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ELECTROLESS COPPER PLATING

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ABSTRACT OF THE DISCLOSURE

No bail-out, formaldehyde odor-reducing or eliminating method for replenishing depleted or spent electroless copper plating baths which eliminates the prior requirement of removing or bailing out material amounts of liquid solution from the bath during replenishing to maintain constant volume, and which considerably reduces or eliminates the irritating ordor of formaldehyde otherwise emanating from the bath. A replenisher concentrate solution is added to the depleted electroless copper plating bath, such replenisher concentrate solution containing the following constituents within the proportion ranges set forth below:

	Percent by weight
Cupric nitrate	About 1 to saturation.
Formaldehyde - methanol reaction product comprising primarily $CH_3—O—CH_2—O—CH_3$	About 1–50.
Formalin	About 15–75.
Methanol, concentrated	About 1–83.

The formaldehyde-methanol reaction product comprising primarily the pleasant smelling methylal, i.e.

$$CH_3—O—CH_2—O—CH_3,$$

is present in the replenisher concentrate solution within the aforesaid proportion range in an effective amount, sufficient to reduce considerably the formaldehyde odor of the electroless copper plating bath.

CROSS REFERENCES TO RELATED APPLICATIONS

This is a continuation-in-part of our copending application. Ser. No. 62,649, filed Aug. 10, 1970 now abandoned.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to electroless copper plating and more particularly to a new and improved method for replenishing depleted or exhausted chemical reduction copper plating baths without having to remove a material amount of liquid plating solution from the bath prior to, during or after the replenishment, except for those amounts of liquid bath solution removed by drag out and evaporation, and for considerably reducing the odor of formaldehyde in the concentrate solution and in the plating bath solution. Additionally this invention is concerned with new and improved concentrate solutions for replenishing depleted or exhausted chemical reduction copper plating baths or from mixing together with another concentrate composition and water in making up new plating baths.

(2) Description of the prior art

All commercial chemical reduction copper plating baths in this country at the present time, to the best of our knowledge, contain the sulfate of copper as the source

of copper ions. Although these copper sulfate containing baths give good results in the chemical reduction plating of copper, they have certain disadvantages and drawbacks when it comes to replenishment of their constituents when in a depleted or spent state. The replenisher concentrate solutions added to the depleted plating baths must necessarily be in large volumes by reason of containing large quantities of water to enable the addition of the desired amount of ionic copper to the bath, which is due to the relatively low solubility of the copper sulfate in water, specifically a solubility of 31.6 g. per 100 ml. water at 0° C. for $CuSO_4 \cdot 5H_2O$. To enable the addition of the large volume of copper sulfate-containing replenisher concentrate solution to the depleted bath, it was necessary to remove or bail-out a considerable volume of the depleted bath to maintain substantially constant volume and to prevent overflow of bath solution from the tank or a dangerous high level of bath solution therein with consequent overflow spillage of bath solution from the tank upon immersing therein the articles to be plated. This requirement of bail-out of plating bath solution resulted in loss of operable plating solution and valuable plating chemicals. It also requires manual labor to bail-out the bath solution. Moreover in automatic plating lines, in some instances, it may be necessary to shut down the line to enable the bail-out.

To illustrate this prior requirement of bail-out of bath solution to enable addition of replenisher concentrate solution, it requires the bail-out of 15 gallons of the depleted copper sulfate containing bath solution to make room for the addition of 25 gallons total of replenisher concentrate solutions when 10 gallons of bath solution have been previously removed by drag out and evaporation loss. Inasmuch as the amount of bath removed by drag out varies with virtually every plating rack, the type of rack design, and the condition and age of the rack, this is illustrative only. However, suffice it to say that considerable quantities of the bath solution are required to be removed prior to replenishing depleted copper sulfate-containing baths.

Further, all or virtually all commercial electroless copper plating baths currently used contain formaldehyde as a consistuent and evolve the characteristic sharp odor of formaldehyde, which may be objectionable from the standpoint of the operator and personnel in the immediate vicinity of the plating tank. The prior formaldehyde-containing replenisher concentrate as well as the concentrates for making up new plating baths also possessed the characteristic unpleasant odor of formaldehyde.

