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PREPARATION OF COLORED METALLO- α -OXIMINO KETONE COMPLEX IMAGES

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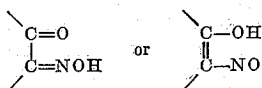
3 Claims. (Cl. 95-88)

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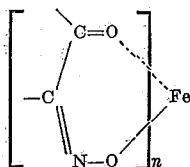
The present invention relates to photographic materials containing colored metallo- α -oximino-ketone complex images, and to a method of preparing such images.

One of the most commonly used methods for forming colored photographic images involves developing an exposed silver halide emulsion with a primary aromatic amino developer in the presence of a color former such as a phenol or a compound containing a reactive methylene group. The oxidation products of the developer react with the color former to produce a colored dye image. Such images suffer from the disadvantage that they are not particularly light-fast.

It is known that α -oximino-ketones having a structure:



are capable of reacting with certain metallic ions such as ferrous ions to yield highly colored products. When an iron salt capable of yielding ferrous ions is used, chelate compounds usually green, blue-green or blue in color and presumably of the following structure



are formed. (In this formula n is equal to 2 or 3.) α -oximino-ketones have found use as reagents for detecting ferrous iron, and the ferrous iron complexes thereof have in certain cases been used as dyestuffs for textiles (see Color Index Nos. 1 to 6).

I have now discovered that intensely colored metallo- α -oximino-ketone complexes containing a thioamide structure, capable of isomerizing to an iso-thioamide structure, may be deposited in situ with a silver halide image by virtue of the fact that such complexes form silver salts less soluble than silver halides. These complexes are conveniently applied from alkaline solutions, i. e., of sodium carbonate, potassium carbonate, etc. in which they are soluble as a result of the presence therein of the aforesaid thioamide group.

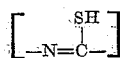
The colored images produced in this way and the preparation of the same constitute the purposes and objects of the present invention.

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The metallo- α -oximino-ketone complexes utilized in the formation of said colored images are produced from a compound containing a thioamide structure capable of isomerizing to an iso-thioamide structure and being capable of yielding an α -oximino-ketone upon nitrosation. Such compounds contain an α -keto methylene structure or a structure capable of yielding an α -keto methylene structure upon isomerization. When such compounds are nitrosated, α -oximino-ketones are produced which react with soluble metal salts to yield the aforesaid highly colored metallo- α -oximino-ketone complexes. If the metal salt employed is a ferrous salt, the complex is a brilliant cyan in color and is soluble in aqueous alkalies.

Compounds within the above category which I have found to be particularly suitable for such use are 2-thiobarbituric acid and the 1-aryl-, 1-alkyl-, 1-aralkyl-, or 1-alkylene- derivatives thereof, such as 1-phenyl-2-thiobarbituric acid, 1-(α -naphthyl)-2-thiobarbituric acid, 1-(β -naphthyl)-2-thiobarbituric acid, 1-toluy-2-thiobarbituric acid, 1-methyl-2-thiobarbituric acid, 1-ethyl-2-thiobarbituric acid, 1-propyl-2-thiobarbituric acid, 1-butyl-2-thiobarbituric acid, 1-octyl-2-thiobarbituric acid, 1-decyl-2-thiobarbituric acid, 1-dodecyl-2-thiobarbituric acid, 1-benzyl-2-thiobarbituric acid, 1-(1-methyl-2-naphthyl)-2-thiobarbituric acid, 1-allyl-2-thiobarbituric acid, 1-isopropenyl-2-thiobarbituric acid and thiourea-substituted on one nitrogen atom by a hydroxy-naphthyl group such as 5-thioureido-1-naphthol, 8-thioureido-1-naphthol, 7-thioureido-2-naphthol, 6-thioureido-1-naphthol.

The above thioureido naphthols are included with the thiobarbituric acids for the reason that, like the thiobarbituric acids, the thioamide grouping therein has the known ability under salt forming conditions to isomerize to the iso-thioamide grouping



and for the further reason that the α - and β -naphthols have the known ability to yield α -oximino-ketone structures upon nitrosation.

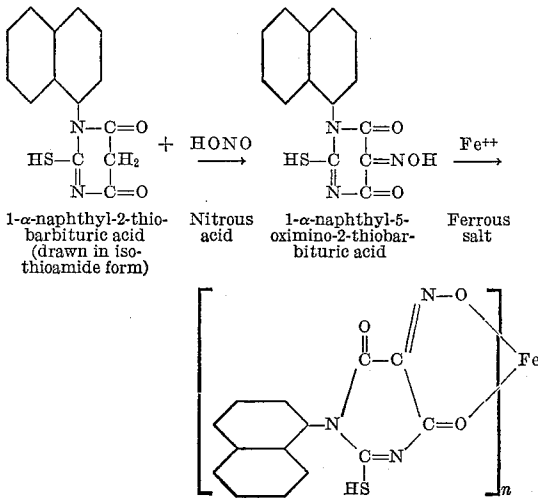
By treating a photographic element containing a silver halide image with an aqueous alkaline solution of the aforesaid colored metal complexes, the metal complex is bound imagewise to the silver halide through the medium of the aforesaid isothioamide group. The "white" areas which contain no silver halide are unaf-

ected by this treatment and the unconverted metal complex is removed from these areas by washing.

In some cases it may be advisable to remove unconverted silver halide by fixing in the usual manner. Such treatment has no effect on the colored complex image.

