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3,770,630

TREATMENT OF ELECTROLESS PROCESS AND STRIPPING SOLUTIONS

David R. Kamperman, Harmony, Pa., assignor to Dart Industries Inc., Los Angeles, Calif.

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8 Claims

ABSTRACT OF THE DISCLOSURE

Solutions that have been used for electroless plating a workpiece of non-conductor material, such as a resin, or for stripping metal from a workpiece are treated in such a manner that they may be discharged as non-polluting waste into a natural body of water. A used solution is first provided in a condition involving a pH of not greater than 8 or 9, with an optimum of below 5, and then if it contains dissolved metal above about 5 g./l., it is diluted with water before further treatment. The solution is then heated to a temperature of at least 120° F. and maintained at such a temperature, while providing alkalinity and using an excess of sodium hydrosulfite of at least about 50 mg./l., but preferably higher, up to a maximum of about 500 mg./l. The solution is then allowed to settle and is decanted with less than one mg./l. of dissolved metal content, and with precipitated solid metal waste being thus removed. Subsequently, the thus treated solution may be recirculated and if necessary, further conditioned for its particular use and then employed in an applicable rinsing operation. On the other hand, if desired, it can be discharged as a substantially non-toxic waste solution.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to an integrated or batch treatment of a used electroless process solution for substantially eliminating its dissolved metal content and particularly, to a treatment which will enable such a solution to be either discarded as non-toxic waste to the environment or to be recirculated and used in accomplishing workpiece washing or rinsing.

Description of the prior art

Copper, nickel, cobalt, are typical electroless plating metals that have been used as a base coating or layer on a workpiece to provide corrosion resistance. They represent the basis for a smooth and bright deposit, such as for a thin final chromium plated deposit, that may serve principally to protect the workpiece against surface oxidation and tarnish. For many years the practice has been in electroplating to reduce the applicable metal on a workpiece employed as a cathode by providing the metal in ionic form, such as is easily available from an acid solution of the metal, or from its cyanide complex. In accordance with this procedure, the anion is reduced by hydrogen to yield the desired metal ion and deposit it on the cathode surface.

A recent trend in the technology has as its aim the deposition of such a representative metal from a neutral or slightly acid solution on a workpiece of a specially prepared plastic or glass or other non-conducting base material. This necessitates at least applying the initial metallic deposit by means of a non-electrolytic process for rendering the surface conductive to make a subsequent electro depositing operation possible. In carrying out the coating of a workpiece having a non-conducting surface, a reducing agent such as formaldehyde, boron hydride, hypophosphite, etc., is used to reduce the metal

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from its salt or salts, as dissolved in the deposition solution, to a metallic form. Such a process generically has been termed making use of an electroless plating solution.

Also, similar types of process solutions of an alkaline or slightly acidic nature but containing an oxidizing rather than a reducing agent have been used to dissolve the same metals in a stripping solution without attacking the basis metal or non-metallic surfaces of a workpiece.

Although the function of the above-described two types of process solution utilizations are quite different, in that the one contains a reducing agent for reducing dissolved metal salt in metallic form, and the second contains an oxidizing agent for actuating and accelerating the dissolution of a metallic film, the basic make-up of the two is somewhat similar. That is, disregarding the respective use of reducing or oxidizing agents and other additives to enhance the particular characteristics and performance of each type of solution, the basic make-up of both types of solutions employs solubilizing agents (chelating agents) for metal salts, such as of copper, nickel, cobalt. Chelating agents are used where the metal salts in an alkaline or slightly acidic solution would otherwise precipitate as insoluble hydroxides, carbonates or oxides of the particular metals. Solubilizing or chelating agents capable of such use are varied and extend from the simplest form as represented by ammonia and phosphates, to an array of organic amine complexes, such as aryl-, alkyl- amines, polyphosphates, organo-phosphate compounds; organic acids such as citric, acetic, boric and tartaric; a variety of hydroxyacetic and hydroxycarboxylic acids and their salts; and finally, a combination of organic acids with the amines. Examples of the latter are well known complexing agents, such as ethylene diamine tetra acetic acid (EDTA), and nitrilo tetra acetic acid (NTA) or their salts.

