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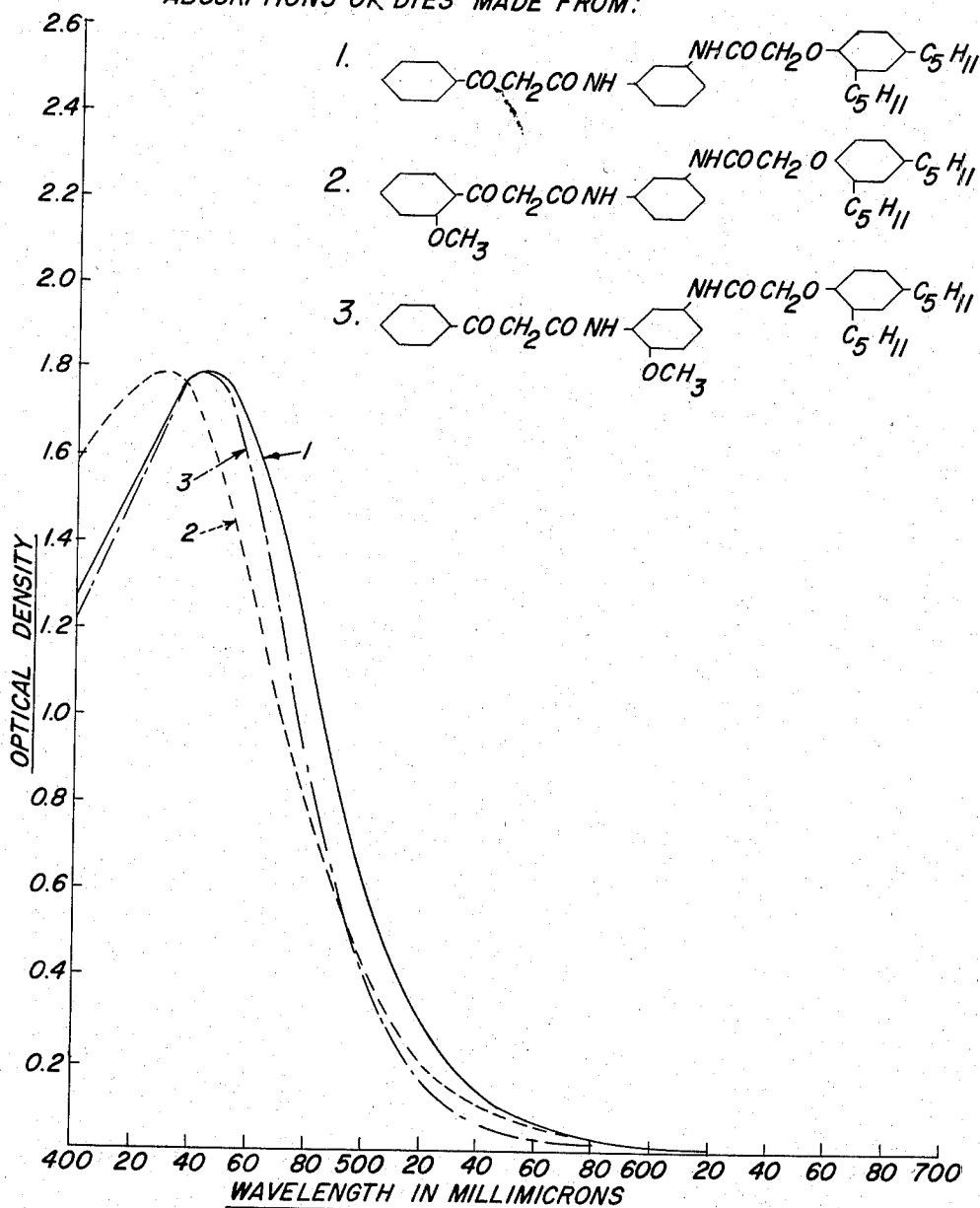
F. C. McCROSSEN ET AL

2,875,057

BENZOYLACET-O-ALKOXYANILIDE COUPLERS FOR COLOR PHOTOGRAPHY

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ABSORPTIONS OF DYES MADE FROM:



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2,875,057

BENZOYLACET-O-ALKOXYANILIDE COUPLERS FOR COLOR PHOTOGRAPHY

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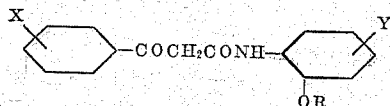
Application March 30, 1956, Serial No. 575,099

10 Claims. (Cl. 96—100)

This application is a continuation-in-part of our U. S. patent application Serial No. 476,159, filed December 20, 1954, now abandoned.

