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# EFFECT OF REPLACING COPPER CYANIDE FOR COPPER SULPHATE IN A BRASS ELECTROLESS BATH

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**Abstract**

Environmental conditions and health protection worldwide, is a search engine solutions for the surface finishing industry, in the sense use bath solutions, which do not contain toxic substances, and difficult to treat waters waste. Here are the results from the replacement of copper cyanide by copper sulphate in the composition of an electroless brass-plating bath; the electroless brass plating process can be applied directly on Zamak alloys, also on low carbon steels and aluminium. The morphological and brass film colour characteristics were evaluated by scanning electron microscopy, optical microscopy, colour parameters L*, a*, b*, with a spectrophotometer and electrochemical techniques, depending on the molar concentration of copper sulphate. This bath was prepared based on a bath of electroless brass patented in Mexico, the composition of this bath using zinc oxide as a source of $Zn^{+2}$ ions, a suitable complexing agent and a stabilizer, with an alkaline pH and a temperature of 75 ° C. The results indicate that we can control the colour of brass plating with $Cu^{+2}/Zn^{+2}$ ratio.

**Keywords**: Brass electroless, Copper Cyanide, Electrochemical Characterization

## 1. Introducción

The brass coating plating is coating alloys most widely used today, its origins come from mid 1600. Dissolving solid brass in nitric acid mixed with cyanide made those solutions. Because the obvious volatility of this process, it was not until 1920 that the electrolytic process starts has be used as a available alternative to solid brass Kowalski A. J (1999).

The interest of brass coating on other materials can be grouped into two main areas: functional and decorative purposes. For decorative purposes we can mention the brass coating on hardware. In this application the colour of brass is very important. The coatings are usually thin, 0.005 mm, and have little protection against corrosion in harsh environments, Blum W (1949) and Strow H. (2005).

Examples of functional purposes of the electrolytic brass include: increased adhesion between rubber and steel with thicknesses less to 0.0025 mm, the corrosion resistance for example marine vessels, its use in the automotive industry as an intermediate layer on the bumpers, its utility as a lubricating film for drawing of steel, etc. Brass electrolytic may be a potential substitute for dyes and resins applied electrolytically, whose technology is relatively new. Although the latter technology is gaining some acceptance, commercial costs, not adaptability of process operations volume and the fact that the finish cannot rust or olden artificially reduce their fields of application, so the brass is an excellent substitute, Kowalski J. A. (1999).

Baths for coating metal objects with brass, both electrolyte and some processes electroless are made based cyanides copper, cyanides of zinc, and sodium cyanide, so that these processes are considered highly hazardous

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to health and highly toxic, and because it still used today, attempts have been made to replace the cyanide salts for the preparation of brass baths.

Attempts have been made to eliminate or reduce cyanides in the brass electrolytic baths or with other metals requiring cyanides as silver coating H. Sanchez et al (1996), gold plating with thiosulfate instead of gold cyanides Sullivan A. M (1997) or electroless gold on electroless Ni-B Sato J. (2002), zinc plating Nabil Z. 2002. By reference in 1988 Fujiwara Y. et al (1998), obtained a brass plating bath free cyanides with commercial applications, based on $CuSO_4$, $ZnSO_4$ and sodium glucoheptonate dihydrate with pH above 10.0 using current densities of 0-5 A/dm$^2$. The thickness brass film was 5-50 □m. Cu70Zn30 brass characteristic colour is obtained with current densities above 1 A/dm$^2$. There is a patent with a free cyanide brass plating based in pyrophosphate and orthophosphate applying a film of brass foil of another metal, the thickness is 0.05 to 0.1 □m Ameen T. (1998). Carlos I. A. et al (2004) also investigated an electrolytic bath of Cu-Zn using sorbitol as the complexing of $Cu^{2+}$ obtaining colours Cu-Zn deposit from yellow to greyish brass.

Studies have also been made to eliminate cyanides in Sn-Zn plating, using sulphate-tartrates baths at pH 4-5 Guaus E. (2005). Another job for the electroplating of Cu-Zn alloy is realize by Juskenas R. et al (2007) in an alkaline solution by adding D-mannitol. In previous studies on brass plating electroless on zamak alloy 5, Dominguez et al (2008), Dominguez et al (2001) and Hurtado Macias et al (2010), will study the effect of sodium-potassium tartrate on the morphological characteristics and the film Cu-Zn composition, obtaining a deposit acicular morphology to low levels of Rochelle salt and morphology nodular coating with levels high of the Rochelle salt in the bath. De Almeida (2011) conducted a research of a plating of Cu-Zn alkaline based on EDTA as complexing of $Cu^{2+}$ cyanides free, obtaining yellow brass. in references latest Ballesteros (2014) study the electrochemical deposition of Cu-Zn using chloride salts of Cu and Zn, pH = 10, glycine is used as complexing agent, this bath is free of cyanides at room temperature. In the most recent reference, Minggang et al (2015) studied the influence of copper sulphate on the Cu-Zn coating, free cyanide using 1-Hydroxyethylidene-1, 1-diphosphonic acid (HEDP), potassium citrate, sulphates Cu and Zn and potassium hydroxide to adjust pH = 13.

