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Effects of polishing grades and Saccharin-550 additive on copper electroplating on NST60Mn and NST50-2 steels

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ABSTRACT: Cathodic protection is still one of most useful methods of corrosion control applicable to metal surfaces. Copper is often applied on steels for its good adhesion and improved appearance. Organic additives to plating baths improve the throwing power, levelling and brightening of the film. Hence the effects of surface polishing grit and Saccharin-550 additive on copper plating of steels were studied. Two standard NST60Mn and NST50-2 steels were electroplated in acid-sulphate bath using saccharin-550 as additive. Copper film thickness reduces as surface polishing grit increased with or without additive. The film properties improve as the substrate surface improves, with the most stable, metallic, lustre and adhesion obtained on 400µm and 600µm finishes without additive. Increasing saccharin-550 concentration from 0.1g/l to 0.5g/l improved film quality. Lower 0.1g/l saccharin-550 concentration produced higher thickness but poor brightening. Optimum plating parameters were obtained at 2V, 200g/l $CuSO_4.H_2O$, 600µm SFG and 0.5g/l saccharin. The density of copper plates is increased while porosity is reduced. The coat becomes more tenacious and protective in nature, and deposited in form of metal sheet rather than the powdery form. Types of steel do not control Cu-deposition but rather the polishing grade of steel surface.

KEYWORDS: Surface polishing grit, Saccharin-550, levelling agent, brightening, copper-plating, carbon steel.

1 INTRODUCTION

The theories of electro-deposition are based on the previous works done by Michael Faraday in 1833 on electrolysis [1]. Electroplating involves the deposition of more protective metal on a metalised surface by passing electric current through the solution of the metal to be deposited, while the coating metal is made the anode and the surface is the cathode [2]. It is electrochemical deposition (of metals or alloys) that involves the reduction of metal ions from aqueous, organic, or fused salt electrolytes. In its simplest form the reaction in aqueous medium at the cathode follows the equation:

$$M^{n+} + ne^- = M \quad (1)$$

$$M = M^{n+} + ne^- \quad (2)$$

This occurs with a corresponding anodic reaction. The anode material can be the metal to be deposited and in this case the electrode reaction is electro-dissolution that continuously supplies the metal ions [3]. For a copper-plating on steel process, the chemistry of the reaction can be represented as

$$Cu^{2+} + Fe = Cu + Fe^{2+} \quad (3)$$

Copper is commonly used in coating of steel surface for use as the earthen rod due to its high conductivity and adhesion to the steel surface. The shape of the work piece and the bath throwing power determine the plate thickness. For this purpose, a few micron thickness layers is necessary. It is often applied for good adhesion and improved appearance. [4,5]. Though copper coating on steel have good resistance to corrosion, but once the base metal is exposed by a pin hole or scratch, a strong voltaic effect is set up at the breaks beneath the coating and this results in peeling away of the coat. Copper coating for a decorative reason is always prevented from oxidation by top coating with clear lacquer. High throwing power baths are often used such as sulphate and fluoborate-acid baths, cyanide and pyrophosphate alkaline baths [6].

A variety of low carbon steels (such as ST30LC, NST44) and mild steels medium (NST50-2), medium carbon steels (NST60Mn) and high carbon steel are produced in Nigeria [7,8.9]. These are used in many areas such as wire drawing, steel rolling and machine parts and machine tools fabrication to mention a few. Steels are characterized by high strength and high workability, but are like other metals susceptible to corrosion when used. The improved service requirement of steel can be achieved by the measures such as heat treatment; coating such as painting, metallising and electroplating; regular lubrication and so on which offer a long lasting protective measure on the machine part under services [10,11,12,13]. Coating and plating as finishing operations are carried out to obtain a good characterized surface finish of the materials for effective corrosion resistance, heat reflection, wear resistance and decorative value [14]. The coating thickness and adhesion are very important. The thickness varies from hundredth of micron to millimetres. There is control of the uniformity in the coating thickness. Some salts are added to increase the brightening and levelling of electroplate, thereby improving the porosity and appearance such as dextrin, lactic acid and saccharin are added to cadmium on steel plating baths [15].

Of recent, Hartikainen et al, 2012 [16] assessed the impact of Cu and Zn on fungi and the growth of 18 taxonomically different saprtrophic fungi such as ascomycete, zygomycete and basidiomycete and their production of oxidative enzymes on 0-400 mkg^{-1} Cu or Zn. It was reported that for all the methods, Cu was found to be more toxic than Zn for all tested fungi, showing that microbial functioning of soil is more vulnerable to Cu than Zn.

