

UNITED STATES PATENT OFFICE

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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, alkyltoluenediamines 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*-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 which enables the oxidation products of the developer

to couple with the color-forming compounds to form a dye image.

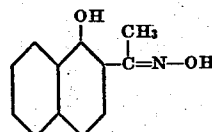
We have found that certain substituted α -naphthols are useful as coupler compounds in photographic developers and emulsion layers to form colored images on photographic development. The compounds which we propose using have the following general formula:



15 in which X is an alkyl group, such as methyl, ethyl, or propyl, and Y is a group which, together with the carbon atom to which it is attached, forms an oxime, hydrazone, or semicarbazone group.

20 The following examples illustrate coupler compounds of this general formula:

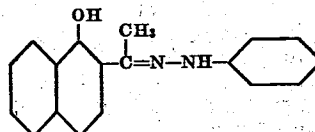
(1)



2-acetyl-1-naphthol-oxime

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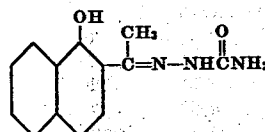
(2)



2-acetyl-1-naphthol phenyl-hydrazone

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(3)

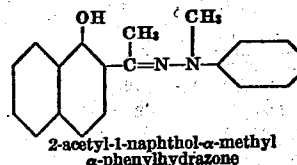


2-acetyl-1-naphthol semicarbazone

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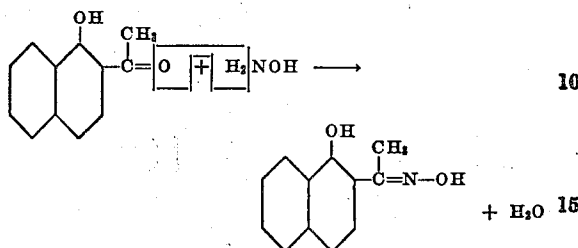
(4)

2-acetyl-1-naphthol- α -methyl
phenylhydrazone

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These compounds may be prepared by reacting a suitable 1-hydroxy-2-naphthyl ketone with a α -substituted hydroxylamine, a α -substituted hydrazine or a 2 or 4 substituted semicarbazide. 2-acetyl-1-naphthol oxime may be prepared in the following manner:



Compounds 1 and 3 are suitable for incorporation in photographic developing solutions and compounds 2 and 4 may be incorporated in emulsion layers and do not diffuse from the layer in which they are incorporated in the case of multi-layer coatings. Blue-green dyes are formed 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	liter	1

B		
Coupler	gram	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.

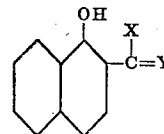
The couplers which are used in the emulsion layer may be incorporated in various ways but we prefer to form a solution of the sodium salt of the coupler in alcohol and add this to the emulsion. For example, 3 grams of coupler may be dissolved or suspended in 50 cc. of ethyl alcohol and sodium hydroxide 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:

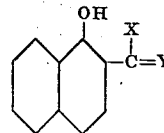
1. The method of producing a colored photographic image in a silver halide emulsion layer which comprises simultaneously developing an image therein and coupling the development product of an aromatic amino developing agent containing a primary amino group with a compound having the formula:



2. in which X is an alkyl group and Y is a group which, together with the carbon atom to which it is attached, produces a group selected from the class consisting of oxime, hydrazone, and semicarbazone groups.

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 2-acetyl-1-naphthol oxime.

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. in which X is an alkyl group and Y is a group comprising the atoms necessary to form a hydrazone 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 2-acetyl-1-naphtholphenyl-hydrazone.

7. 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 2-acetyl-1-naphthol- α -methyl- α -phenylhydrazine.

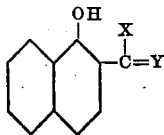
8. The method of producing a colored photographic image in a silver halide emulsion layer which comprises simultaneously developing an image therein and coupling the development product of an aromatic amino developing agent containing a primary amino group with 2-acetyl-1-naphtholsemicarbazone.

9. A color forming photographic developer comprising an aromatic amino developing agent containing a primary amino group and a coupler compound comprising 2-acetyl-1-naphthol oxime.

10. A color-forming photographic developer

comprising an aromatic amino developing agent containing a primary amino group and a coupler compound comprising 2-acetyl-1-naphthol-semicarbazone.

9. 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 X is an alkyl group and Y is a group comprising the atoms necessary to form a hydrazone group.

10. A photographic element for forming colored images comprising a gelatino-silver halide emulsion containing 2-acetyl-1-naphthol phenyl hydrazone as a coupler.

11. A photographic element for forming colored images comprising a gelatino-silver halide emulsion containing 2-acetyl-1-naphthol- α -methyl- α -phenylhydrazone as a coupler.

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