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AUTOCATALYTIC COPPER PLATING PROCESS AND SOLUTION

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The present invention relates to a copper plating process and solution.

More particularly, the invention relates to an autocatalytic chemical reduction process and bath for continuously plating desired thicknesses of copper on objects having catalytic metallic surfaces.

Heretofore, it has been necessary to electroplate copper onto the surfaces of objects where it is desired to have a relatively thick coating of copper (for example up to five thousandths of an inch thick). While this method of copper plating is satisfactory for many purposes, it is objectionable in that it requires the use of rather elaborate and somewhat expensive electrical equipment. Further, because of difficulty in positioning the electrodes used in electroplating processes, it is often difficult, if not impossible, to electroplate irregularly-shaped objects.

There are some known techniques for obtaining flash coatings of chemical plated copper; however, these techniques utilize chemical solutions which decompose spontaneously during the plating process. In order to obtain any substantial thickness of chemically plated copper by these known techniques, it would require a number of such flash coatings. However, because the chemicals in the solutions used in these techniques are spent in obtaining each such flash coating, such a procedure would be wasteful of chemicals, and hence too costly.

It is therefore one object of the present invention to provide new and improved commercially practicable copper plating solution and processes for the autocatalytic chemical plating of copper.

Another object of the invention is to provide new and improved copper plating solutions and processes which are capable of plating any desired thickness of copper, up to a predetermined minimum thickness, onto objects having any desired surface configuration or shape.

A still further object of the invention is to provide new and improved chemical copper plating solutions which are relatively stable, and which do not decompose spontaneously during the plating action.

A still further object of the invention is to provide copper plating solutions and processes having the above listed characteristics which do not require elaborate electrical or other equipment for use in conjunction therewith.

In practicing the invention an autocatalytic chemical reduction process for continuously plating copper on objects having a catalytic metallic surface is provided. This process utilizes an aqueous solution of a complex copper ion, a carbonate radical, a hydroxide radical, formaldehyde, and a complexing agent such as a tartrate or salicylate radical. For best results, the complex copper ion is present in an amount from .06 to .12 mole per liter of solution, the carbonate radical is present in an amount from .06 to .50 mole per liter of solution, and the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution is

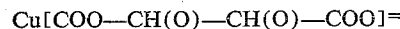
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within the range of .20 to .60. In carrying out the process, the object to be plated is immersed in a solution comprised as stated above, and copper plating by autocatalytic reaction of the solution at the catalytic metallic surface of the object takes place. During the plating action, the plating solution is circulated from a reservoir to a plating bath, and then back to the reservoir. The solution is heated to a temperature between 20° and 100° centigrade before introduction into the plating bath, and is cooled to a temperature between 20° and 30° centigrade before returning the solution to the reservoir. If desired, the solution may be filtered prior to being returned to the reservoir; however, the composition of the plating solution must be maintained by adding to the portion of the solution contained in the reservoir, appropriate amounts of soluble copper, hydroxide and formaldehyde containing reagents.

It has long been known in the copper mirroring industry that copper in alkaline solution can be reduced by formaldehyde. This familiar reaction is set forth in the following equation.

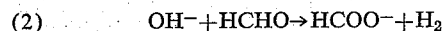


where the term (OH^-) represents a hydroxide radical, the term $HCHO$ represents formaldehyde, the term $Cu(II)$ represents a copper complex having the form

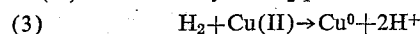


the term $HCOO^-$ is a formate radical, H_2O is water, and Cu^0 the deposited copper. A copper plating solution that utilizes this reaction to achieve chemical copper plating is disclosed in an article entitled "Formation of Copper Films on Non-Conductors"—a survey by Samuel Wein appearing in the Metal Finishing Magazine, August 1948 issue on page 58. The solution disclosed in the above-identified article, and all other previously known chemical copper plating solutions, achieve a flash coating of copper with a simultaneous breakdown or general decomposition of the chemicals of the solution. While the extremely thin films of copper obtained by these known flash coating solutions and techniques may be satisfactory for copper mirroring purposes, the thin films of copper thus obtained are not adequate for use (for example) to form electrical conductors capable of carrying considerable amounts of electric current. In order to obtain sufficiently thick copper films for such a purpose with previously known techniques, it would be necessary to carry out a number of flash coatings of the object to be copper plated. Because the chemicals in these copper plating solutions are decomposed during the flash coating process, the solutions are spent and cannot be regenerated. Hence, such a method of building up comparatively thick coatings of copper would be quite expensive, and prohibits the use of such procedure on a commercial scale.

The present invention is designed to achieve copper plating by the reduction of $Cu(II)$ in a system in



[F. Hartwagner, Z. Anal. Chem. 52, 17-20, 1913], which the reaction represented by Equation 2 is taking place. The above Reaction 2 is catalyzed by a copper surface. $Cu(II)$ is reduced by the H_2 produced



or by the activated complex in Reaction 2. The plating, therefore, is an autocatalytic process. That is, the plated copper surface itself serves as a catalyst to the reaction leading to copper plating. Hence, any desired thickness of copper plating may be built up on the object to be plated. This autocatalytic chemical copper plating action is achieved by stabilizing the plating solution used in

carrying out the plating process. In accordance with the present invention, stabilization of the plating solution is obtained by use of proper proportions of the constituents of the plating solution, operation of the plating solution in a desired temperature range for the particular ingredients used to make up a particular plating solution, and the use of a suitable stabilizing agent in proper amounts. When thus properly constituted, the plating solution does not decompose generally, and will autocatalytically plate copper on certain catalytic metallic surfaces. Further, because this plating reaction takes place without any general decomposition of the plating solution, the plating process can be continued over long periods of time by continuous regeneration of the chemicals of the bath that are spent by reason of the plating action.

COMPOSITION OF PLATING SOLUTION

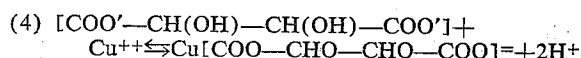
In any copper plating process attempting to carry out the reactions set forth in Equations 2 and 3, it is of course essential that a plating solution be provided wherein all of the constituents listed in Equations 2 and 3 are present. In order to provide a chemical copper plating bath having the proper constituents, and the proper proportions of such constituents, and thereby obtain the stable characteristics required for autocatalytic chemical copper plating in accordance with the invention, it is necessary that the constituents of the plating bath fall within the proportions listed in the below-set-forth Table No. 1. Table No. 1 identifies three general types of plating solutions formed in accordance with the present invention, and identifies the constituents of the solutions. The constituents of the solutions are listed in moles per liter of solution, and the solutions set forth are intended to be operated within the temperature range of 20 degrees to 100 degrees centigrade.

