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2,367,531

ACYLAMINOPHENOL PHOTOGRAPHIC COUPLERS

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11 Claims. (Cl. 95—6)

This invention relates to photographic color forming compounds and particularly to color forming coupler compounds comprising certain acylamino phenols.

The formation of colored photographic images by coupling the development product of aromatic amino developing agents with color forming or coupling compounds is well known. In these processes the subtractive process of color formation is ordinarily used and the image dyes are intended to be of complementary primary colors, cyan or blue-green, magenta and yellow. The couplers which produce the cyan dyes are usually phenols or naphthols, those producing the magenta dyes are ordinarily pyrazolones or cyanoacetyl compounds and those producing the yellow dyes are ordinarily compounds containing a methylene group having two carbonyl groups attached to it. The dyes produced by coupling are azomethines, indamines or indophenols depending upon the composition of the coupler and of the developer.

The principal disadvantages which have been encountered in the use of dyes of this type are undesirable light transmission characteristics and instability of the dyes to heat and light. The most desirable dyes would be those which transmit two of the primary colors completely and absorb the third primary color completely. For example, the cyan or blue-green dye would absorb red light completely and transmit blue and green light completely. It should retain these transmission characteristics over a long period of time and should withstand reasonable exposure to heat and light without appreciable fading or loss of its light transmission characteristics. Many of the available couplers, however, have been found not to produce dyes having these desirable characteristics.

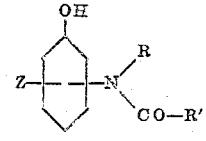
Many of the couplers have been incorporated in photographic emulsion layers in an insoluble or dispersed state and react with the developer upon photographic development to produce a dye image. In such cases it is usually impractical to remove the unused coupler from the emulsion layer after formation of the dye image. Frequently this unused coupler tends to darken or "print out" on exposure of the finished picture to light and this has the effect of darkening the highlights of the picture.

It is, therefore, an object of the present invention to provide novel photographic coupler compounds producing dyes which have desirable properties with respect to heat and light stability. A further object is to provide novel couplers capable of producing blue-green dye images in photographic emulsion layers. A still further object is to provide novel couplers which may be incorporated in photographic emulsion layers. A still further object is to provide novel couplers which may be incorporated in photographic emulsion layers and which do not darken appreciably upon exposure of the finished picture to light. Other objects will appear from the following description of our invention.

These objects are accomplished according to our invention by the use, as coupler compounds, of certain acylamino phenols, especially phenoxyphenylacylamino phenols and phenoxyalkylacylamino phenols.

The couplers of our invention may be incorporated in a photographic emulsion layer by dissolving them in an alkaline solution and mixing the solution with the emulsion. According to the preferred embodiment of our invention, however, the coupler is dissolved in a water-insoluble, water-permeable material and the solution is dispersed in a silver halide photographic emulsion having a water soluble colloid, such as gelatin, as the carrier material. Emulsions produced in this way have certain advantages which will be pointed out more particularly hereinafter.

The couplers which we propose to use have the following general composition:



where R is H, alkyl, or aryl and R' is alkyl or aryl with or without substituents. Other substituents (Z) may or may not be present in the aminophenol nucleus, for example, alkyl, aryl or halogen.

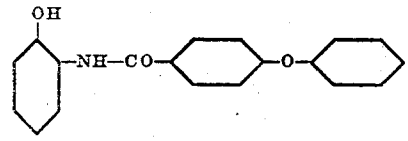
We prefer to use couplers in which R' in the formula above is a phenoxyphenyl or a phenoxyalkyl group. Such couplers have been found to be quite stable to the action of light and produce dyes having excellent transmission and heat stability characteristics.

A further requirement considered necessary with these couplers, as with all couplers of the phenol class which react with the development product of aromatic amino developers, is that the ortho-position or the para position with respect to the phenolic hydroxyl group be unsubstituted or substituted with a readily replaceable group. In the general formula above, we have indicated that there may be an alkyl or or halogen substituent in the phenol nucleus. When the substituent is halogen, it may be present even in the para position with respect to the phenolic hydroxyl group since halogen atoms are replaceable in the coupling reaction. It is de-

sirable, therefore, that the position para to the phenolic hydroxyl group be unoccupied by an irreplaceable group.

