

UNITED STATES PATENT OFFICE

2,369,929

ACYLAMINO PHENOL COUPLERS

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Serial No. 479,610

13 Claims. (Cl. 95-6)

This invention relates to photographic color forming or coupler compounds and particularly to substituted phenolic coupler compounds.

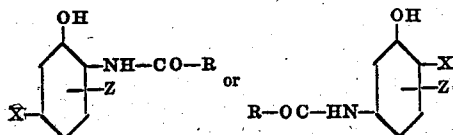
This application is a continuation-in-part of our application Serial No. 422,699, filed December 12, 1941, now U. S. Patent 2,338,676, granted January 4, 1944.

The formation of colored photographic images by using a primary aromatic amino developing agent which couples with a color forming compound on development has been the subject of numerous prior patents. Most of these patents have been directed to coupler compounds which produce on development dyes which meet the requirements of subtractive color photography, that is, dyes which are colored yellow, magenta or blue-green.

Phenolic coupler compounds have been described in prior patents such as Fischer U. S. Patent 1,055,155, March 4, 1913, Mannes & Godowsky U. S. Patent 2,039,730, May 5, 1936, and French Patent 836,144. French Patent 836,144 discloses acetyl-o- and m-amino-phenol as couplers. These acetyl aminophenols have no substituent para to the acetyl amino group, and, therefore, produce dyes which are less stable to heat and light than those produced from acetyl-amino phenols having a substituent para to the acetyl amino group.

It is, therefore, an object of the present invention to provide novel coupler compounds for color photography. A further object is to provide phenolic coupler compounds having the proper spectral absorption characteristics for use in multi-color photography. A still further object is to provide coupler compounds which form photographic images having satisfactory heat and light stability characteristics. Other objects will appear from the following description of our invention.

These objects are accomplished by the use of primary aromatic amino developing agents in conjunction with certain 2,5-disubstituted phenols as coupler compounds. These coupler compounds have substituents in the 2- and 5-positions with respect to the phenolic hydroxyl group, one of the substituents being an alkyl group, and the other substituent being an acylamino group. These compounds having the general formula:



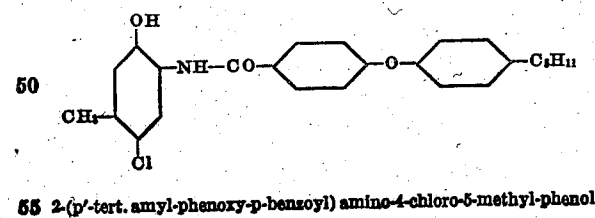
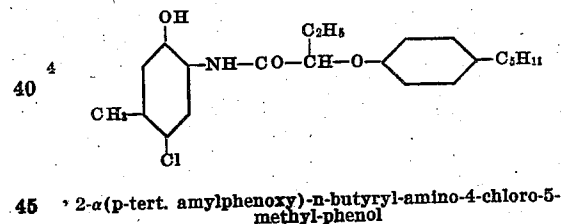
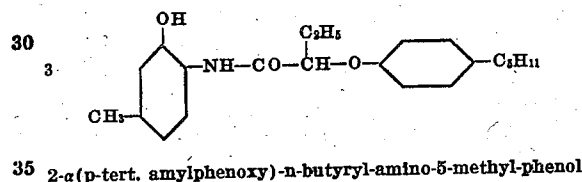
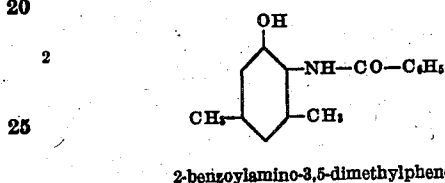
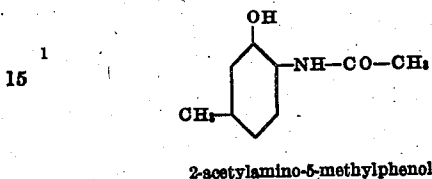
where