These various complexing agents or the chelating compounds have one desirable property for the above particular use, namely, that they form a stable complex with the metal salt and prevent its precipitation. They thus prevent the loss of the metal salt from the solution and act as a solvent molecule insofar as the metal salt is concerned. It is well known that heavy metal ions and particularly those of the metals here of interest, namely, copper, nickel, cobalt, can have adverse toxic effects on the environment if discharged in soluble form within an effluent. Previously, all known efforts to render such metal salts insoluble from these complex solutions by various neutralization treatments have been unsuccessful. However, where ammonia complexes were available, the process set forth in Lancy, Pat. No. 3,218,254 has been satisfactory, but it does require large quantities of caustic soda and a special reactor vessel for ventilation and air scrubbing facilities. Also, it is somewhat costly to boil the solution for, in some instances, two or three hours.

In an endeavor to solve the problem involved, various recommendations of chemical suppliers were investigated, including the adding of high excesses of lime, caustic soda or acidifying the solutions and then neutralizing them, and even adding sulfide compounds to the treated waste solution. However, the metal content of the treated waste solution was only partially reduced, even employing the sulfides. By way of example, a nitro-organic type of nickel stripping solution, even after dilution to 5% of its original concentration, was found to contain 850 mg./l. of soluble nickel. No appreciable reduction in its chemical content occurred even when it was first acidified with sulfuric acid and subsequently neutralized to a pH of about 11, with lime or caustic soda. Such a solution when treated with a high excess of lime, in the range of 20 g./l., had a nickel content that was only reduced from about 850 to 350 mg./l. Attempts to precipitate the soluble nickel content

with subsequent additions of sulfur compounds did not change the amount in solution.

In another experiment, using the same nickel containing solution content, 30 g./l. of ferric chloride was added in an attempt to aid in co-precipitating the nickel. Neutralizing this waste solution with large quantities of lime resulted in a solution that contained 370 mg./l. of nickel, with considerable amounts of iron and lime sludge solids. This increased the waste treatment cost without materially aiding the requirements of nickel precipitation.

As contrasted to the above results, the usual requirement is to in some manner reduce the nickel or copper content of the waste solution to a one mg./l. level or less. This clearly was not obtained and could not be obtained by the above approaches.

SUMMARY OF THE INVENTION

It has therefore been an object of the invention to solve the problem thus presented.

Another object has been to develop a process for after conditioning or treating electroless plating and metal stripping solutions to organically effect a separating-out of substantially the full dissolved metal content, in order that the solution can be reused for rinsing or discarded without adverse results.

A further object of the invention has been to devise chemical means and operating conditions for effectively removing objectionable soluble metal content in a previously used aqueous solution formulated for electroless plating or metal stripping of a workpiece.

These and other objects of the invention will appear to those skilled in the art from the description thereof and particularly, from the standpoint of the preferred embodiment and the claims.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In carrying out the invention, it was discovered that the retention of such representative metals from chelated complexes represented by an electroless plating solution or a metal stripping solution can be reduced in a neutral or slightly alkaline medium by the addition of sodium hydrosulfite, boron hydride or hydrazine reducing agents, or a mixture of these. These chemicals are effective reducing agents in this connection and will reduce copper, silver and gold to a metallic or oxide form. On the other hand, it was determined that nickel and cobalt were reduced to a metallic form only to a very slight extent, and that sulfides of these two metals will be precipitated as a result of the reaction of the reduction and sulfide formation from the breakdown of the sodium hydrosulfite. At room temperature the reaction is relatively slow, the sludge is very fine and is slow in settling.

Further, in carrying out the invention, it was determined that the reaction could not only be greatly accelerated but that the treatment could be effectively completed within a few minutes (less than five), by subjecting the solution to a critical minimum temperature elevation while maintaining an excess of about 50 to 500 mg./l. of hydrosulfite. Nickel and cobalt salts were precipitated and in a dense black form as apparent sulfides. Copper precipitate was found to contain metallic copper, cuprous oxide and a small percentage of cuprous sulfide.

The process has also been found to be well suited for the treatment of a discarded electroless treating solution that has outlived its usefulness, and that may contain a soluble metal concentration within a range of about 3 to 8 g./l. It was found to be equally suitable for treating a discarded metal stripping solution containing metals in a concentration of up to about 50 to 60 g./l. In the latter case, the treatment procedure is effected by first water-diluting the waste until its soluble metal content is reduced to a range of about 3 to 5 g./l. To avoid contamination of rinse water solutions following an electroless plating or a metal stripping process, a process solu-

tion can be made up containing an alkalinity and maintained within a pH range of about 5 to 9, with a sodium hydrosulfite concentration of about 50 to 500 mg./l. Higher concentrations of the sodium hydrosulfite were not found to be harmful.

