

Electroplating of Copper from a Non-cyanide Electrolyte

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A non-cyanide bath useful for electroplating adherent copper deposits directly on mild steel has been developed in a study based on the need for new processes that are more acceptable, environmentally, than earlier processes containing toxic substances.

Electrodeposited copper finds extensive application as undercoat for decorative nickel-chromium plating, for masking in selective case hardening, in copper-bottomed stainless steel cookware and in printed circuit boards, among other applications. Copper is normally deposited from acid baths of the sulfate and from alkaline cyanide baths.¹⁻⁴ When copper is electroplated on a ferrous metal substrate, the application of an initial strike from a cyanide bath is employed to ensure adhesion of the subsequently plated copper. Because of the toxic nature of cyanide electrolytes, which calls for strict pollution control measures, the search for a suitable nontoxic electrolyte as an alternative continues. In the current study, the authors report their attempts to identify a suitable non-cyanide electrolyte and the deposition characteristics of a solution containing copper in its EDTA complex.

Table 1
Immersion Deposit Formation
Of CuSO₄ Solutions (100 g/L) With Various Complexants

| Complexant | Conc. g/L | Stability | Immersion Deposit |
|---------------------------|-----------|--------------|--------------------|
| Citric acid | 100 | clear soln. | yes |
| | 200 | clear soln. | yes |
| | 300 | clear soln. | yes |
| Acetic acid | 100 | clear soln. | yes |
| | 200 | clear soln. | yes |
| | 300 | clear soln. | yes |
| Trisodium orthophosphate | 100 | precipitated | no |
| | 200 | precipitated | no |
| | 300 | precipitated | no |
| Sodium thio-sulfate | 100 | precipitated | yes |
| | 200 | precipitated | yes |
| | 300 | precipitated | yes |
| Sodium potassium tartrate | 100 | precipitated | yes |
| | 200 | precipitated | yes |
| | 300 | precipitated | yes |
| EDTA disodium salt | 100 | clear soln. | yes |
| | 200 | clear soln. | yes-feeble deposit |
| | 300 | clear soln. | yes-feeble deposit |
| Thiourea | 100 | turbid soln. | yes |
| | 200 | precipitated | yes |
| | 300 | precipitated | no |

Experimental Procedure

Galvanic displacement characteristics and stability of solutions were examined by immersing 7.5 x 2.5 x 0.025 cm cold-rolled steel specimens in solutions of different compositions for 10 min. The specimens were inspected by visual observation for immersion deposit formation. Solution stability was ascertained from the clarity of the solutions.

Current efficiency studies were carried out by electroplating 7.5 x 2.5 x 0.025 cm steel specimens and determining the mass of the deposit obtained for a specific quantity of electricity passed in each case. Rate of deposition was calculated in $\mu\text{m/hr}$. Throwing power of the solution finally chosen was determined by the Haring-Blum method for a cathode distance ratio of 5:1.

Adhesion of plated deposits was tested by the bend test with repeated bending through 180° to fracture of the substrate and inspection for lift-off of copper. Microhardness values for deposits were determined by applying a load of 25g for 15 sec. Porosity testing was by the Ferroxy test.

Results and Discussion

Galvanic Displacement Characteristics and Stability of Solutions

Immersion deposition of copper on steel occurs in solutions of divalent copper as a result of galvanic displacement. Complexing of copper is an effective way of shifting its potential to less positive (or to negative) values. This helps prevent immersion deposition leading to electrolytic formation of adherent deposits. The greater the stability constant of the complex, the less tendency to form immersion deposits by galvanic displacement. Prevention of immersion deposition is very important because it hinders adhesion of subsequently plated layers. Dissolution of the substrate during immersion deposition, though small, contributes to bath contamination.