SUMMARY OF THE INVENTION

The substantially no bail-out, formaldehyde odor-reducing method of the present invention for replenishing depleted or spent electroless alkaline aqueous copper plating baths involves adding to the depleted alkaline plating bath solution comprising cupric nitrate, formaldehyde and a complexing agent for the cupric ions a replenisher concentrate solution containing the following constituents in proportions within the proportion ranges hereafter specified:

	Percent by weight
Cupric nitrate	About 1 to saturation.
Formalin	About 15–75.
Methanol, concentrated	About 1–84.

And an effective amount of a formaldehyde-methanol reaction product comprising primarily methylal, i.e. $CH_3—O—CH_2—O—CH_3$.

The formalin specified immediately supra and elsewhere herein is an aqueous formaldehyde solution ordinarily of 37% formaldehyde concentration and is readily ob-

tained in commerce. The formaldehyde-methanol reaction product comprising primarily

$$CH_3—O—CH_2—O—CH_3$$

is present in the concentrate solution in an amount which is sufficient to reduce considerably the irritating formaldehyde odor of the electroless, i.e. chemical reduction, alkaline copper plating bath containing formaldehyde as reducing agent. The formaldehyde-methanol reaction product comprising primarily $CH_3—O—CH_2—O—CH_3$ is formed in situ in the replenisher concentrate solution or other concentrate solution herein by bringing together or admixing the concentrated methanol and formalin in the presence of the cupric nitrate usually at room temperature and for at least a time sufficient to obtain the formaldehyde-methanol reaction product, such reaction time being 1 hour or more.

The methanol and formaldehyde react to form such formaldehyde-methanol reaction product in a molar ratio of 2:1 respectively. The replenishment of the depleted electroless copper plating baths in accordance with this invention constitutes a considerable improvement by reasons of: (1) little or no bail-out of plating bath solution required due to the relatively small replenishment volume required for bath replenishment; (2) usually total elimination of a detectable odor of formaldehyde in the plating bath and concentrate solution, and at most only a nonobjectionable low odor of formaldehyde in both the plating bath and concentrate solution; (3) requiring only relatively small or minimum replenishment volume in at least the preferred embodiment for replenishing the depleted plating bath; (4) loss of valuable plating chemicals avoided due to elimination of the bail-out requirement; and (5) no shut-down of the automatic plating line required for bail-out of plating bath.

The time of the reaction between the formaldehyde and methanol in the presence of the cupric nitrate to form the formaldehyde-methanol reaction product containing primarily the pleasant smelling methylal is 1 hour or more as is disclosed supra and may extend for several days, for instance to about 14 days. The reaction temperature for such reaction is usually room temperature or normal temperature. However, elevated temperatures above room temperature can be employed for the reaction although the elevated temperatures are not preferred. Thus the reaction temperature can be in the range of room temperature to about 120° F. The pH of the reaction solution is on the acid side of pH 7, i.e. below 7, and preferably the pH is in the range of about 1.5 to about 2.5. Maintenance of pH is effected, if required, by addition of small amounts of dilute nitric acid or sulfuric acid solution.

The term "primarily" used herein in specifying the formaldehyde-methanol reaction product as comprising "primarily" the $CH_3—O—CH_2—O—CH_3$, i.e. methylal, means that the formaldehyde-methanol reaction product contains in excess of 50% by weight of the methylal, i.e. $CH_3—O—CH_2—O—CH_3$. The formaldehyde-methanol reaction product may also contain a minor or small amount of the compounds CH_3OCH_2OH and

$$CH_3O(CH_2O)_nH$$

wherein n is a positive integer of 1 or more, the two last-mentioned compounds when present being in lesser amount than the methylal.

Although we do not wish to be bound by theory, it is believed the cupric nitrate takes up or absorbs most, if not all, of the free water in the replenisher and other concentrate of this invention resulting in the concentrates being anhydrous or substantially anhydrous. And this is believed to occur even though H_2O may be added to the formulation.

