Journal homepage: www.fia.usv.ro/fiajournal
Journal of Faculty of Food Engineering,
Ştefan cel Mare University of Suceava, Romania
Volume XIV, Issue 1 - 2015, pag. 45– 52

FOOD AND ENVIRONMENT SAFETY

CONTRIBUTIONS TO ACHIEVEMENT OF A COMPOSITE MATERIAL FOR ADVANCED ELECTROMAGNETIC SHIELDING OF LIVING AND WORK SPACES

Second part - quantitative aspects

Cristian Florin ALEXUC[1], *Gheorghe GUTT[1], Sonia AMARIEI[1]

[1]*Faculty of Food Engineering, Stefan cel Mare University of Suceava, Romania*
g.gutt@usv.ro
*Corresponding author
Received 7th March 2015, accepted 27th March 2015

Abstract: *Quantitative aspects about the composition of copper baths of steel wire nets and technological parameters used are presented in the second part of the paper. The mechanism of copper plating process is described and also the theoretical material balance for the three copper deposition technologies respectively galvanic deposition, electrochemical deposition without external power and deposition by chemical reduction, all described in the first part of the paper. The issue of automation copper plating bath for the latter technology is presented.*

Keywords: *copper plating recipe, technological parameters, reaction mechanism, material balance, productivity*

1. Introduction

In the first part of the paper [1] the authors presented the need for electromagnetic shielding of living and workspaces and the issue of this important environmental need. In the purpose of advanced shielding to electromagnetic radiations of low and high frequency the authors propose a new composite material that takes the form of some fine nets made of thin steel wires. Over these nets are submitting a high purity copper shirt wrapped in turn by a polymer shirt made in order to protect the copper coating against the oxidation. The nets, supplied in rolls, can be integrated under the plaster of working and living spaces performing their advanced electromagnetic shielding throughout the duration of the building which the space belongs [3], [4]. The second part of the paper is dedicated to the description of copper baths composition, technological work parameters, mechanism of galvanic copper deposition and material balances and carry out a benchmark considering quantitative and qualitative aspects of the three technologies proposed for copper plating.

2. Quantitative aspects of steel wire nets coppering for shielding of living and workspaces against electromagnetic radiations of low and high frequency.

2.1. Steel wire nets coppering by galvanic deposition of copper

The authors recommend two types of galvanic copper plating baths, one with alkaline electrolyte based on copper cyanide(recipe 1 with the eletrolyte 6a, fig.1), and the other with acid electrolyte based on copper sulphate(recipe 2 electrolyte 6b, fig.1) [1], [2]. The two galvanic baths composition and operating mode are as follows:

1. recipe 1- alkaline electrolyte 6a based on copper cyanide with the following composition for 1 liter of electrolyte:150 g CuCN , 100 g NaCN, 20 g NaOH.

- current density - 1 A/dm^2 (the surface refer to the steel wire from which it is made the net and it does not refere to the steel net)
- working temperature 60^{o}C
- feed of advancement of steel wire net of 6m / minute
- immersion length of the net in galvanic bath of 2 linear meters
- electrolyte recirculation flow rate - 2 liters / second
- galvanic bath capacity - 500 liters
- thickness of copper deposited about 10 µm

Reactions that occur during galvanic deposition of copper from cyanide bath on steel wire net are:

$$CuCN_{aq} \rightarrow Cu^{+} + CN^{-} - \text{dissociation galvanic bath}$$

$$NaCN_{aq} \leftrightarrow Na^{+} + CN^{-} - \text{dissociation galvanic bath}$$

$$NaOH_{aq} \leftrightarrow Na^{+} + OH^{-} - \text{dissociation galvanic bath}$$

$$H_2O \rightarrow H^{+} + OH^{-} - \text{dissociation galvanic bath}$$

$$Cu^{2+} + OH^{-} \rightarrow Cu(OH)_2 - \text{dissociation galvanic bath}$$

$$Cu - 2e^{-} \rightarrow Cu^{2+} - \text{anode dissolution}$$

$$Cu^{2+} + 2e^{-} \rightarrow Cu - \text{cathode deposition}$$

$$2H^{+} + 2e^{-} \rightarrow 2H \rightarrow H_2 \uparrow - \text{anode emission}$$