Table 1 lists the various solution compositions examined with regard to their relative stabilities and tendency to form immersion deposits on steel. It can be seen that when copper sulfate (100 g/L) is added to solutions containing phosphate, thiosulfate, thiourea or sodium potassium tartrate, precipitation of copper occurs, showing that no soluble complex is formed. Although the addition of cupric sulfate to complexants, such as citric acid, acetic acid, ammonia, EDTA, etc., produces clear solutions, immersion deposits are formed by displacement of copper ions in the solution as copper onto a steel piece immersed in each of them.

Experiments on the effects of complexants in clear solutions containing copper at low concentrations, but higher pH values, showed the usefulness of EDTA (ethylenediamine tetraacetic acid) disodium salt as a complexant. Clear solutions with no tendency to immersion deposition were obtained with copper sulfate (10 g/L) and EDTA (30 g/L) for pH adjusted to 10.5 (Table 2). A lower pH, higher copper content or lower EDTA concentration, results in either precipitation

of the solution or immersion deposit formation. It is clear from the results that the mass ratio of 1:3 of copper sulfate to EDTA with a suitable final pH, would be optimum for avoiding immersion deposition.

Stability of solutions and their immersion deposition characteristics were studied with varying copper concentrations (Copper:EDTA, 1:3), pH and temperature. The results (Table 3) lead to the conclusion that copper ethylenediaminetetraacetate complex-based electrolytes would be suitable for producing copper deposits on steel substrates without the problem of immersion deposition and solution degradation at pH 10.5–12.0 and 30 to 50 °C.

Table 2
Immersion Deposit Formation of CuSO₄-EDTA Solutions

| CuSO ₄ g/L | EDTA disodium salt | | pH | Stability | Nature of Deposit |
|--------------------------|-----------------------|--|------|------------------|-------------------|
| | g/L | | | | |
| 10 | 30 | | 9.0 | turbid soln. | bright adherent |
| 20 | 30 | | 9.0 | slight turbidity | semi-bright adh. |
| 30 | 30 | | 9.0 | clear soln. | dull nonadherent |
| 40 | 30 | | 9.0 | clear soln. | dull nonadherent |
| 50 | 30 | | 9.0 | clear soln. | dull nonadherent |
| 10 | 30 | | 10.5 | clear soln. | none |
| 20 | 30 | | 10.5 | clear soln. | feeble |

Table 3
Effect of Concentration, pH & Temperature on Immersion Deposits Of CuSO₄-EDTA Solutions

| CuSO ₄ g/L | EDTA disodium salt | | Stability, °C | | | Deposition, °C | | |
|--------------------------|-----------------------|------|---------------|----|----|----------------|----|----|
| | g/L | pH | 30 | 40 | 50 | 30 | 40 | 50 |
| | | | | | | | | |
| 10 | 30 | 10.5 | C | C | C | N | N | N |
| 15 | 45 | 10.5 | C | C | C | N | N | N |
| 20 | 60 | 10.5 | C | C | C | N | N | N |
| 25 | 75 | 10.5 | C | C | C | N | N | N |
| 10 | 30 | 12.0 | C | C | C | N | N | N |
| 15 | 45 | 12.0 | C | C | C | N | N | N |
| 20 | 60 | 12.0 | C | C | C | N | N | N |

C - clear solution
N - no immersion deposit

Table 4
Influence of Current Density & Temperature on Nature Of Deposit, Cathode Current Efficiency & Rate of Deposition

(CuSO₄ 10 g/L, EDTA disodium salt 30 g/L, pH 10.5)

| Current Density A/dm ² | Temp. °C | Nature of Deposit | Cathode Current Efficiency, % | Rate of Deposition µm/hr |
|--------------------------------------|-------------|---------------------------|-------------------------------|-----------------------------|
| 1.0 | 30 | uniform, dull brown | 90.5 | 12.1 |
| 1.5 | 30 | uniform, dull brown | 86.8 | 17.3 |
| 2.0 | 30 | uniform, dull brown | 64.8 | 17.3 |
| 2.5 | 30 | dull, uniform, dark brown | 55.0 | 18.3 |
| 1.0 | 40 | uniform, dull brown | 88.2 | 11.8 |
| 1.5 | 40 | uniform, dull brown | 79.7 | 15.9 |
| 2.0 | 40 | uniform, dull brown | 63.9 | 17.0 |
| 2.5 | 40 | uniform, dull brown | 54.6 | 18.2 |
| 1.0 | 50 | uniform, dull brown | 80.6 | 10.7 |
| 1.5 | 50 | uniform, dull brown | 76.4 | 15.3 |
| 2.0 | 50 | uniform, dull, dark brown | 60.6 | 16.1 |
| 2.5 | 50 | uniform, dull, dark brown | 50.3 | 16.7 |