Table No. 1

Plating solution type.....	I		II		III	
	Low	High	Low	High	Low	High
Limits of proportions in moles per liter of solution.....						
Complex copper ion, [Cu(II)].....	0.06	0.12	0.06	0.12	0.06	0.12
Hydroxide radical, (OH).....	0.5	1.5	0.5	1.5	0.5	1.5
Formaldehyde, (HCHO).....	0.3	5.0	0.3	5.0	0.3	5.0
Carbonate, (CO ₃).....	0.06	0.5	0.06	0.5	0.06	0.5
Tartrate, [COO—CH(OH)—CH(OH)—COO].....	0.1	0.4			0.1	0.4
Salicylate, (HO—C ₆ H ₄ —COO).....			0.1	0.4	0.01	0.4
Water, (H ₂ O).....	Remainder to 1 liter					

In addition to the above conditions, for the best results, it is desirable that the ratio between the complex copper ions and the carbonate ions in the plating solution expressed in moles per liter of solution be within the range .20 to .60.

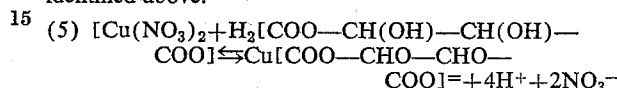
One of the difficulties encountered in providing a chemical copper plating solution is the tendency of the copper ions to go out of solution. To overcome this difficulty, it has proven necessary to complex the copper ions by means of a suitable complexing agent added to the plating solution. One known suitable complexing agent is described in the Journal of the Indian Chemical Society, volume 27, No. 12, 1950, in a series of articles entitled "Metallic Complexes of Tartaric and Citric Acids"; "Part I, Copper-Tartaric Acid," pages 443-454; and "Part II, Copper-Akali Tartrate," pages 683 to 690, by R. N. Sen Sarma. This complexing agent reacts with the copper ions in the following general manner to form a copper complex that is readily maintained in solution.



It can be appreciated from an examination of Equation 4 that the reaction product of the tartrate radical with the copper ion is the copper complex [Cu(II)] identified above as a constituent of the plating solutions comprising

a part of the present invention. It is this copper complex that takes part in the reaction set forth in Equation 3 to effect autocatalytic copper plating on objects having a catalytic metallic surface.

The following lists of copper salts, among others, are suitable for forming the copper complex identified in the reaction of Equation 4. These copper salts are cupric salicylate, cupric tartrate, cupric carbonate, cupric nitrate, cupric chloride, cupric sulfate, and cupric hydroxide. A typical reaction involving one of these copper salts and tartaric acid to form the desired copper complex is set forth in Equation 5, and is exemplary of the complexing action of the tartrate radical on any of the copper salts identified above.



By comparison of Equation 5 to Equation 4, it can be appreciated that the reactions set forth therein are identical except for the fact that Equation 4 expresses the reaction in general terms.

The tartrate radical required in the reaction set forth in Equation 4, may be supplied from any one of the following lists of tartrate bearing compounds, amongst others. These compounds are—tartaric acid, sodium tartrate, potassium tartrate, cupric tartrate and sodium potassium tartrate.

In addition to the tartrate radical, it has been discovered that the salicylate radical will serve as a suitable complexing agent for carrying out a complexing reaction similar to that set forth in Equation 4. No formulation of the salicylate complexing reaction has been worked out at this time; however, it has been observed that

salicylate will hold the copper ions in solution in a fashion similar to tartrate, and for this reason it is believed that salicylate complexes the copper ion in a similar manner. Suitable ingredients for providing a salicylate radical to a plating solution in order to achieve this end are set forth in the following list. These ingredients are—salicylic acid, sodium salicylate, potassium salicylate and cupric salicylate.

In addition to both the tartrate and salicylate radicals, it has been determined that combinations of tartrate and salicylate in a plating bath can achieve complexing of the copper ion in the manner set forth in the reaction of Equation 4. Any of the particular tartrate or salicylate bearing ingredients set forth in the above lists are suitable for use in combination to achieve the desired complexing. From the results obtained by using salicylate alone, and combinations of salicylate with tartrate, as a complexing agent, it appears that the tartrate radical performs somewhat better as a complexing agent. This belief is based on the fact that less filtering of plating solutions using tartrate was required after extended periods of use of the plating solutions; hence indicating, that if the tartrate is used as a complexing agent, or if it is present with salicylate, there is a little less decomposition of the plating solution after extended periods of use.

In addition to the presence of a copper complex, the reaction set forth in Equations 2 and 3 requires the presence of a formaldehyde radical which serves as a reducing agent. This formaldehyde radical may be supplied from a pure or aqueous solution of formaldehyde.

To complete the reaction set forth in Equation 2, it is necessary to provide a hydroxide radical which is believed to catalyze the reaction. Amongst others, suitable sources of the hydroxide radical are—sodium hydroxide, potassium hydroxide and cupric hydroxide.

In order that the copper plating reaction set forth in Equations 2 and 3 take place autocatalytically, it is essential that no general spontaneous decomposition of the bath or plating solution take place. To prevent any such spontaneous general decomposition of the plating solution, it was determined that a stabilizing agent was required in the solutions in order to assure autocatalytic reduction of copper at the surface of objects having catalytic metallic surfaces immersed in the solutions. Further, it was discovered that the carbonate radical provided the most effective stabilizing agent for plating solutions of this character, and that the ratio of the complex copper ions present in the solution to the carbonate ions, was fairly critical. For best results, this ratio expressed in moles per liter of solution should range between .2 and .6. In addition to stabilizing the plating solution, it is believed that the carbonate radical also serves to help keep the copper ions in solution; hence, the carbonate radical serves as a complexing agent in a manner somewhat similar to tartrate and salicylate. Amongst others, suitable sources of carbonate for use as a stabilizing agent are—sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, cupric carbonate, and basic cupric carbonate.

