

UNITED STATES PATENT OFFICE

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PRODUCTION OF COLORED PHOTOGRAPHIC IMAGES BY COLOR-DEVELOPMENT

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10 Claims. (Cl. 95—6)

This invention is for improvements in or relating to the production of colored photographic images by color-development.

There is known a process of producing color pictures in which an exposed silver halide emulsion is developed in the presence of a substance known as a "color-former," the color-former being a substance which reacts with the oxidation products of an aromatic amino photographic developer to form a colored image which can be revealed by bleaching out the silver image with Farmer's reducer or with other suitable photographic bleaching agent.

The property of color-formers to couple with the oxidation products of aromatic amino photographic developers may be ascribed to the presence in the color-former compounds of active groups which are conveniently termed "coupling functions." The commonly known coupling functions include (1) a phenolic hydroxyl group, as for example in α -naphthols, (2) an aromatic amino group as in *p*-phenylene diamine, and (3) an active methylene group in (a) an open chain, as in aceto-acetic esters, or in (b) a heterocyclic nucleus as in a pyrazolone, or (c) adjoining a cyano group, as in *p*-nitro-benzylcyanide.

In the production of photographic color images utilising color-development a number of physical and chemical properties are required of the color-former additional to the power of coupling to produce colored images described above. Such additional properties may include non-diffusibility from the emulsion or other layer, absence of deleterious effect on the speed fog and contrast of the silver halide emulsion in which it is dispersed, the production of coupled dyestuffs of desired hue and of a suitable degree of insolubility in water.

On account of the number of these requirements, which vary with the exact nature of the process employed, it has not always been possible to select from the many substances which have already been proposed, color-formers which are entirely suitable for a particular procedure.

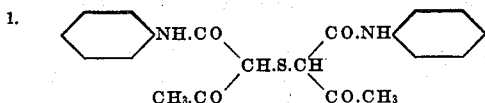
We have now discovered that improved results may be obtained in a process of producing colored images by use of a new series of color-formers conforming to the requirements above-referred to.

According to the present invention, there is provided a process for the development of a reducible silver salt emulsion to produce a colored image which process comprises developing the emulsion by means of an aromatic amino-developing agent containing a primary amino group

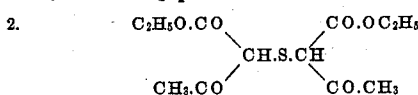
in conjunction with color-former in which the coupling function as above-defined occurs at least twice and in which at least two of the active methylene groups constituting the coupling functions are directly linked by means of one sulphur atom.

The color-former may be incorporated in the emulsion or mixed with the aromatic amino-developing agent, e. g. an aromatic diamino compound, using for this purpose a solution in an alcohol, for example in methyl or ethyl alcohol, or other suitable solvent or solvent mixture or again the color-former may be incorporated in a layer adjacent to one comprising a reducible silver halide emulsion.

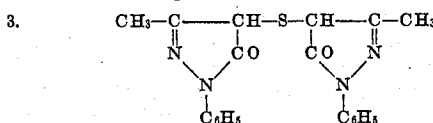
Color-formers employed in accordance with the present invention include the following:



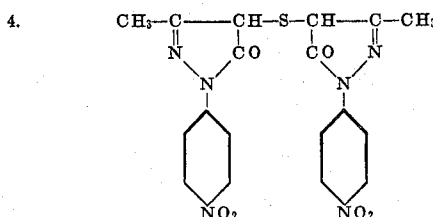
Thio-bis-acetoacetic anilide giving a yellow image on color-development.



Thio-bis-acetoacetic ester giving a yellow image on color-development.



Thio-bis-phenylmethylpyrazolone giving a red image on color-development.



Thio-bis-*p*-nitro-phenylmethylpyrazolone giving a magenta image on color-development.

The pyrazolones and acetoacetanilides are made either by condensing thioacetoacetic ester with a phenyl hydrazine or an amine respectively, or condensing directly the pyrazolones and acetoacetanilides with an inorganic halogen compound such as sulphur dichloride or thionyl chlo-

ride. It is preferable to employ thionyl chloride to sulphur dichloride since sulphur dichloride acts as a powerful desensitizer for the emulsion and if used for the preparation of the color-former very thorough purification of the product is essential.

When the color-formers made by the present invention are basic they may be used as such or in the form of the corresponding inorganic acid salts.

Following is a description by way of example of two methods of carrying the invention into effect.

EXAMPLE I

Thio-bis-(1-phenyl-3-methyl-5-pyrazolone)

To 5 grams of 1-phenyl-3-methyl-5-pyrazolone dissolved in 50 cc. of chloroform 2.2 cc. of thionyl chloride were added. After standing for three days the solid was filtered off, liquid removed by pressing on the funnel and the partially dried solid washed with a little dry ether to remove any thionyl chloride still present. It was then recrystallised several times from methyl alcohol and refluxed for 6 hours in absolute alcohol to which animal charcoal had been added. The clear filtrate was then allowed to cool after adding an equal amount of dry light petroleum ether. The resulting color-former consisting of thio-bis-(1-phenyl-3-methyl-5-pyrazolone) consisted of small white crystals having a melting point of 181°-2° C.

