This work deals with the development of cyanide-free copper-silver electroplated coatings on AISI-1075 steel and its corrosion behavior under a 5% NaClO solution (commercial household bleach). A cyanide-free bath based on sodium thiosulfate was employed to obtain the silver coatings using current densities from 0.2 to 5.0 mA/cm² and different concentrations of EDTA (additive). The evolution of the open circuit potential with time showed that silver is anodic with respect to copper, so there were no intense attacks in the silver pores. Adhesion measurements were made on both coatings by the tape test. The behavior against corrosion was evaluated by polarization resistance (Rp) in samples with the best coating adhesion. The best results were obtained with a silver coating of about 20 μm in thickness deposited on copper coating previously polished with colloidal silica. The best performance was attributed to the formation of AgCl as demonstrated by x-ray diffraction and scanning electron microscopy.

Keywords: corrosion protection, cyanide-free Silver Baths, Cu/Ag coatings on AISI-1075 steel, electroplating, polarization resistance

1. Introduction

Hypochlorites are widely used as bleaches and remain as important chemical disinfectants in healthcare since they are easily available and inexpensive. One in five disinfectants listed by the U.S. Environmental Protection Agency as effective against COVID 19 comprises chlorinated compounds, most of them based on sodium hypochlorite (NaClO) (Ref1, 2). The consumption of NaClO in laundry bleach applications currently represents 67% of its use, and the use of disinfectants represents the remaining 33% (Ref 3). However, hypochlorites are alkaline oxidizing agents, with a strong tendency to attack by pitting, being considered among the most corrosive chemical substances (Ref 4). Their handling and application require metals with high corrosion resistance and/or the use of combined protection systems. For instance, stainless steel valve springs coated with an epoxy system are employed in the packaging of 5% NaClO for household use. However, it has been observed that they have poor adhesion, which result in the detachment of the paint system and leaves the stainless steel unprotected during service. This promotes the corrosion of the stainless steel resulting in a short-term performance since the spring fails in less than 30 days (Ref 5). This time is significantly shorter compared to the life of uncoated stain-
adhesion, or even flaking and cracking problems when cyanides are not used, so that an intermediate substrate between steel and silver is required to obtain deposits with good adhesion (Ref 14). As just mentioned, Cu deposits are well known for their good adhesion on carbon steels (Ref 15). In addition, Cu is one of the preferred substrates for Ag electrodeposits being used for the production of semiconductors (Ref 16) or production of Cd-109 (a radionuclide that can be used as an x-ray fluorescence source) (Ref 17) and for the evaluation of baths without cyanide or additives to improve the quality of the deposits (Ref 11, 13, 14); other applications include integrated circuits (Ref 19, 20), electroless coatings (Ref 21), among others. Finally, the additives used in electroplating are very important and their choice often determines the success or failure of a given coating process (Ref 22). Complexing additives such as EDTA are often used to improve bath stability (avoid precipitation), control the coating rate, the crystallization mechanism, the film uniformity, and the gloss, as they can form complexes with metal ions (Ref 23, 24). EDTA is widely used in industrial applications because it has a strong ability to bind metal cations in aqueous solution (Ref 25).

The main objective of the present investigation is to develop electrolytic Cu–Ag coatings on AISI-1075 carbon steel and evaluate its corrosion behavior under 5% NaClO (commercial bleach). Coatings were obtained by a non-cyanide thiosulfate electroplating bath. The microstructure and the chemical nature of coatings were characterized in detail by scanning electron microscopy, energy dispersive x-ray spectrometry and x-ray diffraction. The adhesion of the Cu intermediate coating and the final Ag coating was measured by the tape test. Corrosion resistance was evaluated by polarization resistance.