Also with trend of increase in price of metals in the world market, the use of pure copper materials as earthen rod is been replaced in practice with copper plated steels in many of the West Africa sub-region. With the view of solving the problem of microbial growth which facilitate high corrosion rate in buried plated metallic materials, perfect adhesion and uniform deposition of coating metal (metal plate) to the substrate has to enhanced and assured. Hence in the present study, the effects of addition of saccharin-550 (a compound of Ortho-sulfobenzoic Acid Imide) as the levelling and brightening additive for improved properties of copper film on steels in acid–sulphate bath were investigated on five degrees of surface polishing grits (SPG) and two varieties of steels (NST50-2 and NST60Mn) which popularly dominate Nigeria steel markets for earthen rod production.

2 Materials and Method

2.1 Materials

The materials used in this study were NST50-2 and NST60Mn steels samples of dimension 100 mm x 100 mm x 150 mm obtained from Osogbo Steel Rolling Mill, Osogbo. The chemical composition of the steel is shown in Table 1. Saccharin 550 insoluble Vardayini's Steamer Brand of Saccharin 550 with molecular formula $C_7H_5NO_3S$ was procured from chemical store and used for the experiment.

2.2 Methods

Saccharin-550 was pis used as levelling and brightening additive. The chemical compositions of the samples were determined at the Universal Steels, Ogba Ikeja, Lagos by optical emission spectrometry using AR430 metal analyser. The results are presented in Table 1.

Table 1: Chemical composition (%) of as-received carbon steel samples

Elements	Fe	C	Si	Mn	P	S	Ni	N_2
NST50[2]	98.3	0.24	0.18	0.40	0.40	0.04	-	0.01
NST60 Mn	97.7	0.35	0.3	0.9	0.04	0.25	0.10	-

2.2.1 Preparation of carbon steel samples

Steel samples were cut to smaller dimension of 40 mm x 15 mm x 5.5 mm thick. The samples surface were smoothened by hand filing with 0.8 mm, 0.6 mm and 0.4 mm hand files and finally polished on the ELE polishing machine (EL 78/260) using five degrees of sand paper grits (60µm, 120µm, 320µm, 400µm and 600µm).

2.2.2 SAMPLES SURFACE PRE-TREATMENT OPERATION

The surface cleaning were carried out by brush cleaning and washing in emulsifying solution made from 1:1 kerosene and detergent at 50 ±5°C for 10 mins, followed by water rinsing for 1 mins at 70 ±5°C, alkaline-washing in 1% NaOH solution operating at 45 ±5°C for 2 mins to degrease the surface, followed by acid-washing in 13% HCl at 50 ±5°C for 1 min with intermittent water rinsing at 27 °C between every stage. The initial weight of the specimen was determined on weight meter

2.2.3 PREPARATION OF COPPER ELECTROPLATING BATH

The acid copper sulphate electrolyte used was formulated based on the patent right of Gupta et al, 1990 [17]. HDPE plastic container was used as the bath containing the prepared formulated electrolyte. Pure copper electrode (anode) rod was carefully selected and prepared based on the B224-04 and B115-00(2004) ASTM Standards.

2.2.4 PLATING REAGENTS AND OPERATING CONDITIONS

The copper electroplating bath (Figure 1) was set up under the following conditions; the acid sulphate bath comprises of three initial plating solutions: 200g/l $CuSO_4.5H_2O$, 50g/l H_2SO_4, 1.0g/l phenol as inhibitor, operated at 50 ±5 °C bath temperature, current density (c.d) = 1A/dm^2, 95% current efficiency. 120 mm maximum electrodes separation, 25 minutes for constant time experiments, Voltage was kept constant at 2V using 0.1A. The surface polishing grade is varied from 60μm to 600μm. Saccharin concentration was varied from 0.1g/l to 0.5g/l.

