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COLOR PHOTOGRAPHY

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This invention relates to color photography, and more particularly to color-forming compounds which form dyes by coupling with the oxidation products of photographic developing agents.

A principal object of this invention is to provide a color photographic element derived from color-forming compounds, which, in combination with certain classes of developing agents, will form dyes in situ with photographic images. A further object is to produce such dyes by color-forming development. Another object is to produce partial color-records in which the individual records are of improved spectral quality for color photography.

It has been formerly taught to prepare colored photographs by developing exposed silver salt emulsion layers in certain developing agents whose oxidation products are water-insoluble dyes. Thus, a silver halide layer, bearing a latent image, can be developed in an alkaline indoxyl solution, whereupon a silver image is produced along with a blue dye image in situ with the silver. The silver image can be removed by Farmers Reducer, revealing the dye image. In like manner, a photographic record can be developed in chlor-indoxyl to produce a green image and in thio-indoxyl for a red image.

It is also known, for the purpose of preparing color pictures, to develop exposed silver halide layers by agents whose oxidation products are not colored but which will chemically unite or couple with other organic agents, called "color-formers" to form intensely colored dyes. These "color-formers" are not photographic developers, are generally water-insoluble and produce dyes in situ with, and simultaneously with the deposition of the metallic silver image. The de-

of the diamino-aryl class, such as p-phenylenediamine or its substitution products, such as for example, di-methyl or di-ethyl p-phenylenediamine. Color-forming compounds already proposed include, for example, thymol, benzoyl acetone, phenacyl chloride and para-nitrobenzyl cyanide.

These prior processes, however, have failed to produce colored images having the correct spectral qualities for color photography. Moreover, these prior color-formers tend to have a harmful effect on the sensitivity of silver halide emulsions, so that, for these reasons, the color-formers already known have not provided a practical means for color photography.

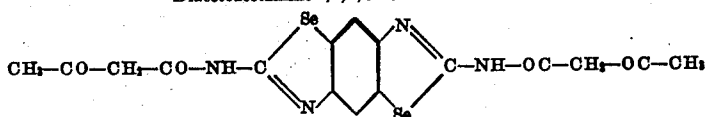
The present invention has demonstrated that amino-aryl-bis-azoles wherein two amino hydrogens of a diaminoaryl-bis-azole are replaced by the radicle of an acyl acetic acid, in conjunction with aromatic amino developing agents, form satisfactory dye images when developing exposed photo-sensitive layers of gelatino-silver salts or bichromatized gelatin. As representative of the type of color-forming compounds contemplated as within the scope of our invention, are diacylacetaminoaryl-bis-azoles wherein two amino hydrogens are replaced by the radicles of an acyl acetic acid e. g., acetoacetic acid, furoyl-acetic acid, benzoyl-acetic acid and naphthoyl-acetic acid and/or cyanacetic acid, malonic acid and the azoles include the thiazoles, oxazoles, selenazoles and tellurazoles. The acylacetamino-aryl-bis-azoles may be made by condensing the diaminoaryl-bis-azole with at least two mols of the ethyl or equivalent ester of the acylacetic acid.

The following preferred examples are given as descriptive of the invention but not in limitation thereof:

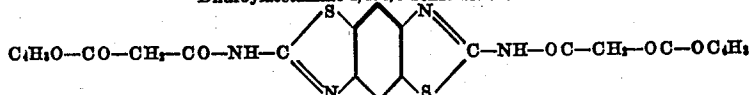
Diacetoacetamino-1, 2, 4, 5-benzo-bis-thiazole



Diacetoacetamino-1, 2, 4, 5-benzo-bis-selenazole



Difuroylacetamino-1, 2, 4, 5-benzo-bis-thiazole



velopers used for these proposed processes are

The preferred color-forming compounds above

described may be used either in developers or as an addition to silver halide emulsions.