The formaldehyde-methanol reaction product is usually added to the electroless or chemical reduction copper plating bath to be replenished as a constituent of the relatively high cupric ion content, replenisher concentrate

solution. The replenisher concentrate solution also contains, in addition to the cupric nitrate and formaldehyde-methanol reaction product, unreacted formaldehyde and unreacted methanol.

The concentrate solution of this invention, in its broader aspects, comprises the following constituents within the proportion ranges set forth below:

	Percent by weight
Cupric nitrate	About 1 to saturation.
Formalin	About 15–75.
Methanol, concentrated	About 1–84.

and an effective amount sufficient to reduce considerably the formaldehyde odor of the electroless copper plating bath, of a formaldehyde-methanol reaction product comprising primarily the methylal. The formaldehyde-methanol reaction product comprising primarily the methylal is prepared or formed in situ in the concentrate solution under the reaction conditions previously disclosed herein, and such formaldehyde-methanol reaction product is ordinarily present in the concentrate solution herein in amount of about 1–50% by weight of the concentrate solution.

The concentrated methanol and formalin are brought together or admixed in the presence of the cupric nitrate in any sequence and in any suitable vessel or container, in the formation of the formaldehyde-methanol reaction product. Thus the concentrated methanol can be added to the formalin and cupric nitrate, the formalin added to the concentrated methanol and cupric nitrate, the concentrated methanol added to the formalin followed by the addition of the cupric nitrate to the resulting admixture, the formalin added to the concentrated methanol followed by the addition of the cupric nitrate to the resulting admixture, or such materials can be admixed in any other sequence. Additional agitating or mixing besides that obtained merely by adding the one or more materials to the other is not required but may be effected, if desired.

The formaldehyde-methanol reaction product comprises primarily methylal, i.e. $CH_3—O—CH_2—O—CH_3$. The methylal is obtained only when formaldehyde and concentrated methanol are brought together or mixed in the presence of the cupric nitrate, the nitrate anions of the cupric nitrate apparently catalyzing the reaction. The reactions for the formation of the methylal are set forth in the following equations:

$$CH_3OH + CH_2O \xrightleftharpoons[\text{nitrate}]{\text{Cupric}} CH_3OCH_2OH$$

$$CH_3OCH_2OH + CH_3OH \longrightarrow \underbrace{CH_3OCH_2OCH_3}_{\text{Methylal}} + H_2O$$

When formaldehyde as formalin and methanol were brought together in the absence of cupric nitrate, no reaction between the formaldehyde and methanol occurred. This evidenced that the nitrate anions catalyzed the reaction to form the formaldehyde-methanol reaction product.

Further it is essential that the formaldehyde-methanol reaction product which comprises primarily methylal as hereinbefore disclosed, be pre-formed prior to introduction into the depleted chemical reduction copper plating bath inasmuch as no formaldehyde-methanol reaction product is formed in the plating bath solution per se or, if formed, is not formed therein in sufficient quantity to mask or reduce the formaldehyde odor of the plating bath to an unobjectionable low level. This is believed due to the relatively large quantity of water present in the plating bath solution, which is a dilute solution, as contrasted with the relatively small amount of water or no water present in the replenisher concentrate solution of this invention, which is a concentrated solution, wherein the formaldehyde-methanol reaction product is usually formed.

The concentrate solution of this invention hereafter specified will usually contain the following constituents in the proportions within the proportion ranges hereafter specified:

	Percent by weight
Cupric nitrate	About 1–30.
Formaldehyde-methanol reaction product comprising primarily $CH_3OCH_2OCH_3$	About 1–25.
Formalin	About 15–75.
Methanol, concentrated	About 1–83.

Formalin is an aqueous solution of 37% formaldehyde concentration readily obtainable in commerce. The concentrated methanol is of 90–100% methanol concentration.