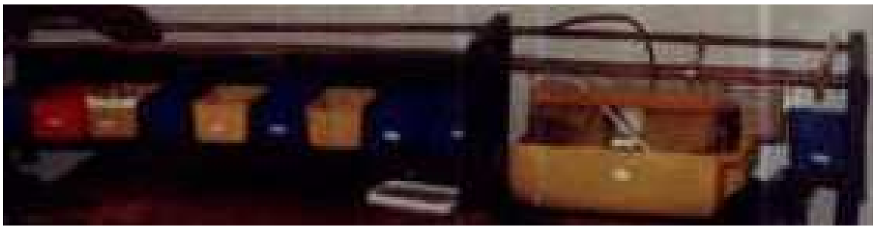

Figure 1: Laboratory set up for copper plating experiment

2.2.5 POST PLATING OPERATION

The plated steel was seal rinsed in water at 80 ±5°C for 1 min, dried in air and kept in the dry saw dust.

2.2.6 COPPER FILM WEIGHT AND THICKNESS DETERMINATION

The final weight of cathode is measured. The copper film weight-gain is determined from the difference in the final and initial weights. The results are presented in Tables 2 to 10. Also, the initial dimensions were subtracted from the final dimensions of the electroplated samples. The values obtained from weight difference and from dimension difference were used in evaluating both the actual weight deposited per unit area and the thickness of deposition. Mathematically expressed as Equations 4 and 5:

$$W_D = W_2 - W_1 \quad (4)$$

$$A_D = A_2 - A_1 \quad (5)$$

where W_1= initial Weight of sample before electroplating,

W_2 = final Weight of sample after electroplating,

W_D = Electrodeposited weight,

A_1 = initial surface area of sample before electroplating.

A_2 = final surface area of sample after electroplating.

The actual electrodeposited weight in g/cm2 was calculated from Equation 6;

$$(W_D/A_D) = (W_2-W_1)/(A_2-A_1) \quad (6)$$

The thickness of electrodeposited copper film was also calculated as Equation 7;

$T_{Cu} = W_D / (A_D \times \rho_{Cu})$ (7)

Where ρ_{Cu} = density of copper given varied from 8.3 to 9 g/cm^3 [18]

The thickness of the metallic Cu-film was measured using micrometer screw gauge and while for powdery film, the electro-deposition thickness per hour has also been determined from the Equation 8

$T = (CD \times W \times CE) / 235 \times \rho_{cu}$ (8)

Where CD = current density, W = weight of metal deposited, CE = current efficiency and ρ_{cu} = copper metal density. The results are presented in Tables 3 to 7; 9, 11 and 13

2.2.7 Visual Observation and Surface Examination

The electroplated samples were observed for physical appearance as colour, brightness, transparency, texture and tenacity and were reported in Tables 2 to 7, and 9.

The surface examination of the copper electroplated samples was carried out using digital camera at ×100 magnification in Plates 1 (a and b). Also the thin film of copper-electroplated sample and as-received substrate was carried out under an optical metallurgical microscope with digital camera at magnification ×160 (Plates 2, 4 and 5).

3 Results and Discussion

3.1 Determining the optimum plating parameters

Table 2: Plot of applied voltage against copper film weight and film thickness

Applied voltage (V)	Film weight (g)	Film thickness (mm)	Appearance of plating
1	0.07	0.018	Pink and smooth
2	0.09	0.023	Pink and transparent
3	0.15	0.038	Red and smooth
4	0.41	0.104	Deep red and rough
5	0.75	0.190	Brownish red and powdery

Table 3: Plot of plating time against copper film weight and film thickness

Plating time (mins)	Film weight (g)	Film thickness (mm)	Appearance of plating
5	0.24	0.061	Pink, bright and metallic
10	0.41	0.104	Pink, bright and metallic
15	0.45	0.114	Pink, bright and metallic
20	0.50	0.126	Pink, bright and metallic
25	0.53	0.134	Pink, bright and metallic

Table 4: Plot of electrolyte concentration against copper film weight and thickness

Concentration (g/l)	Film weight (g)	Film thickness (mm)	Appearance of plating
200	0.05	0.013	Pink, bright, metallic and smooth
210	0.12	0.030	Pink red, metallic and smooth
220	0.21	0.053	Red, metallic and rough
230	0.25	0.063	Deep red colour and rough
240	0.31	0.077	Deep red colour and rough
250	0.35	0.089	Deep red colour, rough and porous

Table 5: Plot of electrode separation against copper film weight and film Thickness

Electrode separation mm	Film weight (g)	Film thickness (mm)	Appearance of plating
140	0.05	0.013	Pink red, metallic and smooth
120	0.08	0.020	Red, metallic and fairly smooth
100	0.12	0.030	Red, fairly smooth, peeling
80	0.17	0.043	Deep red colour and rough
60	0.18	0.046	Brownish red, rough and powdery

3.2 EFFECT OF SURFACE FINISHING GRADES ON COPPER DEPOSITION WITHOUT ADDITIVES

The effects of five surface-finishing grades of steel samples studied on the copper film weight and film thickness in sulphate bath. Figures 2 shows copper-plating on steel using improving surface finishes ranging from 60 to 600µm polishing grades. No additive was used. From the results, the film weight gain and thickness reduce as the surface-finishing grades increased. The physical appearance (colour, porosity, lustre and adhesion) improves as the surface improves.

