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COPYING MATERIALS

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U.S. Cl. 96—114.1 9 Claims

ABSTRACT OF THE DISCLOSURE

A heat-decomposable reaction product of an aryl thiol and a water-soluble silver salt of an inorganic oxyacid is made light-sensitive by treatment with halide ion and when then exposed to light is decomposable at a reduced temperature to give a visible change.

This invention is concerned with improvement in or relating to copying materials. More especially the invention relates to a light sensitive composition which can be coated onto a suitable backing sheet and used in the production of permanent copies of originals.

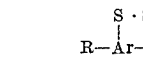
Conventional light sensitive compositions which include silver halides have the disadvantage that when they are used to make permanent copies of an original they require the time consuming and inconvenient steps of wet development, wet fixing, washing and then drying. Many attempts have been made to obtain a light sensitive composition which after exposure to a light image gives a permanent copy with only one simple processing step, such as heating, but no completely successful composition has been prepared.

These difficulties are overcome to a large extent by a light sensitive composition in accordance with the invention which comprises a silver halide and a silver salt of an aryl thiol (a silver mercaptide) containing an excess of silver ions in the form of an inorganic oxyacid silver salt.

Such a light sensitive composition makes use of the known light sensitivity of silver halides but does not have the disadvantage of requiring long and numerous development steps other than a simple heating.

The silver salts used in the compositions in accordance with the invention are decomposed by heat and this decomposition is catalyzed by the silver halide where this has been exposed to light. It appears that the composition is sensitized to light of short wavelength by the silver halide and a latent image is formed in this silver halide by the action of light. The heating decomposes the silver salt of the aryl thiol and the decomposition is catalyzed imagewise by the silver halide so as to give a brownish-black image. After the heat treatment causing development in the light-struck regions to produce a negative image, the unexposed regions are almost insensitive to light and so the image formed is largely fixed.

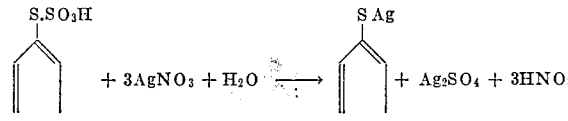
The silver salt of the aryl thiol containing an excess of silver ions combined with an inorganic oxyacid is preferably prepared by reacting an aryl thiosulphuric acid having the general formula:



wherein Ar represents a benzene or naphthalene nucleus, and in which R represents an —NH_2, —NHR', —NR'R'', —OH, —OR', —SH or —SR' group, where R' and R'', which may be the same or different, each represent an alkyl group, a substituted alkyl group, an aralkyl group

or an aryl group, or R' and R'' together form a ring, and R''' either represents a hydrogen atom or a substituent such as an alkyl or alkoxy group or a halogen atom; with a soluble silver salt such as silver nitrate or silver perchlorate. This silver salt should preferably be in excess to an extent of about 1.5 moles of soluble silver salt per mole of aryl thiosulphuric acid.

We believe that in such a composition the excess silver ions combined with an inorganic oxyacid are derived from a reaction such as that exemplified by the following equation:



Compositions prepared as described above are made light sensitive by forming in the composition some silver halide. This can be accomplished, for example, by dispersing the composition in an aqueous medium containing a water soluble binder, such for example as, polyvinyl alcohol, polyvinyl alcohol/acetate copolymer or polyvinyl pyrrolidone, and adding a water soluble halide, e.g. a potassium or cadmium halide.

These light sensitive compositions are particularly sensitive to ultra violet and blue light but the sensitivity can be extended to longer wavelengths by the addition of spectral sensitizers such for example as the cyanine and merocyanine types of dye.

The light sensitive compositions can be used in the form of a coating on a backing sheet of, for example, paper or plastic film.

The invention will now be described with reference to the following examples.

EXAMPLE 1

S-2-aminophenyl thiosulfuric acid (0.66 gram mole) was dissolved in 3 litres of distilled water at 45° C. 700 ml. of an aqueous silver nitrate solution containing 1 gram mole of silver nitrate was then run into the stirred solution of the acid during a period of eight minutes. The yellow precipitate formed was allowed to stand for twelve hours, filtered, washed with water and dried.

10 g. of the above silver salt was ball milled for sixteen hours with 100 ml. of a 5% aqueous solution of "Gelvatol 40/20" a water-soluble polyvinyl alcohol/acetate copolymer formed by partial hydrolysis of polyvinyl acetate, containing 37–42% residual unhydrolyzed ester, having a viscosity, as a 4% solution in water, of 2–3 centipoise, and having an approximate weight average molecular weight of 3000. The resultant dispersion was stirred and 20 ml. of a 0.42 molar aqueous potassium bromide solution was added to make the composition light sensitive. After continued stirring for one hour the dispersion was coated onto a paper base and air dried. Suitable coating weights were found to be within the range of approximately 5 to 100 mg. of silver per square decimeter.

The coating so prepared was exposed through a negative held in contact with it to tungsten light for 10^6 meter candle seconds and was subsequently developed by holding in contact with a heated smooth-surfaced copper cylinder at 175° C. for ten seconds. A black-brown image of the negative on a substantially light insensitive pale yellow background was thereby produced.

