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COUPLERS FOR COLOR PHOTOGRAPHY

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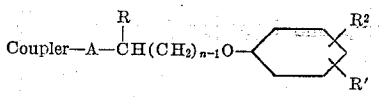
No Drawing. Application July 29, 1957
Serial No. 674,572

1 Claim. (Cl. 96—100)

This invention relates to coupler compounds for color photography which contain n-alkylcyclohexyloxy substituents.

Coupler compounds reactive with the oxidation products of p-phenylenediamine silver halide developing agents to form dye images in photographic emulsion layers and containing cycloaliphatic substituents have previously been described in the literature. However, coupler compounds containing n-alkylcyclohexyloxy substituents have not previously been described as useful in color photography.

Coupler compounds of the invention containing an n-alkycyclohexyloxy substituent may be represented by the following general formula:



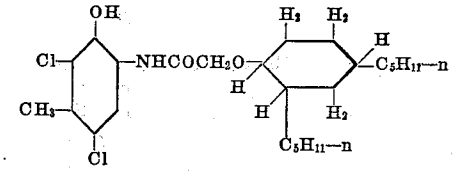
where A represents a functional group linking the n-alkylcyclohexyloxyalkylene substituent to the coupler, R represents a hydrogen atom or an alkyl group of from 1 to 4 carbon atoms, R′ represents a hydrogen atom and R^2 represents an n-alkyl group of at least 5 carbon atoms or both R′ and R^2 represent such n-alkyl groups and *n* represents a positive integer of from 1 to 4. The n-alkylcyclohexyloxyalkylene group is necessarily linked to the coupler molecule in a non-coupling position.

A unique feature of the described n-alkylcyclohexyloxy substituted couplers of the invention lies in the fact that the alkyl groups R′ and R^2 must be n-alkyl groups because secondary or tertiary alkylcyclohexyloxy substituted couplers do not appear to be capable of synthesis. This is based upon the fact that during the hydrogenation step shown in the synthesis hereafter, a cleavage takes place at the oxygen atom of the alkylcyclohexyloxy group if either a secondary alkylcyclohexyl or tertiary alkylcyclohexyl group is attached to the oxygen atom.

A further unique and advantageous characteristic of the n-alkylcyclohexyloxy substituted couplers of the invention lies in the fact that the couplers have much lower melting points than the analogous alkylphenoxy couplers. For example, coupler VII below melts at a temperature 41° C. below the melting point of the analogous alkylphenoxy coupler. This property greatly facilitates the incorporation of the couplers into photographic emulsions by means of coupler solvents. That is, the couplers may be dispersed in a coupler solvent for incorporation into emulsions at about 40° C. lower temperature which avoids degradation of the coupler.

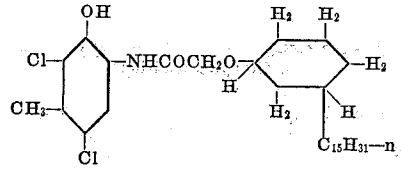
The following are representative of the n-alkylcyclohexyloxy substituted couplers contemplated by the invention:

(I)



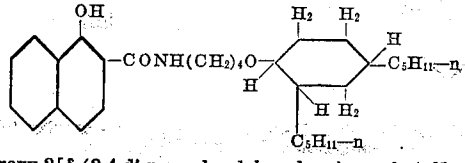
6-[α-(2,4-di-n-amylcyclohexyloxy)acetamido]-2,4-dichloro-3-methylphenol

(II)



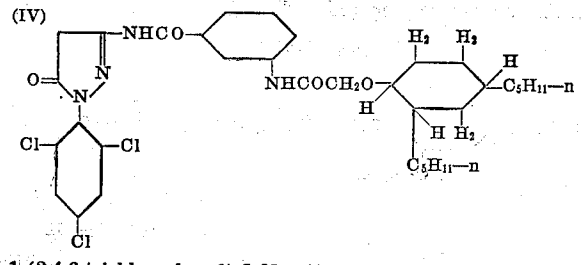
6-[α-(3-n-pentadecylcyclohexyloxy)acetamido]-2,4-dichloro-3-methylphenol