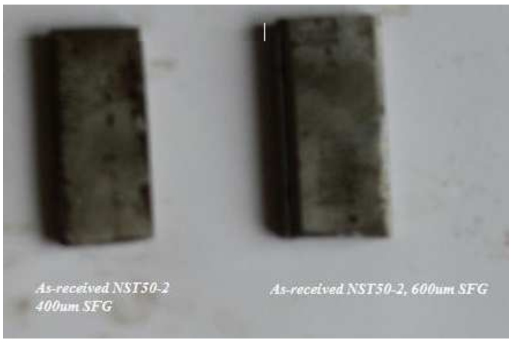

Plate 1: (a) Macroscopic views of as-received 600µm polished steel substrates.

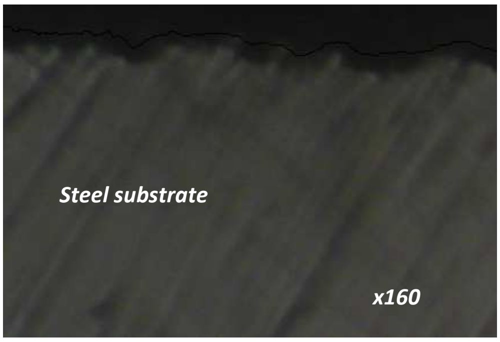

Plate 2: Microscopic views of as-received 600µm polished steel substrates

Table 6: Effect of SFG on copper film weight and film thickness (without additive)

Polishing grade (µm)	Film weight (g)	Film thickness (mm)	Appearance of plating
60	0.14	0.035	Deep red colour and rough
120	0.16	0.041	Deep red colour and rough
320	0.14	0.035	Deep red colour
400	0.10	0.025	Red colour
600	0.06	0.015	Pink colouration and smooth

Observation shows that the most stable plating was obtained from the 600µm surface finishing grade. There were unstable, rough deposits on the 320, 120µm and 60µm grades, while the deposition on 400µm and 600µm finishes were of metallic lustre and better adhesion characteristics. The result shows that a very thin layer (µm) of copper film was deposited on the steel cathode.

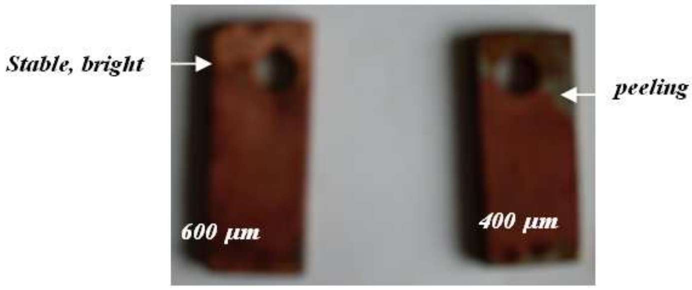

Plate 3: Photographic views of copper film on 600µm and 400µm polished substrates.

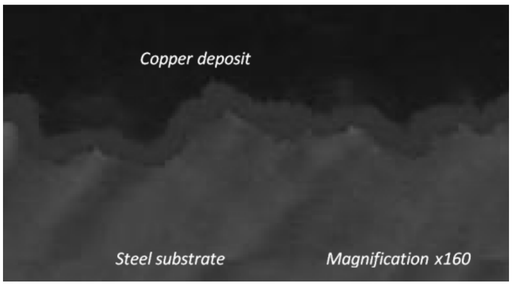

Plate 4: Optical microscopic view of copper film on 600µm polished substrate.

3.3 Effect of surface polishing grits on copper deposition with additives

The results of the effect of organic brightening agent (saccharin 500) on the film weight gain and the film thickness using five surface finishing grades are presented in Figures 3 through 5. These organic additives are used to improve on the throwing power of acid-sulphate electrolyte and the brightening of the copper plating.

