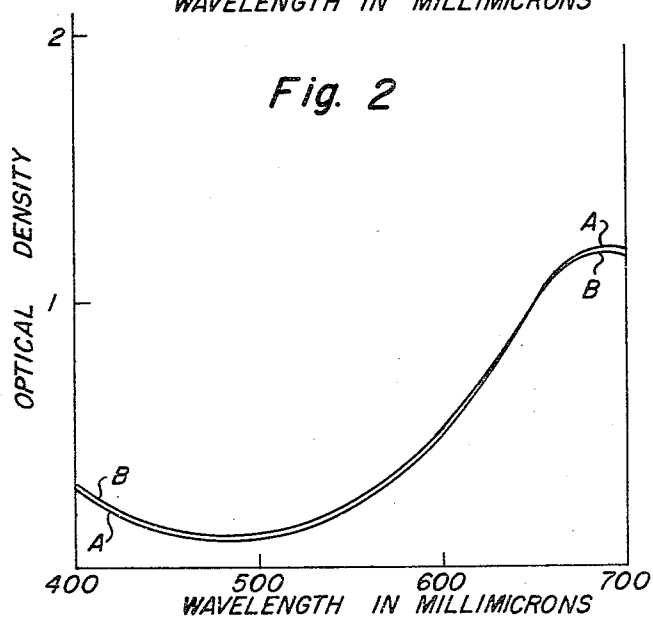
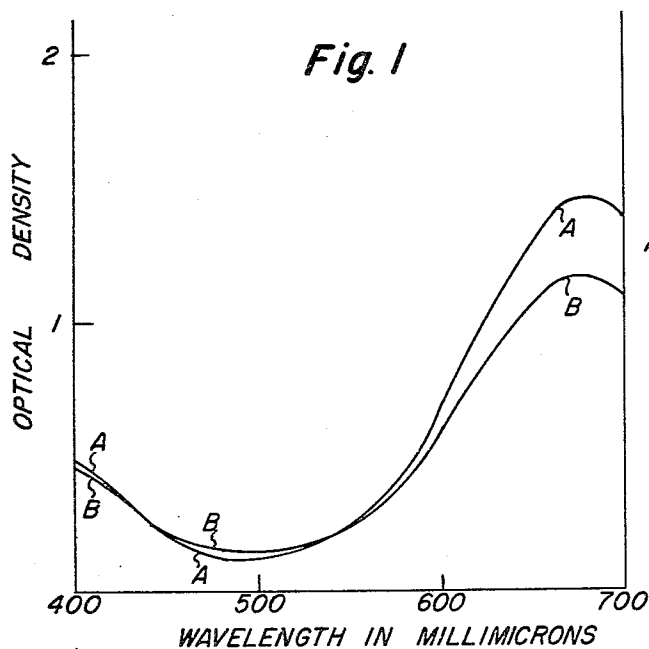


Nov. 27, 1956

I. F. SALMINEN ET AL  
DIACYLAMINOPHENOL COUPLERS

2,772,162

Filed Nov. 3, 1954



ILMARI F. SALMINEN  
CHARLES R. BARR  
INVENTORS

BY *Daniel J. Wayne*  
*R. Frank Smith*  
ATTORNEYS

1

2,772,162

## DIACYLAMINOPHENOL COUPLERS

Ilmari F. Salminen and Charles R. Barr, Rochester, N. Y.,  
assignors to Eastman Kodak Company, Rochester,  
N. Y., a corporation of New Jersey

Application November 3, 1954, Serial No. 466,570

15 Claims. (Cl. 96-55)

This invention relates to color photography and particularly to certain diacylaminophenol coupler compounds.

The formation of colored photographic images by coupling the development product of primary 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, magenta and yellow. The couplers used to produce the cyan dyes are usually phenols or naphthols and produce indophenol dyes upon coupling with the development product of the developing agent.

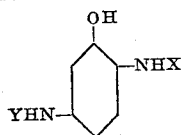
Aminonaphthols have been used as cyan-forming couplers but the heat stability of the dye images formed from them is usually low. Acylaminophenols of the type described in Salminen and Weissberger U. S. Patent 2,423,730, granted July 8, 1947, have also been used, but the dyes produced from these couplers have a rather high absorption in the blue spectral region and also have a somewhat low degree of heat stability. It is, of course, desirable for the absorption of the cyan dyes to be low in the blue region and for the heat stability to be as high as possible.