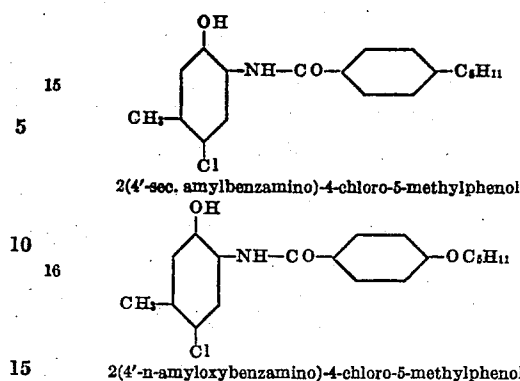
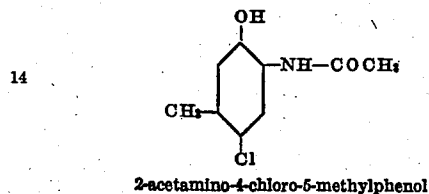
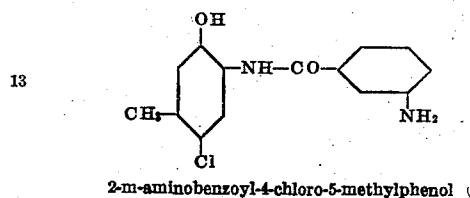
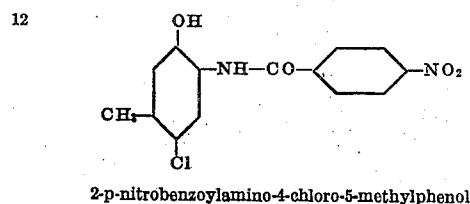
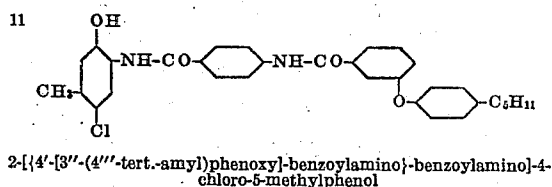
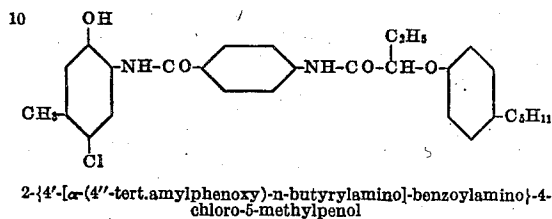
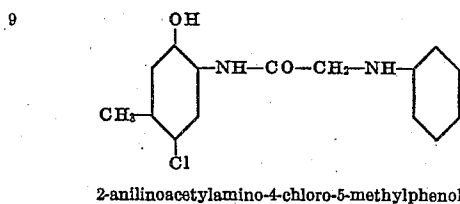
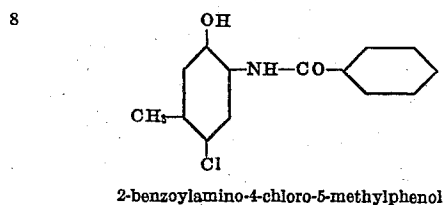
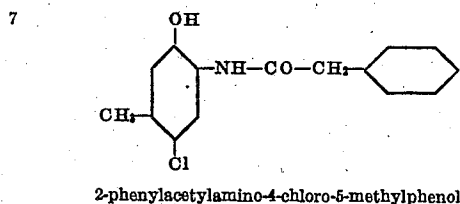
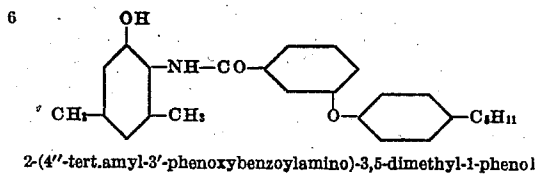
X=alkyl

R=alkyl or aryl, both of which may be substituted or unsubstituted

5 Z=hydrogen or a replaceable substituent, such as chlorine, or an irreplaceable substituent, such as methyl, in a position other than para to the hydroxyl.

