

## UNITED STATES PATENT OFFICE

2,353,754

COLOR PHOTOGRAPHY USING METALLIC  
SALT COUPLER COMPOUNDSWillard D. Peterson, Rochester, N. Y., assignor to  
Eastman Kodak Company, Rochester, N. Y., a  
corporation of New JerseyNo Drawing. Application November 7, 1942,  
Serial No. 464,893

14 Claims. (Cl. 95—6)

This invention relates to photographic color forming or coupling compounds and particularly to coupler compounds which are non-diffusing when incorporated in sensitive emulsion layers.

The production of photographic images by means of a coupling reaction between a photographic developer and an intermediate or coupling compound upon which photographic development takes place is well known, having been described in Fischer U. S. Patent 1,055,155 and numerous patents which have issued more recently. One method of carrying out a color forming of this type is to incorporate the coupling compound in the sensitive emulsion layer prior to coating it on the support. When the coupling compound is incorporated in the sensitive layer in this way, a number of requirements must be met. Probably the most important of these is that the coupling compound must not wander or diffuse from the layer in which it is incorporated. This is especially important when two or more layers are superposed and are differentially sensitive as obviously the wandering of a coupling component would cause inaccurate color rendition. Another requirement is that the coupling compound, when incorporated in the sensitive layer, should not desensitize or otherwise adversely affect the emulsion layer.

In my U. S. Patent 2,296,306, granted September 22, 1942, I have described a color photographic process in which couplers made by combining a compound having a coupling function, with a heterocyclic compound having a free imino or mercapto group, are incorporated in emulsions as metallic salts. In the method described in my prior patent, the coupler was first mixed with the gelatin or other colloidal carrier, and a silver halide then precipitated in the gelatin. I have found that in some cases this method of preparing the emulsion results in fog, and that it is better to form the sensitive silver halide in the gelatin and then add the coupler and produce its silver or other metal salt in the emulsion.

As in the case of the method of my prior Patent 2,296,306, I use as coupling compounds derivatives of well known coupling compounds with certain heterocyclic compounds containing active groups in which a metal atom may be substituted to render the compound as a whole non-diffusing.

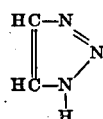
The heterocyclic compounds which react with the coupling compounds are characterized by the fact that they contain an imino (NH) group in the nucleus. These heterocyclic nuclei may also contain a mercapto (SH) group on one of the atoms in the nucleus and the hydrogen atom

of either the NH or the SH group may be replaced by a metallic atom such as a silver atom.

The heterocyclic nuclei suitable for incorporating in coupler compounds according to my invention are characterized by the fact that the imino group or the mercapto group which they contain is not more than two atoms distant from an atom which has an unshared pair of electrons. The atom which has the unshared pair of electrons may be, for example, a nitrogen atom or a sulfur atom and may be in the heterocyclic ring or in a chain or attached to an atom which is a member of the ring. It is a well known principle of chemistry that nitrogen may exist with valences of either three or five and that sulfur may exist with valences of two, four or six. When nitrogen has a valence of three, it has therefore an unshared pair of electrons and when sulfur has a valance of two, it has one or two unshared pairs of electrons.

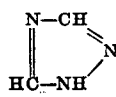
The following are suitable heterocyclic compounds into which coupling groups may be introduced to form compounds capable of being rendered non-diffusing according to my invention:

(1)



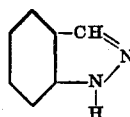
1,2,3-triazole

(2)



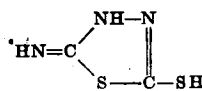
1,2,4-triazole

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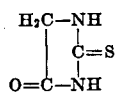
Indazole

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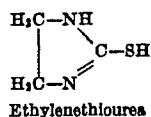
2-mercapto-5-aminothiazazole

(5)