In this paper the results of replacing copper cyanide by copper sulphate in a bath of electroless brass plating are presented, which was developed and patented in Mexico Dominguez-Rios C. et al (1999) and Dominguez C. (2001) Dominguez-Rios et al (2008) and Macias Hurtado et al (2010). In these works the composition bath contain ZnO, CuCN, NaCN, NaOH, Rochelle salt, and $NH_3OH$ $Na_2CO_3$ to adjust the pH. Due to environmental pressures and toxicological reasons we believe that the objective of this work is to replace the CuCN by CuSO4.

## 2. Experimental

Samples of the Zamak alloy 20 mm x 20 mm x 2 mm were obtained, which was roughed with sandpaper 220 and 600, then weighed in groups of three pieces to start the process of brass, three samples were submitted for each To properly prepare the surface of the pieces of zamak for brass electroless process, the following baths were prepared: Alkaline degreasing bath with $Na_2CO_3$ and $Na_3PO_4$-$12H_2O$ was used, recommended for ASTM B252-92; bath temperature 70-85 ° C, current density of 30-55 A/dm$^2$, time 180 s, with a rinse with distilled water.

Cathodic degreasing bath of sodium hydroxide (NaOH) was used to complete the removal of oils and fats, and to ensure good adhesion of the film made of brass (ASTM B 252-92), this bath conditions are; environment temperature, current density of 16 A/dm$^2$, time 40 s, with distilled water rinse. The next step is the immersion brass bath, for which the content of $CuSO_4$ was varied while keeping constant the concentration of the other reagents according to Dominguez (1999), (2001) and (2010). The composition and conditions baths of the tested are shown in Table 1.

**Table 1 Electroless Baths Compositions**

| Reactive | 1 (mol/l) | 2 (mol/l) | 3 (mol/l) | 4 (mol/l) | 5 (mol/l) | 6 (mol/l) | 7 (mol/l) |
|---|---|---|---|---|---|---|---|
| NaOH | 1.12 | 1.12 | 1.12 | 1.10 | 1.12 | 1.12 | 1.12 |
| NaCN | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 |
| ZnO | 0.11 | 0.11 | 0.11 | 0.11 | 0.11 | 0.11 | 0.11 |
| **$CuSO_4$** | **0.05** | **0.07** | **0.08** | **0.10** | **0.11** | **0.13** | **0.15** |
| $Na_2CO_3$ | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 |
| $NaK(C_4H_4O_6)\bullet 4H_2O$ | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 |
| $NH_4OH$ | 0.16 | 0.16 | 0.16 | 0.16 | 0.16 | 0.16 | 0.16 |
| Temperature | 70 ºC | 70 ºC | 70 ºC | 70 ºC | 70 ºC | 70 ºC | 70 ºC |
| Time | 15-30 min. | 15-30 min. | 15-30 min. | 15-30 min. | 15-30 min. | 15-30 min. | 15-30 min. |
| Agitation | Cte. | Cte. | Cte. | Cte. | Cte. | Cte. | Cte. |
| pH | 11 | 11 | 11 | 11 | 11 | 11 | 11 |

The surface characterization and thickness brass coating electroless was performed using scanning electronic microscopy FESEM Jeol JSM 7400, the weight gain was calculated gravimetrically. The measurement of colour parameters L, a, b, Spectrum-one spectrophotometer gloss Gude 45/0 was used, Spectro-guide sphere gloss BYK Gardner. A potentiostat-galvanostat GillAC ACM Instruments was used for electrochemical characterization.

## 3. Results and discussion

### 3.1. Weight and Thickness

In table 2, we can see the results of weight gain and thickness brass coating with three times immersion tested with a different content of $CuSO_4$ in brass electroless bath.

**Table 2 Weight Gain and Thickness of Sample vs $CuSO_4$ Concentration**

| Bath | Weight Gain (mg) | | | Thickness (μm) | | |
|---|---|---|---|---|---|---|
| | 15 min | 20 min | 30 min | 15 min | 20 min | 30 min |
| 1 | 0.8 | 2.4 | 2 | 3.328 | 0.974 | 1.295 |
| 2 | 1 | 1.1 | 1.4 | 2.489 | 1.168 | 2.71 |
| 3 | 1.6 | 0.8 | 1.1 | 1.48 | 1.967 | 2.33 |
| 4 | 1.6 | 0.9 | 1 | 2.554 | 2.777 | 2.654 |
| 5 | 1.5 | 2 | 2.4 | 3.035 | 2.307 | 2.372 |
| 6 | 2.1 | 2.1 | 1.5 | 3.193 | 4.16 | 5.617 |
| 7 | 4.1 | 2.7 | 5.03 | 4.332 | 4.844 | 4.514 |

In figure 1, we can see a graph of the weight gain of the film brass electroless, with increase of the concentration of $CuSO_4$, it is observed that the immersion time of 15 minutes there is an increased in weight gain, but for samples immersion time of 20 and 30 minutes we can see a reduction in weight gain in the first concentrations of $CuSO_4$, up to a maximum of approximately 5.03 mg of brass coating electroless.