3.3.1 Effect of increasing SPG and saccharin 550 concentration on deposition

Figure 3 shows the results of increasing the concentration of saccharin 550 additives used as organic brightener on copper-plating on five surface finishing grades of steels in an acid-sulphate bath. There was reduction in film weight gain and thickness as the surface polishing grits SPG increased. Observation shows that, the increasing saccharin-550 concentration from 0.1g/l to 0.5g/l shows improvement on the physical appearance of the plating. At lower concentrations 0.1g/l saccharin-550, there was a high film weight and thickness value but poor brightening characteristic of the plating. The addition 0.5g/l saccharin 550 to the bath gave stable plating on all the surface finish grades. The trend of curves revealed that there was reduction in copper film weight for all surface-finishing grades used as the concentration of saccharin 550 increased. The deposition on the 600µm finish grade was very thin, bright, protective and stable. Thus, the combination of 600µm SPG and 0.5g/l saccharin produced the most stable plating suitable enough for corrosion prevention.

Table 7: Effect of SFG on copper film weight (with saccharin additive)

Concentration (g/l)	Film weight (g) and appearance of copper deposit using 60µm	120µm	320µm	400µm	600µm
0.0	0.14	0.16	0.14	0.10	0.06
appearance	powdery	rough, metallic	rough red	rough brown	rough red
0.1	0.21	0.22	0.36	0.38	0.13
appearance	powdery	mixed deposit	rough red	rough red	rough red
0.2	0.14	0.16	0.16	0.16	0.02
appearance	rough red	rough red	dull red	dull red	red, peeling
0.3	0.15	0.11	0.14	0.13	0.02
appearance	rough red	rough red	rough red	dull	red, peeling
0.4	0.11	0.07	0.07	0.09	0.03
appearance	rough, red	red-pink	red-pink	red-pink	bright pink
0.5	0.09	0.04	0.03	0.03	0.02
appearance	peeling	bright pink	dull pink	very bright	very bright

Copper film thickness is plotted against five surface polishing grits SPG varied from 60 to 600 µm. The copper film weight (g) reduces as the surface-finishing grade increased. Close values of copper deposition (weight gain) were obtained from the use of 0.5g/l saccharin on 120~600µm finish grades.

In the saccharin based electrolytes, the plating stability increased with increasing SPG.

The physical observation shows that, the organic additives gave stable plating with lower film thickness values on 600µm SFG.

Table 8: Effect of SPG on copper film thickness (with saccharin additive)

Saccharin (g/l)	Film thickness (mm) using 60µm	120µm	320µm	400µm	600µm
0.0	0.036	0.041	0.036	0.025	0.015
0.1	0.053	0.056	0.091	0.096	0.033
0.2	0.036	0.041	0.033	0.041	0.005
0.3	0.038	0.028	0.036	0.033	0.005
0.4	0.028	0.018	0.018	0.023	0.008
0.5	0.023	0.041	0.008	0.008	0.005

Using saccharin, the 600µm surface-finishing grade produced the least copper film weight and thickness with best physical appearance and plating stability. Generally, the organic additive used, yielded better and improved results in terms of brightness and adhesion, though less quantities of cu film (weight and thickness) was produced. Hence, the overall results show that with the use of 0.5g/l saccharin 550, very thin film could be obtained from 120~600µm SFG. Plate 5 illustrates the optical macrographs of copper film on (a) 60µm, (b) 120µm, (c) 320µm and (d) 600µm polished steel substrates. More porous films are obtained on rough surfaces.

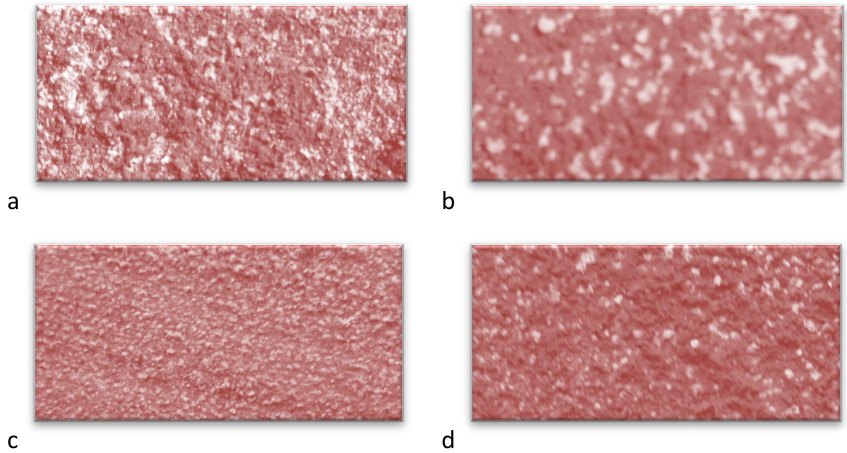

Plate 5: Optical macrographs of copper film on (a) 60µm, (b) 120µm, (c) 320µm and (d) 600µm polished steel substrates.