The above thus-prepared process solution can be used as an integrated treatment wash or rinse following an electroless plating or metal stripping process for the removal of the toxic metal containing chemical film carried-over on the workpiece. The wash solution is then taken-off for treatment from the washing bath or tank (see the tank C of the in-line operation represented by Lancy U.S. Pat. No. 2,725,314). The precipitation treatment of the taken-off solution can then be effected in a separate tank or reservoir (see the reservoir E of the reference patent) and the precipitate removed before the solution is rechanneled and reused, or is discarded by running it into a sewer, for example. Where a wash solution taken-off from the reservoir is to be recirculated for reuse, it is provided with the desired alkalinity by adding alkaline metal hydroxide (hydride) or carbonate, and by adding the sodium hydrosulfite in proportion to the consumption thereof that is involved. It is important to maintain an excess quantity (above about 50 mg./l.) of sodium hydrosulfite and thus, the effectiveness of the reducing condition.

By way of further example, a typical treatment system may employ a batch dumping of the process solution from either an electroless plating solution or metal workpiece stripping treatment. This involves first acidifying the solution to preferably a pH of about 5 and if highly alkaline in nature, to at least reduce the pH to about 8 or 9. Secondly, the batch waste solution should be diluted so that its metal content concentration is not more than 5 g./l. Thirdly, the solution should be heated to at least 120° and preferably or as an optimum to about 140° or higher. Finally, alkalinity is added along with an excess (above a stoichiometric amount) of sodium hydrosulfite so as to provide the solution with an excess of the latter of at least about 50 mg./l., but as an optimum higher, and up to about 500 mg./l. The solution is then allowed to settle and the treated liquid is decanted, resulting in a content of less than one mg./l. of dissolved metal. The solid waste is removed and discarded which, of course, is insoluble and thus suitable for solid waste disposal. The same process may be used for a chemical treatment rinse or for an integrated and recirculated treatment wash solution, with the described chemical conditions being maintained by either adding alkalinity to provide the desired higher pH after an acidic treating process or for an acidic solution. An alkali metal salt such as calcium chloride will tend to precipitate and thereby reduce the pH; it can be used while maintaining the reducing conditions through continuous or intermediate hydrosulfite additions to maintain in the necessary excess.

I claim:

1. In a method of treating a waste rinsing, electroless process or a metal stripping solution containing metals dissolved therein of the class consisting of copper, nickel and cobalt that are in the form of stable complexes due to the presence of a solubilizing complexing agent in the nature of a chelating agent and thus are difficult to precipitate out, the steps of first providing the solution with a slightly acid to slightly alkaline pH within a maximum of about 9, adding water to the solution as may be required to assure a dilute soluble metal content concentration of not more than a maximum of about 5 g./l. heating the solution to a temperature of at least about 120° F., and providing an excess of above a stoichiometric amount of sodium hydrosulfite in the solution and using it as the sole chemical reagent to substantially fully convert the soluble metal content of the solution into an insoluble metal precipitate.

2. In a method as defined in claim 1, decanting the thus-treated solution for discarding it as a non-toxic waste solution.

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3. A method as defined in claim 1 wherein the waste solution after the precipitation of its metal content is reconditioned for use as a rinsing solution.

4. A method as defined in claim 3 wherein an excess of sodium hydrosulfite is added to the solution to further recondition it.

5. A method as defined in claim 1 wherein the sodium hydrosulfite is added to the heated solution in an amount of not less than about 50 mg./l.

6. A method as defined in claim 1 wherein the sodium hydrosulfite is provided in the heated solution in an amount of about 50 to 500 mg./l.

7. A method as defined in claim 1 wherein the solution is first provided with a slightly acid to slightly alkaline pH within a range of about 5 to 9.

8. In a method as defined in claim 1, first acidifying the solution to a pH of less than about 5 and maintaining it slightly on the acid side, then heating it and providing

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the excess of hydrosulfite, and thereafter decanting the thus-treated solution.

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MICHAEL ROGERS, Primary Examiner

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