Patented Dec. 5, 1950

2,533,181

UNITED STATES PATENT OFFICE

2,533,181

PREPARATION OF COLORED METALLO-α-OXIMINO KETONE COMPLEX IMAGES

Donald E. Sargent, Easton, Pa., assignor to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware

No Drawing. Application July 8, 1949, Serial No. 103,757

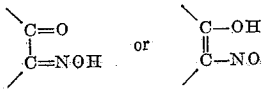
2 Claims. (Cl. 95—88)

1

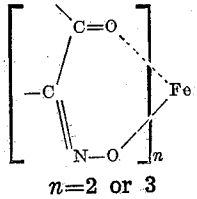
The present invention relates to photographic elements containing colored metallo-α-oximino ketone complex images, and to a method of preparing such images.

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:



n=2 or 3

are formed. 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 these colored metallo-α-oximino-ketone complexes may be formed in situ with a silver halide image by treating a photographic element bearing a silver halide image with a compound capable of reacting with said silver halide to form a less soluble silver compound and capable of yielding an α-nitroso-ketone structure upon nitrosation, nitrosating the silver compound formed by such treatment with aqueous nitrous acid and converting the resultant highly insoluble nitrosated silver salt to a colored metal complex. Where an iron salt is employed for such conversion, a cyan ferrous α-oximino-ketone complex of exceedingly high fastness to light is produced.

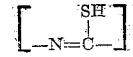
2

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

The compounds which I utilize in my procedure form insoluble nitrosatable silver salts by virtue of the fact that they contain a thioamide grouping which is capable of isomerizing to an isothioamide grouping and contain a nitrosatable methylene group adjacent to a keto group or a structure capable of isomerizing thereto.

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-toluyl-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 thioureas 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 isothioamide grouping:



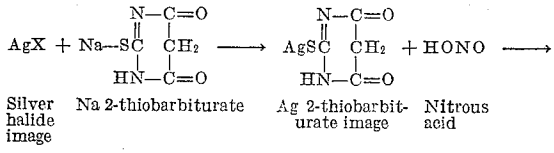
and for the further reason that the α- and β-naphthols have the known ability to yield α-oximino-ketone structures upon nitrosation.

All of the above compounds exhibit solubility in aqueous alkaline solutions, i. e., of sodium carbonate, potassium carbonate, sodium hydroxide, and the like, and are conveniently applied from such solutions in the form of their water soluble alkali salts.

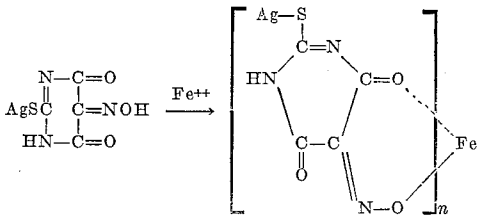
As stated, when a silver halide image is treated with one of the aforesaid compounds, the silver halide is converted into a less soluble silver salt. Assuming that the compound employed is 2-thiobarbituric acid applied as the sodium salt from an aqueous sodium carbonate solution, this treatment produces an image of silver 2-thiobarbi-

turate. The "white" areas of the element, since they contain no silver halide, are unaffected by this treatment and upon subsequent washing the excess of the sodium 2-thiobarbiturate is removed from these areas. The silver 2-thiobarbiturate image is then nitrosated by bathing the element in aqueous nitrous acid, after which the element is washed to remove excess nitrous acid. The nitrosated image is finally converted to a metal complex image by bathing the element in a solution of a water soluble metal salt, preferably a ferrous salt. In this way the silver halide image is replaced by an intensely colored metallo-α-oximino-ketone complex image which is cyan in color when ferrous iron is used as above.

The method involved may be more readily understood by a consideration of the following equations which indicate the reactions involved in forming the complex image:



Silver halide image | Na 2-thiobarbiturate | Ag 2-thiobarbiturate image | Nitrous acid



Ag 5-oximino-2-thiobarbiturate image | Ferrous salt | Cyan ferrous iron complex image

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 final image 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

A film carrying a silver bromide image was treated for 1 minute with a 0.5% solution of 2-thiobarbituric acid in 5% sodium carbonate at 18° C. and then washed to remove the 2-thiobarbituric acid from the white areas. The silver 2-thiobarbiturate image was nitrosated by treatment with a 1% solution of sodium nitrite dissolved in 2% acetic acid for 2 minutes at 18° C. After washing for 3 minutes in running water at

18° C., the film was treated in a 1% solution of ferrous sulfate for 2 minutes. After washing again for 3 minutes, the film was cleared of unconverted silver bromide by treatment in an acid hypo bath.

The above process produced an excellent duplicate in cyan color of the original silver bromide image. This image was found to be extremely light-stable, practically no fading occurring in 75 hours in a Fade-ometer. Many cyan dyes used in color photography fade badly in 5–10 hours.

Example II

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

Example III

The procedure is the same as in Example I excepting that the 2-thiobarbituric acid is replaced by an equivalent amount of 5-thioureido-1-naphthol. A green image of high light stability 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 do not intend to be limited in the patent granted except as necessitated by the appended claims.

I claim:

1. The process of producing α-oximino-ketone complex images in a photographic element which comprises treating a silver halide image in such element with an aqueous alkaline solution of a compound capable of forming silver salts less soluble than silver halides and containing a thioamide grouping capable of isomerizing to an isothioamide grouping and a structure yielding α-oximino-ketone compounds upon nitrosation and selected from the class consisting of α-ketomethylene and 1- and 2-hydroxy naphthalene structures, nitrosating the resulting silver salt with aqueous nitric acid and treating such silver salt with a soluble metal salt selected from the class consisting of soluble ferrous and cobaltous salts to convert the nitrosated silver salt image into an intensely colored metallo-α-oximino-ketone complex image in situ with the original silver halide image.

2. The process of producing a ferrous α-oximino-ketone complex image fast to light in a photographic element which comprises treating a silver halide image in such element with an aqueous alkaline solution of 2-thiobarbituric acid to form a silver 2-thiobarbiturate image, nitrosating the resulting image with aqueous nitrous acid and treating the resulting nitrosated silver salt image with a water soluble ferrous salt to form a cyan ferrous iron α-oximino-ketone complex image in situ with the original silver halide image.

DONALD E. SARGENT.

No references cited.