It is, therefore, an object of the present invention to provide novel photographic coupler compounds for producing cyan dye images. A further object is to provide coupler compounds which produce cyan dyes having low blue light absorption. A still further object is to provide coupler compounds which produce dyes having a high degree of heat stability. Other objects will appear from the following description of our invention.

These objects are accomplished according to our invention by the use of certain diacylaminophenol described below, as coupler compounds.

The accompanying drawing is a reproduction of spectral absorption curves of dye images produced from a typical coupler of the present invention (Fig. 2) and comparison curves of a dye image made from a prior art coupler (Fig. 1), before and after subjecting them to fading tests.

Couplers of the following structure are useful according to our invention:



in which

X=fatty acid acyl  
aromatic carboxylic acyl  
aryloxy-substituted fatty acid acyl

Y=fatty acid acyl  
aromatic carboxylic acyl  
aryloxy-substituted fatty acid acyl  
phenylcarbamyl fatty acid acyl  
furoyl

2

Specific compounds which we may use are those in which X and Y have the structure shown below:

1. 

2-acetamido-5-[alpha-(2,4-di-tert-amylphenoxy)acetamido]phenol
2. 

5-benzamido-2-[gamma-(2,4-di-tert-amylphenoxy)butyramido]phenol
3. 

2-benzamido-5-[gamma-(2,4-di-tert-amylphenoxy)butyramido]phenol
4. 

5-benzamido-2-[alpha-(2,4-di-tert-amylphenoxy)butyramido]phenol
5. 

2,5-di-acetamido-phenol
6. 

2-caproylamido-5-[gamma-(2,4-di-tert-amylphenoxy)butyramido]phenol
7. 

2,5-di-laurylamido-phenol
8. 

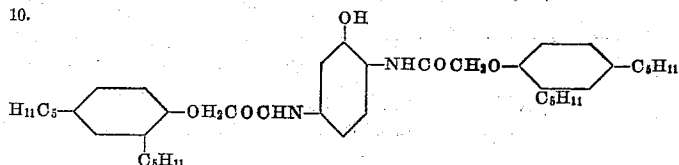
2-lauroylamido-5-furoylamido-phenol
9. 

2,5-di-palmitoylamido-phenol

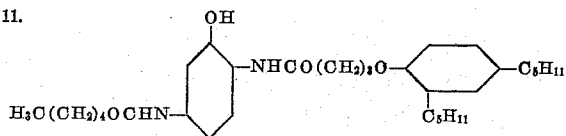
3

4

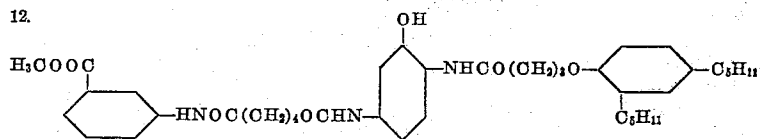
10.

2,5-di- $\alpha$ -(2,4-di-tert-amylphenoxy)-acetamido-phenol

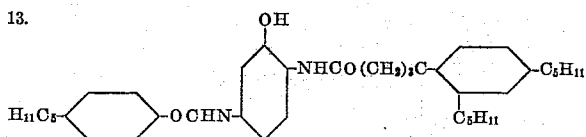
11.

2-[ $\gamma$ -(2,4-di-tert-amylphenoxy)butyramido]-5-caproylamido-phenol

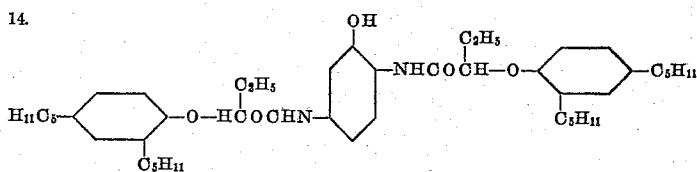
12.

2-[ $\gamma$ -(2,4-di-tert-amylphenoxy)-butyramido]-5-[ $\delta$ -(3,5-dicarboxyphenylcarbamyl)valeramido]phenol

13.

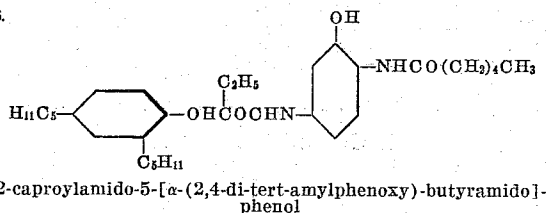
2-[ $\gamma$ -(2,4-di-tert-amylphenoxy)-butyramido]-5-p-tert-amylbenzamido-phenol

14.