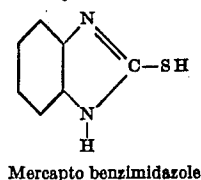


Thiohydantoin

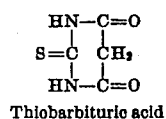
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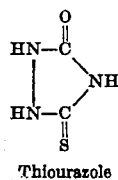
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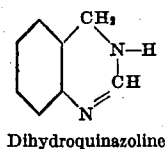
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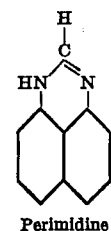
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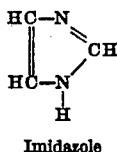
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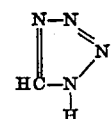
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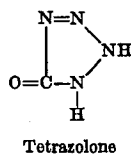
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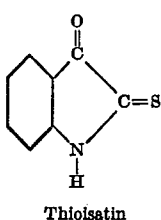
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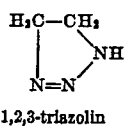
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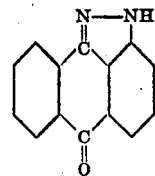
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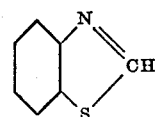


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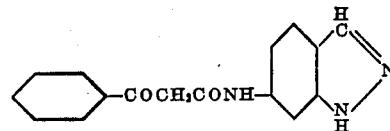


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The coupling compounds which are introduced into the heterocyclic nuclei described above may be any well known types of coupler compounds such as those described in Fischer U. S. Patent 1,055,155, Mannes and Godowsky U. S. Patents 2,039,730, 2,108,602, and 2,113,330, or Mannes, Godowsky and Peterson U. S. Patents 2,115,394 and 2,126,337. It is to be understood that when I refer to the coupler compounds as "being introduced into the heterocyclic nuclei" I do not mean that the final compound is necessarily formed by simple substitution starting with these two materials. The final compound may be formed by any suitable reaction which results in a compound having a heterocyclic portion as described above and a coupler portion or portions containing at least one group capable of reacting to form a dye image.

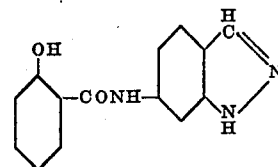
The following compounds are examples of couplers containing heterocyclic rings which may be employed according to my invention:

(1)



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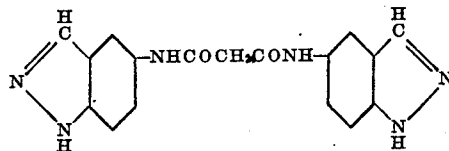
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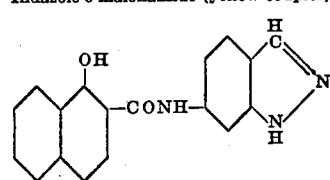
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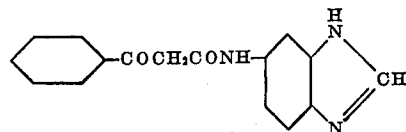
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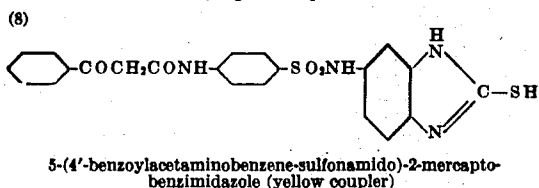
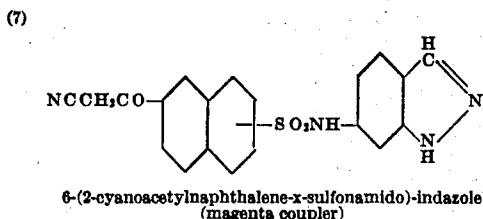
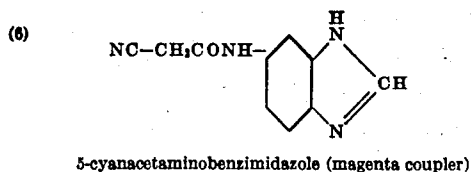
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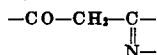


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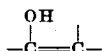
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The functional or reactive group common to the coupler compounds which react with primary aromatic amino developing agents to form a colored image is a reactive methylene or reactive ethenol group and this group may occur at various positions or more than a single position in the coupler molecule. By reactive methylene, I mean a  $\text{CH}_2$  group which is reactive in the coupling process. The  $\text{CH}_2$  group usually is present between two negative centers as, for example, in the groups  $-\text{CO}-\text{CH}_2-\text{CO}-$ ,  $-\text{CO}-\text{CH}_2-\text{CN}$ , or



in a ring system or chain compound. One of the hydrogen atoms of the methylene group may, in many cases, be substituted without destroying chemical activity of the group. By reactive ethenol I mean the group



This group occurs in the phenolic and naphtholic coupler compounds which are reactive in the ortho or para position with respect to the position of the hydroxyl group.