The manner in which the new and improved chemical copper plating solutions are made up, can be quite important in that if the ingredients are placed in the plating solution in an improper order, it may vary well happen that not all the ingredients will become dissolved in the solution. For this reason, the following procedure is suggested for making up copper plating solutions in accordance with the invention. First dissolve the copper containing salt in a quantity of water to form a first solution. Next dissolve the tartrate and/or salicylate salts in a quantity of water to form a second solution. Then dissolve the hydroxide and carbonate bearing ingredients in a quantity of water to form a third solution. Add the first and second solutions together, and to the resulting mixture add the third solution. Finally, add formaldehyde and a quantity of water necessary to bring the total to one liter to make up the plating solution. It is, of course, understood that the quantities of ingredients added are in accordance with teachings of the above tables, and that the solutions are maintained within the temperature range prescribed. Examples of six different plating solutions made up in accordance with the teachings of the invention, are set forth in Table No. 2 below, and brief descriptions of the particular ingredients used in forming each solution are listed. Concentrations in Table No. 2 are given in moles/liter.

Table No. 2

Temperature range in degrees centigrade	20°-30°	40°-52°	70°-75°	75°-80°	80°-100°	25°-30°
Plating solution	#1	#2	#3	#4	#5	#6
Copper complex [Cu(II)]	0.062	0.117	0.07	0.07	0.117	0.12
Hydroxide	0.5	1.25	0.875	0.875	.05	1.25
Formaldehyde	1.1	.88	.55	.55	.33	.22
Carbonate	0.12	.476	.06	.06	.30	.30
Tartrate	.016	.227		.266	.283	.283
Salicylate		.58	.362	.362		
Solvent (H ₂ O)	Remainder of solution up to 1 liter					

The plating baths listed in Table No. 2 were made up of the following ingredients expressed in grams/liter unless otherwise indicated.

Bath #1:

5	Cupric nitrate, Cu(NO ₃).3H ₂ O	15 gm./l.
	Sodium hydroxide (NaOH)	20 gm./l.
	Formaldehyde (HCHO)	100 ml., 36% solution.
10	Sodium bicarbonate (NaHCO ₃)	10 gms./l.
	Sodium potassium tartrate (NaKC ₄ H ₄ O ₆ .4H ₂ O)	30 gms./l.
	Water (H ₂ O), remainder to one liter.	

Bath #2:

15	Cupric chloride (CuCl ₂ .2H ₂ O)	20 gms./l.
	Sodium hydroxide (NaOH)	50 gms./l.
	Formaldehyde (HCHO)	80 ml., 36% solution.
	Sodium bicarbonate (NaHCO ₃)	40 gms./l.
20	Sodium potassium tartrate (NaKC ₄ H ₄ O ₆ .4H ₂ O)	64 gms./l.
	Salicylic acid (HOC ₆ H ₄ COOH)	80 gms./l.
	Water (H ₂ O), remainder to one liter.	

Bath #3:

25	Cupric chloride (CuCl ₂ .2H ₂ O)	12 gms./l.
	Sodium hydroxide (NaOH)	35 gms./l.
	Formaldehyde (HCHO)	50 ml., 36% solution.
	Sodium bicarbonate (NaHCO ₃)	5 gms./l.
30	Sodium potassium tartrate (NaKC ₄ H ₄ O ₆ .4H ₂ O)	75 gms./l.
	Salicylic acid (HOC ₆ H ₄ COOH)	50 gms./l.
	Water (H ₂ O), remainder to one liter.	

Bath #4:

35	Cupric chloride (CuCl ₂ .2H ₂ O)	12 gms./l.
	Sodium hydroxide (NaOH)	35 gms./l.
	Formaldehyde (HCHO)	50 ml., 36% solution.
40	Sodium bicarbonate (NaHCO ₃)	5 gms./l.
	Salicylic acid (HOC ₆ H ₄ COOH)	50 gms./l.
	Water (H ₂ O), remainder to one liter.	

Bath #5:

45	Cupric chloride (CuCl ₂ .2H ₂ O)	20 gms./l.
	Sodium hydroxide (NaOH)	20 gms./l.
	Formaldehyde (HCHO)	30 ml., 36% solution.
	Sodium bicarbonate (NaHCO ₃)	25 gms./l.
50	Sodium potassium tartrate (NaKC ₄ H ₄ O ₆ .4H ₂ O)	80 gms./l.
	Water (H ₂ O), remainder to one liter.	

Bath #6:

55	Cupric sulfate (CuSO ₄)	30 gms./l.
	Sodium hydroxide (NaOH)	50 gms./l.
	Formaldehyde (HCHO)	200 ml., 36% solution.
	Sodium bicarbonate (NaHCO ₃)	25 gms./l.
60	Sodium potassium tartrate (NaKC ₄ H ₄ O ₆ .4H ₂ O)	80 gms./l.
	Water (H ₂ O), remainder to one liter.	

AUTOCATALYTIC COPPER PLATING PROCESS

The present invention further comprises an autocatalytic chemical reduction process for plating catalytic metallic surfaces with copper. This process has been found to provide selective chemical deposition of copper on catalytic metallic surfaces with no appreciable copper being precipitated to the bottom of the reaction vessel containing the plating solution, or being deposited on its walls. The copper is deposited in substantially pure, metallic form, and has good adhesion to the catalytic metallic surface being plated. In tests, the autocatalytically chemically plated copper has been found to have substantially the same properties as electro-deposited copper plating.

In carrying out the process, the source of plating copper is a complex copper ion contained in the plating solution, and upon an object to be plated being immersed in the plating bath, the reaction set forth in Equation 2 is catalyzed by the catalytic metallic surface of the object. Metals which serve to catalyze the reaction set forth in Equation 2 include copper, and as copper is produced by Reaction 3, it can be stated that the reaction is autocatalytic, and that copper can be plated to any desired thickness within certain practical limits. Other metals which are known to catalyze the reaction set forth in Equation 2 are nickel, silver, palladium, platinum, and gold. It is, of course, possible to provide an object with a catalytic metallic surface in order to copper plate the same by means of the present invention. For example, nickel is known to be a catalytic material and all of the following list of elements can be nickel-plated by means of the autocatalytic chemical reduction of nickel in the presence of a low concentration of hypophosphite as taught by Brenner and Ridell in an article entitled "Nickel Plating on Steel by Chemical Reduction," Journal of Research of the National Bureau of Standards, volume 37, July 1946, pages 31 to 34. These materials are copper, silver, gold, beryllium, boron, germanium, aluminum, thallium, silicon, carbon, vanadium, molybdenum, tungsten, chromium, selenium, tellurium, titanium, iron, cobalt, nickel, palladium, and platinum. Additionally, by proper treatment of the surface thereof in a known manner, it is possible to provide a sheet of insulating material, such as a phenolic plastic, with a catalytic metallic surface. This may be achieved, for example, by providing the sheet of insulating material with a flash coating of silver or nickel or other metallic crystals on the areas desired to be copper plated, and subsequently immersing the catalyzed sheet of material in a bath prepared in accordance with the present invention. In this manner, it is possible to autocatalytically deposit a layer of copper on the sheet of insulating material which is sufficiently thick to serve as an electrical conductor, for example.

