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3,005,709
**PHOTOGRAPHIC COUPLERS CONTAINING
 ACYLAMINO GROUPS**

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 No Drawing. Filed Jan. 13, 1958, Ser. No. 708,374
 4 Claims. (Cl. 96-55)

This invention relates to photographic color-forming compounds and particularly to color-forming coupler compounds containing highly branched acylamino groups.

The production of colored photographic images where by a primary aromatic amino developing agent couples with color-forming compounds on development has long been known in the art. In most methods of color photography, the subtractive color principle is ordinarily employed resulting in dye images of the complimentary primary colors, i.e., cyan or blue-green, magenta and yellow. The dyes formed in this way must be sufficiently stable and insoluble in order to withstand processing in ordinary photographic developing and fixing baths so that the simultaneously formed silver images can be removed from the photographic layers to leave therein the pure dye images.

The coupler compounds, when used as described above, may be added directly to the developer solution or they can be incorporated in the photographic layer prior to exposure.

In the former case, the coupler compounds must be sufficiently soluble in the developer solution and readily diffusible into the emulsion layers so that amounts can be used which will produce adequate dye densities in the final photographic images.

On the other hand, when the coupling components are incorporated in the photographic layer, it is essential that they remain immobile and not wander or diffuse through the emulsion from their original site; otherwise, color separation will be imperfect and result in final dye images that are degraded.

A method commonly employed to render color formers non-diffusing is to introduce into the coupler molecule a bulky substituent such as a carbon chain of from 10 to 20 carbon atoms. The function of the bulky carbon chain serves as an anchor and holds the coupler firmly in the emulsion layer.

The aforesaid non-diffusing couplers may have, in addition, a salt-forming group, i.e., a carboxylic acid or sulfonic acid grouping, whereby the couplers can be dissolved in the photographic emulsion in the form of their soluble alkali salts.

Alternately, color-forming compounds may be incorporated in photographic emulsions by forming dispersions. Such a method for dispersing color formers in emulsion layers is disclosed in U.S.P. 2,269,158 and 2,284,877 by Martinez and in U.S.P. 2,304,939 and 2,304,940 by Mannes and Godowsky, wherein a mixture of a water-insoluble colloid such as a natural or synthetic resin or cellulose ester and a coupler is dissolved in a water-immiscible low boiling solvent and the resulting solution emulsified in a gelatin emulsion. The volatile solvent is subsequently removed leaving behind a dispersion composed of a coupler in admixture with a water-insoluble colloid distributed throughout the gelatin matrix.

In preparing color coupler dispersions in this way, various difficulties are encountered. One such difficulty is due to the limited solvent action which the solid colloid has for the coupler and the dye derived therefrom with the result that the coupler and the dye often crystallize in the emulsion. This manifests itself in inefficient coupling on color development and dye images of diminished

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brilliance. Although in some cases it is possible to select a water-insoluble colloid having the proper solvent action for the couplers and dyes produced therefrom, such particles often prove to be insufficiently permeable to the processing solutions.

Another process for dispersing color formers in photographic emulsions is described in U.S.P. 2,322,027. According to this method, a coupler is converted into a liquid at room temperature by dissolving it in a high boiling oily liquid and the resulting coupler solution dispersed in a photographic colloid as minute droplets or globules. Since it is desirable that the concentration of the coupler in the oil be as high as possible, this system calls for couplers of extreme solubility so as to prevent crystallization, a condition which limits the number of couplers suitable for such applications.

By employing highly concentrated coupler solutions, emulsion layers can be prepared containing smaller quantities of coupler solvents and, as a consequence, less coupler is needed per unit area to produce a given dye density.

Although it has been claimed that couplers dispersed in admixture with water-immiscible colloids or high boiling solvents are not required to be non-diffusing, molecular weights in excess of 400 appear to be expedient. This is particularly true for color formers employed in mixed grain where the problem of coupler diffusion occurs to a greater degree than in the conventional three layer emulsions.

