

UNITED STATES PATENT OFFICE

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PHOTOGRAPHIC COLOR-FORMING COMPOUNDS

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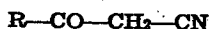
No Drawing. Application October 14, 1936, Serial No. 105,617

12 Claims. (Cl. 95-88)

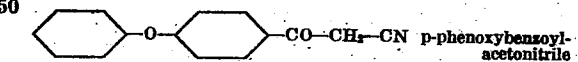
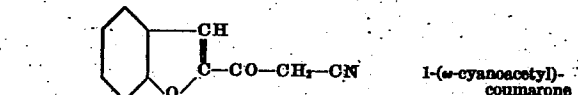
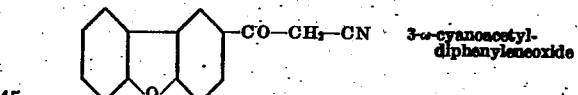
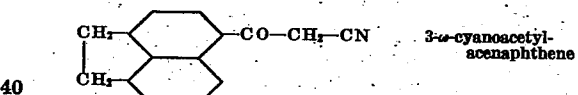
This invention relates to photographic developers and more particularly to compounds which form dyes by coupling with the developing compound on development.

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. The present invention relates to a process in which the color-forming compound is contained preferably in the developing solution, but might also be incorporated in the sensitive material and forms a dye simultaneously and in situ with the development of the silver image by coupling with the oxidation product of the photographic developer. In U. S. Patent No. 2,039,730, granted May 5, 1936, to L. D. Mannes and L. Godowsky, Jr., there is disclosed the use of hydroxylated diphenyl compounds for this purpose. The use of other types of compounds was also described in application, Serial No. 8519, of L. D. Mannes and L. Godowsky, Jr.

We have found that certain organic compounds containing the cyanoacetyl group as a substituent are useful as coupler compounds in photographic developers and form colored images on photographic development. The compounds which we contemplate using have the following general formula:



in which R may be one of the following groups: acenaphthenyl, dibenzofuryl, coumaronyl or phenoxyphenyl. The compounds containing these groups attached to a cyanoacetyl group will have the following formulae:



These compounds when present in a developer solution containing an aromatic amino develop-
ing compound coupler with the oxidation prod-

uct of the aromatic amino developing compound form a dye simultaneously with the formation of the silver image. The coupling occurs in each case at the methylene group contained between the carbonyl group and the cyano group of the coupler compound.

The coupler compounds used may be substituted in the aromatic ring with groups including halide, nitro, amino, substituted amino, alkyl, aryl and carboxyl groups. These groups may be substituted in the ring at any position since the ring is not reactive in the coupling to form the dye.

As developing agents we contemplate using the aromatic amino compounds which function as photographic developers. The compounds preferred for this purpose are para phenylenediamine and its substituted derivatives. These developers may be substituted in the amino groups as well as in the ring with alkyl, ester, or halide groups. We prefer to use as developers para phenylenediamine dialkyl substituted in one amino group, the other amino group remaining unsubstituted. These compounds are ordinarily used in the salt form, such as the hydrochloride or sulfate, since these compounds are more stable than the amines themselves. Developing agents which may be used include diethyl para phenylenediamine, monomethyl para phenylenediamine hydrochloride and diethylene para phenylenediamine sulfate.

A developing formula which may be used is the following:

A

Diethyl para phenylenediamine hydrochloride	gram	1
Sodium sulfite	do	0.5
Sodium carbonate	grams	20
Water	litre	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 colors formed by the compounds of the present invention on coupling with the oxidation product of the developer are various shades of red and magenta. The colors may, of course, be altered by inserting various substituent groups into the molecule of the coupler compounds.

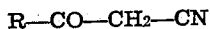
Although we have described our invention with particular reference to the use of the coupling compound in the developing solution itself, our invention is in no way limited to this method.

- 5 As an alternative method, the coupler compound may be incorporated in the photographic layer before development, or before exposure and development. It may be adsorbed to the sensitive silver halide grain or chemically combined with the sensitive salt, or, in some cases, the silver salt of the coupler compound itself, without halide, may exhibit light sensitivity and coupling properties on development.

- Our compounds may be used to form colored photographic images in films plates, or paper, when gelatin or other suitable colloid is used as the carrier for the silver halide constituting the sensitive salt. The emulsion treated to form the colored image may be on one side or on both sides of the support or superposed emulsion layers may be coated on one or both sides of the support. Where a plurality of layers is used the layers may be differently sensitized to form natural colored images on development, according to the process described in application, Serial No. 8,516, filed February 27, 1935, by L. D. Mannes and L. Godowsky, Jr.

What we claim is:

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



- where R is selected from the class consisting of acenaphthenyl, dibenzofuryl, coumaronyl, and phenoxyphenyl groups.

2. A color-forming photographic developer comprising a dialkyl amino paraphenylene diamine and a coupler compound having the formula



- where R is selected from the class consisting of acenaphthenyl, dibenzofuryl, coumaronyl, and phenoxyphenyl groups.

3. A color-forming photographic developer comprising a diethyl paraphenylene diamine hydrochloride and a coupler compound having the formula



- where R is selected from the class consisting of acenaphthenyl, dibenzofuryl, coumaronyl, and phenoxyphenyl groups.

4. A color-forming photographic developer

comprising an aromatic amino developing compound containing a primary amino group and 3- ω -cyanoacetyl-acenaphthene.

5. A color-forming photographic developer comprising a dialkyl amino paraphenylene diamine developing compound and 3- ω -cyanoacetyl-acenaphthene.

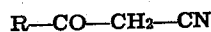
6. A color-forming photographic developer comprising diethyl paraphenylene diamine hydrochloride and 3- ω -cyanoacetyl-diphenylene-oxide.

7. A color-forming photographic developer comprising an aromatic amino developing compound containing a primary amino group and 1-(ω -cyanoacetyl)-coumarone.

8. A color-forming photographic developer comprising a dialkyl amino paraphenylene diamine developing compound and 1-(ω -cyanoacetyl)-coumarone.

9. A color-forming developer comprising diethyl para phenylenediamine hydrochloride and 1-(ω -cyanoacetyl)-coumarone.

10. A photographic image comprising a dye formed by the coupling of the development product of an aromatic amino developing compound containing a primary amino group with a compound having the formula



where R is selected from the class consisting of acenaphthenyl, dibenzofuryl, coumaronyl, and phenoxyphenyl groups.

11. A photographic image comprising a dye formed by the coupling of the development product of a dialkyl amino paraphenylene diamine with a compound having the formula



where R is selected from the class consisting of acenaphthenyl, dibenzofuryl, coumaronyl, and phenoxyphenyl groups.

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



where R is selected from the class consisting of acenaphthenyl, dibenzofuryl, coumaronyl, and phenoxyphenyl groups.

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