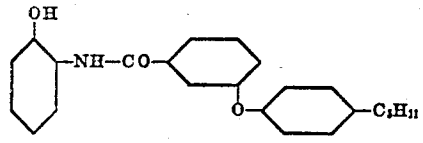
The following compounds illustrate the general class which we have found suitable for use as couplers:

(1)



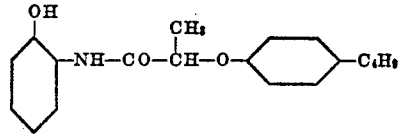
2-(4'-phenoxybenzoylamino)-phenol

(2)



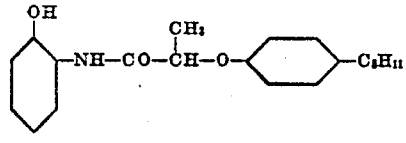
2-(4''-tert. amyl-3'-phenoxybenzoylamino) phenol

(3)



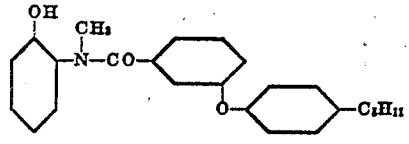
2-[α-(4'-tert. butylphenoxy)-propionylamino]-phenol

(4)



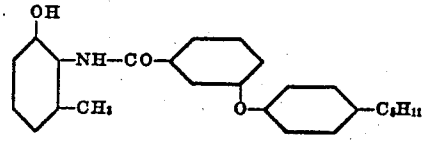
2-[α-(4'-tert. amyl)-phenoxypropionylamino]-phenol

(5)



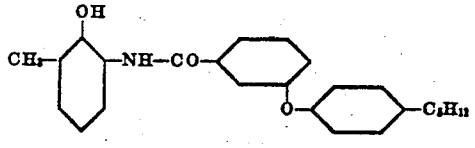
2-(n-methyl-n-4''-tert. amyl-3'-phenoxybenzoylamino)-phenol

(6)



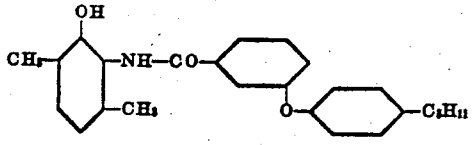
2-(4''-tert. amyl-3'-phenoxybenzoylamino)-3-methyl-1-phenol

(7)



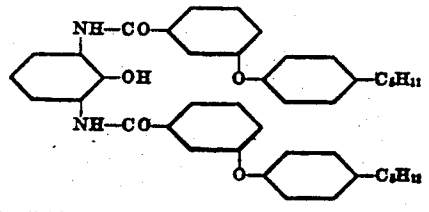
2-(4''-tert. amyl-3'-phenoxybenzoylamino)-6-methyl-1-phenol

(8)



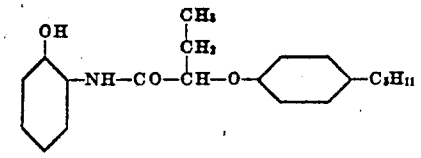
2-(4''-tert. amyl-3'-phenoxybenzoylamino)-3,6-dimethylphenol

(9)



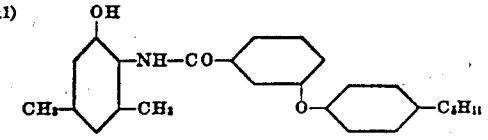
2,6-di-(4''-tert. amyl-3'-phenoxybenzoylamino)-1-phenol

(10)



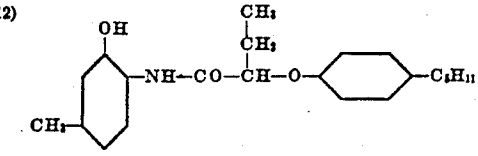
2-α-(4'-tert. amylphenoxy)-butyryl-amino-1-phenol

(11)



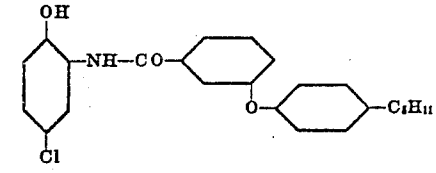
2-(4''-tert. amyl-3'-phenoxybenzoylamino)-3,5-dimethyl-1-phenol

(12)



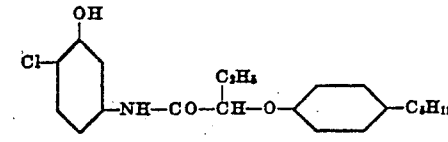
2-[α-(4'-tert. amylphenoxy)-n-butyrylamino]-5-methyl-1-phenol

(13)



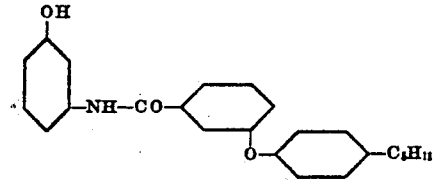
2-(4''-tert. amyl-3'-phenoxybenzoylamino)-4-chloro-1-phenol