To perform the theoretical material balance, expressing the theoretical consumption coefficients, the Faraday's law governing galvanic processes is used:

$$m = K \cdot I \cdot t \cdot \eta \qquad (1)$$

where:

K - electrochemical constant K =A/zF

A - atomic mass

z - valence

F - Faraday number, (96.500 C)

m - mass of metal deposited on the cathode or dissolved from the anode [g]

I - galvanic current intensity [A]

t - time passing of electrical current through the cell [s]

η - current efficiency taking into consideration theoretical material balance as 100%

In the case of coppering from cyanide baths of thin steel wire nets, the quantity of copper theoretical deposited is:

$$m_{Cu1} = \frac{A_{Cu}}{96.500} \cdot I_1 \cdot 20 = \frac{64}{96.500} \cdot I_1 \cdot 20 = 0{,}0133 I_1 \qquad (2)$$

where:

m_{Cu1} - mass of copper deposited on the cathode, respectively dissolved at the anode in conditions of 100% current yield η of anode and cathode

64 - atomic mass of copper

96.500 - Faraday number

20 - time, in seconds, as electric current passes through a segment of thin steel wire net from its entry to the exit of galvanic bath (feed rate of the mesh in the galvanic bath of 6m / minute, immersion length in galvanic bath - 2 meters), [s],

I_1 - calculated current intensity of electrolysis at a current density of 1A / dm^2 considered on the surface of the steel wire, diameter of 0,3 mm, which form meshes of metal net, with an immersion length of 2 meters, at a given moment in the galvanic bath.