Having provided the object to be copper plated with a catalytic metallic surface, if the object is not formed from a catalytic metallic material, the object is then ready to be plated by immersing the same in a plating solution prepared in accordance with the teachings set forth above. No special pre-plating treatment of the object is required other than providing it with a catalytic metallic surface, and seeing that the catalytic metallic surface is clean. Any of the conventional methods of cleaning metallic surfaces may be used insofar as cleaning of the catalytic metallic surface is concerned. For example, water rinsing has been proven to be quite adequate in many instances. The object to be plated is then immersed in the plating bath in a manner such that all of the surface to be plated is exposed to the plating solution. It has been determined, that the size of the object or surface to be plated with respect to the size of the reaction vessel in which the plating solution is contained, is not too critical. As is to be expected, however, the larger the object to be

plated with respect to the total amount of plating solution available, the faster the ingredients of the plating solution will be used in the plating reaction, and the faster such ingredients must be replenished. For this reason, there is an optimum relationship to be maintained between these two parameters in order that the proportions of the constituents of the solutions be maintained within the range of values listed in Table No. 1. It is of course essential that the objects being plated be immersed in the plating solution for a sufficiently long period of time to build up the thickness of the plated copper to a desired value.

Upon immersion of the object to be plated in the copper plating solution, the immersed object is copper plated by autocatalytic reaction of the solution at the catalytic metallic surface of the object. This reaction is depicted by Equations 2 and 3 and results in the deposition of copper on the catalytic metallic surface of the object. In carrying out the copper plating reaction depicted by Equations 2 and 3 the copper salts, the hydroxide radical and the formaldehyde radical become depleted, consequently, it is necessary to continually replenish the supply of these constituents during the plating action. Accordingly, if the plating reaction is to be carried out on a commercial scale wherein large numbers of objects are plated over extended periods of time, it is desirable that a suitable installation for continuous regeneration of the plating solution be provided. For this reason, any installation that is designed to carry on extended plating operations by means of the present invention, should include both a reservoir for the plating solution, and a reaction vessel or plating bath in which plating takes place, together with equipment for circulating the plating solution between the reservoir and the plating bath. Additionally, means must be provided for heating the plating solution to a temperature between 20 degrees and 100 degrees centigrade before introduction into the plating bath, and means should be provided for cooling the plating solution to a temperature between 20 degrees and 30 degrees centigrade before returning the solution to the reservoir. It is also desirable that the plating solution be filtered at some stage subsequent to cooling of the solution, and prior to its being reheated. Further, in order to revitalize the constituents of plating solution that are depleted during the plating action, the portion of the plating solution contained in the reservoir should have appropriate amounts of soluble copper, hydroxide and formaldehyde containing reagents added thereto. In this manner the proportions of the constituents of the plating solution are maintained so that they always fall within the prescribed range of values set forth in Table No. 1.

By means of the present invention, it has been possible to build up chemically deposited copper coatings having a total thickness as great as .004 inch, at a rate of about .00008 inch per hour. The resulting copper coatings were determined to have good mechanical adhesion to the objects upon which they were plated, and to provide a coating comparable to electrodeposited copper.

From the foregoing description, it can be appreciated that the invention provides a commercially practicable chemical copper plating solution and process for the autocatalytic chemical plating of copper on objects having catalytic metallic surfaces. By means of the invention relatively thick coatings of copper may be plated without requiring the use of elaborate and expensive electrical equipment, and yet, any desired thicknesses of copper plating may be formed up to predetermined maximum thickness limits. Further, chemical copper plating may be readily formed on irregularly shaped objects and surfaces, and assures that such irregularly shaped objects and surfaces will receive a uniform coating of copper. Also the invention provides a plating solution and process capable of carrying out the above objectives which is

relatively stable, and easy to operate. This characteristic allows those portions of the plating solution which are exhausted during continuous and extended plating operations to be continuously renewed by supplying to the plating solution appropriate amounts of the depleted reagents, thereby making feasible chemical copper plating operations on a commercial scale.

Obviously, other modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that changes may be made in the particular embodiments of the invention described which are within the full intended scope of the invention as defined by the appended claims.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. A bath for the autocatalytic chemical plating of copper on a catalytic metallic surface, the bath essentially comprising an aqueous solution of a complex copper ion present in an amount from .06 to .12 mole per liter of solution, a carbonate radical present in an amount from .06 to .50 mole per liter of solution, a hydroxide radical, formaldehyde and a complexing agent.

2. The bath set forth in claim 1 wherein the catalytic metallic surface essentially comprises an element selected from the group consisting of nickel, silver, palladium, copper, platinum and gold, the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution is within the range .20 to .60, and the temperature of the bath is maintained between 20 degrees and 100 degrees centigrade.

3. A bath for the autocatalytic chemical plating of copper on a catalytic metallic surface, the bath essentially comprising an aqueous solution of a complex copper ion present in an amount from .06 to .12 mole per liter of solution, a carbonate radical present in an amount from .06 to .50 mole per liter of solution, a hydroxide radical, formaldehyde, and a complexing agent comprising a tartrate radical.

4. The bath set forth in claim 3 wherein the catalytic metallic surface essentially comprises an element selected from the group consisting of nickel, silver, palladium, copper, platinum, and gold, the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution is within the range .20 to .60 and the temperature of the bath is maintained between 20 degrees and 100 degrees centigrade.

5. A bath for the autocatalytic chemical plating of copper on a catalytic metallic surface essentially comprising an element selected from the group consisting of nickel, silver, palladium, copper, platinum and gold, the bath essentially comprising an aqueous solution of a complex copper ion present in an amount from .06 to .12 mole per liter of solution, a carbonate radical present in an amount from .06 to .50 mole per liter of solution, a hydroxide radical, formaldehyde, and a complexing agent comprising a salicylate radical, the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution being within the range .20 to .60, and the temperature of the bath being maintained between 20 degrees and 100 degrees centigrade.

