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## COLOR FORMER CONTAINING BIS COUPLING FUNCTIONS

Donald E. Trucker, Binghamton, N.Y., assignor to General Aniline & Film Corporation, New York, N.Y., a corporation of Delaware  
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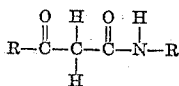
This invention relates to color photography. More particularly the invention relates to the production of yellow photographic images, to certain bis color formers for producing such images and to silver halide photographic emulsions containing the color formers.

It is, of course, well known in the art to produce colored photographic images by reacting imagewise quantities of the oxidation products of a primary aromatic amino developing agent with a color forming component or a color coupler. The present day multilayer color packs are based on the aforementioned reaction. In fabricating a modern multilayer photographic element, at least three continuous layers are individually sensitized to a different primary color aspect. Thus one layer responds to red rays, the second layer to green rays and the third layer to the blue rays. After exposure the film is color developed using a primary aromatic amino developing agent whereby subtractively colored images are formed in each layer, that is a cyan image is obtained in the red sensitive layer, a magenta image in the green sensitive layer and a yellow image in the blue sensitive layer. The dye in the images is produced in quantities inversely proportional to the exposure of the layer. When such subtractively colored images are superimposed and viewed through white light, there is rendered a color reproduction of the subject being photographed.

The color coupler employed for obtaining cyan images is characteristic of a phenolic compound such as phenol or naphthol; a magenta image is produced from a pyrazolone and the yellow image is formed from an  $\alpha$ -benzoylacetylacetanilide. It is this latter type of color coupler with which the present invention is concerned.

The yellow color formers generally used are as above stated  $\alpha$ -benzoylacetylacetanilide, which can be formulaistically depicted as follows:

(1)



wherein R represents an aliphatic or aromatic residue. It is to be noted that couplers of this type are known as reactive methylene compounds, i.e., a structure characterized by the presence of a methylene bridge linked to various negative groupings which, in the present instance, are keto functions on either side of the methylene bridge. It is the methylene portion of a couple which couples with the oxidized primary aromatic amino developing agent to produce the colored dye images.

Since the advent of color photography based upon color couplers and which was first proposed by Rudolph Fischer in 1912, much work and endeavor has been expended in refining the system of Fischer. Much of this work which is documented in various photographic publications and patents is directed to improving the stability of the colored photographic images particularly to such agencies as light and conditions of excessive humidity. Since the dye images arise from the coupling component, it follows that the latter must also be a stable entity. For instance, the coupler and the dye images produced therefrom must not be decolorized or otherwise changed when

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subjected to the various steps or stages of the color development process. It is, furthermore, essential that the dye images be of the proper spectral and optical qualities; cheapness and ease of manufacture are also important factors. A color coupler must possess a wide variety of rather specific properties to be suitable for use in color photography.

Although the couplers in use today are generally satisfactory, the dye images produced therefrom are still lacking in desired stability, particularly as to light and excessive humidity. In the case of the yellow color couplers, most of the proposals heretofore have proceeded along similar paths, namely, modifications of an  $\alpha$ -benzoylacetylacetanilide of the type depicted in Formula 1. To improve this situation, many proposals have been suggested for producing superior coupler structures.

I have evolved a type of yellow color former which represents a departure from the structures previously contemplated and which, on color development with a primary aromatic amino developing agent, produces yellow photographic images of excellent stability to light and excessive humidity.

It is, therefore, the primary theme and purpose of this invention to provide such a yellow coupler and a method for producing said coupler.

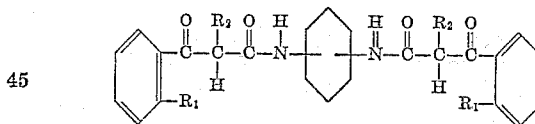
It is a further object of the invention to provide yellow photographic images produced from said yellow coupler.

It is still a further object to provide silver halide photographic emulsions containing such a yellow coupler.

Other objects will be apparent as the description proceeds.