2. Experimental Procedure

2.1 Materials

An AISI-1075 carbon steel sheet was used as the metallic substrate, considering that this material fulfills the requirements of the mechanical properties needed to fabricate valve springs. The chemical composition of the experimental steel was determined by infrared absorption spectroscopy (ASTM E 1019) and optical spark emission spectrometry (ASTM E 415): 0.80 wt.% C, 0.67 wt.% Mn, 0.022 wt.% Si, 0.036 wt.% P, 0.006 wt.% S, 0.015 wt.% Al (balance Fe) (Ref 26, 27). Steel samples with dimensions of 10 cm length × 5 cm width × 1.3 mm thickness were degreased with a hot 30% NaOH solution, pickled and activated with a 30% HCl + 10% H2SO4 solution with inhibitors for 15 min, rinsed with deionized water and then dried using compressed air. The samples were immediately coated with a copper intermediate coating at a current of 15 mA/cm2 for 15 min in a commercial acidic bath.

Table 1 Composition of the electrolytic bath and operating conditions for silver deposits

| Compound    | Concentration (g/L) |
|-------------|---------------------|
| AgNO3       | 30                  |
| Na2S2O3     | 225                 |
| K2S2O7      | 40                  |
| CH3COONH4   | 25                  |
| CH4N2S      | 0.8                 |

| Operating conditions |
|----------------------|
| pH                   | 5.5-6.0             |
| Temperature          | 22 °C               |
| Current densities    | 0.2, 1.0, 5.0 mA/cm²|
| Concentrations of EDTA | 0, 5, 10 mM         |

reduce porosity, the Cu-coated samples were polished with 0.06 μm colloidal silica to obtain a mirror like finish, activated with 10% HCl or 7% HNO3 and then coated with Ag. To evaluate the effect of roughness on the quality and corrosion resistance of Cu and Ag coatings, this property was measured prior to and after coating with a Mitutoyo Sj-301 surface roughness tester, reporting the roughness average (Ra) value obtained from three tests, considering the same area in each measurement.

Another batch of specimens were coated in the thiosulfate bath during a time long enough to obtain a thickness of around 20 μm. The formation of AgCl was promoted on the surface of the Ag coating, this due to the low solubility of AgCl (Kps = 1.7 × 10^-10) (Ref 28). To promote the formation of AgCl, an electrolytic chloride reduction process was used by polarization of the Ag-plated steel sheet in contact with a 0.1 M HCl solution. A voltage of 9 V and stainless-steel electrodes were used for the cell (Ref 29). After these operations, a dark grayish coloration, which is characteristic of the silver/silver chloride (Ag/AgCl) electrodes, was observed on the surface of coatings. Finally, porosity was evaluated using a variant of the standard ASTM B 765-93, as proposed by Jayakrishnan et al. (Ref 30). To this end a filter paper (grade 40) soaked with a NaCl solution (50 g/L) was placed in contact with the coating and polarized with a current of 2 mA/cm² for 5 min. The solution also contained potassium ferrocyanide in a concentration of 10 g/L, which promoted the precipitation of the iron dissolution products on the filter paper, producing an impression of the pores present in the coating.