It is therefore an object of the present invention to provide color-forming compounds having extremely high solubility in oily type organic solvents.

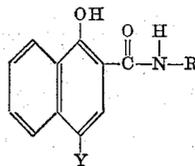
A further object is to provide coupler compounds which do not diffuse from one emulsion layer into another when incorporated in a multilayer coating.

A further object is to provide coupler compounds having highly branched substituents.

A further object is to provide couplers which possess low melting points and resist crystallization.

Other objects will appear hereinafter as the description proceeds.

These objects can be realized by the use of coupler compounds having certain highly branched acylamino side chains as depicted in the following general formula:



wherein R represents a highly branched tertiary alkyl group of from 8 to 24 carbon atoms and Y is hydrogen or halogen.

The coupling compounds herein described are either liquid at room temperature or low melting solids having extremely high solubility in solvents used to disperse them in a photographic emulsion according to conventional methods. They have a high resistance to crystallization and yield dyes of excellent stability and spectral characteristics. All of these advantages make them desirable couplers for use in color photography.

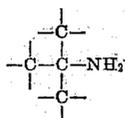
In general, the coupler compounds of my invention can be prepared by reacting a phenyl ester of an aromatic carboxylic acid containing an ortho hydroxy group with a highly branched tertiary alkyl amine containing from 8 to 24 carbon atoms. The reaction can be carried out in the presence or absence of a solvent. In some instances, an excess of the tertiary aliphatic amine is used and can function as a solvent.

A highly branched tertiary alkyl amine, which I have

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found to give excellent results, is a product sold under the trade name of "Primene JM-T" by the Rohm and Haas Company, Washington Square, Philadelphia 5, Pennsylvania.

In a technical brochure (SP-33; 12-51) published by the aforesaid company, "Primene JM-T" is described as a mixture of highly branched primary amines having a tertiary alkyl structure of the following formula:



the predominate portion being t-C₁₈₋₂₄H₃₇₋₄₉NH₂. "Primene JM-T" is further characterized by the following physical constants:

Molecular weight..... Principally 269-353.
 Specific Gravity, 25° C..... 0.853.
 Refractive Index, 25° C..... 1.460.
 Boiling Point (or Range)..... 5-70% at 133-191° C. (15 mm.); 5-70% at 275-324° C. (760 mm.).
 Neutralization Equivalent..... 344.
 Flash-Point (Tag., open cup)--- 265° F.

Since the "Primene JM-T" is a mixture of tertiary aliphatic amines of from 8 to 24 carbon atoms, the couplers produced therefrom, according to this invention, are extremely low melting and soluble and are usually liquids at room temperatures. This can be attributed to two well-known physical principles: (1) the melting points of highly branched organic carbon compounds are usually lower than their straight-chained counterparts of the same number of carbon atoms (2) the melting points of organic compounds composed of mixtures of homologs are usually lower than any one of the homologs making up the mixture, in this case, couplers containing tertiary alkyl groups having from 8 to 24 carbon atoms.

Other suitable highly branched tertiary alkyl amines are:

Tert.-octylamine
 Isobutylethylpropylamine
 Diethylisoamylamine
 Di(isobutyl)ethylamine
 Isoamyl-di(propyl)amine
 Propyl-di(isobutyl)amine

As examples of tertiary amines, in the range C₁₂₋₁₅, the "Primene 81" can be used. This latter, highly branched tertiary alkylamine is a product sold by the Rohm & Haas Company, Washington Square, Philadelphia 5, Pennsylvania.

"Primene 81" is a mixture of highly branched amines and has the same type of tertiary alkyl structure as "Primene JM" but with the number of carbon atoms varying principally from 12 to 15.

The "Primenes" are available in two grades, refined and technical, and are designated by "R." and "T." respectively.

The following examples will illustrate the present invention but are not to be construed as imposing any limitations on the invention.