In accordance with the present invention, I prepare a yellow coupler or a yellow color-forming component wherein two color-forming moieties or groupings are present within the same molecular species. A structure is thus created heretofore not contemplated in the color former art. The color formers as described herein can be represented by the following general formula:

(2)



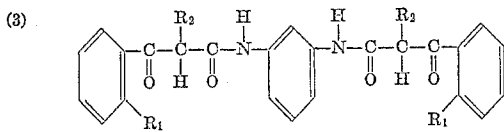
wherein R<sub>1</sub> is hydrogen or alkoxy, e.g., CH<sub>3</sub>O-, C<sub>2</sub>H<sub>5</sub>O-, C<sub>3</sub>H<sub>7</sub>O-, C<sub>4</sub>H<sub>9</sub>O-, C<sub>5</sub>H<sub>11</sub>O-, C<sub>6</sub>H<sub>13</sub>O-, C<sub>7</sub>H<sub>15</sub>O-, C<sub>8</sub>H<sub>17</sub>O-, C<sub>9</sub>H<sub>19</sub>O-, C<sub>10</sub>H<sub>21</sub>O-, C<sub>11</sub>H<sub>23</sub>O-, C<sub>12</sub>H<sub>25</sub>O-, C<sub>13</sub>H<sub>27</sub>O-, C<sub>14</sub>H<sub>29</sub>O-, C<sub>15</sub>H<sub>31</sub>O-, C<sub>16</sub>H<sub>33</sub>O-, C<sub>17</sub>H<sub>35</sub>O-, C<sub>18</sub>H<sub>37</sub>O-, C<sub>19</sub>H<sub>39</sub>O-, C<sub>20</sub>H<sub>41</sub>O-, etc. and R<sub>2</sub> is hydrogen or halogen, e.g., chlorine, bromine, etc.

I prepare my novel yellow color couplers by reacting a benzoylacetic ester and a phenylenediamine. Preferably, the reaction is carried out by refluxing the ester and diamine under reflux in the presence of an aromatic solvent such as xylene. Alternately, it may be desirable to carry out the reaction in the absence of any solvent or an excess of one of the reactants may serve in lieu of a solvent. In certain instances, it may be desirable to carry out the reaction at relatively low temperatures if the particular color former being prepared is thermodynamically unstable. Other and different modifications for preparing the color formers will occur to those skilled in the art.

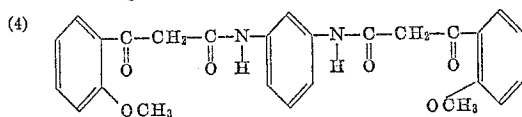
I have found that particularly desirable yellow color couplers are produced in the above described manner when the benzoylacetic ester has or contains an ortho alkoxy substituent and the phenylenediamine is a meta-

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phenylenediamine. The resulting couplers are characterized by the following general formula:



wherein  $R_1$  and  $R_2$  have the values given above. These yellow color couplers on color development yield dye images which are exceedingly stable to light and conditions of excess humidity and in this respect are superior to yellow color couplers heretofore used for the production of photographic yellow dye images. To demonstrate the stability and excellent photographic property of the dye images prepared from my yellow couplers, I subjected the images to light fade and high humidity tests. For these tests, I used as the yellow coupler a structure prepared by reacting ortho methoxybenzoylacetate with metamethoxyphenylenediamine and characterized by the following:



I further established the structure of this coupler by preparing it from o-benzoylacetate ester and nitro aniline, reducing the so obtained 3'-nitro- $\alpha$ -benzoylacetanilide to the corresponding amino derivative which, in turn, was reacted with another portion of the benzoylacetate ester to give the product represented by Formula 4.

In some instances, it may be desirable to replace one of the hydrogen atoms in the reactive methylene group with halogen. The advantage of employing in color coupling reactions a coupler having one of the hydrogen of the methylene group replaced by halogen is that only half the molar proportion of silver halide is required. This technique is sometimes resorted to when it is desired to conserve silver halide. Such halogenation is conveniently effected by treating the coupler with a halogenating agent such as a sulfur halide as for example sulfonyl chloride.

The following examples are presented as methods of preparing the color formers of this invention. It is to be understood, however, that these examples are given by way of illustration only and are not to be taken as in any way limiting the invention.

#### Example 1

This example relates to one method of preparing the compound 1,3-bis-(benzoylacetamido)benzene.

In this method, 3-(benzoylacetamido)nitrobenzene was first prepared as follows:

m-Nitroaniline, 55.2 g. (0.40 mole), in 150 ml. of xylene was brought to reflux in a 500 ml., 3-neck flask equipped with stirrer and water take-off trap with attached condenser. After traces of water were removed, 84.5 g. (0.44 mole) of ethyl benzoylacetate was added in one portion. The water take-off trap and condenser were replaced with a steam condenser and refluxing was continued for 3½ hours. After cooling overnight, the product was filtered, washed twice with 200 ml. portions of xylene, ground under 90° C. petroleum ether, filtered and washed twice with 200 ml. portions of petroleum ether. The solid was suspended twice in 200 ml. portions of 95% ethanol followed by filtration and drying under vacuum at 60° C., 94.6 g. 83% yield, M.P. 126–128.5° C. (Literature value, M.P. 137–138° C.)

