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DIALKYL-5-(OXANILAMIDO) ISOPHTHALATE COUPLERS FOR COLOR PHOTOGRAPHY

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9 Claims. (Cl. 95—6)

This invention relates to color photography, and particularly to color couplers for use in photographic emulsions.

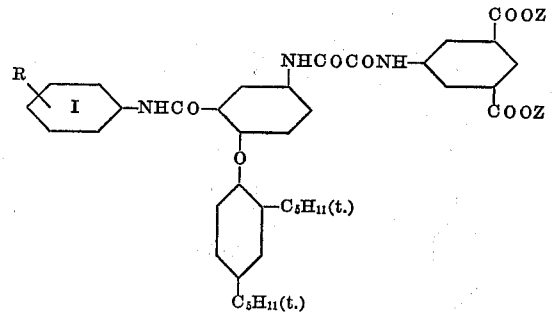
The use in color photography of color-forming compounds which react with the oxidation or development product of primary aromatic amino developing agents to form colored images upon photographic development is well known. The coupler compounds employed in this way may be added to the developing solution or incorporated in the sensitive emulsion.

When used in the emulsion, the couplers must be soluble in the medium in which they are incorporated. In the case of direct incorporation in gelatin or other hydrophilic medium, as in Fischer U. S. Patent 1,102,028, the couplers must have groups rendering them water-soluble, such as carboxylic acid groups. In the case of incorporation in an organic solvent, as in Mannes and Godowsky U. S. Patent 2,304,940 or Jelley and Vittum U. S. Patent 2,322,027, the couplers must be soluble in the organic solvent used to dissolve them.

In the manufacture of emulsions containing couplers, considerable difficulty has been encountered in purifying couplers containing carboxylic acid groups, prior to incorporating them in the emulsion. Because of the presence of the carboxylic acid radical, soluble salts are formed which are difficult to purify by recrystallization. This is especially true if there are two or more carboxylic acid groups in the molecule.

It is therefore an object of the present invention to provide a novel class of color couplers which can be readily purified by recrystallization. A further object is to provide color couplers which can be incorporated in gelatin emulsions either by direct incorporation or by dispersion when dissolved in organic solvents. Other objects will appear from the following description of my invention.

These objects are accomplished by using as the coupler a compound having the formula:



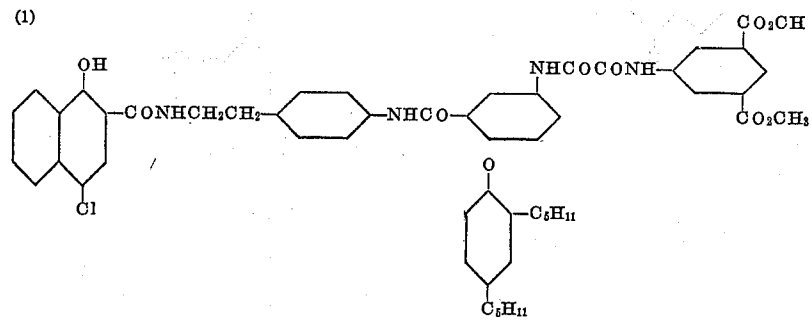
wherein R is attached either directly or indirectly in the meta or para position to radical I and represents a coupling group such as a 5-pyrazolone or a phenol group. Z represents either an alkyl, e. g., methyl, ethyl, propyl, butyl, or an alkali metal, e. g., sodium or potassium.

I have found that the radical of isophthalic acid is a valuable solubilizing component for couplers which are incorporated directly in gelatin emulsions, but compounds containing this radical are difficult to purify by recrystallization. If the esters of phthalic acid are used instead of the free acid, the compounds may be purified by recrystallization, and the esters hydrolyzed to the free acid before incorporation in the gelatin emulsions. The compounds are then introduced into the emulsion as an alkali metal salt, usually the sodium salt.

The isophthalic acid esters of the couplers may also be incorporated in the emulsion in solvent dispersion, as described in Mannes and Godowsky U. S. Patent 2,304,940 and Jelley and Vittum U. S. Patent 2,322,027.