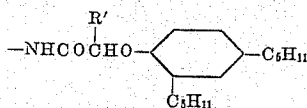
This invention relates to photographic emulsions containing coupler compounds for forming yellow dye images by means of color-forming development. In particular, the invention concerns the use of certain benzoylacetanilide couplers as color-forming coupler compounds.

The coupler compounds of the invention are benzoylaceto-o-alkoxyanilide coupler compounds having the general structure



wherein R represents an alkyl group of from 1 to 20 carbon atoms and either one of the groups X and Y represents a hydrogen atom and the other represents an acylamido group.

A particularly efficacious group of the coupler compounds of the invention have the above general formula wherein either one of the groups X and Y represents a hydrogen atom and the other represents the group

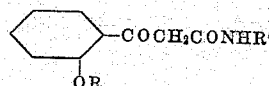


wherein R' represents a hydrogen atom or an alkyl group of from 1 to 4 carbon atoms. These compounds are illustrated by Compounds I to V, X, XIV and XV hereinafter.

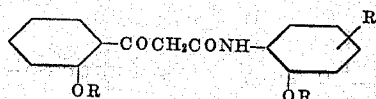
A distinctive feature of the coupler compounds having the above formulas resides in the presence of the alkoxy group in the ortho position of only the anilide nucleus.

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That is, alkoxybenzoylacetanilide couplers are known having the formula



are shown by Weissberger et al. U. S. Patent 2,407,210, September 3, 1946, and similar alkoxyated couplers having the formula

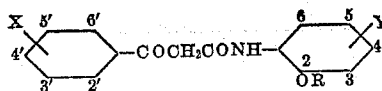


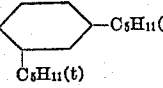
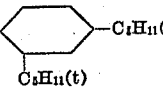
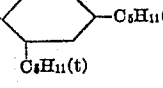
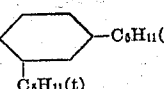
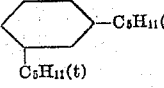
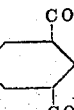
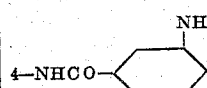
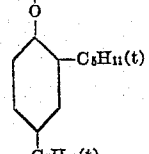
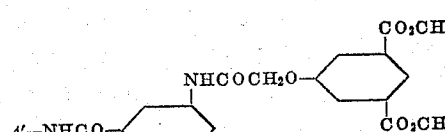
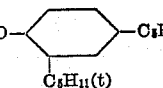
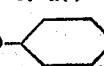
are shown by U. S. Patent 2,678,882. It will be apparent from these last two formulas that the couplers of the patents always contain an alkoxy group in the ortho position of the benzoyl nucleus and in the latter formula there is also present an alkoxy group in the ortho position of the anilide group.

We have discovered that if the benzoylacetanilide coupler compounds contain an alkoxy group of from about 1 to 20 carbon atoms in the ortho position of the anilide group but contain no alkoxy group on the benzoyl group but do contain an acylamido group attached directly to either the benzoyl or the anilide group of the coupler, as in the first general formula above, the coupler compounds possess properties separate and distinct from the coupler compounds of the mentioned patents.

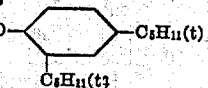
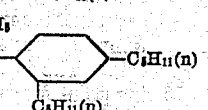
The accompanying drawing illustrates the distinctive features of the compounds of the invention. In the drawing are shown the absorption curves 1, 2 and 3 of dyes obtained by development of a silver halide emulsion with a primary aromatic amino silver halide developer in the presence of the compounds 1, 2 and 3 having the structures shown in the legend of the drawing. A comparison of curves 1 and 2 shows that the effect of the introduction of the methoxyl group in the ortho position of the benzoyl group of compound 1 to obtain compound 2, is to shift the whole absorption curve toward the shorter wave lengths without altering its shape or sharpness of absorption. However, when the methoxyl group is introduced into the ortho position of only the anilide group as in compound 3 of the invention, as shown in curve 3, the absorption maximum is not shifted appreciably but the sharpness of absorption is increased as shown by the increased gradient of curve 3 compared to curves 1 and 2. Accordingly, this results in a distinct reduction in green light absorption of the yellow dye without effectively changing the blue light absorption of the dye. Similar results can be expected when a comparison is made of the coupler compounds of the invention with other known alkoxyated couplers, for example, of U. S. Patent 2,678,882, having alkoxy groups on both the benzoyl and anilide nuclei of the benzoylacetanilide couplers.