Example I

A mixture of recrystallized phenyl 1-hydroxy-2-naphthoate (80 g., 0.3+ mole) and (175 g.) redistilled "Primene JM-T" (Rohm and Haas Company, B.P. 90-140° C./0.5 mm.) was heated at 160-170° C. for 2 hours. The excess amine and phenol was removed at reduced pressure and the residue dissolved in glacial acetic acid. The acetic acid solution was poured with stirring into water. The oil which separated was collected and dissolved in 1 liter of petroleum ether of B.P. 30-60° C.

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The solution was dried and passed through a column of activated magnesium silicate of 40-80 mesh. The resulting nearly colorless solution was evaporated at reduced pressure to give a light tan viscous oil. The product was extremely soluble in most organic solvents.

Example II

The same procedure was followed as in the case of Example I, but the 4-chloro-1-hydroxy-2-naphthoate was used in place of the unsubstituted naphthoic ester. The product thus obtained displayed similar properties.

Example III

A solution of 3 g. of coupler prepared according to Example I was dissolved in a suitable solvent such as 3 g. of tricresyl phosphate. The solution was dispersed in 20 ml. of 6% gelatin plus 0.5 ml. of 25% lauryl sulfate by means of a small Waring Blender. The resulting dispersion was added to 50 g. of a silver-halide gelatin emulsion and the mixture coated on clear film base.

On exposure and development of the resulting coating with a developing solution employing 2-amino-5-diethylaminotoluene as the developing agent and subsequent removal of silver, a cyan image was obtained.

Various photographic developing agents can be employed with the couplers of my invention. The primary aromatic amino developing agents generally suitable include the phenylenediamines and aminophenols. The alkyl phenylenediamines may be substituted in the amino group as well as in the ring. Suitable compounds are 4-aminoaniline, 4-ethylaminoaniline, 2-diethylaminoaniline, 4-dialkylaminoaniline, e.g., 4-dimethylaminoaniline, 4-diethylaminoaniline, 4-[N-(β-hydroxyethyl)-N-ethyl]-aminoaniline, 4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-2-methylaniline sulfate, and the like. The above developing agents are preferably used in the form of their salts such as the hydrochloride or hydrosulfate as they are more soluble and stable than the free bases. All of these compounds have a primary amino group which enables the oxidation product of the developer to couple with the color compounds to form dye images. After removal of the silver image by bleaching and fixing in a manner well-known to the art, the color image remains in the emulsion. A suitable developing solution can be prepared as follows:

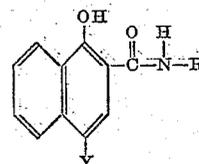
	G.
2-amino-5-diethylaminotoluene	2
Sodium carbonate (anhydrous)	20
Sodium sulfite (anhydrous)	2
Potassium bromide	0.2
Water to make 1 liter.	

The exposed silver-halide emulsions containing the color formers are developed in the above solution in the usual manner.

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

I claim:

1. A silver-halide emulsion containing a coupler compound of the following general formula:



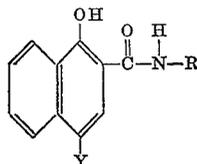
wherein R represents a branched tertiary alkyl group of from 8 to 24 carbon atoms in which the carbon atom connected to the nitrogen atom of the amide grouping is always tertiary, and Y is selected from the class consisting of hydrogen and halogen.

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2. The product as defined in claim 1 wherein Y is hydrogen.

3. The product as defined in claim 1 wherein Y is halogen.

4. The process of producing a cyan dyestuff image in a silver-halide emulsion which comprises exposing said emulsion to light and developing the same with a primary aromatic amino developer in the presence of a color former for cyan having the following general formula:



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wherein R represents a branched tertiary alkyl group of from 8 to 24 carbon atoms in which the carbon atom connected to the nitrogen atom of the amide grouping is always tertiary, and Y is selected from the class consisting of hydrogen and halogen.

References Cited in the file of this patent

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