**a** **b**

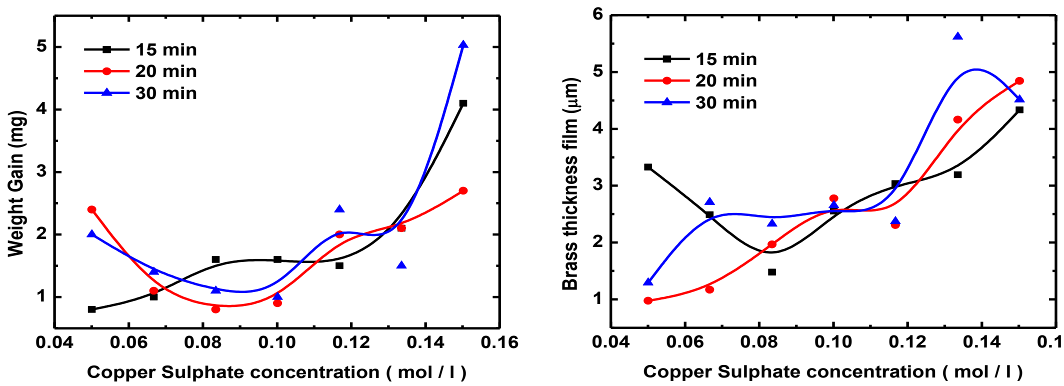


**Figure 1 Copper Sulphate Concentration vs (a) Weight Gain of the Brass Film and (b) Thickness Brass Film**

### 3.2. Characterization of Colour of the Brass Film Electroless

Furthermore, in table 3, can see the results of the variables that describe the colour with ***L****, ***a****, ***b****, with increase content the copper sulphate in the bath. The letter ***L**** correspond to the quantitative determination of clarity or whiteness of coating, ***a**** indicates the tendency to red if the value of ***a**** is positive, or green if the value of ***a**** is negative, and the tendency of yellow if ***b**** is positive and blue if it is negative.
Thus in Figure 2(a) shows the graph of ***L**** which indicates that with increasing content of copper sulphate can be seen a light yellow, thus also, the Figure 2(b) can be seen that with increasing content of copper sulphate trend towards red decreases with the content of copper sulphate and colour yellow initially a greater tendency but after remain approximately even, indicating that the colour yellow brass is obtained even with low concentrations of copper sulphate.

**Table 3 Results of the L, a, b Sistem (corresponding to Lightness, Redness and Yellowness, respectively)**

| Bath | L* | | | a* | | | b* | | |
|---|---|---|---|---|---|---|---|---|---|
| | 15 min | 20 min | 30 min | 15 min | 20 min | 30 min | 15 min | 20 min | 30 min |
| 1 | 69.98 | 70.49 | 74.83 | 0.26 | 5.90 | 0.40 | 30.31 | 39.23 | 35.09 |
| 2 | 70.24 | 72.20 | 72.18 | 2.58 | 8.27 | 7.22 | 36.29 | 29.35 | 32.62 |
| 3 | 76.20 | 71.73 | 67.93 | 0.85 | 0.49 | 0.51 | 28.66 | 30.30 | 26.96 |
| 4 | 77.59 | 78.13 | 76.23 | 0.49 | 0.69 | 7.59 | 29.08 | 30.29 | 26.80 |
| 5 | 78.54 | 78.34 | 78.39 | 0.01 | 0.16 | 1.75 | 31.18 | 31.25 | 33.17 |
| 6 | 83.30 | 79.09 | 75.01 | 1.38 | 9.58 | 3.72 | 30.00 | 26.85 | 33.15 |
| 7 | 84.21 | 84.45 | 77.24 | 2.34 | 1.42 | 4.08 | 30.41 | 28.25 | 30.93 |

