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Polymer Additives For High Quality Coating Obtainment

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ABSTRACT

This article is devoted to the development of new polymer additives for the process of copper electroplating from sulfate solutions with a purpose of copper coating obtaining. Copper coating, obtained from electrolytes in the presence of DEA-PAN additives and thiourea are of high-quality: they are thick, fine-grained, and in some cases, shiny. Increase of temperature can significantly speed up the process without compromising the high quality of the coatings obtained from electrolyte DEA-PAN or with a combined additive thiourea and DEA-PAN. Current output is close to 90 %. Electrolyte composition and the mode of copper plating electrolyte is given. Flow diagram of metal-crystalline and thick copper coatings on the articles of ST (Steel) - 3, and also from the copper electrolyte proposed by us includes the following process operations: mechanical surface cleaning and preparation details, electrochemical degreasing, etching, pickling, copper plating.

Keywords: surfactants, coating, sediment, copper, electro crystallization, electro reduction, thiourea, additives.

INTRODUCTION

New polymeric additives for the electro deposition process of copper from sulfate solutions were developed and recommended [1,2] in order to obtain high-quality copper coatings. Study of the adsorption and the inhibitory effect of HM surfactant were conducted under their influence upon the electro reduction of Cu (II) ions on a mercury electrode and the copper solid one. Polymeric reagents of "DEA-PAN» series are used in the process of copper ions reduction on the mercury-dropping electrode from the $CuSO_4$• H_2O 10-3 mol/l solution on the background of 1M H_2SO_4 at 293C. The tested additives significantly reduce the current limit reduction of copper. The probable reason for this may be the electrostatic interactions of functional groups with the electrode surface. [3-4]. There were received two provisional patents (on copper plating electrolyte and electrolyte galvanizing).

MATERIALS AND METHODS

Research of the influence of polymeric reagents adsorption on electro-reduction kinetics of metal ions on a mercury electrode was carried out by classic and AC Polarographic methods on polarograph IP-1 in the three-electrode thermostatic cell. The working electrode was a mercury-dropping electrode with r = 6,2 s, the auxiliary electrode - bottom mercury and the reference electrode - silver chloride. Working solution was $2x10^{-3}$ mol L^{-1} $CuSO_4 \cdot 5H_2O$ on the background of 1M H_2SO_4. Metallic mercury was purified by multiple passes through the solution of 0.5% nitric acid and then washed several times with bidistillate for Polarographic curves obtaining.

The kinetics of ion discharge on the copper solid electrode was studied by obtaining classical dynamic potency curves on the potentiostat P-5827M at the rate of potential sweep 0.12 V min^{-1} in a temperature controlled cell with separated cathode and anode space. The working electrode was copper of brand "Highly pure" in a Teflon sheath. The working surface of the electrode is a disc with the surface of 0.46 cm^2. The working electrode potential was measured in the working cell. Stirring of the solution was carried out with a stirrer at a speed of 600 rev min^{-1}. The speed of rotation was controlled by frequency meter CH3-38. Terms of performing the experiments with aqueous solutions of polymeric reagents are given in the sections that discuss relevant results.

RESULTS AND DISCUSSION

The efficiency of copper current and the quality of the copper coatings obtained in the presence of HM surfactants DEA-PAN investigated conditions as shown in table 1 are significantly different from the current output and the quality of the electrolytic precipitation of the electrolyte obtained without surfactant.

Table 1. Copper coatings formed from the electrolyte with the composition (mol L^{-1})

Position	Surfactant	Concentration gr/l	T, K	BT Cu, %	Coating appearance
1	without surfactant	-	293	97,4	Bright, coarsely crystalline
2	DEA-PAN	0,5	293	98,35	Light, compact
3	thiourea DEA-PAN	0,1 0,5	293	98,6	Bright, shiny, tight
4	thiourea DEA-PAN	0,1 2	293	98,15	Light, compact with dark spots
5	without surfactant	-	333	98	Bright, coarsely crystalline
6	DEA-PAN	0,5	333	98,65	Light, compact semi-bright
7	thiourea DEA-PAN	0,1 0,5	333	98,6	Bright, shiny, tight
8	thiourea DEA-PAN	0,1 2	333	98,45	Dense with dark spots

copper sulfate -1, sulfuric acid - 0.5 in the presence DEA-PAN and in combination with thiourea. Current density is $2A/dm^2$

The sediment of copper derived from the electrolyte without additives, has a coarse structure.When HM surfactant DEA-PAN is added to the electrolyte copper plating the sediment structure changes: size of the crystals reduce, the number of crystallization centers significantly increases.

At a temperature of 293^0C a surfactant mixture of thiourea and DEA-PAN (0.5 g L^{-1}) significantly improves the quality of the coating: graininess decreases, shine is enhanced (Table 1). DEA-PAN (2 g L^{-1}) strengthening deteriorates the quality of copper sediments: dark spots appear on the light basis, the output metal current is reduced. (Table 2).

