

UNITED STATES PATENT OFFICE

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PRODUCTION OF COLORED PHOTOGRAPHIC IMAGES

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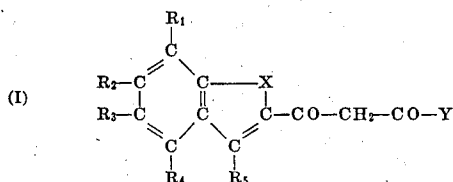
18 Claims. (Cl. 95—6)

This invention relates to the production of colored photographic images by color development.

It is known that a colored image may be formed simultaneously with the silver image obtained by developing a silver halide emulsion with an aromatic amino developing agent, if a substance known as a color former is present, for example, in the developing solution or in the silver halide emulsion. The colored image may be revealed by bleaching out the silver image with Farmer's Reducer or other photographic bleaching agent.

The present invention has for an object the production of new color formers which are useful in color photography. A further object is the preparation of photographic emulsions which contain new and improved color formers which are substantially water insoluble and which yield dyes by coupling with the oxidation products of aromatic amino developing agents. A further object is the provision of new photographic developing processes. A still further object is the preparation of photographic elements bearing an emulsion which contains one or more of the new color formers, which do not migrate; another object is the preparation of multi-layer photographic films containing color formers which do not migrate from layer to layer or into the processing baths. Yet another object is the preparation of finished photographs which contain stable dyed images which are formed of water-insoluble dyes. Other objects include the preparation of color photographs and color forming emulsions upon opaque or transparent supports. Still other objects will appear hereinafter.

The above and other objects are accomplished by the preparation and use in photographic processes and emulsions of color formers which are esters, amides and substituted amides of the general formula:



where R_1 , R_2 , R_3 and R_4 are the same or different and are hydrogen atoms or substituent groups, e. g. hydrocarbon groups, halogen atoms, nitro groups, amino groups, hydroxy groups and alkoxy groups, R_5 is a hydrogen atom or a hydrocarbon

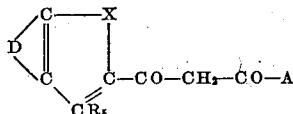
group, X is an oxygen atom or a sulphur atom and Y is an $-OR_6$ group or a



group where R_6 is a hydrocarbon group and R_7 and R_8 are the same or different and are hydrogen atoms or hydrocarbon groups or together form a heterocyclic residue.

Any of the pairs of groups R_1 and R_2 , R_2 and R_3 and R_3 and R_4 may together form a further cyclic nucleus fused to the benzene nucleus of the formula.

For simplicity these compounds may be defined as compounds of the general formula:



where D is the residue of any substituted or unsubstituted aromatic nucleus, X is an oxygen atom or a sulphur atom, R_5 is a hydrogen atom or a hydrocarbon group and A is an ester, amide or substituted amide group.

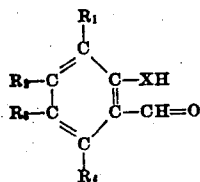
The general formula includes coumarinyl-acetic esters, substituted coumarinyl-acetic esters, thionaphthyl- α -acetic acid esters and substituted thionaphthyl- α -acetic acid esters, and the amides and substituted amides which correspond to them.

As indicated above, the groups R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 and R_8 in the general formula (I) may be hydrocarbon groups. Thus they may be straight or branched chain primary, secondary, tertiary or iso alkyl groups of 1 to 18 or more carbon atoms (e. g. methyl, ethyl, propyl, butyl or higher alkyl groups, e. g. dodecyl, octadecyl etc., cycloalkyl groups, e. g. cyclohexyl, methyl cyclohexyl, dodecyl-cyclohexyl etc., aryl groups (e. g. phenyl or naphthyl groups), or aralkyl groups (e. g. benzyl, methylbenzyl or naphthylmethyl groups). Such groups may themselves be substituted, for example, aryl groups may be substituted with hydroxy, alkoxy, oxyalkyl, amino or nitro groups or with halogen atoms. Suitable groups include methoxy, ethoxy, hydroxyethyl, hydroxymethyl, methylamino, ethylamino, chlorine, bromine etc. The groups R_1 and R_2 , R_2 and R_3 and R_3 and R_4 may together constitute the residues of cyclic nuclei, e. g. benz nuclei, methylene dioxy groups and other heterocyclic nuclei. Also, as indicated above, R_7 and R_8 may form a