(III)



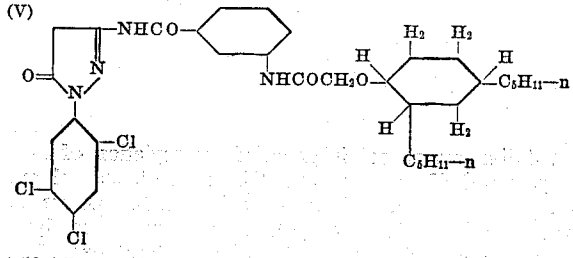
1-hydroxy-2[δ-(2,4-di-n-amylcyclohexyloxy)-n-butyl]naphthamide

(IV)



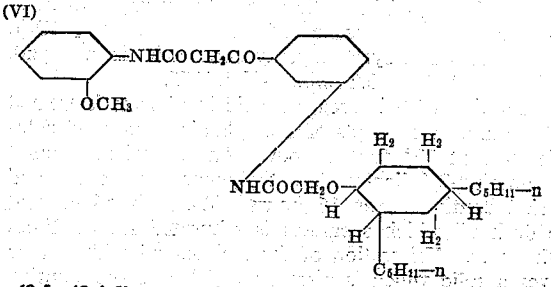
1-(2,4,6-trichlorophenyl)-3-[3-α-(2,4-di-n-amylcyclohexyloxy)-acetamido]benzamido-5-pyrazolone

(V)



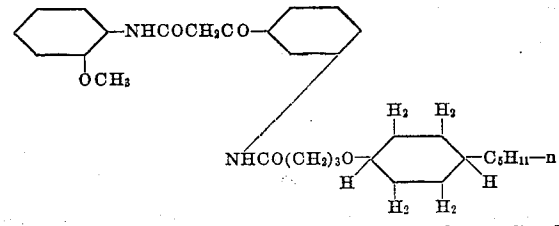
1-(2,4,5-trichlorophenyl)-3-[3-α-(2,4-di-n-amylcyclohexyloxy)-acetamido]benzamido-5-pyrazolone

(VI)



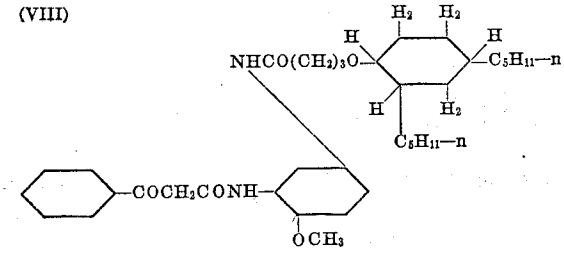
α-(3-[α-(2,4-di-n-amylcyclohexyloxy)acetamido]benzoyl)-2-methoxyacetanilide

(VII)



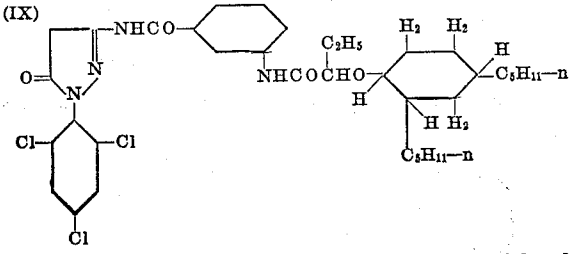
α-{3-[γ-(4-n-amylcyclohexyloxy)butyramido]benzoyl}-2-methoxyacetanilide

(VIII)