The following table illustrates the couplers of the invention having the above general formulas:

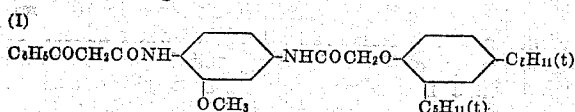


Coupler No.	R	X	Y
I.....	CH ₃	H	4-NHCOCH ₂ O-  -C ₆ H ₁₁ (t)
II.....	CH ₃	H	5-NHCOCH(O-C ₂ H ₅)CHO-  -C ₆ H ₁₁ (t)
III.....	CH ₃	H	5-NHCOCH ₂ O-  -C ₆ H ₁₁ (t)
IV.....	CH ₃	3'-NHCOCH ₂ O-  -C ₆ H ₁₁ (t)	H
V.....	CH ₃	4'-NHCOCH ₂ O-  -C ₆ H ₁₁ (t)	H
VI.....	C ₁₈ H ₃₇	4'-NHCOCH ₂ O-  -C ₆ H ₁₁ (t)	H
VII.....	CH ₃	H	4-NHCO-  -OCH2CO2CH ₃
VIII.....	CH ₃	H	4-NHCO-  -OCH2CO2CH ₃
IX.....	CH ₃	4'-NHCO-  -CO2CH ₃	H
X.....	C ₆ H ₅	H	4-NHCOCH ₂ O-  -C ₆ H ₁₁ (t)
XI.....	C ₆ H ₁₁	H	4-NHCO- 

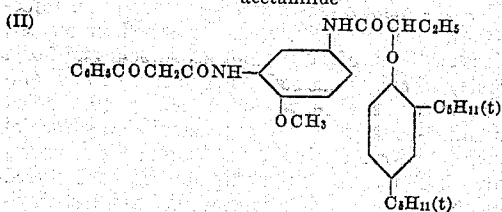
Table—Continued

Coupler No.	R	X	Y
XII XIII	C ₁₀ H ₃₇ C ₂₆ H ₄₁	$\begin{array}{c} \text{H} \\ \\ 4\text{-NHCOCH}_3 \end{array}$	$\begin{array}{c} 4\text{-NHCOCH}_3 \\ \\ \text{H} \end{array}$
XIV	CH ₃	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ 3\text{'-NHCOCH}_2\text{O} \end{array}$ 	H
XV	CH ₃	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ 3\text{'-NHCOCH}_2\text{O} \end{array}$ 	H

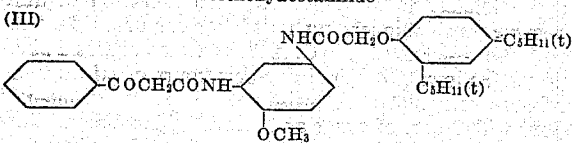
Accordingly, the mentioned efficacious group of coupler compounds of the invention having the general formula above are illustrated by Compounds I to V and XIV having the structures



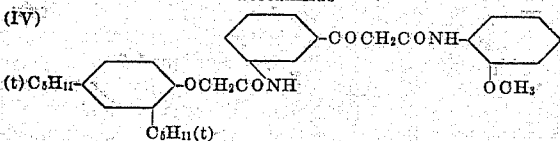
4-benzoylacetamido-3-methoxy-(2',4'-di-tert-amylphenoxy)-acetanilide



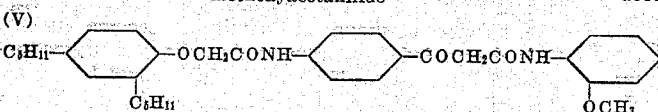
α -Benzoyl-5-[α -(2,4-di-tert-amylphenoxy)butyramido]-2-methoxyacetanilide