EXAMPLE 2

10 g. of the silver salt prepared as in Example 1 was ball milled for sixteen hours with 100 ml. of a 5% aqueous solution of polyvinyl alcohol/acetate copolymer. The resultant dispersion was stirred and 7 ml. of a 0.42 M

aqueous potassium bromide solution were added. After continued stirring for 45 minutes 14 ml. of a 0.42 M potassium iodide solution was added. Stirring was continued for a further 45 minutes after which the dispersion was coated onto paper base and dried.

Exposure of the coating through a negative to tungsten light for 10^6 meter candle seconds followed by development at 175° C. for 10 seconds gave a brown black positive image of negative on a substantially light insensitive pale yellow background.

EXAMPLE 3

To a stirred solution of 3.1 g. of S-2-aminophenyl thiosulphuric acid in 100 ml. of water was added a solution of 6.2 g. of silver perchlorate in 20 ml. of water. After stirring for three minutes, the yellow precipitate so formed was filtered off, well washed with water and dried at 50° C.

10 g. of the silver salt prepared by the above procedure was dispersed in 100 ml. of a 5% aqueous solution of water-soluble polyvinyl alcohol/acetate copolymer by ball milling for 16 hours. The resultant dispersion was sensitized to light by the addition of 20 ml. of 0.42 M aqueous potassium bromide solution. After stirring for one hour the dispersion was coated onto paper base and dried.

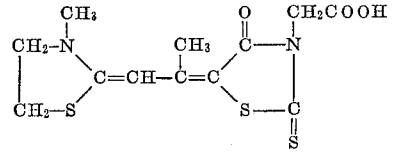
The coating so prepared was exposed through a negative to 10^6 meter candle seconds of tungsten light followed by development at 175° C. A brown-black positive image was formed on a substantially light insensitive pale yellow background.

EXAMPLE 4

10 g. of the yellow precipitate prepared as in Example 1 were ball milled for 16 hours with 100 ml. of a 5% aqueous solution of a polyvinyl alcohol/acetate copolymer (Gelvatol 40/20). The resunltant dispersion was stirred and 20 ml. of 0.42 M aqueous potassium chloride solution were added. After continued stirring for 45 minutes, the dispersion was coated onto paper base and dried. Exposure of the coating through a negative to tungsten light for 10^6 metre candle seconds followed by development at 175° C. for 10 seconds gave a brown-black positive image on a pale yellow background.

EXAMPLE 5

2.5 g. of the yellow precipitate prepared as in Example 1 were ball milled for 16 hours with 25 ml. of a 5% aqueous solution of polyvinyl alcohol/acetate copolymer (Gelvatol 40/20). The resultant dispersion was stirred and 2.5 ml. of a 0.42 M aqueous potassium bromide solution were added, followed by 4 ml. of a 0.001 molar aqueous solution of the following merocyanine dye:



After stirring for 5 minutes the dispersion was coated onto paper base and dried.

Exposure of such a sheet to white light behind a negative and a series of narrow cut spectral filters followed by development at 175° C. for 10 seconds showed an extended photographic response into the green region of the spectrum.

It will be apparent from the above examples that the light sensitive compositions and coatings, prepared in accordance with the invention, yield an image which is largely fixed by the simple step of heating the coating after it has been exposed to a light image; such time consuming steps as wet development, wet fixing, washing and drying are not required.

What we claim is:

1. A light-sensitive composition formed by a process comprising mixing together aqueous solutions of S-2-aminophenylthiosulfuric acid and of soluble silver salt to form a silver-containing heat-decomposable precipitate, and treating said precipitate with halide ion.

2. Composition of claim **1** wherein the molar ratio of said S-2-aminophenylthiosulfuric acid and said soluble silver salt is between 1:1.5 and 1:3.

3. Composition of claim **1** wherein the precipitate is treated in aqueous suspension by addition of a water-soluble halide.

4. Composition of claim **1** wherein said soluble silver salt is silver nitrate or silver perchlorate.

5. Composition of claim **1** wherein is included a cyanine or merocyanine spectral sensitizer dye.

6. Sheet material capable of exhibiting a stable visible image on exposure to a light-image followed by heating, said sheet material comprising a backing having over one surface thereof the dried residue of a coating of the composition of claim **1** in which is included a binder.

7. Sheet material capable of exhibiting a stable visible image on exposure to a light-image followed by heating, said sheet material comprising a backing having over one surface thereof the dried residue of a coating of the composition of claim **5** in which is included a binder.

8. Method of producing a visible image comprising exposing a sheet material as defined in claim **6** to a light-image having a radiant energy within the range including visible and ultraviolet light and heating the exposed sheet to a temperature and for a time sufficient to develop a corresponding visible image.

9. A method of producing a visible image comprising exposing a sheet material as defined in claim **7** to a light image having radiant energy within the range including visible and ultraviolet light and heating the exposed sheet to a temperature and for a time sufficient to develop a corresponding visible image.

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