



Light sensitive cuprous oxide compositions (Rowland G Mowrey and Richard C Sutton)

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This disclosure relates to light-sensitive cuprous oxide coatings, additives thereto and photographic uses thereof.

Positive dye images are produced from negative copper metal images by the incorporation of dyes such as azo dyes or formazan dyes into a cuprous oxide-containing, light-sensitive layer. The layer is imagewise exposed to actinic light and developed by disproportionation. After treatment with a conventional dye bleach solution, a positive dye image is obtained.

Suitable cuprous oxide coatings are prepared by adding cuprous oxide (Cu_2O) to an acidic solution such as hydrochloric acid and adjusting the pH to between 2.0 and 4.0. A polymeric peptizing agent such as poly(3-thiopentyl acrylate-co-3-acryloyloxypropane-1-sulfonic acid sodium salt) is added. The solution is chilled and water is added to form an emulsion.

The emulsion is exposed and processed in a disproportionating solution such as sulphuric acid to yield a negative image in copper.

The negative copper image is then immersed in a dye bleach solution containing, for example, thiourea. Acids to bring the pH to below about 3.0 such as hydrochloric acid may be added as well as dye bleach catalysts such as phenazine, pyrazines, phenazine N-oxides and the like.

Generally, the development may take about 1 minute and the dye bleaching about 5 minutes.

The fading or decomposition of the finely divided copper metal can be prevented by the addition of plugging agents by imbibition to the image. Plugging agents useful herein include sulfurous compounds such as phenylmercaptotetrazole or its derivatives. The plugging agents can be used in a concentration range of from about 0.1 gram/liter to 10 gram/liter.

The photographic speed, coating uniformity and development rate of the cuprous oxide emulsion can be improved by replacing the gelatin coating vehicle with a crosslinkable polymer such as poly(3-thiopentylacrylate-co-acrylic acid-co-3-acryloyloxypropane-1-sulfonic acid sodium salt), poly(3-thiopentylacrylate-co-3-acryloyloxypropane-1-sulfonic acid sodium salt), poly[N-(3-thiobutyl)acrylimide-co-3-acryloyloxypropane-1-sulfonic acid sodium salt], poly(3-thiopentylmethacrylate-co-3-methacryloyloxypropane-1-sulfonic acid sodium salt) and the like.

It is noted that a print-out image can be formed using the cuprous oxide coatings described herein by simultaneously exposing and heating the coating at a temperature of from 100°C to 200°C . The resulting image does not fade and the non-image areas do not print out under the influence of further heat and/or exposure to light.

It is further noted that T-salts can be incorporated in light-sensitive cuprous oxide coatings as described herein. After exposure and development by disproportionation and fixing whereupon a dye image replaces the copper metal image, the remaining T-salt can be transferred to a receiver sheet. On reduction, a positive dye image is obtained in the receiver. The T-salts are incorporated in the cuprous oxide emulsion prior to coating. Generally, the coating contains from about 25 mg/ft^2 to about 300 mg/ft^2 of T-salt. T-salts useful herein include triphenyl tetrazolium chloride and other tetrazolium salts such as those described in US Patent 3,278,366, issued October 11, 1966. The

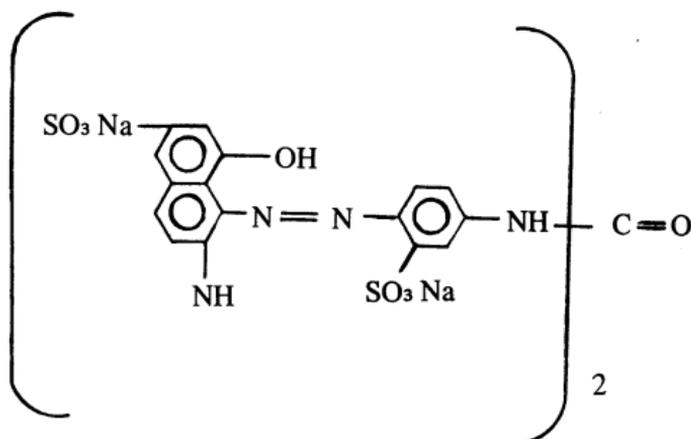
images are fixed, for example, in a hypo solution.

A positive image can be formed on a receiver sheet by placing the fixed strips in contact with a gel coated receiver sheet and after separation dipping into a solution of dithionite.

The following examples are presented.

Example 1

A cuprous oxide coating containing 200 mg/ft² of a dye having the formula:



is exposed to actinic light and processed in a 1/5 N solution of sulphuric acid to give a negative reproduction of the image in copper and then immersed in a bleach solution having the following composition:

1/5 N sulphuric acid	800	ml
Thiourea	100	g
Phenazine	0.20	g
1/5 sulphuric acid to 1 liter		

The copper image is dye bleached and a positive dye reproduction remains.

Example 2

A cuprous oxide emulsion coating prepared as in Example 1 is exposed and developed as in Example 1. The fixing is accomplished by adding 6% ammonium hypo containing 5 grams/liter of the sodium salt of phenylmercaptotetrazole. No fading is observed after drying.

Example 3

An emulsion is prepared as follows:

A solution of 20 g of Cu₂O in 120 ml of hydrochloric acid 89 g of calcium chloride is brought to 24°C and added slowly with stirring to a solution of 150 g of calcium chloride and 14.4 g of sodium hydroxide in 480 ml of water. When 1/2 of the volume of the cuprous oxide solution has been added to the alkaline, 50 ml of 20% poly(3-thiopentyl-acrylate-co-3-acryloyloxypropane-1-sulfonic acid sodium salt) (having a molar ratio of 1:6) is added and the addition is continued until the solution pH is between 7.0 and 9.5. Stirring is stopped and some settling occurs giving a heavy precipitate up to 1/3 of the total volume. The supernatant is poured off and to it with stirring is added an equal volume of ethanol. The curds which separate are added to the original precipitate and this is stirred as again an equal volume of ethanol is added. The total curds are now washed with about 200 ml ethanol and it is then redispersed in 100 ml of distilled water. The coagulation with alcohol is repeated to remove excess halide ion. To this is added 25 ml of the above polymer and 100 ml of ethanol. A sticky mass forms which is washed with alcohol and stirred until viscous and excess alcohol is removed. The mass is brought to a volume of 100 ml with distilled water giving an emulsion with about 400 mg/ml of cuprous oxide.

A 1.5 ml aliquot of the above emulsion is removed and added to 10 ml of a terpolymer of n-isopropylacrylamide, 3-acryloyloxypropane-1-sulfonic acid (sodium salt), and 2-acetoacetoxymethylmethacrylate (7:2:1/4).

Example 4

A cuprous oxide emulsion is prepared by the procedure described in Example 1, coated on a paper support, and simultaneously exposed to a test object and heated for 10 seconds at a temperature of 100°C. A heavy black image appears. Image and background in the sample remain unchanged under the influence of further heat and light.

Example 5

A coating is prepared from a Cu₂O emulsion containing 50 mg/ft² of triphenyltetrazolium chloride. The coating is exposed to a graduated density test object and developed in 1/5 sulphuric acid for one minute and fixed in 'Kodak' F-5 fixing solution ('Kodak' is a trade mark) until a negative image consisting of the formazan dye is formed.

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