2,5-di- $\alpha$ -(2,4-di-tert-amylphenoxy)butyramido-phenol

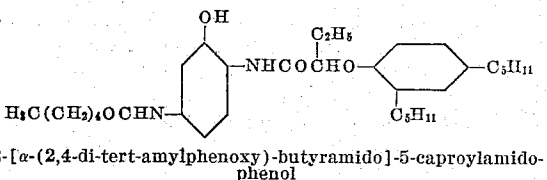
10 16.

15

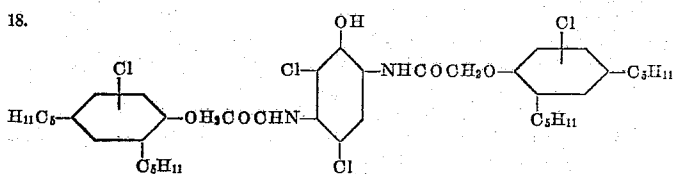
2-caproylamido-5-[ $\alpha$ -(2,4-di-tert-amylphenoxy)-butyramido]-phenol

30 17.

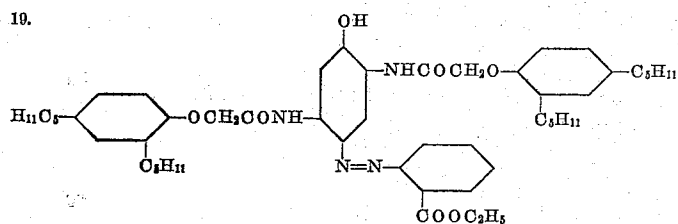
35

2-[ $\alpha$ -(2,4-di-tert-amylphenoxy)-butyramido]-5-caproylamido-phenol

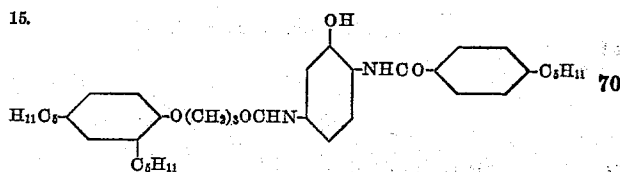
18.

2,5-bis[ $\alpha$ -( $\alpha$ -chloro-2,4-di-tert-amylphenoxy)-acetamido]-4,6-dichlorophenol

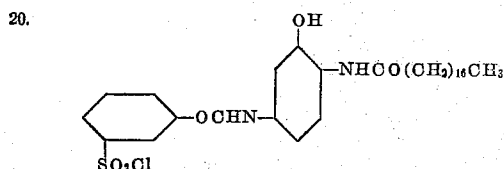
19.

2,5-di-[ $\alpha$ -(2,4-di-tert-amylphenoxy)acetamido]-4-(2-carbethoxyphenylazo)-phenol

15.

2-p-tert-amylbenzamido-5-[ $\gamma$ -(2,4-di-tert-amylphenoxy)butyramido]-phenol

20.



5-(3-chlorosulfonylbenzamido)-2-stearamidophenol

5

The couplers of our invention are produced by treating 2-amino-5-nitrophenol (Beil., 13, 390) with the appropriate acyl chloride, reducing the nitro group to an amine and then treating with the same or a different acyl chloride. The preparation of the compounds of our invention is illustrated by the following examples:

*Coupler 1.—2-acetamido-5-[ $\alpha$ -(2,4-di-tert-amylphenoxy)-acetamido]-phenol*

To a solution of 1 part of 2-acetamido-5-aminophenol and 1.5 parts of anhydrous sodium acetate in 20 volumes of glacial acetic acid was added a solution of 2 parts of 2,4-di-tert-amylphenoxyacetyl chloride in 10 volumes of glacial acetic acid. The temperature rose from 25–32° and a white solid separated. The mixture was stirred for one-half hour and poured into 100 volumes of water. The gummy solid was collected and recrystallized from 25 volumes of absolute ethyl alcohol and dried.

*2-acetamido-5-nitrophenol*

To a mixture of 6 parts of 2-amino-5-nitrophenol (Beil., 13, 390), 8 parts of anhydrous sodium acetate, and 60 volumes of glacial acetic acid was added, with stirring, a solution of 3 parts of acetyl chloride in 20 volumes of glacial acetic acid. The reaction mixture was stirred for one hour, and the product which separated was filtered, washed with water, and dried.

