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New Alkaline Copper Electroplating Bath Based on an Inorganic Complexing Agent

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Abstract

A new alkaline electrolytic solution based on ammonia for copper electroplating has been investigated. Upon addition of alkaline metal hydroxide solution and ammonia followed by the immediate addition of a strong inorganic acid, a highly exothermic reaction takes place. At optimum solution condition ammonia remains in solution as NH_2 and forms a complexing agent..

Keywords: copper electroplating, alkaline bath, non-cyanide.

Introduction

Electroplating of copper from cyanide solutions is a long-established industrial practice [1–9]. Despite the good adherence, brightness and colour hazardous issues has resulted in search for an alternative to the cyanide solutions. Some of the alternative electrolytes used in the previous works include EDTA [10-14], citrate [15], fluoroborate [6], acid sulphate [16-18] and pyrophosphate [19].

Indeed some of these electrolytic solutions ("electrolytes") such as sulphuric acid, citric acid, acetic acid and fluoroboric acid have been used commercially. There are also available some non-cyanide commercial alkaline solutions which utilise chelating ligands such as carboxylates, phosphates and amines. In contrast to acidic non-cyanide solutions these solutions need no pretreatment in a cyanide solution (Tables 1 and 2).

In this paper, a new alkaline solution based on ammonia as the ligand is presented.

The new ammonia-based solution studied in this work is based on the findings by McCoy *et al*. [20] in a U.S. patent article. It is reported in this article that when the addition of solution of ammonium hydroxide to an alkaline metal hydroxide solution is followed by the immediate addition of a strong inorganic acid, a highly exothermic reaction takes place. In this reaction, ammonia is not evolved

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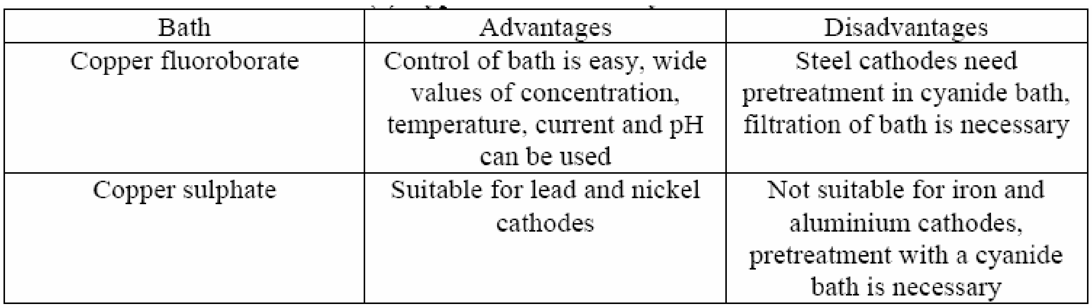
but rather stays in solution as NH_2 and forms complexes with metal ions in solution.

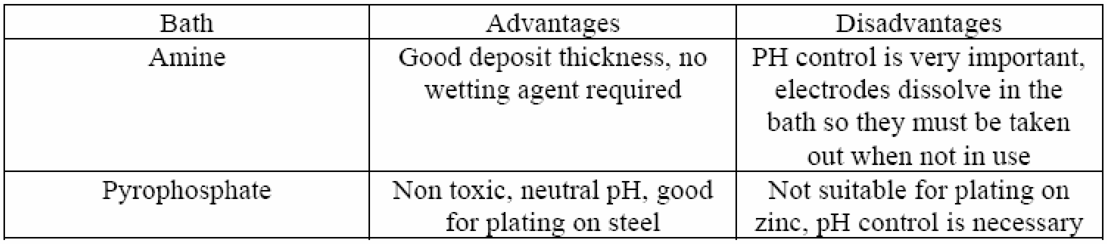
The results of copper electroplating in the new alkaline solution were compared with the results in commercial high speed/high efficiency cyanide solutions.

Table 1. Typical acidic non-cyanide electrolytic solutions.



Bath	Advantages	Disadvantages
Copper fluoroborate	Control of bath is easy, wide values of concentration, temperature, current and pH can be used	Steel cathodes need pretreatment in cyanide bath, filtration of bath is necessary
Copper sulphate	Suitable for lead and nickel cathodes	Not suitable for iron and aluminium cathodes, pretreatment with a cyanide bath is necessary

Table 2. Typical alkaline non-cyanide electrolytic solutions.