heterocyclic group. Suitable heterocyclic nuclei are, for example, pyridine, quinoline, thiazole, benzthiazole, naphthathiazole, oxazole, benzoxazole, selenazole, pyrimidine, quinazoline, thiophene, coumarane and other heterocyclic nuclei.

The color-formers of the type where Y in the above general formula is an $-OR_4$ group may be prepared by condensing an acylacetic ester with a substituted or unsubstituted coumarilyl chloride or a substituted or unsubstituted thionaphthenyl- α -carboxylic acid chloride, followed by removal of the acyl group by hydrolysis.

They may also be prepared by the process described in our co-pending application No. 345,010 entitled "The production of new organic compounds" corresponding to British application No. 23,263/39, i. e. by condensing an aldehyde of the general formula:



with a γ -halogen aceto-acetic ester of the general formula:



the groups R_1, R_2, R_3, R_4 and X having the significance indicated above, and Z being a halogen atom, e. g. chlorine bromine or iodine.

Color formers of the type in which Z is an



group may be prepared by reacting a compound of the above general formula where Z is $-OR_4$ with ammonia or a primary or secondary amine of the formula



Examples of suitable amines are mono- or dialkylamines e. g. ethylamine, diethylamine and higher homologues, aliphatic diamines e. g. ethylene diamine hexylenediamine etc., mono- and di-arylamines, e. g. aniline, diphenylamine and naphthylamines, mono- and di-aralkylamines, e. g. benzylamine, alkyl arylamines, e. g. N-ethylaniline, alkyl aralkyl amines, e. g. N-ethyl benzylamine, aralkyl arylamines, e. g. benzyl aniline, heterocyclic amines, e. g. pyridine, piperidine, methyl piperidine, quinoline, thiazoles, oxazoles, pyrimidines, quinazolines and the like and aromatic diamines, e. g. o- and p-phenylenediamine, benzidine, dianisidine, diamino stilbenes and dinaphthylamines. Aryl nuclei present in the amines may themselves be substituted, e. g. by alkyl nitro, halogen, alkoxy or oxyalkyl groups. Where the amine employed is a diamine, reaction may take place at both amino groups so that the final product contains two coumarilyl or thionaphthenoyl nuclei.

The new color formers may be incorporated in color-coupling or -forming amino developing solutions or in photographic silver halide emulsions. As color coupling amino developing agents the diamino aryl compounds such as p-phenylene diamine and its substitution products are preferred. These developers may be substituted in the amino groups as well as in the ring, prefer-

ably the former, to constitute compounds such as the mono- and di-alkyl arylene-diamines including the mono- and di-alkyl naphthylene diamines, alkyl phenylene diamines and alkyl toluylene diamines. The developing compounds must, of course, have one free or unsubstituted amino group which enables the oxidation product of the developer to couple with the color formers.

As examples of developers which may be employed there may be mentioned the following: p-phenylene diamine, mono ethyl-p-phenylene diamine, di-ethyl-ortho-phenylene diamine, chloro-p-phenylene diamine, amino-p-phenylene diamine 1,2,5-toluene diamine, 2-amino-5-diethylamine toluene, p-amino phenylene piperidine, methyl-oxyethyl-p-phenylene diamine, ethyl-oxyethyl-p-phenylene diamine, butyl-oxyethyl-p-phenylene diamine, 2-amino-5-oxyethyl-1-butylaminotoluene and its dihydrochloride, β - γ -dioxypentyl-p-phenylene diamine, 4,4'-diamino-diphenylamine and α -aminoacetoacetic acid ethyl ester. These compounds are preferably used in the form of their salts either of organic or inorganic type, since the salts are more soluble and stable than the free bases. The hydrochlorides, sulphates and acetates are examples of suitable salts.