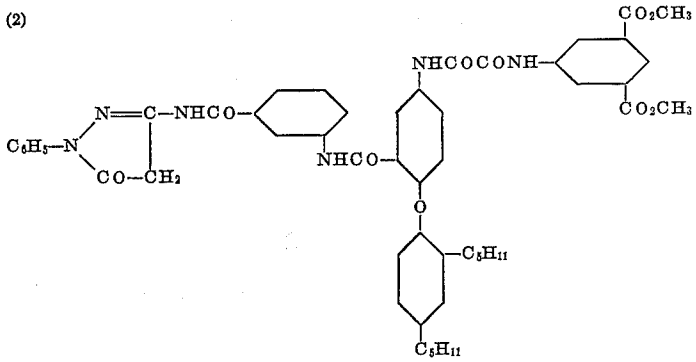
The following compounds illustrate esters which may be used according to my invention:

(1)



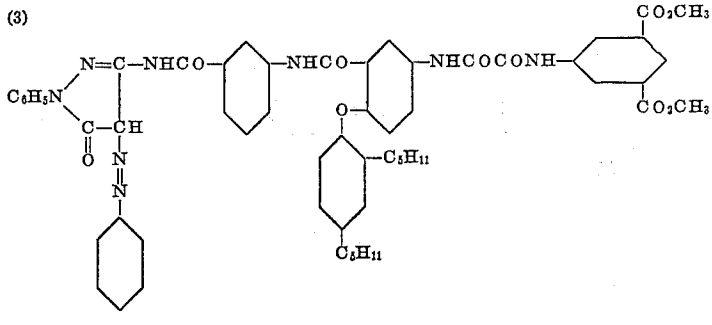
1-hydroxy-4-chloro-N-{4-[2-(2,4-di-tert-amylphenoxy)-5-(3,5-dicarbomethoxyoxanilamido)benzamido]phenethyl}-2-naphamide

(2)



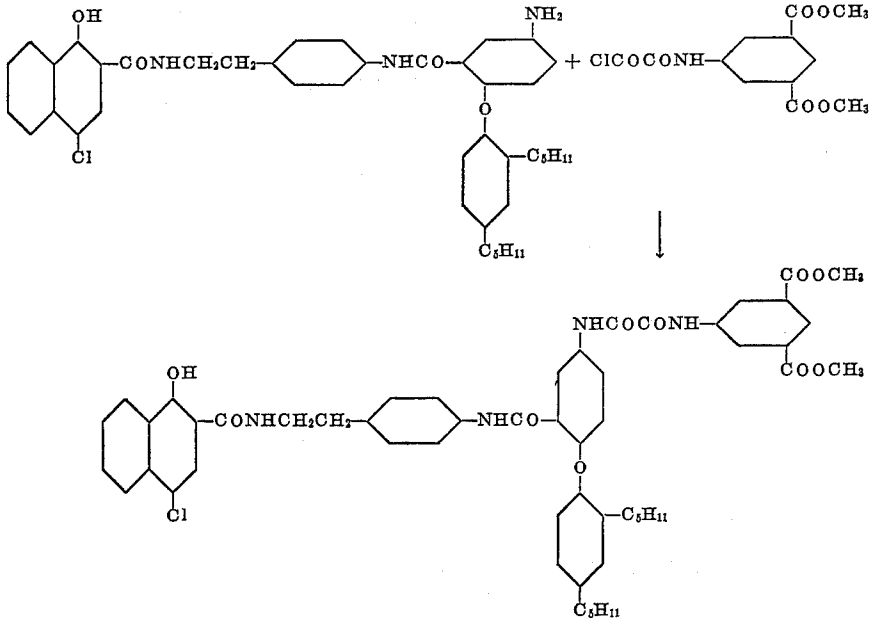
1-phenyl-3-{3-[2-(2,4-di-tert-amylphenoxy)-5-(3,5-dicarbomethoxyoxanilamido)benzamido]benzamido}-5-pyrazolone

(3)