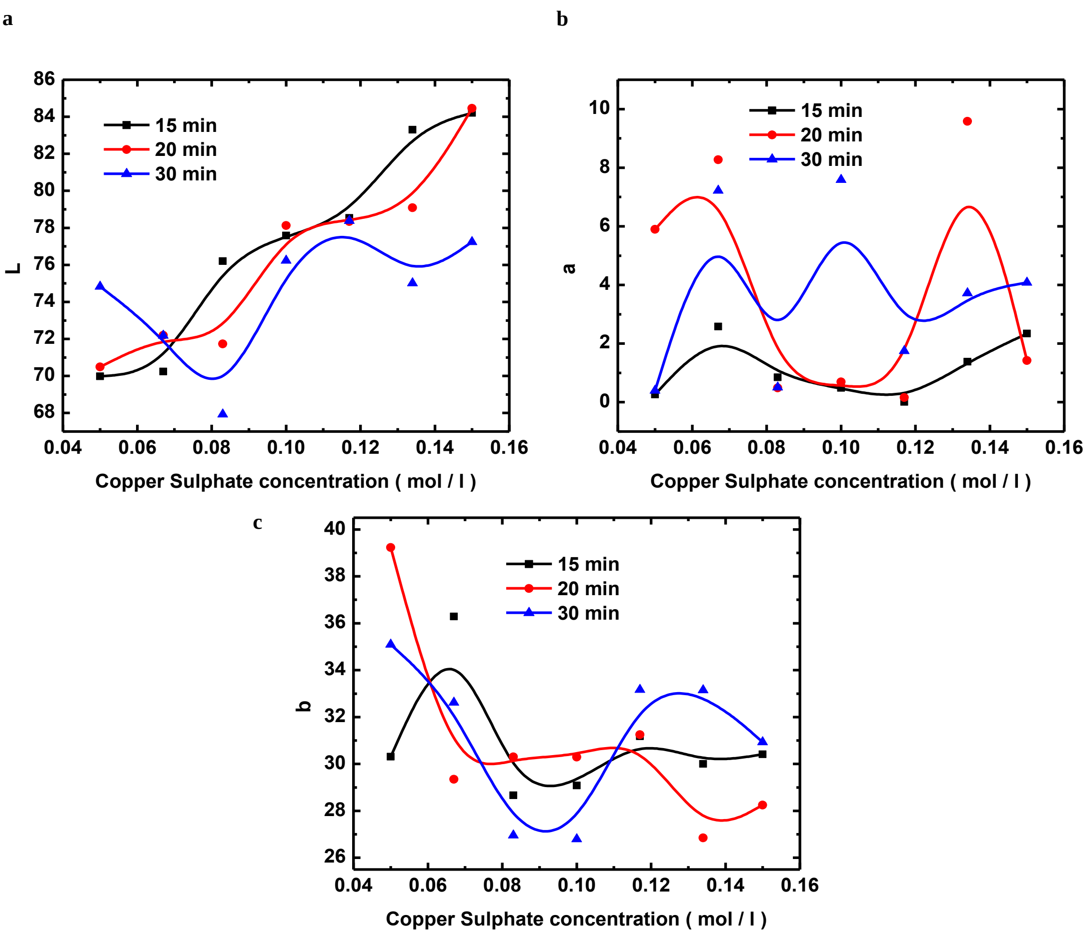


**Figure 2 System L*, a*, b* for definition the brass film electroless colour**

### 3.3. SEM Characterization

Figure 3 shows the surface normal coating electroless brass samples with immersion time of 15 minutes with different concentrations of $CuSO_4$, it can be observed nodular structure where each node has in appearance cauliflower; this characteristic growth occurs in almost all samples, but with $CuSO_4$ content of 0.150 mol/l, we can see a growth of needles which are Zn and in the background can see the structure cauliflower coating. For samples with 20 minutes of immersion time, Figure 4, can be seen that the nodule size is less for this series of samples but the cauliflower structure is also seen in the nodules, is also presented growth needles of Zn with $CuSO_4$ content of 0.05 and 0.150 mol/l.

In Figure 5, we can see the surface morphology of the samples with immersion time of 30 minutes, can see a nodular structure with the characteristics of cauliflower and needles Zn not are observed which indicates that virtually the coating is brass. This surface morphology, can be associated with the low gloss of the brass coating, but if we can see the characteristic yellow colour of brass Cu70Zn30 is obtained.

In Figure 6, can see a micrograph of the cross section of a brass film electroless of the sample with immersion time of 30 minutes in the bath and a $CuSO_4$ concentration of 0.13 mol/l; can be seen that there is excellent adhesion between the brass film and Zamack alloy, the film has not pores and is very homogeneous. with EDS equipment adapted to SEM microanalysis were performed to determine the ratio of Cu/Zn with increasing content CuSO4, the results of this ratio are shown in the graph of figure 7; it may be noted that the ratio increases with increasing content of $CuSO_4$, indicating that there is greater deposition rate of Cu when the content of $CuSO_4$ is increased, see figure 7.