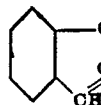
By way of example a suitable developing solution (referred to for convenience in the subsequent examples as "Developing solution A") containing a color-former in accordance with the present invention may be made up as follows:

35	p-Diethylamino aniline hydrochloride	grams	1.0
	Sodium carbonate crystals, $Na_2CO_3 \cdot 10H_2O$	do	80.0
	Sodium sulphite crystals, $Na_2SO_3 \cdot 7H_2O$	do	12.5
40	Color-former solution (i. e. a 1% solution or a saturated solution at room temperature, in alcohol or other solvent, e. g. ethylene glycol mono methyl ether, whichever is the weaker solution)	ccs.	100
45	Distilled water to make	ccs.	1000

The solution sulphite may be omitted if desired. The following examples illustrate the method of production of the color-formers of the invention:

EXAMPLE 1

α -Coumarilylacetic acid ethyl ester



63 gms. of ethylacetoacetate were added to a solution of 11.2 gms. of sodium in 197 ccs. of ethyl alcohol contained in a 3-litre, 3-necked flask fitted with a mercury seal, a double surface condenser, a mechanical stirrer and a dropping funnel. 84 gms. of coumarilyl chloride were slowly added to the resulting solution by means of the dropping funnel, the addition being effected over a period of two hours and the temperature being maintained at 0°C . to -5°C . The temperature was then raised to 15°C . for one hour and maintained at $10-15^\circ \text{C}$. for a further two hours. At the end of this period 102 ccs. of ammonia solution (S. G. 0.920) were added rapidly and the temperature raised to 40°C . The solution was maintained at this tempera-

ture for fifteen minutes and then cooled to 20° C.

200 ccs. of water were then added to the cooled solution (which had set solid) and a solution of 66.1 grams of copper sulphate in 181 ccs. of water then run in, the temperature not being allowed to exceed 35° C.

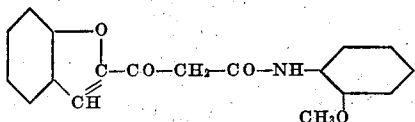
The resulting thick suspension of green copper salt was then cooled to 10° C. with stirring over a period of one hour, and filtered. The solid residue was then washed with water and ethyl alcohol, dried, pulverised and then suspended in 300 ccs. of water. The suspension was rendered acid with 22 ccs. of 24% hydrochloric acid and stirred for half an hour, care being taken not to add an excess of acid. An oil separated which was extracted with ether, dried over sodium sulphate and distilled at 15 m. m. pressure. The resulting liquid had a boiling point of 200-220° C. and was α -coumarilyl-acetic acid ethyl ester.

This compound was included in "Developing solution A" and used for the development of an exposed silver halide photographic emulsion and yielded a red image together with the silver image.

The corresponding 5-nitro- α -coumarilyl acetic acid ethyl ester may be similarly produced by starting with the corresponding 5-nitro-coumarilyl chloride. When included in "Developing solution A" and used as above it yields a magneta image together with the silver image.

EXAMPLE 2

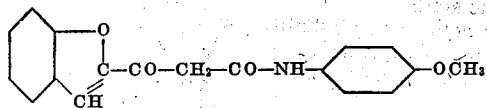
α -Coumarilylaceto-o-anisidide



2.32 gms. of α -coumarilyl acetic acid ethyl ester prepared as in Example 1 were dissolved in 10 ccs. of xylene containing three drops of pyridine, in a 100 cc. distilling flask fitted with a dropping funnel. The solution was gently boiled on a sand bath and then a solution of 1.23 grams of o-anisidine in 10 ccs. of xylene was run in slowly over a period of ten minutes. At the end of this time the solution was boiled for fifteen minutes during which time some of the xylene was distilled off. The residual solution was cooled and diluted with petroleum ether when α -coumarilyl-acetic acid-o-anisidide separated as a yellow solid having a melting point of 100° C. This product when included in "Developing solution A" and used for developing an exposed silver halide photographic emulsion yielded a yellow image together with the silver image.

