

UNITED STATES PATENT OFFICE

2,652,329

COLOR COUPLERS CONTAINING ISO-PHTHALIC ACID RADICALS

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7 Claims. (Cl. 95-6)

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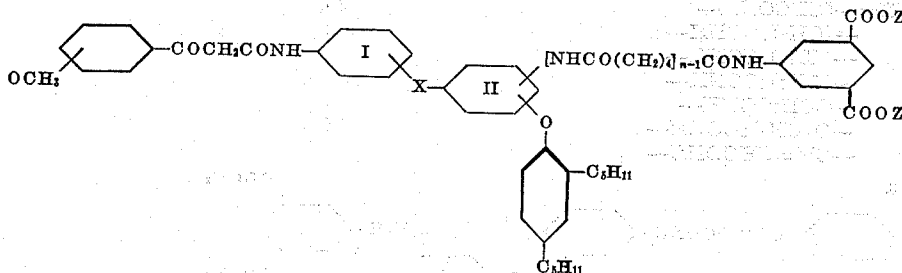
This invention relates to color photography, and particularly to color couplers for use in photographic emulsions.

The use in color photography of color-forming

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appear from the following description of our invention.

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



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

where

- 20 X=—CONH—
—CH₂CONH—
—(CH₂)₂CONH—
—(CH₂)₃CONH—
—(CH₂)₄CONH—
25 —OCH₂CONH—
—O(CH₂)₃CONH—
—CH=CHCONH—

Z=an alkyl radical, e. g., methyl or ethyl, or an alkali metal, e. g., sodium or potassium,
30 n=1 or 2,

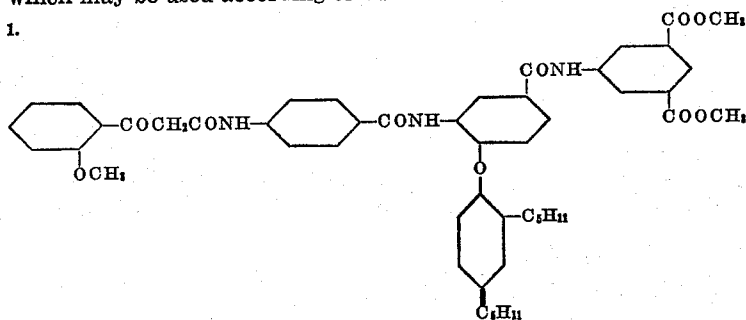
radical I is connected to X in the meta or para position, and radical II is substituted in the positions ortho or meta to X.

35 We 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.

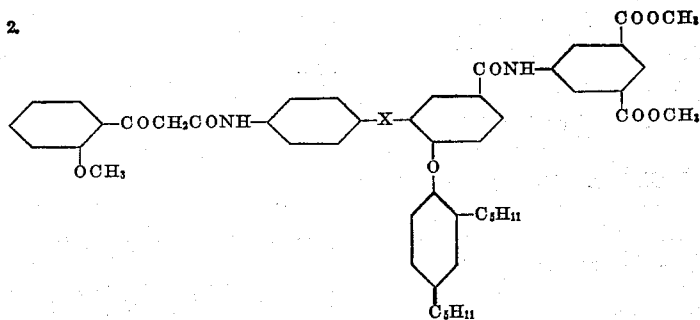
45 The isophthalic acid esters of the couplers may also be incorporated in the emulsion in solvent dispersion, as described in Mannes and Godowsky U. S. Patent 2,304,940 and Jelley and Vittum U. S. Patent 2,322,027.

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

1.



2.