2.3 Characterization

Morphology and composition of electroplated coatings and corrosion products were analyzed by x-ray diffraction (XRD) and determined by scanning electron microscopy (SEM) with a Link System electron microprobe analyzer (EMPA), respectively. The cross sections of the Cu-coated AISI-1075 steel samples were polished using an argon beam for their observation by SEM (Ref 31). X-ray diffraction analysis were conducted in a Bruker D8 Advance x-ray diffractometer using Cu-Kα radiation (λ = 1,54,060 Å) and operated at 40 kV and 35 mA. Scanning was done in the 2θ range of 25-100°, with a step size of 0.02°, a data collecting time of 0.5 s, and total diffraction time of 31 min for each sample. The adhesion of the Cu intermediate coating and the final Ag coating with respect to the substrate was tested according to procedure B of standard
ASTM D 3359–09 (Ref 32). A grid mesh pattern of about 5 mm², divided into squares of 1 mm × 1 mm, was scratched on the coatings surface using a single razor blade type cutter with safety lock system. The blade was dragged across the coating tracing six parallel cuts, followed by a second set of cuts intersecting the first ones as close to a 90-degree angle as possible, forming a lattice pattern. A pressure-sensitive tape, with adhesive force of 6.3-7.0 N/cm² (350-400 g/cm²), was applied and then removed at a 180-degree angle. The results were evaluated by comparing the tested grid meshes with a standard classification chart provided by the standard mentioned before. According to this standard, a score of 5 is optimal, indicating that all the squares remained intact. Duplicate experiments were done considering the same grid area. The results of the adhesion tests were complemented by macro and micrographs obtained by stereoscopy and scanning electron microscopy, and by microhardness measurements conducted in steel and across the coating. Microhardness measurements were conducted in a microhardness tester Shimadzu HMV-G using the lowest load of the equipment (0.01 kgf) and the shortest dwell time (10 s). The electrochemical cell was constructed by adhering a quartz cylinder (3.3 cm internal diameter) to the coated surface, having an area of 8.55 cm² exposed to the electrolyte (commercial 5% NaClO bleach, pH = 12.8). A saturated calomel electrode (sce) and two high-density graphite rods were used as reference and auxiliary electrodes, respectively, and the Ag-coated steel sample as the working electrode. The open circuit potential (OCP) was continuously recorded before the polarization resistance (Rp) tests using a Gamry reference 3000 potentiostat/galvanostat/ZRA. The Rp values were obtained by imposing a pulse of ±10 mV with respect to the OCP at a scan rate of 1 mV/s (potentiodynamic polarization curves), recording the response of the system for the current intensity. All measurements were taken in triplicate at room temperature (≈ 21 °C).

3. Results and Discussion

3.1 Microstructure of Ag Coatings Electrodeposited on Cu Intermediate Coatings

The Cu intermediate coating required for good adhesion between the Ag coating and the carbon steel substrate was satisfactorily obtained with a thickness of about 7.7 μm, which lies within the range of values recommended by the corresponding standard (Ref 33). Activation of the Cu surface with 10% HCl promoted the formation of porous, opaque black Ag coatings with very poor adhesion, which did not cover the entire surface. However, activation with 7% HNO₃ led to a dense and silver colored surface of the Ag coating with uniform color and gloss. The effect of current density on the size of the Ag crystals was as expected, the size decreased as the current density increased for deposits without EDTA, while deposits with 5 mM and 10 mM EDTA an opposite behavior was observed (not shown). Figure 1 shows the surface morphology of deposits obtained at 1.0 mA/cm² with different EDTA contents. Figure 1(a), (b) and (c) is directly comparable, but Fig. 1(d) corresponds to a total thickness of 22 μm, with subsequent formation of AgCl on its surface. Figure 1(a), (b) and (c) shows granular crystals with a wide size distribution; those obtained without EDTA show angular sides as polygons, while those with EDTA exhibit an irregular morphology (Fig. 1b and c). The voids or grooves observed between the crystals can enable effective penetration of the electrolyte causing the attack of the Cu coating and/or accelerating the dissolution of Ag by the galvanic effect. Figure 1(d) shows larger crystals, which have mainly a nodular or spongy morphology and in a lesser extent polygonal; the coating is more compact, has shorter grooves and exhibits, apparently, underlying crystals in the grooves. The formation of granular structures is attributed to a higher rate of electrodeposition as reported elsewhere (Ref 9). The effects of the absence of EDTA were not observed, considering that it is used to promote the development of uniform-thickness coatings and inhibit the dendritic crystal growth (Ref 34).

Figure 2 shows the cross-sectional analysis of coatings obtained at 1.0 mA/cm² without EDTA. Apparently, the voids present on the surface of the Ag coating do not continue to the Cu substrate; the coating is homogeneous and exhibits a good coating-substrate adhesion. The presence of voids is more significant in the thickest coating on the surface and at the steel-Cu interface (Fig. 2b). The steel shows some cavities (dark areas), which were possibly formed by the removal of nonmetallic inclusions during mechanical polishing. Figure 3 shows an elemental map obtained by scanning electron microscopy across the cross section of Cu-Ag coating on 1075 carbon steel surface. Figure 3(a) shows the electron image, and Fig. 3(b), (c) and (d) shows the dot maps corresponding to Ag, Cu and Fe, respectively. As can be seen, the intermediate coating is constituted by copper; the outer coating is constituted by silver and the substrate is mainly constituted by a Fe-based alloy (steel).

