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*Nickel-free galvanic treatments are increasingly requested, although at times it is very complicated to find replacements for galvanic baths containing Nickel. This is due either to the increased process costs or to difficulty in managing the processes or more simply, for both reasons.*

*One very widely used treatment in decorative galvanic baths uses Palladium and Palladium alloys. In particular, Palladium/Nickel baths are very popular and less expensive than pure Palladium as well as much more versatile (it can be used to obtain deposits of various microns) and simple to use.*

*For this treatment too, alternatives have been studied in the last few years, but none are as good as Palladium/Nickel.*

*This publication describes a process to replace Palladium/Nickel, which offers the same level of performance as its predecessor, although it is completely anallergic and also allows for ammonia-free processing.*

*The result is a bath that as well as being eco-friendly, also offers shiny, white plating, even with high thickness. It is a bath that is easy to manage and allows galvanic companies to replace Palladium/Nickel naturally.*

# Thickness Plating with Nickel-free Palladium alloys

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## 1. Introduction

In the last few years, the European Community has sent out strong signals of a trend towards more eco-friendly *galvanic plating*; suffice to remember gold electroforming, where Cadmium has been eliminated, or the reclassification of Nickel compounds<sup>1</sup> where the release limit was lowered as a result.<sup>2</sup>

A toxic/noxious chemical component in a galvanic bath may not just be hazardous to the environment. It can also endanger those who work on the treatment bath every day and also, of course, end users, who wear the treated items in direct and prolonged contact with their skin.

The ideal galvanic bath should not contain any hazardous components, but in actual fact, we know all too well that this is a very difficult condition to achieve.

One of the wider used baths in the galvanic and jewellery industry is Palladium, especially in alloy form with Nickel and at a ratio of 80/20 or 90/10.

The Palladium/Nickel bath has various advantages compared to the pure Palladium bath: it is extremely more versatile because it can be used to work with a wider range of current density; it reaches much higher thicknesses and, by depositing an alloy, means plating costs can be reduced.

It is also very easy to use, maintains its shine – even at high thickness – and has a high degree of resistance to corrosion. For these reasons it is used in many specifications, especially for the galvanic treatment of fashion accessories.

Until now, this bath seemed almost irreplaceable, given that all attempts to create a nickel-free bath gave poorer reliability and characteristic performance as a result.

The Palladium/Iron bath is the result of a lengthy research programme, which began four years ago, starting with a treatment that simply eliminated Nickel to arrive at a process that in terms of versatility is even better than its predecessor.

## 2. The research stages

When the research project was begun four years ago, the aim was to find a treatment that was ammonia free.

Removing ammonia from the process was in itself a very important achievement, since this removed a noxious component from the bath, improving overall operating conditions. But above all, it made technical management simpler, given that ammonia baths require daily pH adjustment.

Proceeding with experiments in the laboratory, it became possible to achieve a stable process that was also Nickel free and the result was a pure Palladium bath with an extremely white, shiny deposit that was easy to control up to 0.5 micron.

There were still some limits, especially in terms of achievable thickness meaning that in spite of the numerous benefits, the bath was not yet able to be considered an alternative to Palladium/Nickel.

This led to a new stage of experiments, testing numerous metals as alloys, including Zinc and Indium, but Iron was the metal that gave the best results.

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<sup>1</sup> Directive 2008/58/EC of 21 August 2008

<sup>2</sup> UNI EN 1811:2011

### 3. Palladium/Iron bath characteristics and operating conditions

The operating conditions of the Palladium/Iron bath are shown in the following Table:

**PALLADIUM/IRON SYSTEM OPERATING CONDITIONS**

PALLADIUM	3.5 g/l
IRON	0.6 g/l
pH	6.8 – 7.0
TEMPERATURE:	50° C
BATH DENSITY:	11.5° Bè
CURRENT DENSITY:	0.8/1 A/dm <sup>2</sup>
DEPOSIT SPEED:	1 µ in 4' to 1.0 A/dm <sup>2</sup>
CATHODE PERFORMANCE:	29 mg/Amin

*Table 1: Palladium-Iron bath operating characteristics*

The bath is calibrated for a 90/10 alloy and it is in these conditions in the laboratory, it has been tested to a maximum of 10 micron thickness, where the deposit was still ductile and shiny

Used in production, the deposits are still shiny and polished at a thickness of 3 microns.

Even under stress, the process turned out to be easy to carry out; the colour is white with silver reflections and the plating is extremely shiny.

As far as concerns distribution, the Palladium/Iron bath has a far more even result in the different points of the frame compared to Palladium/Nickel.

The most interesting characteristic is its levelling power: the higher the thickness, the better the results for the surface of the item treated.

On the silver rhodium market, it has been found that applying a layer of Palladium/Iron before the Rhodium will enhance colour and shine characteristics. It is also an excellent barrier layer for the silver, notably improving its corrosion resistance.

