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2,436,130

ACYL SUBSTITUTED REACTIVE METHYLENE COLOR COUPLERS

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No Drawing. Application November 25, 1944, Serial No. 565,190

6 Claims. (Cl. 95—6)

1

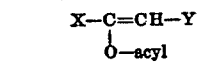
This invention relates to color photography and particularly to color-forming or coupling compounds.

The formation of colored photographic images by using a primary aromatic amino developing agent which couples with color-forming compounds on development has been the subject of numerous prior patents. Most of these patents have been directed to coupler compounds which produce on development dyes which meet the requirements of subtractive color photography, that is, dyes which are colored yellow, magenta or blue-green and many have been directed to methods for rendering the couplers non-diffusing in the silver halide emulsion.

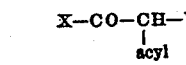
One method of rendering the coupler non-diffusing in the emulsion layer is to incorporate in the non-coupling portion of the molecule a long chain or other complex group which hinders diffusion of the coupler. This diffusion preventing group remains in the final dye image and renders the resulting dye needlessly complex, since it generally does not contribute to the light absorption properties of the dye.

We have found that if an acyl group is attached to the carbon atom of the reactive methylene group of couplers containing such group, or through an oxygen atom to a carbon atom adjacent to the reactive methenyl group of the enolic form of such couplers, compounds result which have desirable properties for purposes of color photography. The coupling reaction is a vigorous one which splits off the acyl group and presumably forms the same dye as would be produced from the coupler not containing the acyl group. The presence of the acyl group, however, introduces desirable properties into the coupler, as will be explained more fully hereinafter.

The couplers which we propose to use have one of the following general formulas:

(1) 

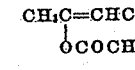
or

(2) 

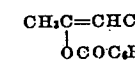
where X=alkyl or aryl, Y=—$COOC_2H_5$ or —CONH-aryl, or X and Y together represent the atoms necessary to complete a pyrazolone ring.

2

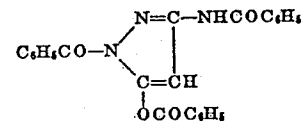
The following examples illustrate compounds which may be used according to our invention:

1. 

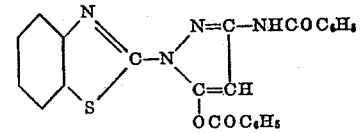
Ethyl O-acetyl-acetoacetate

2. 

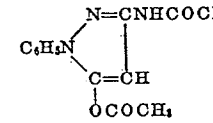
Ethyl-O-benzoyl-acetoacetate

3. 

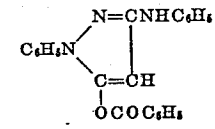
1-benzoyl-3-benzoylamino-5-benzoyloxypyrazole

4. 

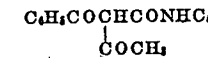
1-(2'-benzothiazolyl)-3-benzoylamino-5-benzoyloxypyrazole

5. 

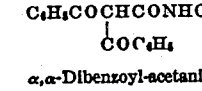
1-phenyl-3-acetylamino-5-acetoxypyrazole

6. 

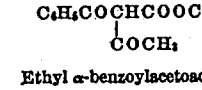
1-phenyl-3-anilino-5-benzoyloxypyrazole

7. 

α-Benzoyl-acetoacetanilide

8. 

α,α-Dibenzoyl-acetanilide

9. 

Ethyl α-benzoylacetoacetate

10.
$$CH_3CO\underset{\underset{COCH_3}{|}}{C}HCOOC_2H_5$$

Ethyl diacetyl-acetate

11.
$$C_6H_5CH_2CO\underset{\underset{COCH_3}{|}}{C}HCOOC_2H_5$$

Ethyl γ-(phenylacetyl) acetoacetate

The acyl radical in the general Formulas 1 and 2 above may be a radical such as acetyl, propionyl, butyryl, or benzoyl, or a higher fatty acid acyl radical such as lauroyl. If the acyl group is a radical of appropriate size, the coupler may be incorporated in an emulsion layer of a multilayer material and is non-diffusing in the layer. When coupling occurs, the acyl group is split off and the resulting dye is a simple molecule containing no long chain or other complex group which is unnecessary in the final dye. Obviously, the lower fatty acid acyl groups may be used in couplers which are to be incorporated in the developing solution. In certain cases, however, couplers containing such acyl groups might be non-diffusing and suitable for incorporation in an emulsion of a multi-layer coating by reason of other groups in the molecule.

The alkyl and aryl groups in the general Formulas 1 and 2 above may be substitued or unsubstituted. A benzyl group is considered a substituted alkyl radical and it is within the scope of our general formula and claims where we refer to an alkyl radical.

The following example illustrates the use of one of our couplers in the developing solution:

A. 2-amino-5-diethyl-aminotoluene HCl	grams	2
Sodium sulfite	do	5
Sodium carbonate	do	30
Water to	liter	1
B. Ethyl-O-acetylacetoacetate	grams	2
Sodium hydroxide (10% solution)	cc	10

For use B is added to A.