Deposition Characteristics:

Cathode Current Efficiency

The results of cathode current efficiency studies carried out with copper-EDTA solutions at pH 10.5 are given in Tables 4 to 7. When the copper sulfate concentration is 10 g/L (Table 4), the current efficiency decreases with increase in current density at all three temperatures employed. This should be attributed to the fact that the very low concentration of metal ions at the cathode (with respect to bath metal content) results in substantial hydrogen evolution, especially at high current densities. The current efficiency decreases with increase in temperature for a given current density. Similar trends of decreasing current efficiency with increasing current density and temperature were observed at a copper sulfate concentration of 15 g/L as well (Table 5).

Current efficiency studies with solutions containing 20 and 25 g/L copper sulfate at pH 10.5 are given in Tables 6 and 7. In these cases, it is seen that current efficiency remains more or less steady with change in current density, as well as temperature. The current efficiency values are found to be in the range of 90 to 100 percent in most of the cases studied. This suggests that the copper-EDTA-based electrolyte is a viable plating composition.

The results of current efficiency studies carried out at pH 12.0 for different concentrations of copper sulfate at varying current densities and temperatures are plotted graphically in Figs. 1 and 2. The efficiency is found to increase with temperature (Fig. 1), whereas an increase in current density reduces current efficiency (Fig. 2). These results show that adherent copper deposits with 100 percent current efficiency are possible under specific conditions of solution composition, temperature, current density and pH 12.0. The stability of the solution is also good.

Rate of Build-up

The rate of build-up values included in Tables 4-7 show that at higher copper concentrations (20–25 g/L) and at higher operating temperature (50 °C), the rate of build-up increases proportionately with

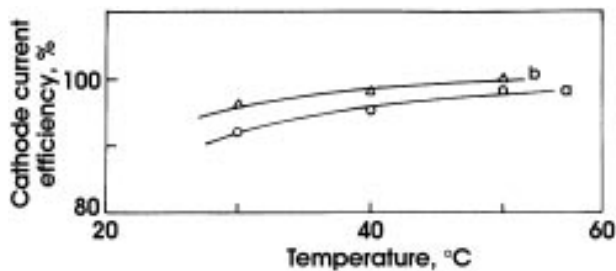


Fig. 1--Influence of temperature on cathode current efficiency; 2 A/dm², pH 2.0, conc. CuSO₄ (a) 20 g/L, (b) 25 g/L.

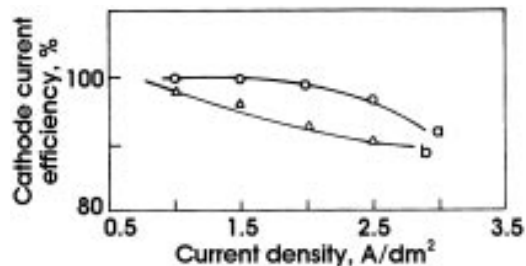


Fig. 2--Influence of current density on cathode current efficiency at pH 12.0: (a) 25 g/L CuSO₄, 50 °C; (b) 20 g/L CuSO₄, 30 °C.

current density. At a lower copper concentration and a lower operating temperature, the increase in build-up rate with current density is much less, as a result of decreased current efficiency with increasing current density.