The same applies for gold-based alloys, especially for those with low carat weight: in this case, a limitation in the palladium/iron system is that it is white and therefore, lowers concentration but it does add shine to the item as well as giving it resistance to corrosion as it is an excellent barrier layer against the diffusion of alloy copper.

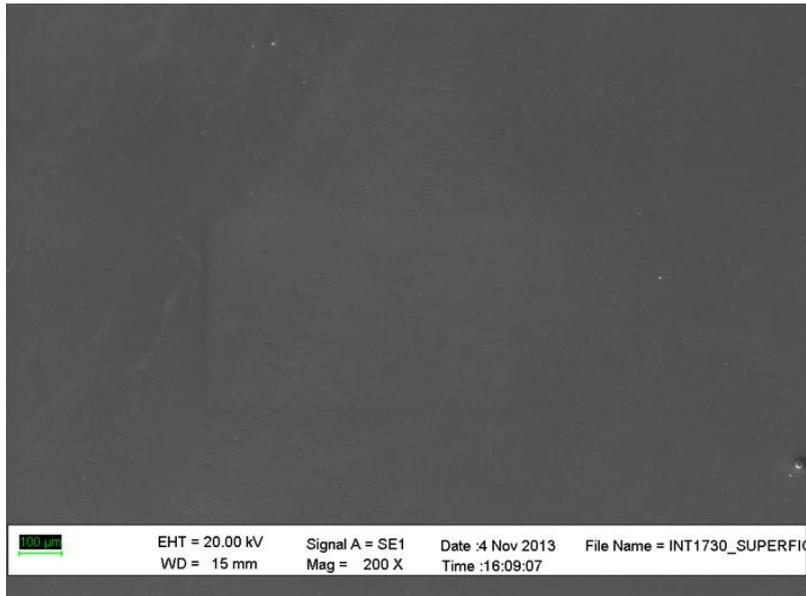
Of course, the traditional use of Palladium and Palladium alloys is in the fashion accessory industry, and in this case, too its characteristics make it the ideal bath when it is necessary to follow nickel-free processing specifications.

### 4. Surface morphology survey for Palladium-Iron alloy plating.

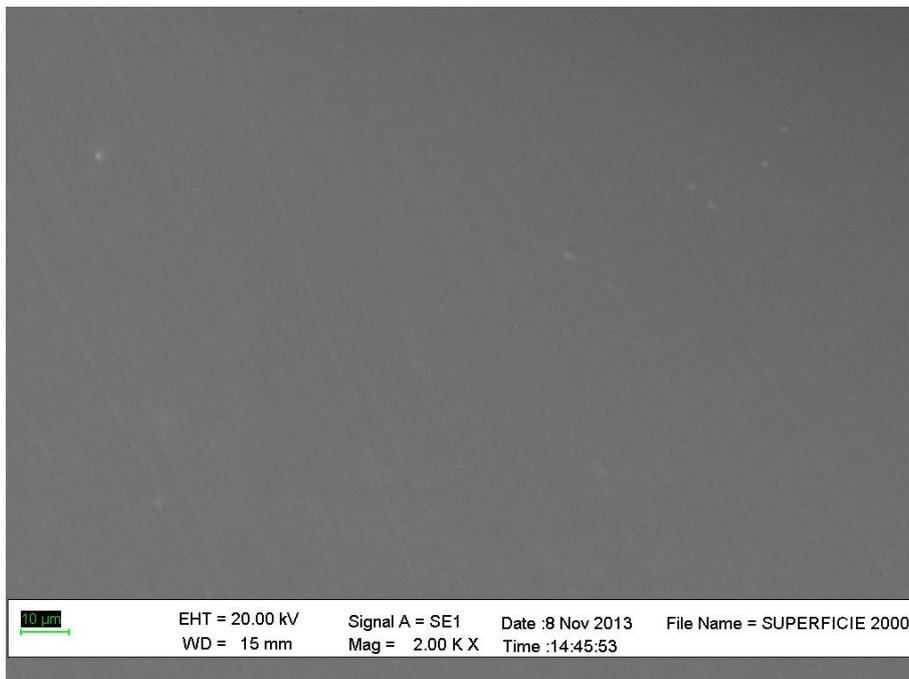
The morphology of the Palladium-Iron alloy plated from the bath has been extensively studied using scanning electron microscope (SEM) techniques.

The identification of different surface images, enlarged a varying number of times, from a brass sample on which a thickness of about 3 microns of Palladium-Iron alloy was deposited has made it possible to check how the morphology of the deposit of thickness palladium is practically even and compact, without any unwanted cracks or splitting, and this is diffused over the whole treated surface.