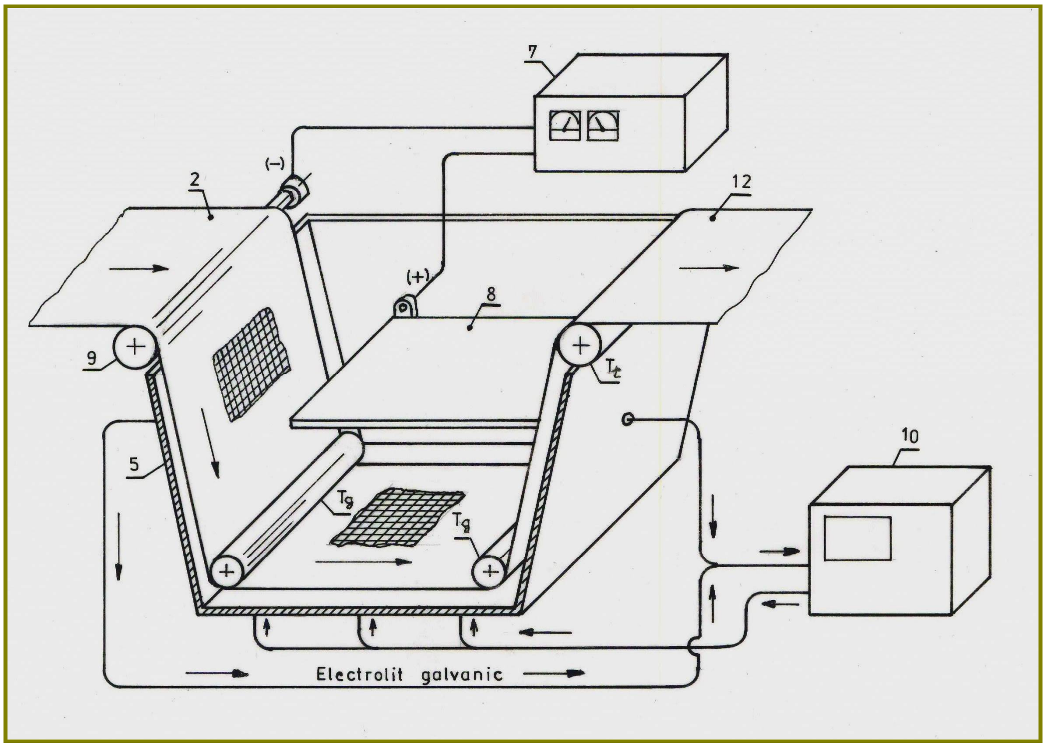

Fig. 1. Constructive details of electroplating bath from the technological process of copering of wire nets on galvanic way, work flow represented in the papers [1], [2]. 2-primary steel wire net, 5a- thermostated galvanic bath used for copper galvanic deposition[1], electrolyte 6a, 7-DC power supply, 8-soluble anode from electrolytic copper, 9-metal drum to power-up, 10-thermostat, 12- intermediate metallic net having steel wire encased in a copper shirt, Tg-drums of guiding- stretching role, Tt-drums of tensile- return role

2. Recipe 2- with acid electrolyte 6b, based on copper sulphate (electrolyte composition for 1 liter of galvanic solution):

- 150 g $CuSO_4 \cdot 5H_2O$
- 20 ml H_2SO4 96%
- 100 ml ethanol 96%
- current density - 0.5 A / dm^2 (area refers to steel wire that mesh is made and not on the surface of the steel net)

- working temperature 45^{o}C
- feed speed of steel wire net - 4m / minute
- immersion length of the net in galvanic bath- 2 linear meters
- electrolyte recirculation flow - 2 liters / second
- galvanic bath capacity - 500 liters
- deposited copper thickness about 4 μm

Reactions that occur during galvanic deposition of copper from sulfate bath on steel wire net are:

$$CuSO_{4aq} \leftrightarrow Cu^{2+} + SO_4^{2-} \text{ – dissociation in the galvanic bath}$$

$$H_2O \rightarrow H^+ + OH^- \text{ – dissociation in the galvanic bath}$$

$$Cu^{2+} + OH^- \rightarrow Cu(OH)_2 \text{ – dissociation in the galvanic bath}$$

$$Cu - 2e^- \rightarrow Cu^{2+} \text{ – anode dissolving}$$

$$Cu^{2+} + 2e^- \rightarrow Cu \text{ – cathode deposition}$$

$$2H^+ + 2e^- \rightarrow 2H \rightarrow H_2 \uparrow \text{ – anode release}$$

For the case of electrolytic coppering of thin steel wire net from sulfate baths, theoretical mass balance expressed by weight deposited on the cathode m_{Cu2} or dissolved from the anode, under a current efficiency η of the anode and cathode of 100%, has the same general expression that of equation (2):

$$m_{Cu2} = \frac{64}{96.500} \cdot I_2 \cdot 30 = 0,0199 \cdot I_2 \qquad (3)$$

The difference from coppering with copper cyanide is in working mode, respectively the time that electric current passes through a net segment from its entry to the exit from galvanic bath, in this case in 240 seconds (speed advance of the net 0.3m/ minute). The intensity of the electrolysis current value I_2 is calculated at a current density of 0.5 A/dm^2. Whereas the yield of anodic dissolution of copper is not equal to that of cathodic deposition at an interval of approximately 48 hours a chemical analysis of galvanic bath on copper ion content is required. Depending on the result of the analysis copper salts is added or electrolyte is extracted from galvanic bath, and the remaining electrolyte is diluted to the optimal concentration.