Bath	Advantages	Disadvantages
Amine	Good deposit thickness, no wetting agent required	PH control is very important, electrodes dissolve in the bath so they must be taken out when not in use
Pyrophosphate	Non toxic, neutral pH, good for plating on steel	Not suitable for plating on zinc, pH control is necessary

Experimental procedure

All chemicals were analytical grades. A (1×1) cm^2 iron plate with a thickness of 1 mm as cathode and a (1×2) cm^2 copper plate as anode, 1 cm apart, were placed in a 25 cm^3 beaker.

Current and voltage were measured using a FLUKE digital multimeter and a rectifier was used as the source of direct current. Thickness of the deposited layer was measured by taking Scanning Electron Microscopy photographs.

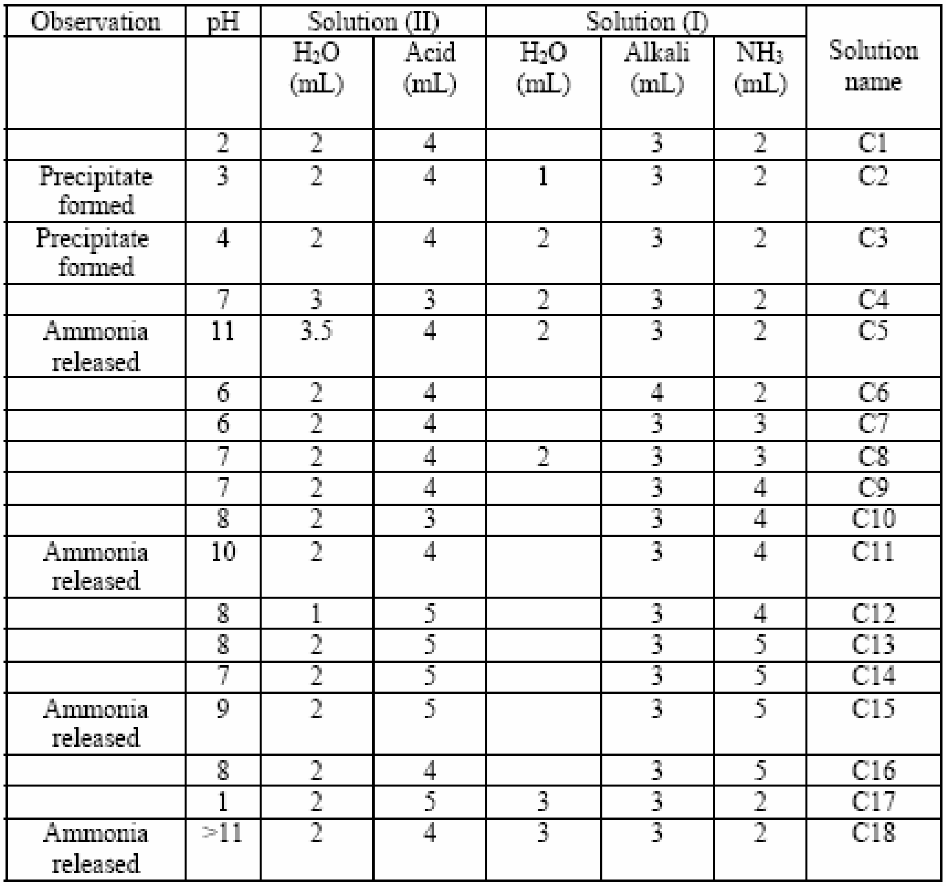
Prior to using in the solution the surfaces of iron plates were sand papered using sand papers of increasing fineness (88 µm, then 18 µm, and then 8 µm). The surfaces were then cleansed of grease using a solution made up of 30 g washing powder, 5 g texaphone, 15 g Na_3PO_4, 30 g Na_2CO_3 and 15 g NaOH made up to 1000 cm^3. The cleansing solution was heated to 70-90 ºC into which iron plates were immersed.

First solutions were prepared to observe the claimed complex formation according to the procedure described by McCoy *et al.* [20]. First an alkaline solution (I) was prepared using ammonia and potassium hydroxide of different concentrations and the resulting solution was cooled to 5 ºC. Then an acid solution (II) was prepared using different inorganic acids and left to cool down. Then the acid solution (II) was poured suddenly into the alkaline solution (I) and the resulting solution was stirred magnetically until it reached room temperature.