10 The following compounds illustrate couplers suitable for use according to our invention:





The following example, which is illustrative only, is a developing solution using one of the couplers of our invention:

A. 2-amino-5-diethylamino toluene HCl	
grams	2
Sodium sulfite	5
Sodium carbonate	30
Water to	1
B. 2-acetyl-amino-5-methylphenol	2
Sodium hydroxide (10% solution)	10

In use, B is added to A.

In addition to their use in the developing solution, the coupler compounds of our invention may be incorporated in the photographic layer prior to exposure, and the colored images formed by development in a primary aromatic amino developing solution. In the case of a multi-layer film in which color-forming compounds are incorporated in the emulsion layers, the coupler molecule may be suitably enlarged, as in compounds 3 to 10, 11, 15 and 16, to render it non-diffusing in the gelatin.

Our couplers may be incorporated in emulsions in the manner described in Mannes & Godowsky U. S. Patent 2,304,940, granted December 15, 1942, or Jelley & Vittum U. S. Patent 2,322,027 granted June 15, 1943.

The aromatic amino developing agents used with the coupler compounds of our invention include the mono-, di- and tri-aminoaryl compounds and their derivatives formed by substitution in the amino group as well as in the ring such as alkyl phenylene diamines and alkyl toluenylenediamines. These compounds are usually employed in the salt form such as the hydrochloride or the sulfate which is more stable than the amines themselves. Suitable compounds are diethyl-p-phenylenediamine hydrochloride, mono-methyl-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 developing agents have an unsubstituted amino group at which the oxidation products of the developer couple with the color forming compounds to form dye images.

As stated above, the coupling compounds used according to our invention produce dyes which are greenish-blue in color and hence are suitable for use in three color subtractive processes of color photography. These compounds have been found to yield dyes which are more stable to heat and light than those produced from the corresponding phenols in which the 5-position relative to the hydroxyl group carries no substituent.

In addition to the substituents in the 2- and 5-positions with respect to the phenolic hydroxyl group, the coupler used according to our invention may also have other substituents such as

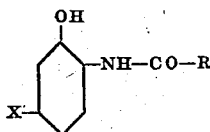
halogen, alkyl, etc. in other positions in the molecule as illustrated by Examples 2 and 4 to 16. The additional substituents illustrated in Examples 2 and 4 to 16 have not been found to confer increased stability upon the resulting dyes but may be used for purposes of making the preparation of the coupler easier or of altering the color of the dyes or changing the solubility and diffusion characteristics or the original couplers. The chlorine atom in the 4-position of couplers 4, 5, and 7 to 16 is lost during coupling and does not affect the characteristics of the resulting dye.

Our development process may be employed for the production of colored photographic images in layers of gelatin or other carrier such as collodion, organic esters of cellulose, or synthetic resins. The carrier may be supported by a transparent medium such as glass, cellulose ester, or a non-transparent reflecting medium such as paper or an opaque cellulose ester. The emulsion may be coated as a single layer or as multiple layers on the support or in the case of a transparent support as superposed layers on both sides of the support. The superposed layers may be differentially sensitized and the dyes formed therein by coupling may be bleached by an oxidizing agent such as chromic acid to colorless soluble compounds. The destruction of the dye in this way does not destroy the silver image and the silver may be resensitized to develop a color a number of times thus permitting the formation of natural color images in superposed layers as described, for example, in Mannes & Godowsky U. S. Patent 2,113,329. Colored images may also be formed in the manner described in Mannes, Godowsky and Wilder U. S. Patent 2,252,718.

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

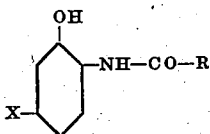
We claim:

1. A color-forming photographic developer comprising a primary aromatic amino developing agent and a phenol coupler having the general formula:



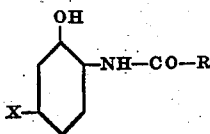
where X is an alkyl radical and R is selected from the class consisting of alkyl and aryl groups.