2.2. Electrochemical coppering of steel wire nets without external power

The embodiment [1-Fig.2] is a manufacturing flux of continuous production of the metal nets for shielding based on electrochemical deposition of copper of high purity, without external power, on the thin steel wire that forms meshes of primary net that in its turn is in a form of winding drum. Copper deposition on iron without exterior power is based on electrochemical potential difference of the two metals in the electrochemical potential series of metals. In this serie the normal electrochemical potential for Fe/Fe^{2+} is - 0.440 V and the normal potential for Cu/Cu^{2+} is + 0.337 V. In these conditions the ions from the more electronegative metal surface (iron) go into solution, and on iron are reduced the ions of more electropositive metal (copper), the deposition are taking place only to obtain an uniform layer of copper on steel wire metal net. Manufacturing flux consists of a power unit comprised a rolling drum 1 of a primary net 2 of thin steel wire, a pickling bath 3 for steel wire of primary net 2, a rinse bath 4 of primary net, a thermostated bath 5b, Fig.2 from [1] and Fig.2 from the present paper for electrochemical deposition of copper without external power, containing an electrolyte 6c based on copper sulphate used for electrolytic deposition of a thin coating of pure copper on the steel wire of primary net 2 on the basis of electrochemical potential difference between copper and iron, another rinsing bath 11 of the intermediate metal mesh with steel wire wrapped in a shirt of pure copper, a drying tunnel 13 of intermediate metalic net, an impregnating bath 14 for wire of intermediate metalic net with a monomer in order to provide advanced protection from oxidation of electro-deposited copper, a line 15 for polymerization with ultraviolet radiations of the monomer deposited on the metalic wire of intermediate net, an initiating drum 16 and winding drum 17 of final shielding net 18, the latter having a composite structure type thin wire steel-electrolitic copper shirt –polymeric shirt. The operative mode to obtain electromagnetic shielding nets by electrochemical deposition without external current is the same as the galvanic deposition of copper with the difference that the bath 5a, Fig.1 [1] and 5a from Fig.1 in the present paper, equipped with DC power source and soluble copper anodes is replaced with a thermostated bath 5b, Fig.2 comprising a thermostat 10, an automatic system for analyzing of copper ion concentration from the thermostatic bath 5b. Composition of 6c electrolyte, based on 1 liter of the solution used for the electrochemical deposition without external current, is as follows: 200g $CuSO_4 \cdot 5H_2O$, 10ml H_2SO_4 98%, 1g NaOH, 5 ml HCl

- working temperature 50^oC
- feed rate of steel wire net 7m / min
- length immersion of net in galvanic bath - 2 linear meters
- electrolyte recirculation debit - 2 liters / second
- thickness of the deposited copper layer of the order of nm

The reactions that occur during electrochemical deposition without external current of copper on steel wire net are:

$$CuSO_{4aq} \rightarrow Cu^{2+} + SO_4^{2-} \text{ dissociation in coppering bath}$$

$$Fe \rightarrow Fe^{2+}_{aq} + 2e^- - \text{oxidation}$$

$$Cu^{2+}aq + 2e^- \rightarrow Cu - \text{reduction}$$

$$Cu^{2+}SO_4^{2-}{}_{aq} + Fe \rightarrow Cu + Fe^{2+}SO_4^{2-}{}_{aq} - \text{global reaction}$$

In this case the theoretical balance of materials corresponds to the real balance of materials.

Performing material balance aims to determine the time at which the coppering bath must be filled with copper sulfate for it to remain in work setpoints.

In this regard will be taken into account as may be allowed a decrease in the concentration of copper ions by 20% which still allows uniform deposition of a layer of 300 nm thickness as (about two copper atomic diameter) pure copper on the thin steel wire that forms meshes of metalic nets.

