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# UNITED STATES PATENT OFFICE

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## PHOTOGRAPHIC DEVELOPER FOR COLOR PHOTOGRAPHY

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9 Claims. (Cl. 95—88)

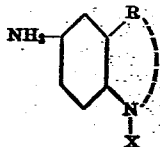
This invention relates to photographic developers and particularly to a new class of developers containing heterocyclic ring systems and adapted for use in various processes of color photography.

In the processes of color photography in which a colored image is formed in a photographic layer by a color-forming development in which the development product of the photographic developer combines with a coupler compound, special types of developing agents must be used. The developing agents suitable for this purpose must contain a primary amino group and such developers are usually chosen from the classes of p-phenylene diamines and p-amino phenols or their various substitution products. A process of this type is described in the U. S. patent to Fischer No. 1,102,028, June 30, 1914.

The choice of developer of these classes is somewhat limited and for this reason developing agents having suitable characteristics cannot always be chosen. For example, the use of the p-phenylene diamines is somewhat limited on account of their insolubility in the developing solution. When an attempt is made to introduce solubilizing groups into these developers, valuable properties, such as the color of the dye generated, are sometimes destroyed, and in the case of the p-amino phenol developers, the compounds are frequently too soluble for color processes in which it is desired to form an insoluble dye image. With both the p-phenylene diamine and p-amino phenol developers, the number and kind of substituents which may be introduced into the molecule is, of course, limited.

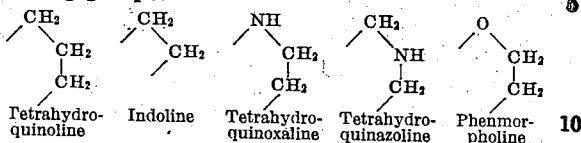
It is, therefore, an object of the present invention to provide a new class of photographic developers particularly adapted for color-forming processes. A further object is to provide a class of photographic developers having suitable solubility properties and which form insoluble and stable dyes by coupling with color-forming compounds. A still further object is to provide a class of photographic developers which develop a color image at an optimum rate. A still further object is to provide a class of photographic developers which penetrate the gelatin of the photographic layer in a sufficiently short time to make them practical for photographic use. Other objects will appear from the following description of my invention.

These objects are accomplished by the use of photographic developers containing a nitrogen-heterocyclic ring system and having the following general formula:

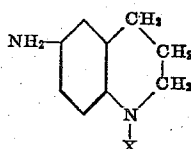


in which R represents the atoms necessary to complete a heterocyclic ring system, and X is an alkyl, hydroxyalkyl, or an allyl group.

In the above formula, R may be one of the following groups:

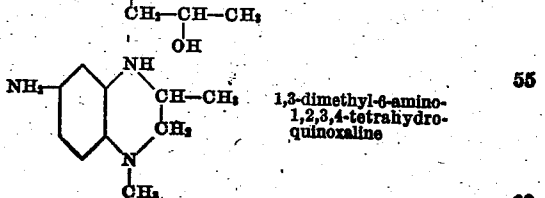
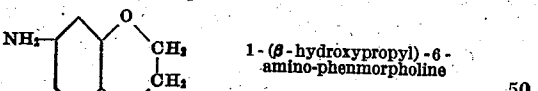
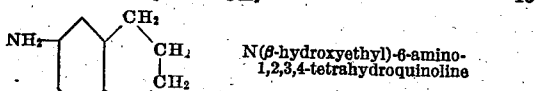
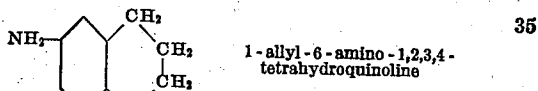
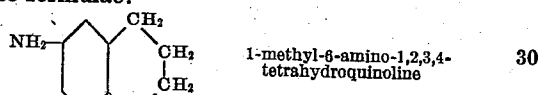


Compounds which I prefer to use as developers are the tetrahydroquinolines of the following general formula:



in which X is an alkyl, hydroxyalkyl, or an allyl group.

