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Martino Gardan is graduated in Industrial Chemistry at Università of Padua, Faculty of Mathematical, Physical and Natural Science since 2004. In 2009 he gets his Ph. D. in Molecular Sciences, specialising in Chemical Sciences at the same University. In 2010 he joined Legor Group where is currently Technical Manager of the Plating Division.

*Ceramic nano – composite cataphoretic coating (e – coating) is an innovative product ideal for the protection of metal surfaces. Thanks to the presence of ceramic nano-particles in its formula, its wear resistance is improved as well as its feeling sensation to the touch with respect to the traditional e-coatings available on the market today. Moreover, as it is colorable by the addition of pigments, it offers the possibility to combine either protective and decorative purposes on jewelry components. This paper is focused on presenting both transparent and several colored e-coatings aside experimental results confirming their exceptional resistance to wear and tarnish in comparison with traditional coatings obtained by chemical passivation, electroplating and PVD technique.*

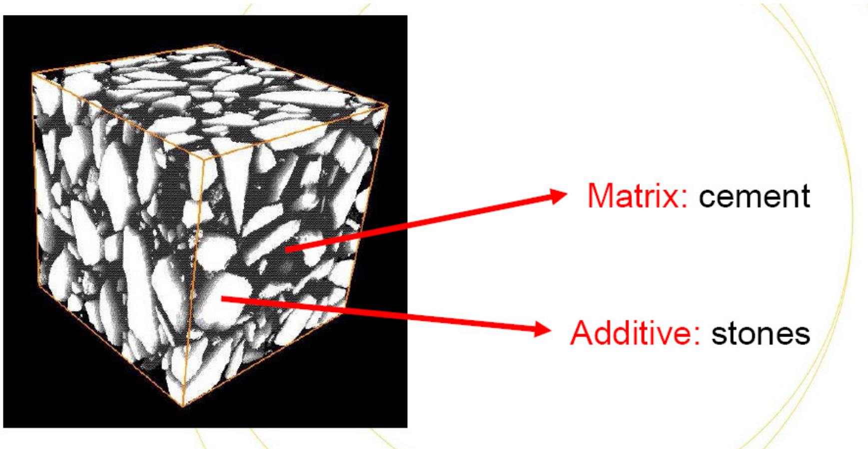
# THE NEW NANO COMPOSITE CERAMIC E-COATINGS. COMPARATIVE STUDY OF ABRASION AND TARNISHING RESISTANCE

## INTRODUCTION

Coatings, the decorative ones too, must be characterized by resistance to abrasion and wearing as well as providing a good resistance to tarnishing.
In order to obtain them, up to now deposition techniques that allow to achieve good surface hardness were used, that is galvanic processes and, in some cases, PVD (Physical Vapour Deposition).
There is no doubt that these techniques guarantee a good resistance to abrasion but they offer rather limited opportunities in terms of colours and effects.
At the same time, a technique that would allow a wide range of colours and shades is the painting, but the latter presents characteristics of low surface hardness and, therefore, a very limited resistance to abrasion.
In this way, it is rather obvious that the ideal would be a depositing technique either with the features of resistance typical of a metal or an alloy but at the same time versatile as a paint.
By using ceramic nano-particles it is possible to match these requirements, because a perfectly transparent or coloured bright coating is achieved, but with a higher resistance to abrasion with respect the normal nowadays used finishing technique.
This new coating presents some other advantages, such easiness of use: it does not require any particular and expensive installations, as it happens for instance for PVD, and can be applied with immersion techniques, as normal plating systems.
This product is revolutionizing the way of intending decorative coating.

## NANOTECHNOLOGY AND NANO-COMPOSITE MATERIALS

"Nanotechnology" is referred to the application of materials which are made of particles with dimensions less than 100 nm.
"Nano" is referred to the particles dimensions while "Composite" is referred to the combination of two or more different materials giving a new one material with different characteristics.
In general a composite material is made of a main component (Matrix) to which one ore more additives are added.
As example of composite material we can consider concrete reinforced with stones as in the following picture.




***Picture 1.*** *Example of composite material*

The addition of stones in a concrete matrix allows to achieve a final products with higher characteristics with respect to the only starting matrix.