5 grams of the color-former prepared as described above were dissolved in 50 cc. of ethylene glycol and 50 cc. of methyl alcohol and the solution was mixed with an aromatic amino-developing solution consisting of:

N-N-diethyl-p-phenylenediamine	
hydrochloride	grams-- 2.5
Sodium sulphite cryst.	do---- 20.0
Sodium carbonate cryst.	do---- 40.0
Water to	cc-- 1,000

The mixed solution of coupler and developing agent was employed as a developer for a silver halide photographic emulsion in the production of a colored image by such development to give simultaneously color and image consisting of metallic silver and the colored combination of the coupler and the oxidation products of the developer such colored image being revealed after removal of the unchanged silver halide by treatment with sodium thiosulphate and by removal completely or in part of the developed silver by means of the reducing agent, e. g. Farmer's reducer.

EXAMPLE II

Thio-bis-acetoacetanilide

8.75 grams of acetoacetanilide were dissolved in 150 cc. dry benzene and 1.66 cc. sulphur dichloride added drop by drop. After standing for 3 days the solid was filtered off, liquid removed by pressing on the funnel and the partially dried solid washed as before with a little dry ether. It was then recrystallised several times from methyl alcohol and refluxed for 6 hours in carbon disulphide and for a further 6 hours in benzene to which animal charcoal had been added. The filtrate was then allowed to cool after adding an equal amount of dry light petroleum ether. The color-former consisting of white silky needles of thio-bis-acetoacetanilide had a melting point of 146° C.

5 grams of the color-former prepared as de-

scribed above were dissolved in 50 cc. of ethylene glycol and 50 cc. of methyl alcohol and the solution was mixed with an aromatic amino-developing solution consisting of:

N-N-diethyl-p-phenylenediamine	
hydrochloride	grams-- 2.5
Sodium sulphite cryst.	do---- 20.0
Sodium carbonate cryst.	do---- 40.0
Water to	cc-- 1,000

The mixed solution of coupler and developing agent was employed as a developer for a silver halide photographic emulsion in the production of a colored image as described in Example I.

I claim:

1. A process for the development of a reducible silver salt emulsion to produce a colored image which process comprises developing the emulsion by means of an aromatic amino-developing agent containing a primary amino group in conjunction with a color-former in which the coupling function occurs at least twice and in which at least two of the active methylene groups constituting the coupling functions are directly linked by means of a single sulphur atom.

2. A process for the development of a reducible silver salt emulsion to produce a colored image which process comprises developing the emulsion by means of an aromatic amino-developing agent containing a primary amino group in conjunction with a color-former in which the coupling function occurs at least twice and in which at least two of the active methylene groups constituting the coupling functions are directly linked by means of a single sulphur atom, the said color-former being incorporated in the emulsion.

3. A process for the development of a reducible silver salt emulsion to produce a colored image which process comprises developing the emulsion by means of an aromatic amino-developing agent containing a primary amino group in conjunction with a color-former in which the coupling function occurs at least twice and in which at least two of the active methylene groups constituting the coupling functions are directly linked by means of a single sulphur atom, the said color-former being mixed with the amino-developing agent.

4. A process for the development of a reducible silver salt emulsion to produce a colored image which process comprises developing the emulsion by means of an aromatic diamino-developing agent containing a primary amino group in conjunction with a color-former in which the coupling function occurs at least twice and in which at least two of the active methylene groups constituting the coupling functions are directly linked by means of a single sulphur atom.

5. A process for the development of a reducible silver salt emulsion to produce a colored image which process comprises developing the emulsion by means of an aromatic diamino-developing agent containing a primary amino group in conjunction with a color-former in which the coupling function occurs at least twice and in which at least two of the active methylene groups constituting the coupling functions are directly linked by means of a single sulphur atom, the said color-former being incorporated in the emulsion.

6. A process for the development of a reducible silver salt emulsion to produce a colored image which process comprises developing the emulsion by means of an aromatic diamino-developing

agent containing a primary amino group in conjunction with a color-former in which the coupling function occurs at least twice and in which at least two of the active methylene groups constituting the coupling functions are directly linked by means of a single sulphur atom, the said color-former being mixed with the diamino-developing agent.

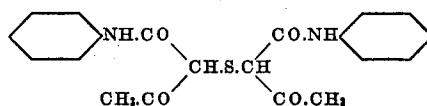
7. A process for the development of a reducible silver salt emulsion to produce a colored image which process comprises developing the emulsion by means of an aromatic amino-developing agent containing a primary amino group consisting of an N-N-dialkyl-*p*-phenylenediamine in conjunction with a color-former in which the coupling function occurs at least twice and in which at least two of the active methylene groups constituting said coupling functions are directly linked by means of a single sulphur atom.

8. A process for the development of a reducible silver salt emulsion to produce a colored image which process comprises developing the emulsion by means of an aromatic amino-developing agent containing a primary amino group consisting of an N-N-dialkyl-*p*-phenylenediamine in conjunction with a color-former in which the coupling function occurs at least twice and in which at least two of the active methylene groups constituting said coupling functions are directly linked by

means of a single sulphur atom, the said color-former being incorporated in the emulsion.

9. A process for the development of a reducible silver salt emulsion to produce a colored image which process comprises developing the emulsion by means of an aromatic amino-developing agent containing a primary amino group consisting of an N-N-dialkyl-*p*-phenylenediamine in conjunction with a color-former in which the coupling function occurs at least twice and in which at least two of the active methylene groups constituting said coupling functions are directly linked by means of a single sulphur atom, the said color-former being mixed with the said N-N-dialkyl-*p*-phenylenediamine developing agent.

10. A process for the development of a reducible silver halide emulsion to produce a colored image which process comprises developing the emulsion by means of an aromatic amino-developing agent containing a primary amino group in conjunction with a color-former consisting of thio-bis-acetoacetic anilide



BRUNO GLUCK.