α-benzoyl-5-[γ-(2,4-di-n-amylcyclohexyloxy)butyramido]-2-methoxyacetanilide

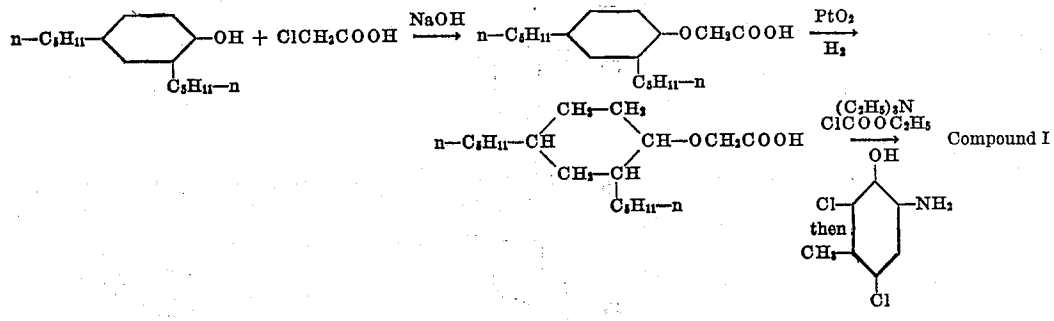
(IX)



1-(2,4,6-trichlorophenyl)-3-[3-α-(2,4-di-n-amylcyclohexyloxy)-butyramido]benzamido-5-pyrazolone

The n-alkylcyclohexyloxy substituted couplers of the invention can be prepared as described below.

Compound I



2,4-di-n-amylphenol is prepared by acylation of p-n-amylphenol (Sandulesco and Girard, Bull. soc. chim., 47, 1300 (1930)), with valeric acid (cf. McLamore, J. Am. Chem. Soc., 73, 2221 (1951)), followed by catalytic hydrogenation using copper chromite as the catalyst. The 2,4-di-n-amylphenoxyacetic acid, formed by well-known methods, is treated in acetic acid with hydrogen at 500–1000 p.s.i. in the presence of Adams' catalyst (PtO_2). The 2,4-di-n-amylcyclohexyloxyacetic acid is a liquid, distilling at 161° at 0.2 mm., n_D^{25} 1.4655.

A solution of the foregoing acid in dioxane is treated with equimolar amounts of triethylamine and ethyl chloroformate at 10° for ½ hour. An equivalent amount of 6-amino-2,4-dichloro-3-methylphenol is added and stirring continued for 16 hours. Water is added and the dark oil which separates is triturated several times with water. Trituration of the residual oil with hexane leaves a solid which is discarded. The hexane solution is concentrated and distilled giving Compound I as a viscous oil, distilling at 235–255° and 0.1 mm. *Analysis.*—Calculated for $C_{25}N_{39}Cl_2NO_3$: C, 63.4; H, 8.3; Cl, 15.0; N, 3.0. Found: C, 63.8; H, 8.6; Cl, 14.5; N, 3.1.

The analogous diamylphenoxy compound prepared in the same manner except omitting the platinum reduction step was a solid melting at 100° C.

When it was attempted to carry out the synthesis of the isomeric di-tertiary compound using 2,4-di-tertiary-amylphenol, it was found that during the hydrogenation step cleavage took place at the ether linkage.

Compound II

m-Pentadecylphenoxyacetic acid (M.P. 103–5°) is prepared in the usual manner and hydrogenated as described above. The acid is treated with triethylamine, ethyl chloroformate and 6-amino-2,4-dichloro-3-methylphenol as described for Compound I.

Compound III

2,4-di-n-amylphenol is treated with γ-chlorobutyronitrile and sodium hydroxide yielding γ-(2,4-di-n-amylphenoxy)butyronitrile. The latter is hydrogenated to the corresponding diamylcyclohexyloxybutylamine which reacts readily with phenyl 1-hydroxy-2-naphthoate.

Compound IV

The compound is prepared as described for Compound I except using the amine 1-(2,4,6-trichlorophenyl)-3-(m-aminobenzamido)-5-pyrazolone prepared as described in the Loria et al. U.S. Patent 2,600,788, granted June 17, 1952, in place of 6-amino-2,4-dichloro-3-methylphenol.

Compound V

This compound is prepared as Compound IV was except using the amine 1-(2,4,5-trichlorophenyl)-3-(m-aminobenzamido)-5-pyrazolone.