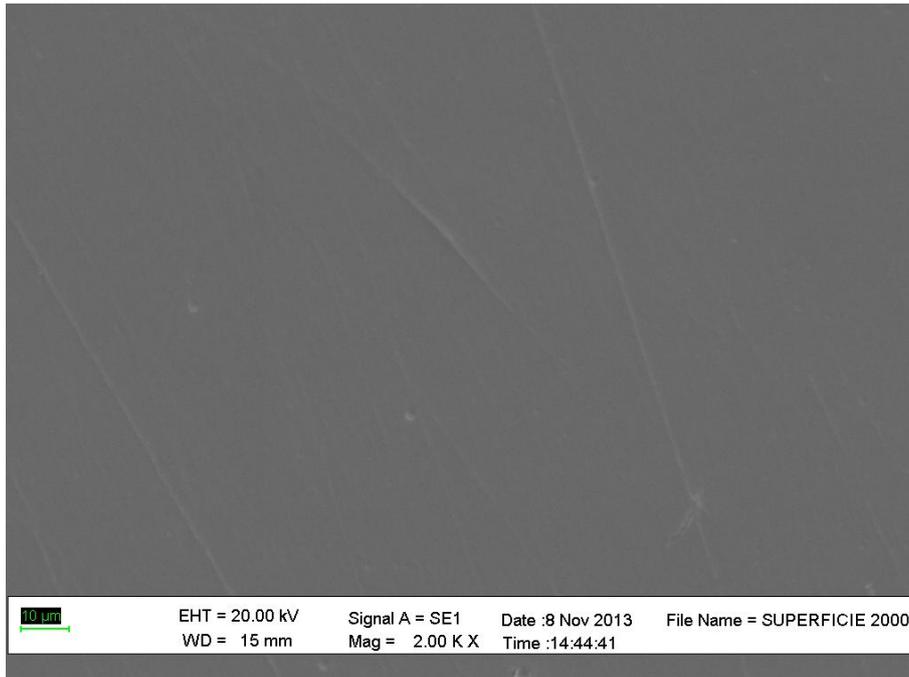
This allows us to state that the system is useful not only from a strictly decorative viewpoint, but also has a barrier layer (in this case, also intermediate, according to the specifications to be followed) to protect against oxidation (*tarnishing*) of materials with low carat weight made with copper-based alloys (brass, bronze) and silver: or those materials normally used in fashion jewellery and accessories in general.



**Photo 1. SEM surface image of a palladium-iron alloy plate enlarged 200 times.**



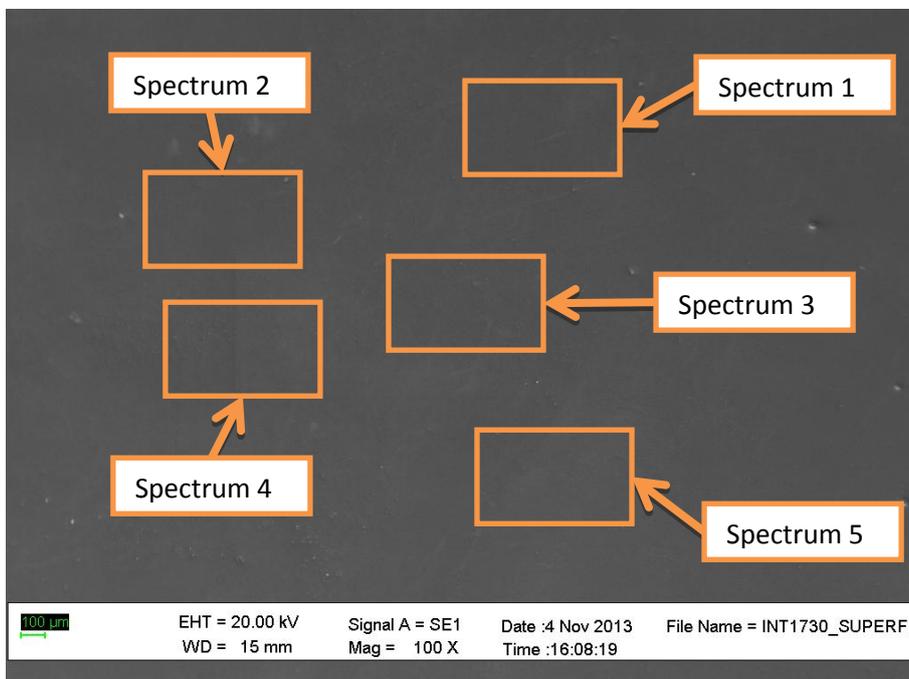
**Photo 2. SEM image of the same surface enlarged 2000 times. In this enlargement mode too, there are no cracks or splits. It is possible to see some small surface undulations only.**



**Photo 3. Other SEM image taken enlarged 2000 times. It is possible to see just a very small amount of localised lining and in any case, it is present on surfaces where the deposit increased in areas with high current density, which confirms that for the most part the plating is smooth and even.**

The fact that the alloy plating is even over the whole surface examined, is confirmed in quantity terms by microanalysis conducted through SEM imaging.

