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UNITED STATES PATENT OFFICE

2,308,023

COLORED PHOTOGRAPHIC IMAGE

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2 Claims. (Cl. 95—6)

This invention relates to photographic materials and the processing thereof and particularly to a method of forming colored photographic images.

Colored images are produced in photographic layers in a variety of ways. Colored images may be introduced into photographic layers for the production of colored pictures by simple toning, by color development in which a dye intermediate present in the developer or in the layer reacts with the photographic developer to form a colored image or by the destruction of a dye present in the photographic layer in the region of a silver image, and in other ways. Colored images may be produced for the purpose of forming colored monochromes or additive or subtractive color pictures for multi-color photography. In all of these processes it is desired that the colors produced should be clear and transparent, that the resulting colors should be stable and non-diffusing from the photographic layer, and that there should be a wide choice of available colors.

I have found that these advantages may be achieved by forming images comprising metallic salts of colored organic compounds in which the metal has replaced the hydrogen atom of an (—NH—) group in a heterocyclic nucleus in which the nitrogen atom is not more than two atoms distant from an atom which has an unshared pair of electrons. The organic compound whose metallic salt is used may have the imino group in one of its tautomeric forms.

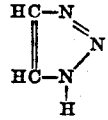
The invention comprises, in its broader aspects, the displacement of hydrogen in the imino group of a colored organic compound, by the metallic atom of a metallic salt more soluble than the salt formed by the replacement. The general reaction for this substitution may be indicated as follows:

$$R{-}NH{+}M{-}X{\rightarrow}R{-}NM{+}HX$$

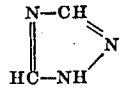
where R is an organic radical, M is a metallic radical, and X is an anion.

It will be most convenient first to give by way of example a list of organic compounds which may be regarded as parent bodies from which the compounds capable of forming the metallic salts employed in the present invention may be derived.

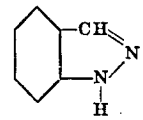
Parent bodies

1. 

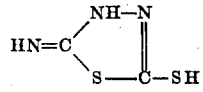
1,2,3-triazole

2. 

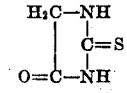
1,2,4-triazole

3. 

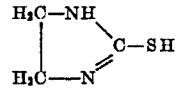
Indazole

4. 

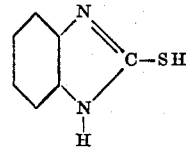
2-mercapto-5-imino-thiobiazole

5. 

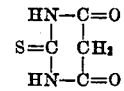
Thiohydantoin

6. 

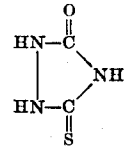
Ethylenethiourea

7. 

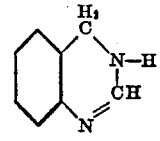
Mercapto benzimidazole

8. 

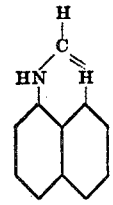
Thiobarbituric acid

9. 

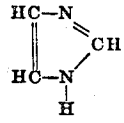
Thiourazole

10. 

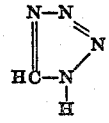
Dihydroquinazoline

11. 

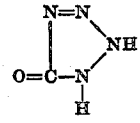
Perimidine

12. 

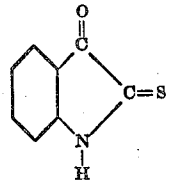
Imidazole

13. 

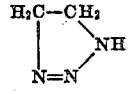
Tetrazole

14. 

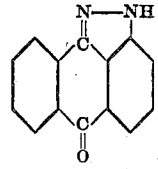
Tetrazolone

15. 

Thioisatin

16. 

1,2,3-triazolin

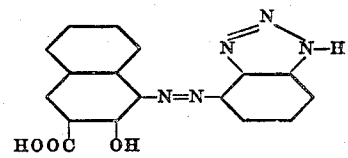
17. 

Pyrazole anthrone

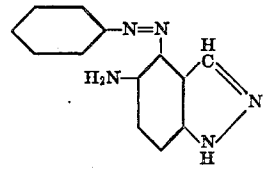
These parent bodies are heterocyclic compounds containing an NH group in the nucleus. These heterocyclic nuclei may also contain an SH group attached to the nucleus and in some cases the hydrogen of the SH group may be replaced by the metallic atom.

The heterocyclic compounds suitable as parent bodies, according to my invention, are characterized by the fact that the imino 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 or a sulfur atom and may be in the heterocyclic ring or attached to 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 2, 4 or 6. When nitrogen is present with a valence of 3, it, therefore, has an unshared pair of electrons and when sulfur is present with a valence of 2 it has at least one unshared pair of electrons. For example, in the parent body 1,2,3-triazole (1) the imino group is adjacent a nitrogen atom which has a valence of 3. This compound, therefore, is capable of forming insoluble silver salts according to my invention. The parent body imidazole (12) contains an imino group which is separated from a 3-valent nitrogen atom by a carbon atom, and also is an operative compound.