Table 2. Electrodepositing copper from the electrolyte (mol/l): $CuSO_4$ -1, H_2SO_4- 0,5 in the presence DEA-PAN and thiourea+DEA-PAN

Position	Additives	Concentration, g/l	Temperature, C	I к, А/дм^2	Current output Cu	Coating appearance
1.	Thiourea DEA-PAN	-	293	2	98,6	Light, compact
2.	Thiourea DEA-PAN	0,5	293	2	98,1	Light, compact with dark spots
3.	Thiourea DEA-PAN	0,1 0,5	293	3	98,0	Light, exfoliate
4.	Thiourea DEA-PAN	0,1 2	293	3	98,4	Light, compact with dark spots
5.	Thiourea DEA-PAN	-	333	2	98,65	Light, compact
6.	Thiourea DEA-PAN	0,5	333	2	98,0	Light, compact with dark spots
7.	Thiourea DEA-PAN	0,1 0,5	333	3	98,45	Light, compact with dark spots
8.	Thiourea DEA-PAN	0,1 2	333	3	98,15	Dark spots

With an increase of temperature to 333^0C the quality of copper coatings obtained from the electrolyte with two additives remains. However, at high concentrations of DEA-PAN (2 g L^{-1}) the sediments darken. The output of copper current is 98.6 %. As follows from the given material, copper coatings obtained from the electrolyte with DEA-PAN and thiourea with DEA-PAN, are of high quality: thick, fine-grained, and in some cases, shiny. Rise of temperature can significantly speed up the process without compromising the high quality of the coatings obtained from electrolyte DEA-PAN or with a combined thiourea with DEA-PAN. Current output is close to 90 %.

Polarization measurements on solid copper cathode in the studied conditions confirm the high adsorption property of surfactants (DEA-PAN), capable of separately and in combination with thiourea to increase the braking of copper electro crystallization process the reduction of which takes place at a low negative charge of the surface.[7-8] As a result, the copper plating obtained from the electrolyte with the indicated additives are of high quality: they are thick, fine-grained, shiny and porousless.

Development of new electrolyte copper plating: Based on the above it can be concluded that certain additives affect the quality of the coatings, it noticeably increases when a surfactant is combined with thiourea. Table 2 shows the experimental results on the study of the conditions of deposition of copper coatings from sulfuric acid electrolyte in the presence of both individual and combined additives.
High-quality coating of copper (as can be seen from the table 3) obtained from sulphate solutions with the addition of thiourea and DEA-PAN (0.5 g L^{-1}) (pos. 2). By increasing the DEA-PAN concentration up to 2 g L^{-1} the coating remains bright and even, but scales off on the edges, the current output is reduced (pos. 3).

The simultaneous increase in DEA-PAN concentration up to 2 g L^{-1} and a current density of 3 a/dm2 adversely affect the quality of coating; its surface is covered with dark spots, the sediment scales off on the edges (pos.5).

Raising the temperature to 333C at a concentration of DEA-PAN 0.5 g L^{-1} in the electrolyte and a current density of 2 a/dm2 does not degrade the quality of electroplating (pos. 6), the coating is thick, shiny, and the current efficiency is 98%. The increase in current density up to 3 a/dm2 degrades the quality of the sediments. They are shiny, but the edges scale off (p. 8.), the current output is reduced.

Table 3. Copper plating electrolyte composition and mode of electrolyte

Composition and mode	Electrolyte g/l	
	I	II
$CuSO_4 \cdot 5H_2SO_4$	180-250	180-250
H_2SO_4	130-150	150-180
DEA-PAN	0,5-0,15	0,5-0,5-1,0
Thiourea	-	0,05-1,0
Current density, A/dm^2	2-3	2-3
Temperature, C	293 и 333	293 и 333

Flow diagram of metal-crystalline and thick copper coatings on the articles of ST (Steel) - 3, and also from the copper electrolyte proposed by us includes the following process operations.

Mechanical cleaning and preparation details: After mechanical cleaning the parts to be coated are subjected to degreasing by Viennese lime in solutions or electrochemically in the following solution (g L^{-1}): NaOH- 10, Na_2CO_3 - 30, Na_3PO_4 – 20, soap - 1 at a current density of 5.3 A/dm^2 and temperature of 343C. Duration of degreasing is 0.5-2 min. Then the items are washed in hot and cold water [5-6].

In order to remove oxide films from the surface of the item it should undergo the process of etching. Etching is performed in 20% sulfuric acid solution for 5 min at room temperature. To remove residual etchant the item is washed with cold water.

Immediately before dipping into a copper plating bath, the parts are decanted to remove a very thin oxide layer on the surface with the help of the solution, g L^{-1}: H_2SO_4 - 30, HCl - 30 for one minute at room temperature, after which the items are loaded into a copper plating bath.
Electrolysis is carried out in a copper plating bath composition, g L^{-1}:

Electrolyte – I:
$CuSO_4$ $5H_2O$ – 180-250;
H_2SO_4 – 130-150;
thiourea – 0,05-1,5;
DEA-PAN – 0,5 – 1,5

Electrolyte – II:
$CuSO_4$ $5H_2O$ – 180-250;
H_2SO_4 – 130-150;
DEA-PAN – 0,5 – 1,5

at a current density of 2 - 3 A/dm^2 and a temperature of 293^0 C and 333^0 C.