*2-acetamido-5-aminophenol*

In a 500-cc. low-pressure reduction bottle was placed a solution of one part of 2-acetamido-5-nitrophenol in 25 volumes of dioxane. To this solution was added one part of Raney nickel catalyst, and the bottle was placed on the Parr hydrogenation apparatus. The hydrogen pressure was brought up to 50 lb. and shaking commenced. The reduction was complete after approximately one hour. The mixture was filtered, and the filtrate was concentrated in vacuo on steam. The solid residue was dried to constant weight in air at room temperature.

*2,4-di-tert-amylphenoxy acetic acid*

In a 3–1 three-necked flask equipped with a stirrer, thermometer, and reflux condenser was placed 40 cc. of water and 660 cc. of denatured alcohol, and 80 g. (2.0 moles) of sodium hydroxide. The solution was stirred, 234 g. (1.0 mole) of redistilled 2,4-di-tert-amylphenol was added and the solution refluxed for five minutes. It was then cooled to 60° and 94.5 g. (1.0 mole) of chloroacetic acid added. The mixture was refluxed with stirring for three hours, cooled to room temperature, diluted with 1 liter of ice water and acidified with 200 cc. of concentrated hydrochloric acid. The di-*tert*-amylphenoxy acetic acid, separated as an orange-brown oil, was extracted with 200 cc. of ether and the wet ether layer concentrated under reduced pressure on the steam-bath. The heavy oil was vacuum distilled, collecting at 172–176° at 1 mm./Hg. Yield: 127 g. (43%). The viscous oil soon solidified to a wax-like solid. The di-*tert*-amylphenoxy acetic acid can be purified by recrystallization from hexane, M. P. 116–117°; snow-white powder.

*$\alpha$ -(2,4-di-tert-amylphenoxy)acetyl chloride*

Eighty grams (0.27 mole of 2,4-di-tert-amylphenoxy) acetic acid was melted on the steam-bath and cooled to 50°. To the semi-solid was added 88 g. (0.74 mole) of thionyl chloride (redistilled over quinoline) and the mixture stirred until all of the solid dissolved. The clear liquid was placed in a 500 cc. flask equipped with stirrer and thermometer and heated with stirring at 40–45° for 4 hours. Excess thionyl chloride was removed by warming under reduced pressure at a water pump. The product was collected at 143–146°/2 mm. Yield 65 g. (76.5%).

6

*Coupler 2.—5-benzamido-2-[ $\gamma$ -(2,4-di-tert-amylphenoxy)butyramido]-phenol*

To a solution of 2 parts of 5-amino-2-[ $\gamma$ -(2,4-di-tert-amylphenoxy)butyramido]phenol and 1.3 parts of quinoline in 36 volumes of dioxane was added 0.71 part of benzoyl chloride in 11 volumes of dioxane. The temperature rose from 26–31°. The clear reaction mixture was stirred for one-half hour and poured into 400 volumes of dilute hydrochloric acid. The solid product was collected and recrystallized from 114 volumes of acetonitrile and dried.

*$\gamma$ -(2,4-di-tert-amylphenoxy)butyric acid*

In a suitable vessel provided with stirrer, thermometer, and coil condenser were placed 500 volumes of absolute methyl alcohol and 46 parts of sodium. To the sodium methoxide thus made was added 468 parts of 2,4-di-tert-amylphenol and stirred 15 minutes. Butyrolactone (198 parts) was added and the mixture refluxed 15 minutes. The condenser was inverted and the excess methyl alcohol distilled up to 115°. Concentrated hydrochloric acid (500 volumes) in 1400 volumes of distilled water was added continuously with stirring, and the acidic mixture poured into a glass tray to cool. The solid was washed and filtered, 650 parts being obtained. The product was crystallized from 1500 volumes of ligroin, 300 grams of product melting at 98–100° being obtained.

*$\gamma$ -(2,4-di-tert-amylphenoxy)butyryl chloride*

In a suitable vessel, provided with a condenser, was placed 32 parts of  $\gamma$ -(2,4-di-tert-amylphenoxy)butyric acid to which was added 22 volumes of thionyl chloride. The mixture was heated for 3 hours at 40°; at the end of this time the excess thionyl chloride was removed under vacuum, the temperature being allowed to reach 55°. The crude acid chloride was purified by distillation, B. P. 165–166°/1 mm.