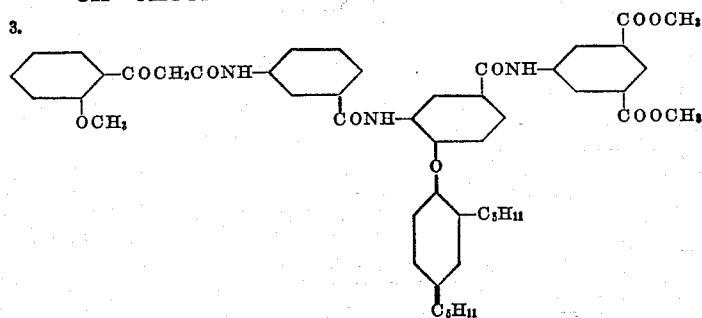


X=—CH₂CONH—
 —(CH₂)₂CONH—
 —(CH₂)₃CONH—
 —(CH₂)₄CONH—
 —OCH₂CONH—
 —O(CH₂)₃CONH—
 —CH=CHCONH—

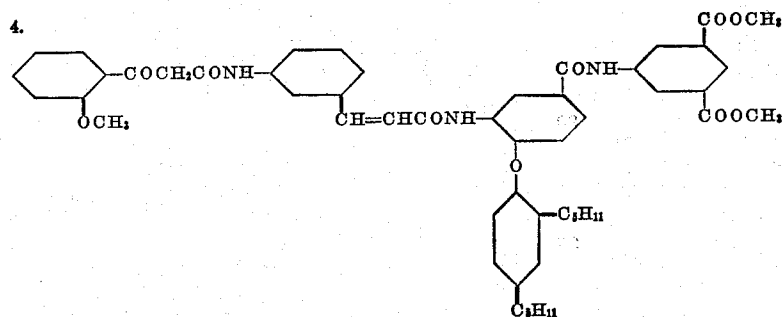
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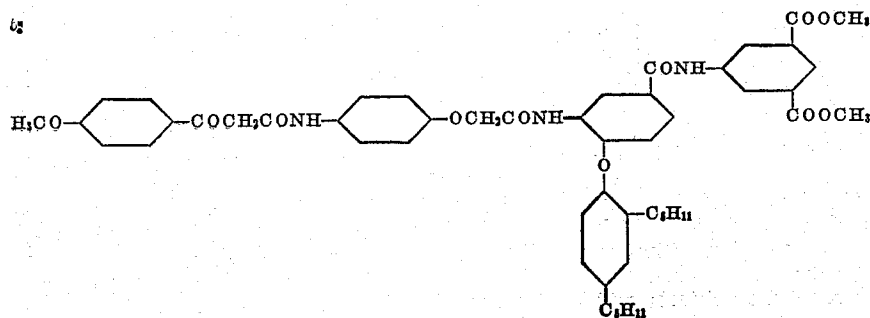
3.

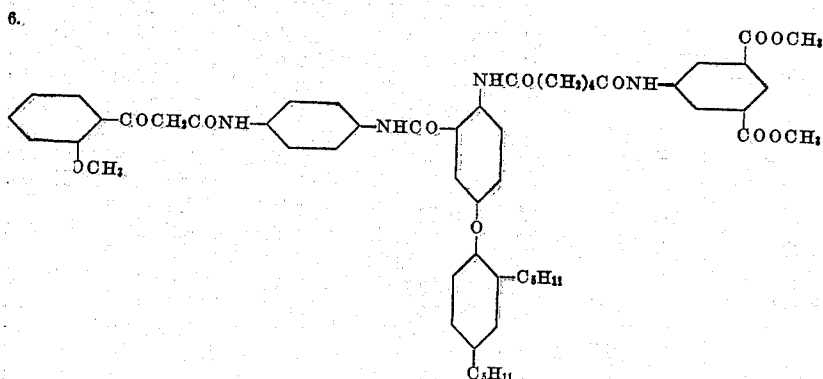


4.



5.

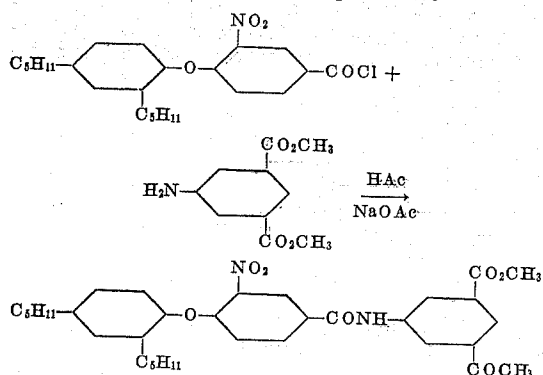




α -2'-methoxybenzoyl-4-[2''(3''',5'''-dicarbomethoxyphenyl-carbamylvaleramido)-5''-(2''',4'''-di-tert.-amylphenoxy)benzamido]-acetanilide