Specific compounds which may be used as developers according to my invention are the following, it being understood that these are exemplary only, and that they may contain other substituent groups as well as those included in these formulae:



An important feature of the compounds used as developers, according to my invention, is the substituent group on the heterocyclic nitrogen atom of the developer molecule. This group in many cases has the property of increasing the solubility of the developing compound and also aids in the formation of a colored image when the photographic layer is developed in the presence of a coupler compound. I have found that developing agents of the type described above, when used in the presence of a coupler compound, do not produce a colored image if the developing molecule does not contain a substituent group in this position. The substituent groups attached to the heterocyclic nitrogen atom therefore possess a critical and important function in the production of a colored image.

According to my invention a gelatino-silver halide emulsion layer, after exposure, is developed in a solution containing as the developing agents one of the compounds described above. The solution may contain in addition a coupler compound, or the coupler compound may be present in the sensitive layer prior to exposure. The layer may be developed to a colored negative image directly or may be developed first to a black and white negative by development in the ordinary way and then developed in the coupler developer to produce a positive colored image. The silver is then removed from the film leaving a pure dye image.

The following example, which is illustrative only, indicates a method of developing a colored image, according to my invention.

A gelatino-silver halide emulsion layer was exposed behind a step tablet, developed in a metol-hydroquinone developer, washed, exposed to white light, and then developed for ten minutes at 70° F. in the following developer solution:

|                        |            |      |
|------------------------|------------|------|
| Developer.....         | grams..... | 1.5  |
| Sodium sulfite.....    | do.....    | 2.0  |
| Sodium carbonate.....  | do.....    | 50.  |
| Potassium bromide..... | do.....    | 2.   |
| Coupler.....           | do.....    | 2.   |
| Sodium hydroxide.....  | do.....    | 1.   |
| Water to.....          | c. c.....  | 1000 |

The film was then washed thoroughly and the silver removed in the usual way with a two-bath Farmer's reducer.

The coupler compounds which may be used according to my invention include any of the compounds suitable for use with the p-phenylene diamine developing agents. These include the phenolic compounds described in Fischer U. S. Patent No. 1,102,028, the pyrazolones of Seymour U. S. Patent 1,969,479, the hydroxydiphenyls of Mannes and Godowsky U. S. Patent No. 2,039,730, the aceto- or cyano-acetamides of Mannes and Godowsky U. S. Patent No. 2,108,602, the acetyl or benzoyl acetones of Mannes and Godowsky U. S. Patent No. 2,113,330, the cyanoacetyl compounds of Mannes, Godowsky and Peterson U. S. Patent No. 2,115,394, and the hydroxy styryl compounds of Mannes, Godowsky and Peterson No. 2,126,337.

Specific coupler compounds which I have found suitable are the following:

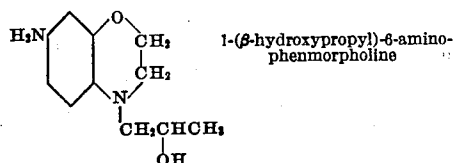
To produce blue or blue-green dyes, o-cresol, thymol, o-phenylphenol, 4-chloro-2-phenylphenol, 2,4-dichloro-B-naphthol; to produce red or magenta dyes, 1-phenyl-3-methyl-5-pyrazolone and 2-naphthoylacetoneitrile; to produce yellow or orange dyes, acetoacet-2,5-dichloroanilide and

The compounds described above may be used to produce a colored photographic image in a single photographic layer or may be used to produce a natural colored image in a multi-color layer or may be used for any of the dye images produced in a multi-layer film by coupler development.

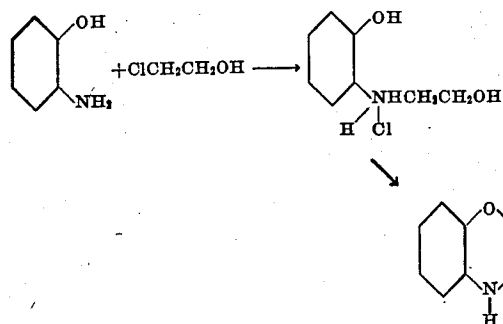
The compounds used as developing agents, according to my invention, are made in various ways. For example, the compounds N( $\beta$ -hydroxyethyl)-6-amino-1,2,3,4-tetrahydroquinoline and 1-( $\beta$ -hydroxypropyl)-6-amino-phenmorpholine are made as follows:

N( $\beta$ -hydroxyethyl)-1,2,3,4-tetrahydroquinoline is prepared by the action of 1 part by weight of ethylene oxide upon 2 parts of 1,2,3,4-tetrahydroquinoline in a bomb (100°-160° C.) for four to nine hours. The resulting N( $\beta$ -hydroxyethyl)-1,2,3,4-tetrahydroquinoline is purified by rectification and boils at 190-195° C./15 mm.

