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REDUCTION OF METALLIC SALTS BY AMINE OXIDE PYROLYSIS

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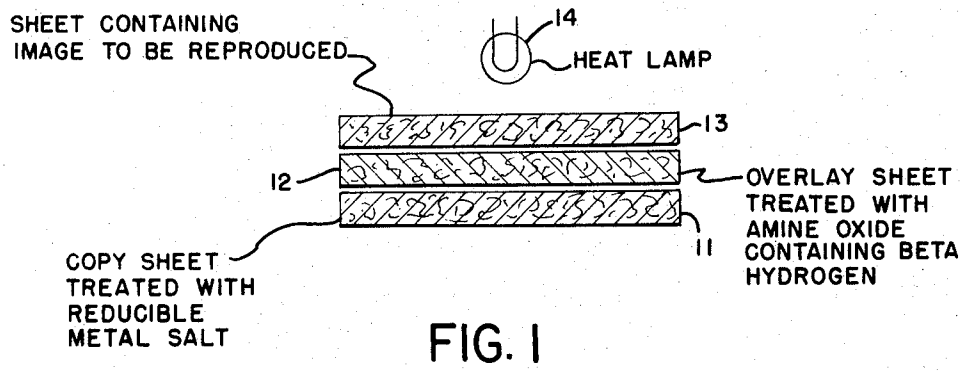


FIG. 1

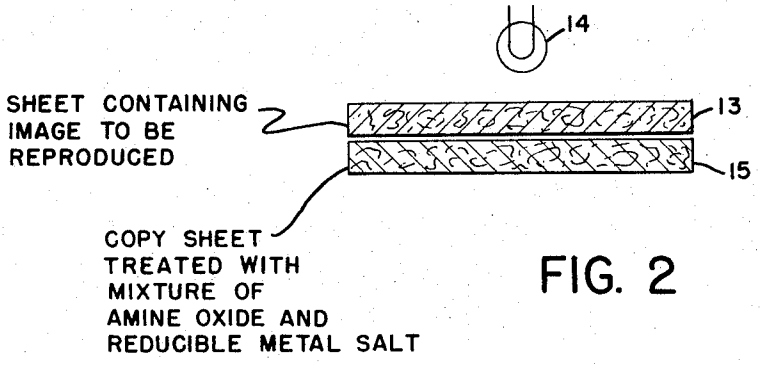


FIG. 2

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REDUCTION OF METALLIC SALTS BY AMINE OXIDE PYROLYSIS

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Reduction of metallic salts by amine oxide pyrolysis

This invention relates to a new and useful combination of a reducible metallic salt and a compound which forms reducing agents on heating. More particularly, this invention relates to the reduction of heavy metal salts by reducing agents formed by the pyrolysis of amine oxides.

The process of reducing metallic ions through the use of heat and reducing compounds is well known. The most widely known concept is that of the reduction of iron ore to the free metal. Less drastic procedures have been developed utilizing controlled reduction of metallic ions to produce visible images such as that required in heat-sensitive copy paper.

Thermal reproduction processes generally require reducing agents possessing properties such as long-term stability at room temperature and rapid reactivity at elevated temperatures. The exacting requirements of reducing agents for thermal reproduction greatly limits their number. Aromatic acids, such as protocatechuic acids have been suggested as reducing agents for metallic soaps used in heat-sensitive copy sheets. There are, however, several disadvantages in using an acid of this type. One disadvantage is that the acid reducing agent and the metallic soap both remain in the reaction area subsequent to thermo reproduction on the copy sheet. Because of this, the copy sheet will darken and lose its graphic image on exposure to further heating.

This invention is based on the fact that amine oxides when subjected to heat, produce compounds which are excellent reducing agents for metallic salts.

It is therefore an object of this invention to provide an improved composition which is stable at room temperature and which is capable upon heating of forming a reducing agent in situ and a free metal.

It is another object of this invention to provide a composition comprising reducible metallic salts and amine oxides, which when subjected to heat produces a reducing agent in situ and a free metal.

Another object of this invention is to provide a process of reducing metallic salts to free metal by contacting the salts with an amine oxide under conditions of elevated temperatures.