2.3. Coppering steel wire nets by chemical reduction of copper

Cell for electrochemical copper deposition without external current on steel wire mesh shown in Figure 2 of the present paper, can be used to copper deposition by its chemical reduction on steel wire mesh. For this purpose it is used an electrolyte 6d, based on copper sulphate and copper chloride and a reducing agent, in the specific case of formaldehyde. The coppering bath composition 6d by chemical reduction and operating mode are:

- 10g $CuSO_4 \cdot 5 H_2O$
- 5g $CuCl_2 \cdot 2H_2O$
- 10 ml formaldehyde
- 1g NaOH
- 15g EDTA
- working temperature 60°C
- feed rate of steel wire net 4m / min
- length immersion of net in galvanic bath - 2 linear meters
- electrolyte recirculation debit - 2 liters / second
- thickness of the deposited copper layer about 10 µm

As in the case of copper depositing electrochemically without external power also in chemical reduction of copper on steel wire net theoretical balance of materials corresponds to the real balance of materials. In this type of deposit the balance of materials aims to determine the time at which the coppering bath must be filled with copper sulfate or copper chloride as the copper concentration variation does not exceed 5% which is the limit which provides another deposition copper in prescribed parameters.

For a concrete example the net of steel wire with a diameter of 0.3 mm, with net width of 1m and side meshes of 2 mm, the feed rate of 4m /minute, in an hour copper is deposited on a net with 240 m length of linear steel wire-containing of 19,200 m length. Taking into account that on this wire is deposited a pure copper jacket of about 10 micrometres thick (thickness required technology) also considering the copper density of 8.92 g/cm^3, in one hour it is consumed about 28 g of copper from galvanic bath which requires the completion of electrolyte for coppering with copper sulfate and copper chloride. Given that in this type of coppering, copper chloride has the role of ensuring a fine crystalline structure and increasing the adhesion of copper to the steel substrate and that copper ions are not consumed in equal ratio from copper sulphate and chloride, a system of automatic control of copper concentration in bath is needed correlated with an automatic dosing of the two substances providing copper ions.

This system, Fig.2, consists of spectrometer 19, a flow cell 20 continuously fed by a peristaltic pump 21 with solution of electrolyte *6c* from bath *5b* of deposition. The spectrometer is coupled by means of microprocessor 22 to an automatic dosing system 23 of concentrated solution of copper sulphate and a system 24 for automatically dosing the copper chloride solution.

In the system of control and automatic dosing the coppering bath is filled continuously with two copper salts maintaining the prescribed concentration, according to the recipe of the coppering by means of microprocessor.

