## Silver Metallization and Selective Metallization by Spraying on Film.

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*Abstract* — This paper starts with the description of a new direct chemical plating method for silver, called the JET METAL (JMT) process and of the JET SELECTIVE process, which allows to obtain a selective metallization on any substrate which can be metallized with the JET METAL process [1]. This technology is based on spraying simultaneously two REACH compliant aquous solutions, an oxidant containing silver metallic ions, and a reducing agent. This process allows to plate chemically silver at twelve micron / hour at room temperature and at ambient pressure and is already used in industrial processes for metallizing plastics, composites and non-conductive materials in general and this in different formats (3 dimensional pieces, foils, ...). In the second part, some functional applications like EMI shielded textiles and antennas on films are being discussed.

I. Introduction

Today several metallization technologies for the deposition of Ag on flexible substrates (like plastic films, textiles, metal foils ...) exist and are widely used in a variety of applications. Such technologies are for example evaporation, sputtering or plating, ... But even such technologies have been in use for some time most of them have some disadvantages like an important investment cost (vacuum technologies), dependency of the choice of substrate material (like plating), treating thermosensitive films (vacuum technologies working at higher temperatures)...

A new "direct plating" technology, executed at room temperature and ambient pressure, has been developed which avoids quite some disadvantages listed above. In few seconds, it is possible to metallize non - conducting surfaces (like plastics or composites) with an Ag film [2,3,4].

The novelty of this plating method is based on a sequentially highly controlled supply of the material (metallic ions Ag+) and the energy source (CMR and Pd free reducing agent) to the substrate. In other words it can be described as a metal plating process using continuous and simultaneously spraying of two solutions. Using compressed air and a double nozzle paint spraying gun, the reducing and oxidizing agent are sprayed simultaneously onto a substrate surface (can be both a conducting or a non-conducting surface; with or without a complex geometry, big or small dimensions) forming a very thin liquid film as shown in Figure [1]



Figure [1]. Principle of the Jet Metal metallization process

This film is adsorbed on the surface and contains the active components. The film is thermodynamically unstable which means that the oxidation - reduction reaction will occur spontaneously. But under some well-defined conditions, this spontaneous reaction can be controlled to avoid coarse precipitation. These conditions are the following:

The sprayed liquid film, which is adsorbed on the substrate, must be thin enough so the redox reaction occurs on the surface.
The ratio of the sprayed oxidizing and reducing solutions must be adapted to give an optimal stoichiometric electrochemical reaction on the surface. This corresponds to the ratio of electrons exchanged between the oxidizing and the reducing agents for a fixed sprayed volume of solutions.

• The polymer substrate must have a uniform wettability and a relatively high surface energy ( $\gamma > 56 \text{ mJ} / \text{m}^2$ ).

When the above conditions are fulfilled, the redox reaction will be induced on the surface instead of a spontaneous precipitation of the metallic ions in the adsorbed liquid film. This will result in a compact, dense and adherent silver film on the substrate surface.

The JMT technology overcomes some of the disadvantages of using the Tollens reagents: JMT's sprayed autocatalytic chemical process vs Ag precipitation in a bath with the Tollens reagents, high kinetic JMT silver plating process, JMT's spraying process allows to control the supply of chemical species and thus the silver thickness deposited. Controlling the Ag layer thickness in the JMT process in based on time as the reaction speed is known and this deposited Ag layer thickness can be controlled off-line via measuring the conductivity with a 4 points probe or X-Ray.

## II. Selective metallization process

By adding one additional step to the above described metallization process, a selective, conductive pattern can be realized: an alkali sensitive organic ink, which will be used as a negative mask, is printed on the substrate with the help of an ink jet printer or screen printing system.

As the oxidant and reducing agent have a pH >10, these pH values allows the modification / loss of adhesion of the printed ink towards the substrate. During the final step of the Jet Metal process (spraying with deionized water) the ink layer is removed again, leaving only metallization where there was no ink printed: a selective coating is achieved, and the result is the exact opposite of the pattern designed with the ink.



Figure [2] Principle of the Jet Selective metallization process

The obtained resolution of the realized selective metallized Ag patterns is directly related to the resolution of the printed negative pattern: the higher the resolution of the printed negative pattern, the higher the final resolution of the Ag metallized lines. Today conductive Ag line widths of ~70  $\mu$ m wide can be obtained.

The process of depositing Ag via this Jet Selective metallization technology can be industrialized and used for large scale mass-produce of e.g. antenna's, flexible electronics, RFID tags,...