Figure 4 shows the XRD patterns of Ag coatings before and after being exposed to 5% NaClO solution. Both patterns show the diffraction reflections corresponding to the crystal planes (111), (200), (220), (311) and (222) of Ag (Ref 12). It is evident that characteristic reflections of AgCl appear once Ag reacts with sodium hypochlorite promoting the formation of AgCl. The initial average surface roughness (Ra) values measured on the surface of the Cu coating prior to and after polishing with colloidal silica were 2.09 μm and 1.66 μm, respectively. Table 2 presents the Ra values of the Ag coating as a function of current density. As can be seen, the roughness increases as the current density is increased.

3.2 Thermodynamic Behavior of Ag and Cu in 5% NaClO

The thermodynamic stability of metals such as Ag and Cu can be evaluated for many corrosive media by the Eh–pH (Pourbaix) diagrams, since they provide information regarding the possible thermodynamically stable phases, formation of insoluble compounds that can be passivants, and metallic dissolution at selected values of potential and pH. Figure 5 shows the Eh–pH diagrams for silver and copper, calculated for a 5% aqueous solution of NaClO at 25 °C, by using the HSC Chemistry 5.1 software (Ref 35). As mentioned above, the concentration and pH of NaClO solution correspond to the average values of sodium hypochlorite for household use. The potential values determined by placing in contact both metals with the bleach for 3000 s were 246 mV_she and 836 mV_she (5 mV_sce and 595 mV_sce see Fig. 10) for Ag and Cu, respectively. The calculated diagrams show that, at pH = 12.8, a protective layer of AgCl will form on Ag, and Cu will be
between the two insoluble compounds above the dissolved form of CuCl₂. In the case of Ag (Fig. 5a), there were included AgCl and AgClO₄, which were identified by x-ray diffraction in the sample used to determine the potential. Although other chemical species could have been formed, they should be crystalline and present in concentrations greater than 100 ppm to be detected by XRD. In the case of Cu, information reported in the literature was used as reference (Ref 36). At first instance,
the probable behavior of Ag in the AgCl zone was understood, however, this information is not enough to predict its behavior, since silver could be dissolved in the medium forming Ag⁺ ions or form AgCl in a proportion equal to, or less than the silver content present in the system. For a better understanding of this, the equilibrium phase fraction and concentration diagrams for Ag in 5% NaClO were calculated (Fig. 6a and b), respectively, with the same software mentioned above.
The concentrations of the main ions that may be present are indicated at the top of Fig. 6(a). In presence of 5% NaClO, chloride ions (ClO$_3^-$) will be dissolved in the medium and Ag will tend to form AgCl. This latter will precipitate on the surface of Ag considering the low concentrations of free chlorides (Cl$^-$) present in the hypochlorite (Ref 37). As shown in Fig. 6(b), AgCl will be inert in the medium since Ag will not form another compound. It will not be solubilized in the medium either, considering the low solubility product value of AgCl. It is also observed in this diagram that even though hydroxyl free radicals (OH$^-$) may react with silver and form silver hydroxides such as AgOH and Ag (OH)$_2^-$, Ag will mainly promote the formation of AgCl due to the electronegativity of chlorides. The concentration of AgCl will be approximately equal to the amount of Ag present as ions, and only one-thousandth or less will form the ionic compounds AgCl$_2^-$ and AgCl$_3^{2-}$; this, considering that the equivalent concentration is equal to the inverse logarithm of its corresponding value (Fig. 6b), having in this way the concentrations of the compounds from the following formula: [C] = 10$^{-log [c]}$, where [C] represents the concentration in molar scale and superscript [c] represents the values of concentrations plotted in Fig. 6(b). The concentrations values obtained from Fig. 6(b) were [AgCl$_{s}$] = 10 mM, [AgCl$_2^{-}$] = 0.01 mM, [AgCl$_3^{2-}$] = 0.0063 mM and [AgCl$_{dissolved}$] = 1 x 10$^{-7}$ mM. As observed in Fig. 4(a), Ag reacts with 5%-NaClO promoting the formation of AgCl.