6. A bath for the autocatalytic chemical plating of copper on a catalytic metallic surface essentially comprising an element selected from the group consisting of nickel, silver, palladium, copper, platinum and gold, the bath essentially comprising an aqueous solution of a complex copper ion $[\text{Cu}(\text{II})]$ present in an amount from .06 to .12 mole per liter of solution, a carbonate radical (CO_3^-) present in an amount from .06 to .50 mole per liter of solution, a hydroxide radical (OH^-), formaldehyde (HCHO), a tartrate radical



and a salicylate radical ($\text{HOC}_6\text{H}_4\text{COO}^-$), the ratio between the complex copper ions and the carbonate ions

in the bath expressed in moles per liter of solution being within the range .20 to .60, and the temperature of the bath being maintained between 20 degrees and 100 degrees centigrade.

7. A bath for the autocatalytic chemical plating of copper on a catalytic metallic surface, the bath essentially comprising an aqueous solution of a complex copper ion present in an amount from .06 to .12 mole per liter of solution, a carbonate radical present in an amount from .06 to .50 mole per liter of solution, a hydroxide radical present in an amount from .50 to 1.50 moles per liter of solution, and formaldehyde present in an amount from 1.0 to 5.0 moles per liter of solution.

8. The bath set forth in claim 7 wherein the catalytic metallic surface essentially comprises an element selected from the group consisting of nickel, silver, palladium, copper, platinum and gold, the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution is within the range .20 to .60, and the temperature of the bath is maintained between 20 degrees and 100 degrees centigrade.

9. A bath for the autocatalytic chemical plating of copper on a catalytic metallic surface essentially comprising an element selected from the group consisting of nickel, silver, palladium, copper, platinum and gold, the bath essentially comprising an aqueous solution of a complex copper ion present in an amount from .06 to .12 mole per liter of solution, a carbonate radical present in an amount from .06 to .50 mole per liter of solution, a hydroxide radical present in an amount from .50 to 1.50 moles per liter of solution, formaldehyde present in an amount from .30 to 5.0 moles per liter of solution, and a tartrate radical, the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution being within the range .20 to .60, and the temperature of the bath being maintained between 20 degrees and 100 degrees centigrade.

10. A bath for the autocatalytic chemical plating of copper on a catalytic metallic surface essentially comprising an element selected from the group consisting of nickel, silver, palladium, copper, platinum and gold, the bath essentially comprising an aqueous solution of a complex copper ion present in an amount from .06 to .12 mole per liter of solution, a carbonate radical present in an amount from .06 to .50 moles per liter of solution, a hydroxide radical present in an amount from .50 to 1.50 moles per liter of solution, formaldehyde present in an amount from .30 to 5.0 moles per liter of solution, a tartrate radical, and a salicylate radical, the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution being within the range .20 to .60, and the temperature of the bath being maintained between 20 degrees and 100 degrees centigrade.

11. A bath for the autocatalytic chemical plating of copper on a catalytic metallic surface essentially comprising an element selected from the group consisting of nickel, silver, palladium, copper, platinum and gold, the bath essentially comprising an aqueous solution of a complex copper ion present in an amount from .06 to .12 mole per liter of solution, a carbonate radical present in an amount from .06 to .50 mole per liter of solution, a hydroxide radical present in an amount from .50 to 1.50 moles per liter of solution, formaldehyde present in an amount from .30 to 5.0 moles per liter of solution, and a salicylate radical, the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution being within the range .20 to .60, and the temperature of the bath being maintained between 20 degrees and 100 degrees centigrade.

12. A bath for the autocatalytic chemical plating of copper on a catalytic metallic surface, the bath essentially comprising an aqueous solution of a complex copper ion present in an amount from 0.6 to .12 moles per liter of solution, a carbonate radical present in an amount from .06

11

to .50 mole per liter of solution, a hydroxide radical present in an amount from .50 to 1.50 moles per liter of solution, formaldehyde present in an amount from .30 to 5.0 moles per liter of solution, a tartrate radical present in an amount from .10 to .40 mole per liter of solution, and a salicylate radical present in amount from 0 to .40 mole per liter of solution.

13. The bath set forth in claim 12 wherein the catalytic metallic surface essentially comprises an element selected from the group consisting of nickel, silver, palladium, copper, platinum and gold, the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution is within the range .20 to .60, and the temperature of the bath is maintained between 20 degrees and 100 degrees centigrade.

14. A bath for the autocatalytic chemical plating of copper on a catalytic metallic surface, the bath essentially comprising an aqueous solution of a complex copper ion present in an amount from .06 to .12 mole per liter of solution, a carbonate radical present in an amount from .06 to .50 mole per liter of solution, a hydroxide radical present in an amount from .50 to 1.50 moles per liter of solution, formaldehyde present in an amount from .30 to 5.0 moles per liter of solution, and a salicylate radical present in amount from .10 to .40 mole per liter of solution.

15. The bath set forth in claim 14 wherein the catalytic metallic surface essentially comprises an element selected from the group consisting of nickel, silver, palladium, copper, platinum, and gold, the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution is within the range .20 to .60, and the temperature of the bath is maintained between 20 degrees and 100 degrees centigrade.

16. A bath for the autocatalytic chemical plating of copper on a catalytic metallic surface, the bath essentially comprising an aqueous solution of a complex copper ion formed from a copper salt selected from the group consisting of cupric salicylate, cupric tartrate, cupric carbonate, cupric nitrate, cupric chloride, cupric sulfate, and cupric hydroxide, a carbonate radical selected from the group consisting of sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, cupric carbonate, basic cupric carbonate, formaldehyde selected from pure or an aqueous solution of formaldehyde, a hydroxide radical selected from the group consisting of sodium hydroxide, potassium hydroxide, and cupric hydroxide, and a complexing agent.

17. The bath set forth in claim 16 wherein the catalytic metallic surface essentially comprises an element selected from the group consisting of nickel, silver, palladium, copper, platinum and gold, the complex copper ion is present in the solution in an amount from .06 to .12 mole per liter of solution, the carbonate radical is present in the amount from .06 to .50 mole per liter of solution, the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution is within the range .20 to .60, and the temperature of the bath is maintained between 20 degrees and 100 degrees centigrade.