III. EMI Shielding of textiles

The evaluation of the JMT Ag coating characteristics for its EMI shielding properties were done at EMITECH FRANCE (COFRAC accredited). The measurement tests that were done followed the GAM T20 norm, which are the shielding attenuation measurement test for high end applications like military applications.

The methodology consists of using a Faraday cage to shield the environment and place the metallized sample as the "only" way to pass for the Electro Magnetic waves. The other objective of the reverberation chamber is to obtain a field which is constant on average, which has many polarization directions, and which is statistically uniform.

Electro Magnetic waves are generated by a first antenna, waves will pass through the metallized sample and the second antenna will receive the attenuated signal. A scheme of the test set – up principle of this measurement is show in Figure [3].



Figure [3]. Test set - up for GAM T 20 test

Results and discussion

In all of the tests a 500 nm thick Ag layer deposited with the above described JMT technology was used.



Figure [4]. Shielding Effectiveness for GAM T20 test conditions for a 500 nm thin Jet Metal Ag layer

The first observation that we can made is about the average shielding value. A JMT Ag coating gives between 60 to 75 dB (in the frequency range of 10 MHz to10 GHz) for a layer thickness of 500 nm. These results are good enough for several markets like RF, Cell phones, medical devices and military applications.

Obviously, using a 500 nm thick layer, the absorption impact is not the main mechanism to shield for HF, VHF and UHF but Ag reflectivity is so high that a high level of shielding can be reached. We can imagine to combine absorption & reflectivity effects with a thicker JMT Ag coating or to add an electroplating process once non-conductive parts are metallized with a 150 nm Ag JMT layer. As reflectivity is the main JMT Ag shielding mechanism and it is based on conductivity of the Ag layer, a study on the JMT Ag electrical resistivity was made in order to define it and better understand the evolution in function of the thickness. It's well known that electrical properties as resistivity is directly linked to the thickness of the metal layer in the nanometre scale. The measurements were made using a 4 point electrical probe in order to define R $\square$  called also R Sheet (m $\Omega\square$ ) and following the Van der Pauw method.



Figure [5] RSheet vs thickness of JMT Ag layers

We can observe that the measured RSheet values for a 500 nm thick JMT layer is 50 m $\Omega$  $\square$ .



Figure [6] Resistivity vs thickness of JMT Ag layers

We can observe that the resistivity decreases with the increase of the thickness. Indeed, a JMT Ag layer approaches the standard value of silver resistivity which is around 1,59.10<sup>-8</sup>  $\Omega.m$  or conductivity which is 6,3.10<sup>7</sup> S.m<sup>-1</sup> when the JMT Ag layer is 2,5 - 3  $\mu m$  thick.

IV. Using Selective Metallization to make antennas

In order to characterize a JMT patch, a classical 2.45 GHz Cu patch (left on Figure [7]) [5] was compared with patches made via the selective metallization technology as discussed above via the standard methods on FR4 substrates.



Figure [7] 2,45 GHz Cu patch vs Ag patches

Two families of patches were made:

- Patches with sprayed silver radiating planar element and copper ground plane
- Patches with both radiating planar element and ground plane made with sprayed silver

In each family, three different layer thicknesses were realized in order to obtain information about the impact of the metal layer thickness for the radiating planar element. In fact, the conductivity depends of the metal thickness, but has also an impact on the determination of the resonating frequency.

	3AgCu	5AgCu	3AgAg	5AgAg
Radiating element	Ag			
Thickness (nm)	600	1 000	600	1 000
Ground plane	Cu		Ag	
Thickness (nm)	35 000		1 000	

Table [1] Description of different patch antennas

These different combinations of antennas were tested a.o. on their intrinsic gains



Figure [8]: Intrinsic gain in function of frequency

Results of antennas made via the Jet Selective metallization technology gave similar results as classic copper antennas.

As such patch antenna patterns also can be realized on plastic films like PET, PP or other, this selective metallization technology could also be applied to manufacture antennas in a R2R production process.

V. Conclusions

In this abstract we showed that the JET METAL TECHNOLOGIES metallization technology is a new, green and effective metallization process for a.o. non – conductive substrates like plastics foil.

The EMI shielding effectiveness of a 500 nm JMT silver coating reach high performances up to 70 dB for frequencies between 10 MHz to 10 GHz.

Antennas made via the Jet Selective metallization technology gave similar performance as the standard Cu patch antennas.

Based on these results and in combination with a proven industrial track record, the JMT metallization technology is a viable alternative for existing metallization processes like PVD, plating, evaporation... in R2R processes.

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