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2,938,805

PROCESS OF STABILIZING AUTOCATALYTIC COPPER PLATING SOLUTIONS

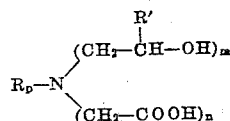
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10 Claims. (Cl. 106—1)

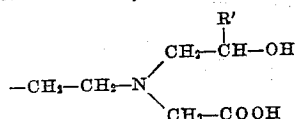
The present invention relates to a process for stabilizing copper plating solutions used to autocatalytically plate copper onto metals or onto non-metallic surfaces. More particularly, this invention relates to a stabilization process which comprises producing oxidizing conditions within said plating solutions whereby the formation of cuprous oxide, which causes these solutions to become unstable, is greatly minimized or substantially prevented without the prevention of the reducing reaction which causes the copper to plate.

In my copending application S.N. 725,449, the copending applications of Robert M. Lukes, S.N. 725,450 and S.N. 725,452, all of which are filed concurrently herewith and assigned to the same assignee as the present invention, in the patent of A. E. Cahill et al., U.S. 2,874,072 and assigned to the same assignee as the present invention, and in the pamphlet Wein, Samuel, "Copper Films," PB 111, 237, U.S. Department of Commerce, Office of Technical Services, 1953, there are disclosed plating solutions comprising aqueous, alkaline solutions containing formaldehyde and cupric ion complexed to prevent precipitation of cupric hydroxide to which my process is applicable.

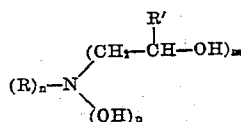
Specifically, Cahill discloses complexing agents which are tartrates and salicylates used in the presence of carbonates all of which are water soluble. Lukes discloses in his application S.N. 725,450 complexing agents which are ethyleneaminoacetic acids which are selected from the class consisting of ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid and 1,2-cyclohexylenediaminetetraacetic acid. In application S.N. 725,452, Lukes discloses complexing agents corresponding to the formula:



where m and n are both integers and are at least 1 and not more than 2, p is an integer and is at least 0 and not more than 1, the sum of m , n and p equaling 3; R is a member of the group consisting of hydrocarbon radicals having from 1 to 10 carbon atoms, and the

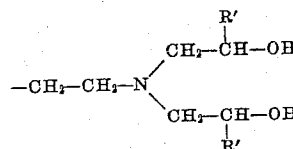


grouping and R' is a member of the group consisting of hydrogen and methyl. In my copending application I disclose complexing agents which correspond to the formula:



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where R is a hydrocarbon radical having from 1 to 10 carbon atoms and, in addition, when $p=0$ and $n=1$, R also represents the



grouping. R' is a substituent selected from the group consisting of hydrogen and methyl, m is an integer and is at least 1 and no more than 4, n is an integer and is at least 0 and no more than 3, p is an integer and is at least 0 and not more than 1. The particular values of m , n , and p must be so chosen that they fulfill the following equation:

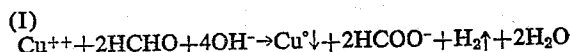
$$n+p=3+p$$

Further details concerning the use of these solutions are shown by the examples and by reference to the Cahill patent and the above-mentioned copending applications.

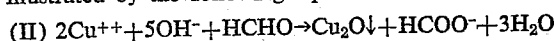
Many of the solutions disclosed in the Wein publication can form copper films or mirrors on surfaces that have not been sensitized with metallic films.

All of these solutions autocatalytically plate copper. By this terminology I mean that the solutions are capable of plating copper without the application of an external force, e.g., electricity.

Solutions known to autogenously plate copper as a smooth, adherent coating do so according to the following equation:



A subordinate and yet significant, reaction also occurs as illustrated by the following equation:



Since the reaction expressed by Equation II does not require activation by an extraneous material, it will occur merely upon the solution standing at room temperature and is hastened by heating. The cuprous oxide product is reduced by the alkaline formaldehyde solution to copper metal which is one of the metals that is catalytically active in initiating the plating reaction expressed by Equation I. Therefore, the reaction of Equation II causes these solutions to spontaneously decompose and to become useless upon standing for long periods. Although the complexing agents used in any of the above copending applications greatly suppress the reaction expressed by Equation II, nevertheless, high concentrations of cupric ion and the high alkalinity of the solutions over-ride some of the effect of these complexing agents. Furthermore, it is not possible to completely suppress Equation II with any complexing agent.