Another object of this invention is to provide a process of reducing metallic salts to free metal by bringing into contact with the salts a reducing agent formed by the pyrolysis of an amine oxide.

A further object of this invention is to provide heat-sensitive copy sheets containing reducible metallic salts and amine oxides.

A further object of this invention is to provide a method of producing heat-sensitive copy sheets which are stable to heating subsequent to the reproduction of a visible graphic image thereon.

Another object of this invention is to provide a method of thermally reproducing visible graphic images and conductive circuits.

The objects of this invention are accomplished by the process which comprises heating amine oxides in contact with easily reducible metallic salts and obtaining thereby free metal.

The method and compositions of this invention overcome the disadvantages of other thermal reproduction methods in that the reducing agent is not formed until subjected to heat. In one aspect of the invention, an amine oxide is intimately mixed with a reducible metallic salt. When subjected to heat, the reducing agent is formed in situ and reduces the metallic salt to the free metal.

In another aspect of the invention by the proper selection of the amine oxide, the reduction of the metallic salt may take place by vapor transfer. In this manner, the amine oxide is heated and the reducing agent in the form of a vapor is contacted with the metallic salt thereby reducing it to the free metal. This procedure permits the use of an overlay containing the amine oxide which only contacts the medium containing the reducible metal salt during the heating step. Thereafter, the overlay may be removed from the metallic salt-containing medium which renders the medium inert to further heating.

By the procedures of this invention, it is possible to utilize compounds which are very stable at room temperatures but yet form reducing agents on heating to a temperature in the range of 70° C. to 150° C. Temperatures up to about 250° C. may be employed to accelerate the reduction reaction but are not normally required.

FIG. 1 of the accompanying drawing shows, in partial cross section, one aspect of this invention for thermally reproducing images, and FIG. 2 shows another aspect of this invention for thermally reproducing such images.

The metallic salts useful in this invention are easily reducible salts of the heavy metals and are metals contained in groups I–B, II–B, III–A, IV–A, V–A, VI–A and VIII of the Periodic Chart of the Elements as shown on pages 56 and 57 of Lange's Handbook of Chemistry, Eighth Edition. These groups include titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, technetium, rhenium, iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum, copper, silver, gold, zinc, cadmium, mercury, aluminum, gallium, indium, thallium, germanium, tin, lead, antimony, bismuth and polonium. The preferred metals are silver, bismuth, platinum, palladium, gold, mercury, lead and tin.

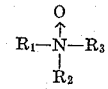
The "easily reducible salts" referred to are those salts which will be reduced by heating in the presence of amine oxides at temperatures between 70° C. and 250° C. The term, "reducible metallic ions," is defined as the metal ions of the organic and inorganic salts of heavy metals.

For purposes of this invention, amine oxides are classified into two categories; those containing available beta hydrogen and those which do not have an available beta hydrogen. Both classes of amine oxides are useful in this invention but are distinguished because the availability of the beta hydrogen determines the characteristic of the reducing agents obtained from the amine oxides. Amine oxides containing a beta hydrogen form volatile reducing agents when heated to a temperature of 70° C. to 150° C. and therefore are particularly suitable for reduction of heavy metal ions by vapor transfer.

The term "vapor transfer" is used herein to describe a procedure of bringing volatile reducing agents into contact with reducible metallic salts.

Amine oxides which do not contain an available beta hydrogen group form reducing agent upon heating which are not volatile but will reduce metallic ions in situ rather than by vapor transfer.

The amine oxides of this invention are represented by the formula:



wherein R_1, R_2 and R_3 each designates a hydrocarbon radical containing 1 to 26 carbon atoms or a substituted

alkyl, the substituents being heterocyclic, aryl, alkyl, cycloalkyl, or halo-substituted alkyl. R_1, R_2 and R_3 may include fatty saturated and unsaturated chains, such as lauryl, stearyl, oleyl, linoleyl and behenyl, shortchain hydrocarbon, such as methyl, ethyl, propyl, butyl and hexyl, heterocyclic radicals such as (3-furfuryl) ethyl, (2-pyridyl) ethyl, and (3-sulfolanyl) ethyl, aryl such as phenyl and substituted phenyl and halo-substituted alkyl such as 3,4-dichlorohexyl. Alternately, two R groups can be part of a ring system such as a cycloalkyl as that found in N,N-methyaza-cyclo-octane oxide.