The concentrate solution of this invention is usually added to the depleted plating bath to replenish its constituents in combination with another replenisher concentrate solution, which is usually separately added to the depleted bath, in a volume ratio of the invention concentrate solution to the other replenisher concentrate solution within the volume ratio range of about 1:¼ to about 1:2 respectively. The last-mentioned replenisher concentrate will usually contain the following constituents within the proportion ranges hereinafter specified:

	Percent by weight
Rochelle salt	0 to about 30.
NaOH (50% solution)	10 to 100.
Na_2CO_3	0 to about 2.
H_2O	0 to about 90.

The other replenisher concentrate solution, which is mixed together with the cupric nitrate-and formaldehyde-methanol reaction product-containing concentrate solution of this invention and water in making up a new chemical reduction copper plating solution, will usually contain the following constituents within the proportion ranges specified:

	Percent by weight
Rochelle salt	5–30
NaOH	3–10
Na_2CO_3	1–8
Methanol (concentrated)	0–20
Water	32–91

The methanol is of 90–100% methanol concentration. The last-mentioned complexing agent-containing solution is mixed together with the cupric nitrate- and formaldehyde-methanol reaction product-containing concentrate solution of this invention and water in making up a new plating bath usually in a volume ratio range of about ¼:½:9¼ to about 2:4:4 respectively.

A chemical reduction copper plating bath containing as prepared and before use, by weight, 1.4% of

$Cu(NO_3)_2 \cdot 3H_2O$,

5.0% of formaldehyde aqueous solution of 37% concentration, 3.0% of a complexing agent such as Rochelle salt, 2.0% of methanol, 1.0% of NaOH, 0.3% of Na_2CO_3 and 87.3% of water may contain in its depleted or spent state and after 1 hour of use for copper plating 1 ft.^{2} of surface/gallon typically about 1.6% of the $Cu(NO_3)_2 \cdot 3H_2O$, 4.5% of the formaldehyde of 37% concentration, 2.8% of the Rochelle salt, 1.7% of methanol, 0.8% of the NaOH, 0.2% of the Na_2CO_3 and 88.4% of water. The exact amounts of these constituents remaining in a depleted bath will of course vary depending on the length of time the bath has been used for plating, the number of articles to be plated put through the bath during that time, and the extent of plating required on different articles.

The pH of the depleted plating baths is usually in the range of 10–13, and the pH of the plating baths after replenishing and of the newly made-up plating baths is usually in the range of 10–13, preferably 12–12.6.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The concentrate solution of this invention preferably contains the following constituents within the proportion ranges specified:

	Percent by weight
Cupric nitrate	About 17–21.
Formaldehyde-methanol reaction product comprising primarily $CH_3—O—CH_2—O—CH_3$	About 5–10.
Formalin	About 60–70.
Methanol (90%–100%)	About 5–15.

The methanol is a concentrated methanol of 90–100% methanol concentration.

The following examples further illustrate the invention:

Example I

The following concentrate solutions were utilized to replenish a depleted chemical reduction copper plating solution, and also to make-up a new chemical reduction copper plating solution or bath, as indicated and in accordance with the present invention, in the manner hereinafter set forth. The Concentrate A Solution is a concentrate of the present invention.

CONCENTRATE A SOLUTION

	Percent by weight
$Cu(NO_3)_2 \cdot 3H_2O$	10.0
Formalin	48.7
Methanol (95%)	30.8
Formaldehyde-methanol reaction product comprising primarily methylal, i.e. $CH_3—O—CH_2—O—CH_3$	7.0
H_2O	3.5

The Concentrate A Solution set forth immediately supra was prepared by admixing at room temperature the $Cu(NO_3)_2 \cdot 3H_2O$, the Formalin and the methanol in the proportions, by weight, of 10.0% of the $Cu(NO_3)_2 \cdot 3H_2O$, 55% of the Formalin and 35% of the methanol. The Formalin and methanol were maintained together in admixture in the presence of the cupric nitrate for a reaction time of 14 days to form in situ in the concentrate solution the formaldehyde-methanol reaction product containing primarily the methylal, e.e. $CH_3—O—CH_2—O—CH_3$.