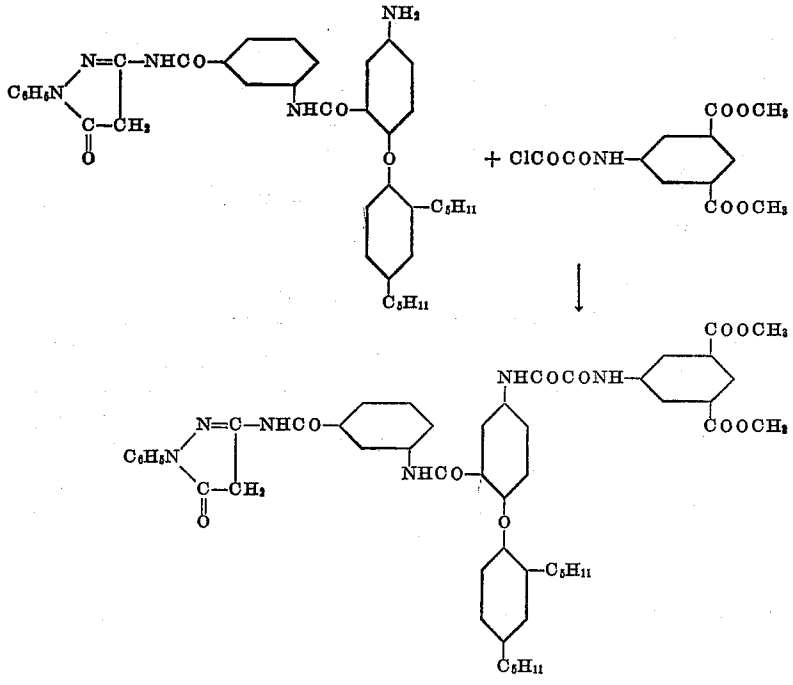
1-phenyl-3-{3-[2-(2,4-di-tert-amylphenoxy)-5-(3,5-dicarbomethoxyoxanilamido)benzamido] - benzamido} - 4 - [4 -(carboxymethoxy)-phenylazo]-5-pyrazolone

Compound 1 was prepared as follows:



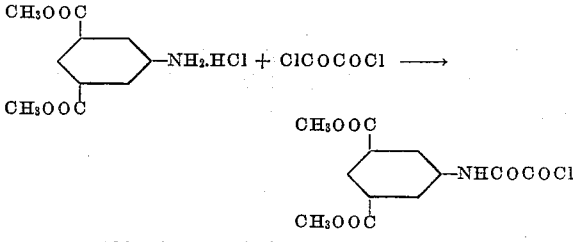
In a 200-ml. Erlenmeyer flask equipped with a stirrer were placed 0.5 g. (0.006 mole) of anhydrous sodium acetate, 100 ml. of glacial acetic acid, and 3.3 g. (0.005 mole) of 4-chloro-1-hydroxy-2{β-{4'[2''(2''',4'''-diamylphenoxy) - 5'' - aminobenzamido]} - phenethyl} - naphthamide. The mixture war warmed to 50° to dissolve the amine and 1.5 g. (0.005 mole) of dimethyl 5-(chloroglyoxyl-amido)isophthalate was added with good stirring. After two hours the solution with diluted with 100 ml. of water. The precipitate was filtered, washed with water, and dried. On crystallization from acetonitrile 2 g. (42%) of white powder melting at 235–237° was obtained.

Compound 2 was prepared as follows:



To a solution of 3.2 g. (0.005 mole) of 1-Phenyl-3-{3'-[2''-(2,4-di-tert-amylphenoxy)-5''-amino]benzamido} benzamido-5-pyrazolone in 500 ml. of refluxing acetonitrile was added 3.0 g. (0.01 mole) of dimethyl 5-chloroglyoxylamido)isophthalate. After 20 hours' reflux a solid precipitated, was filtered, and dried. Recrystallization from acetonitrile gave 4.3 g. (95%), melting at 205°.

Dimethyl 5-(chloroglyoxylamido)isophthalate



In a 100-ml. round bottom standard taper flask equipped with a stirrer was placed 38 g. (0.3 mole) of oxalyl chloride. With good stirring at 15°, 8 g. (0.033 mole) of dimethyl 5-amino-isophthalate hydrochloride was added portionwise during ten minutes. After stirring for one hour the reaction mixture was left at room temperature for five days. The excess oxalyl chloride was removed in vacuo and the residue was recrystallized from 375 ml. of dry benzene to give 7.5 g. (75%) of white needles melting at 160–165° with decomposition.

Compound 3 which is a colored coupler was prepared from compound 2 as follows:

p-Aminophenoxyacetic acid was prepared by reduction of p-nitrophenoxyacetic acid in aqueous solution over 5% palladium on carbon, and the free amine obtained was converted to the hydrochloride for storage. M. P. 222–223° C. The desired coupler was then obtained by dissolving compound 2 in pyridine at 0° C. and treating the solution with the diazotized aniline derivative at 0° C., followed by drowning the reaction mixture in cold, dilute hydrochloric acid, filtering and washing with cold water on the filter.