*2-[ $\gamma$ -(2,4-di-tert-amylphenoxy)butyramido]-5-nitrophenol*

To a solution of 3 parts of 2-amino-5-nitrophenol (Beil., 13, 390), 5 parts of quinoline, and 50 volumes of dioxane was added a solution of 7 parts of  $\gamma$ -(2,4-di-tert-amylphenoxy)butyryl chloride in 10 volumes of dioxane. The reaction mixture was stirred at room temperature for one-half hour, and poured into 300 volumes of dilute hydrochloric acid. The oil which separated solidified on scratching, was filtered, washed with water, and dried.

*5-amino-2-[ $\gamma$ -(2,4-di-tert-amylphenoxy)butyramido]-phenol*

In a 500-cc. low-pressure reduction bottle was placed 10 parts of 2-[ $\gamma$ -(2,4-di-tert-amylphenoxy)butyramido]-5-nitrophenol in 250 volumes of absolute ethyl alcohol. To this solution was added one part of Raney nickel catalyst, and the bottle was placed on the Parr hydrogenation apparatus. The hydrogen pressure was brought up to 50 lb. The reduction was completed after approximately one hour. The mixture was filtered, and the filtrate was concentrated in vacuo on steam. The residual solid was slurried in petroleum ether, and dried.

*Coupler 3.—2-benzamido-5-[ $\gamma$ -(2,4-di-tert-amylphenoxy)butyramido]-phenol*

To a solution of 4.5 parts of 5-amino-2-benzamido-phenol in 100 volumes of dioxane were added simultaneously at 10° C. a solution of 5 parts of quinoline in 10 volumes of dioxane and a solution of 6.8 parts of  $\gamma$ -(2,4-di-tert-amylphenoxy)butyryl chloride in 10 volumes of dioxane. The temperature rose to 20° C. The clear reaction mixture was left to stand for 2 days and

poured into 500 volumes of dilute hydrochloric acid. The solid product was collected and recrystallized from 150 volumes of acetonitrile and dried.

*2-benzamido-5-nitrophenol*

To a solution of 3 parts of 2-amino-5-nitrophenol (Beil., 13, 390) and 5 parts of quinoline in 60 volumes of dioxane was added a solution of 3 parts of benzoyl chloride in 10 volumes of dioxane. The mixture was stirred for approximately one hour, after which time it was poured into 250 volumes of dilute hydrochloric acid. The solid which separated was filtered, washed with water, and dried.

*5-amido-2-benzamidophenol*

In a 500-cc. low-pressure reduction bottle was placed 10 parts of 2-benzamido-5-nitrophenol in 200 volumes of dioxane. To this solution was added one part of Raney nickel catalyst, and the bottle was placed on the Parr hydrogenation apparatus. The hydrogen pressure was brought up to 50 lb. The reduction was completed after approximately one hour. The mixture was filtered, and the filtrate was kept under CO<sub>2</sub> until the amine was used in preparing the final coupler.

*Coupler 4.—5-benzamido-2-[α-(2,4-di-tert-amylphenoxy)butyramido]-phenol*

To a solution of 7 parts of 5-amino-2-[α-(2,4-di-tert-amylphenoxy)butyramido]phenol and 4 parts of quinoline in 50 volumes of dioxane was added a solution of 2.3 parts of benzoyl chloride in 10 volumes of dioxane. The temperature rose from 30–38°. The clear reaction mixture was stirred for 3 hours and poured into 300 volumes of dilute hydrochloric acid. The gummy product was collected and recrystallized from 125 volumes of acetonitrile and dried.

*2-[α-(2,4-di-tert-amylphenoxy)butyramido]-5-nitrophenol*

To a solution of 3 parts of 2-amino-5-nitrophenol (Beil., 13, 390) and 5 parts of quinoline in 40 volumes of dioxane was added a solution of 6 parts of α-(2,4-di-tert-amylphenoxy)butyryl chloride (see Fierke and Chechak Serial No. 476,561 filed December 20, 1954) in 20 volumes of dioxane. The mixture was stirred for approximately one hour and left standing at room temperature overnight, after which time it was poured into 250 volumes of dilute hydrochloric acid. The solid which separated was filtered, washed with water, and dried.