CONCENTRATE B SOLUTION

	Percent by Weight
H_2O	84.0
NaOH	5.0
Na_2CO_3	1.0
Rochelle Salt	10.0

CONCENTRATE C SOLUTION

	Percent by Weight
H_2O	64.0
NaOH (50% solution)	30.0
Na_2CO_3	1.0
Rochelle Salt	5.0

The Concentrate B Solution and Concentrate C Solution set forth immediately supra were prepared by admixing the constituents specified at room temperature in the proportions specified. For replenishing the depleted chemical reduction copper plating solution containing residual amounts of cupric nitrate, formaldehyde, Rochelle salt, NaOH and Na_2CO_3, ⅓rd volume of the Concentrate A Solution and ⅔th volume of the Concentrate C Solution, totalling ⅚th volume, were added to the depleted plating solution. No bailout or removal of plating solution was required to maintain substantially constant volume of the plating bath as sufficient plating solution had been re-

moved by drag out and evaporation losses to accomplish this. The Concentrate A Solution and the chemical reduction copper plating solution contained only a non-objectionable low odor of formaldehyde due to the formaldehyde odor masking effect of the formaldehyde-methanol reaction product.

For makeup of a new, ready-to-use chemical reduction copper plating solution or bath, 1 volume of Concentrate A Solution, 2 volumes of Concentrate B Solution and 7 volumes of deionized water were mixed together. The resulting plating bath solution had only a low odor of formaldehyde, which was unobjectionable to workers in the immediate vicinity of the plating solution due to the formaldehyde odor-masking or eliminating effect of the formaldehyde-methanol reaction product comprising primarily the methylal.

EXAMPLE II

The concentrate solutions hereafter set forth were employed to replenish an exhausted chemical reduction copper plating solution, and to make up a new chemical reduction copper plating solution, as indicated and in accordance with the prior art:

CONCENTRATE A SOLUTION

	Percent by weight
$CuSO_4 \cdot 5H_2O$	5.0
H_2SO_4	0.03
Formaldehyde (37%)	20.0
H_2O	74.97

CONCENTRATE B SOLUTION

	Percent by weight
H_2O	85.3
NaOH	6.0
Na_2CO_3	0.5
Rochelle Salt	8.2

CONCENTRATE C SOLUTION

	Percent by weight
H_2O	77.0
NaOH	20.0
Rochelle salt	2.0
Na_2CO_3	1.0

For replenishing the depleted chemical reduction copper plating solution containing residual amounts of cupric sulfate, formaldehyde, Rochelle salt, NaOH, Na_2CO_3, H_2SO_4 and methanol, 1 volume of the Concentrate A Solution and ½ volume of the Concentrate C Solution, bath of this Example II and totalling 1½ volumes, were added to the depleted plating solution. It was necessary to bail-out or remove 1 volume of the plating solution prior to replenishment to maintain constant volume of the plating solution. The Concentrate A Solution of this Example II reeked of an objectionable, strong odor of formaldehyde, and the replenished chemical reduction copper plating solution also had an objectionable, strong odor of formaldehyde.

For make up of a new, ready-to-use chemical reduction copper plating solution or bath, 3 volumes of Concentrate A Solution, 3 volumes of Concentrate B Solution and 4 volumes of deionized water were mixed. The resulting plating solution had a strong odor of formaldehyde, which was objectionable to personnel in the immediate vicinity of the plating solution.

Although Rochelle salt is the preferred cupric ion complexer in the concentrate compositions and plating baths provided by this invention, other complexing agents are utilizable therein in place of the Rochelle salt such as, for example, EDTA or amines.

Additional examples of concentrate solutions of the present invention follows:

Example III

	Percent by weight
$Cu(NO_3)_2 \cdot 3H_2O$	10.0
Formalin	8.0
Methanol (95% methanol concentration)	28.8
Formaldehyde-methanol reaction product comprising primarily methylal	35.3
H_2O	17.9

The concentrate solution set forth immediately supra is prepared by admixing at room temperature the $Cu(NO_3)_2 \cdot 3H_2O$ the formalin, and methanol in the proportions, by weight of 10% of the $Cu(NO_3)_2 \cdot 3H_2O$, 40% of the formalin, and 50% of the methanol. The formalin and methanol are held together in the presence of the cupric nitrate for a sufficient reaction time to form in situ in the concentrate solution the formaldehyde-methanol reaction product containing primarily the methylal.