The couplers of the invention are particularly adapted to use in one of the emulsion layers of a multilayer color film to form dye images therein by methods well known in the art. Compound 3 is representative of colored coupler compounds comprising a part of my invention which are useful in emulsion layers for masking purposes as described in Hanson U. S. Patent 2,449,966.

The couplers may be incorporated into emulsion layers in the form of their alkali metal salts. This is accomplished by first heating the coupler in alcoholic alkali to hydrolyze the isophthalyl ester groups, followed by dilution of the reaction mixture and reducing the pH to about 6.5 to 7.0. The solution of the alkali metal salt of the coupler is then incorporated in the desired amount into a melted silver halide emulsion and coated as usual.

When incorporating the couplers in solvent dispersion into an emulsion the coupler may be heated in a suitable volume of a coupler solvent such as dibutylphthalate at about 165° C. until solution is obtained and this solution is milled into a gelatin solution containing a suitable dispersing agent. The resulting dispersion is then introduced into a melted silver halide emulsion.

Various photographic developing agents can be employed with the couplers of my invention. The primary aromatic amino developing agents are generally suitable including the phenylene-diamines and aminophenols. The alkyl phenylenediamines may be substituted in the amino group as well as in the ring. Suitable compounds are diethyl-p-phenylenediamine, monomethyl-p-phenylene-diamine, dimethyl-p-phenylenediamine and p-aminophenol. These compounds are usually employed in the salt form, such as the hydrochloride or the sulfate which are more stable than the free amines. All of these compounds have a primary amino group which enables the oxidation product of the developer to couple with the color-forming compounds to form dye images.

The following developing solution is suitable for developing gelatino-silver halide layers containing colored couplers according to my invention incorporated either directly in the emulsion or in solvent dispersion:

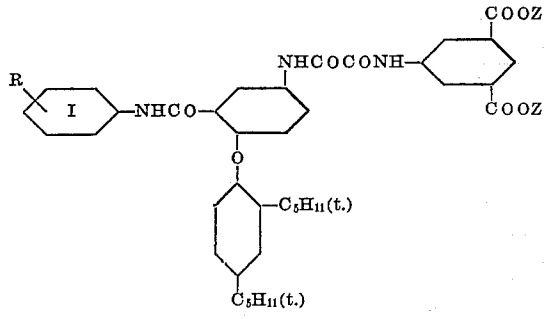
	Grams
2-amino-5-diethylamino toluene HCl	2
Sodium sulfite	2
Sodium carbonate	20
Potassium bromide	2
Water to 1 liter.	

It will be understood that the examples and modifications set forth herein are illustrative only and that my

invention is to be taken as limited only by the scope of the appended claims.

What I claim is:

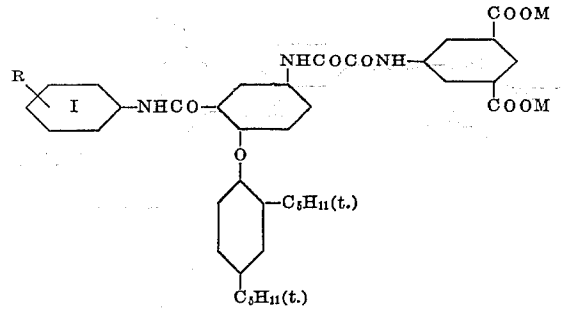
1. A photographic silver halide emulsion containing a coupler compound having the general formula



wherein R is attached to a position of radical I other than ortho and represents a group of atoms containing a coupling group capable of reaction with a primary aromatic amino silver halide developing agent to form a dye, and Z represents a member of the group consisting of an alkyl group and an alkali metal.

2. A photographic silver halide emulsion containing

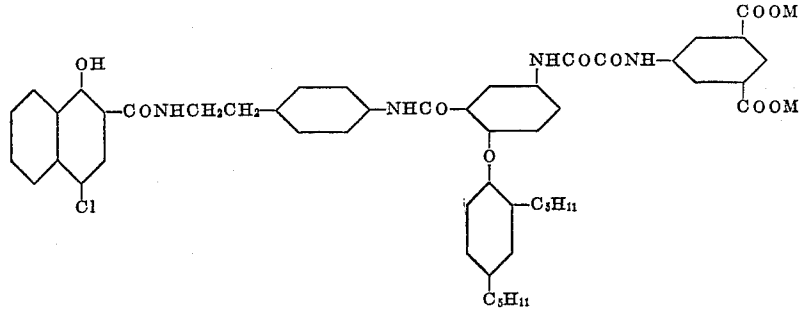
a coupler compound having the general formula



wherein R is attached to a position of radical I other than ortho and represents a group of atoms containing a 5-pyrazolone group capable of reacting in the 4-position with a primary aromatic amino silver halide developing agent to form a dye, and M represents an alkali metal.