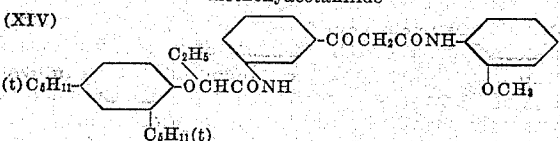
3-benzoylacetamido-4-methoxy-(2',4'-di-tert-amylphenoxy)-acetanilide



α -[3-[α -(2,4-di-tert-amylphenoxy)acetamido]benzoyl]-2-methoxyacetanilide



α -[4-[α -(2,4-di-tert-amylphenoxy)acetamido]benzoyl]-2-methoxyacetanilide



α -[3-[α -(2,4-di-tert-amylphenoxy)butyramido]benzoyl]-2-methoxyacetanilide

The coupler compounds provided above for illustration of our invention can be prepared as follows:

Example 1

Coupler No. I is prepared as follows:

α -Benzoyl-2-methoxy-4-nitroacetanilide.—In a 250-ml. round-bottom flask equipped with a partial condensing stillhead were placed 33.6 g. (0.2 mole) of 2-methoxy-4-nitroaniline (Ber. 13, 390) and 75 ml. of histological

xylene. The mixture was refluxed for five minutes before 40 ml. (0.22 mole) of ethyl benzoyl acetate was added. About 9 ml. of distillate was collected in two hours. The brown solution was filtered from mechanical impurities and allowed to stand at room temperature overnight. The precipitate was filtered, washed with 100 ml. of xylene, washed with 100 ml. of petroleum ether, slurried with 200 ml. of denatured alcohol, and dried. The yield was 39 g. (62%) of a yellow solid which melted at 179–180° C.

α -Benzoyl-4-amino-2-methoxyacetanilide hydrochloride.—In a one-liter 3-necked flask equipped with a reflux condenser were placed 31.4 g. (0.1 mole) of α -benzoyl-2-methoxy-4-nitroacetanilide, 200 ml. of 50% aqueous denatured alcohol, and 150 ml. of glacial acetic acid. The mixture was brought to a boil, the heat was removed, and 31.4 g. of iron powder was added as rapidly as possible. When the initial reaction had subsided, heat was again applied and the reaction mixture was refluxed 20 minutes. After filtration the filtrate was diluted as rapidly as possible with one liter of water and 300 ml. of concentrated hydrochloric acid. The solution changed from a deep brown to a deep yellow. After chilling overnight at 5° C., the hydrochloride was filtered, washed well with 500 ml. of 5% hydrochloric acid and 500 ml. of cold water. After drying, 24.8 g. (77%) of an off-white solid was obtained which turned red in patches ca. 150° C., losing HCl ca. 200° C., and melted with decomposition at 206–209° C.

4-benzoylacetamido-3-methoxy-(2',4'-di-tert-amylphenoxy)-acetanilide.—In a 500-ml. Erlenmeyer flask equipped with a stirrer were placed 16 g. (0.05 mole) of α -benzoyl-4-amino-2-methoxyacetanilide hydrochloride and 10 g. (0.1+ mole) of anhydrous sodium acetate in 200 ml. of glacial acetic acid. With good

stirring 16 g. (0.051 mole) of 2,4-di-tert-amylphenoxy-acetyl chloride were added. After stirring at room temperature for one hour, the reaction mixture was heated to 60° C. for one-half hour, cooled, and poured with very vigorous stirring into two liters of cold water. After stirring until the precipitate was filterable, the solid was filtered, washed with 500 ml. of water, and sucked as dry as possible. The moist solid was recrystallized from 5–10 parts of denatured alcohol to give 16.3 g. (58.4%) of white material which melted at 163–165° C.

Example 2

Coupler No. II is prepared as follows:

α -Benzoyl-5-[α -(2,4-di-tert-amylphenoxy)butyramido]-2-methoxyacetanilide.—In a 1 liter Erlenmeyer flask equipped with a stirrer is placed 500 ml. of glacial acetic acid, 20 g. of anhydrous sodium acetate, and 32.1 g. of α -benzoyl-5-amino-2-methoxyacetanilide

(as the hydrochloride) (Example 3). After stirring 10–15 minutes, 33.9 g. of α -(2,4-di-*tert*-amylphenoxy)-*n*-butyryl chloride is added all at once. The reaction mixture is stirred overnight at room temperature, drowned in 3–4 liters of cold water, and stirred until the precipitate is filterable. The tan product is filtered, washed well with water, and dried. The amorphous solid is recrystallized from 10–15 parts of methyl alcohol to yield 33 g. (56%) of white product which sinters at 72° C. and melts at 135–137° C., but occasionally contains alcohol of solvation and melts at 75–78° C.

