

UNITED STATES PATENT OFFICE

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COLOR PHOTOGRAPHY

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This invention relates to the production of colored photographic images by color development, and more particularly to methylenebis-coumarins as new color forming coupler compounds therefor.

The formation of colored photographic images by coupling the development product of an aromatic amino developing agent with color forming or coupling compounds is well known, and is generally referred to as color forming development. In these methods the subtractive process of color formation is ordinarily used and the image dyes are intended to be of the complementary primary colors, cyan or blue-green, magenta and yellow. The couplers which produce magenta dyes are ordinarily pyrazolones or cyano acetyl compounds. The dyes produced by coupling are azomethines, indamines or indolphenols, depending upon the composition of the coupler and of the developer. The coupler or color former may be present in the emulsion or in the developing solution which during the development process couples with the oxidation product of the aromatic amino developer to form a dye image in the emulsion. The developed emulsion may then be bleached for removal of the silver image leaving the color image in the emulsion.

I have discovered that methylenebis-coumarins are especially valuable color formers which couple with the oxidation product of an aromatic primary amino developer to form a magenta dye image in the emulsion. The methylenebis-coumarins have short absorption bands and a high transmission in the blue-green region of the spectrum, with the result that a satisfactory color for subtractive color processes is obtained upon coupler development.

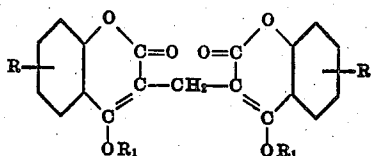
The principal object of this invention is to provide a new class of color formers for producing magenta dye images by color forming development.

A further object is to provide photographic developer solutions and emulsions which contain a new class of color formers for producing magenta dye images in situ with photographic images.

A still further object is to provide finished photographs which contain stable dye images.

Still other objects will appear hereinafter.

The above and other objects are accomplished according to the present invention by the use of methylenebis-coumarins of the general formula:



wherein R represents hydrogen, or an alkyl radi-

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cal, e. g., methyl, ethyl, propyl, butyl, octyl, decyl, octadecyl or any other aliphatic radical containing up to 24 carbon atoms, acyl, e. g., acetyl, propionyl, butyryl, lauroyl, palmityl, stearyl, benzoyl, naphthoyl, etc., aryl, e. g., phenyl, naphthyl, anthranyl, diphenyl, etc., aralkyl, e. g., benzyl, methyl benzyl, ethyl benzyl and the like, or halogen, e. g., chlorine, bromine and iodine, and R₁ represents either hydrogen, alkyl, or acyl group of the same value as above. Said alkyl, acyl, aryl and aralkyl radicals given as values for R may be substituted by a halogen such as chlorine, bromine or iodine, amino group, e. g., primary amino, secondary amino such as methyl amino, phenyl amino and the like, or a tertiary amino such as dimethyl amino, diphenyl amino, etc., sulfoamino, or solubilizing groups such as sulfonic or carboxylic acid groups.

Compounds which fall under this general classification are, 3,3'-methylenebis (4-hydroxycoumarin), 6,6'-stearyl-3,3'-methylenebis (4-hydroxycoumarin), 7,7'-stearyl-3,3'-methylenebis (4-hydroxycoumarin), disulfo 7,7'-stearyl-amino-3,3'-methylenebis (4-hydroxycoumarin), 3,3'-methylenebis (4-hydroxycoumarin), 3,3'-methylenebis (4-hydroxycoumarin) mono methyl ether, 3,3'-methylenebis (4-hydroxycoumarin) dimethyl ether, 3,3'-methylenebis (4-hydroxycoumarin) dibenzoate, 6,6'-dioctadecyl-3,3'-methylenebis (4-hydroxycoumarin), 6,6'-diphenyl-3,3'-methylenebis (4-hydroxycoumarin), 7,7'-dibenzyl-3,3'-methylenebis (4-hydroxycoumarin), 6,6'-dibromo-3,3'-methylenebis (4-hydroxycoumarin), 6,6'-dioctadecyl - 7,7' - disulfo - 3,3' - methylenebis (4-hydroxycoumarin), 6,6'-dioctadecyl - 3,3'-methylenebis (4-hydroxycoumarin), 3,3'-methylenebis (4-hydroxycoumarin) diacetate, 3,3'-methylenebis (4-hydroxycoumarin) dipropionate, 3,3'-methylenebis (4-hydroxycoumarin) di-n-butyrate, 3,3'-methylenebis (4-hydroxycoumarin) diisocaproate, 3,3'-methylenebis (4-hydroxycoumarin) di-n-heptanoate, and 3,3'-methylenebis (4-hydroxycoumarin) di-trimethylacetate.