Therefore, all of the solutions used to autocatalytically plate copper, such as those described in the above-identified applications have a finite life, that would be very desirable to extend. I have now found a very simple and easy method for performing this function. My invention comprises aerating these solutions with an oxygen-containing gas during storage or other periods of non-use, and also while it is being used to plate copper. Aeration can be accomplished with pure oxygen or oxygen diluted with any inert gas such as argon, neon, krypton, nitrogen, and the like, the simplest gaseous mixture to use being air itself even though it does contain a minor amount of carbon dioxide which reacts with the alkali in the solution. From what I can determine by experiment, the effect of oxygen is to either prevent the formation of cuprous oxide or to reoxidize the cuprous oxide back to soluble cupric compounds so quickly that no noticeable

precipitate can be observed. This is based on my observations that the plating solutions remain clear and free of any precipitate for extended periods of time providing a gas containing elemental oxygen, more commonly referred to as an oxygen-containing gas, is blowing through the solutions. If I stop the flow of gas, a precipitate will form in time which will disappear almost as soon as I start aerating again. However, if I delay the start-up of the gas stream for a period long enough that the cuprous oxide is converted to copper, the copper will not dissolve. To restore stability in this case, the copper must be removed from contact with the solution, for example by filtration, centrifugation, decantation, etc. Furthermore, I have found that best results are obtained if I have the gas dispersed as very fine bubbles which are uniformly distributed throughout the entire solution. Should I fail to do this, I have noticed that precipitation will occur in those portions of the solution not contacted by the gas stream. Immediate correction of this condition can be effected by vigorous agitation. I have found that the best method of carrying my invention into effect is to introduce the oxygen-containing gas stream through a disperser such as a fritted glass disk or a porous ceramic disk so that the gas is broken up into very fine bubbles, and to use vigorous agitation to insure that these bubbles are distributed throughout the entire volume of the plating solution. Since all metals that are not attacked by the alkaline solutions are catalytically active with the plating solution, the gas inlet and disperser must be non-metals. Alternatively, of course, more than one stream of gas can be introduced into the solution. Providing the gas inlets are properly placed, and the volume of the incoming gas is sufficient, no further agitation is required since the gas streams themselves will provide sufficient agitation of the solution. Preferably, the entire liquid phase should be saturated with the oxygen-containing gas at all times. Filters can be used in conjunction with the aeration to remove any solid material. Superatmospheric gas pressure can be used but is not required. Sub-atmospheric pressure is not desirable since it does not permit as effective saturation of the solution with the oxygen-containing gas as do higher pressures.

I have also found that aeration can be accomplished by flowing thin films of the plating solutions over the surfaces to be plated. By this means, a small volume of liquid is exposed to a large volume of oxygen-containing gas. By inclining the surfaces so that the liquid flows rapidly, agitation is also provided. The surfaces to be plated can be arranged in a step-wise fashion so that the liquid cascades from one surface to the next in series. If non-metallic spray equipment is used, the plating solution can be sprayed as an atomized mist to provide aeration. In any of these applications, if a reservoir of liquid is present, additional aeration of the liquid in the reservoir will usually be required. A filter can also be installed in the line to remove any solid material.

Since the amount of oxygen actually consumed is extremely small, there is no critical concentration of oxygen required in the gas composition used in my process. The actual amount of oxygen is dependent on the cupric ion concentration. This amount can be supplied by low oxygen concentration at fast flow rates or high concentration at low flow rates. From a practical standpoint, there is no advantage in using a gas containing less oxygen than the approximately 20% contained in air, since this is the cheapest and most readily available oxygen-containing gas. Oxygen in a compressed gas cylinder is a convenient source to use where there is no source of compressed air, or where mobility of the plating equipment is desired. However, my results with pure oxygen have shown no added benefits over the results I obtain with air. The oxygen-containing gas should be free of oils, greases and other contaminants that would affect the quality of the copper plate produced by the solutions. Preferably, the container for the plating solutions should

be so arranged that the exit gases do not entrap any more than the minimum amount of reagents. In this regard, some loss of formaldehyde will always occur, due to its volatilization in the gas stream. This loss can be compensated for by additions of aqueous formaldehyde continuously or at prescribed intervals so as to maintain the concentration required to produce the plating reaction.