Compound 5 was prepared as follows:

Methyl-5[4'(2'',4''-di-tert.-amylphenoxy)-3'-nitrobenzamido]-isophthalate

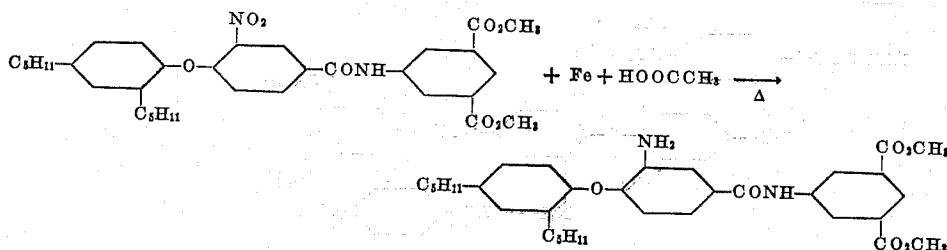


In a 5-l. flask, equipped with a mechanical stirrer and condenser carrying a drying tube and a thermometer, were placed 157 g. (0.75 mole) of methyl-5-aminoisophthalate and 1 l. of glacial acetic acid. The mixture was heated to 60° C. and 300 g. (0.74 mole) of crude 4(2',4'-di-tert.-amylphenoxy)-3-nitrobenzoyl chloride in 500 ml. of glacial acetic acid was added to it all at once, followed by 62 g. (0.76 mole) of anhydrous sodium acetate. The mixture was heated on the steam bath with stirring for 1.5 hrs. longer.

There was practically complete solution for a short time and then the sodium chloride formed came out of solution in very fine crystals. The reaction was stopped, the sodium chloride filtered out by gravity while the solution was still hot, and the filtrate diluted with 200 ml. of boiling water and let stand overnight. The next morning the reaction was cooled to 15° C. and the white crystalline product filtered. It was slurried in 3 l. of cold water, filtered again and washed as free of acetic acid as desired with cold water.

The dry material melted at 112-114° C. and was pure enough to use in the next step.

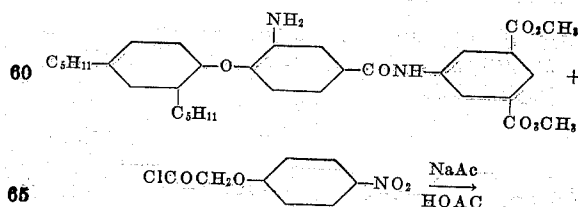
Methyl-5[4'(2'',4''-di-tert.-amylphenoxy)-3'-aminobenzamido]-isophthalate



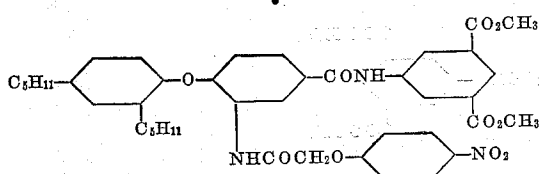
A 12-l. wide mouth flask was equipped with a mechanical stirrer and two wide bore coil condensers. In it were placed 380 g. (0.645 mole) of methyl-5[4'(2'',4''-di-tert.-amylphenoxy)-3'-nitrobenzamido]isophthalate and 4.5 l. of 90% acetic acid, and the mixture was heated to reflux with vigorous stirring. At this point the source of heat was removed and 380 g. of active iron (Fe) was added in 40-50-g. portions through one of the condensers. A very vigorous reaction took place on the addition of the iron, but the two water-cooled condensers were sufficient to control it, if the iron is added in a period of 15 min. A more rapid addition of the iron would require external cooling of the flask, which might be accomplished by playing a jet of running water on it. After the reaction had subsided somewhat, heating was again applied and vigorous refluxing continued for 10 min. longer. The reaction mixture was allowed to cool just below its boiling point and filtered free of the excess iron, excluding air as much as possible. Hot (just below its boiling point) 50% acetic acid (4.5 l.) was added to the filtrate and the flask was shaken by hand for complete mixing, and stoppered immediately. The solution was allowed to cool spontaneously with occasional shaking and finally let stand overnight.

