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2,427,910

# UNITED STATES PATENT OFFICE

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## ACETOACET-METHINE COLOR FORMERS

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8 Claims. (Cl. 95—6)

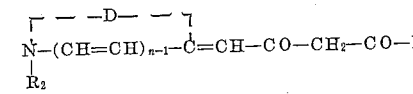
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This invention relates to colour photography and particularly to dyestuff intermediates for use in colour photographic processes.

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, and homologues thereof and 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 compound of the general formula:



where D is the residue of a heterocyclic nitrogen nucleus, $n$ is an integer less than 3, $R_1$ is a hydrocarbon or heterocyclic group, and $R_2$ is an alkyl or aralkyl group.

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The heteroclyclic nucleus may be five-membered or six-membered. Examples are thiazoles, oxazoles, selenazoles and their polycyclic homologues, such as those of the benzene and naphthalene series, pyridine and its polycyclic homologues, such as quinoline and $\alpha$ and $\beta$-naphthoquinolines, lepidines, picolines, indolenines, diazines (e. g., thio $\beta\beta'$-diazole) oxazolines, thiazolines and selenazolines. The polycyclic compounds of this series may be substituted in the carbocyclic rings with one or more groups such as alkyl, aryl, amino, hydroxy, alkoxy and methylene-dioxy groups, or by halogen atoms.

The group $R_1$ may be an alkyl, aryl or aralkyl group, e. g., methyl, ethyl or higher alkyl; phenyl or naphthyl; or benzyl or naphthylmethyl. Or $R_1$ may be a heterocyclic group, e. g., a furoyl, coumaryl, thionaphthenyl or a residue of any of the heterocyclic nitrogen compounds referred to above. $R_2$ may be any of the alkyl or aralkyl groups referred to above.

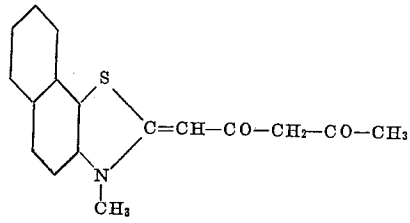
The compounds employed in accordance with the present invention may be prepared by any convenient method. One suitable method is to condense a heterocyclic nitrogen quaternary salt containing a methyl group in $\alpha$ or $\gamma$ position to the quaternary nitrogen atom with an acyl acetic ester in the presence of a solvent and a base. Thus, for example, 1-aceto acetyl methine-2-methyl benzthiazole may be prepared by refluxing 1-methyl benzthiazole methiodide with acetoacetic ester in the presence of xylene as solvent and in the presence of a small quantity of triethylenine or other base, e. g., sodium ethoxide. Under these conditions the alcohol liberated in the reaction may be distilled off and the residue, after filtering, removal of the xylene and recrystallisation, is the desired product. This product, M. Pt. 124° C., yields a strong yellow image on colour-coupling development in accordance with this invention, and the image is strongly resistant to sulphite, i. e., its depth is not substantially reduced by the presence of sulphite in the developer used.

Other compounds for use in the present invention may be prepared from quaternary salts of any of the heterocyclic nitrogen compounds referred to above, which contain a methyl group

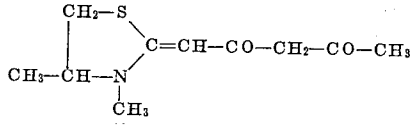
in the $\alpha$ or $\gamma$ position to the quaternary nitrogen atom. Instead of aceto acetic ester there may be employed: ethyl benzoylacetate, ethyl furoylacetate, ethyl picolinoylacetate and similar compounds.

Particular compounds of use in the present invention are:

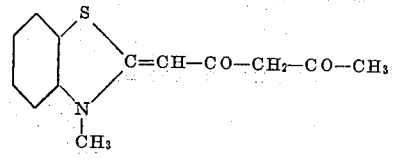
1-acetoacet-methine-2-methyl-5-6-dihydronaphtha-thiazole (prepared from ethyl acetoacetate and 1-methyl-5.6-naphthathiazole ethiodide)



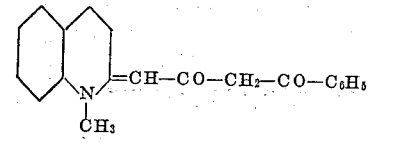
2-acetoacet-methine-3:4-dimethyl thiazoline (prepared from ethyl acetoacetate and 2.4-dimethyl thiazole methiodide)



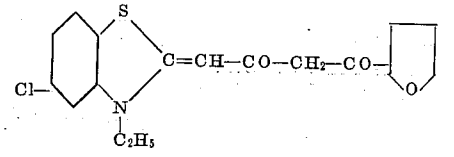
1-acetoacet-methine-2-methyl-dihydrobenzthiazole (prepared from ethyl acetoacetate and 1-methyl-benzthiazole methiodide)



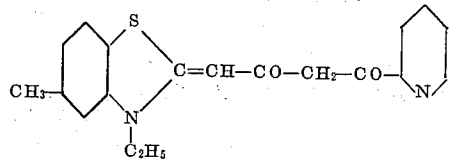
2-benzoylacet-methine-1-methyl-dihydroquinoline (prepared from ethyl benzoylacetate and quinaldine methiodide)



1-furoylacet-methine-2-ethyl-4-chlorodihydrobenzthiozole (prepared from ethyl furoyl-acetate and 1-methyl-4-chlor-benzthiazole ethiodide



1-picolinoylacet-methine-2-ethyl-4-methyl-dihydrobenzthiazole (prepared from ethyl picolinoylacetate and 1:4-dimethyl benzthiazole ethiodide)



All these compounds are prepared by the general method described above. They all yield yellow to orange azomethine dyes on colour-coupling development.