18. The bath set forth in claim 14 wherein the catalytic metallic surface essentially comprises an element selected from the group consisting of nickel, silver, palladium, copper, platinum and gold, the complex copper ion is present in the solution in an amount from 0.6 to .12 mole per liter of solution, the carbonate radical is present in an amount from .06 to .50 mole per liter of solution, formaldehyde is present in an amount from .30 to 5.0 moles per liter of solution, the hydroxide radical is present in an amount from .50 to 1.5 moles per liter of solution, the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution is within the range .20 to .60, and the temperature of the bath is maintained between 20 degrees and 100 degrees centigrade.

12

19. A bath for the autocatalytic chemical plating of copper on a catalytic metallic surface, the bath essentially comprising an aqueous solution of a complex copper ion formed from a copper salt selected from the group consisting of cupric salicylate, cupric tartrate, cupric carbonate, cupric nitrate, cupric chloride, cupric sulfate, and cupric hydroxide, a carbonate radical selected from the group consisting of sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, cupric carbonate, and basic cupric carbonate, a hydroxide radical selected from the group consisting of sodium hydroxide, potassium hydroxide and cupric hydroxide, formaldehyde from pure or an aqueous solution of formaldehyde, a tartrate radical selected from the group consisting of tartaric acid, sodium tartrate, potassium tartrate, cupric tartrate, and sodium-potassium tartrate, and a salicylate radical selected from the group consisting of salicylic acid, sodium salicylate, potassium salicylate, and cupric salicylate.

20. The bath set forth in claim 19 wherein the catalytic metallic surface essentially comprises an element selected from the group consisting of nickel, silver, palladium, copper, platinum and gold, the complex copper ion is present in the solution in an amount from .06 to .12 mole per liter of solution, and the carbonate radical is present in the amount from .06 to .50 mole per liter of solution, the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution is within the range .20 to .60, and the temperature of the bath is maintained between 20 degrees and 100 degrees centigrade.

21. The bath set forth in claim 19 wherein the catalytic metallic surface essentially comprises an element selected from the group consisting of nickel, silver, palladium, copper, platinum and gold, the complex copper ion is present in the solution in an amount from .06 to .12 mole per liter of solution, the carbonate radical is present in an amount from .06 to .50 mole per liter of solution, formaldehyde is present in an amount from .30 to 5.0 moles per liter of solution, the hydroxide radical is present in an amount from .50 to 1.5 moles per liter of solution, the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution is within the range .20 to .60, and the temperature of the bath is maintained between 20 degrees and 100 degrees centigrade.

22. The bath set forth in claim 19 wherein the catalytic metallic surface essentially comprises an element selected from the group consisting of nickel, silver, palladium, copper, platinum and gold, the complex copper ion is present in the solution in an amount from .06 to .12 mole per liter of solution, the carbonate radical is present in an amount from .06 to .50 mole per liter of solution, formaldehyde is present in an amount from .30 to 5.0 moles per liter of solution, the hydroxide radical is present in an amount from .50 to 1.50 moles per liter of solution, the tartrate radical is present in an amount from .10 to .40 mole per liter of solution, and the salicylate radical is present in an amount from 0 to .40 mole per liter of solution, the ratio between the complex copper ions and the carbonate ions in the bath is within the range of .20 to .60, and the temperature of the bath is maintained between 20 degrees and 100 degrees centigrade.

23. A bath for the autocatalytic chemical plating of copper on a catalytic metallic surface, the bath essentially comprising an aqueous solution of a complex copper ion formed from a copper salt selected from the group consisting of cupric salicylate, cupric tartrate, cupric carbonate, cupric nitrate, cupric chloride, cupric sulfate, and cupric hydroxide, a carbonate radical selected from the group consisting of sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, cupric carbonate and basic cupric carbonate, a hydrox-

ide radical selected from the group consisting of sodium hydroxide, potassium hydroxide, and cupric hydroxide, formaldehyde selected from pure or an aqueous solution of formaldehyde, and a tartrate radical selected from the group consisting of tartaric acid, sodium tartrate, potassium tartrate, cupric tartrate, and sodium-potassium tartrate.

24. The bath set forth in claim 23 wherein the catalytic metallic surface essentially comprises an element selected from the group consisting of nickel, silver, palladium, copper, platinum, and gold, the complex copper ion is present in the solution in an amount from .06 to .12 mole per liter of solution, and the carbonate radical is present in the amount from .06 to .50 mole per liter of solution, the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution is within the range .20 to .60, and the temperature of the bath is maintained between 20 degrees and 100 degrees centigrade.

25. The bath set forth in claim 23 wherein the catalytic metallic surface essentially comprises an element selected from the group consisting of nickel, silver, palladium, copper, platinum, and gold, the complex copper ion is present in the solution in an amount from .06 to .12 mole per liter of solution, the carbonate radical is present in an amount from .06 to .50 mole per liter of solution, formaldehyde is present in an amount from .30 to 5.0 moles per liter of solution, the hydroxide radical is present in an amount from .50 to 1.5 moles per liter of solution, the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution is within the range .20 to .60, and the temperature of the bath is maintained between 20 degrees and 100 degrees centigrade.

26. A bath for the autocatalytic chemical plating of copper on a catalytic metallic surface, the bath essentially comprising an aqueous solution of a complex copper ion formed from a copper salt selected from the group consisting of cupric salicylate, cupric tartrate, cupric carbonate, cupric nitrate, cupric chloride, cupric sulfate, and cupric hydroxide, a carbonate radical selected from the group consisting of sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, cupric carbonate, and basic cupric carbonate, a hydroxide radical selected from the group consisting of sodium hydroxide, potassium hydroxide, and cupric hydroxide, formaldehyde selected from pure or an aqueous solution of formaldehyde, and a salicylate radical selected from the group consisting of salicylic acid, sodium salicylate potassium salicylate, and cupric salicylate.

27. The bath set forth in claim 26 wherein the catalytic metallic surface essentially comprises an element selected from the group consisting of nickel, silver, palladium, copper, platinum and gold, the complex copper ion is present in the solution in an amount from .06 to .12 mole per liter of solution, and the carbonate radical is present in the amount from .06 to .50 mole per liter of solution, the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution is within the range .20 to .60, and the temperature of the bath is maintained between 20 degrees and 100 degrees centigrade.