The precipitate formed (just off-white needles) was filtered and washed successively with 50%, 25%, 10% and 5% acetic acid, about 4 l. of each. It was then freed of any acetic acid, either by slurrying in or washing with water. The hot oven-dried product melted at 210-212° C. and was of excellent quality. Yield 320 g. (88.5%).

Methyl-5[4'(2'',4''-di-tert.-amylphenoxy)-3'(4'-nitrophenoxyacetamido)-benzamido]-isophthalate



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Methyl - 5[4'(2'',4'' - di-tert.-amylphenoxy) - 3' - aminobenzamidol - isophthalate 99 g. (.177 mole) was suspended in 1 l. of glacial acetic acid and heated to 60 C. on a steam bath in a 2-l. flask with occasional shaking. To it were added successively 38 g. (.177 mole) p-nitrophenoxy-acetyl chloride and 20.5 g. (.25 mole) of anhydrous sodium acetate. The mixture was heated on a steam bath for 1 hr. under a condenser carrying a drying tube.

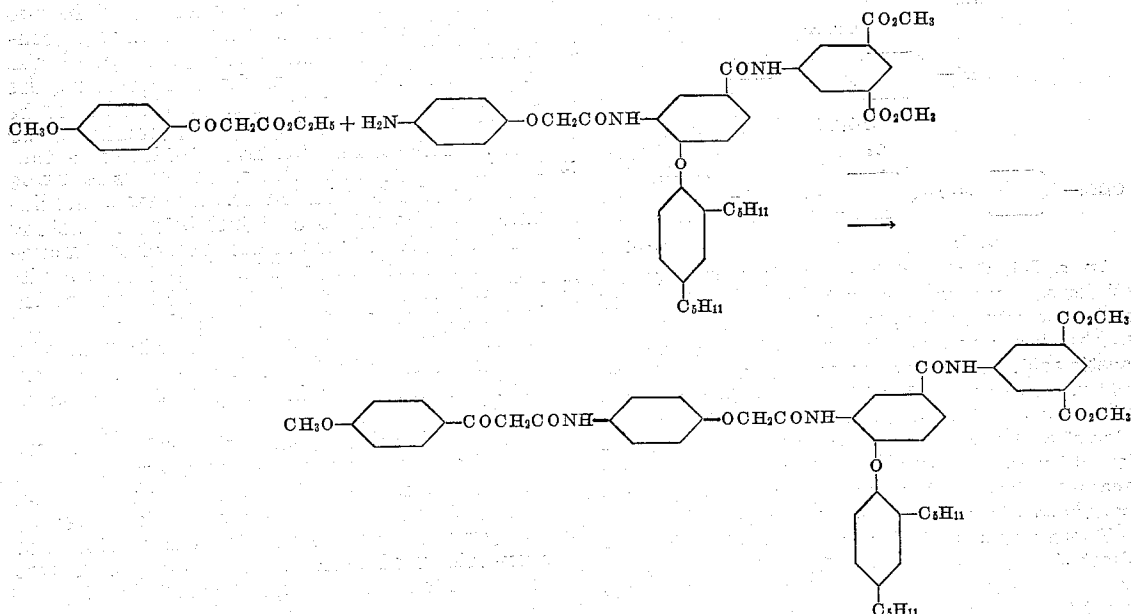
There was practically complete solution at first and then a very fine precipitate of sodium chloride was formed. The hot solution was filtered by gravity and allowed to cool, slowly at first until crystallization was well on the way, and finally by external cooling to 15° C. with stirring. The solid formed was filtered, slurried with 2 l. of water, filtered again and washed free of acetic

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Methyl - 5[4'(2'',4'' - di-tert-amylphenoxy) - 3'(4'''-nitrophenoxyacetamido)-benzamido]-isophthalate 50 g. (.064 mole) and 200 ml. of absolute alcohol were charged into a 375-ml. capacity magnesia bottle. To it was added 2 g. of sodium carbonate and about 3 g. of Raney nickel catalyst. The bottle was placed on a Parr hydrogenating machine and a pressure of about 50 lbs. of hydrogen was applied on the system. The bottle was shaken while it was externally heated with a jet of steam.