The product thus produced was then hydrogenated to form 3-(benzoylacetamido)aniline as follows:

3-(benzoylacetamido)nitrobenzene, 15.7 g. (0.055 mole), was hydrogenated in 250 ml. of ethyl acetate using 1.0 g. of a 30% palladium on charcoal catalyst. With the Parr apparatus initially at 50 p.s.i.g. the reduction was

complete in 30 min. The solution was filtered from catalyst, evaporated in half and chilled overnight to obtain 4.7 g., 34% yield, of material melting at 157–157.5° C.

A sample was crystallized three additional times from methanol, M.P. 163–163.5° C.

Calcd. for  $C_{15}H_{14}N_2O_2$ : C, 70.85; H, 5.55; N, 11.02. Found: C, 71.07; H, 5.34; N, 10.80.

2.5 grams (0.01 mole) of the 3-(benzoylacetamido)aniline produced as above was refluxed with 2 g. (0.01 mole) ethyl benzoylacetate and 30 ml. of xylene in a 100 ml., 1-neck flask equipped with a steam-jacketed condenser, and the apparatus was topped by a water-cooled condenser and take-off assembly. After an 18-hour reflux, the solution was filtered hot. The oily layer was separated, cooled and the solid washed six times with ether prior to drying, 2.18 g., 54% yield, M.P. 131–135° C.

The crude product was dissolved in about 35 ml. of glacial acetic acid and added dropwise to 500 ml. of cold water with stirring. The precipitate was made filterable by warming on a steam bath and cooling before filtration. This crude product was crystallized twice from benzene. Some oiling was noted but rubbing the oil under the solvent converted it to a solid, M.P. 173–174° C. The solid was 1,3-bis-(benzoylacetamido)benzene.

#### Example 2

Another more simple method of producing the compound 1,3-bis-(benzoylacetamido)benzene used by me was as follows:

A mixture of 76.8 g. (0.40 mole) of ethyl benzoylacetate, 21.6 g. (0.20 mole) m-phenylene diamine and 300 ml. of xylene was refluxed under a steam-jacketed condenser for 5 hours. A solid was observed in the refluxing solution. After cooling overnight, the solid was filtered and washed twice with 150 ml. portions of xylene. The solid was melted under the xylene to improve washing; the product was solidified for filtration. The solid was washed three times with 30–60° C. petroleum ether, 68 g., 85% yield, followed by two washings with ether and an additional six washings with 30–60° C. petroleum ether.

The solid was dissolved in about 500 ml. of acetic acid and filtered into ice water. The precipitate was filtered and crystallized twice from methanol, 9.36 g., 23%, M.P. 162–165° C. An analytical sample was prepared by crystallization of the crude three times from benzene instead of methanol, M.P. 173–174° C.

Calcd. for  $C_{24}H_{20}N_2O_4$ : C, 71.99; H, 5.04; N, 7.00. Found: C, 72.27; H, 4.51; N, 6.67.

#### Example 3

The compound 1,3-bis-( $\alpha$ -chloro-benzoylacetamido)benzene was prepared as follows:

Crude 1,3-bis-(benzoylacetamido)benzene, 4.0 g. (0.01 mole), was dissolved in 90 ml. of chloroform in a 250 ml., 3-neck flask equipped with stirrer and vacuum take-off. Sulfuryl chloride, 2.7 g. (0.02 mole) was added dropwise. The solution was stirred for 45 minutes at room temperature, then heated to 50° C. for 15 minutes. The mixture was taken to dryness under vacuum and ground in a mortar. The light yellow material, 4.22 g., 90% yield, sintered at 80° C. and appeared to melt from 100° C. to the decomposition point of 125° C.

The sample was dissolved in methanol, treated with decolorized charcoal and added dropwise to ice water with stirring. The precipitate was filtered, washed and dried. The product sinters in a sealed tube at 75° C. and appears to melt from 82–102° C.

#### Example 4

The compound 1,3-bis-(2-methoxybenzoylacetamido)benzene was prepared as follows:

A mixture of 1.08 g. (0.01 mole) of m-phenylenediamine, 4.36 g. (0.02 mole) of ethyl o-methoxybenzoylacetate and 100 ml. of xylene was refluxed 4 hours in 150 ml., 1-neck flask topped by a steam-jacketed condenser. On

cooling over a weekend, 3.7 g., 81% yield, mixed yellow and white solid was obtained. The solid was washed three times with ether, once with xylene and once with 30–60° C. petroleum ether. Three crystallizations from methanol were required for purification, 0.6 g., 13% yield, M.P. 153–155° C.