Solution Throwing Power

The throwing power for the solution (Table 8) was found to be good, as well as comparable to cyanide copper baths.

mild steel has the following composition, with a copper sulfate to EDTA disodium salt ratio of 1:3:

- Copper sulfate 20–25 g/L
- EDTA disodium salt 60–75 g/L
- pH 10.5–12.0
- Temperature 40–50 °C
- Current density 0.5–2.5 A/dm²

Properties of Deposits:

Nature

At 10 g/L copper sulfate concentration and bath pH 10.5, the deposits obtained are dull brown, but uniform (Table 4). For a concentration of 15 g/L, uniform semibright deposits are obtained at 50 °C and at 1.0 to 1.5 A/dm² (Table 5). When the concentration of copper is further increased (Tables 6 and 7) deposits are mostly dull at all temperatures and operating current densities.

Experiments done at pH 12 show that for copper sulfate concentration of 20 g/L, semibright deposits can be obtained at 40 to 50 °C and at 1.0 to 2.5 A/dm² (Table 9).

Deposit Adhesion

Specimens of steel, copper-plated under varying conditions of composition and operation, showed no peeling or flaking of the deposited layer when they were subjected to the bend test for adhesion. Good adhesion of electrolytically deposited copper, and nonformation of immersion copper deposits are highly favorable factors of the bath composition discussed so far.

Deposit Microhardness

Microhardness values for the semibright deposits are listed in Table 9. The values of 120–160 kg/mm² are higher than those for deposits obtained from conventional cyanide solution.⁵

Deposit Porosity

From the results of porosity tests (Table 10), it is clear that the deposits would be pore-free at thicknesses greater than 7.0 to 7.5 μm.

Findings

A non-cyanide bath useful for electroplating adherent copper deposits directly on

Table 5
Influence of Current Density & Temperature on Nature of Deposit, Cathode Current Efficiency & Rate of Deposition

(CuSO₄ 15 g/L, EDTA disodium salt 45 g/L, pH 10.5)

| Current Density A/dm ² | Temp. °C | Nature of Deposit | Cathode Current Efficiency, % | Rate of Deposition μm/hr |
|-----------------------------------|----------|---------------------------|-------------------------------|--------------------------|
| 1.0 | 30 | dull, uniform, dark brown | 92.0 | 12.3 |
| 1.5 | 30 | dull, uniform, dark brown | 83.0 | 16.6 |
| 2.0 | 30 | dull, uniform, dark brown | 62.2 | 16.6 |
| 2.5 | 30 | dull, uniform, dark brown | 57.5 | 19.1 |
| 1.0 | 40 | dull, uniform, dark brown | 90.6 | 12.1 |
| 1.5 | 40 | dull, uniform, dark brown | 76.8 | 15.3 |
| 2.0 | 40 | dull, uniform, dark brown | 60.4 | 16.1 |
| 2.5 | 40 | dull, uniform, dark brown | 56.9 | 18.9 |
| 1.0 | 50 | semi-bright, uniform | 88.0 | 11.7 |
| 1.5 | 50 | semi-bright, uniform | 75.8 | 15.4 |
| 2.0 | 50 | uniform, dull, dark brown | 58.4 | 15.1 |
| 2.5 | 50 | uniform, dull, dark brown | 54.3 | 18.0 |

Table 6
Influence of Current Density & Temperature on Nature of Deposit, Cathode Current Efficiency & Rate of Deposition

(CuSO₄ 20 g/L, EDTA disodium salt 60 g/L, pH 10.5)

| Current Density A/dm ² | Temp. °C | Nature of Deposit | Cathode Current Efficiency, % | Rate of Deposition μm/hr |
|-----------------------------------|----------|---------------------------|-------------------------------|--------------------------|
| 1.0 | 30 | uniform, dull brown | 97.9 | 13.0 |
| 1.5 | 30 | uniform, dull brown | 95.0 | 19.0 |
| 2.0 | 30 | uniform, dull brown | 92.6 | 24.7 |
| 2.5 | 30 | dull, streaky, brown | 90.3 | 30.1 |
| 1.0 | 50 | uniform, semi-bright | 99.8 | 13.3 |
| 1.5 | 50 | dull, uniform, dark brown | 99.0 | 19.8 |
| 2.0 | 50 | dull, uniform, dark brown | 98.5 | 26.2 |
| 2.5 | 50 | dull, uniform, dark brown | 95.0 | 31.6 |

