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Study of reaction conditions and substrate for the development of flexible antennas by the electroless method[1]

Estudo das condições reacionais e substrato para o desenvolvimento de antenas flexíveis pelo método electroless

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Abstract

The method of surface coating, known as electroless, is based on the deposition of metals without the presence of an electric current, being an alternative for the deposition of metals using direct printing, thus avoiding the need to use photoresist to standardize the metal layer. The present work aims to study substrates, based on polyethylene terephthalate (PET), and their covering using the electroless technique. In this study, factors such as plasma, temperature and immersion time were investigated, when covering the surface, using a silver nitrate solution and a copper bath. The results showed that these factors interfere in obtaining a homogeneous coating with efficient conductivity. In addition, it is concluded that the electroless technique is a low-cost, fast and efficient method for coating flexible surfaces with metallic materials, being, therefore, very promising.

Keywords: Electroless. Antenna. RFID.

Resumo

O método de recobrimento de superfícies, conhecido como electroless, baseia-se na deposição de metais sem a presença de corrente elétrica, sendo uma alternativa para a deposição de metais utilizando impressão direta, assim evitando a necessidade da utilização de um fotorresiste para padronizar a camada de metal. O presente trabalho tem como objetivo o estudo de substratos, à base de tereftalato de polietileno (PET), e seu recobrimento, utilizando a técnica electroless. Neste estudo, fatores como plasma, temperatura e tempo de imersão foram investigados, frente ao recobrimento da superfície, utilizando uma solução de nitrato prata e um banho de cobre. Os resultados demonstraram que esses fatores interferem na obtenção de um revestimento homogêneo e com eficiente condutibilidade. Ainda, conclui-se que a técnica electroless trata-se um método de baixo custo, rápido e eficiente para o revestimento de superfícies flexíveis com materiais metálicos sendo, portanto, bastante promissora.

Palavras-chave: *Electroless. Antena. RFID.*

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1 Introduction

The ubiquitous barcode labels that have sparked a revolution in identification systems are considered inadequate in an increasing number of cases. Barcodes can be extremely cheap, but their obstacle is low storage capacity and the fact that they cannot be reprogrammed. The most common form of electronic device data transport is the smart card, based on a contact field (cell phone smart card, bank cards). However, for a number of applications the mechanical contact used on the smart card is impractical. A contactless data transfer between the data transport device and its reader is much more flexible. In the ideal case, the energy needed to operate the electronic data transport device would also be transferred from the reader, using contactless technology. Due to the user's procedures for transferring energy and data, non-contact identification systems are called radio frequency identification or RFID systems. Due to the several advantages of RFID systems, compared to other identification systems, this system is conquering several new markets (FINKENZELLER, 2010).

The term "electroless" is used to describe a system in which metals are deposited on a surface immersed in a solution without the presence of an electrical current. The coating process takes place in a metal ion bath, similar to electroplating, but in this case there is a reaction called reduction-oxidation (redox), in which one species is oxidized, while another is reduced (ATKINS; PAULA, 2014).

When a metallic substrate, for example, an iron one, is immersed in a solution of copper sulfate or silver nitrate, dissolution of one of the components (in this case iron) is observed and deposition of the other (copper or silver) under the substrate surface. This process is called immersion, which can be explained by the mechanism of redox reactions and the electrochemical series, whose principle is based on the transfer of electrons between the participating species, when they are brought into contact. The most electropositive redox system will be reduced (deposition will occur), while the most electronegative redox will be oxidized (dissolution will occur). Using the substances mentioned above as an example, it is known from the literature that the standard redox potential of silver (E°red = + 0.799 V) and copper (E° red = + 0.337 V) are more electropositive than for iron (E°red = - 0.44V), therefore, the reactions occur on the surface of the iron substrate. Standard electrode potentials are values that represent the potential differences measured between an electrode and a standard reference electrode under standard conditions (ATKINS; PAULA, 2014).

Below is an example of the reduction reactions for iron, copper and silver.