(14)



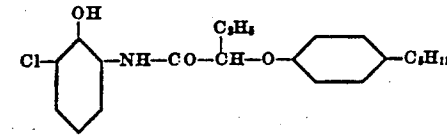
2-[α-(4'-tert. amylphenoxy)-n-butyrylamino]-6-chloro-phenol

(15)



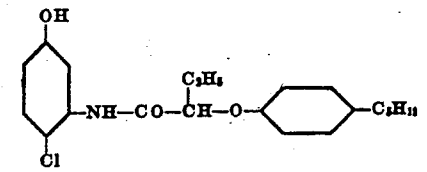
2-(4''-tert. amyl-3'-phenoxybenzoylamino)-phenol

(16)



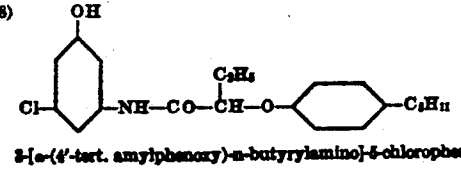
2-[α-(4'-tert. amyl-phenoxy)-n-butyrylamino]-6-chlorophenol

(17)



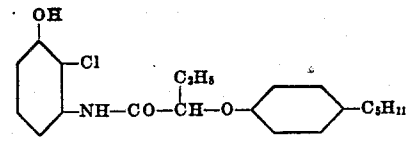
2-[α-(4'-tert. amylphenoxy)-n-butyrylamino]-4-chlorophenol

(18)



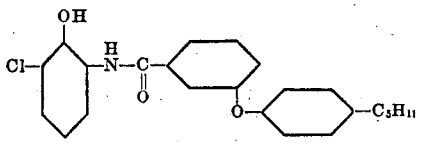
2-[α-(4'-tert. amylphenoxy)-n-butyrylamino]-5-chlorophenol

(19)



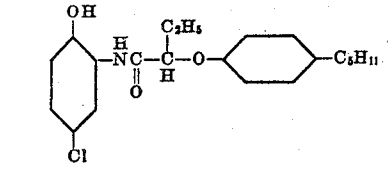
3 [α-(4'-tert. amylphenoxy)-n-butyrylamino]-2-chlorophenol

(20)



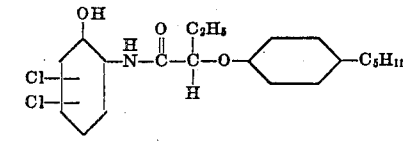
2-(4''-tert. amyl-3'-phenoxybenzoylamino)-6-chlorophenol

(21)



2-α(4'-tert. amylphenoxybutyrylamino)-4-chlorophenol

(22)

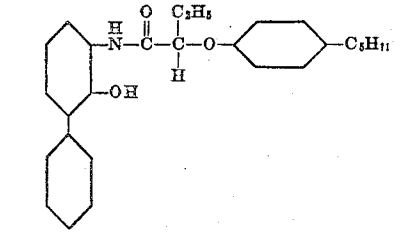


2-α(4'-tert. amylphenoxybutyrylamino)-x.x-dichlorophenol

(23) Prepared from 2-α(4'-tert. amylphenoxybutyrylamino) phenol by chlorination with sulfuryl chloride

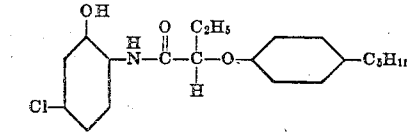
2-α(4'-tert. amylphenoxybutyrylamino) tetrachlorophenol

(24)



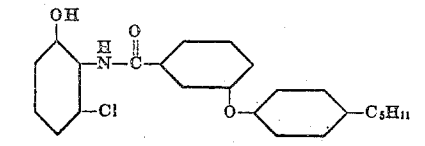
3-(α-[4'-tert.amylphenoxy]-butyrylamino)-2-hydroxy diphenyl

(25)



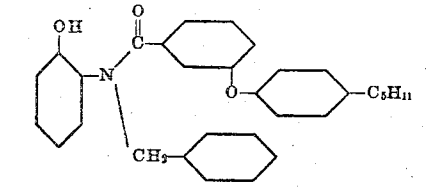
2-α(4'-tert. amylphenoxybutyryl amino)-5-chlorophenol

(26)



2-(4''-tert. amyl-3'-phenoxybenzoylamino)-3-chlorophenol

(27)



2-(N-[4''-tert. amyl-3'-phenoxybenzyl]-N-benzoylamino)-phenol

These couplers are produced by replacement of one of the hydrogen atoms of the amine group of the aminophenol by an acyl group and further substitution in the acyl group. For example, 1 mole of acid chloride may be condensed with 2 moles of the appropriate amine.