The results of the microanalysis conducted on a sample treated with a palladium-iron bath are as follows:



**Photo 4. SEM image highlighting the areas in which scanning electron microscope analysis was made of the surface composition.**

The following table shows the composition of the alloy, as recorded in the five different areas shown in the top photo:

Spectrum	Fe	Pd	Total
Spectrum 1	8.81	91.19	100.00
Spectrum 2	8.21	91.79	100.00
Spectrum 3	8.87	91.13	100.00
Spectrum 4	8.41	91.59	100.00
Spectrum 5	8.77	91.23	100.00
Media	8.61	91.39	

**Table 2. Results of the microanalysis carried out on the SEM in BSE (Back Scattered Electron) mode.**

It is obvious how the results shown in Table 2 confirm the even composition of the alloy deposited on all of the points of a certain surface treated and how this has a Pd/Fe ratio of 90/10, as already mentioned in the introductory paragraph about the characteristics of the electrolyte solution itself.

## **5. Palladium-Iron distribution on pieces treated and fitted on the same frame**

The distribution of plated surfaces are studied and assessed in parallel to the morphological analysis of the surface on a set of sample tags hooked to the same frame.

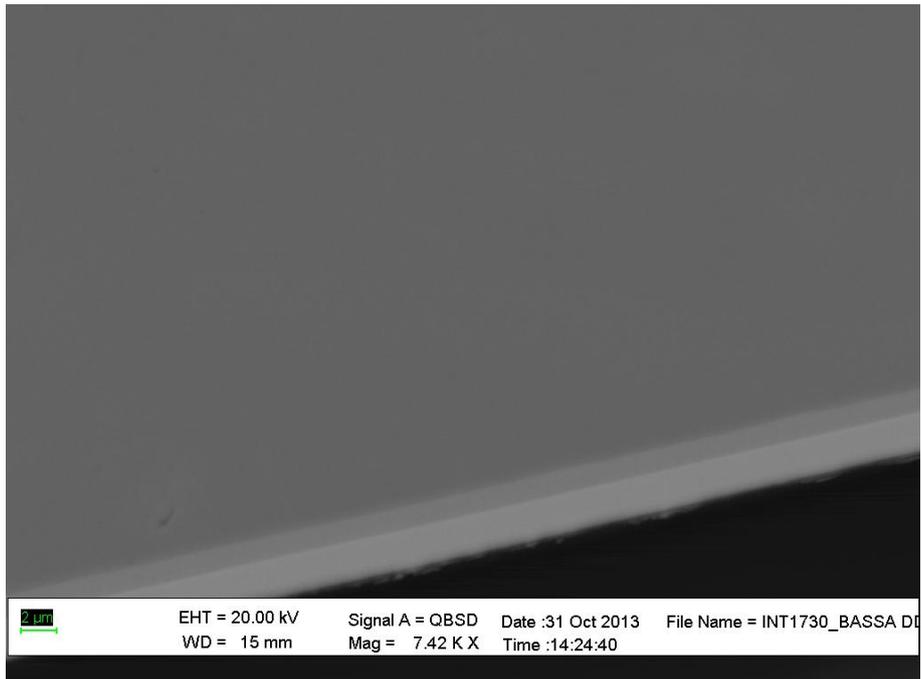
This survey has the purpose of checking the evenness of thickness increase among pieces in high and low density current respectively.

It is in fact known that one of the main problems that the galvanic technician finds during the different procedures with the various processes that s/he interfaces with every day, there is the problem of having to guarantee an even thickness on all pieces loaded onto the same frame. This problem increases in line with the number of pieces loaded, the dimensions of the frame and therefore, the dimensions and volumes of the baths used on an industrial scale.

This problem in fact not only has the repercussion of having to guarantee different clients compliance with certain specifications, but since s/he has to calculate the costs regarding the consumption of materials used, minimising the underestimate margin as far as possible, above all when dealing with precious metals of high value, the galvanic technician is also involved.