Electroplating obtained from the above electrolyte, is characterized by density and gloss. Output of current is 100%. Copper anodes (M -O GOST 859-41) are soluble. Ratio of the anode surface equals the surface of the covered parts.

Preparation of electrolytes: Electrolyte salts are dissolved sequentially in warm water, the solution is filtered as required[7-8]. Surfactant additive DEA-PAN is pre-soaked for 5-7 h in cold water until

complete dissolution then thiourea (previously dissolved in hot water) is introduced into the electrolyte. The electrolyte is adjusted to a suitable volume. For a long time, the electrolyte remains transparent, once it grows turbid the electrolyte is filtered (once a month), major components are analyzed and after the filtering a new portion of the surfactant is introduced. The pH of the electrolyte is regularly controlled by pH -meter.

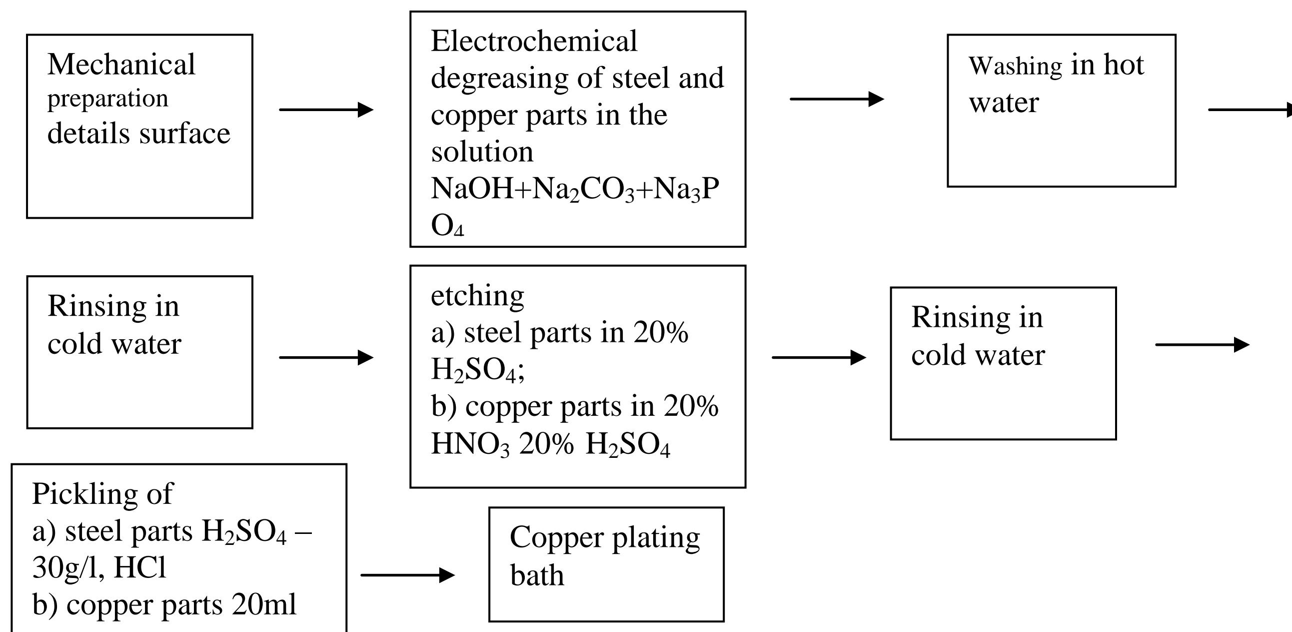

Figure 1. Technological operations of copper plating

Sediments of copper having a smooth surface, gloss (or a matte surface), fine-grained structure and meeting the requirements of modern standards are prepared from surfactants -containing electrolytes.

APPLICATIONS

This work is useful for the development of new polymer additives for the process of copper electroplating from sulfate solutions with a purpose of copper coating obtaining. Copper coating, obtained from electrolytes in the presence of DEA-PAN additives and thiourea are of high-quality: they are thick, fine-grained, and in some cases, shiny.

CONCLUSIONS

1.Copper coatings obtained from electrolytes in the presence of additives DEA -PAN and thiourea together with DEA-PAN, are of high quality: thick, fine-grained, and in some cases, shiny. The temperature rise can significantly speed up the process without compromising the high quality of the coatings obtained from electrolytes with DEA-PAN or thiourea combined with DEA-PAN.

2. Based on the concepts of action of surfactants on the cathode processes the factor having a large effect on the value of the cathode potential, and consequently the structure of the sediment, would be a definite orientation and densification of particles or molecules of "extension agent". Such substances compaction on the interfacial metal- solution occurs due to adsorption. Often, in addition to physical adsorption, flowing under the action of electrostatic forces, there is the phenomenon of specific adsorption associated with surface chemical reactions. In such cases, the "compaction" may occur not only on the outer surface but also in the pores and crevices of the crystals. Adsorption of polymeric compounds on mercury and

solid electrodes is characterized by the same laws as in the case of simple organic substances, however, polymeric compounds are adsorbed to a much greater degree.

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