The N( $\beta$ -hydroxyethyl)-6-amino-1,2,3,4-tetrahydroquinoline is prepared by nitrosating the foregoing product by adding dropwise the calculated quantity of an aqueous solution of sodium nitrite to an excess of chilled 17% hydrochloric acid solution of the product. The resulting nitroso compound is reduced by the slow addition of zinc dust, the end of the reduction being determined by the decolorization of the solution. The zinc sludge is filtered, the filtrate made strongly basic and the amino derivative extracted with amyl alcohol. The 1-( $\beta$ -hydroxyethyl)-6-amino-1,2,3,4-tetrahydroquinoline is obtained by rectification and boils at 208-215° D./4 mm.



Phenmorpholine is readily prepared by the action of ethylene-chlorohydrin on ortho-amino-phenol according to the equations:

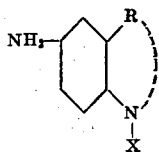


With propylene oxide the N-( $\beta$ -hydroxypropyl) group is introduced and upon nitrosation and subsequent reduction the desired 6-amino derivative is obtained.

The developers used according to my invention may contain other substituent groups and other heterocyclic groupings than those specifically listed in the present specification. The examples given are illustrative only and other modifications may be made within the scope of the appended claims.

What I claim is:

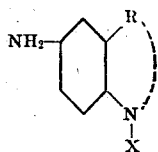
1. A photographic developer comprising a compound of the general formula



- 10 in which X is selected from the class consisting of alkyl, hydroxyalkyl, and allyl groups, and R represents the atoms necessary to complete a heterocyclic ring.

- 15 2. A photographic developer comprising a 6-amino-1,2,3,4-tetrahydroquinoline having on the heterocyclic nitrogen atom a substituent selected from the class consisting of alkyl, hydroxyalkyl, and allyl groups.

- 20 3. A photographic developing solution comprising a developing agent of the general formula



- 25 in which X is selected from the class consisting of alkyl, hydroxyalkyl, and allyl groups, and R represents the atoms necessary to complete a heterocyclic ring, and a coupling compound which combines with the oxidation product of the developing agent on photographic development to produce a colored image.

- 30 4. A photographic developing solution comprising as a developing agent a 6-amino-1,2,3,4-tetrahydroquinoline having on the heterocyclic nitrogen atom a substituent selected from the class of alkyl, hydroxyalkyl, and allyl groups, and, as a coupling agent, a compound which combines with the oxidation product of the developing agent on photographic development to produce a colored image.

5. A photographic developing solution comprising as a developing agent a 6-amino-1,2,3,4-tetrahydroquinoline having an alkyl substituent on the heterocyclic nitrogen atom, and as a coupling agent, a compound which combines with the oxidation product of the developing agent on photographic development to produce a colored image.

6. A photographic developing solution comprising as a developing agent a 6-amino-1,2,3,4-tetrahydroquinoline having a hydroxyalkyl substituent on the heterocyclic nitrogen atom, and as a coupling agent, a compound which combines with the oxidation product of the developing agent on photographic development to produce a colored image.

7. A photographic developing solution comprising as a developing agent a 6-amino-1,2,3,4-tetrahydroquinoline having as allyl substituent on the heterocyclic nitrogen atom, and as a coupling agent, a compound which combines with the oxidation product of the developing agent on photographic development to produce a colored image.

8. The method of producing a colored photographic image in a gelatino-silver halide emulsion layer, which comprises coupling the development product of a 6-amino-1,2,3,4-tetrahydroquinoline having on the heterocyclic nitrogen atom a substituent selected from the class consisting of alkyl, hydroxyalkyl, and allyl groups, with a phenolic coupler compound.

9. The method of producing a colored photographic image in a gelatino-silver halide emulsion layer, which comprises coupling the development product of a 6-amino-1,2,3,4-tetrahydroquinoline having on the heterocyclic nitrogen atom a substituent selected from the class consisting of alkyl, hydroxyalkyl, and allyl groups, with an acetamide coupler compound.

WILLARD D. PETERSON.