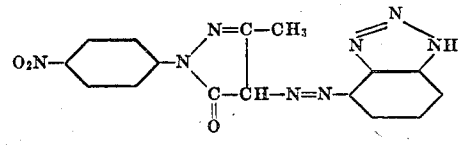
The parent bodies are attached to groups containing chromophoric groups, such as azo groups. They, therefore, are colored compounds although the colored salt formed by replacement of the hydrogen atom of the imino group by a metallic atom are not necessarily of the same color as the original compound. The following are specific examples of compounds derived from some of the parent bodies listed above which are capable of forming colored insoluble salts with metals such as silver.



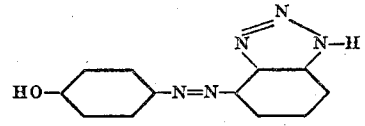
1-(benzotriazole-4-azo)-2-hydroxy-3-naphthoic acid



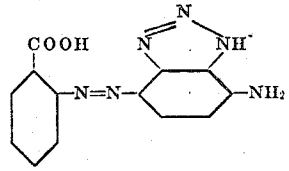
4-phenylazo-5-amino-indazole



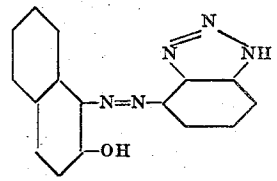
1-(p-nitrophenyl)-3-methyl-4(-benzotriazole-4-azo)-5-pyrazolone



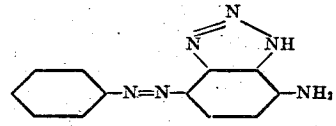
4-(p-hydroxyphenylazo)-benzotriazole



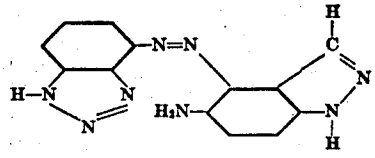
4-amino-7-(o-carboxyphenylazo) benzotriazole



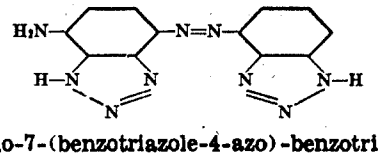
1-(benzotriazole-4-azo) β-naphthol



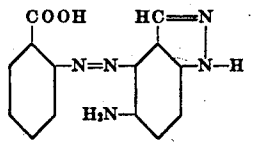
4-amino-7-phenylazo benzotriazole



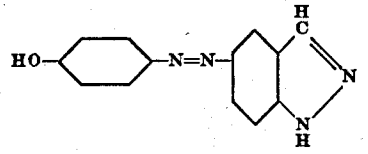
4-(benzotriazole-4-azo)-5-aminoindazole



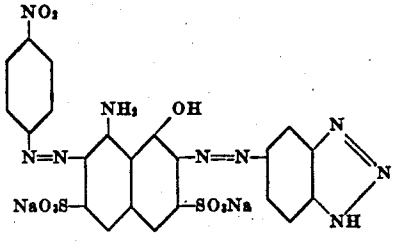
4-amino-7-(benzotriazole-4-azo)-benzotriazole



5-amino-4-(o-carboxyphenylazo) indazole



5-(p-hydroxyphenylazo) indazole



1-hydroxy-2-(5-benzotriazylazo)-7-(p-nitrophenylazo)-8-amino-3,6-naphthalene disodiumdisulfonate

The metallic salt present in the photographic layer, the metallic atom of which replaces the hydrogen of the imino group to form a colored insoluble salt will usually be a silver salt such as silver halide. Any salt may be used which is more soluble than the silver metallic salt formed by replacement of the hydrogen of the imino group by the metallic atom. Silver halide, such as silver chloride or silver bromide, is the commonest example of a metallic salt of this type although other metallic salts which are capable of generating a colored silver salt more insoluble than the original silver salt are silver ferricyanide, silver orthophosphate, silver aresenate, silver oxalate, silver cyanate and silver citrate. The colored insoluble salts need not be limited to those of silver but may be generated from other metallic ions such as copper, lead, and nickel.

Colored metallic salts formed according to my invention may be used for the production of monochromatic images in photographic layers or by the choice of suitable salts may be used for the formation of multi-color especially three color images.

The imino-containing compounds used to form insoluble metallic salts according to my invention are usually dissolved in a dilute alkaline solution such as 2% to 6% solution of sodium carbonate or up to a ½% solution of sodium hydroxide depending on the solubility of the compound. The amount of the imino containing compound in the solution may vary from about ½% to 5% depending upon its solubility. Usually a saturated solution of the compound will be somewhere in this region. Some of the compounds are readily soluble in acid solution and generate the insoluble salts in such a medium.

The following examples, which are illustrative only, indicate methods of forming colored photographic images according to my invention.