In general, the coupling compounds of the present invention which do not contain solubilizing groups, are water insoluble. Their solubility in water, however, is accomplished by the introduction of suitable solubilizing groups, e. g., sulfonic or carboxylic acid groups into the groups represented by R in the above general formula.

The new color coupling compounds of the present invention are prepared from methylenebis (4-hydroxycoumarin) substituted by suitable groups according to the methods known in the art. The methylenebis (4-hydroxycoumarin) is readily synthesized by condensing formaldehyde with 2 molecular equivalents of 4-hydroxycoumarin as described in Jour. Amer. Chem. Soc., 65, page 2288, 1943. The di-esters of 3,3'-methylenebis (4-hydroxycoumarin) listed above are pre-

pared according to the methods described in U. S. Patent 2,345,635.

The color formers may be added to the developer, providing they are not fast to diffusion in gelatin, or to the silver-halide emulsion in the form of a solution or a suspension in a suitable solvent, such as, 1-N-alcoholic sodium or potassium hydroxide, acetone, ethyl alcohol, isopropyl alcohol, etc. Dispersing agents such as isopropyl naphthalene sulfonic acid or any of the dispersing agents disclosed in U. S. 2,186,717 may be used in preparing the suspensions of the water insoluble color formers for incorporation into developers or silver-halide emulsions. Instead of gelatin, the color formers may be incorporated in other colloidal materials such as, organic esters of cellulose, super-polyamides, polyesters or synthetic resins. The emulsion may be carried by a transparent medium such as cellulose esters, super-polyamides, synthetic resins or a nontransparent reflecting medium such as paper or an opaque cellulose ester. The emulsion may be coated as a single layer on the support, or superposed layers containing the couplers may be coated on one or both sides of the support. The superposed layers may be differentially sensitized for the formation of a color image in the well known manner.

When incorporating the color formers into photographic silver-halide emulsions, it is essential that the substituents of R in the above general formula be such that they will prevent the color formers from migrating from one layer to another, otherwise color distortion will result upon color-forming development. Several methods have been proposed to prevent migration of color formers from silver-halide emulsion layers by rendering such color formers "fast to diffusion in gelatin." This result may be accomplished in several ways, as for example, by substituting the methylenebis coumarin nucleus with suitable groups which impart substantive characteristics to the color formers which combine permanently with the gelatin and other colloidal materials of the silver-halide emulsion, or by enlarging the substituent group of the color former with a long chain alkyl radical so that the color former is incapable of diffusing from the gelatin or other colloidal material. Examples of such methods which render color formers fast to diffusion by imparting substantive characteristics thereto are disclosed in U. S. 2,179,228. Examples of color formers which are rendered fast to diffusion by enlarging the substituent groups are disclosed in U. S. Patents 2,178,612; 2,179,244; 2,186,045; 2,186,719; 2,186,732; 2,186,849; and 2,186,734. By reference to the latter patents, it will be noted that the color formers are modified by the inclusion of radicals of resins, polypeptides, hydrogenated ring systems, carbohydrates, long alkyl chains, and by having the substituent radical recur a number of times in the final molecule. It is to be understood that the substituent groups of the color forms of the present invention in addition to those previously mentioned, include substantive groups or molecular enlarging groups for the purpose of rendering the methylenebis coumarins fast to diffusion.

As examples of suitable aromatic primary amino developing agents which may be employed with the color coupling compounds of the present invention, there may be mentioned p-phenylene diamine, mono ethyl-p-phenylene diamine, diethyl-o-phenylene diamine, 4,4'-diamino-diphenylamine, p-amino dialkyl anilines, e. g., p-amino

dimethyl aniline and p-amino-diethyl aniline. These developing agents are preferably used in the form of their salts such as the hydrochloride, since they are more soluble and stable than the free base. They are characterized by the presence of a free or primary amino group in the phenyl nucleus which enables the oxidation product of the developer to couple with the color former to form a dye image in the emulsion adjacent to the individual particles of the silver image. The silver image may be removed by bleaching in the well known manner to leave the color image in the emulsion.

A suitable developing solution is prepared as follows:

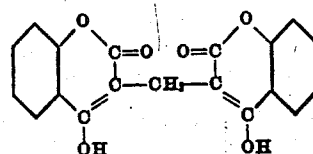
p-Amino-diethylaniline HCl	grams	2.0
Sodium carbonate (anhydrous)	do	50.0
Sodium sulfite (anhydrous)	do	2.0
Potassium bromide	do	0.2
Water to make	liters	1

The exposed silver-halide emulsions are developed in the above solution in the usual manner. A solution or suspension of the color former is only added to the developing solution where the color former is not present in the silver-halide emulsion.

