 or 4 position are useful as coupler compounds in photographic developers and emulsion layers. These compounds have the following general formula:



in which one X is a hydrogen atom, and the other X is a valeryl or cinnamoyl group.

The following compounds illustrate couplers of this class:

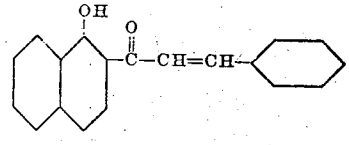
(1)



2-n-valeryl-1-naphthol

Prepared by the method given for the 2-acetyl derivative. Ber. 47, 3216 (1914.)

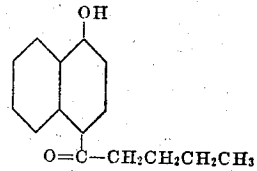
(2)



2-cinnamoyl-1-naphthol

Prepared as in Ber. 31, 706 (1898)

(3)

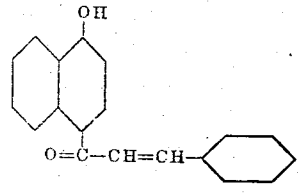


4-n-valeryl-1-naphthol

Prepared by the method given for the 4-acetyl derivative. Ber. 47, 3228 (1914)

Prepared by the method as given for Example 2.

(4)



4-cinnamoyl-1-naphthol

In the compounds listed above, the valeryl-substituted α-naphthols, compounds 1 and 3, are suitable for use in the developing solution and the

cinnamoyl substituted α-naphthols, compounds 2 and 4, may be used in the emulsion layer. These compounds form blue-green dyes on photographic development.

A developing formula which may be used is the following:

A

Diethyl para phenylenediamine hydrochloride	grams	1
Sodium sulfite	do	0.5
Sodium carbonate	do	20
Water to	liters	1

B

Coupler	grams	1
Acetone	cc	50

Add B 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.

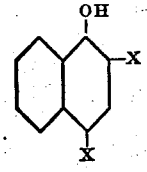
The couplers which are used in the emulsion layer may be incorporated in various ways but we prefer to form a solution of the sodium salt of the coupler in alcohol and add this to the emulsion. For example, 3 grams of coupler may be dissolved or suspended in 50 cc. of ethyl alcohol and sodium hydroxide added in the amount of 1½ equivalent weights of the coupler. The sodium hydroxide may be added as solid or as a concentrated solution. The sodium salt of the coupler is thereby generated in a solution of 50 cc. of alcohol and this solution is added to one liter of a gelatino silver halide. The pH of the emulsion may be adjusted if desired by adding a suitable acid such as acetic or sulfuric acid to neutralize all or part of the sodium hydroxide used to form the sodium salt of the coupler.

The coupling compounds may be incorporated either in gelatin or in other colloidal materials such as collodion, organic esters of cellulose or synthetic resins. In case the coupler is incorporated in the emulsion or is used in the developing solution, the emulsion may be carried by a transparent medium such as glass, cellulose ester or synthetic resin or a non-transparent reflecting medium such as paper or an opaque cellulose ester. The emulsion may be coated as a single layer on the support or superposed layers containing the couplers may be coated on one or both sides of the support. The superposed layers may be differentially sensitized for the formation of a neutral color image in the well known manner.

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

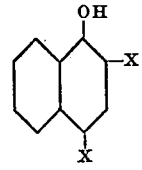
We claim:

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



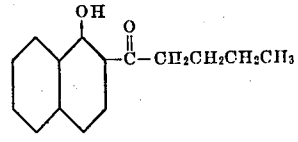
in which one X is a hydrogen atom and the other X is an acyl group selected from the class consisting of valeryl and cinnamoyl groups.

2. The method of producing a colored photographic image in a silver halide emulsion layer which comprises simultaneously developing an image therein and coupling the development product of an aromatic amino developing agent containing a primary amino group with a compound having the formula:

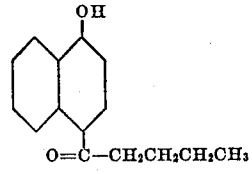


in which one X is a hydrogen atom and the other X is a valeryl group.

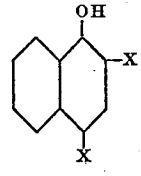
3. The method of producing a colored photographic image in a silver halide emulsion layer which comprises simultaneously developing an image therein and coupling the development product of an aromatic amino developing agent containing a primary amino group with a compound having the formula:



4. The method of producing a colored photographic image in a silver halide emulsion layer which comprises simultaneously developing an image therein and coupling the development product of an aromatic amino developing agent containing a primary amino group with a compound having the formula:

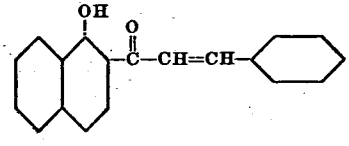


5. The method of producing a colored photographic image in a silver halide emulsion layer which comprises simultaneously developing an image therein and coupling the development product of an aromatic amino developing agent containing a primary amino group with a compound having the formula:

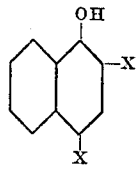


in which one X is a hydrogen atom and the other X is a cinnamoyl group.

6. The method of producing a colored photographic image in a silver halide emulsion layer which comprises simultaneously developing an image therein and coupling the development product of an aromatic amino developing agent containing a primary amino group with a compound having the formula:

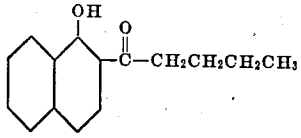


7. A color forming photographic developer comprising an aromatic amino developing agent containing a primary amino group and a coupling compound having the formula:

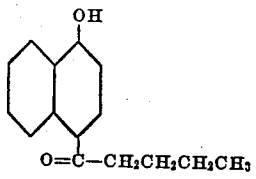


in which one X is a hydrogen atom and the other X is a valeryl group.

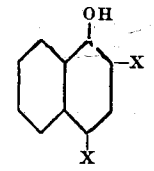
8. A color forming photographic developer comprising an aromatic amino developing agent containing a primary amino group and a coupling compound having the formula:



9. A color forming photographic developer comprising an aromatic amino developing agent containing a primary amino group and a coupling compound having the formula:

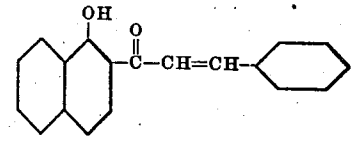


10. A photographic emulsion for forming colored images comprising a colloidal carrier containing a sensitive silver halide and a coupler compound having the formula:



in which one X is a hydrogen atom and the other X is a cinnamoyl group.

11. A photographic emulsion for forming colored images comprising a gelatino-silver halide emulsion containing a coupler compound having the formula:



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