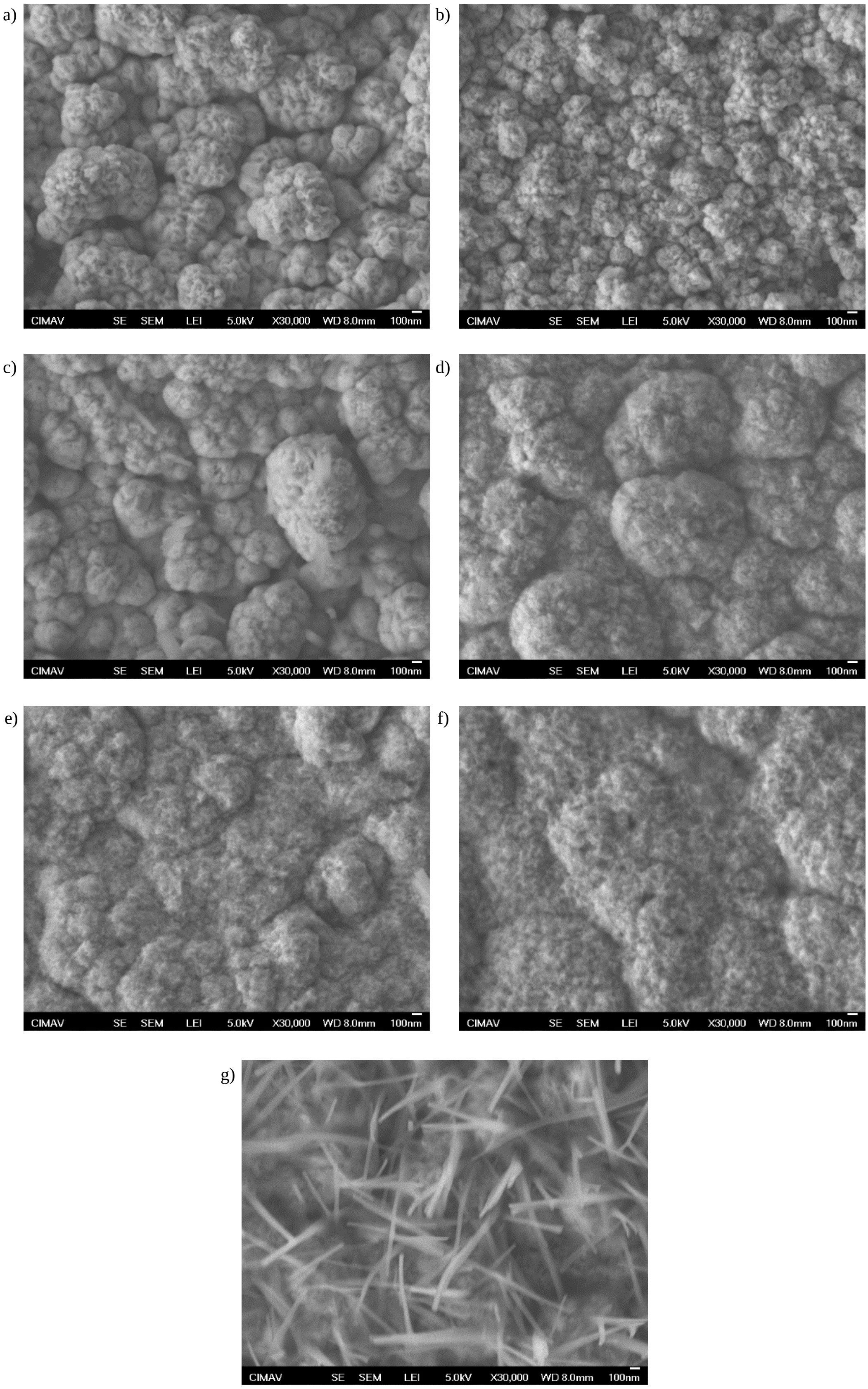


**Figure 3 FESEM Microphotographs of samples with immersion time of 15 min., Copper Sulphate concentrations, a) 0.050, b) 0.067, c) 0.084, d) 0.100, e) 0.117, f) 0.134 y g) 0.150 mol/l.**