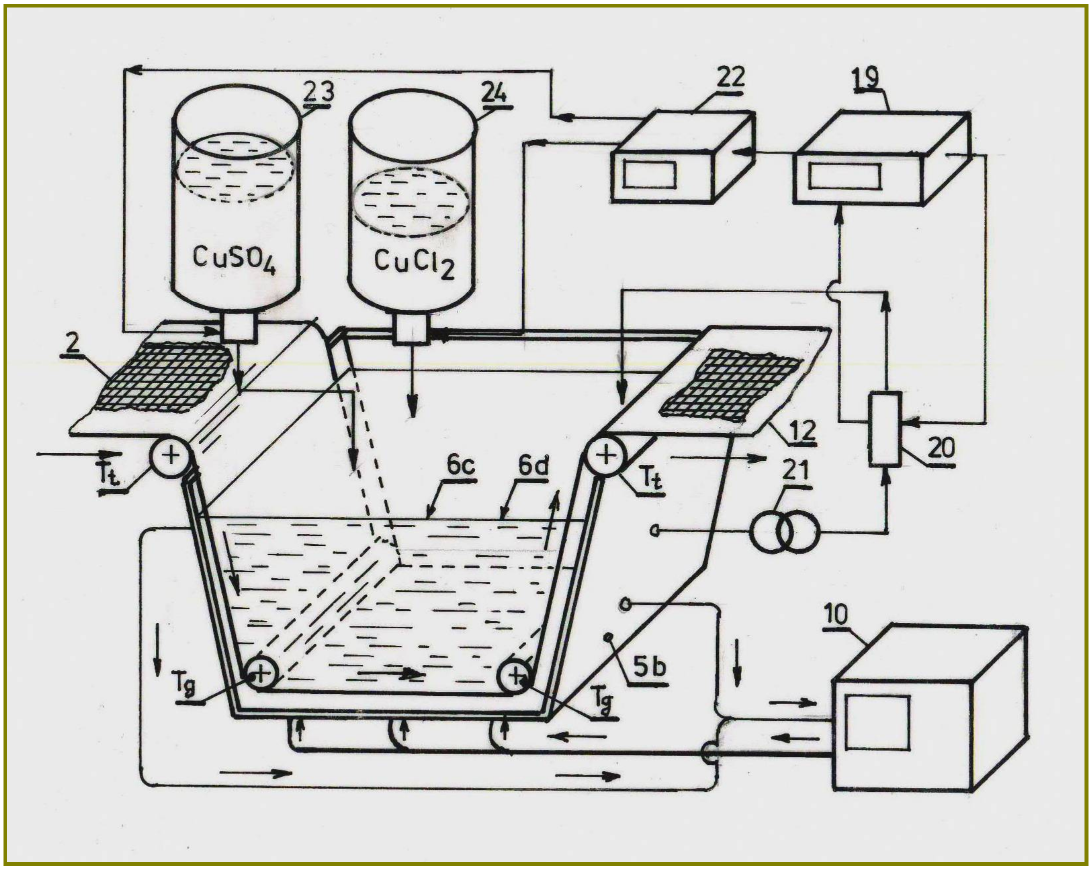

Fig.2 Constructive details of electrolytic bath from coppering process of thin steel wire nets [1], [2], using chemical reduction process and automation related the coppering bath to maintain the nominal operating parameters. 2-primary steel wire net, 5b-reduction thermostatic bath for depositing copper used either without external current (electrolyte 6c) or for depositing copper using chemical reduction process (electrolyte 6d), 10-thermostat, 12- intermediate metalic net of coated steel wire having a copper jacket, 19- the spectrometer, 20-flow cell, 21-peristaltic pump, 22- microprocessor, 23- automatic system of dosing automatically concentrated solution of copper sulfate, 24- automatic dosing system of copper concentrated chloride solution. Tg-drums of guiding –stretching role, Tt-drums of tensile- return role.

3. Conclusions

Steel wire net coated with copper according to the technology, methods and recipes for coppering described is an advanced composite material that through the steel net provides advanced electromagnetic shielding of low-frequency currents, through the copper layer deposited on the steel wire mesh provides shielding of high-frequency currents, and by the thin film of polymer reduced on the copper layer provides protection thereof against oxidation allowing fixing nets shielding under plaster of workspaces or housing thereby assuring a lifetime equal to that of the building.

These nets from composite material can be used in the furniture industry to be secured non-detachably and invisible in stratified wood panels, coated with melamine, being mounted during manufacture of plates by hot pressing between core laminated wood and melamine plate.Detailed description of recipes for coppering and theoretical material balances as well as advanced description of process flow of manufacturing enable immediate approach of production of this shielding material. The comparative study of three coppering methods that may be used reveals that the most efficient in terms of quality, productivity and layer thickness is the method of galvanic deposition of copper from cyanide solutions instead the lowest price presents electrolytic deposition method without external power.

4. References

[1]. ALEXUC C., GUTT G., AMARIEI S., Contributions to achievement a composite material for advanced electromagnetic shielding of living and workspaces, First part - Shielding material, Food and Environment Safety 12 (4), 283-289, (2014)

[2]. ALEXUC C.,F., GUTT G., AMARIEI S., Metallic material for electromagnetic shielding of radiations and its achieving technology, Proposal for invention, OSIM File A00684/09.09.2014

[3]. GUTT G., GUTT S., STROE S., ALEXUC C.F., A process for electromagnetic shielding, Patent RO 126.682/2011

[4]. GUTT G., GUTT S., ALEXUC C.F., Building materials for housing electromagnetic shielding, Patent, RO 126.683/2011