In addition, trialkylamine oxides, such as trimethyl, triethyl, tributyl, trioctyl, and the like, mixed alkylamine oxides, as dimethylethyl, methyldiethyl, ethyl, dibutyl, and the like, mixed alkylarylamine oxides, as dimethylaniline oxide, diethylaniline oxide, methyl butyl aniline oxide, and the like, aralkylamine oxides, as tribenzyl, dimethylbenzyl, diethylbenzyl, and the like, heterocyclic amine oxides, as N-ethylpiperidine, furfuryldimethylamine oxide, thienyldiethylamine oxide and the like, alicyclic amine oxides, as dimethylcyclohexyl, diethylcyclopropyl, cyclopentylcyclohexylmethyl, alpha-pinyldimethyl, cholesteryldimethyl and the like, functionally substituted amine oxides, as dimethyl-3-hydroxypropylamine oxide, dimethyl cyanoethylamine oxide, dibutyl carboxyethylamine oxide, and the like, are useful in the practice of this invention.

The amine oxides preferred for vapor transfer reduction of metallic ions are those amine oxides which contain at least one available beta hydrogen on one R group. Amine oxides which do not contain a beta hydrogen are useful for homogeneous in situ reduction of the metallic ions. When an amine oxide is used, which does not contain beta hydrogen, the amine oxide must be in intimate admixture with the metal salts.

Examples of amine oxides which do not contain a beta hydrogen include benzyldimethylamine oxide, methyldineopentylamine oxide, trimethylamine oxide and the like. Examples of amine oxides containing an available beta hydrogen which yield volatile reducing agents by pyrolysis include triethylamine oxide, dimethyllaurylamine oxide, diethyl (3-furfuryl) ethylamine oxide, dimethyl-beta-phenylethylamine oxide and the like.

Amine oxides decompose in the temperature range of 70° C. to 150° C. The pyrolytic decomposition of an amine oxide containing beta hydrogen yields an olefin and a volatile hydroxyl amine reducing agent. If the amine oxide does not contain an available beta hydrogen, the pyrolytic decomposition proceeds to an aldehyde when in contact with heavy metal ions. Both the hydroxylamines and the aldehydes, rapidly reduce the heavy metal salts of this invention to free metal. The various reducing agents formed lend versatility to the several methods of reducing metallic ions within the scope of this invention.

The metallic salts which are useful in the practice of this invention are both the organic and inorganic salts of the easily reducible heavy metals referred to heretofore. The anion of the salt is not critical. For use in copy sheets, however, the organic salts are preferred. Inorganic salts such as nitrates and halogenates are not preferred because of the tendency to attack the copy sheet, especially if it is paper. The use of inorganic salts necessitates the addition of additives or stabilizer to retard the decomposition of the paper. Inorganic salts can readily be used in the productoin of electrical circuits or mossy metal where the base sheet is relatively inert to chemical attack by the anions.

The preferred organic salts are the carboxylates and acetates of heavy metal ions. The preferred inorganic salts are the nitrates and halogenates of heavy metal ions.

The processes of this invention are useful wherever it is desirable to reduce easily reducible heavy metallic ions to free metal. This invention is particularly applicable to thermal duplication processes, the formation of mossy metal, and the reproduction of printed electrical circuits.

There are two methods in which the processes of this invention can be carried out. One method is to utilize the vaporous decomposition products of amine oxides containing beta hydrogen to reduce metallic ions by vapor transfer. Another method which is particularly applicable to amine oxides which do not have beta hydrogen, is the use of an intimate admixture of amine oxides and easily reducible metal salts.

The vapor transfer method is most desirable for use in paper copy sheets. This permits thermal reproduction by use of an overlay which can be mechanically removed after the duplication process has been completed. The use of vapor transfer to produce visible graphic images has a distinct advantage over copy sheets containing a homogeneous mixture of reducible metallic salts and a reducing agent. Once the overlay is removed from the copy sheet, further darkening or loss of graphic image does not take place on subsequent heating. This is in marked contrast to most previously known thermal copy sheets.