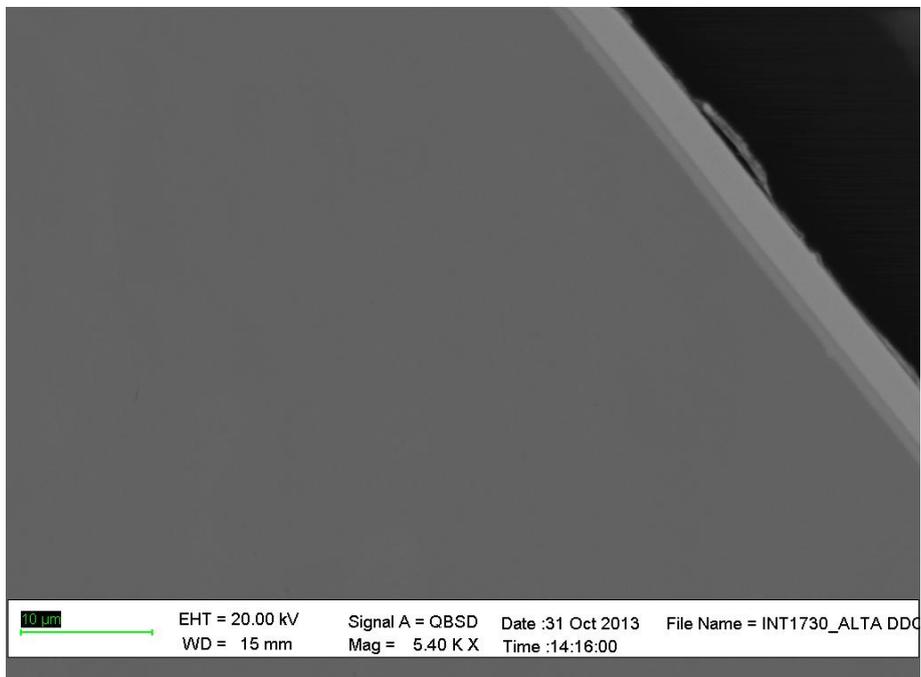
With the help of a scanning electron microscope (SEM) technique, used on a section of samples taken in high-density current areas (i.e., localised close to pieces loaded into the outermost parts or in the corners of a rectangular sheet) and also taken in low-density current areas (i.e. localised in proximity to pieces loaded in the innermost or central parts of a rectangular frame), we checked the difference in the thicknesses found and then compared them with the pieces loaded onto the other areas of the same frame.

The SEM images recorded are shown here.



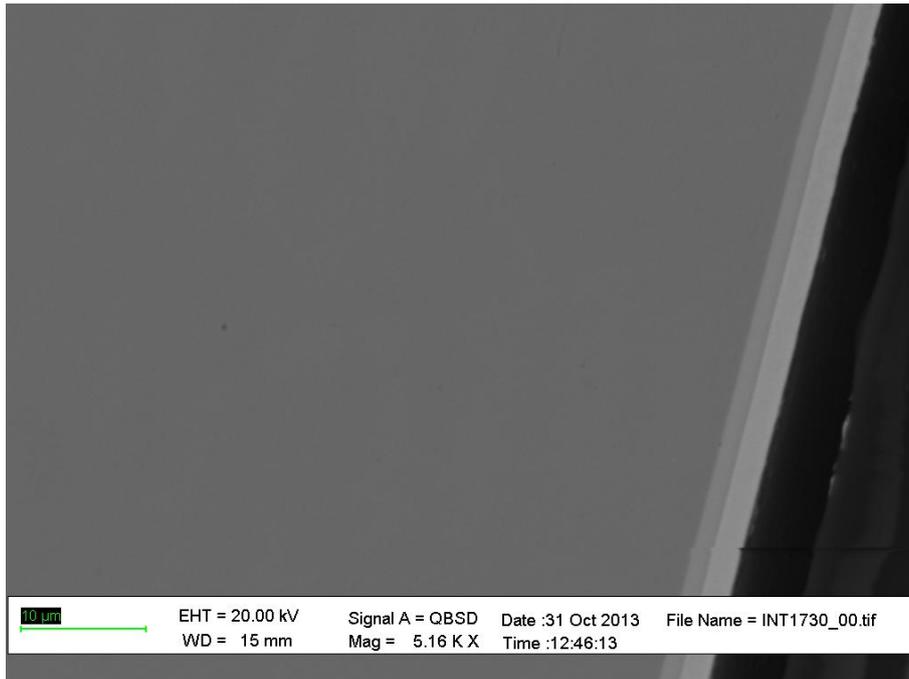
**Average outermost thickness: 2.26 micron.**