### 3.3 Adhesion of Electroplated Coatings

The intermediate (Cu) and final (Ag) coatings were evaluated by the adhesion test and by inspection of the surface appearance as indicated above. Several Ag coatings obtained with different current densities and EDTA contents were opaque black, non-homogeneous and present some brittle areas.
experiencing detachment during the adhesion tests, others exhibited very good adhesion, but were porous. The best results were observed with coatings obtained at 1.0 mA/cm². Figure 7 shows representative images of the cutting patterns obtained after the coating adhesion testing conducted in: (a) intermediate and (b) final coatings (Cu/steel, Ag/Cu, respectively). The latter, obtained without EDTA at 1.0 mA/cm², after polishing the Cu coating surface with colloidal silica and further activation with 7% HNO₃. Both images show the absence of abscission or fragmentation at the edge of the cutting lines. According to ASTM D 3359-09, the bond strength of both coatings is classified as 5B (optimal adherence in this test), indicating that the coating remained adhered to the substrate. Similar results were reported for Ag–Cu coatings, but unlike this work, they were obtained in a cyanide bath and with a current density of 10 mA/cm² (Ref 38). In the present work, the Cu intermediate coating was also evaluated by the bend test according to ASTM A 125 using a bending angle of 14° (Ref 39). Coatings did not show any fracture after bending, which confirms they have a good adhesion to the substrate (Ref 40). Figure 8 shows a macrograph (Fig. 8a) and a micrograph (Fig. 8b) showing steel cross sections with the Cu intermediate coating, after the bend test. As can be seen, the cross section of the steel shows that the coating is preserved on the steel surface without showing detachment or cracks, which is consistent with the results of the adhesion test. The average microhardness values obtained in the steel substrate and in the Cu/Ag coating were 266 HV and 164 HV, respectively. It was observed that the indent covered the whole thickness of the Cu/Ag coating; however, after such measurements, the coating did not show detachment, which in addition to the characteristics observed in the macro and micrographs presented in Fig. 8, confirmed the well adhesion of the coating to the substrate.

3.4 Corrosion Estimations and Electrochemical Measurements

The OCP was measured to set the best conditions that would lead to obtaining more protective coatings in different stages of the work, for example, to determine the best acid to activate the Cu surface after polishing with colloidal silica. Figure 9 shows a comparison between the corrosion behavior of Ag coatings on

![Fig. 7 Results of scratch adhesion testing of electroplated coatings: (a) Cu deposited on AISI-1075 steel and (b) Ag deposited on Cu intermediate coating](image)

![Fig. 8 Macrograph and micrographs showing cross sections of steel with the Cu intermediate coating after the bend test](image)
samples activated either with HCl or HNO₃ after being in contact with 5% NaClO. In samples activated with 10% HCl, the OCP value decreases toward more active potentials during the first 3000 s of measurement, first sharply and then slightly, but its stabilization is not observed. Activation with 7% HNO₃, leads to a slightly increase of the OCP value at the beginning of the measurement, but then remains practically constant after 2000 s indicating its stabilization. For this reason, this latter acid was used for the surface activation of Cu intermediate coatings. The evolution of the OCP was measured during 3000 s prior to Rp measurements.

