

## UNITED STATES PATENT OFFICE

2,441,491

## CYANACETYLAMINO PHENOL COLOR FORMERS FOR COLOR PHOTOGRAPHY

John David Kendall and Douglas James Fry,  
Ilford, England, assignors to Ilford Limited,  
Ilford, England, a British company

No Drawing. Application May 3, 1945, Serial No.  
591,828. In Great Britain May 12, 1944

8 Claims. (Cl. 95—6)

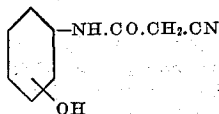
1

This invention relates to colour photography and particularly to dyestuff intermediates for use in colour photographic processes.

Processes of colour photography are well known in which coloured images are produced by the development of reducible silver salt images by means of aromatic primary amino developing agents in the presence of compounds, generally known as "colour-formers" or "colour-couplers," which couple with the oxidation products of such developers, formed during development, to form quinone-imine or azomethine dyes. The colour-couplers may be present in the developing solution employed, or may be included in a photographic emulsion layer which contains the reducible silver salt image, or in an adjacent layer or a layer separated from the said emulsion layer only by a thin water-permeable layer. The developing agent may be, for example, p-phenylene diamine or its N.N.-dialkyl derivatives, e. g. N.N.-dimethyl and N.N.-diethyl p-phenylene diamines, or a homologue, e. g. 5-diethylamino-2-amino-toluene.

Large numbers of colour-couplers have been described in the extensive literature dealing with this type of colour photographic process. The requirements for a satisfactory colour-coupler, however, are rather strict. Thus it must be capable of ready incorporation into the developing bath or photographic layer into which it is desired to include it, and where it is included in a photographic layer, neither it nor the dye derived from it must have any substantial tendency to diffuse from such layer, either into adjacent layers of the photographic element, or into processing baths. Moreover, it must be selected so that the colour of the dye obtained from it is suitable for the particular colour process with which it is intended to be used.

According to the present invention a process of colour photography comprises developing a reducible silver salt image by means of an aromatic primary amino developing agent in the presence of a cyanacetyl amino phenol of the general formula:



where the indicated hydroxy group is in the ortho or meta position to the indicated amino residue and the para position to the hydroxy group is unsubstituted or substituted only by sul-

2

phonic, carboxyl, or halogen (or other atom or group readily removed during the dye-coupling reaction), or in the presence of a corresponding naphthol or higher homologous compound.

Such compounds may be prepared by reacting together an aminophenol (or naphthol or higher homologous compound) which is unsubstituted in the para position to the hydroxy group, or contains a carboxyl, sulphonic, halogen or other easily removable atom or group in such position, with ethyl cyanacetate. Thus, for example, cyanacet-o-hydroxy-anilide may be prepared from o-amino-phenol and ethyl cyanacetate in hot xylene solution in the presence of piperidine or other base. The product separates on cooling, and after purification has a melting point of 178° C. Similarly, using 2-amino-5-methyl phenol, the compound cyanacet-o-hydroxy-p-toluidine, M.Pt. 189° C., is obtained. Both these compounds yield deep blue to blue-green dyes on colour-coupling development in accordance with this invention.

Other amino phenols and amino naphthols which may be similarly employed as initial reagents are, for example, m-amino-phenol, β-amino-α-naphthol, 2-amino-5-ethoxy-phenol, 2-amino-3-methyl phenol and 2-amino-5-chlor phenol.

Particular compounds which may be employed are:

- 1-cyanacetyl amino-2-hydroxy-4-ethoxy benzene
- 2-cyanacetyl amino-1-hydroxy naphthalene
- 1-cyanacetyl amino-2-hydroxy-6-methyl benzene

These compounds are made by the general process described above, using the appropriate reagents.

As will be clear from the foregoing discussion of the compounds, the benzene, naphthalene or other ring system present may contain other substituent groups, e. g. hydrocarbon groups or alkoxy groups.

The colour-couplers of this invention may be included in a developing solution containing an aromatic primary amino developing agent, or may be included in a silver halide emulsion layer, or in a water-permeable colloid layer coated next to a silver halide emulsion layer, or separated therefrom only by a thin water-permeable layer.

Thus, for example, the colour-couplers of this invention may be used in any of the colour processes of U. S. Patents Nos. 2,350,380, 2,363,764 and 2,369,171 and British Patents Nos. 551,116, 551,117, 554,302 and 556,858.

The formation of coloured images by means

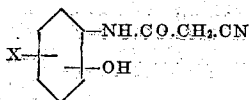
3

of the colour-couplers of this invention may be applied to the development of a reducible silver salt image which is an original latent image formed in the emulsion layer by exposure to light, or which is an image obtained by the conversion of a silver image to a reducible silver salt image by the usual bleaching technique.

Although this invention is primarily concerned with colour photographic processes in which the dye is formed by the coupling of the colour-couplers of the invention with the oxidation products of an aromatic primary amino developing agent formed in situ during the development of a reducible silver salt image, the colour-couplers of the invention may also be employed in other colour photographic processes, e. g. processes in which the dye is formed by direct coupling between the colour-coupler and a nitroso aniline, e. g. p-nitroso dialkyl aniline, or between the colour-coupler and a diazo compound. As an example of this latter type of process a colour-coupler may be present in a layer containing a reducible silver salt image, such image developed with an aromatic primary amino developing agent forming an azomethine dye image in situ with the developed silver image, the residual colour-coupler coupled with a diazo compound applied in solution to the photographic element, and the original azomethine dye image bleached out, leaving only the azo dye image in the layer.