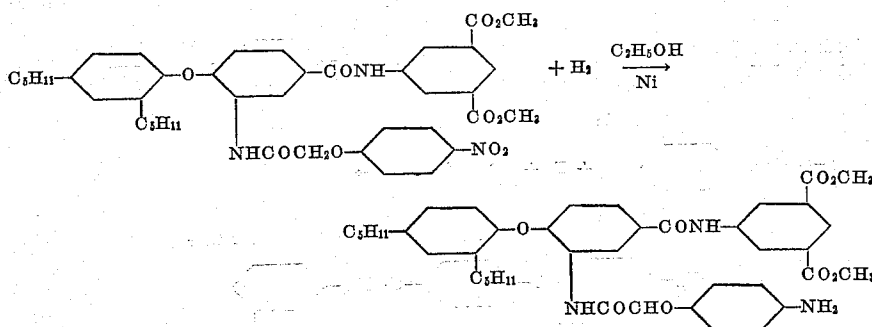
Reduction started very shortly and within 30 min. the required amount of hydrogen was taken up. The bottle was allowed to cool and the reaction mixture was filtered by gravity and let stand overnight in a stoppered vessel. The partly crystallized reaction mixture was cooled to about 10° in an ice bath and the white crystalline solid was filtered and washed once with 50 m. of cold alcohol and dried. The dry product weighed 39 g. and melted at 171-172° C. Yield 86%.

a - (4 - methoxybenzoyl) - 4 - { α - [2 - (2,4 - di-tert-amylphenoxy) - 5 - (3,5-dicarboxymethoxyphenylcarbamyl) phenylcarbamyl] methoxy} - acetanilide



acid with water. The dry product melted at 208-210° C. Yield 100.5 g., 77% of theory.

Methyl - 5[4'(2'',4'' - di - tert. - amylphenoxy) - 3'(4'''-aminophenoxyacetamido)-benzamido]-isophthalate



In a 1-liter flask were placed 35.5 g. (0.05 mole) of methyl 5-[4'-(2'',4'')-di-tert-amylphenoxy) - 3'-(4'''-aminophenoxyacetamido) benzamidoliso-phthalate and 500 cc. of histological xylene. The solution was heated to boiling before 11 g. (0.05 mole) of ethyl p-methoxybenzoylacetate was

added. This mixture was heated in an oil bath at 150° C. under a steam-jacketed ester column carrying a downward water-cooled condenser. About 3 cc. of distillate boiling at 75–80° was collected during two hours. As the solution cooled, an oil separated. It was stirred under petroleum ether until it became crystalline. Recrystallization from 500 cc. of benzene gave 31 g. (70% of the theoretical amount) of white solid, M. P. 177–179°.

Compounds 1 to 4 were made in the same way as compound 5, using the appropriate acetyl chloride in place of p-nitrophenoxycetyl chloride and o-methoxybenzoyl acetate in place of p-methoxybenzoyl acetate.

The preparation of compound 6 is described in application Serial No. 301,961, filed concurrently herewith by McCrossen, Salminen and Weissberger.

The following example illustrates the method of hydrolysis of the ester of the coupler and incorporation in a gelatin emulsion:

3.7 grams of compound 1 were dissolved in a mixture of 15 cc. of 95 per cent ethyl alcohol and 7.5 cc. of 20 per cent sodium hydroxide solution. The mixture was warmed gently (if necessary) to complete solution of the coupler and then poured into 200 cc. of water at 40° C. If desired, the mixture may be added directly to a gelatin solution. The resulting solution was brought to a pH of 6 to 7 by addition of 2 per cent citric acid solution. The coupler solution was then mixed with a suitable amount of melted silver halide gelatin emulsion e. g. 400 cc. of a positive type gelatino silver halide emulsion at 40° C. After

grams of 1,2-dimethoxy benzene was added to 200 cc. of water containing 2.0 grams of the wetting agent Gardinol WA. The whole mixture was stirred to effect preliminary emulsification, then passed through a colloid mill several times while the temperature of the solution and the mill was maintained at about 20° C. In this way a very stable and very fine emulsion was obtained which was added to 1000 cc. of a melted silver halide gelatin emulsion. The emulsion containing the added coupler dispersion was coated on a suitable support, set and dried in the usual manner. On exposure and development of this emulsion with a developing solution employing 2-amino-5-diethylaminotoluene as the developing agent and subsequent removal of silver, a yellow dye image was obtained.