Figure 10 shows the OCP values of the three metallic materials measured separately in 5% NaClO. Its behavior is monotonous, separated by wide ranges of potential, which can

![Figure 9](image)

**Fig. 9** Evolution of the open circuit potential of AISI-1075 steel samples coated with Cu/Ag coatings (1 mA/cm²) activated with different acids, in contact with 5% NaClO (commercial bleach)

![Figure 10](image)

**Fig. 10** Evolution of the open circuit potential of the three metals exposed separately to 5% NaClO solution
cause considerable galvanic couples. At the end of the test, Cu (595 mV) is cathodic with respect to Ag (5 mV) and therefore, in presence of pores or discontinuities in the Ag coating, the dissolution of Cu will not be intense. On the other hand, the steel substrate (−408 mV) is anodic with respect to the two coatings and thus, pores or discontinuities will represent sites for an intense dissolution of steel. It is usual to consider Ag noble compared to Cu, but in 5% NaClO, fortunately, the opposite behavior happens. Figure 11 presents the evolution of the OCP of samples coated with different current densities and concentrations of EDTA, compared with the evolution of Ag. The values of the coated samples are slightly more noble than those of Ag, probably due to porosity that allows the electrolyte penetration to the underlying Cu coating with a much nobler potential. After an initial decrease, the values stabilize showing no increase or decrease in potential, which may suggest a tendency toward passivity or localized attack, respectively.

As is well known, very high localized currents may exist in the electrochemical test and lead to rapid removal of plated coatings. The polarization resistance (Rp) method offers the advantage of being a nondestructive test considering that very small polarizations are required for its measurement (Ref 41). The Rp and the corrosion current density (i_corr) are related by the Stern-Geary equation \( i_{\text{corr}} = B/R_p \), where B is a constant that is a function of the Tafel slopes (Ref 42). The measurement of Rp is probably the safest electrochemical test for the i_corr determination. Figure 12 shows the type of graphs obtained from measurements of Rp, −10 to +10 mV/OCP, where the experimental data are connected by a line that represents the scan performed at a rate of 1.0 mV/s. Data fitting made by the Echem Analyst® Software is represented by the thicker straight line from which the corresponding Rp value was determined. The experimental data fit well with the straight line, as observed for all the conditions investigated. The small variations of current correspond to inhomogeneous coatings. Because coating properties such as grain size and porosity are critically affected by local current density, the ability of a coating to protect the substrate would be expected to vary from one point to another (Ref 41).

Figure 13 presents the average values of Rp for all the samples as a function of the deposit current density and EDTA concentration. For comparison, the Rp values corresponding to the steel substrate and to the metals used as coatings (Cu and Ag) are also included. There is no proportionality between the Rp values and the additive concentration, since the two maximum values at 1 mA/cm² are present in extreme concentrations (0 mM and 10 mM), the highest one for deposits without EDTA. Both values are higher than that corresponding to Cu.

Considering that the maximum value of Rp was presented at a deposit current density of 1 mA/cm² without EDTA, the fact that electrodeposited coatings applied to thicknesses less than ~25 μm are porous, and because increasing the thickness is the most practical method to reduce porosity and increase the protection value, it was proceeded to thicken the Ag coating and promote the subsequent formation of AgCl on its surface (Ref 34, 41). The average value of Rp, 312 Ω cm², of samples with the largest thickness (~20 μm) is also shown in Fig. 13. As can be seen, this value is higher than those obtained for thinner samples (~10 μm) at the same current density. Since the Tafel slopes were not determined, a value of 120 mV/decade (default value provided by the equipment software to calculate the i_corr) was used for both. Figure 14 shows a comparison between the i_corr values as function of EDTA concentration, calculated for the deposits obtained at 1 mA/cm² and those corresponding to the metallic materials calculated separately. Since \( i_{\text{corr}} \) is inversely proportional to Rp, the 20-micron thickness plus the subsequent formation of AgCl Ag coating has the lowest i_corr value. It is notable that i_corr increases for both concentrations of EDTA used. This result may be
related to the refinement of crystals, which is clearly observed in the SEM images of coatings obtained with EDTA (Fig. 1b and c). The smaller the crystals, the higher the boundary area between crystals, which causes a larger surface through which NaClO-5% penetrates and corrodes the coating.