Many specific objects, features and advantages of my invention will become apparent to those skilled in the art from the specific examples appearing below. The following examples are not to be considered as limiting my invention but are merely illustrative of methods of carrying it out.

EXAMPLE I

3,3'-methylenebis (4-hydroxycoumarin)

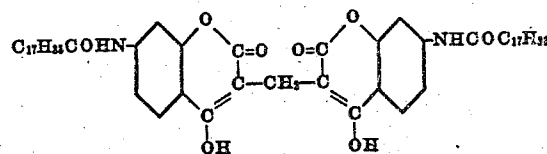


This compound was prepared according to the method given in Jour. Amer. Chem. Soc., 65, p. 2289, 1943, by adding 9 grams of 4-hydroxycoumarin to a mixture of 30 cc. of formaldehyde and 60 cc. of absolute ethyl alcohol and refluxing the mixture for an hour. The reaction mixture was allowed to cool. The precipitated product was then filtered and recrystallized from ethyl alcohol.

1 gram of the above product was dissolved in 20 cc. of ethyl alcohol. 2 cc. of the solution were then added to the developing solution and used for the development of an exposed silver-halide emulsion. A magenta image was obtained together with the silver image.

EXAMPLE II

7,7'-stearyl-amino-3,3'-methylenebis (4-hydroxycoumarin)



This compound was prepared according to Example I of U. S. 2,186,045, by dissolving 3.38 grams of 3,3'-methylenebis (4-hydroxycoumarin) in 25 cc. of concentrated sulfuric acid and nitrating the mixture by the addition of 0.2 mol of sodium

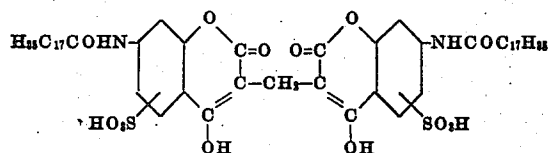
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nitrate with cooling. The reaction product was precipitated by pouring out the mixture on ice, and after recrystallization from water was reduced with stannous chloride and hydrochloric acid. The tin was removed with H_2S and the whole concentrated by evaporation. The resulting product was then acylated with 0.1 mol of stearyl chloride in pyridine. After recrystallization from benzene the product was dried in an oven for about 2 hours at $75^\circ C$.

1.8 grams of the above color former were dissolved in 2.0 cc. of 1-N-alcoholic KOH and added with thorough mixing to 100 cc. of a gelatin silver bromide-iodide emulsion. After coating the emulsion containing the color former onto a suitable support and drying, the film was exposed and developed to yield a magenta image together with the silver image.

EXAMPLE III

Disulfo 7,7'-stearyl-amino-3,3'-methylenebis (4-hydroxycoumarin)

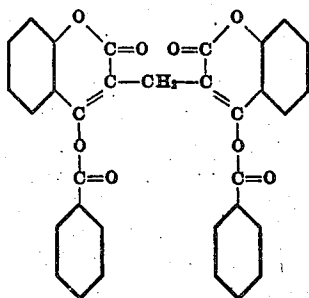


This compound was obtained by sulfonating the product of Example II with sulfuric acid containing 30% SO_3 with cooling.

After recrystallization from water, 1.8 grams of the resulting product were dissolved in 2.0 cc. of water and the solution added to 100 cc. of gelatin silver bromide-iodide emulsion. The emulsion was coated onto a cellulose acetate base and after drying, the film was exposed and developed. A dye image of excellent magenta color was formed in the emulsion.

EXAMPLE IV

3,3'-methylenebis (4-hydroxycoumarin) dibenzoate



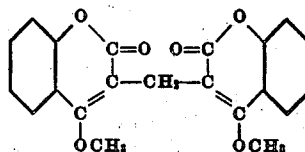
This compound was prepared according to the directions given in Jour. Amer. Chem. Soc., 65, p. 2295, 1943 by dissolving or suspending 1.5 grams of 3,3'-methylenebis (4-hydroxycoumarin) in 5 cc. of pyridine and an equal volume of benzoyl chloride. The mixture was allowed to stand about twelve hours, during which time the di-ester crystallized out. The product was recrystallized from benzene and dried.

1.8 grams of the above color former were dissolved in 2.0 cc. of 1-N-alcoholic KOH and added with thorough mixing to 100 cc. of a gelatin silver bromide-iodide emulsion. After coating the emulsion containing the color former onto a suitable support and drying, the film was exposed and developed to yield a magenta image together with the silver image.