The reactive NH or SH group of the heterocyclic systems herein disclosed reacts with metal salts to permit the formation of an insoluble salt such as a silver, gold, nickel, mercury, cadmium or tin salt. Silver salts are preferred since a silver salt is ordinarily used in the production of sensitive photographic layers and common silver salts such as silver chloride or silver bromide are suitable for the purpose of my invention. Other silver salts which may be used are silver ferricyanide, silver orthophosphate, silver arsenate, silver oxalate, silver cyanate, and silver citrate.

The reaction of the metal salts with the herein described heterocyclic system of the coupling compounds is ionic and rapid and involves a simple replacement of the hydrogen atom of the NH or SH group by the metal atom of the metallic salt employed.

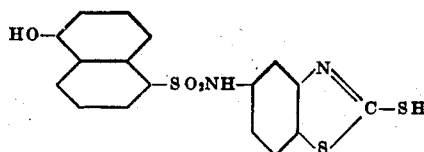
Not all of the heterocyclic parent bodies listed above may be used to produce couplers which are suitable for incorporation in all types of emulsions. With some of the compounds the silver salts produced in the emulsion would not be more insoluble than the silver halide. All of the heterocyclic parent bodies listed can be employed in

silver chloride emulsions since all of them produce silver salts which are less soluble than silver chloride. Many of the heterocyclic compounds such as Nos. 4 to 8, inclusive, can be employed in silver bromide emulsions and produce silver salts more insoluble than silver bromide.

The non-diffusing metal salts made according to my invention may be incorporated in single gelatin layers or layers of other colloidal materials such as cellulose esters or natural or synthetic resins. Non-diffusing silver salts according to my invention may also be incorporated in gelatino-silver halide emulsions intended for coating as superposed layers to form multi-color photographic elements.

The following example, which is illustrative only, indicates a method of forming a multi-layer photographic element according to my invention.

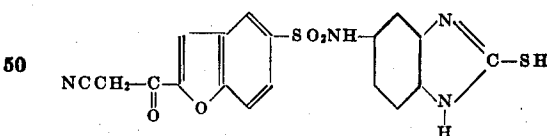
The coupler compound 2-mercapto-5-(1'-naphthol-5'-sulfonamido)-benzothiazole having the following formula:



is incorporated in a red-sensitive gelatino-silver halide emulsion of the chlorobromide type.

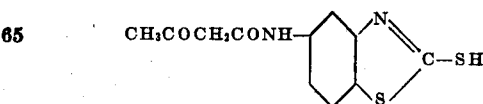
The emulsion contains 30 to 40 grams of silver chlorobromide, about half chloride and half bromide and 50 grams of gelatin per liter. It is chilled, noodled, washed and red-sensitized. One liter of the emulsion is melted at  $45^\circ\text{C}$ . and an aqueous solution containing from 4 to 8 grams of the sodium salt of the coupler in 200 cc. of water is added to it. The amount of coupler depends on the silver halide grain size, the finer the grain, the more coupler being used. The mixture is stirred for 30 minutes at  $45^\circ\text{C}$ ., chilled to room temperature overnight and coated.

A second emulsion is produced in the same way with a green sensitized emulsion and the coupler 2-mercapto-5-(2'-cyanoacetyl coumaronyl-5-sulfonamido)benzimidazole having the following formula:



The coupler is added to the emulsion as an aqueous solution containing from 3 to 6 grams of the sodium salt of the coupler in 200 cc. of water. The emulsion formed in this way is coated directly over the first emulsion layer.

A third emulsion is formed according to the same method using a non-optically-sensitized emulsion and the coupler 2-mercapto-5-acetylacetaminobenzothiazole having the following formula:



The coupler is added to the emulsion as an aqueous solution containing 3 to 6 grams of the sodium salt of the coupler in 200 cc. of water. Prior to coating this emulsion on the previously coated emulsions, a yellow filter layer is coated on the second emulsion. The yellow filter layer may consist of any suitable material such as colloidal

silver in gelatin or may be prepared from gelatin containing the metallic salt of a dye such as described in my prior Patent 2,266,441, granted December 16, 1941. A filter layer of this type is prepared as follows:

To a freshly prepared fine grain silver chloride emulsion containing 8.4 grams of silver chloride per liter of 2% gelatin, there is added at 40° C. an aqueous solution containing 7 grams of the sodium salt of p-sulfophenylazothiobarbituric acid in 150 cc. of water. This layer is coated on the second emulsion layer and the third emulsion layer is then coated directly on it.

