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PHOTOGRAPHIC SILVER HALIDE EMULSIONS CONTAINING 1-CARBOMYLMETHYL-PYRAZOLONE COUPLERS

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5 Claims

ABSTRACT OF THE DISCLOSURE

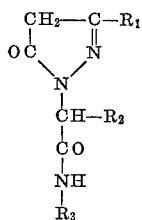
Photographic silver halide emulsion containing a magenta-forming 1-carbomylmethyl-pyrazolone coupler.

This invention relates to a color photographic material which has at least one silver halide emulsion layer which contains a magenta-forming coupler.

The term color couplers is understood to mean compounds which will react with the oxidation products of color photographic developers, especially those of the phenylene diamine type, to form colored compounds. Such couplers must satisfy many requirements; for example they should couple as rapidly as possible with the oxidised color developer to form the dye. The resulting dye should, as far as possible, only adsorb in the required region of the spectrum whereas any side absorptions in other regions of the spectrum are undesirable. Furthermore the dyes produced should be as light-fast as possible and be stable even under extreme conditions of high temperature and atmospheric moisture such as occur in the tropics. Adequate resistance to tropical conditions is, of course, also necessary for the color couplers which are incorporated in the light-sensitive layer. The previously known magenta-forming couplers have been particularly unsatisfactory in this last respect. Also, the known magenta-forming couplers do not produce dyes on color development of the required brilliance.

It is the object of the invention to find magenta-forming couplers which not only have these required properties but also show satisfactory stability under tropical conditions and have high brilliance and good fastness to light.

It has now been found that particularly suitable magenta-forming couplers for photographic silver halide emulsion layers are 1-carbomylmethyl-pyrazolone compounds of the following formula:



in which

R₁ is (1) alkyl preferably with up to 20 carbon atoms, (2) an arylamino group, preferably a phenylamino group, in which the phenyl group may be further substituted, e.g. with halogen, such as chlorine or bromine, alkyl, alkoxy, sulfo or carboxyl, or (3) an acylamino group in which the acyl groups may be derived from long chain aliphatic carboxylic acids or from benzene carboxylic acids which may carry further substituents such as halogen, alkyl, alkoxy, phenoxy, sulfo or carboxyl; the acyl groups can