Compound VI

This compound is prepared in the manner of Compound I except using as the amine α-(m-aminobenzoyl)-2-methoxyacetanilide prepared as described in Example 4 of the McCrossen et al. U.S. patent application Serial No. 575,099, filed March 30, 1956. The compound had a melting point of 57° C. compared to 83° C. for the n-diamylphenoxy analogue prepared in the same manner except omitting the platinum hydrogenation step.

Compound VII

γ-(p-n-Amylphenoxy)butyric acid is prepared by the reaction of the sodium salt of p-n-amylphenol with γ-butyrolactone. The acid is hydrogenated as for Compound I above and the product caused to react with the amine α-(m-aminobenzoyl)-2-methoxyacetanilide.

Compound VII had a melting point of 106° C. compared to 147° C. for the analogous p-n-amylphenoxy compound made in the same manner except omitting the hydrogenation step.

Compound VIII

This compound (M.P. 128°) is prepared in the manner of Compound I except using the amine α-benzoyl-5-amino-2-methoxyacetanilide (McCrossen et al. invention above) and the hydrogenated acid prepared by reducing γ-(2,4-di-n-amylphenoxy) butyric acid.

Compound IX

This compound is prepared in the manner of Compound IV except using α-(2,4-di-n-amylcyclohexyloxy) butyric acid.

The following table compares the dissolution temperature of representative couplers I, VI and VII with the analogous phenoxy couplers. The comparison was made by noting the temperature at which a given amount of the coupler dissolves in an equal amount of the coupler solvent n-butylphthalate.

	Dissolution temperature (° C.)
Coupler I	25
Coupler I analog	63
Coupler VI	69
Coupler VI analog	72
Coupler VII	83
Coupler VII analog	115

As mentioned, the lower dissolution temperature of the couplers of the invention prevents degradation of the couplers during incorporation in photographic emulsions.

The coupler compounds of the invention may be incorporated in sensitive silver halide emulsion layers as described in Mannes and Godowsky U.S. Patent 2,304,940 or Jelley and Vittum U.S. Patent 2,322,027. In a typical procedure, a suitable quantity of the coupler is dissolved in di-n-butylphthalate by heating and stirring. This solution is then mixed with a 10 percent gelatin solution containing a dispersing agent and this passed through a colloid mill several times to disperse the coupler well. The dispersion may then be mixed with a suitable quantity of gelatino silver halide emulsion and coated in the normal manner on a film base.

The aromatic amino developing agents used with the coupler compounds of our invention include the mono-, di- and tri-amino aryl compounds and their derivatives formed by substitution in the amino group as well as in the ring such as alkyl phenylene diamines and alkyl toluylene 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. Suitable compounds are di-ethyl-p-phenylene diamine hydrochloride, monoethyl-p-phenylene diamine hydrochloride, di-methyl-p-phenylene diamine hydrochloride, di-methyl-p-phenylene sulfate and 2-amino-5-di-ethyl amino toluene sulfate. The p-amino phenols and their substitution products may also be used where the amino group is unsubstituted. All of these compounds 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.

The following is a color developing solution which may be used to develop colored images in emulsion layers containing the coupler compounds of the invention:

p-Aminodiethylaniline sulfate	grams	2
Sodium sulfite (anhydrous)	do	5
Sodium carbonate (anhydrous)	do	20
Potassium bromide	do	2
Water to	liter	1

The colloid vehicle of the emulsions containing the coupler compounds of the invention may be gelatin or other carriers such as collodion, organic esters of cellulose or synthetic resins. The support for the emulsion may be a transparent material such as glass, cellulose ester or a non-transparent reflecting material 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 to form natural color photographic images in the well-known manner. For example, in a multilayer material sensitized to red, green and blue light, respectively, our couplers would ordinarily be used in the green-sensitive emulsion layer to form the magenta image.

What we claim is:

A photographic silver halide emulsion containing the coupler compound 6-[α-(3-n-pentadecylcyclohexyloxy)-acetamido]-2,4-dichloro-3-methylphenol.

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