Anodic: $Fe_{(s)} \rightarrow Fe^{2+} + 2e$

Cathodic: $Cu^{2+} + 2e \rightarrow Cu_{(s)}$

$2\,Ag^{2+} + 2e \rightarrow 2Ag_{(s)}$

The surface of the metallic substrate consists of a variety of anodic and cathodic sites, with a continuous coating process with the other metallic substrate, in this case, copper. However, when the oxidation process ceases, the coating is interrupted, with a limit on the thickness of the obtained film, whose average values observed in the study by Bindra and White (1990) are in the order of magnitude of 1 μm. Other limitations of this method are associated with processes of adhesion, porosity and contamination with ions of the base metal. In order to overcome these limitations and obtain thicker deposits, an alternative oxidation reaction has been studied, which occurs initially in the metallic substrate and later in the deposit itself.

The selection of the reducing agent must also be evaluated, since the redox reaction must occur only in the substrate, without causing homogeneous reduction (decomposition) of the solution. An example is the addition of formaldehyde (E°red = + 0.56 V) to a silver nitrate solution, which causes spontaneous precipitation of metallic silver.

Other reaction criteria that need to be monitored refer to the pH and the stabilization of the metal in the reaction medium. Changes in pH can lead to precipitation of the metal in solution. To remedy this behavior, complexing agents are added to the coating bath, in order to keep the metal ion in solution, which lower the concentration of free metal ion (related to the dissociation constant of the metal complex), preventing precipitation within the solution and allowing the bath to be operated at higher pH values. On the other hand, an excessively low concentration of complexant can also influence the efficiency of the deposition process. Therefore, it is necessary to monitor both the type and the concentration of complexing agent used in electroless deposition processes.

In addition, the oxidation of reducing agents used in the electroless process involves the formation of hydrogen (H +) or hydroxyl (OH-) ions. Consequently, the pH of the coating solution changes, during plating and, therefore, affects the deposition rate and deposit properties. In this case, buffer solutions (buffers) have been used to stabilize the pH of the solution. These include carboxylic acids in an acid medium (which also act as complexers) and organic amines in alkaline solutions. In addition, the rate of deposition or coating can be influenced by the addition of substances called accelerators or exaltants, usually anions (BINDRA; WHITE, 1990).

The general coating process involves the steps described below:

- Surface preparation;
- Surface activation by sowing catalytic metal particles on plated surfaces;
- Coating bath to recover the metal on the activated surfaces.

Within the surface coating sector, metals such as gold and silver have been widely studied in printed devices as conductive coating bases on flexible substrates. Due to its high electrical conductivity and low cost, copper has recently attracted great attention in the field of printed circuits. Currently, the most commonly used conductive copper inks are suspensions of copper nanoparticles with plastic binders (KANG *et al.*, 2010; LIAO; KAO, 2012).

Silver is a metal of low electrical resistivity and stable to oxidation, which has been used to connect circuits or, as a passive component, use submicrometric silver particles. Furthermore, silver can also act as an activator for the copper electrolytic coating reaction as a substitute for conventional colloid activators such as: SnCl2, PdCl2 or Pd. (LIAO; KAO, 2012; LIU *et al.*, 2005; SCHAEFERS; RAST; STANISHEVSKY, 2006; YANG; WAN; WANG, 2004).

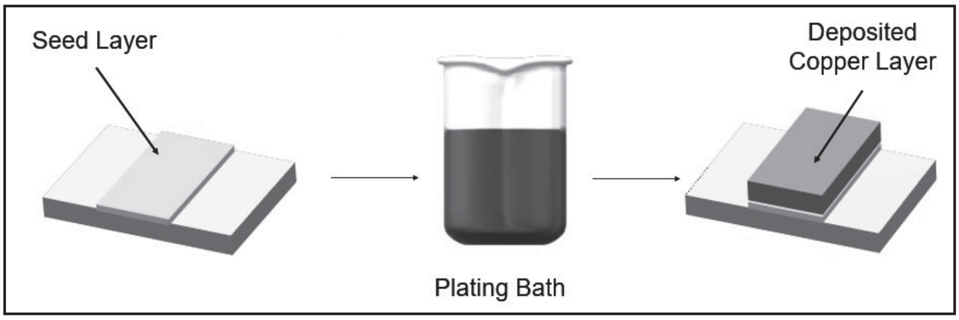
Studies carried out by Shah, Kevrekidis and Benziger (1999), using the electroless process for the coating of metallic platinum, demonstrate the importance of the substrate and its treatment to obtain an adequate covering surface. Better results were observed, when using Nafion (ionomeric material) or polymeric substrate, based on pre-treated PET (polyethylene terephthalate) as substrate.