An analytical sample was prepared by crystallizing the solid three more times from methanol, 0.26 g., M.P. 156.0–156.5° C.

Calcd. for  $C_{26}H_{24}N_2O_8$ : C, 67.81; H, 5.25; N, 6.09. Found: C, 68.29; H, 5.30; N, 5.99, 5.93.

The yellow color couplers as above described are lipophilic in nature, that is, they are soluble in oily type organic solvents and are, therefore, incorporated in a photographic emulsion by the well known dispersion technique. In this method the color former is dissolved in an oily solvent immiscible with the carrier of the photographic emulsion and the resulting color former solution then dispersed or homogenized in the emulsion. Typically, photographic coatings are prepared by dissolving one gram of the color former in 6 to 9 millimeters of the solvent mixture consisting of 5 parts of phenethyl alcohol, 4 parts of tricresyl phosphate and 1 part of dibutyl phthalate. The resulting oily solution is then homogenized in 20 millimeters of 6% aqueous gelatin to which had been added 0.5 millimeter of a 25% dispersing agent such as lauryl sulfate. The homogenization of the coupler solution in the gelatin is conveniently carried on in a high energy laboratory type mixer such as, for instance, a Waring blender which appliance is well known among laboratory equipment. The so obtained dispersion is then blended or mixed with a gelatino silver halide emulsion and a mixture coated on the suitable film base such as glass, paper, triacetate film base, polyester film base, or any of the other typical photographic supports common to the art.

Alternately, the color formers described herein can be incorporated in a gelatino silver halide emulsion in the form of a water soluble alkali metal salt. Such couplers contain water solubilizing groups as COOH or  $SO_3$  but otherwise are identical to the previously described lipophilic type. Solubilizing groups may be introduced into the completely formed coupler, or intermediates having such groups may be employed in synthesizing the coupler. The methods employed for introducing the aforesaid solubilizing groups into couplers are well known in the organic chemical field and is not deemed necessary to discuss such methods at length in the present instance.

Suitable developing agents for compounding developer formulations as used herein include the various alkylphenylenediamines such as 4-aminoaniline, 4-ethylaminoaniline, 2-dimethylaminoaniline, 4-dialkylaminoaniline, e.g., 4-dimethylaminoaniline, 4-diethylaminoaniline, 4-[N-( $\beta$ -hydroxyethyl) - N - ethyl] aminoaniline, 4-amino-N-ethyl - N - ( $\beta$ -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 freer basis. All of these compounds have a primary amino group which enables the oxidation product of the developer to couple with the color com-

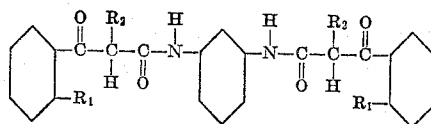
pounds to form dye images. After removal of the silver image by bleaching and fixing in a manner well known to the art, the color image remains in the emulsion.

A developer formulation suitable for developing the coatings prepared in accordance with the instant invention has the following composition:

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

I claim:

1. A light-sensitive silver halide emulsion having incorporated therein a compound having the following general formula:



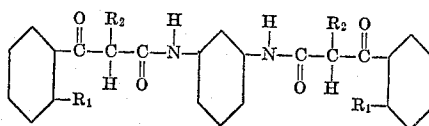
wherein  $R_1$  is selected from the class consisting of hydrogen and lower alkoxy and  $R_2$  is selected from the class consisting of hydrogen and chlorine.

2. A light-sensitive silver halide emulsion as recited in claim 1 wherein both  $R_1$  and  $R_2$  are hydrogen.

3. A light-sensitive silver halide emulsion as recited in claim 1 wherein  $R_1$  is hydrogen and  $R_2$  is chlorine.

4. A light-sensitive silver halide emulsion as recited in claim 1 wherein  $R_1$  is  $OCH_3$  and  $R_2$  is hydrogen.

5. A film for use in color photography comprising a base having a coating of a silver halide light-sensitive emulsion thereon, said emulsion containing a coupling compound having the following general formula:



wherein  $R_1$  is selected from the class consisting of hydrogen and lower alkoxy and  $R_2$  is selected from the class consisting of hydrogen and chlorine.

6. A film as recited in claim 5 wherein both  $R_1$  and  $R_2$  are hydrogen.

7. A film as recited in claim 5 wherein  $R_1$  is hydrogen and  $R_2$  is chlorine.

8. A film as recited in claim 5 wherein  $R_1$  is  $OCH_3$  and  $R_2$  is hydrogen.

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