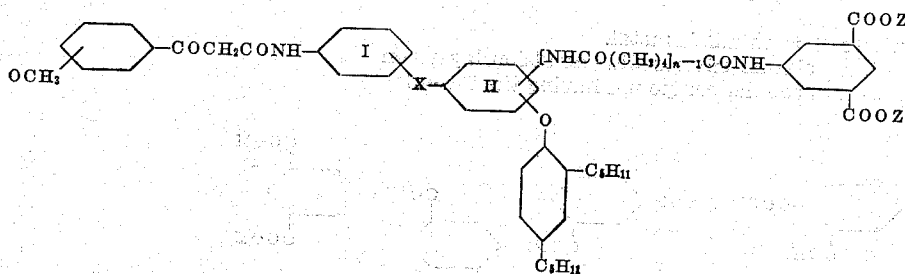
The following developing solution is suitable for developing silver halide emulsion layers containing the couplers incorporated either directly in the emulsion or in solvent dispersions:

	Grams
2-amino-5-diethylaminotoluene hydrochloride	2
Sodium sulfite	2
Sodium carbonate	2
Potassium bromide	2
Water to 1 liter.	

It will be understood that the examples and modifications set forth herein are illustrative only and that our invention is to be taken as limited only by the scope of the appended claims.

We claim:

1. A gelatino-silver halide emulsion layer containing a coupler compound having the formula



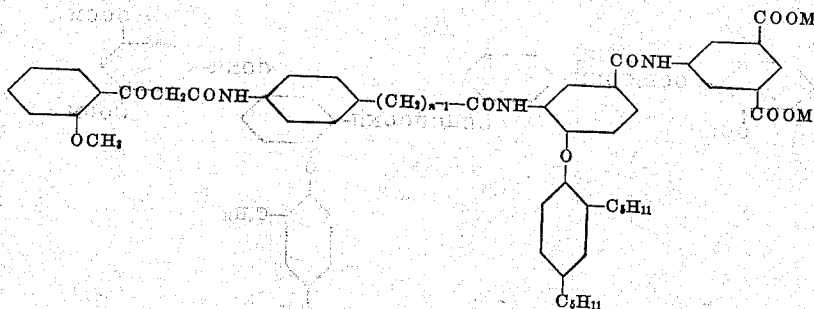
coating, the emulsion layer thus obtained may be subjected to the usual exposure and processing steps of color photography.

In hydrolyzing the couplers other means may be used such as acid or alkaline hydrolysis in lower aliphatic alcohol or aqueous media provided that the conditions employed do not cause splitting of the coupler at points in the molecule such as at the —NHCO— linkage.

The following example illustrates incorporation of the methyl ester of the coupler in solvent

where X is selected from the class consisting of —CONH—, —CH2CONH—, —(CH2)2CONH—, —(CH2)3CONH—, —(CH2)4CONH—, —OCH2CONH—, —O(CH2)3CONH—, and —CH=CHCONH—, Z is selected from the class consisting of alkyl and alkali metal, n is an integer from 1 to 2, radical I is connected to X in a position other than ortho, and radical II is substituted in a position other than para to X.

2. A gelatino-silver halide emulsion layer containing a coupler compound having the formula



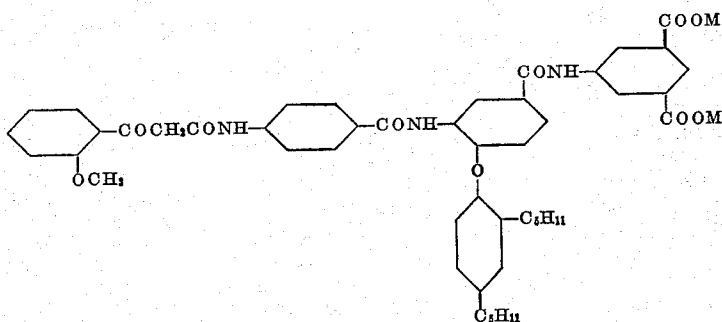
dispersion in a gelatin emulsion:

where n is an integer from 1 to 5 inclusive, and M is an alkali metal.