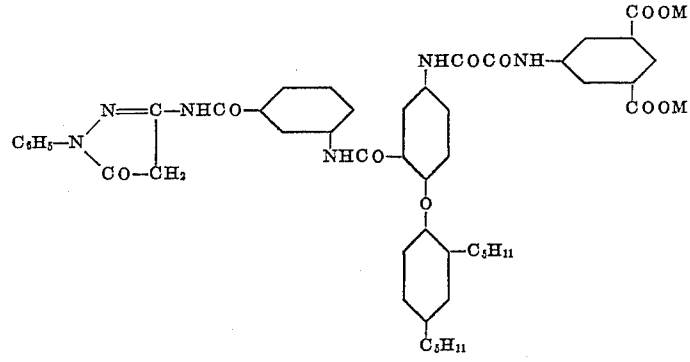
3. A photographic silver halide emulsion containing a coupler compound having the formula defined in claim 2 wherein R represents a group of atoms containing a phenolic hydroxyl group the aromatic nucleus of which contains a position free to react with a primary aromatic amino silver halide developing agent to form a dye.

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



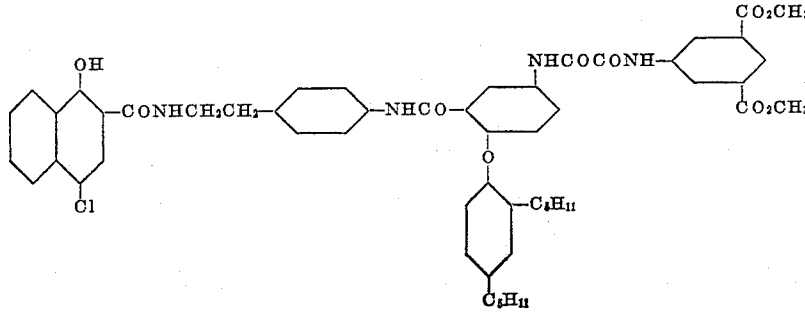
wherein M represents an alkali metal.

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

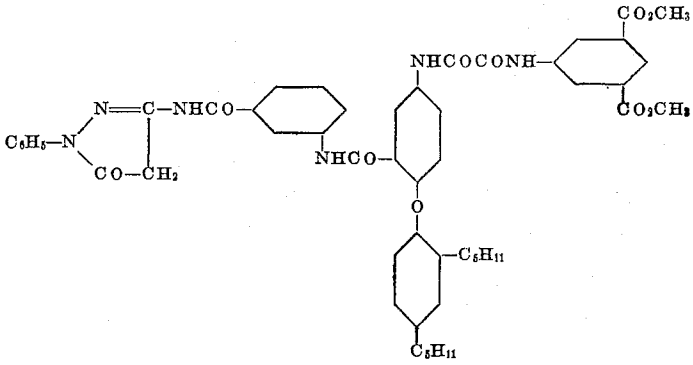


wherein M represents an alkali metal.

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

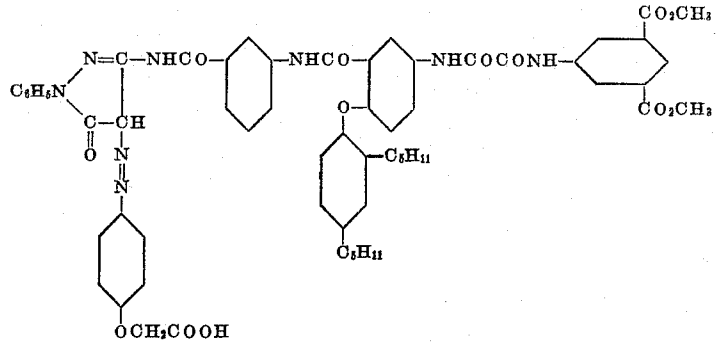


7. A photographic silver halide emulsion containing a coupler compound having the formula



8. A photographic silver halide emulsion containing a coupler compound having the formula defined in claim 2 wherein R represents a group of atoms containing a 5-pyrazolone group having an azo group in the 4-position.

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



References Cited in the file of this patent

UNITED STATES PATENTS

2,511,231 Weissberger et al. ------ June 13, 1950