As preferred color-forming developers, the following produce excellent results:

<i>Formula 1</i>	
Diethyl-p-phenylenediamine, hydrochloride	
gms---	2
Sodium sulfite, anhydrous-----	5
Sodium carbonate, anhydrous-----	20
Water to-----	1
To which is added:	
Diacetoacetamino-1,2,4,5-benzo-bis-thiazole	
gm---	1.0
Ethyl alcohol-----	100

<i>Formula 2</i>	
Diethyl-p-phenylenediamine, hydrochloride	
gms---	2
Sodium sulfite, anhydrous-----	5
Sodium carbonate, anhydrous-----	20
Water to-----	1
To which is added:	
Diacetoacetamino-1,2,4,5-benzo-bis-selenazole	
gm---	1.0
Ethyl alcohol-----	100

<i>Formula 3</i>	
Dimethyl-p-phenylenediamine, hydrochloride	
gms---	2
Sodium sulfite, anhydrous-----	5
Sodium carbonate, anhydrous-----	20
Water to-----	1
To which is added:	
Difuroylacetamino-1,2,4,5-benzo-bis-thiazole	
gm---	1.0
Ethyl alcohol-----	100

In place of the di-alkyl-substituted p-phenylenediamine, the mono-alkylated substitution products may be used or the un-substituted p-phenylenediamine may be used as well as the bases and/or acid salts of these developing agents. In place of the ethyl alcohol, methyl alcohol or acetone may be used.

If it is desired to add the color-forming compound directly to the emulsion, a preferred procedure is as follows: 10 grams of the color-former is dissolved in 200 mls. of ethyl alcohol to which is added about 50 grams of gelatin in 500 mls. of water and then thoroughly mixed. This color-forming solution is then added, with vigorous stirring, to 1 liter of silver-gelatino-emulsion. Emulsions containing these color-forming compounds may be coated as layers on one or both sides of a photographic support either as individual or superposed emulsion layers.

While it is preferred to employ silver-gelatine emulsions, other emulsions comprising other well known sensitizers and binding agents may also be used. Examples of these are the well known silver collodion emulsions, albuminoid emulsions, or bichromated emulsions.

In the form of color-forming developers, the

above described compounds may also be used to re-develop bleached silver images. Thus, a silver image may be bleached in potassium ferrocyanide or a mixture of chromic and hydrobromic acids and re-exposed, whereupon the bleached image can be re-developed to silver and a dye image by the color-forming developers above described. After development, the silver is removed by any of the well known reducers such as Farmers Reducer.

While the foregoing specification sets forth the preferred exemplifications of the present invention, it is intended to include all variations and modifications within the spirit and scope of the appended claims.

We claim:

1. A color-forming photographic developer comprising an aromatic amino photographic developing agent and a diacylacetaminoaryl-bis-azole.

2. A color-forming photographic emulsion comprising a binding agent, a light sensitive compound, an aromatic amino photographic developing agent, and a compound taken from the group consisting of diacylacetaminoaryl-bis-oxazoles, -thiazoles, and -selenazoles.

3. A color-forming photographic emulsion comprising a binding agent, a light sensitive compound, a compound selected from the group consisting of N-dialkyl-p-phenylenediamine and the acid salts thereof, and a compound taken from the group consisting of diacylacetaminoaryl-bis-oxazoles, -thiazoles, and -selenazoles.

4. A color-forming photographic emulsion comprising a binding agent, a salt of silver and a diacylacetaminoaryl-bis-azole.

5. A color-forming photographic layer comprising a sensitized gelatino-silver-halide emulsion and a diacylacetaminoaryl-bis-azole.

6. A color-forming photographic developer comprising an N-di-alkyl-p-phenylenediamine and a diacylacetaminoaryl-bis-azole.

7. A color-forming photographic emulsion comprising a binding agent, a silver halide and a diacylacetamino-aryl-bis-thiazole.

8. A color-forming photographic emulsion comprising a binding agent, a silver halide and a diacetoacetaminobenzo-bis-thiazole.

9. A color-forming photographic emulsion comprising a binding agent, a silver halide and a diacylacetaminoaryl-bis-selenazole.

10. A color-forming photographic emulsion comprising a binding agent, a silver halide and a diacetoacetaminobenzo-bis-selenazole.

11. A color-forming photographic emulsion comprising a binding agent, a silver halide and a dinaphthoylacetaminoaryl-bis-azole.

12. A color-forming photographic emulsion comprising a silver halide and a dinaphthoylacetaminobenzo-bis-thiazole.

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