The addition of increasing organic additives increases the solution resistance to current flow as understood from the equation M=ZVt (1/R) based on Ohm's law and Faraday's laws. It is known that I =V/R, where 1/R is equal to conductance of solution. Hence, with much quantity of additive in solution large quantity of current I have to be drawn into the cell before substantial quantity of Cu could be plated on steel.

It is known that most organic additives are reagents with large molecular composition. They are not as conducting in solution as copper sulphate or H_2SO_4 aqueous solutions. Hence, their addition on large quantity may reduce solution conductance to certain extent.

Mayana et al, 1989 [15] reported the addition of dextrin and lactic acid as levelling and brightening agent on cadmium plating on steel. The density of copper plates is increased while porosity is reduced. The coat becomes more tenacious and protective in nature, and deposited in form of metal sheet rather than the powdery form. From the result, it becomes more evident that, with increasing surface finish grade value, (Smoother surfaces), less quantity of Cu is deposited on steel surface. The rougher surfaces have more crevices and pits, which increase the total surface area of steel obtainable (Cathode).

3.3.2 DETERMINATION OF EFFECT OF SFG AND STEEL COMPOSITION ON COPPER PLATING.

The results of copper film weight and film thickness (Tables 9 and 10) on five surface finishing grades of $NST50^2$ and NST60Mn steels are compared in Fig. 5. The plating was done using the optimum plating values of V=2V, 200g/l $CuSO_4$ for 10 minutes.

The trend of both $NST50^2$ and NST60Mn curves show that the film weight and film thickness decrease with increasing SFG from 60-600µm while observation revealed that plating become more stable from 400 to 600µm SFG. Both curves show a decrease in film weight and thickness for SFG from 60 to 320µm and from 400 to 600µm. From 320 to 400µm, $NST50^2$ maintained a constant film weight and thickness values while on the NST60Mn curve, the film weight and thickness increased with SFG. The little difference in Cu-deposition on the steel surfaces might have been influenced by some other imperfections (scratches etc) rather than the composition of the steel. Hence, it is evident that the level (degree) of surface smoothness has more pronounced influence on deposition rather than the steel types. Best Cu-plating was obtained for the two types of steels when 400 and 600µm grades were used showing that better degree of copper adhesion would be enhanced on very smooth steel substrate. The plating is sufficient enough to offer protection against corrosion of both steels when copper plated and intended to be used as earthen rods.

Table 9: Effect of SFG on copper film weight on NST50-2 and NST60Mn steels

teel type	Film weight (g) using 60µm	120µm	320µm	400µm	600µm	Remark
NST50-2	0.09	0.05	0.03	0.03	0.02	
appearance	peeling, red	bright pink	red-pink	very bright	very bright	Good as from 120µm
NST60Mn	0.08	0.05	0.02	0.03	0.02	
appearance	red	bright	bright	very bright	very bright	All good

Table 10: Effect of SFG on copper film thickness on NST50-2 and NST60Mn steels

Steel type	Coat thickness (mm) using surface finish grades 60µm	120µm	320µm	400µm	600µm
NST50-2	0.018	0.013	0.008	0.008	0.005
NST60Mn	0.016	0.013	0.005	0.008	0.005