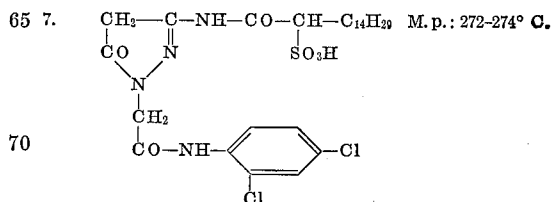
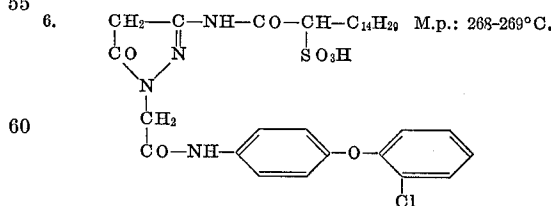
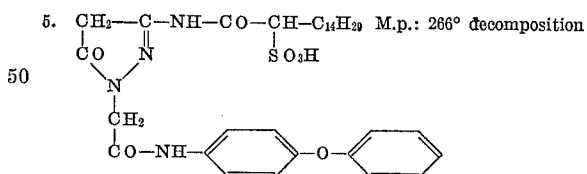
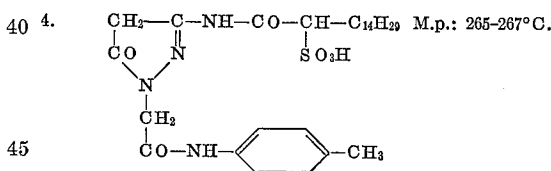
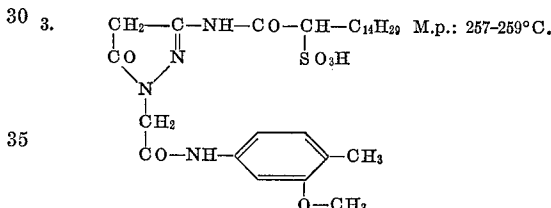
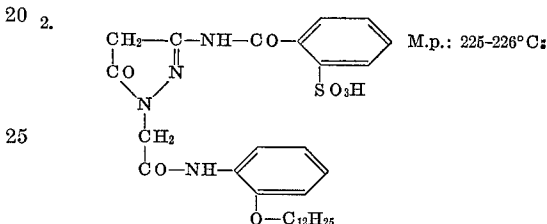
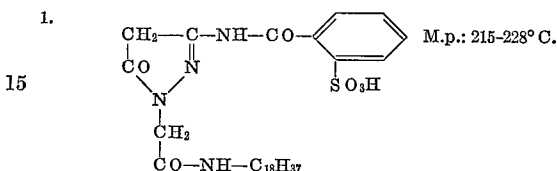
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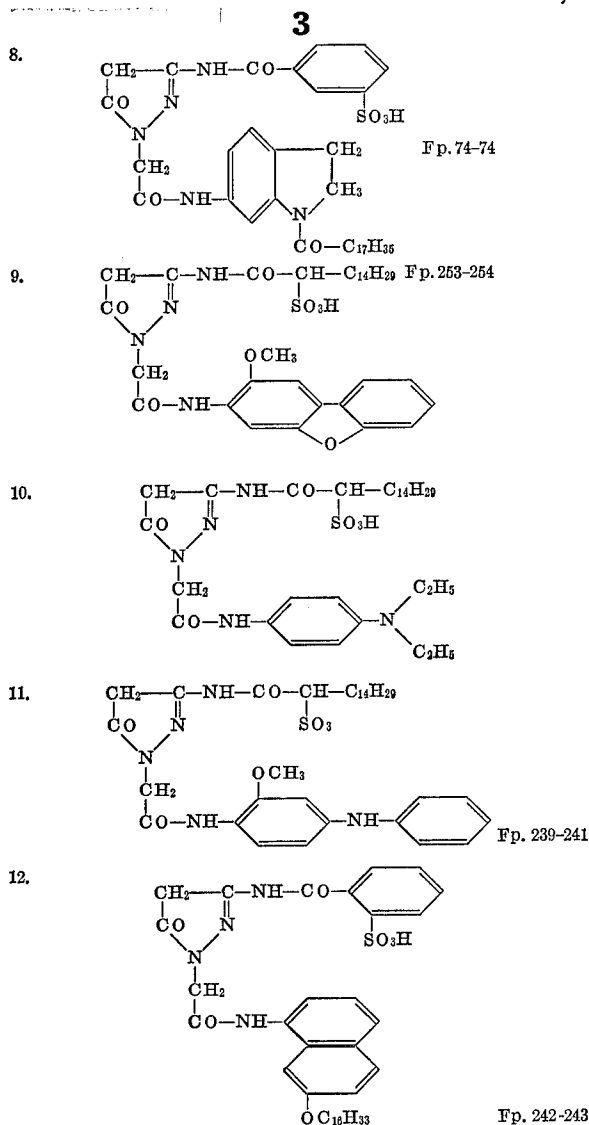
also be derived from aliphatic or aromatic monoesters of carbonic acid.

R₂ is hydrogen or alkyl having up to 18 carbon atoms;

R₃ is (1) hydrogen, (2) alkyl having up to 20 carbon atoms, (3) an aryl group, especially phenyl, which may carry one or more substituents such as alkyl or alkoxy with up to 20 carbon atoms, phenoxy, halogen, such as chlorine or bromine, sulfo or carboxyl, or (4) a heterocyclic group which may be further substituted, e.g. with alkyl, alkoxy, halogen or acyl groups.

The following couplers are suitable for example:





The compounds according to the invention are prepared by methods known per se. The method of preparation of coupler 2 is described in detail below. The other compounds are prepared in a similar way.

PREPARATION OF COUPLER NO. 2

(I) 2-dodecyl-acetanilide

532.8 g. of 2-acetaminophenol and 540 g. of dodecyl bromide were suspended in 2 litres of absolute alcohol. A solution of 46 g. of sodium in 1 litre of absolute alcohol was added to the mixture. The mixture was boiled under reflux for 5 hours. It was then filtered while hot and mixed while stirring into 8 litres of water to which 40 ml. of concentrated hydrochloric acid had been added. It was filtered under suction and the product was washed with water and methanol. The crude product was recrystallized from methanol. The yield was 612 g. of melting point 61-63° C.