The emulsion layers coated in this way produce, respectively, cyan, magenta and yellow images upon development with a developing agent containing a primary aromatic amino group such as a p-phenylenediamine. The element may be exposed and developed directly to form a negative colored image or a positive image may be obtained by first developing in an ordinary black and white developer followed by color development of the residual silver halide.

A developing solution suitable for development of the material such as described above is as follows:

|                                     |       |     |
|-------------------------------------|-------|-----|
| p-Aminodiethylaniline hydrochloride | grams | 1   |
| Sodium sulfite                      | do    | 2   |
| Sodium carbonate                    | do    | 30  |
| Potassium bromide                   | do    | 2.5 |
| Sodium hydroxide                    | do    | 1   |
| Water to                            | liter | 1   |

Development is preferably carried out for about 5 minutes at 65° F. after which the element is treated with a weak acid stop bath (acetic acid) followed by ferricyanide and hypo baths to remove the silver and any undeveloped silver halide which the film contains. These baths also remove any unused coupler.

Instead of incorporating the coupler in the emulsion as the sodium salt, a metallic salt dispersion, such as a silver or cadmium, of the coupler may be produced in gelatin, and this dispersion mixed with the gelatino-silver halide emulsion.

It will be apparent that my process has many advantages over prior color processes of the type in which couplers are incorporated in photographic emulsion layers. Since the couplers are incorporated in the colloid as salts much more insoluble than silver halides, they are absolutely non-diffusing in the colloid. This lack of diffusion of the couplers makes it possible to coat one emulsion layer directly on another without the use of insulating layers between the emulsion layers.

Another advantage is the ready removability of the unused couplers in the usual fixing baths. The alkali salts of the couplers diffuse readily through gelatin and when the silver or other metal is removed from the coupler in the usual solvents such as alkaline cyanides or alkaline hypo solutions the unreacted coupler is readily removed. In many multi-layer processes the residual coupler constitutes a serious problem because of the degradation or discoloration of the final image.

A further advantage of my process is that the couplers have fog inhibiting properties because of the presence of the heterocyclic ring system. I have found that the silver salts of the couplers which I employ, when incorporated in silver halide emulsions, act strongly as fog inhibitors

both in Elon-hydroquinone black and white developers and in phenylenediamine color-forming developers. The emulsions are capable of being developed to intensely colored dye images with clear highlight areas.

A further advantage of my process is that the final dye image may be mordanted to increase the stability of the final dye. The dye formed by coupling still contains the heterocyclic portion of the molecule and this may be treated with the customary mordanting salts such as alum to introduce a metallic atom into the molecule. The final dye is thereby rendered more stable to humidity and heat than the original dye image. For example, the dyes produced as described in the specific example above can be washed with a 5% solution of silver nitrate for 5 minutes, then washed thoroughly with water for several minutes. The image thus produced is more stable to ultra-violet light than the untreated image.

A still further advantage in my process is that the emulsions may be developed by simple tray processing because of the rapid color formation. Development time may be as short as one minute although it is usually preferably to develop for a longer time because of the greater ease of control.

It will be apparent that the emulsion layers made according to my invention may be coated on any suitable support such as cellulose nitrate, cellulose acetate, glass or synthetic resins or on opaque supports such as paper or pigmented cellulose ester.

My invention is capable of numerous variations and it is to be understood that it is to be taken as limited only by the scope of the appended claims.

I claim:

1. The method of producing a color-forming photographic emulsion which comprises forming a sensitive silver salt in a colloidal material and then incorporating in said material a coupler compound containing a heterocyclic nucleus having therein a group selected from the class consisting of imino and mercapto groups, the hydrogen atom of which is replaceable by a metal atom to render the compound non-diffusing, said group being not more than two atoms distant from an atom which has an unshared pair of electrons, and forming a metallic salt of said coupler compound less soluble than said sensitive silver salt by replacement of the hydrogen atom of said group with the metallic atom.

2. The method of producing a color-forming photographic emulsion which comprises forming a sensitive silver halide in a colloidal material and then incorporating in said material, a coupler compound containing a heterocyclic nucleus having therein a group selected from the class consisting of imino and mercapto groups, the hydrogen atom of which is replaceable by a metal atom to render the compound non-diffusing, said group being not more than two atoms distant from an atom which has an unshared pair of electrons, and forming a silver salt of said coupler compound less soluble than said sensitive silver halide by replacement of the hydrogen atom of said group with a silver atom.