*5-amino-2-[α-(2,4-di-tert-amylphenoxy)butyramido]-phenol*

In a 500-cc. low-pressure reduction bottle was placed 10 parts of 2-[α-(2,4-di-tert-amylphenoxy)butyramido]-5-nitrophenol in 100 volumes of dioxane. To this solution was added 1 part of Raney nickel catalyst, and the bottle was placed on the Parr hydrogenation apparatus. The hydrogen pressure was brought up to 50 lb., and the reduction was completed after approximately one hour. The mixture was filtered, and the filtrate was kept under CO<sub>2</sub> until the amine was used in preparing the final coupler.

*Coupler 10.—2,5-di-[α-(2,4-di-tert-amylphenoxy)acetamido]-phenol*

To a solution of 8 parts of 5-amino-2-[α-(2,4-di-tert-amylphenoxy)acetamido]phenol and 5 parts of quinoline in 50 volumes of dioxane was added 6 parts of α-(2,4-di-tert-amylphenoxy)acetyl chloride in 20 volumes of dioxane. The mixture was left standing at room temperature overnight, during which time some solid separated. The mixture was then poured into 125 volumes of dilute hydrochloric acid, and the solid which separated was filtered, washed with water, and dried.

*2-[α-(2,4-di-tert-amylphenoxy)acetamido]-5-nitrophenol*

To a solution of 3 parts of 2-amino-5-nitrophenol (Beil., 13, 390) and 5 parts of quinoline in 50 volumes of dioxane was added 6 parts of α-(2,4-di-tert-amylphenoxy)acetyl chloride in 20 volumes of dioxane. The mixture was left standing overnight at room temperature, after which time it was diluted with 250 volumes of dilute hydrochloric acid and a solid separated. This solid was filtered, washed with water, and air-dried.

*5-amino-2-[α-(2,4-di-tert-amylphenoxy)acetamido]-phenol*

In a 500-cc. low-pressure reduction bottle was placed 8 parts of 2-[α-(2,4-di-tert-amylphenoxy)acetamido]-5-nitrophenol in 200 volumes of ethyl acetate. To this solution was added 1 part of Raney nickel catalyst, and the bottle was placed on the Parr hydrogenation apparatus. The hydrogen pressure was brought up to 50 lb., and the reduction was completed after approximately one hour. The mixture was filtered, and the filtrate was concentrated in vacuo and air-dried.

*Coupler 19.—2,5-di-[α-(2,4-di-tert-amylphenoxy)acetamido]-4-(2-carbethoxyphenylazo)phenol*

To the solution of 3 parts of 2,5-di-[α-(2,4-di-tert-amylphenoxy)acetamido]phenol (coupler No. 10) in 25 volumes of pyridine at 0° C. was added a solution of 1 part of o-carbethoxybenzenediazonium chloride in 10 volumes of pyridine. This mixture was left standing at room temperature for one hour, after which time it was diluted with 100 volumes of water. The product which separated was filtered and dried.

*Coupler 20.—5-(3-chlorosulfonylbenzamido)-2-stearamidophenol*

To the solution of 3.9 parts of 5-amino-2-stearamidophenol and 2.6 parts of quinoline in 60 volumes of dioxane was added a solution of 2.5 parts of 3-chlorosulfonylbenzoyl chloride in 15 volumes of dioxane with stirring at 25° C. The temperature rose rapidly to 33° C. and a complete solution resulted. In about five minutes a thick light tan slurry formed. The mixture was left standing at room temperature overnight, after which time the solid was filtered off and slurried in 100 volumes of water and dried. This solid was recrystallized from ethyl acetate.

The remaining compounds were prepared similarly, using the following acyl chlorides: Acetyl chloride for coupler 5, caproyl chloride for couplers 6, 11, 16 and 17, lauroyl chloride for couplers 7 and 8, palmitoyl chloride for coupler 9, furoyl chloride for coupler 8, γ-2,4-di-tert-amylphenoxy butyryl chloride for couplers 6, 11, 12, 13 and 15, α-2,4-di-tert-amylphenoxy butyryl chloride for couplers 14, 16 and 17, p-tert-amylbenzoyl chloride for couplers 13 and 15, chloro-2,4-di-tert-amylphenoxy-acetyl chloride for coupler 18, and δ-3,5-dicarbomethoxy phenyl carbamyl valeryl chloride for coupler 12. This intermediate was prepared as described in U. S. Patent 2,688,544.