A solution of 7.5 grams of compound 1 in 15

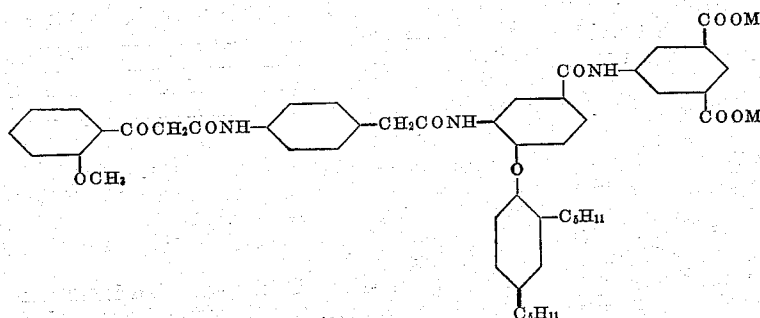
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3. A gelatino-silver halide emulsion layer containing a coupler compound having the formula



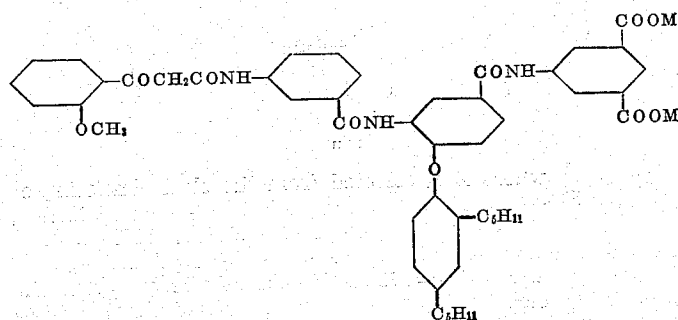
where M is an alkali metal.

4. A gelatino-silver halide emulsion layer containing a coupler compound having the formula



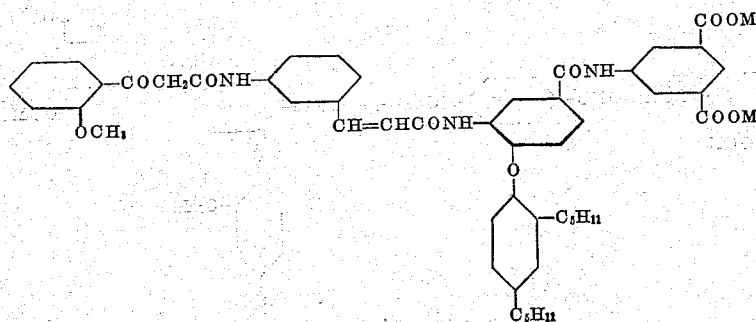
where M is an alkali metal.

5. A gelatino-silver halide emulsion layer containing a coupler compound having the formula



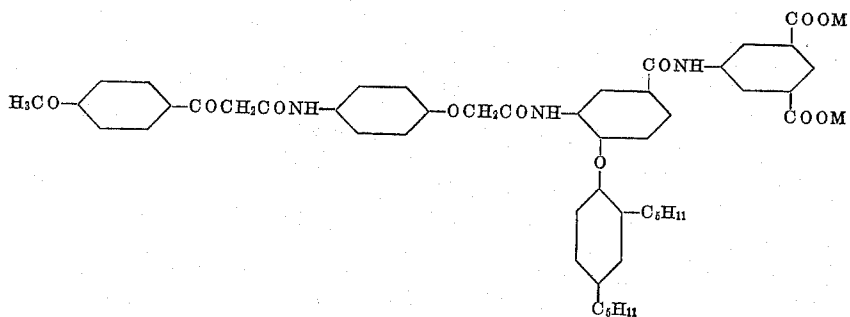
where M is an alkali metal.

6. A gelatino-silver halide emulsion layer containing a coupler compound having the formula



where M is an alkali metal.

7. A gelatino-silver halide emulsion layer containing a coupler compound having the formula



where M is an alkali metal.

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No references cited.