While our couplers may be incorporated directly in photographic emulsion layers from alkaline solution, we prefer to dissolve them in a water-insoluble, water-permeable solvent and to disperse the resulting solution in the emulsion layer. Water-insoluble, water-permeable solvents for the couplers include materials such as cellulose esters, natural and synthetic resins, and high boiling crystalloidal materials such as triphenyl phosphate. Methods for the incorporation of couplers in this way are described in Martinez U. S. Patent 2,269,158, granted January 6, 1942, Mannes and Godowsky U. S. Patent 2,304,940 granted December 15, 1942, and Jelley and Vittum U. S. Patent 2,322,027, granted June 15, 1943.

The following examples illustrate our invention:

Example 1

For the incorporation of a coupler in an emulsion by dissolving it in a water-permeable, water-insoluble solvent and dispersing the resulting solution in the emulsion the following procedure may be used:

1 gram of 2-(4''-tert. amyl-3'-phenoxybenzoylamino)-phenol is dissolved in a mixture of 4 cc. of N-n-amylphthalimide and 50 cc. of ethyl acetate. This solution is emulsified with a solution of 0.2 gram of sodium lauryl sulfate in 60 cc. of water by passing the mixture several times through a colloid mill. The ethyl acetate and part of the water are evaporated from the emulsion by heating on a steam bath while stirring, leaving a fine dispersion of the solution of coupler in N-n-amylphthalimide. This dispersion is added to 100 cc. of a gelatino-silver halide emulsion and coated in the usual manner.

After exposure, this emulsion may be developed in the following solution:

2-amino-5-diethylaminotoluene HCl	grams	2
Sodium sulfite	do	2
Sodium carbonate	do	20
Potassium bromide	do	2
Water to	liter	1

After development it may be fixed in the usual acid-alum fixing bath, washed and the silver removed by successive treatments in ferricyanide-bromide solutions and hypo.

Example 2

The direct incorporation of a coupler in an emulsion is illustrated by the following example:

A solution is prepared containing 1 gram of 2-(4''-tert. amyl-3'-phenoxybenzoylamino)-3,5-dimethyl-1-phenol, 13 cc. of 95% ethyl alcohol and 1 cc. of 20% sodium hydroxide solution. This solution is mixed with 100 cc. of a melted red-sensitized gelatino-silver bromide emulsion and to the resulting mixture is added enough 10% citric acid solution to bring the pH of the emulsion back to its original value. This emulsion is then coated in the normal manner and may be processed as described in Example 1.

The couplers proposed according to our invention yield dyes having better absorption characteristics and fastness to light and heat than dyes from previously known couplers suitable for addition to emulsion layers to produce cyan dyes. This stability of the coupler is particularly evident where the coupler is incorporated in the emulsion as a dispersion in a water-insoluble, water-permeable carrier material as described in Example 1. The dyes resulting from the incorpora-

tion of a coupler in this way are appreciably more stable to heat and light than those incorporated in the emulsion by direct mixing as described in Example 2. Another important advantage of the couplers of our invention is that they do not darken upon exposure of the finished picture to light. This is important because in those processes where couplers are added to the emulsion layers and the unused portion cannot easily be removed, the finished pictures contain residual coupler. If the coupler turns dark upon exposure to light, the finished picture will darken in the highlights on exposure to light and degrade the purity of the resulting picture.

In the development of exposed silver halide emulsion layers using the couplers of our invention, any color-forming developer containing a primary amino group may be used. These include developers having two primary amino groups as well as those having one of the amino groups substituted or having substituents in the ring such as alkyl phenylenediamines. These compounds are usually employed 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, dimethyl-p-phenylene diamine hydrochloride and 2-amino-5-diethylaminotoluene hydrochloride. The p-aminophenols and their substitution products may also be used where the amino group is unsubstituted. All of these developers have an unsubstituted amino group which enables the oxidation product of the developer to couple with the color forming compounds to form a dye image.

Our couplers may be incorporated in gelatino-silver halide emulsion layers or in silver halide emulsions in other carriers such as water-soluble 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 on the support or as superposed layers on one or 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 image may be developed, bleached and developed to color images in superposed layers as described, for example, in Mannes and Godowsky U. S. Patent No. 2,113,329. Since the couplers of our invention produce cyan dyes, they will usually be incorporated in the red-sensitive emulsion layer of a multilayer coating although they may be incorporated in layers otherwise sensitized when false colors are to be produced.