EXAMPLE 3

α -Coumarilyl-acet-p-anisidide

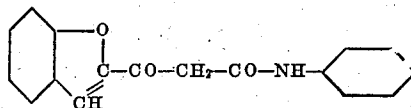


This compound was prepared by a method similar to that of Example 2, but using 1.16 grams of α -coumarilylacetic acid ethyl ester dissolved in 10 ccs. of xylene containing three drops of pyridine and 0.61 grams of p-anisidine dissolved in 10 ccs. of xylene. The re-crystallised product has a melting point of 161° C. When included in "Developing solution A" and used

for the development of an exposed silver halide photographic emulsion it yielded an orange-red image together with the silver image.

EXAMPLE 4

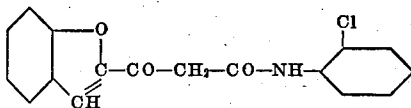
α -Coumarilyl-acet-anilide



This compound was prepared by a method similar to Example 2 using 1.16 grams of α -coumarilylacetic acid ethyl ester dissolved in 10 ccs. of xylene containing three drops of pyridine and 0.45 gram of aniline dissolved in 10 ccs. of xylene. The recrystallised product had a melting point of 150° C. When included in "Developing solution A" and used for the development of an exposed silver halide emulsion it yielded an orange-red image in addition to the silver image.

EXAMPLE 5

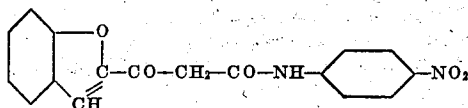
α -Coumarilyl-acet-o-chloranilide



This compound was prepared by a method similar to Example 2 using 1.16 grams of α -coumarilylacetic acid ethyl ester dissolved in 10 ccs. of xylene containing three drops of pyridine and 0.63 gram of o-chloraniline dissolved in 10 ccs. of xylene. The white solid product, when included in "Developing solution A" and used for the development of an exposed silver halide emulsion yielded a yellow image in addition to the silver image.

EXAMPLE 6

α -Coumarilylacet-p-nitranilide



1.16 grams of α -coumarilyl acetic acid ethyl ester dissolved in 10 ccs. of xylene and containing three drops of pyridine were gently boiled and then 2.69 grams of p-nitraniline dissolved in 50 ccs. of xylene were added slowly.

At the same time the xylene was steadily distilled off so that the bulk of the reaction mixture at no time exceeded 10-15 cc. Finally the mixture was boiled for fifteen minutes, cooled and filtered. The product, separated by filtration, was recrystallised from ethyl alcohol solution and had a melting point of 193° C. When included in "Developing solution A" and used for the development of an exposed silver halide photographic emulsion it yielded a brown image together with the silver image.

In the foregoing examples the tests were effected using silver chloride emulsions. However, other tests show that similar colors are obtained using emulsions of any other silver halides, e. g. silver bromide, silver iodobromide and silver chloro bromide.

EXAMPLE 7

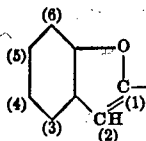
This example illustrates the incorporation of the color-formers of this invention in emulsion layers. 20 ccs. of a 1% solution in ethylene gly-

col monomethyl ether of α -coumarilylacetic acid ethyl ester were added to 25 ccs. of a 10% aqueous solution of gelatin and the mixture added to 50 ccs. of a melted photographic "Gaslight" emulsion containing approximately 20 grams of silver halide, chiefly silver chloride, per pound weight of emulsion. The emulsion thus prepared was coated on a paper support and dried. The emulsion coated paper was exposed under a negative and was then developed with a "Developing solution A" excluding the color-former but including an equivalent quantity of the water miscible liquid such as ethylene glycol mono-methylether. A red image was produced together with the silver image.