***Photo 5. Sample section processed on an area of the frame with LOW current density.***



**Average thickness: 2.76 micron**

***Photo 6. Sample section processed on an area of the frame with HIGH current density***



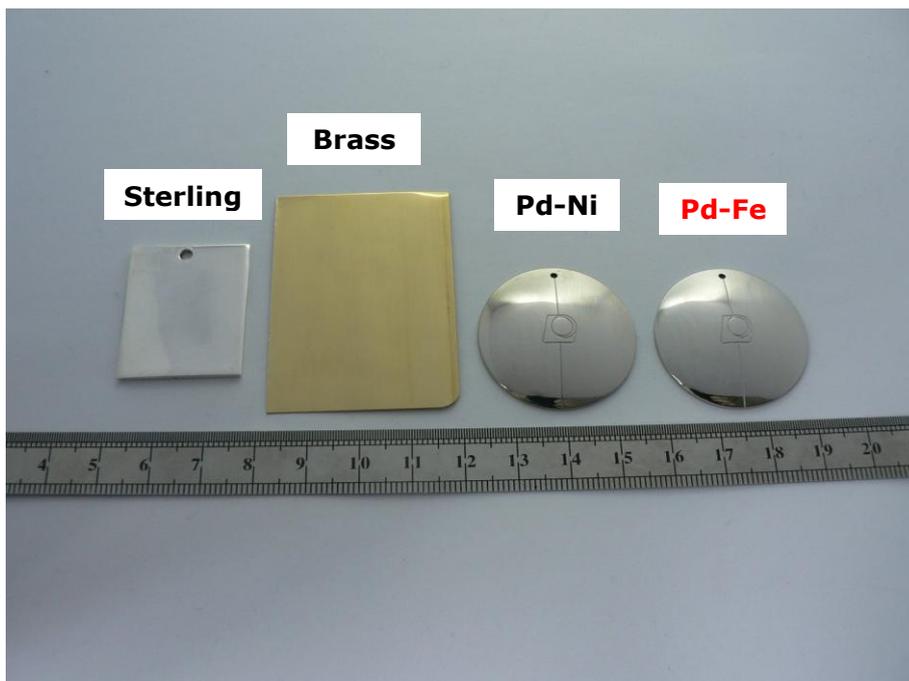
**Average thickness: 2.28 micron**

**Photo 7. Sample section processed on an area of the frame with INTERMEDIATE current density**

## 6. Comparative corrosion tests

The collected samples coated with 3 microns of palladium-iron were subjected to four different oxidation (tarnish) tests in severe conditions: UV test, ACTIVE CHLORINE test, Thioacetamide (TAA) test and perspiration test for 24 and 48 h respectively.

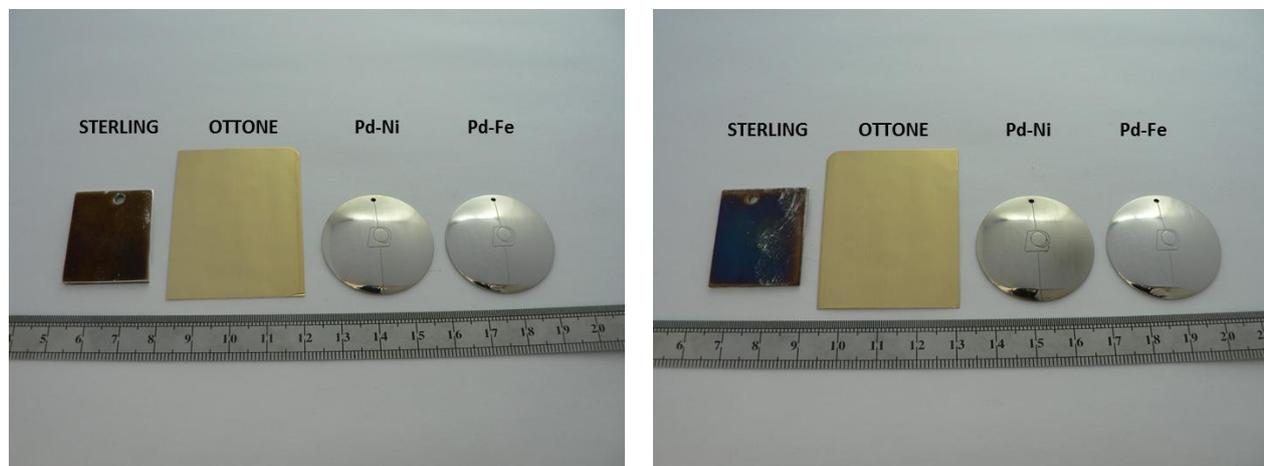
As far as regards the methods used, please see the internal procedure references attached to Annex I. For each test, a small sheet of sterling silver was inserted and examined as a reference, together with a non-treated brass, a sample tag with galvanic Palladium-Nickel plating to compare the two different thickness coatings of Palladium directly, as well as the sample tag treated with Palladium-Iron.



**Photo 8. Test Sample set before testing**

The following section contains the photos and comments for each single test performed.