Analysis.—Product M. P. 135–137° C. Calc.: C, 73.8; H, 7.85; N, 4.8. Found: C, 73.6; H, 7.9; N, 4.8.

Example 3

Coupler No. III is prepared as follows:

α -Benzoyl-2-methoxy-5-nitroacetanilide.—In a 250-ml. round bottom flask equipped with a partial condensing still-head were placed 100 ml. of histological xylene and 16.8 grams (0.1 mole) of 4-nitro-2-aminoanisole (Ber. 13, 389). The mixture was brought to a boil and 19.2 grams (0.1 mole) of ethyl benzoylacetate was added all at once. After refluxing 2 hours, about 3–5 ml. of ethyl alcohol had been collected. The yellow solution was filtered hot and allowed to cool to room temperature. The yellow solid which separated was filtered, washed with 50 ml. of xylene, and finally with 100 ml. of petroleum ether. A crude yield of 26 grams (83 percent) was obtained which melted at 170–175° C. On recrystallization from 18 parts of glacial acetic acid, 22.4 grams (71 percent) of fine light yellow needles, M. P. 177–179° C., was obtained.

α -Benzoyl-5-amino-2-methoxyacetanilide.—In a Parr hydrogenation bottle were placed 16 grams (0.051 mole) of α -benzoyl-2-methoxy-5-nitroacetanilide, 250 ml. of absolute ethyl alcohol, and 2–5 grams of Raney nickel. The reaction mixture was shaken under 2–3 atmospheres of hydrogen overnight at room temperature. The nickel was removed by filtration and the filtrate cooled in an ice bath. The light yellow solid was filtered, washed with 50 ml. of cold methyl alcohol, and dried. The yield was 13 grams (90 percent) of a solid which melted at 108–110° C.

3-benzoylacetamino-4-methoxy-(2',4'-di-*tert*-amylphenoxy)-acetanilide.—In a 250-ml. Erlenmeyer flask were placed 5.68 grams (0.02 mole) of α -benzoyl-5-amino-2-methoxyacetanilide, 2 grams (0.02+ mole) of anhydrous sodium acetate, and 100 ml. of glacial acetic acid. With good stirring 6.2 grams (0.02 mole) of 2,4-di-*tert*-amylphenoxyacetyl chloride in 25 ml. of glacial acetic acid was added all at once. The reaction mixture was stirred 1 hour at room temperature and ½ hour at 60° C. After cooling to room temperature, the reaction mixture was poured with vigorous stirring into 1 liter of cold water. The moist solid was filtered, washed with cold water, sucked as dry as possible, and recrystallized from 200 ml. of denatured alcohol. The yield was 7.5 grams (67 percent) of a tan powder which melted at 124–126° C. Recrystallization from 200 ml. of alcohol gave 6.2 grams (55%) of a product which melted at 132–134° C.

The couplers isomeric to I and III are prepared similarly from the isomeric α -benzoyl methoxynitroacetanilides.

Example 4

Coupler No. IV is prepared as follows:

α -(*m*-Nitrobenzoyl)-2-methoxyacetanilide.—To a refluxing mixture of 22 g. (0.93 mole) of ethyl α -(*m*-nitrobenzoyl)-acetate (Bülow and Hailer, Ber. 35, 915 (1902)) in 150 ml. of histological xylene was added in one portion 11 g. (0.09 mole) of *o*-anisidine. The mixture was heated at the reflux temperature (oil bath at 145–55° C.) for two hours under a steam-jacketed still-head, which permitted the removal of the alcohol-xylene

azeotrope. The product which separated from the cooled reaction mixture was filtered and sucked dry on a Büchner funnel; the yield of yellow product was 24 g. (82%), M. P. 166–7° C.