The couplers or our invention are preferably incorporated in the photographic emulsion layers by dissolving them in a water-insoluble, water-permeable solvent and dispersing 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 tri-o-cresyl phosphate, di-n-butyl phthalate and 2,4-di-tert-amylphenol. Other coupler solvents described in Jelley and Vittum U. S. Patent 2,322,027, granted June 15, 1943, may be used with our couplers.

The following examples illustrate our invention:

EXAMPLE 1

One gram of coupler No. 11 was dissolved in a mixture of 4 cc. of 2,4-di-tert-amylphenol and 50 cc. of ethyl ace-

tate. This solution was emulsified with a solution of 0.2 g. of sodium lauryl sulfate in 60 cc. of water by passing the mixture several times through the colloid mill. The ethyl acetate and part of the water were evaporated from the emulsion by heating on a steam bath while stirring, leaving a fine dispersion of the solution of coupler with 2,4-di-tert-amylphenol. This dispersion was added to 100 cc. of a gelatino-silver halide emulsion and coated in the usual manner.

After exposure, this emulsion was developed in the following solution:

2-amino-5-diethylaminotoluene HCl.....	grams--	2
Sodium sulfite (desiccated).....	do----	2
Sodium carbonate, monohydrate.....	do----	20
Potassium bromide.....	do----	2
Water to .....	liter--	1

After development, the emulsion was fixed in the usual acid-alum fixing bath, washed, and the silver removed by successive treatments in ferricyanide-bromide solution and hypo.

#### EXAMPLE 2

Certain of the couplers of our invention may be incorporated in the developing solution, where no coupler is present in the emulsion layer as in certain processes. A developing solution suitable for developing the fine image is as follows:

##### A.

2-amino-5-diethylaminotoluene .....	grams--	2
Sodium sulfite, anhydrous .....	do----	2
Sodium carbonate, monohydrate .....	do----	20
Potassium bromide .....	do----	1
Water to .....	liter--	1

##### B.

Coupler No. 5 .....	grams--	2
Sodium hydroxide, 10% solution .....	cc----	10

For use, B is added to A

The value of our couplers in producing dyes which have less blue absorption and which are more stable to heat treatment is illustrated in the drawing. As shown therein, Fig. 1 illustrates the curves obtained upon development of an emulsion layer containing the coupler 2-[ $\alpha$ -(4'-tert. amylphenoxy)-n-butyryl amino]-4-chloro-5-methyl phenol (Compound 15 of U. S. Patent 2,423,730), incorporated in the emulsion and developed as described in Example 1. A illustrates the curve obtained immediately after development and B illustrates the curve obtained after treatment of the emulsion at 140° F. for one week. The blue light absorption between 400 and 500 millimicrons is appreciable in both cases but the red light absorption in the region about 460 to 480 millimicrons is considerably lower after heat storage, showing that the dye has faded to an appreciable extent.

Fig. 2 illustrates the curves obtained upon treatment in an identical manner of an emulsion containing coupler No. 16 of the present invention. In this case, the blue light absorption between 200 and 400 millimicrons is lower than in the previous case and the absorption in the red spectral region has not changed appreciably upon heat treatment from curve A illustrating the absorption of the dye immediately after development to curve B illustrating the dye after heat storage as in the preceding case. This illustrates the improved stability obtained with dyes made from our couplers.

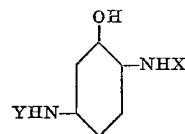
Our couplers may be incorporated in gelatino-silver halide emulsion layers or in silver halide emulsions or other carriers such as organic acid esters of cellulose or synthetic resins. The support may be a transparent medium such as glass or cellulose ester or a non-transparent reflecting medium such as paper or an opaque cellulose ester. The emulsion may be coated as a single

layer on the support or superposed layers may be coated on one or both sides of the support. The superposed layers may be differentially sensitized to form a natural color element in the known manner. Our couplers produce cyan dyes and will usually be incorporated in the red-sensitive emulsion layer of a multi-layer coating or 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.

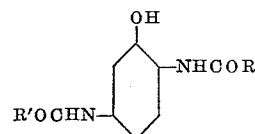
We claim:

1. The method of producing a cyan photographic image in silver halide emulsion layer, which comprises exposing the layer and developing it with a primary aromatic amino developing agent in the presence of a 2,5-diacylaminophenol coupler compound, in which the acyl is derived from carboxylic acid.
2. The method of producing a cyan photographic image in 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 having the formula:



in which X is selected from the class consisting of fatty acid acyl radicals, aromatic carboxylic acyl radicals and aryloxy-substituted fatty acid acyl radicals, and Y is selected from the class consisting of fatty acid acyl radicals, aromatic carboxylic acyl radicals, aryloxy-substituted fatty acid acyl radicals, phenylcarbonyl fatty acid acyl radicals and furoyl radicals.