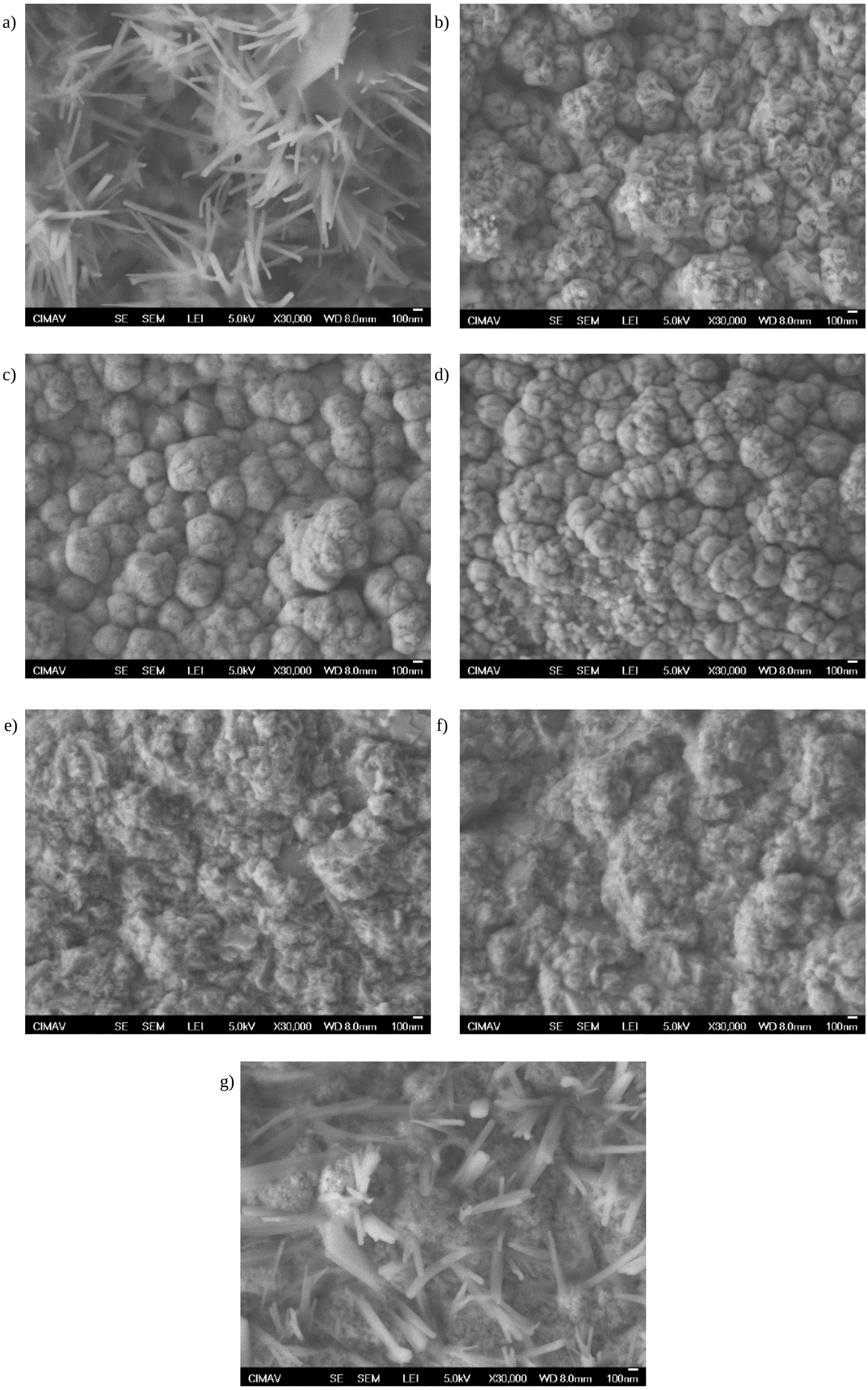


**Figure 4 FESEM Microphotographs of samples with immersion time of 20 min., Copper Sulphate concentrations, a) 0.050, b) 0.067, c) 0.084, d) 0.100, e) 0.117, f) 0.134 y g) 0.150 mol/l.**