The method involved, assuming the formation and use of the cyan colored ferrous iron complex of 1- α -naphthyl-5-oximino-2-thiobarbituric acid may be more readily understood from the following equations which indicate the reactions believed to be involved in forming the metal complex image:

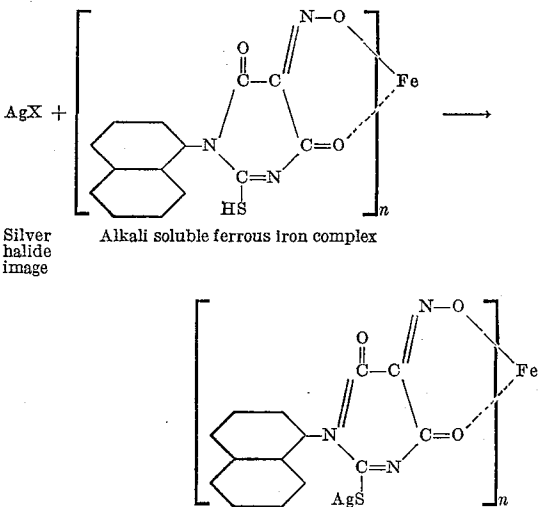
Preparation of iron complex



Alkali soluble ferrous iron complex (cyan dye)

wherein $n=2$ or 3 .

Deposition of colored complex image



Insoluble silver salt of cyan ferrous iron complex

wherein $X=$ halogen and $n=2$ or 3 .

It is to be understood that these equations are merely indicative of my theory of the reaction and is not to be construed as the exact mechanism by which the complex images are produced.

In the nitrosation step, it is preferable to use a bath containing a small amount of sodium nitrite dissolved in a weak organic acid such as acetic acid, formic acid, and the like. Excellent results have been obtained when employing a

1-3% solution of sodium nitrite dissolved in 2-5% of acetic acid.

The metal salts which may be employed for producing the metallo- α -oximino-ketone complex are any water soluble ferrous or cobaltous salts, such as ferrous sulfate, ferrous nitrate, ferrous acetate, ferrous chloride, cobaltous sulfate, cobaltous acetate, cobaltous chloride, and the like. Where a cobaltous salt is used for forming the metal complex, the resulting image is orange in color rather than cyan.

The invention is further illustrated by the following examples, it being understood that the invention is not restricted thereto.

Example I

An alkali soluble cyan colored ferrous iron complex was prepared from 1- α -naphthyl-2-thiobarbituric acid in the following manner: A solution of 1.35 parts of 1-(α -naphthyl)-2-thiobarbituric acid in 20 parts of glacial acetic acid was cooled to 10° C. and heated with stirring with 3.5 parts of a 10% aqueous sodium nitrite solution. During the addition of the nitrite, which took 5 minutes, the temperature was not allowed to rise above 12° C. There resulted a yellowish-brown solution of the 5-oximino compound. This cold solution was then poured with rapid stirring into a solution of 2.78 parts of ferrous sulfate ($FeSO_4 \cdot 7H_2O$) in 100 parts of water. The blue-green product was precipitated immediately as a very fine powder. This was filtered off, washed with water and dried at 50° C. The yield was practically quantitative.

A film bearing a silver bromide image was bathed in a 1% solution of this 1-(α -naphthyl)-2-thio-5-oximino barbituric acid-ferrous iron complex in 5% sodium carbonate solution. The film was washed to remove unreacted complex. There resulted an insoluble brilliant cyan image, the white areas being unaffected. This is presumably due to the formation of an insoluble silver salt in situ with the silver halide.

Alkaline solutions of dyes of this type penetrate gelatin only with difficulty and the cyan image produced may easily be restricted to the top layer in multilayer photographic materials, if desired.

The cyan image prepared in this way showed no appreciable fading after 50 hours' exposure in an accelerated light-aging test (Fade-Ometer).

Example II

The procedure is the same as in Example I excepting that the 1-(α -naphthyl)-2-thiobarbituric acid is replaced by an equivalent amount of 2-thiobarbituric acid. The image formed is cyan in color and possesses a light fastness comparable to the image of Example I.

Example III

The procedure is the same as in Example I excepting that the 1-(α -naphthyl)-2-thiobarbituric acid is replaced by an equivalent amount of 5-thioureido-1-naphthol. An image of a greener shade but of high light fastness is formed.

Example IV

The procedure is the same as in Example I excepting that the ferrous sulfate is replaced by an equivalent amount of cobaltous acetate. There is produced a bright orange image which is extremely fast to light.

Various modifications of the invention will occur to persons skilled in this art, and I therefore

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do not intend to be limited in the patent granted except as necessitated by the appended claims.

I claim:

1. The process of depositing a metallo- α -oximino-ketone complex image in situ with a silver halide image contained in a photographic element which comprises treating a silver halide image in such element with an aqueous alkaline solution of a complex metal compound containing a thioamide group capable of isomerizing to an isothioamide group and capable of forming silver salts less soluble than silver halides, said complex metal compound being obtained by nitrosating a compound containing a thioamide group capable of isomerizing to an isothioamide group and yielding α -oximino-ketone structures upon nitrosation, and having a structure selected

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from the class consisting of α -keto methylene and 1- and 2-hydroxy naphthalene structures, and reacting the resulting nitrosated compound with a soluble metal salt selected from the class consisting of soluble ferrous and cobaltous salts.

2. The process as defined in claim 1 wherein the compound subjected to nitrosation is 1-(α -naphthyl)-2-thiobarbituric acid and the water soluble metal salt is a ferrous salt.

3. The process as defined in claim 1 wherein the compound subjected to nitrosation is 2-thiobarbituric acid and the water soluble metal salt is a ferrous salt.

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No references cited.