The aromatic amino developing agents used with the coupler compounds of our invention include the mono-, di-, and tri-amino aryl compounds and their derivatives formed by substitution in the amino group as well as in the ring, such as alkyl, phenylene diamines and alkyl toluene diamines. These compounds are usually employed in the salt form, such as the hydrochloride or the sulfate which is more stable than the amines themselves. Suitable compounds are diethyl - p - phenylenediamine hydrochloride, monomethyl-p-phenylene diamine hydrochloride, dimethyl-p-phenylene diamine sulfate, and 2-amino-5-diethylaminotoluene hydrochloride. The p-aminophenols and their substitution products may also be used where the amino group is unsubstituted. All of these developing agents have an unsubstituted amino group to which the oxidation products of the developer couple with the color-forming compounds to form dye images.

In addition to the advantage of having a diffusion-preventing group in a portion of the molecule which is split off during formation of the dye image, our couplers have the advantage that the activity of the methylene group with compounds other than the oxidized developer is greatly reduced. The couplers cannot participate in undesirable side reactions which tend to produce stain because the activity of the reactive methylene group to many of these reactions is reduced by the presence of the acyl radical. The color-forming reaction, however, is more powerful than many of these side reactions and immediately splits off the acyl group and forms a coupled dye image.

Our development method may be employed for the production of colored photographic images in layers of gelatin or other carrier such as collodion, organic esters of cellulose or synthetic resins. The carrier may be supported by a transparent medium, such as glass, cellulose ester, or a non-transparent reflecting medium, such as paper or an opaque cellulose ester. The emulsion may be coated as a single layer or as multiple layers on the support or in the case of a transparent support as superposed layers on both sides of the support. The superposed layers may be differentially sensitized and the dyes formed therein by coupling may be bleached by an oxidizing agent, such as chromic acid to colorless soluble compounds. The destruction of the dye in this way does not destroy the silver image and the silver may be resensitized to develop a color a number of times, thus permitting the formation of neutral colored images in superposed layers as described for example in Mannes and Godowsky U. S. Patent 2,113,329. Colored images may also be formed in the manner described in Mannes and Godowsky and Wilder U. S. Patent 2,252,718.

The examples and compounds set forth in the present specification are illustrative only and it will be understood that our invention is limited only by the scope of the appended claims.

We claim:

1. A color-forming photographic developer comprising a primary aromatic amino developing agent and a coupler compound having a formula selected from the group consisting of

$$X\text{—}\underset{\underset{O\text{—}R}{|}}{C}\text{=}CH\text{—}Y \quad \text{and} \quad X\text{—}CO\text{—}\underset{\underset{R}{|}}{C}H\text{—}Y$$

where R is a carboxylic acid acyl group, and X and Y are selected from the class consisting of groups in which X is selected from the class consisting of alkyl and aryl, Y is selected from the class consisting of $—COOC_2H_5$ and —CONH-aryl, and X and Y together represent the atoms necessary to complete a pyrazolone ring.

2. A color-forming photographic developer comprising a primary aromatic amino developing agent and a coupler compound having the formula

$$X\text{—}\underset{\underset{O\text{—}R}{|}}{C}\text{=}CHCOOC_2H_5$$

where R is a carboxylic acid acyl group and X is an alkyl group.

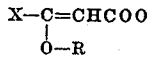
3. The method of producing a colored photographic image in a gelatino-silver halide emulsion layer which comprises exposing the layer and developing it with a primary aromatic amino developing agent in the presence of a coupler compound having a formula selected from the group consisting of

$$X\text{—}\underset{\underset{O\text{—}R}{|}}{C}\text{=}CH\text{—}Y \quad \text{and} \quad X\text{—}CO\text{—}\underset{\underset{R}{|}}{C}H\text{—}Y$$

where R is a carboxylic acid acyl group, and X and Y are selected from the class consisting of groups in which X is selected from the class consisting of alkyl and aryl, Y is selected from the class consisting of $—COOC_2H_5$ and —CONH-aryl, and X and Y together represent the atoms necessary to complete a pyrazolone ring.

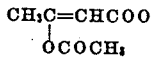
4. The method of producing a colored photographic image in a gelatino-silver halide emul-

sion layer which comprises exposing the layer and developing it with a primary aromatic amino developing agent in the presence of a coupler compound having the formula:

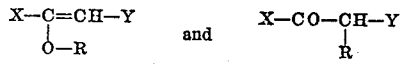


where R is a carboxylic acid acyl group and X is an alkyl group.

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



6. A photographic emulsion for forming colored images comprising a water-permeable, colloidal carrier containing a sensitive silver halide and a coupler compound having a formula selected from the group consisting of



where R is a carboxylic acid acyl group, and X and Y are selected from the class consisting of groups in which X is selected from the class consisting of alkyl and aryl, Y is selected from the class consisting of —$COOC_2H_5$ and —CONH-aryl, and X and Y together represent the atoms necessary to complete a pyrazolone ring.

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CHARLES J. KIBLER.
HENRY D. PORTER.

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