28. The bath set forth in claim 26 wherein the catalytic metallic surface essentially comprises an element selected from the group consisting of nickel, silver, palladium, copper, platinum and gold, the complex copper ion is present in the solution in an amount from .06 to .12 mole per liter of solution, formaldehyde is present in an amount from .30 to 5.0 moles per liter of solution, the hydroxide radical is present in an amount from .50 to 1.5 moles per liter of solution, the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution is within the range .20 to .60, and the temperature of the bath

is maintained between 20 degrees and 100 degrees centigrade.

29. The bath set forth in claim 26 wherein the catalytic metallic surface essentially comprises an element selected from the group consisting of nickel, silver, palladium, copper, platinum, and gold, the complex copper ion is present in the solution in an amount from .06 to .12 mole per liter of solution, the carbonate radical is present in an amount from .06 to .50 mole per liter of solution, formaldehyde is present in an amount from .30 to 5.0 moles per liter of solution, the hydroxide radical is present in an amount from .50 to 1.50 moles per liter of solution, the salicylate radical is present in an amount from .10 to .40 mole per liter of solution, the ratio between the complex copper ions and the carbonate ions in the bath is within the range .20 to .60, and the temperature of the bath is maintained between 20 degrees and 100 degrees centigrade.

30. An autocatalytic chemical reduction process for continuously plating copper on objects having a catalytic metallic surface comprising the steps of providing an aqueous solution of a complex copper ion, a carbonate radical, a hydroxide radical, formaldehyde, and a complexing agent, immersing an object to be plated in said solution, and copper plating said immersed object by autocatalytic reaction of said solution at the catalytic metallic surface of the object.

31. The process set forth in claim 30 wherein the catalytic metallic surface essentially comprises an element selected from the group consisting of nickel, silver, palladium, copper, platinum and gold, the temperature of the aqueous solution is maintained between 20 degrees and 100 degrees centigrade, and the solution is continuously regenerated during plating by adding thereto appropriate amounts of soluble copper, hydroxide and formaldehyde containing reagents.

32. An autocatalytic chemical reduction process for continuously plating copper on objects having a catalytic metallic surface comprising the steps of providing an aqueous solution of a complex copper ion present in an amount from .06 to .12 mole per liter of solution, a carbonate radical present in an amount from .06 to .50 mole per liter of solution, a hydroxide radical, formaldehyde, and a complexing agent, immersing an object to be plated in said solution, and copper plating the immersed metal object by autocatalytic reaction of said solution at the catalytic metallic surface of the object.

33. The process set forth in claim 32 wherein the catalytic metallic surface essentially comprises an element selected from the group consisting of nickel, silver, palladium, copper, platinum and gold, the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution is within the range .20 to .60, the temperature of the aqueous solution is maintained between 20 degrees and 100 degrees centigrade, and the solution is continuously regenerated during plating by adding thereto appropriate amounts of soluble copper, hydroxide and formaldehyde containing reagents.

34. An autocatalytic chemical reduction process for continuously plating copper on objects have a catalytic metallic surface comprising the steps of providing an aqueous solution of a complex copper ion present in an amount from .06 to .12 mole per liter of solution, a carbonate radical present in an amount from .06 to .50 mole per liter of solution, a hydroxide radical present in an amount from .50 to 1.50 moles per liter of solution, and formaldehyde present in an amount from .30 to 5.0 moles per liter of solution, and a complexing agent, immersing an object to be plated in said solution, and copper plating the immersed object by autocatalytic reaction of said solution at the catalytic metallic surface of the object.

15

35. The process set forth in claim 34 wherein the catalytic metallic surface essentially comprises an element selected from the group consisting of nickel, silver, palladium, copper, platinum and gold, the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution is within the range .20 to .60, the temperature of the aqueous solution is maintained between 20 degrees and 100 degrees centigrade, and the solution is continuously regenerated during plating by adding thereto appropriate amounts of soluble copper, hydroxide and formaldehyde containing reagents.

36. An autocatalytic chemical reduction process for continuously plating copper on objects having a catalytic metallic surface comprising the steps of providing an aqueous solution of a complex copper ion present in an amount from .06 to .12 mole per liter of solution, a carbonate radical present in an amount from .06 to .50 mole per liter of solution, a hydroxide radical present in an amount from .50 to 1.50 moles per liter of solution, formaldehyde present in an amount from .30 to 5.0 moles per liter of solution, a tartrate radical present in an amount from .10 to .40 mole per liter of solution, and a salicylate radical present in an amount from 0 to .40 mole per liter of solution, immersing an object to be plated in said solution, and copper plating the immersed object by autocatalytic reaction of said solution at the catalytic metallic surface of the object.

37. The process set forth in claim 36 wherein the catalytic metallic surface essentially comprises an element selected from the group consisting of nickel, silver, palladium, copper, platinum and gold, the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution is within the range of .20 to .60, the temperature of the aqueous solution is maintained between 20 degrees and 100 degrees centigrade, and the solution is continuously regenerated during plating by adding thereto appropriate amounts of soluble copper, hydroxide and formaldehyde containing reagents.

38. An autocatalytic chemical reduction process for continuously plating copper on objects having a catalytic metallic surface comprising the steps of providing an aqueous solution of a complex copper ion present in an amount from .06 to .12 mole per liter of solution, a carbonate radical present in an amount from .06 to .50 mole per liter of solution, a hydroxide radical present in an amount from .50 to 1.50 moles per liter of solution, formaldehyde present in an amount from .30 to 5.0 moles per liter of solution, and a salicylate radical present in an amount from .10 to .40 mole per liter of solution, immersing an object to be plated in said solution, and copper plating said immersed object by autocatalytic reaction of said solution at the metallic surface of the object.

39. The process set forth in claim 38 wherein the catalytic metallic surface essentially comprises an element selected from the group consisting of nickel, silver, palladium, copper, platinum and gold, the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution is within the range .20 to .60, the temperature of the aqueous solution is maintained between 20 degrees and 100 degrees centigrade, and the solution is continuously regenerated during plating by adding thereto appropriate amounts of soluble copper, hydroxide and formaldehyde containing reagents.