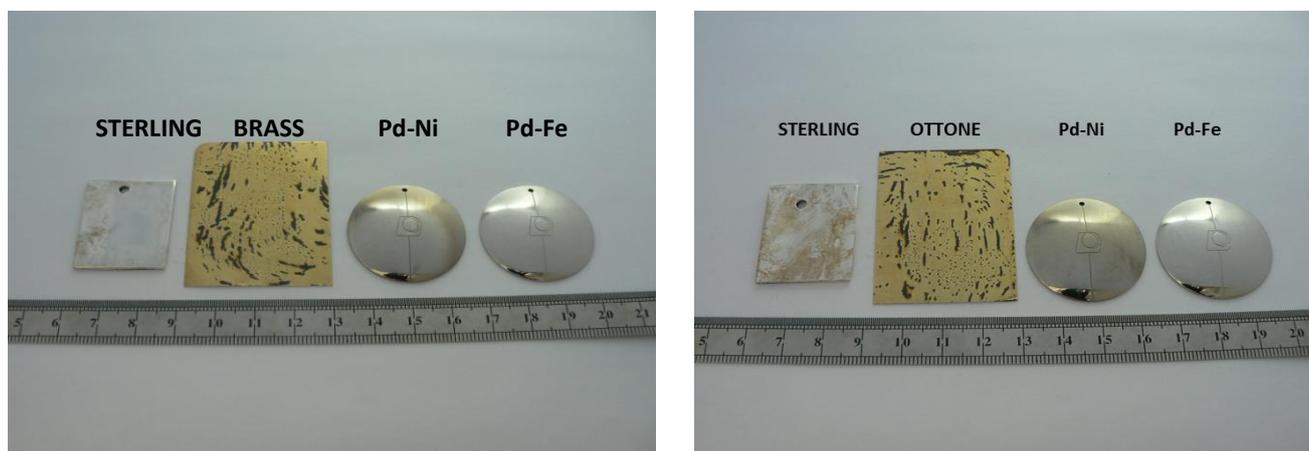
### 6.1. UV Test



**Photo 9. UV Test for 24h (left) and 48 h (right).**

The test of exposure to ultra-violet radiation (a test used to reproduce the exposure conditions inside a shop window, in an amplified manner), shows how both palladium coatings (Nickel and Iron alloys respectively) are quite resistant to oxidation within the 48-hour monitoring period. However, it is possible to see a more marked tarnishing on the brass and on the Palladium-Nickel surface compared to the one with the Palladium-Iron coating, which has shown itself to be more resistant in these conditions.

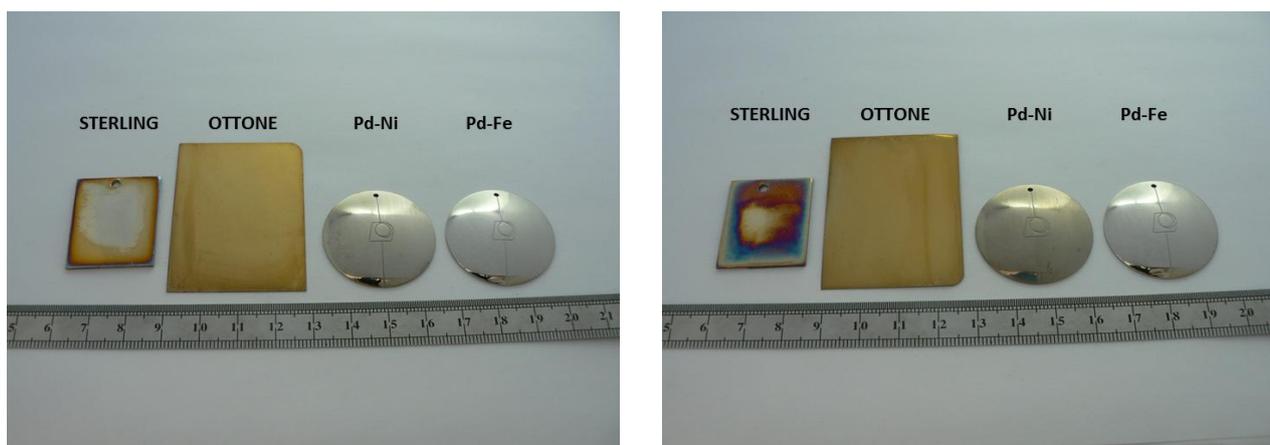
### 6.2. Active chlorine test



**Photo 10. Active Chlorine Test for 24h (left) and after 48h (right).**

The active chlorine test was found to be the harshest for the untreated brass and also for the Palladium-Nickel, which show colour variations compared to the original after just 24 hours, compared to the UV radiation exposure test. In the case of the Palladium-Iron coating, the exposure test to active chlorine shows only a small drop in brightness after 48h, revealing it to be the most resistant system in this case too. The purpose of this test is to reproduce, on an amplified scale, the conditions of exposure to chlorinated water, such as in swimming pools, for example or chlorinated substances like bleach.