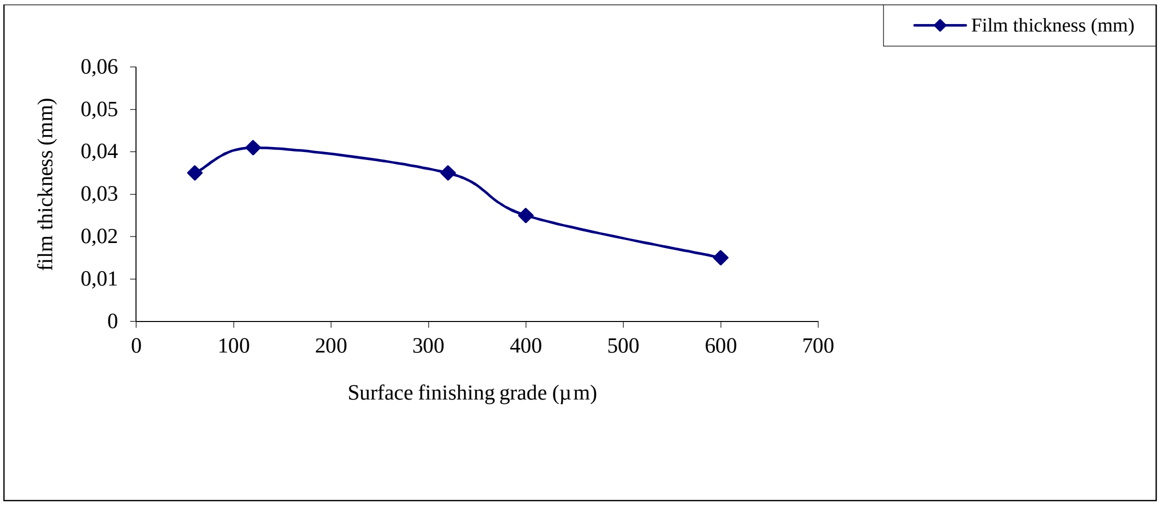

Figure 2: Effect of SFG on copper film thickness (in bath without additive)

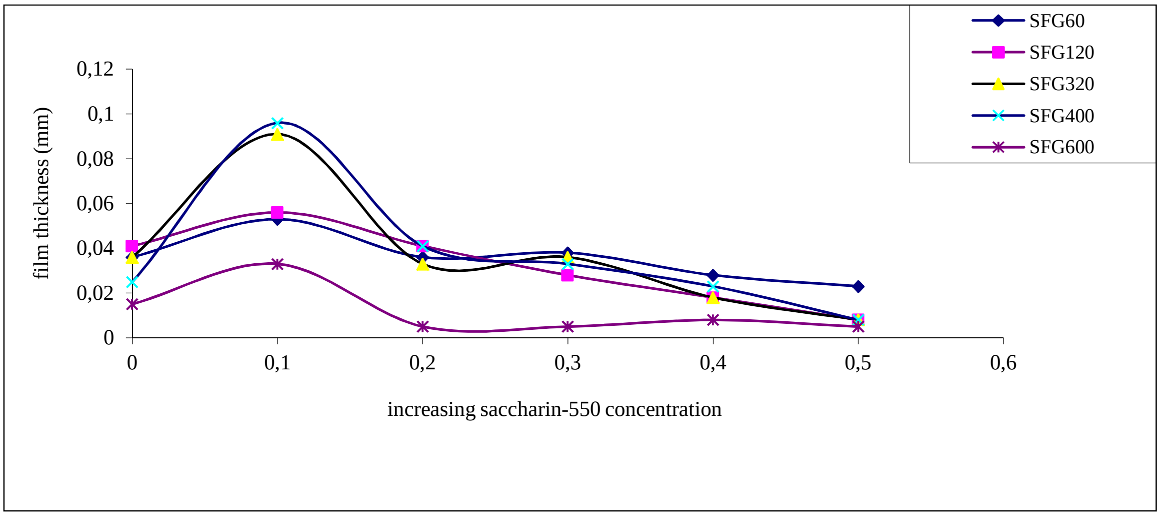

Figure 3: Effect of varying SFG and saccharin concentration on film thickness on NST50-2