α -(*m*-Aminobenzoyl)-2-methoxyacetanilide.—In a 5-liter, three-necked flask, equipped with stirrer, reflux condenser and addition tube, are placed 104 g. of technical-grade sodium sulfide (0.8 mole) and 200 ml. of water. The mixture is stirred gently on a steam bath until solution is complete, and 3200 ml. of ethyl alcohol is added. The mixture is boiled and 126 g. (0.4 mole) of α -(*m*-nitrobenzoyl)-2-methoxyacetanilide is added portionwise over a period of fifteen minutes with good stirring. The brown reaction mixture is heated at the boiling point for one-half hour and poured on about an equal volume of ice. To the cold solution is added 212 g. (4 moles) of solid ammonium chloride. The mixture is stirred manually until the ammonium chloride is dissolved, and allowed to stand for forty minutes. The product is filtered by suction and washed on the funnel with several liters of water, until the washings are colorless. The pale-yellow product is dissolved in 1600 ml. of boiling alcohol and 100 ml. of hot water added. A small amount of Darco is added, and the solution is filtered while hot. The cooled filtrate yields 89.1 g. (78.5%) of fluffy yellow product, M. P. 139.5–40° C.

α -[3-[α -(2,4-di-*tert*-amylphenoxy)acetamido]benzoyl]-2-methoxyacetanilide.—In a 500-cc. three-necked flask, provided with a stirrer and thermometer, were placed 300 cc. of 90 percent acetic acid and 30 g. (0.36 mole) of anhydrous sodium acetate. To this solution, at room temperature, was added 32.0 g. (0.1 mole) of α -(*m*-amino-benzoyl)-2-methoxyacetanilide hydrochloride, an easily stirrable mixture resulting as the temperature dropped 2° C. After this mixture had been stirred for one-half hour, 37 g. (0.19 mole) of 2,4-di-*tert*-amylphenoxyacetyl chloride (see above) was added during approximately one-half minute. The reaction mixture became much thinner, but failed to clear up as the temperature rose from 25.5° C. to 33.5° C.; color was a pink-gray. Following one and one-half hours of stirring, the mixture was diluted dropwise over a period of one-half hour with 30 cc. of water and seeded with coupler. Further stirring overnight caused separation of product as a finely divided white mass.

The reaction mixture was drowned with stirring during fifteen minutes in 600 cc. of water, the product separating in white granules. Stirring was continued for forty-five minutes and the mixture filtered readily through a 5-inch Büchner funnel. The white solid was washed on the funnel with 2 liters of water, not over 20° C. Immediately, when the cake was no longer covered by water, it shrank in a characteristic manner away from the edge of the funnel as though threatening to become gummy. This change failed to occur as the cake was sucked and pressed thoroughly. The solid, which could be broken up easily, was air-dried, 60 g. being obtained; it had an indistinct melting range, starting at about 95° C.

Twelve hundred cc. of cyclohexane was heated to a boil on the steam bath and the 60 g. of crude product dissolved therein, forming a pink solution. It was treated with 2 g. of Darco and the solution filtered hot through 2 g. of Darco on a 4-inch Büchner funnel. Clear filtrate was only slightly less colored than prior to the Darco treatment. The coupler was permitted to crystallize undisturbed overnight. It was filtered readily, washed on the funnel with three 100-cc. portions of fresh cyclohexane. The yield was 47 g. (82% of the theoretical amount) of white coupler, which melted at 126–127° C.

Example 5

Coupler No. V is prepared as follows:

α -(*p*-Nitrobenzoyl)-2-methoxyacetanilide.—In a one-liter flask fitted with a steam-jacketed column containing a downward water-cooled condenser were placed 73.8 g.

Example 6

Example 7

α -benzoyl-4-[2-(2,4-di-*tert*-amylphenoxy)-5-(2,4-dicarbomethoxymethoxybenzamido)benzamido]-2-meth-

Example 8

Example 9

α -[4-(2-{2,4-di-*tert*.-amylphenoxy}-5-[α -(3,5-dicarbo-
methoxyphenoxy)-acetamido]benzamido benzoyl]-2-
methoxyacetanilide.—A mixture of 0.6 g. of α -[4-[2-(2,4-
di-*tert*.-amylphenoxy)-5-aminobenzamido]benzoyl]-2-
methoxyacetanilide, 0.3 g. of α -(3,5-dicarbo-methoxyphenoxy)-

noxy)acetyl chloride, 0.2 ml. of N,N-diethylaniline and 100 ml. of acetone was heated at the boiling point for one hour. After cooling, it was poured onto 300 g. of ice containing 2 ml. of concentrated hydrochloric acid. The solid was filtered, washed with water, and dried. The white solid was recrystallized from 25 ml. of ethanol; yield 0.7 g. (78%), M. P. 150-3° C. The melting point was unchanged after another crystallization from the same solvent.