3. The method of producing a color-forming photographic emulsion which comprises forming a sensitive silver halide in a colloidal material and then incorporating in said material a coupler compound containing a benzothiazole nucleus having a free mercapto group, and forming a silver salt of said coupler compound less soluble

than said sensitive silver halide by replacement of the hydrogen atom of the mercapto group of said coupler compound with a silver atom.

4. The method of producing a color-forming photographic emulsion which comprises forming a sensitive silver halide in a colloidal material and then incorporating in said material an insoluble metallic salt of a coupler compound containing a heterocyclic nucleus having therein a group selected from the class consisting of imino and mercapto groups, the hydrogen atom of which is replaceable by a metal atom to render the compound non-diffusing, said group being not more than two atoms distant from an atom which has an unshared pair of electrons.

5. The method of producing a color-forming photographic emulsion which comprises forming a sensitive silver halide in a colloidal material and then incorporating in said material a silver salt of a coupler compound containing a heterocyclic nucleus having therein a group selected from the class consisting of imino and mercapto groups, the hydrogen atom of which is replaceable by a metal atom to render the compound non-diffusing, said group being not more than two atoms distant from an atom which has an unshared pair of electrons.

6. The method of producing a color-forming photographic emulsion which comprises forming a sensitive silver halide in a colloidal material and then incorporating in said material a cadmium salt of a coupler compound containing a heterocyclic nucleus having therein a group selected from the class consisting of imino and mercapto groups, the hydrogen atom of which is replaceable by a metal atom to render the compound non-diffusing said group being not more than two atoms distant from an atom which has an unshared pair of electrons.

7. The method of producing a color-forming photographic emulsion which comprises forming a gelatino-silver bromide emulsion and then incorporating in said emulsion a cadmium salt of a mercaptobenzimidazole coupler.

8. The method of producing a color-forming photographic emulsion which comprises forming a gelatino-silver bromide emulsion and then incorporating in said emulsion a cadmium salt of a mercaptobenzothiazole coupler.

9. The method of producing a colored photographic image in a gelatino-silver halide emulsion layer containing as a coupler a metallic salt of a heterocyclic compound having therein a group selected from the class consisting of imino and mercapto groups, and having attached thereto

a group reactive with the development product of a primary aromatic amino developing agent, which comprises exposing said layer and developing it with a primary aromatic amino developing agent to form a dye image, removing substantially all silver, silver halide, and unused coupler from the layer, and mordanting the dye with a metallic salt.

10. The method of producing a colored photographic image in a gelatino-silver halide emulsion layer containing as a coupler a silver salt of a heterocyclic compound having therein a group selected from the class consisting of imino and mercapto groups, and having attached thereto a group reactive with the development product of a primary aromatic amino developing agent, which comprises exposing said layer and developing it with a primary aromatic amino developing agent to form a dye image, removing substantially all silver, silver halide, and unused coupler from the layer, and mordanting the dye with a metallic salt.

11. The method of reducing the fog in a color-forming gelatino-silver halide emulsion layer, which comprises incorporating in said layer a coupler having attached thereto a metallic salt of a fog-inhibiting heterocyclic compound having therein a group selected from the class consisting of imino and mercapto groups.

12. A light-sensitive gelatino-silver halide emulsion layer containing as a fog-inhibiting and coupling compound, a coupler reactive with the development product of a primary aromatic amino developing agent and having attached thereto a metallic salt of a fog-inhibiting heterocyclic compound having therein a group selected from the class consisting of imino and mercapto groups.

13. A light-sensitive gelatino-silver halide emulsion layer containing as a fog-inhibiting and coupling compound, a coupler reactive with the development product of a primary aromatic amino developing agent and having attached thereto a silver salt of a fog-inhibiting heterocyclic compound having therein a group selected from the class consisting of imino and mercapto groups.

14. A light sensitive gelatino-silver halide emulsion layer containing as a fog-inhibiting and coupling compound, a coupler reactive with the development product of a primary aromatic amino developing agent and having attached thereto a cadmium salt of a fog-inhibiting heterocyclic compound having therein a group selected from the class consisting of imino and mercapto groups.

WILLARD D. PETERSON.