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.

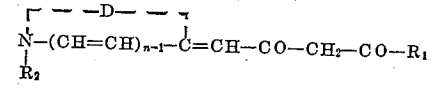


The formation of coloured images by means of the colour-couplers of this invention may be applied to the development of a reducible silver salt image which is an original latent image formed in the emulsion layer by exposure to light, or which is an image obtained by the conversion of a silver image 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 anilene, e. g., p-nitroso dialkyl anilene, 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.

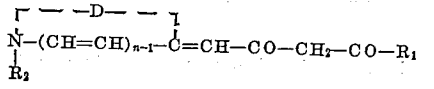
What we claim is:

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:



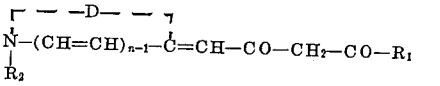
where D is the residue of a heterocyclic nitrogen nucleus, $n$ is an integer less than 3, $R_1$ is a group selected from the class consisting of hydrocarbon and heterocyclic groups, and $R_2$ is a group selected from the class consisting of alkyl and aralkyl groups.

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 D is the residue of a heterocyclic nitrogen nucleus, $n$ is an integer less than 3, $R_1$ is a group selected from the class consisting of hydrocarbon and heterocyclic groups, and $R_2$ is a group selected from the class consisting of alkyl and aralykyl groups.

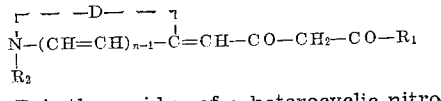
3. A photogrphic element for colour photography which comprises a support bearing at least one layer of a light-sensitive silver halide emulsion containing a compound of the general formula:



where D is the residue of a heterocyclic nitrogen nucleus, $n$ is an integer less than 3, $R_1$ is a group

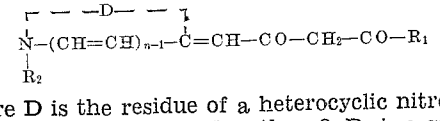
selected from the class consisting of hydrocarbon and heterocyclic groups, and $R_2$ is a group selected from the class consisting of alkyl and aralkyl groups.

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:



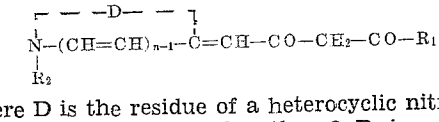
where D is the residue of a heterocyclic nitrogen nucleus, $n$ is an integer less than 3, $R_1$ is a group selected from the class consisting of hydrocarbon and heterocyclic groups, and $R_2$ is a group selected from the class consisting of alkyl and aralkyl groups.

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 D is the residue of a heterocyclic nitrogen nucleus, $n$ is an integer less than 3, $R_1$ is a group selected from the class consisting of hydrocarbon and heterocyclic groups, and $R_2$ is a group selected from the class consisting of alkyl and aralkyl groups, and developing said image with an aromatic primary amino developing agent.

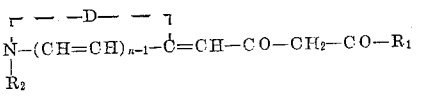
6. A process of colour photography which comprises forming a reducible silver salt image in an emulsion layer of a photographic element which contains a compound of the general formula:



where D is the residue of a heterocyclic nitrogen nucleus, $n$ is an integer less than 3, $R_1$ is a group selected from the class consisting of hydrocarbon and heterocyclic groups, and $R_2$ is a group selected from the class consisting of alkyl and aralkyl groups, and developing said image with an N,N-dialkyl-p-phenylene diamine.

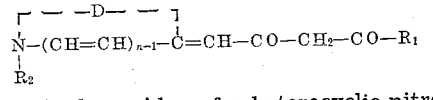


7. A process of colour photography which comprises forming a reducible silver salt image in an emulsion layer of a photographic element which includes, adjacent thereto, a layer containing a compound of the general formula:



where D is the residue of a heterocyclic nitrogen nucleus, $n$ is an integer less than 3, $R_1$ is a group selected from the class consisting of hydrocarbon and heterocyclic groups, and $R_2$ is a group selected from the class consisting of alkyl and aralkyl 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 D is the residue of a heterocyclic nitrogen nucleus, $n$ is an integer less than 3, $R_1$ is a group selected from the class consisting of hydrocarbon and heterocyclic groups, and $R_2$ is a group selected from the class consisting of alkyl and aralkyl groups, and developing said image with an N,N-dialkyl-p-phenylene diamine.

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