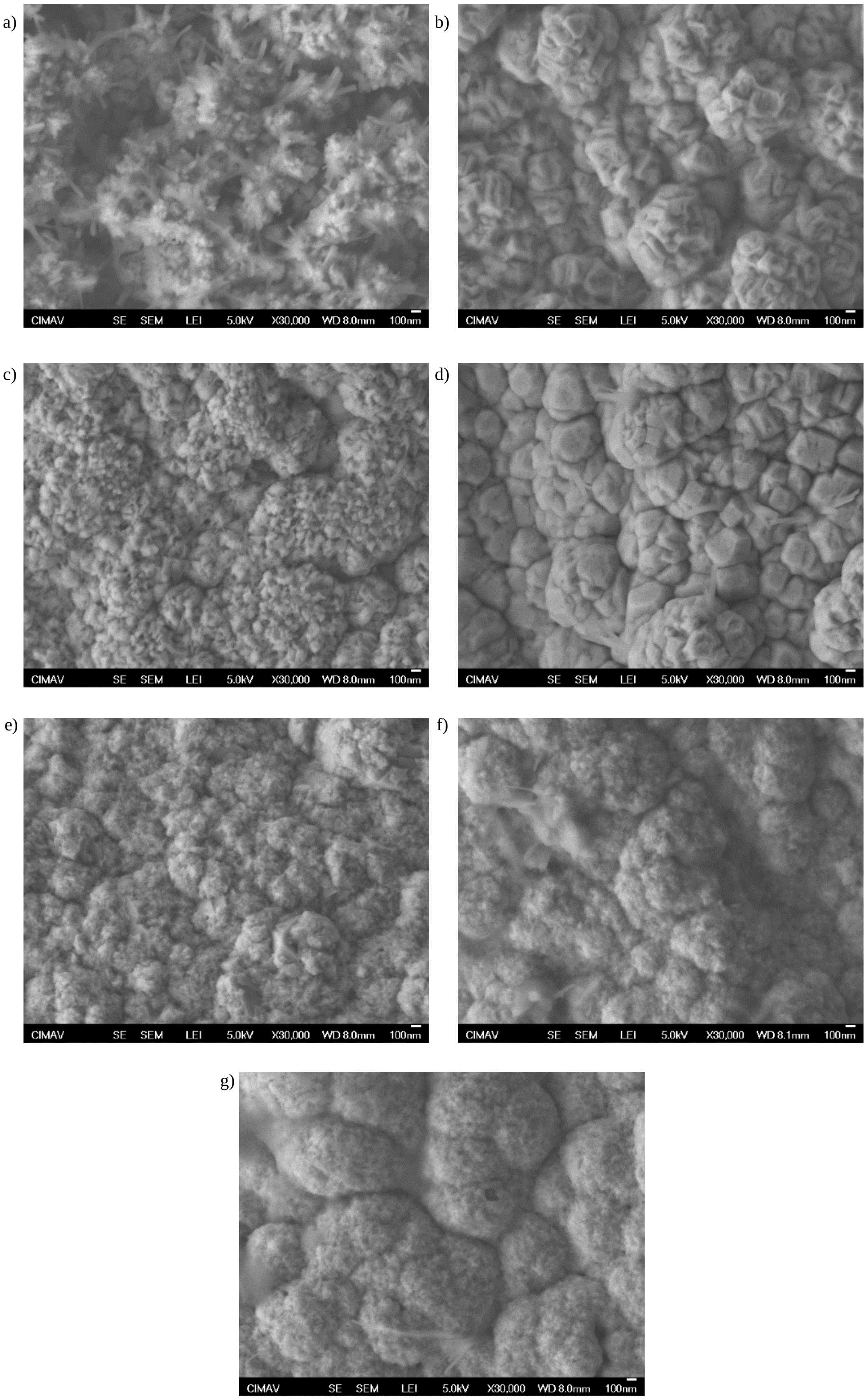


**Figure 5 FESEM Microphotographs of samples with immersion time of 30 min., Copper Sulphate concentrations, a) 0.050, b) 0.067, c) 0.084, d) 0.100, e) 0.117, f) 0.134 y g) 0.150 mol/l.**