2. A color-forming photographic developer comprising a primary aromatic amino developing agent and a phenol coupler having the general formula:



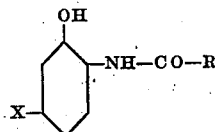
where X is an alkyl radical and R is an alkyl radical.

3. A color-forming photographic developer comprising a primary aromatic amino developing agent and a phenol coupler having the general formula:



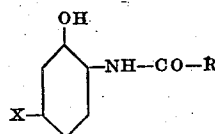
where X is an alkyl radical and R is an aryl radical.

4. The method of producing a colored photographic image in a gelatino-silver halide emulsion layer, which comprises exposing and developing it with a primary aromatic amino developing agent in the presence of a phenol coupler having the general formula:



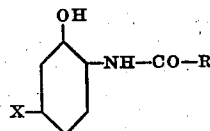
where X is an alkyl radical and R is selected from the class consisting of alkyl and aryl groups.

5. A photographic emulsion for forming colored images comprising a water-permeable carrier containing a sensitive silver halide and a phenol coupler having the general formula:



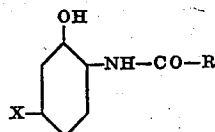
where X is an alkyl radical and R is selected from the class consisting of alkyl and aryl groups.

6. The method of producing a colored photographic image in a gelatino silver halide emulsion layer which comprises exposing and developing it with a primary aromatic amino developing agent in the presence of a phenol coupler having the general formula:



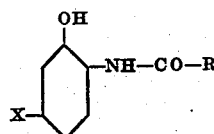
where X is an alkyl radical and R is an alkyl radical.

7. The method of producing a colored photographic image in a gelatino silver halide emulsion layer which comprises exposing and developing it with a primary aromatic amino developing agent in the presence of a phenol coupler having the general formula:



where X is an alkyl radical and R is an aryl radical.

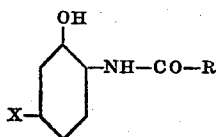
8. The method of producing a colored photographic image in a gelatino silver halide emulsion layer which comprises exposing and developing it with a primary aromatic amino developing agent in the presence of a phenol coupler having the general formula:



where X is an alkyl radical and R is an aryloxy alkyl radical.

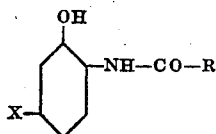
9. The method of producing a colored photographic image in a gelatino silver halide emulsion layer which comprises exposing and developing it with a primary aromatic amino developing

agent in the presence of a phenol coupler having the general formula:



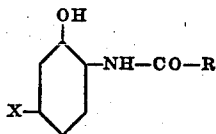
where X is an alkyl radical and R is an aryloxy aryl radical.

10. A photographic emulsion for forming colored images comprising a water-permeable carrier containing a sensitive silver halide and a phenol coupler having the general formula:



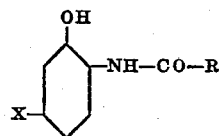
where X is an alkyl radical and R is an alkyl radical.

11. A photographic emulsion for forming colored images comprising a water-permeable carrier containing a sensitive silver halide and a phenol coupler having the general formula:



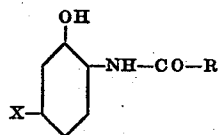
where X is an alkyl radical and R is an aryl radical.

12. A photographic emulsion for forming colored images comprising a water-permeable carrier containing a sensitive silver halide and a phenol coupler having the general formula:



where X is an alkyl radical and R is an aryloxy alkyl radical.

13. A photographic emulsion for forming colored images comprising a water-permeable carrier containing a sensitive silver halide and a phenol coupler having the general formula:



where X is an alkyl radical and R is an aryloxy aryl radical.

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WILLARD D. PETERSON.