To prepare paper-like duplicating sheets, referring to FIG. 1, a base sheet **11** on which the image will be reproduced, is treated with a metallic salt. An overlay **12** is prepared by treating another sheet with an amine oxide containing beta hydrogen. A visible graphic image is reproduced on the base sheet, often called a copy sheet, by placing the overlay in physical contact with the prepared base sheet. The original **13** to be copied is placed over the overlay sheet as to sandwich the overlay between the original and the base sheet. The sandwiched copy sheets are then placed so that the original is nearest a heat source. A visible positive graphic image is reproduced on the base sheet by heating at a temperature of 70° C. to 250° C. for a dwell time of about 0.1 to about 5 minutes by means of heat lamp **14**. At the higher temperatures, the shorter dwell time is required. Normally, temperatures up to 150° C. are sufficient to complete the reduction. A high contrast facsimile of the original is reproduced on the copy sheet. Shading will be in colors ranging from brown to blue-black depending on the metallic salt used. The background will be white, grey or buff when using white base sheets, depending on the metallic ion used.

There are numerous methods of constructing the overlay. Besides the individual sheet, the overlay can be in the form of a continuous belt which is fed through the thermal duplicating device. The belt can be exchangeable or permanent. The permanent type belt would be sprayed, dipped or brushed with an amine oxide containing solution and dried prior to reuse. This is easily done by incorporating a dipping, spraying or brushing means into the duplicating machine.

Copy sheets can also be made without the use of an overlay. This is accomplished, referring to FIG. 2, by treating a copy sheet **15** with an intimate admixture of amine oxide and easily reducible metallic salt. An alternate procedure is to first treat the copy sheet with an easily reducible metallic salt and then the same sheet with an amine oxide with or without available beta hydrogens. Reproduction of a visible graphic image from the original **13** is effected without the use of an overlay by subjecting to a temperature of 70° C. to 250° C. for a dwell time of about 0.1 minute to about 5 minutes.

The process of this invention can be utilized to reproduce any original graphic image which is composed of thermally conductive material such as ink, carbon containing compositions, pigmented compositions and the like.

Printed electrical circuits can also be produced using the overlay procedure. In addition, circuits can be produced utilizing an intimate admixture of metallic salts and amine oxides, both those containing available beta hydrogen and those without available beta hydrogen. Since electrical circuits usually are printed on a relatively inert substrate or base sheet such as plastic, glass, cardboard and the like, the inorganic metallic salts can be

readily used. Relatively inert base sheet materials permit rinsing to remove excess amine oxide subsequent to the formation of the desired free metal.

The amine oxides and metallic salts can be applied to the base sheets in solution or slurry form by spraying, dipping or coating.

The reduction of the metallic ions takes place by heating with a suitable heating means including heat lamps, hot plates, heated styluses, heated stamps or patterns and the like.

The following examples are included to illustrate certain preferred embodiments of the present invention and are not to be limiting in any sense. All parts and percentages are by weight.

Example 1

A copy sheet was prepared by soaking a sheet of flax paper in 5% bismuth chloride solution in aqueous ethanol. The paper was allowed to air dry. The paper to be duplicated, called the original, had a message written on it in pencil, and was soaked in a 5% dimethyllaurylamine oxide solution of ethyl acetate and air dried. The original was placed upright on a glass sheet and the copy sheet was placed in contact with it. The original and copy sheet were then passed through a heating zone with original nearest the heat source so that a temperature of 125° C. for a dwell time of 45 seconds was produced on the face of the original. A positive facsimile of the original graphic image was obtained having a high contrast of black against a white background.

With the original copy removed from the duplicate, the duplicate was again heated for several minutes at 125° C. without darkening or loss of the graphic image.

Example 2

A copy sheet was prepared by soaking onionskin paper in a 5% silver stearate solution in acetone and allowed to dry. A 5% dimethyllaurylamine oxide solution in aqueous ethanol was then sprayed onto the copy sheet and allowed to dry. The prepared copy sheet was stable at room temperature for many months. A graphic image was reproduced on the copy sheet from a printed original by passing both through a heated zone as shown in Example 1. Copy sheets made in this manner would darken on repeated heating unlike those produced when the amine oxide is contained in an overlay.