40. The continuous process of autocatalytically chemically plating objects having a catalytic metallic surface with copper which comprises providing a plating bath essentially comprising an aqueous solution of complex copper ions, a carbonate radical, a hydroxide radical, formaldehyde, and a complexing agent, circulating the solution from the reservoir to the plating bath and

16

then back to the reservoir, heating the solution to a temperature between 20 degrees centigrade to 100 degrees centigrade before introduction into the plating bath, cooling the solution to a temperature between 20 degrees centigrade and 30 degrees centigrade before returning the solution to the reservoir, immersing the object to be plated in the plating bath for a time interval corresponding to the thickness of the copper plating desired, copper plating said object by autocatalytic reaction of the solution at the catalytic metallic surface of the object, and maintaining the composition of the plating solution by adding to the portion thereof contained in the reservoir appropriate amounts of soluble copper, hydroxide, and formaldehyde containing reagents.

41. The continuous process of autocatalytically chemically plating objects having a catalytic metallic surface with copper which comprises providing a plating bath essentially comprising an aqueous solution of complex copper ions, a carbonate radical, a hydroxide radical, formaldehyde, and a complexing agent, circulating the solution from a reservoir to the plating bath and then back to the reservoir, heating the solution to a temperature between 20 degrees to 100 degrees centigrade before introduction into the plating bath, cooling the solution to a temperature between 20 degrees and 30 degrees centigrade before returning the solution to the reservoir, filtering the solution subsequent to cooling and prior to reheating the same, immersing the object to be plated in the plating bath for a time interval corresponding to the thickness of the copper plating desired, copper plating the object by autocatalytic reaction of the solution at the catalytic metallic surface of the object, and maintaining the composition of the plating solution by adding to the portion thereof contained in the reservoir appropriate amounts of soluble copper, hydroxide, and formaldehyde containing reagents.

42. The process set forth in claim 41 wherein the catalytic metallic surface essentially comprises an element selected from the group consisting of nickel, silver, palladium, copper, platinum and gold, the complex copper ion is present in the solution in an amount from .06 to .12 mole per liter of solution, the carbonate radical is present in the amount from .06 to .50 mole per liter of solution, and the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution being within the range .20 to .60.

43. The process set forth in claim 41 wherein the catalytic metallic surface essentially comprises an element selected from the group consisting of nickel, silver, palladium, copper, platinum and gold, the complex copper ion is present in the solution in an amount from .06 to .12 mole per liter of solution, the carbonate radical is present in an amount from .06 to .50 mole per liter of solution, formaldehyde is present in an amount from .30 to 5.0 moles per liter of solution, the hydroxide radical present in an amount from .50 to 1.5 moles per liter of solution, and the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution is within the range .20 to .60.

44. The continuous process of autocatalytically chemically plating objects having a catalytic metallic surface with copper which comprises providing a plating bath essentially comprising an aqueous solution of complex copper ions, a carbonate radical, a hydroxide radical, formaldehyde, and a tartrate radical, circulating the solution from a reservoir to the plating bath and then back to the reservoir, heating the solution to a temperature between 20 degrees to 100 degrees centigrade before introduction into the plating bath, cooling the solution to a temperature between 20 degrees and 30 degrees centigrade before returning the solution to the reservoir, filtering the solution subsequent to cooling and prior to reheating the same, immersing the object to be plated in the plating bath for a time interval corresponding to the

thickness of the copper plating desired, copper plating the object by autocatalytic reaction of the solution at the catalytic metallic surface of the object, and maintaining the composition of the plating solution by adding to the portion thereof contained in the reservoir appropriate amounts of soluble copper, hydroxide, and formaldehyde containing reagents.

45. The continuous process of autocatalytically chemically plating objects having a catalytic metallic surface with copper which comprises providing an aqueous solution of complex copper ions, a carbonate radical, a hydroxide radical and formaldehyde, a tartrate radical, and a salicylate radical, circulating the solution from a reservoir to the plating bath and then back to the reservoir, heating the solution to a temperature between 20 degrees to 100 degrees centigrade before introduction into the plating bath, cooling the solution to a temperature between 20 degrees and 30 degrees centigrade before returning the solution to the reservoir, filtering the solution subsequent to cooling and prior to reheating the same, immersing the object to be plated in the plating bath for a time interval corresponding to the thickness of the copper plating desired, copper plating the object by autocatalytic reaction of the solution at the catalytic metallic surface of the object, and maintaining the composition of the plating solution by adding to the portion thereof contained in the reservoir appropriate amounts of soluble copper, hydroxide, and formaldehyde containing reagents.

46. The process set forth in claim 45 wherein the catalytic metallic surface essentially comprises an element selected from the group consisting of nickel, silver, palladium, copper, platinum, and gold, the complex copper ion is present in the solution in an amount from .06 to .12 mole per liter of solution, the carbonate radical is present in an amount from .06 to .50 mol per liter of solution, the hydroxide radical is present in an amount from .50 to 1.50 moles per liter of solution, formaldehyde is present in an amount from .30 to 5.0 moles per liter of solution, the tartrate radical is present in an amount from .10 to .40 mole per liter of solution, the salicylate radical is present in an amount from 0 to .40 mole per liter of solution, and the ratio between the complex copper ions and the carbonate ions in the bath expressed in moles per liter of solution is within the range .20 to .60.

47. The continuous process of autocatalytically chemically plating objects having a catalytic metallic surface with copper which comprises providing an aqueous solution of complex copper ions, a carbonate radical, a hydroxide radical, formaldehyde, and a salicylate radical

circulating the solution from a reservoir to the plating bath and then back to the reservoir, heating the solution to a temperature between 20 degrees to 100 degrees centigrade before introduction into the plating bath, cooling the solution to a temperature between 20 degrees and 30 degrees centigrade before subsequent to cooling and prior to reheating the same, immersing the object to be plated in the plating bath for a time interval corresponding to the thickness of the copper plating desired, copper plating the object by autocatalytic reaction of the solution at the catalytic metallic surface of the object, and maintaining the composition of the plating solution by adding to the portion thereof contained in the reservoir appropriate amounts of soluble copper, hydroxide, and formaldehyde containing reagents.

48. The process set forth in claim 47 wherein the catalytic metallic surface essentially comprises an element selected from the group consisting of nickel, silver, palladium, copper, platinum and gold, the complex copper ion is present in the solution in an amount from .06 to .12 mol per liter of solution, the carbonate radical is present in an amount from .06 to .50 mole per liter of solution, formaldehyde is present in an amount from .30 to 5.0 moles per liter of solution, the hydroxide radical is present in an amount from .50 to 1.50 moles per liter of solution, the salicylate radical is present in an amount from .10 to .40 mole per liter of solution, and the ratio between the complex copper ions and the carbonate radical in the bath is within the range .20 to .60.

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