Example IV

	Percent by weight
$Cu(NO_3)_2 \cdot 3H_2O$	5.0
Formalin	17.5
Methanol (95%)	65.0
Formaldehyde-methanol reaction product comprising primarily methylal	8.3
H_2O	4.2

Such concentration solution set forth immediately supra is prepared by mixing together at room temperature the $Cu(NO_3)_2 \cdot 3H_2O$, the formalin, and methanol in the proportions, by weight, of 5% of the $Cu(NO_3)_2 \cdot 3H_2O$, 25% of the formalin and 70% of the methanol. The formalin and methanol are maintained together in the presence of the cupric nitrate for a sufficient reaction time to form in situ in the solution the formaldehyde-methanol reaction product comprising primarily the methylal.

The percentage of the formaldehyde-methanol reaction product comprising primarily the methylal set forth in Examples I, III and IV and elsewhere herein was calculated as methylal, i.e. $CH_3—O—CH_2—O—CH_3$.

What is claimed is:

1. In a method for replenishing a depleted electroless alkaline aqueous copper plating bath solution comprising cupric nitrate, formaldehyde and a complexing agent for the cupric ions, the improvement comprising adding to the depleted bath solution a replenisher concentrate solution containing the following constituents in proportions within the proportion ranges hereafter specified:

	Percent by weight
Cupric nitrate	About 1 to saturation.
Formalin	About 15–75.
Methanol, concentrated	About 1–84.

and an effective amount, sufficient to reduce considerably a formaldehyde odor of the electroless copper plating bath solution, of a formaldehyde-methanol reaction product comprising primarily $CH_3—O—CH_2—O—CH_3$, the formaldehyde-methanol reaction product being formed in situ in the concentrate solution as a constituent thereof by bringing together the concentrated methanol and Formalin in the presence of cupric nitrate for a time sufficient to obtain said formaldehyde-methanol reaction product.

2. The method of claim **1** wherein the concentrated methanol and formaldehyde are brought together in the presence of the cupric nitrate at a temperature in the range of room temperature to 120° F. inclusive and for a reaction time of at least one hour.

3. The method of claim **2** wherein the reaction time is in the range of one hour to about fourteen days.

4. The method of claim 1 wherein another replenisher concentrate solution comprising a complexing agent for the cupric ions, an alkaline material, and water is also added to the depleted plating bath solution.

5. The method of claim 4 wherein the cupric ion complexing agent in the depleted plating bath is Rochelle salt and the other complexing agent-containing replenisher concentrate contains Rochelle salt as the cupric ion complexing agent, and an alkali metal hydroxide and an alkali metal carbonate as the alkaline material.

6. A concentrate solution for use in chemical reduction copper plating solutions comprising the following constituents in proportions within the proportion ranges hereafter specified:

	Percent by weight
Cupric nitrate	About 1 to saturation.
Formalin	About 15–75.
Methanol, concentrated	About 1–84.

and an effective amount, sufficient to reduce considerably a formaldehyde odor of the chemical reduction copper plating bath utilizing formaldehyde as reducing agent, of a formaldehyde-methanol reaction product comprising

primarily $CH_3—O—CH_2—O—CH_3$, the formaldehyde-methanol reaction product being formed in situ in the concentrate solution as a constituent thereof by bringing together the concentrated methanol and formalin in the presence of the cupric nitrate for a time sufficient to obtain said formaldehyde-methanol reaction product.

7. The concentrate solution of claim 6 wherein the concentrated methanol and formaldehyde are brought together in the presence of cupric nitrate at a temperature in the range of room temperature to 120° F. inclusive and for a reaction time of at least one hour.

8. The concentrate solution of claim 7 wherein the reaction time is in the range of one hour to about fourteen days.

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