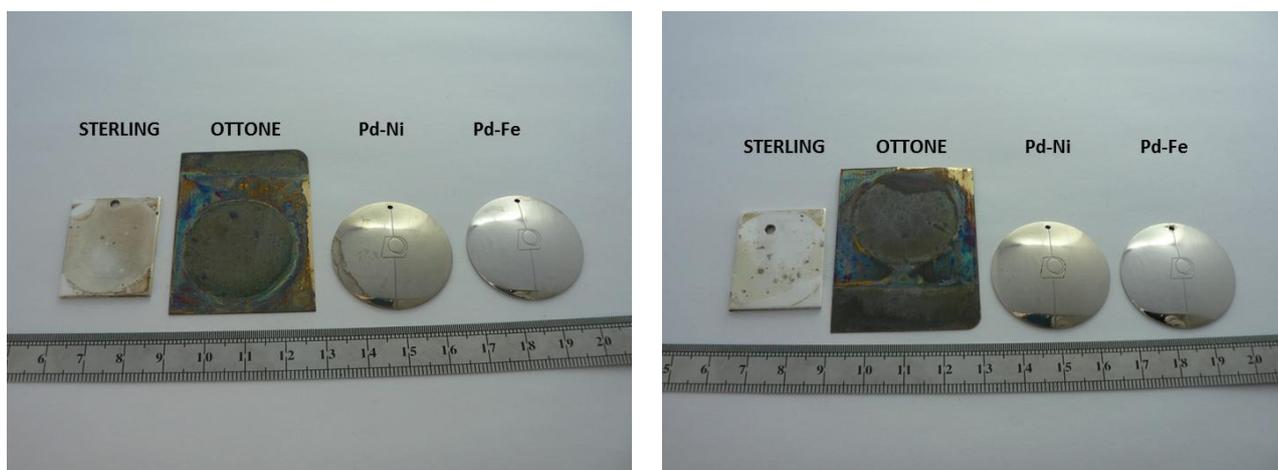
### 6.3. Thioacetamide (TAA) Test



**Photo11: Thioacetamide Test for 24h (left) and after 48h (right).**

The thioacetamide (TAA) exposure test gave practically the same results as the test for active chlorine exposure, confirming the greater resistance of the palladium-iron plating compared to this aggressive atmosphere. The TAA test serves to amplify the conditions of exposure to atmospheres containing sulphurised compounds, which are normally mostly responsible for metal silver and copper-based alloys.

### 6.4. Perspiration Test



**Photo 12: Perspiration Test for 24h (left) and 48h (right).**

The perspiration test shows how untreated brass reacted completely by the end of the first 24h of testing, while the two palladium alloy coatings once again confirmed the results of the other tests, i.e., that the palladium-iron alloy plating is more resistant than the palladium-nickel. In fact, where palladium-nickel begins to lose its shine partially, after the first 24-hour test period, the palladium-iron alloy only showed a very slight loss of shine after the total 48-hour monitoring.

### Tarnishing Test Conclusions

Cross-analysis of the four different situations with exposure to aggressive atmospheres that lead to rapid oxidation of metal surfaces has shown that the palladium-iron alloy thickness plating is decidedly better than the traditional palladium-nickel plate. We consider that this is in part due to the morphology of the plate (see previous section) which, since it has no localised cracks or splits of any kind, it creates quite a compact surface barrier. This barrier prevents the underlying base material from undergoing an oxidation process through direct contact with the external atmosphere and it stops oxidation by propagation through to the outermost layers from making treated items aesthetically unacceptable.

## 7. Remarks and Conclusions

Elimination of ammonia and Nickel as an alloy metal from Palladium baths is an achievement on the cutting edge and makes Palladium-Iron plating a next-generation process.

The result is an *eco-friendly* treatment that is very easy to manage and requires no changes to existing machinery and equipment or any additional outlay.

For Nickel-free specifications, this type of bath is a turning point that will make it notably easier to disseminate specifications for completely non-allergic processes.

And last but not least, there is the very important consideration of the high degree of resistance to surface oxidation which is the most responsible for unsightly markings on embellished or decorated items and which may occur after a certain and variable amount of time.

The resistance to oxidation of the palladium-iron system is even better than that of the traditional palladium-nickel method.

## APPENDIX I – Experimental Section

### SEM-EDX Tests

All of the photographic images referring to the thickness and morphology studies of the different samples studied for this paper were recorded by scanning electron microscope which uses the emission of X-rays generated by an accelerated electronic beam that affects the sample (SEM-EDX technique). Similarly, the same technique made it possible to perform the microanalysis in section 4 and Table 2.

### Corrosion Tests

**Perspiration test:** performed using the in-house procedure used by Legor Group and directly derived from the integration of ISO12870:2004, standard perspiration test used by the eyewear industry. Pieces are exposed to a saturated atmosphere of synthetic perspiration vapour and monitored over a period of 48 hours, with a double check after 24 hours.

**Thioacetamide (TAA) test:** The thioacetamide test was performed using an in-house procedure to assess the tarnishing resistance of a certain type of metal material. The procedure is based on the standard ISO4538 procedure for corrosion tests. Pursuant to this procedure, pieces are exposed over a 48-hour period, with a double check after 24 hours, to a sulphide saturated atmosphere inside a closed environment, set to 20°C for the purpose of reproducing a normal ambient temperature. The occurrence of browning on the surfaces of the pieces studied points to sensitivity to tarnishing: the greater the amount of browning, the greater the sensitivity.

**Active chlorine test:** The active chlorine test is a Legor Group in-house procedure for the purpose of checking resistance to metal materials tested in a solution containing 5 ppm of sodium hypochlorite. The test was performed over a 48-hour period with a double check after 24 hours.

**Test of exposure to ultraviolet (UV) rays:** The test of exposure to UV rays is a Legor Group in-house procedure for the purpose of checking the resistance of the metal materials tested to exposure to UV-A and UV-C radiation from a special lamp at 500 W. The purpose is that of reproducing, in a more extreme fashion, the conditions of exposure under the lights of a shop window display.