Studies by Kao and Chou (2007) for printing on alumina (Al^2O^3) substrates either by inkjet or by means of a profile drawn with an appropriate pen, using colloidal silver have shown that it is possible to obtain an electrolytic layer through the process called electroless. In their research they report obtaining a copper film with a thickness between 3-6 μm obtained quickly, since the surface density of the silver particles is greater than $1.5.10^9$ cm^{-2} with an average growth rate of 7.2 μm per hour. Since most thermoplastic polymeric substrates can melt at high temperatures, the sintering process has a limit of applicability.

Studies carried out by Liao and Kao (2012) on the electroless technique for covering a polymeric substrate with copper demonstrate that it is possible to obtain a good adhesion on substrates, based on PET or polyimide, provided that appropriate reaction conditions used. In their studies, free silver particles were printed on both substrates as an activating agent for copper coating. They observed the efficiency of the silver particles in activating the PET surface, as well as the influence of the deposition time on the thickness and resistivity obtained. Since PET is hydrophobic, ethanol needed to be added to contribute to the wettability process.

The electroless method, exemplified in figure 1, has proven to be a quick synthetic route for copper standards with dimensions ranging from micrometers to centimeters and is an alternative for applications in printed electronic devices such as RFID antennas.

Figure 1 - Schematic of the electroless coating process



Source: The authors (2020).

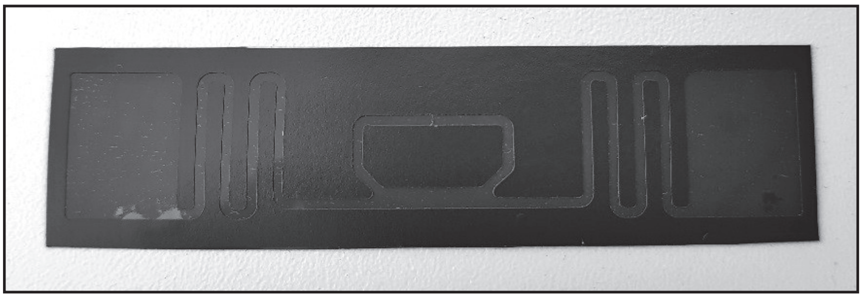
2 Development

2.1 Definition of the antenna layout

First, different substrates, based on polyethylene terephthalate (PET), were studied to verify the adhesion of the coating material. Tests were carried out on three different substrates: Melinex, KIJ 900, HSPL20, where PET HSPL20 obtained a superior result, regarding copper adhesion, in relation to the others.

The desired layout was obtained using a vinyl adhesive (Arlon) and cut on a plotter and adhered to the surface of the PET substrate, as shown in figure 2. Afterwards, the PET substrate with vinyl adhesive was submitted to oxygen plasma in 200 W for 10 minutes for surface cleaning.

Figure 2 - Top image of the PET substrate with vinyl adhesive



Source: The authors (2020).

2.2 Silver and copper baths

Two solutions called solution A and solution B were prepared. The silver nitrate solution (solution A), whose composition is described in table 1, is subsequently filtered through a 0.45 μm filter to remove suspended particles. The PET is then immersed in the solution for a period of 5 seconds and dried at a temperature of approximately 55 ºC until the surface is completely dry.

Table 1 - Composition of the silver nitrate solution (solution A)

Components	**Quantity (in 50 mL of solvent)**
Silver nitrate	0,1698 g
Ethanol	42,5 mL
Ethylene glycol	2,5 mL
Deionized water	5 mL

Source: The authors (2020).