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



in which R represents an alkyl radical of from 4 to 15 carbon atoms and R' represents an aryloxyalkyl radical in which the alkyl radical contains from 1 to 3 carbon atoms.

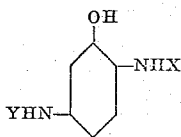
4. The method of claim 3 in which the aryloxy radical is a 2,4-di-tert. amyl phenoxy radical.
5. The method of producing a cyan photographic image in silver halide emulsion layer, which comprises exposing the layer and developing it with a primary aromatic amino developing agent in the presence in said emulsion layer prior to development, of the coupler 2-(2,4-di-tert. amylphenoxybutyramido)-5 - capronylaminophenol.
6. The method of producing a cyan photographic image in silver halide emulsion layer, which comprises exposing the layer and developing it with a primary aromatic amino developing agent in the presence in said emulsion layer prior to development, of the coupler 2-(2,4-di-tert. amylphenoxybutyramido)-5-p-tert. amylbenzoylaminophenol.
7. The method of producing a cyan photographic image in silver halide emulsion layer, which comprises exposing the layer and developing it with a primary aromatic amino developing agent in the presence in said emulsion layer prior to development, of the coupler

11

2-capronylamino - 5 -  $\alpha$  - (2,4-di-tert. amylphenoxybutyramido)-phenol.

8. A color-forming photographic emulsion comprising a gelatino-silver halide emulsion layer containing dispersed particles of a water-insoluble, water-permeable coupler solvent selected from the class consisting of cellulose esters, natural and synthetic resins, and organic crystalloidal materials having a boiling point above about 175° C., having dissolved therein a 2,5-diacylamino-phenol coupler compound in which the acyl is derived from carboxylic acid.

9. A color-forming photographic emulsion comprising a gelatino-silver halide emulsion layer containing dispersed particles of a water-insoluble, water-permeable coupler solvent selected from the class consisting of cellulose esters, natural and synthetic resins, and organic crystalloidal materials having a boiling point above about 175° C., having dissolved therein a coupler compound having the formula:

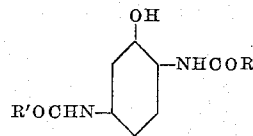


in which X is selected from the class consisting of fatty acid acyl radicals, aromatic carboxylic acyl radicals and aryloxy-substituted fatty acid acyl radicals, and Y is selected from the class consisting of fatty acid acyl radicals, aromatic carboxylic acyl radicals, aryloxy-substituted fatty acid acyl radicals, phenylcarbamyl fatty acid acyl radicals and furoyl radicals.

10. A color-forming photographic emulsion comprising a gelatino-silver halide emulsion layer containing dispersed particles of a water-insoluble, water-permeable

12

coupler solvent having dissolved therein a coupler compound having the formula:



in which R represents an alkyl radical of from 4 to 15 carbon atoms and R' represents an aryloxyalkyl radical in which the alkyl radical contains from 1 to 3 carbon atoms.

11. The emulsion of claim 8 in which the coupler compound is 2-(2,4-di-tert. amylphenoxybutyramido)-5-capronylamino-phenol.

12. The emulsion of claim 8 in which the coupler compound is 2-(2,4-di-tert. amylphenoxybutyramido)-5-p-tert. amylbenzoyl-amino-phenol.

13. The emulsion of claim 8 in which the coupler compound is 2-capronylamino-5- $\alpha$ -(2,4-di-tert. amylphenoxybutyramido)-phenol.

14. The emulsion of claim 8 in which the coupler compound is 2,5-bis-[ $\alpha$ -(x-chloro-2,4-di-tert. amylphenoxy)-acetamido]-4,6-dichlorophenol.

15. The emulsion of claim 8 in which the coupler solvent is 2,4-di-tert. amyl phenol.

#### References Cited in the file of this patent

##### UNITED STATES PATENTS

2,367,531	Salminen et al. ....	Jan. 16, 1945
2,423,730	Salminen et al. ....	July 8, 1947

##### FOREIGN PATENTS

651,958	Great Britain .....	Apr. 11, 1951
---------	---------------------	---------------