Example 1

A photographic silver halide emulsion layer is exposed and developed in the usual way to form a metallic silver image. The silver image formed in this way is dissolved in a silver solvent such as permanganate in H_2SO_4 solution or dichromate solution and the film containing the remaining silver halide image is immersed for a few minutes in a 2% sodium carbonate solution containing 3% of 4-amino-7-(ortho-carboxyphenylazo)-benzotriazole. This forms a brilliant red to magenta positive image depending upon the pH of the bath.

Example 2

A negative colored image may be formed in a single layer photographic film in the following manner. A silver halide photographic emulsion is exposed and developed in the usual way and the unexposed silver halide is removed in acid hypo. The remaining black silver image is bleached in a solution containing 3% potassium ferricyanide and 3% potassium bromide or chloride and is then washed with water. The film is then placed in a bath having the following composition:

Sodium carbonate	grams 6
4(o-carboxyphenylazo-5-aminoindazole	do 1
Water to	cc 200

The film is allowed to remain in this bath for six minutes at 65° F. after which an orange-yellow dye is deposited in proportion to the amount of metallic silver in the original image. The intensity of this colored image may be reduced by treatment for 4 to 5 minutes in a slightly alkaline 10% solution of hypo.

Example 3

A multi-layer photographic film, for example, a film having three superposed layers sensitive to the blue, green and red regions of the spectrum is exposed and developed in such a way as to form metallic silver color separation images in the three layers. The metallic silver is removed from each of the layers by treatment in a silver salt bath, for example, acid permanganate or bicromate and the film is then treated in a weakly alkaline solution of a salt containing an imino group capable of generating a yellow insoluble salt image in the layer of the film which was originally blue sensitive. A solution of 1-(p-nitrophenyl)-3-methyl-4-(benzotriazole-4-azo)-5-pyrazolone in 4% sodium carbonate solution is suitable for this purpose. If the layer in which the yellow image is to be formed is the top layer of the film, the penetration of the solution into the lower layers may be prevented by adding a loading agent, such as those disclosed in Mannes and Godowsky U. S. Patent 2,059,887, to the solution. The film may also be hardened to prevent penetration into the lower layers and similarly permeable intervening layers are also helpful in controlling diffusion.

The film is then thoroughly washed with cold water and the dyeing process is repeated using

a weakly alkaline solution of a dye capable of generating an unsoluble magenta silver salt in the layer which was originally green sensitive. A compound suitable for this purpose is 1-(benzotriazole-4-azo)-β-naphthol. If it is desired to prevent the penetration of this solution into the layer which was originally red sensitive, the penetration may be controlled as described above.

After coloring the magenta image, the film is again thoroughly washed in cold water and is then treated with a sodium carbonate solution of a compound capable of generating a blue-green silver salt. A compound suitable for this purpose is 1-hydroxy-2(5-benzotriazyl-azo)-7-(p-nitrophenylazo)-8-amino-3,6 napthylene disodium disulfonate.

The intensity of the final picture may be reduced by bathing in a solution of alkaline hypo or in some cases a dilute solution of ammonium hydroxide.

My process for the production of colored images in photographic layers is more simple than most processes heretofore known since it involves merely the metathesis between the original silver salts and the compounds which are capable of generating colored insoluble silver salts. There are many advantages in this process. In the first place, since it does not depend upon the photographic reducability of the silver salt and hence upon the oxidation of the developer, many different silver salts may be used. That is to say, the silver salt need not be light-sensitive and the transformation into a colored insoluble compound is not dependent upon a photographic process. The process is not dependent upon a complex set of conditions which involve simultaneously the rates of diffusability of a developer and a coupler into the photographic layer and it is not necessary to control the hydrogen ion concentration. It eliminates the necessity of stabilizing the solutions against aerial oxidation and because the reaction is fairly rapid it can readily be controlled. A further important advantage in multicolor photography is that it eliminates the necessity for sensitizers which must withstand photographic development. A large number of dyes may be used since many well known dyes can be attached to the parent bodies described above and a wide choice of colors is, therefore, available.

My process is suitable for the formation of both picture images and sound track images on motion picture film, as well as being suitable for making still picture images on both transparent and opaque supports.

The specific examples of compounds and reagents included in the present specification are illustrative only and it is to be understood that my invention is intended to be limited only by the scope of the appended claims.

I claim:

1. The method of forming a colored image in a photographic layer containing a silver salt image, which comprises treating the layer with a solution of a colored indazole derivative containing an imino group and also containing at least one azo group, the hydrogen of the imino group being replaceable by silver to form a colored silver salt, and the original silver salt in the layer being more soluble than the silver salt formed by the replacement.

2. The method of forming a colored image in a photographic layer containing a silver salt image, which comprises treating the layer with a solution of a colored azo dye derivative of an indazole containing an imino group in the indazole nucleus, the hydrogen of the imino group being replaceable by silver to form a colored silver salt, and the original silver salt in the layer being more soluble than the silver salt formed by the replacement.

WILLARD D. PETERSON.