Compounds X to XIII can be prepared in the manner of the above examples and will be found to exhibit physical and chemical properties similar to Compounds I to IX.

Example 10

Compound XIV, (α -{3-[α -(2,4-di-*t*-amylphenoxy)butyramido]benzoyl}-2-methoxyacetanilide), is prepared as follows:

A slurry of 56.8 g. of α -(3-aminobenzoyl)-2-methoxyacetanilide in 250 cc. of glacial acetic acid and 25 cc. of water was heated until complete solution occurred (ca. 70° C.). To this solution was added 74.5 g. of α -(2,4-di-*t*-amylphenoxy) butyryl chloride all at once with vigorous stirring. After several moments, a solution of 18 g. of sodium acetate in 40 cc. of water was added and stirring continued for two hours without heating. The solution was poured into two liters of ice water, and the resulting solid was filtered. After drying, the solid (106 g.) was purified by recrystallization from ligroin. 52 grams of a white solid melting at 105° C. was obtained.

The isomeric Compound XV, (α -{3-[α -(2,4-di-*n*-amylphenoxy)butyramido]benzoyl}-2-methoxyacetanilide), was prepared in the same manner except using 2,4-di-*n*-amylphenol instead of 2,4-di-*t*-amylphenol and was a white solid having a M. P. of 80° C.

Compounds XIV and XV are particularly valuable since they have lower melting points than, e. g., Compound IV which facilitates the incorporation of the compounds into gelatin emulsions by means of coupler solvents.

The coupler compounds of the invention can be incorporated into silver halide emulsion layers by use of oily coupler solvents as described in the Mannes and Godowsky U. S. Patent 2,304,940, December 15, 1942, and the Jelley and Vittum U. S. Patent 2,322,027, June 15, 1943. However, coupler compounds such as VI to IX containing terminal ester groups can also be hydrolyzed with alkali and when dissolved in aqueous alkaline solution can be incorporated directly into a silver halide emulsion.

The following example illustrates the use of the coupler Compound IV in an emulsion:

0.6 gram of coupler IV is dissolved in a mixture of 0.3 gram of di-*n*-butyl phthalate and 2.5 ml. of ethyl acetate by heating with stirring. This solution is mixed with 17.7 ml. of 10% gelatin solution containing 2 ml. of 5% Alkanol B. The mixture is put through a colloid mill four times to effect dispersion. Fourteen ml. of water is used to rinse out the colloid mill and this is added to the dispersion. The dispersion is then chilled and allowed to set. It is then shredded and dried on a stainless steel screen to remove the water and the ethyl acetate. The dried dispersion is then added to 33 ml. of water and allowed to soak for 20 minutes. The mixture is then warmed to 40° C. to melt the gelatin. The melted dispersion is mixed with 8.5 ml. of a sensitive silver halide emulsion and the resulting mixture is coated in the normal manner upon a film base support.

The resulting film is then exposed under an image and developed in a color developing composition as follows:

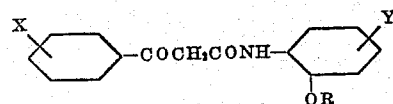
	Grams
2-amino-5-diethylamino toluene HCl-----	2
Sodium sulfite (anhydrous)-----	2
Sodium carbonate (anhydrous)-----	20
Potassium bromide-----	1
Water to 1 liter.	

The result is to obtain a silver and yellow dye image in the emulsion layer from which the silver image can be removed by well-known methods. The dye image thus obtained has light absorption properties similar to that obtained from compound 3 (Compound III of Example 3) as shown in the drawing. Similar results are obtained when the other couplers of the invention are incorporated into silver halide emulsion layers and developed by means of p-phenylenediamine developer compositions. In the development of exposed photographic 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 the alkyl phenylene diamines. These compounds are usually used in the salt form, such as the hydrochloride or the sulfate which are more stable than the amines themselves. The suitable compounds are diethyl-p-phenylenediamine hydrochloride, monomethyl-p-phenylenediamine hydrochloride, dimethyl-p-phenylenediamine 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 products of the developer to couple with the color-forming compounds to form a dye image.