Different concentrations of ammonia, potassium hydroxide, sodium hydroxide and also different types of acid such as phosphoric acid, nitric acid and hydrochloric acid, were used as shown in Table 3.

Conventional chemistry predicts that addition of a strong acid solution to a strong alkaline solution produces the precipitation of a salt and also evolution of ammonia is observed. For example addition of phosphoric acid to ammonia produces ammonium di-phosphate and also ammonia is evolved. As addition of a strong acid to a strong alkaline solution produces a buffer solution, the resulting solution was also tested for its buffer properties. It can be seen that solutions c6-c9, c12-c14 and c16 do not indicate observable changes and additionally pH remains neutral.

Table 3. Experimental schemes to verify complex formation.



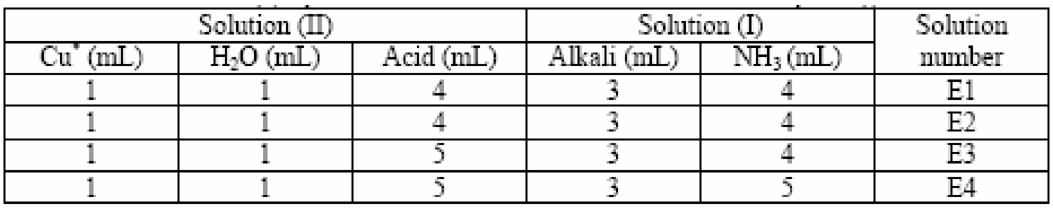
Observation	pH	Solution (II)		Solution (I)			Solution name
		H_2O (mL)	Acid (mL)	H_2O (mL)	Alkali (mL)	NH_3 (mL)	
	2	2	4		3	2	C1
Precipitate formed	3	2	4	1	3	2	C2
Precipitate formed	4	2	4	2	3	2	C3
	7	3	3	2	3	2	C4
Ammonia released	11	3.5	4	2	3	2	C5
	6	2	4		4	2	C6
	6	2	4		3	3	C7
	7	2	4	2	3	3	C8
	7	2	4		3	4	C9
	8	2	3		3	4	C10
Ammonia released	10	2	4		3	4	C11
	8	1	5		3	4	C12
	8	2	5		3	5	C13
	7	2	5		3	5	C14
Ammonia released	9	2	5		3	5	C15
	8	2	4		3	5	C16
	1	2	5	3	3	2	C17
Ammonia released	>11	2	4	3	3	2	C18

The following tests were carried out further to verify complex formation in the solution:

- buffer properties;
- effect of change in temperature;
- effect of addition of hydrogen peroxide;
- effect of the presence of different metallic ions in solution such as Fe, cobalt and copper;
- effect of increase of copper concentration in solution.

After preliminary experiments to check for the above effects the baths shown in Table 4 at a pH of 8 were prepared.

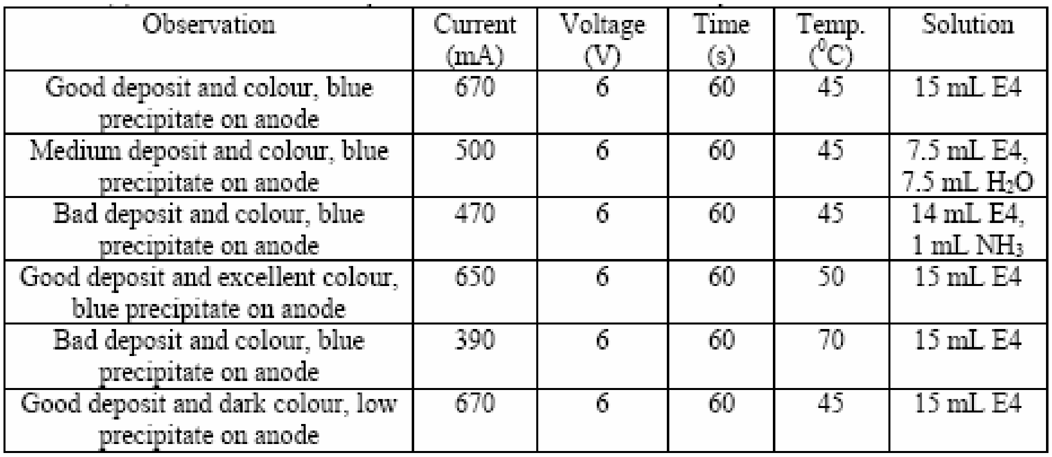
Table 4. Optimised bath formulation used for electroplating.