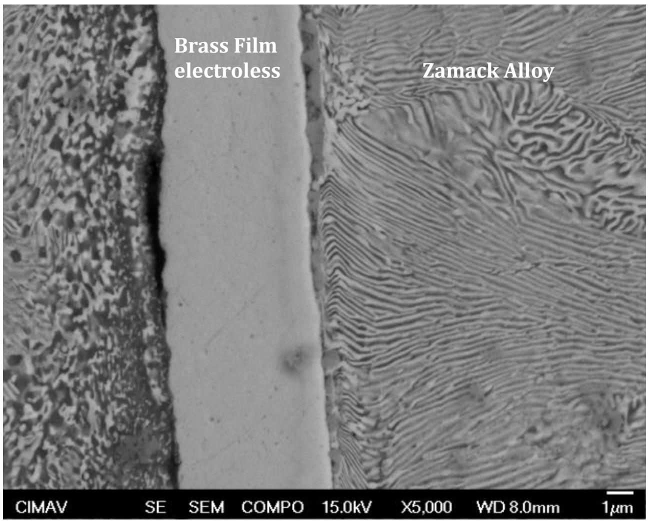


**Figure 6 Cross section of the sample with immersion time 30 min. and $CuSO_4$ 0.13 mol/l**

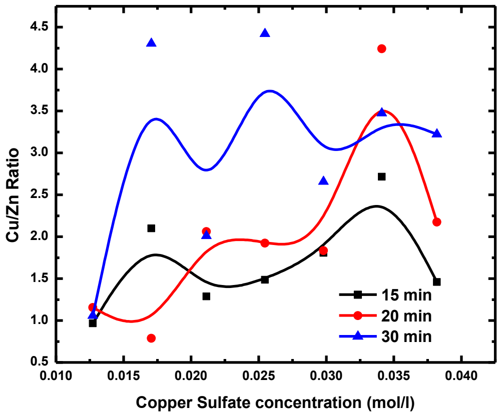


**Figure 7 Graph Cu/Zn ratio obtained from EDS microanalysis**

### 3.4. Electrochemical Techniques of the Brass Electroless Baths

For this characterization, only the results of an electroless brass bath are presented with $CuSO_4$ containing 0.11 mol/l, compared with an bath electroless with CuCN, this is because all baths exhibit the same behaviour. Because the autocatalytic reduction or electroless is a technique through which metal deposits are obtained by a redox reaction, which occurs within the solution between the metal ions to be deposited and the reducing agent, without input current external, and also the coating process is autocatalytic, since once the metal begins to deposit, it will be responsible for catalysing the reduction reaction, thus, figure 8 (a) shows the behaviour potential (mV) versus time (s), for 1800 seconds for two baths used, it is observed that the electrochemical potential or redox, presents a very similar behaviour with same tendency throughout the test time, initiating the process with values of potential of about -1510 mV and ending in values close to -1375 mV, the behaviour shown in both cases may be associated with both the anodic and cathodic reaction carried out simultaneously, developed in the process have potential very similar, that is to say, oxidation and reduction potentials maintain very close values in both tests, however, we can see a shift of the curve obtained in the bath with CuCN was potentials more negative, which indicates the possibility of having a more negative potential in the reducing agent causing increased kinetics reduction. Figure 8 (b) shows the behaviour of the density current ($mA/cm^2$) versus time (s) to a bath of electroless brass with $CuSO_4$ containing 0.11 mol/l, compared with a electroless bath with CuCN; the behaviour shown for test 05 starts with values of positive current until a time of 300 seconds, showing that there is a greater presence of oxidizing species (reducing agent) at the start of the process, after this

time is seen a current changes to negative values (predominating the reducing species) reaching a maximum value of approximately -0.9 mA/cm$^2$ in about 700 sec, from this value a begins downward trend until the end of test, reaching a value of approximately -0.6 mA/cm$^2$, this latter trend is indicative of the consumption of reducing species. On the other hand, the test With CuCN presents in the first few seconds large positive values in the current, predominant oxidizing species, but immediately those values become negative indicating the presence of the reducing species (greater amount of metal ions present in the bath) showing a similar decrease in these values, in the same way that the tendency shown by the test 05. This behaviour shown in both tests must be reflected in the quality of the coating, good adhesion, and compact, continuous, free of pores.
In both tests, peaks are seen in descending upstream, which are known as transient or anodic and cathodic peaks, this behaviour can be observed in both series of potential and current, in which there exists a reciprocity according to the Ohm Law, indicating abrupt changes in both potential and current demand. Associating at high magnifications (very localized or point) in both the amount of the reducing agent and the oxidizing species, however, in all cases the same trend return.

a b

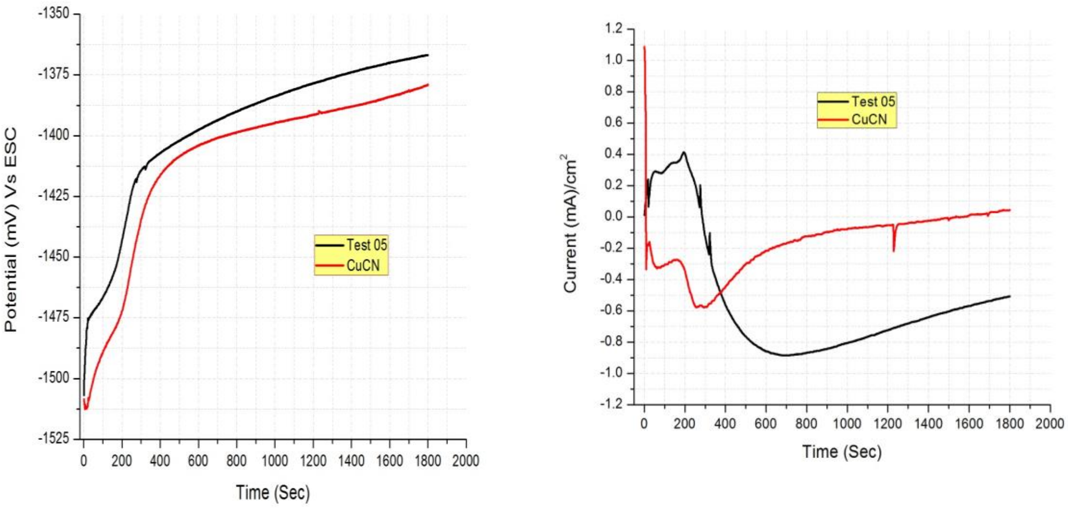


**Figure 8 Graphs (a) Potential vs time (b) Current vs time, for bath 5 and bath with CuCN brass electroless**

## 4. Conclusions

i. Can be replaced CuCN by $CuSO_4$ in the brass electroless bath
ii. The surface morphology of the brass electroless film is nodular with the surface of the cauliflower-shaped nodules.
iii. We can get different brass alloys, modifying the content of $CuSO_4$.
iv. With this bath we can get the yellow brass Cu70Zn30.
v. According to the results of the electrochemical tests, baths with $CuSO_4$ have almost the same kinetics deposit bathrooms with CuCN.

## 5. Acknowledgements

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