Example 3

A copy sheet was prepared by spraying flax paper with a 5% bismuth behenate solution in acetone. The sheet was then air dried. A second flax sheet was then prepared by soaking in a 5% dimethyl-beta-phenylethylamine oxide solution in ethyl acetate. This sheet was also air dried. A graphic image was thermally reproduced on the copy sheet containing the bismuth behenate by placing the sheet containing the amine oxide between the original and the copy sheet and passing through a heated zone as in Example 1. The high contrast facsimile of the original did not darken or lose contrast on subsequent heating with the overlay removed.

Example 4

Highly conductive mossy silver was precipitated on a glass plate by coating the plate with a mixture of 15% silver stearate in acetone and 15% beta phenethyldimethylamine oxide in ethanol. The plate was heated on a 100° C. hot plate for one minute. A silver metal deposit was formed on the glass plate. This deposit appeared spongy when viewed under a microscope. The silver deposit was highly conductive giving a reading of less than 1 ohm on a strip 3 mm. wide by 10 cm. long. A 150-watt light bulb was connected in series with the 3 mm. by 10 cm. strip. The circuit was completed and the light glowed brightly even after the printed circuit had been reduced in width in less than 0.5 mm. for a length of 5 mm.

Example 5

A printed circuit was made by reducing a silver salt to free silver in the form of a geometric pattern onto a plastic base sheet. A 5% silver stearate solution in acetone was sprayed onto a 4" x 6" plastic sheet. This was allowed to dry. A 5% dimethyllaurylamine oxide solution in aqueous ethanol was then sprayed over the dried silver stearate. After the solvent had evaporated, the plastic base sheet was passed under a heat source which was derived from a 500-watt heating lamp. A pattern cut out of an opaque heat shielding material was placed between the heat source and the plastic base sheet. The heat passed through the pattern to produce a temperature of 145° C. on the plastic base sheet where not shielded by the opaque shield. The dwell time was 30 seconds. A conductive circuit was produced by the precipitated silver where the heat passed through the precut shielding pattern. The excess dimethyllaurylamine oxide and silver stearate remaining on the plastic base sheet was removed by rinsing in acetone and a protective coating of plastic was placed over the printed circuit.

Example 6

A printed circuit was formed on a plastic base sheet by coating the sheet with a 50–50 mixture of silver laurylate and methyldilaurylamine oxide in a 50% acetone slurry. The coating was allowed to dry. Silver metal was precipitated by bringing a heated pattern of the desired design to within about ⅛ inch of the coated surface on the plastic base sheet. The temperature produced on the surface of the base sheet immediately adjacent to the pattern was about 125° C. The dwell time was 1 minute. Silver metal was precipitated in the shape of the heated pattern. The excess silver salt and amine oxide was removed by rinsing with acetone.

The usefulness of this new reducing agent is readily apparent to one skilled in the art from the description and examples shown. The amine oxides have particular utility in thermal reproducing processes including the making of copy sheets and electrical circuits.

What is claimed is:

1. A composition comprising a tertiary amine oxide and a reducible metallic salt.

2. A composition comprising a tertiary amine oxide and a reducible metallic salt wherein the metal is selected from the group consisting of groups I–B, II–B, III–A, IV–A, V–A, VI–A, and VIII of the periodic table.

3. A composition comprising a tertiary amine oxide and a reducible metallic salt wherein the anion of said salt is selected from the group consisting of carboxylate, nitrate and halogenate.

4. A process for reducing a metallic salt to free metal comprising heating a tertiary amine oxide in the presence of said metallic salt to a temperature in the range of about 70° C. to 250° C.

5. A process for reducing a metallic salt to free metal comprising heating a tertiary amine oxide in the presence of said metallic salt to a temperature in the range of about 70° C. to 250° C., said metal selected from the group consisting of groups I–B, II–B, III–A, IV–A, V–A, VI–A and VIII of the periodic table, and the anion of said salt selected from the group consisting of carboxylate, nitrate and halogenate.