(II) 2-dodecyl-oxy-aniline

420 g. of 2-dodecyl-oxy-acetanilide were dissolved in 1,300 ml. of alcohol, and a solution of 430 g. of potassium hydroxide in 430 ml. of water was added. The mixture was boiled under reflux for 20 hours. It was then cooled to a low temperature, suction filtered and washed with methanol. 320 g. of 2-dodecyl-oxy-aniline of melting point 37-39° C. were obtained on recrystallization from methanol.

(III) 2-dodecyl-oxy-chloroacetanilide

273 g. of 2-dodecyl-oxy-aniline were suspended in 2.5 litres of alcohol. 40.8 g. of chloroacetyl chloride were

added dropwise with stirring at -5° to 0° C. At this temperature the following reagents were added dropwise successively: 150 ml. of an alcoholic potassium hydroxide solution (55.3 g. KOH in 480 ml. of alcohol), 40.8 g. of chloroacetyl chloride, 150 ml. of alcoholic KOH of the above concentration, 40.8 g. of chloroacetyl chloride, 180 ml. of alcoholic KOH of the above concentration, 40.8 g. of chloroacetyl chloride and lastly another 150 ml. of alcoholic KOH. The mixture was stirred for 10 minutes, poured into 2.5 litres of water and acidified with 5 N HCl until acid to Congo red. The reaction mixture was suction filtered and washed with a large quantity of water. The air-dried crude product was recrystallized from alcohol. The yield was 175 g., melting point 72-74° C.

(IV) 2-dodecyl-oxy-hydrazinoacetanilide

175 g. of 2-dodecyl-oxy-chloroacetanilide were suspended in a solution of 96 g. of hydrazine hydrate in 500 ml. of alcohol. The mixture was heated up to a temperature of +70° C., at which temperature all the reactants went into solution. The solution was then stirred for 30 minutes at 70° C. The mixture was then poured while stirring into 2 litres of ice water, acidified until acid to Congo red, filtered with suction and washed with 2 N HCl and lastly with water. The hydrochloride was dissolved in 750 ml. of warm methanol, adjusted to pH 10 with 5 N NaOH and then diluted with 2 litres of ice water. The product was filtered with suction and washed with a large amount of water. The yield of pure, colorless crystals was 117 g., melting point 44-46° C.

(V) 1-[N-(2-dodecyl-oxyphenyl)-carbamylmethyl]-3-amino-pyrazolone-(5)

117 g. of 2-dodecyl-hydrazinoacetanilide are suspended in 150 ml. of pyridine. 74 g. of diethyl monoimino-malonate hydrochloride were added at temperatures between 0 and +5° C. The reaction is exothermic. The reaction mixture was stirred for 2 hours at 0-10° C. and then for 2 hours without cooling. 220 ml. of methylate solution (85 g. of Na/litre of methanol) were then added to the solution and the solution was boiled under reflux for 30 minutes. The reaction mixture was then poured into a mixture of 300 ml. of 5 N HCl and ice and then made acid to Congo red with 5 N HCl. The waxy product was separated by suction filtration and washed with water. The crude product was stirred up with a little methanol, separated by suction filtration and washed with methanol. The crude product was purified by recrystallization from 250 ml. of alcohol with the addition of active charcoal. The yield of yellowish crystals was 50 g., the melting point 103-105° C.

(VI) Coupler 2

50 g. of the above aminopyrazolone were suspended in 300 ml. of ethyl acetate and heated to boiling. 23 g. of o-sulfo-benzoic acid anhydride were added near the boiling point of the solution. The whole reaction mixture first dissolved to form a clear solution but after 3 minutes, the coupler started to precipitate in crystalline form. The reaction mixture was boiled under reflux for 30 minutes. The mixture was cooled to +50° C., filtered under suction and washed with ethyl acetate until the washings were colorless. The yield was 50 g. of colorless crystals of melting point 225-226° C.

The color couplers according to the invention have excellent stability to moist heat. The dyes produced from them in the course of the color-producing development are also stable under extreme climatic conditions at elevated temperatures and in very humid conditions. In addition, they have excellent fastness to light. Their absorption properties are very good. The color couplers according to invention couple extremely rapidly with the usual developers. The dyes obtained on color development with the color couplers according to the invention have an exceptionally high brilliance.