The results of the porosity test were evaluated according to standard ASTM B 765. Ten different areas were analyzed on the Ag coatings surface reporting the average value as the number of pores/cm² (Ref 43). As expected, porosity decreased with the increase in thickness as observed in Fig. 15 for coatings obtained at 1 mA/cm² without EDTA. Figure 16 shows a surface chemical analysis conducted by energy dispersive spectrometry (EDS) on the surface of Ag coatings after the corrosion tests. As can be seen, the spectrogram shows mainly the presence of Ag and Cl. This result is consistent with the result obtained by XRD. As shown in Fig. 4(b), Ag

Fig. 12 Polarization curves obtained by potentiodynamic polarization for Cu-plated and Ag-plated AISI-1075 steel sheets exposed to 5% NaClO. Deposit current density of 0.2 mA/cm², without EDTA

Fig. 13 Average values of Rp as a function of deposit current densities and EDTA contents for Cu-plated and Ag-plated AISI-1075 steel sheet samples exposed to 5% NaClO. The values corresponding to the three metals measured separately are also included
coatings promote the formation of AgCl after contact with 5\% NaClO solution. Due to the differences of potential and area exposed to the electrolyte, which exist between a cathodic coating and its substrate, the substrate corrosion rate will increase, and the effect could be even greater than in absence of coating. Ideally, to provide complete protection against corrosion, an electrodeposited cathodic metal should be completely free of defects (Ref 44). However, during the electroplating process pores and defects form in the deposit, probably due to the substrate roughness or to insulating substances deposited on these materials such as oil, dust particles, residues, even hydrogen bubbles released during the electrodeposition process (Ref 45). Generally, a coating deposited on a rough metal surface will be more porous and will therefore have less protective value than a coating deposited on a smooth surface (Ref 46). A rough surface can be detrimental due to it can affect the electrochemical behavior of the deposit and make it difficult to protect the substrate from corrosion. This, because a very rugged topography requires special care to ensure that the peaks of the rough surface are covered by an adequate coating thickness. However, the effect of roughness is not always detrimental, in some cases, a rough surface can improve adhesion of coatings on the substrate (Ref 45). It seems to be the case for coatings presented in Fig. 7. Some authors deposited Ag on Cu in baths with different compositions, which mainly contain cyanide. It was observed a relationship
between the charge transfer resistance (determined by electrochemical impedance spectroscopy), and the roughness of deposits, which exhibited good uniformity at nanoscale level. For silver coatings with the same real surface area, it was seen that the higher the average roughness $R_A$, the higher the corrosion rate, independently of the deposit texture and deposition conditions (Ref 16). By comparing the results of $R_A$ and Rp (Table 2 and Fig. 13, respectively), this relationship between roughness and resistance to corrosion is not observed, since in the present work, a lower roughness does not lead to a greater the corrosion resistance, as reported elsewhere for a nano-level roughness (Ref 16).

4. Conclusions

Silver was successfully deposited on the surface of copper by a non-cyanide thiosulfate electroplating bath. From the three current densities employed, 1 mA/cm$^2$ was the one with which the highest resistance to the 5% NaCl solution was obtained at each of the three EDTA concentrations. The samples without EDTA had the best performance, the Ag coatings with thickness of 20 $\mu$m, in which the formation of AgCl was electrolytically induced on their surface, showed the highest resistance to corrosion (Rp = 312 $\Omega$.cm$^2$) and the best adhesion (5B). According to the measurements of the open circuit potential in 5%-NaCl solution, the Cu intermediate coating used between the outer Ag layer and the AISI-1075 steel substrate presented a more noble (cathodic) behavior with respect to the Ag coating, and therefore, in presence of pores or discontinuities in the Ag coating, the dissolution of Cu was not intense. However, both Cu and Ag coatings are cathodic with respect to the AISI-steel substrate.

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