In order that those skilled in the art may understand how my invention can be carried into effect, the following examples are given by way of illustration, and not by way of limitation.

Example 1

One liter of a plating solution was made by dissolving the following ingredients in enough water to make one liter of solution:

	Grams
Cupric sulfate pentahydrate	25
Triethanolamine	60
Sodium hydroxide	16
Aqueous 37% formaldehyde, 25 ml.	

The above solution was divided into two portions; one portion was used as a control and was allowed to stand at room temperature without any further treatment. The other portion was aerated by introduction of air into the solution through a fritted glass disk. It was not mechanically stirred. At the end of approximately two hours, the control had started to decompose, as evidenced by the precipitation of copper. The aerated sample remained clear and unchanged. After leaving the solutions overnight, the control sample had completely decomposed, as evidenced by the solution being colorless and all of the copper being a precipitate in the bottom of the container. The aerated sample was still blue in color and had a pH of 11.5. There was a small amount of copper metal present in the solution indicating that the solution had not been well stirred. The example was repeated, except that this time the solution was stirred vigorously in addition to being aerated. At the end of 12 hours, no decomposition of the plating solution had occurred, the pH was 11.9. A piece of sand-blasted paper-base, phenolic-resin laminate was sensitized by immersing it for one minute in a stannous chloride solution made by dissolving 10 grams of stannous chloride and 10 milliliters of 12 molar hydrochloric acid in one liter of water, rinsed with water, dipped for one minute into a palladium chloride solution made by dissolving 0.5 gram of palladium chloride and 10 milliliters of 12 molar hydrochloric acid in one liter of water, and again rinsed in water. When the sensitized laminate was placed in the aerated solution, a coherent, bright film of copper plated onto the laminate simultaneously with the evolution of hydrogen from the surface.

Example 2

The solution as described in Example 1 was duplicated and divided into two portions. Into one portion, a stream of nitrogen was admitted at the rate of 0.4 cubic foot per hour. In the second portion, a flow of pure oxygen was admitted at the rate of 0.4 cubic foot per hour. At the end of 1½ hours, the solution aerated with the nitrogen was beginning to decompose and at the end of 2½ hours, was completely decomposed, as evidenced by the solution being colorless. The solution aerated with oxygen was still bright blue in color, with no signs of decomposition at the end of 48 hours, but there had been some depletion of formaldehyde. The amount of formaldehyde lost was replaced and the pH adjusted to 12.8. When a piece of paper-base, phenolic-resin laminate which had been sensitized as in Example 1 was placed in this solution, it was found that the copper plated on the sensitized surface at a rate of about 1 mil per hour. When 4 mils of copper had built up on the board, it was removed from the solution. The solution was aerated with oxygen for an additional 24 hours. When a sensitized piece of phenolic-resin laminate was inserted into the

plating solution, the copper deposited at the same fast rate of 1 mil per hour. After a film of 3 mils of copper had been plated onto the sample, it was removed. Altogether, the solution had remained clear and useful as a plating bath for about 80 hours with no signs of decomposition.