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EXAMPLE V

3,3'-methylenebis (4-hydroxycoumarin) mono-methyl ether



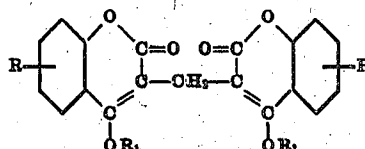
This compound was prepared according to the directions given in Jour. Amer. Chem. Soc., 65, p. 2295, 1943 by refluxing 1.5 grams of 3,3'-methylene-4,4'-epoxydicoumarin with 60 cc. of 0.5 N-sodium methylate in methyl alcohol for 30-60 minutes. The solution was then poured into water and acidified with HCl. The crude product was collected by filtration and recrystallized from a methyl alcohol water mixture.

Following the procedure of Example I, the color former was incorporated into the developing solution. After exposing the silver-halide emulsion and developing it in the developing solution, a magenta dye image of marked clarity of color was formed in the emulsion.

While I have disclosed the preferred embodiments of my invention and the preferred modes of carrying the same into effect, it will be readily apparent to those skilled in the art that many variations may be made therein without departing from the spirit thereof. Accordingly, the scope of my invention is to be limited solely by the following claims.

I claim:

1. A color forming photographic developer comprising an aromatic primary amino developing agent and a coupler compound having the general formula:



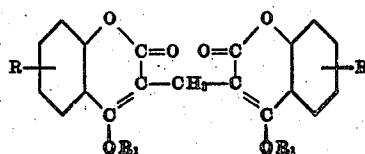
in which R is selected from the class consisting of hydrogen, halogen, alkyl, acylamino, sulfo-acylamino, aryl and aralkyl groups, and R_1 is selected from the class consisting of hydrogen, alkyl and acyl groups.

2. A color forming photographic developer comprising an aromatic primary amino developing agent and 3,3'-methylenebis (4-hydroxycoumarin).

3. A color forming photographic developer comprising an aromatic primary amino developing agent and 7,7'-stearyl-amino-3,3'-methylenebis (4-hydroxycoumarin).

4. A color forming photographic developer comprising an aromatic primary amino developing agent and disulfo 7,7'-stearyl-amino-3,3'-methylenebis (4-hydroxycoumarin).

5. The method of producing a magenta color photographic image in a gelatin silver-halide emulsion layer which comprises exposing the layer and developing it with an aromatic primary amino developing agent in the presence of a coupler compound having the general formula:



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in which R is selected from the class consisting of hydrogen, halogen, alkyl, acylamino, sulfoacylamino, aryl and aralkyl groups, and R₁ is selected from the class consisting of hydrogen, alkyl and acyl groups.

6. The method of producing a magenta colored photographic image in a gelatino silver-halide emulsion layer which comprises exposing the layer and developing it with an aromatic primary amino developing agent in the presence of 3,3'-methylenebis (4-hydroxycoumarin) as a coupler compound.

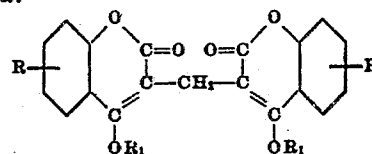
7. The method of producing a magenta colored photographic image in a gelatino silver-halide emulsion layer which comprises exposing the layer and developing it with an aromatic primary amino developing agent in the presence of 7,7'-stearyl-amino-3,3'-methylenebis (4-hydroxycoumarin) as a coupler compound.

8. The method of producing a magenta colored photographic image in a gelatino silver-halide emulsion layer which comprises exposing the layer and developing it with an aromatic primary amino developing agent in the presence of disulfo 7,7'-stearyl-amino-3,3'-methylenebis (4-hydroxycoumarin) as a coupler compound.

9. A photographic silver-halide emulsion con-

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taining a coupler compound having the general formula:



10 in which R is selected from the class consisting of hydrogen, halogen, alkyl, acylamino, sulfoacylamino, aryl and aralkyl groups, and R₁ is selected from the class consisting of hydrogen, alkyl and acyl groups.

15 10. A photographic silver-halide emulsion for forming colored images comprising a colloidal carrier containing a sensitive silver-halide and disulfo 7,7'-stearyl-amino-3,3'-methylenebis (4-hydroxycoumarin).

20 11. A photographic silver-halide emulsion for forming colored images comprising a colloidal carrier containing a sensitive silver-halide and 7,7'-stearyl-amino-3,3'-methylenebis (4-hydroxycoumarin).

25 12. A photographic silver-halide emulsion for forming colored images comprising a colloidal carrier containing a sensitive silver-halide and 3,3'-methylenebis (4-hydroxycoumarin).

ABRAHAM BAVLEY.