In addition to the color formers specifically referred to above, the following specific color formers which can be prepared in like manner from the reactants described may be instanced as yielding dye images of especial value according to this invention:

- 4:6 dibrom- α -coumarilylacetic acid ethyl ester, M. pt. 210° C., yielding a bright red dye image
- 6 bromo- α -coumarilylacetic acid ethyl ester, M. pt. 110° C., yielding a bright red dye image
- 4 brom- α -coumarilylacetanilide, M. pt. 180° C., yielding an orange dye image
- 6 brom- α -coumarilylaceto-*o*-anisidide, M. pt. 179° C., yielding an orange dye image
- 6 brom- α -coumarilyl acet-*p*-nitranilide, M. pt. 227° C., yielding a red dye image
- 4:6 dibrom- α -coumarilylaceto-*o*-anisidide, M. pt. 220-230° C., yielding an orange dye image
- 3:4 benz- α -coumarilylacetic acid ethyl ester, M. pt. 100° C., yielding a red dye image
- 3:4 benz- α -coumarilylaceto-*o*-anisidide, M. pt. 160° C., yielding a yellow dye image
- α -Thionaphthenoylacetic acid ethyl ester, boiling point 220-228° C./25 mm., yielding a red dye image
- α -Thionaphthenoylaceto-*o*-anisidide, M. pt. 144° C., yielding a yellow dye image
- α -Thionaphthenoylacetanilide, M. pt. 166° C., yielding an orange brown image
- α -Thionaphthenoyl-*p*-chlor-anilide, M. pt., 210° C., yielding an orange brown image
- Di - (α -thionaphthenoylacetamino) - diphenyl, M. pt. above 305° C., yielding a red image
- p,p'*-Di-(coumarilyl-acetamino)-diphenyl, M. pt. 226° C., yielding an orange dye image
- p,p'*-Di-(coumarilyl-acetamino)-benzene, M. pt. 227° C., yielding an orange dye image

(In naming the above compounds the coumarilyl nucleus is numbered as follows:



The process of development employing the color-formers in accordance with the present invention may be applied to a latent image in an emulsion of silver halide which has been exposed to the action of light, for example, in a camera or behind a photographic negative image. The process may also be applied to a silver salt image which has been obtained by dissolving away an initial reduced silver image and exposing to light the residual unaltered silver salt, for example, in the reversal process of development. The process may also be applied to a developable silver salt image obtained by removing the unal-

tered silver halide by means of solvents from a developed photographic image in metallic silver and then converting the metallic silver to a developable silver salt by means of known photographic bleaching agents. The process may also be applied to the development of silver halide photographic emulsions which have been rendered developable by means other than exposure to light, for example, by chemical means. The color formers and processes are not limited to any one type of reducible silver salt. Any developable silver halide may be used. Thus, as indicated above, simple and mixed silver halides such as silver chloride, silver bromide, silver-chloride bromide, silver bromide iodide etc., may be employed.

As a modification, the production of colored images by means of the color-formers of this invention may be applied to colloid layers sensitized by bi-chromate. Thus the color-formers may be incorporated in bichromate-sensitized colloid layers (e. g. gelatin, gum arabic or albumin), the layers exposed, the unexposed colloid removed, for example by treatment with hot water, and the color developed in the exposed portions by treatment with *p*-nitroso-dialkyl-aniline or its derivatives.

The color formers are also useful in various processes of color photography, wherein azo dye images are formed. The color formers couple with the usual types of diazo compound, e. g. diazotized *p*-nitroaniline, tetrazotized dianilidine solutions etc. Thus, the color-formers may be employed to form such azo dyes and the dyes then differentially bleached by known processes to yield azo dye images.

The new color formers of this invention possess many advantages. As indicated above they do not migrate from one emulsion layer to another and they do not tend to diffuse from the emulsion layers during processing treatments. Moreover, the new color formers are strongly resistant to the bleaching action of the sulphite commonly contained in photographic developing solutions; that is, they yield dye images of satisfactory depth even though sulphite is present in the developer employed. Moreover, the dye images produced are very stable.