As will be apparent, the coupler compounds of the invention find greatest use in the yellow image-forming layer of multi-layer color films. As such, emulsion layers containing the couplers contain as the emulsion vehicle gelatin or other water-permeable organic colloids such as albumin, partially hydrolyzed cellulose esters and partially hydrolyzed polyvinyl esters, polyvinyl alcohol, etc. The carrier may be supported by a transparent medium such as glass, a cellulose ester or synthetic resin 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 one of a number of superposed layers on one or both sides of the support. The superposed layers may be differentially sensitized as is conventional in color photography.

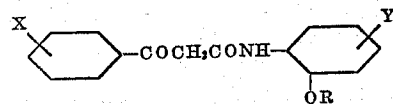
What we claim is:

1. A photographic silver halide emulsion containing a coupler compound having the general formula

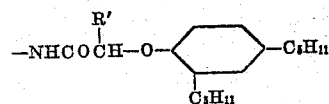


wherein R represents an alkyl group of from 1 to 20 carbon atoms and one of the groups X and Y represents a hydrogen atom and the other represents a photographically inactive carboxylic acid acylamido group.

2. A photographic silver halide emulsion containing a coupler compound having the general formula



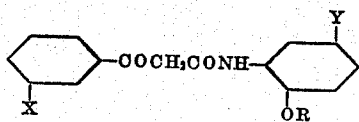
wherein R represents an alkyl group of from 1 to 20 carbon atoms and one of the groups X and Y represents a hydrogen atom and the other represents the group



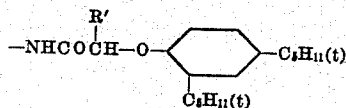
wherein R' represents a member of the class consisting of a hydrogen atom and an alkyl group of from 1 to 4 carbon atoms.

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3. A photographic silver halide emulsion containing a coupler compound having the general formula

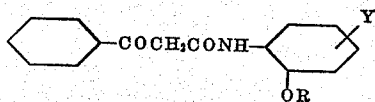


wherein R represents an alkyl group of from 1 to 20 carbon atoms and one of the groups X and Y represents a hydrogen atom and the other represents the group

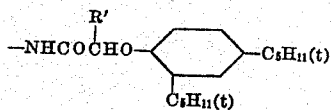


wherein R' represents a member of the class consisting of a hydrogen atom and an alkyl group of from 1 to 4 carbon atoms.

4. A photographic silver halide emulsion containing a coupler compound having the general formula



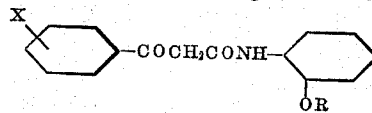
wherein R represents an alkyl group of from 1 to 20 carbon atoms and Y represents the group



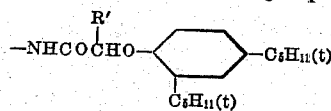
wherein R' represents an alkyl group of from 1 to 4 carbon atoms.

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5. A photographic silver halide emulsion containing a coupler compound having the general formula



wherein R represents an alkyl group of from 1 to 20 carbon atoms and X represents the group



wherein R' represents an alkyl group of from 1 to 4 carbon atoms.

6. A photographic silver halide emulsion containing the coupler compound 4-benzoylaceto-3-methoxy-(2',4'-di-tert-amylphenoxy)-acetanilide.

7. A photographic silver halide emulsion containing the coupler compound α -{3-[α -(2,4-di-n-amylphenoxy) butyramido]-benzoyl}-2-methoxyacetanilide.

8. A photographic silver halide emulsion containing the coupler compound 3-benzoylaceto-4-methoxy-(2',4'-di-tert-amylphenoxy)-acetanilide.

9. A photographic silver halide emulsion containing the coupler compound α -{3-[α -(2,4-di-tert-amylphenoxy) acetamido]-benzoyl}-2-methoxyacetanilide.

10. A photographic silver halide emulsion containing the coupler compound α -{3-[α -(2,4-di-tert-amylphenoxy) butyramido]-benzoyl}-2-methoxyacetanilide.

References Cited in the file of this patent

UNITED STATES PATENTS

35 2,678,882 Barr et al. May 18, 1954