Example 3

Two liters of solution were prepared containing the following ingredients in the stated concentrations:

	Molarity
Cupric sulfate	0.10
Ethylenediaminetetraacetic acid	0.10
Potassium hydroxide	0.80
Formaldehyde	0.30

A piece of paper-base, phenolic-resin laminate having an area of 50 sq. inches which had been sensitized with palladium as in Example 1 was placed in this solution. Air was bubbled in through a fritted glass filter diffuser at the rate of 0.2 liter per minute, while the solution was stirred vigorously with a mechanical stirrer. At the end of 5 hours an additional 25 milliliters of formaldehyde was added and 2 milliliters of a wetting agent comprising an ethylene oxide and propylene oxide polymer was added. The thickness of the copper coating was 0.6 to 0.7 mil thick and no decomposition of the plating solution had occurred. At the end of an additional 1½ hours, the solution was plating satisfactorily and was left overnight, for 15 hours. No decomposition of the solution occurred during this time and the solution was still plating, however, at a very slow rate. An additional 50 milliliters of formaldehyde was added and enough potassium hydroxide was added to increase the initial molarity of the base by an additional 0.80. This caused the solution to start plating rapidly again. At the end of 4½ hours, the solution was still plating at a rate of about 0.1 mil per hour and the total thickness of the copper plate was about 2½ mils. Although no undesirable decomposition of the solution occurred, the plating reaction was stopped at this point by acidifying the solution to a pH of 2, whereby 56 of the original 60 grams of the ethylenediaminetetraacetic acid was recovered by filtration of the solution, since this reagent is insoluble in the reaction mixture at this pH.

Example 4

One liter of solution was made containing the following ingredients:

	Grams
Cupric nitrate trihydrate	15
Sodium hydroxide	20
Sodium bicarbonate	10
Sodium potassium tartrate	30

This solution was divided into four equal portions of 250 milliliters each, and into each portion 25 milliliters of 37% aqueous formaldehyde was added. One portion was left standing at room temperature as a blank; the second portion was aerated with air using a fritted glass disk to disperse the gas stream. A paper-base, phenolic-resin laminate which had been sensitized as in Example 1 was placed in each of the third and fourth portions. The third portion was not aerated and the fourth portion was aerated in the same way as the second portion. In both the third and fourth solutions, the seeded board was plated rapidly with copper. At the end of about 20 minutes, both the first and third solutions which had not been aerated, were starting to decompose as was evidenced by the formation of precipitate of cuprous oxide. Both the second and fourth solutions were still clear, with no evidence of decomposition at the end of 7 hours.

Example 5

A plating composition comprising three solutions useful in making copper mirrors was made up as follows.

Solution A:

Cupric sulfate pentahydrate	g--	20
Glycerol	ml--	80
Aqueous ammonia (28%)	ml--	20

5 Solution B:

Sodium hydroxide (9% aqueous sol.)	ml--	400
Sucrose (10% aqueous sol.)	ml--	200
Nitric acid	ml--	0.5
Water	ml--	250

10 Solution C:

Aqueous formaldehyde (37%)	ml--	80
Water	ml--	1250

The three solutions combined in the proportion

15 Solution A	ml--	120
Solution B	ml--	850
Solution C	ml--	1330

The resulting plating solution was divided into two portions. One portion was aerated with air at the rate of 0.5 cubic foot per hour while the other portion was permitted to stand at ambient temperature as a control. When a piece of paper base-phenolic-resin laminate that had been sensitized with palladium as in Example 1 was placed in each of the two portions copper plated onto the sensitized area. The pieces of laminate were removed and the solutions allowed to stand overnight. In the morning the non-aerated sample had formed a smooth mirror over the entire area of the glass beaker contacted by the solution which was now depleted of copper. No sensitization of the non-metallic (glass) surface is necessary with this solution to obtain the mirror. The aerated sample had not decomposed either by forming a copper mirror or by precipitating cuprous oxide. At the end of three days it was still stable and plated copper on the sensitized laminate. By stopping the aeration of a sample of this solution, a copper mirror will form on the walls of the container on standing overnight.

Example 6

One liter of solution was made containing the following concentration of ingredients:

	Molarity
Cupric sulfate	0.1
Glycerol	0.45
45 Ammonium hydroxide	0.4
Sodium hydroxide	0.6
Formaldehyde (37% aqueous sol.), 80 ml.	

This solution was divided into two portions, one of which was aerated with air as in Example 5. Both portions plated copper on a piece of phenolic laminate sensitized as in Example 1. The non-aerated portion decomposed in 15 to 20 minutes while the aerated sample was still plating on the laminate at the end of five hours when the test was discontinued.