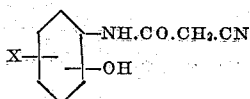
What we claim is:

1. A process of colour photography which comprises developing a reducible silver salt image in a photographic element by means of an aromatic primary amino developing agent in the presence of a compound of the general formula:



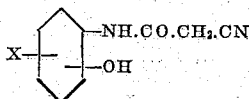
where the hydroxy group is in a position taken from the group consisting of ortho and meta positions to the cyanacetyl group and where X is para to the hydroxy group and is a member selected from the class consisting of the hydrogen and halogen atoms and sulphonie and carboxyl groups.

2. A process of colour photography which comprises developing a reducible silver salt in a photographic element by means of a solution of an aromatic primary amino developing agent containing a compound of the general formula:



where the hydroxy group is in a position taken from the group consisting of ortho and meta positions to the cyanacetyl group and where X is para to the hydroxy group and is a member selected from the class consisting of the hydrogen and halogen atoms and sulphonie and carboxyl groups.

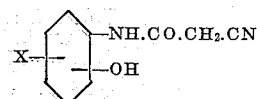
3. A photographic element for colour photography which comprises a support bearing at least one layer of a light-sensitive silver halide emulsion containing a compound of the general formula:



4

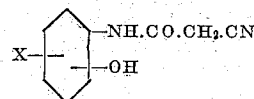
where the hydroxy group is in a position taken from the group consisting of ortho and meta positions to the cyanacetyl group and where X is para to the hydroxy group and is a member selected from the class consisting of the hydrogen and halogen atoms and sulphonie and carboxyl groups.

4. A photographic element for colour photography which comprises a support bearing at least one layer of a light-sensitive silver halide emulsion and, adjacent thereto, a layer containing a compound of the general formula:



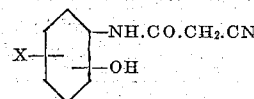
where the hydroxy group is in a position taken from the group consisting of ortho and meta positions to the cyanacetyl group and where X is para to the hydroxy group and is a member selected from the class consisting of the hydrogen and halogen atoms and sulphonie and carboxyl groups.

5. A process of colour photography which comprises forming a reducible silver salt image in an emulsion layer of a photographic element which contains a compound of the general formula:



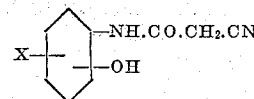
where the hydroxy group is in a position taken from the group consisting of ortho and meta positions to the cyanacetyl group and where X is para to the hydroxy group and is a member selected from the class consisting of the hydrogen and halogen atoms and sulphonie and carboxyl groups, and developing said image with an aromatic primary amino developing agent.

6. A process of colour photography which comprises forming a reducible silver salt image in an emulsion layer of a photographic element which contains a compound of the general formula:



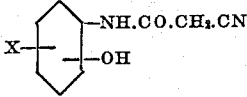
where the hydroxy group is in a position taken from the group consisting of ortho and meta positions to the cyanacetyl group and where X is para to the hydroxy group and is a member selected from the class consisting of the hydrogen and halogen atoms and sulphonie and carboxyl groups, and developing said image with an N,N-dialkyl-p-phenylene diamine.

7. A process of colour photography which comprises forming a reducible silver salt image in an emulsion layer of a photographic element which includes, adjacent thereto, a layer containing a compound of the general formula:



where the hydroxy group is in a position taken from the group consisting of ortho and meta positions to the cyanacetyl group and where X is para to the hydroxy group and is a member selected from the class consisting of the hydrogen and halogen atoms and sulphonie and carboxyl groups, and developing said image with an aromatic primary amino developing agent.

8. A process of colour photography which comprises forming a reducible silver salt image in an emulsion layer of a photographic element which includes, adjacent thereto, a layer containing a compound of the general formula:



where the hydroxy group is in a position taken from the group consisting of ortho and meta positions to the cyanacetamino group and where X is para to the hydroxy group and is a member selected from the class consisting of the hydrogen and halogen atoms and sulphonic and carboxyl groups, and developing said image with an N,N-dialkyl-p-phenylene diamine.

JOHN DAVID KENDALL.  
DOUGLAS JAMES FRY.

5

10

15

20

## REFERENCES CITED

The following references are of record in the file of this patent:

## UNITED STATES PATENTS

| Number    | Name                   | Date          |
|-----------|------------------------|---------------|
| 2,108,602 | Mannes et al. _____    | Feb. 15, 1938 |
| 2,133,937 | Middleton et al. _____ | Oct. 18, 1938 |
| 2,181,944 | Kleine _____           | Dec. 5, 1939  |
| 2,220,908 | Kendall et al. _____   | Nov. 12, 1940 |
| 2,269,481 | Reindorp _____         | Jan. 13, 1942 |
| 2,303,380 | Frochlich _____        | Dec. 1, 1942  |
| 2,328,652 | Kirby et al. _____     | Sept. 7, 1943 |
| 2,350,380 | White _____            | June 6, 1944  |
| 2,367,531 | Salminen et al. _____  | Jan. 16, 1945 |
| 2,369,929 | Vittum et al. _____    | Feb. 20, 1945 |
| 2,380,809 | Verkindern _____       | July 31, 1945 |