To perform the copper bath, solution B, described in table 2, add copper sulfate pentahydrate, followed by sodium and potassium tartrate, sodium hydroxide and deionized water. After homogenization, it is placed on a heating plate until it reaches a temperature of 40ºC, with subsequent addition of the glyoxal solution, promoting the copper reduction reaction.

The PET is then inserted into the bath for about 5 minutes and washed in deionized water and dried in an oven for about 10 minutes at 70 ºC.

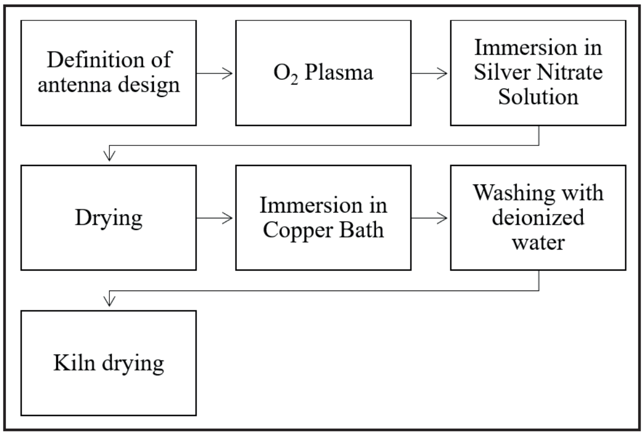
Figure 3 shows the antenna manufacturing process schematically.

Table 2 - Composition of the copper bath (solution B)

Components	**Quantity (in 100 mL of solvent)**
Copper sulphate penta hydrate (source of copper ions)	2,164 g
Sodium and potassium tartrate (stabilizer)	6,52 g
Sodium hydroxide in pearls	2,6 g
Deionized water	80 mL
Glyoxal (reducing agent)	20 mL

Source: The authors (2020).

Figure 3 - Schematic process for obtaining a metallic coating on a flexible surface in order to obtain RFID antennas



Source: The authors (2020).

3 Results and discussion

Preliminary and comparative tests, regarding the use of oxygen plasma in the substrate, demonstrated greater efficiency in terms of homogeneity of copper deposition with the use of it. Analyzes, using time greater than 10 minutes, showed a decrease in the deposition on the substrate, when compared to samples that were not submitted to plasma.

Preliminary formulations of solution A were tested, where the amount of silver nitrate was varied. A test was performed with 3mM of silver nitrate, diluted in the same amounts of solvent as solution A, the results of which showed very little copper deposit on the substrate used. In tests containing 1 mol of silver nitrate, the process of crystallization of silver nitrate on the surface of the substrate was noted, causing the copper to deposit in a heterogeneous manner. The amount of immersion of the PET substrate was also monitored, where no significant differences were observed for one or several immersions.

Different temperatures of the copper bath were evaluated, where a great difference was observed, considering the temperature levels with the final quality of the coating. Color changes from blue to green, when the bath reaches a temperature above 50ºC, after the introduction of glyoxal in the solution, with no reduction of copper or deposition of it to the substrate.

Therefore, the subsequent tests were performed by submitting the samples in 200 W plasma oxygen for 10 minutes, with subsequent immersion in solution A, where the 20 mM silver nitrate concentration was used. The temperature used for the copper bath, solution B, which obtained a higher copper deposition rate was 40ºC.

The pH of the copper bath was evaluated in three different stages of the process, the results of which are shown in table 3.