Example 7

One liter of solution was made containing the following ingredients in the stated concentration:

	Molarity
Cupric sulfate	0.1
Glycerol	0.45
Sucrose	.15
65 Ammonium hydroxide	0.4
Sodium hydroxide	0.4
Aqueous formaldehyde (37%), 80 ml.	

The procedure of Example 6 was repeated with almost identical results. The test for the aerated sample was discontinued at the end of eight hours with no sign of decomposition.

Example 8

In order to obtain some explanation as to the function of oxygen in preventing the decomposition of these plat-

ing solutions, a solution was made up containing the following ingredients in the stated concentrations:

	Molarity
Ethylenediaminetetraacetic acid -----	0.10
Potassium hydroxide -----	0.60

Into this solution, 0.05 mole of cuprous oxide was added, mechanical agitation was supplied, and air at the rate of 0.4 cubic foot per hour was bubbled through the solution. At the end of 4 hours, all of the cuprous oxide had dissolved, thus demonstrating that oxygen is capable of dissolving cuprous oxide in such a solution. Formaldehyde had been purposely omitted, since if it had been present, it would have reduced the cuprous oxide to copper.

Example 9

The following example was carried out to see whether or not aeration could stop decomposition once it had been initiated. One liter of solution was made up containing the following ingredients:

	Grams
Cupric sulfate pentahydrate -----	25
Ethylenediaminetetraacetic acid -----	60
Sodium hydroxide -----	52

Twenty-two milliliters of 37% aqueous formaldehyde solution was added to 875 milliliters of the above solution, which was agitated with a mechanical stirrer and aerated with oxygen at the rate of 0.4 cubic foot per hour. A sample of this solution showed a light transmission of 98½% when measured in a spectrophotometer using light of a wavelength of 450 millimicrons. The mechanical stirrer was shut off and the stream of oxygen stopped. At the end of approximately 1 hour, the solution became turbid, indicating that it was starting to decompose. At this point, the light transmission was found to have dropped to approximately 2%. The stream of oxygen and the stirring were again started, which immediately caused the turbidity to disappear. After 15 minutes of aeration, a sample was taken and it was found that the light transmission had increased to 90%. During the entire experiment the pH of the solution had remained at 12.8. This example shows that aeration with an oxygen-containing gas can stop decomposition of these plating solutions if initiated in the early stages of the decomposition.

As illustrated by the above examples, my method of stabilization is applicable to all plating solutions which

are based on the reaction of formaldehyde with a cupric salt complex in an alkaline solution to produce a film of copper metal. This stabilization is apparently caused by the ability of the oxygen-containing gas to prevent the precipitation or formation of cuprous oxide by the secondary reaction outlined above.

The above examples have illustrated many of the modifications and variations of the present invention, but obviously other modifications and variations are possible in light of the above teaching. For example, the plating solutions aerated according to my invention can be used at higher temperatures than the non-aerated plating solutions. 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 I claim as new and desire to secure by Letters Patent of the United States is:

1. The process for stabilizing aqueous, alkaline, formaldehyde-containing copper plating solutions used to autocatalytically plate copper onto metals or non-metallic surfaces which comprises aerating such solutions with a gas containing elemental oxygen.
2. The process of claim 1 wherein the gas is air.
3. The process of claim 1 wherein the gas is substantially pure oxygen.
4. The process of claim 1 wherein the plating solutions are saturated with the gas.
5. The process of claim 1 wherein aeration is used in conjunction with mechanical agitation.
6. The process of claim 1 wherein the gas is dispersed throughout the entire volume of plating solution.
7. A solution for autocatalytically plating copper which is stabilized against self-decomposition comprising an aqueous, alkaline solution of formaldehyde and a cupric ion which has been complexed so that the solution is free of cupric hydroxide, said solution containing a gas containing elemental oxygen.
8. The solution of claim 7 wherein the gas is air.
9. The solution of claim 7 wherein the gas is substantially pure oxygen.
10. The solution of claim 7 wherein the solution is saturated with the gas.

References Cited in the file of this patent

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