6. A process for reducing a metallic salt to free metal comprising heating a tertiary amine oxide containing a beta hydrogen to a temperature in the range of about 70° C. to 250° C., and contacting the volatile products formed with said metallic salt.

7. The process of claim 6 wherein said metal of said salt is selected from the group consisting of groups I–B, II–B, III–A, IV–A, V–A, VI–A and VIII of the periodic table.

8. The process of claim 6 wherein the anion of said metallic salt is selected from the group consisting of carboxylate, nitrate and halogenate.

9. A process for reducing a metallic salt to free metal comprising heating a tertiary amine oxide in intimate admixture with said metallic salt to a temperature in the range of about 70° C. to 250° C.

10. The process of claim 9 wherein said metal of said salt is selected from the group consisting of group I–B, II–B, III–A, IV–A, V–A, VI–A, and VIII of the periodic table.

11. The process of claim 9 wherein the anion of said metallic salt is selected from the group consisting of carboxylate, nitrate and halogenate.

12. A composite thermographic copying system which comprises a base medium containing a reducible metallic salt and an overlay containing a tertiary amine oxide containing a beta hydrogen.

13. The copying system of claim 12 wherein the metal of said metallic salt is selected from the group consisting of groups I–B, II–B, III–A, IV–A, V–A, VI–A, and VIII of the periodic table and the anion of said metallic salt is selected from the group consisting of carboxylate, nitrate and halogenate.

14. The copying system of claim 12 wherein said base medium comprises a paper sheet.

15. A thermographic copy sheet comprising a base medium containing a tertiary amine oxide and a reducible metallic salt.

16. The copy sheet of claim 15 wherein the metal of said metallic salt is selected from the group consisting of groups I–B, II–B, III–A, IV–A, V–A, VI–A, and VIII of the periodic table and the anion of said metallic salt is selected from the group consisting of carboxylate, nitrate and halogenate.

17. The copy sheet of claim 15 wherein said base medium comprises a paper sheet.

18. A thermographic copying process which comprises placing an overlay containing a tertiary amine oxide containing a beta hydrogen between an original graphic image desired to be copied and a base sheet containing a reducible metallic salt, heating said overlay, base sheet and original to a temperature in the range of about 70° C. to 250° C. for about 0.1 minute to about 5 minutes.

19. The process of claim 18 wherein the metal of said metallic salt is selected from the group consisting of groups I–B, II–B, III–A, IV–A, V–A, VI–A, and VIII of the periodic table and the anion of said metallic salt is selected from the group consisting of carboxylate, nitrate and halogenate.

20. A thermographic copying process which comprises placing an original graphic image desired to be copied adjacent to a copy sheet comprising a tertiary amine oxide and a reducible metallic salt, heating said original and copy sheet to a temperature in the range of about 70° C. to 250° C. for about 0.1 minute to about 5 minutes.

21. The process of claim 20 wherein the metal of said metallic salt is selected from the group consisting of groups I–B, II–B, III–A, IV–A, V–A, VI–A, and VIII of the periodic table and the anion of said metallic salt is selected from the group consisting of carboxylate, nitrate and halogenate.

22. A process for the production of mossy metal on a base medium comprising heating on said medium an intimate admixture of a tertiary amine oxide and a reducible metallic salt to a temperature in the range of about 70° C. to about 250° C.

23. A process for the production of printed electrical circuits on a base medium comprising forming on a base medium an intimate admixture of a reducible metallic salt and a tertiary amine oxide, placing a pattern conforming to the desired electrical circuit between said base medium and a heat source, and heating said admixture to a temperature in the range of about 70° C. to 250° C., and removing non-reduced metallic salt and amine oxide from said base medium.

24. A process for the production of printed electrical circuits on a base medium comprising forming a coating of a reducible metallic salt on a base medium, placing a pattern conforming to the desired electrical circuit adjacent said base medium, placing an overlay containing a tertiary amine oxide containing a beta hydrogen over said pattern, heating said base medium, pattern and overlay to a temperature in the range of about 70° C. to 250° C., and removing non-reduced salt from said base medium.

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