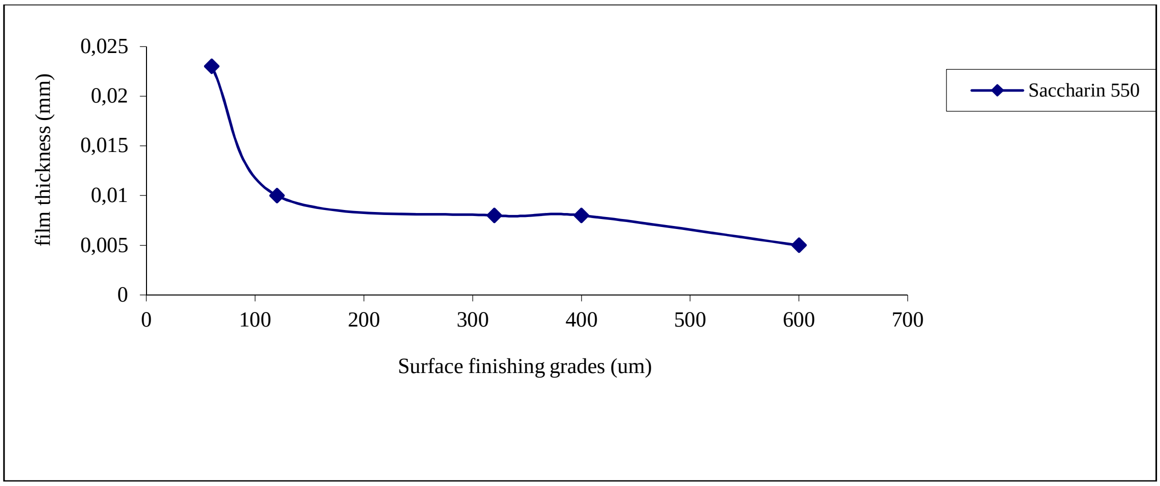

Figure 4: Effect of SFG on film thickness on NST50-2 steels (with 0.5g/l saccharin)

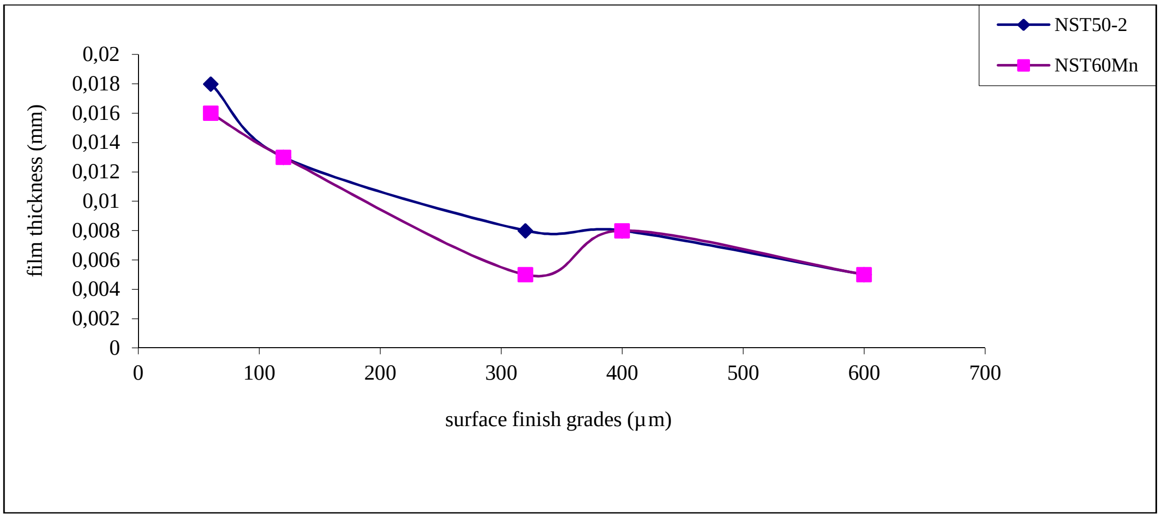

Figure 5: Effect of SFG on film thickness on NST50-2 and NST60Mn (with 0.5g/l saccharin)

4 CONCLUSION

NST50 and NST60Mn Steels were coated using copper by electroplating process. The optimum plating parameters for copper plating on steel substrates were obtained at 2V applied voltage, 200g/l $CuSO_4.H_2O$ electrolyte concentration, 120mm minimum electrodes separation, 600µm surface finishing grade and 0.5g/l saccharin concentration (used as organic brightening agent).

Copper film thickness reduces as surface polishing grades increased with or without additive. The film properties improve as the substrate surface improves, with the most stable, metallic, lustre and adhesion obtained on 400µm and 600µm finishes without additive. Increasing saccharin-550 concentration from 0.1g/l to 0.5g/l improved film quality. Lower 0.1g/l saccharin-550 concentration produced higher thickness but poor brightening. Optimum plating parameters were obtained at 2V, 200g/l $CuSO_4.H_2O$, 600µm SFG and 0.5g/l saccharin. The density of copper plates is increased while porosity is reduced. The coat becomes more tenacious and protective in nature, and deposited in form of metal sheet rather than the powdery form. The types of steel used do not show much pronounced effect on Cu-deposition but rather by the grade of smoothness of surface finishing of steel material.

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