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 emulsion comprising a gelatino-silver halide layer containing dispersed particles of a water-insoluble, water-permeable material having dissolved therein an acylamino phenol selected from the class consisting of phenoxyphenyl acylamino phenols and phenoxyalkyl acylamino phenols capable of coupling with the development product of primary aromatic amino developing agents to form a heat-stable dye.

2. A color-forming photographic emulsion comprising a gelatino-silver halide layer containing dispersed liquid particles of a water-insoluble, water-permeable material having dissolved therein an acylamino phenol selected from the class consisting of phenoxyphenyl acylamino phenols and phenoxyalkyl acylamino phenols capable of coupling with the development product of primary aromatic amino developing agents to form a heat-stable dye.

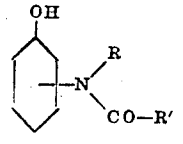
3. A color-forming photographic emulsion comprising a gelatino-silver halide layer containing dispersed particles of a water-insoluble, water-permeable material having dissolved therein a phenoxyphenyl acylamino phenol coupler capable of coupling with the development product of primary aromatic amino developing agent to form a heat-stable dye.

4. A color-forming photographic emulsion comprising a gelatino-silver halide layer containing dispersed particles of a water-insoluble, water-permeable material having dissolved therein a phenoxyalkyl acylamino phenol coupler capable of coupling with the development product of primary aromatic amino developing agents to form a heat-stable dye.

5. A color-forming photographic emulsion comprising a gelatino-silver halide layer containing dispersed liquid particles of a water-insoluble, water-permeable material having dissolved therein a phenol coupler having a phenoxyphenyl acylamino group in a position other than the para position with respect to the phenolic hydroxyl group.

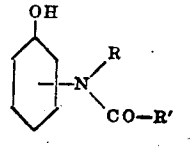
6. A color-forming photographic emulsion comprising a gelatino-silver halide layer containing dispersed liquid particles of a water-insoluble, water-permeable material having dissolved therein a phenol coupler having a phenoxyalkyl acylamino group in a position other than the para position with respect to the phenolic hydroxyl group.

7. A gelatino-silver halide emulsion for color photography containing a substantially non-diffusing, non-obscurative color-forming compound having the following structural formula:



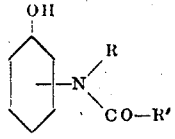
where R is selected from the class consisting of hydrogen, alkyl groups, and aryl groups, and R' is selected from the class consisting of phenoxyphenyl and phenoxyalkyl groups, and the position para to the phenolic hydroxyl group is unoccupied by an irreplaceable group.

8. The method of producing a blue-green photographic image in a gelatino-silver halide emulsion layer which comprises exposing the layer and developing it with a primary aromatic amino developing agent in the presence of a coupler compound present in said emulsion layer prior to development, said coupler compound having the formula:



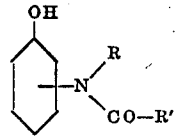
where R is selected from the class consisting of hydrogen, alkyl groups, and aryl groups, and R' is selected from the class consisting of phenoxyphenyl and phenoxyalkyl groups, and the position para to the phenolic hydroxyl group is unoccupied by an irreplaceable group.

9. The method of producing a blue-green photographic image in a gelatino-silver halide emulsion layer which comprises exposing the layer and developing it with a primary aromatic amino developing agent in the presence of a coupler compound present in said emulsion layer prior to development, said coupler compound having the formula:



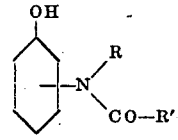
where R is hydrogen and R' is selected from the class consisting of phenoxyphenyl and phenoxyalkyl groups, and the position para to the phenolic hydroxyl group is unoccupied by an irreplaceable group.

10. The method of producing a blue-green photographic image in a gelatino-silver halide emulsion layer which comprises exposing the layer and developing it with a primary aromatic amino developing agent in the presence of a coupler compound present in said emulsion layer prior to development, said coupler compound having the formula:



where R is hydrogen and R' is a phenoxyphenyl group, and the position para to the phenolic hydroxyl group is unoccupied by an irreplaceable group.

11. The method of producing a blue-green photographic image in a gelatino-silver halide emulsion layer which comprises exposing the layer and developing it with a primary aromatic amino developing agent in the presence of a coupler compound present in said emulsion layer prior to development, said coupler compound having the formula:



where R is hydrogen and R' is a phenoxyalkyl group and the position para to the phenolic hydroxyl group is unoccupied by an irreplaceable group.

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