Table 3 - pH of the copper bath at different stages of the process

Phases	pH	Temperature
Before the addition of glyoxal	13,22	22,1
After the addition of glyoxal	10,49	25,5
At the end of the process	8,42	33,3

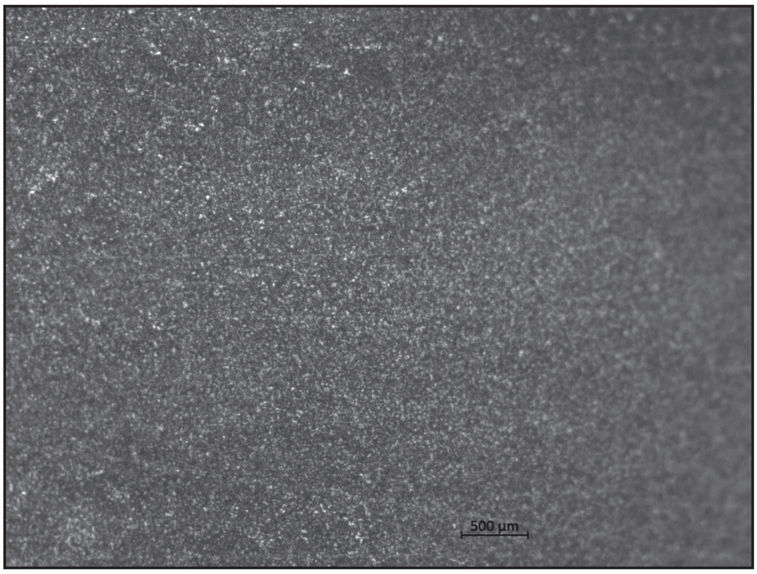
Source: The authors (2020).

From the results shown in table 3, it can be seen that the reaction takes place in an alkaline medium. The influence of the pH of the reaction medium was mentioned by Glenn O. Mallory and co-workers, who infers that it affects deposition rate and deposit properties.

The samples were obtained in duplicate or triplicate to observe the repeatability of the results. Tests were performed on all samples, whose results showed good repeatability.

Complementing the studies, an optical microscopy (ZEISS Axio Lab.A1) of an antenna region, figure 4, was performed, where it is possible to observe the copper particles deposited in the PET in a wide coverage area, which is quite homogeneous.

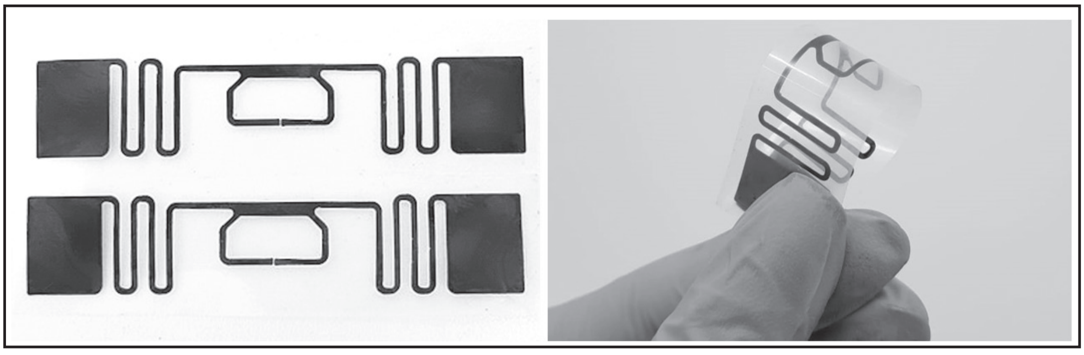
Figure 4 - Optical microscopy of the RFID antenna



Source: The authors (2020).

It is also possible to observe a good coverage of the antenna by this process, demonstrating, in figure 5, a good and homogeneous covering from the reaction method used.

Figure 5 - (a) Top view of the RFID antennas; (b) Flexible RFID antenna



Source: The authors (2020).

4 Conclusion

From the present work, it is concluded that the control of variables such as process temperature, sample immersion time and concentration of solutions is essential to obtain a homogeneous deposition of copper on the PET substrate. The control of these variables is also necessary to obtain a good adhesion of the metallic layer, being essential in the use of flexible substrates, thus avoiding the delamination of the coating.

The pH analysis of the copper bath is essential, given its correlation with the metal deposition rate and the properties of this deposit. Other factors, such as quality and composition of the substrate and the use of plasma facilitate this methodology and significantly affect the final quality of the RFID antenna.

In addition, as demonstrated above, the electroless technique is an efficient and promising alternative to the traditional methods of metal coating on flexible surfaces, added to the low cost and speed of the process.

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