Solution (II)			Solution (I)		Solution number
Cu^* (mL)	H_2O (mL)	Acid (mL)	Alkali (mL)	NH_3 (mL)	
1	1	4	3	4	E1
1	1	4	3	4	E2
1	1	5	3	4	E3
1	1	5	3	5	E4

Copper electroplating at a voltage of 6 V and current of 670 mA was carried out. Solutions E1 and E3 did not produce a good deposit layer but solutions E2 and E4 produced good deposit layer with the colour of deposit in solution E4 better than in solution E2. Following these results, solution E4 was used as the main formulation and experiments were carried out to optimise the electroplating conditions.

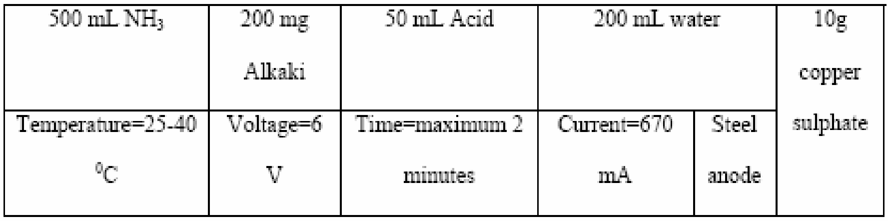
Table 5. Effect of various experimental conditions on the optimized bath formulation.



Observation	Current (mA)	Voltage (V)	Time (s)	Temp. (°C)	Solution
Good deposit and colour, blue precipitate on anode	670	6	60	45	15 mL E4
Medium deposit and colour, blue precipitate on anode	500	6	60	45	7.5 mL E4, 7.5 mL H_2O
Bad deposit and colour, blue precipitate on anode	470	6	60	45	14 mL E4, 1 mL NH_3
Good deposit and excellent colour, blue precipitate on anode	650	6	60	50	15 mL E4
Bad deposit and colour, blue precipitate on anode	390	6	60	70	15 mL E4
Good deposit and dark colour, low precipitate on anode	670	6	60	45	15 mL E4

Following these results the best formulation is therefore:

Table 6. Proposed formulation for copper electroplating bath.



500 mL NH_3	200 mg Alkaki	50 mL Acid	200 mL water		10g copper sulphate
Temperature=25-40 °C	Voltage=6 V	Time=maximum 2 minutes	Current=670 mA	Steel anode	

The results of electroplating in this new bath were compared with the results in a high speed/high efficiency cyanide bath as suggested in [21]. The high speed/high efficiency bath was prepared as follows: 9.4 g potassium cyanide was weighed and dissolved in 40 mL of distilled water with 6 g of copper.

Table 7. Comparison of the new bath with high speed/high efficiency cyanide bath.

Ammonia based bath	**High speed/high efficiency cyanide bath**	**Deposit layer and bath condition**
Strong	Strong	Deposit layer colour
2μm and uniform	3-4μm and non-uniform	Deposit layer thickness (for same deposition time)
Blue	Transparent	Bath colour
None	Some	Particulate matter in the bath
Copper is not usable	Copper	Anode type
670 mA	350 mA	Current
Stable	Unstable	Bath stability with time
Cheap	Expensive	Cost

Cyanide was added to this solution and then 1.5 g potassium carbonate and 4.3 g sodium hydroxide were added to this solution. The solution was made up to a volume of 100 mL with distilled water. 15 mL of the resulting solution were placed in a 25 mL beaker and the iron and copper plates were placed in the bath. A voltage of 6 V and current of 500 mA was applied to the plates and a temperature of 70 ºC was maintained in the bath. After several experiments, and examination of deposit layer, it was decided to add 4 mL of brightening agent and 8 mL of co-brightening agent to the bath. Scanning Electron Microscopy revealed a deposit layer thickness of 3-4 μm with good colour.

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