We claim:

1. A light sensitive photographic emulsion taken from the group consisting of silver halide and bichromate emulsions containing as a color former a compound selected from the class consisting of esters, amides and substituted amides of α -coumarilyl acetic acid, substituted- α -coumarilyl acetic acid, thionaphthenyl- α -acetic acid and substituted thio-naphthenyl- α -acetic acid.
2. A photographic element comprising a light sensitive silver halide emulsion containing as a color former an ester of an α -coumarilyl acetic acid.
3. A photographic element containing at least one colloid layer comprising a light sensitive silver halide emulsion containing as a color former an amide of an α -coumarilyl acetic acid.
4. A photographic element comprising a light sensitive silver halide emulsion containing as a color former an amide of a halogen substituted α -coumarilyl acetic acid.
5. A photographic color forming developer which comprises a color coupling amino developing agent and a color former which is a compound selected from the class consisting of esters, amides and substituted amides of α -coumarilyl acetic acid, substituted α -coumarilyl acetic acid,

thio-naphthhenyl- α -acetic acid and substituted thio-naphthhenyl- α -acetic acid.

6. A photographic color forming developer which comprises an aromatic amino developing agent containing an unsubstituted amino group and a color former which is an ester of an α -coumarilyl acetic acid.

7. A photographic color forming developer which comprises an aromatic amino developing agent containing an unsubstituted amino group and a color former which is an amide of an α -coumarilyl acetic acid.

8. A photographic color forming developer which comprises an aromatic amino developing agent containing an unsubstituted amino group and a color former which is an amide of a halogen substituted α -coumarilyl acetic acid.

9. A method of producing a colored image in a silver halide emulsion which has a latent image formed in it which comprises color developing the emulsion in the presence of a compound selected from the class consisting of esters, amides and substituted amides of α -coumarilyl acetic acid, substituted- α -coumarilyl acetic acid, thio-naphthhenyl- α -acetic acid and substituted thio-naphthhenyl- α -acetic acid with an aromatic amino developing agent containing an unsubstituted amino group.

10. A method of producing a colored image in a silver halide emulsion which has a latent image formed in it which comprises developing the emulsion in the presence of an ester of an α -coumarilyl acetic acid in the presence of an aromatic amino developing agent containing an unsubstituted amino group.

11. A method of producing a colored image in a silver halide emulsion which has a latent image formed in it which comprises developing the emulsion in the presence of an amide of an α -coumarilyl acetic acid in the presence of an aromatic amino developing agent containing an unsubstituted amino group.

12. A method of producing a colored image in a silver halide emulsion which has a latent image formed in it which comprises developing the emulsion in the presence of an amide of a halogen substituted α -coumarilyl acetic acid in the presence of an aromatic amino developing agent containing an unsubstituted amino group.

13. A method of producing a color image in a photographic element bearing a silver halide emulsion layer having a latent image formed in it which comprises color developing said element in the presence of alpha-coumarilyl-acetic acid ethyl ester with an aromatic amino developing agent containing an unsubstituted amino group.

14. A photographic color forming developer containing an aromatic amino developing agent having an unsubstituted amino group and alpha-coumarilyl-acetic acid ethyl ester.

15. A method of producing a colored image in a photographic element bearing a silver halide emulsion layer containing a latent image which comprises color developing said element in the presence of alpha-coumarilyl-acet-anilide with an aromatic amino color developing agent having an unsubstituted amino group.

16. A photographic color forming developer containing an aromatic amino developing agent having an unsubstituted amino group and alpha-coumarilyl-acet-anilide.

17. A photographic color forming developer containing an aromatic amino developing agent having an unsubstituted amino group and alpha-coumarilyl-acet-ortho-chloranilide.

18. A method of producing a color image in a photographic element bearing a silver halide emulsion layer having a latent image formed in it which comprises color developing said element in the presence of alpha-coumarilyl-acet-ortho-chloranilide with an aromatic amino color developing agent having an unsubstituted amino group.

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