Table 7
Influence of Current Density & Temperature on Nature of Deposit,
Cathode Current Efficiency & Rate of Deposition

(CuSO₄ 10 g/L, EDTA disodium salt 30 g/L, pH 10.5)

| Current Density A/dm ² | Temp. °C | Nature of Deposit | Cathode Current Efficiency, % | Rate of Deposition µm/hr |
|-----------------------------------|----------|---------------------------|-------------------------------|--------------------------|
| 1.0 | 30 | uniform, dull brown | 97.5 | 13.0 |
| 1.5 | 30 | uniform, dull brown | 96.7 | 19.3 |
| 2.0 | 30 | uniform, dull brown | 96.4 | 25.7 |
| 2.5 | 30 | uniform, dull brown | 91.4 | 30.4 |
| 1.0 | 50 | dull, uniform, dark brown | 100.0 | 13.3 |
| 1.5 | 50 | dull, uniform, dark brown | 100.0 | 20.0 |
| 2.0 | 50 | dull, uniform, dark brown | 99.0 | 26.4 |
| 2.5 | 50 | dull, uniform, dark brown | 96.0 | 32.0 |

Table 8
Throwing Power
(CuSO₄ 25 g/L, EDTA disodium salt 75 g/L
pH 12.0, Current Density 1.0 A/dm²)

| Temperature, °C | Throwing Power, % |
|-----------------|-------------------|
| 30 | 24 |
| 40 | 30 |
| 50 | 36 |

Table 9
Influence of Current Density & Temperature on Nature
& Microhardness of Deposits

(CuSO₄ 20 g/L, EDTA disodium salt 60 g/L, pH 12.0)

| Current Density A/dm ² | Temp. °C | Nature of Deposit | Microhardness, V |
|-----------------------------------|----------|---------------------------|------------------|
| 1.0 | 30 | uniform, dull brown | — |
| 1.5 | 30 | uniform, dull, dark brown | — |
| 2.0 | 30 | uniform, dull, dark brown | — |
| 2.5 | 30 | uniform, dull, dark brown | — |
| 1.0 | 40 | semi-bright, uniform | 120 |
| 1.5 | 40 | semi-bright, uniform | 136 |
| 2.0 | 40 | semi-bright, uniform | 151 |
| 2.5 | 40 | dull, uniform brown | — |
| 1.0 | 50 | semi-bright, uniform | 130 |
| 1.5 | 50 | semi-bright, uniform | 150 |
| 2.0 | 50 | semi-bright, uniform | 158 |
| 2.5 | 50 | uniform, dull brown | — |

This bath has the desirable characteristic of no tendency to immersion deposition, as well as ability to produce adherent deposits with good throwing power and current efficiency. Accordingly, it is a viable substitute for toxic cyanide-based solutions, not only for copper strikes, but plating as well.

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References

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Table 10
Results of Porosity Tests
On Copper-Plated Steel

(CuSO₄ 25 g/L,
EDTA disodium salt 75 g/L)

| pH | Deposit | |
|------|---------------|-------------|
| | Thickness, µm | Porosity, % |
| 10.5 | 2.0 | 75 |
| | 4.5 | 40 |
| | 5.5 | 29 |
| | 6.0 | 24 |
| | 6.5 | 20 |
| | 7.0 | 9 |
| | 7.5 | nil |
| | 8.0 | nil |
| | 9.3 | nil |
| | 10.3 | nil |
| 12.0 | 2.0 | 80 |
| | 4.7 | 33 |
| | 5.4 | 25 |
| | 6.4 | 16 |
| | 7.0 | nil |
| | 7.7 | nil |
| | 8.9 | nil |
| | 9.5 | nil |

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