## NANO COMPOSITE CERAMIC COATINGS

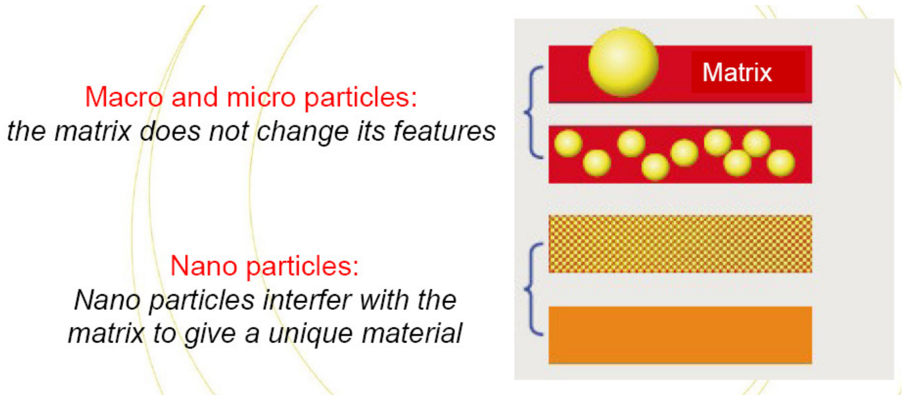
In this sense clearly appears that a nano composite ceramic coating is a material in which a resin (an organic chemical-nature material) is used as matrix and ceramic nano-particles (inorganic chemical-nature meterials) have been used as additive. By this combination, we can get a resin with higher wearing resistance without loosing all its other features.

Why use additive particles so small?

For sure, the first important advantage is that nano-particles are invisible to the human eye. The addition of nano-particles to a transparent resin does not absolutely affect its transparency, neither its brilliance affording the same time a good feeling in touch of the same coating.

We can consider that such small particles make a sort of homogeneous amalgam with the matrix-resin as the system is a solution rather than a dispersion.

In order to show better this concept, see the following scheme where two different composite materials with macro and micro particles are compared.




***Scheme 1.*** *Comparison between composite materials made respectively with macro, micro and nano-particles*

It is quite easy to understand that by using either macro and micro particles, the features of the matrix does not change so much, while by using nano particles, which interacts with the main component in a single system, a totally new material with new features is obtained.

In order to get a nano-composite coating, nano-particles used as additive in its structure must to have specific features which are listed here below:

- Stable during time;
- Diameter range should be as small as possible, close to the optimal value;
- Find the optimum ratio of the quantity of such nano-particles with respect to the resin-matrix;
- Nano-particles made of substances compatible with respect to those making the resin

## DEVELOPMENT OF HYBRID CERAMIC NANO COATINGS AND EXPERIMENTAL RESULTS OBTAINED BY COMPARATIVE STUDIES OF ABRASION AND TARNISHING RESISTANCE WITH RESPECT TO THE MOST USED PASSIVATING TECHNIQUE

On the basis of such information, a new hi-tech Product Line has been designed: ***Kliar-Line®.***

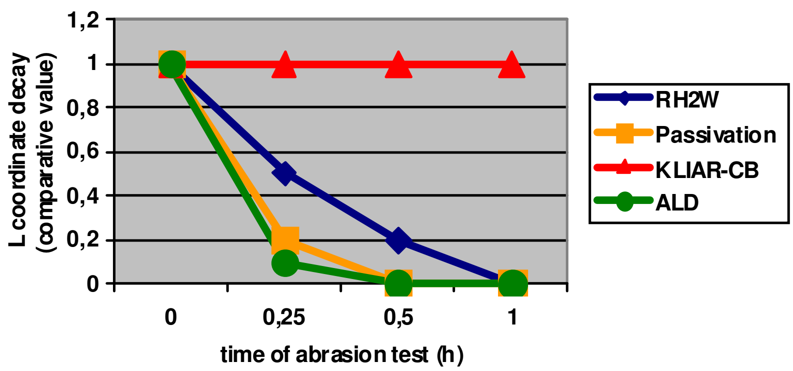
This line consists of different nano-ceramic coatings both coloured and transparent to be applied on jewellery or costume jewellery items rather than on fashion accessories to maintain their best properties unchanged during time with the opportunity to give them particular colour shades, otherwise very difficult to achive by traditional plating processes.

As the application is by means an electrodeposition, these products are commonly called ***e-coatings***.

Different studies run in our R&D laboratories confirmed improved abrasion, wearing and tarnishing resistance with respect to the top passivating agents available nowadays on the market in the jewellery sector and with respect to the other traditional e-coatings.

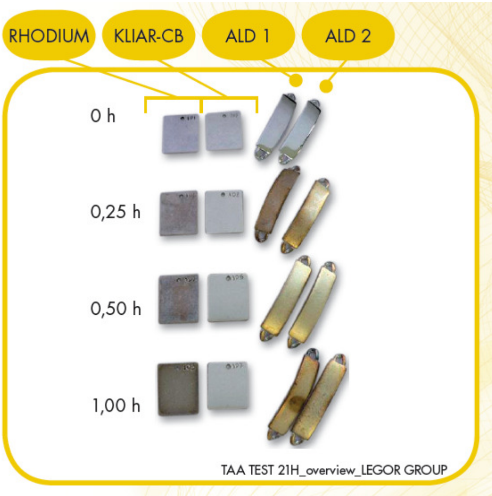

***Picture 2.*** *Oxidation resistance test (TAA test for 70h) for KLIAR-CB (the new transparent e-coating) and for most effective passivating agents on the market today in Sterling Silver sample-plates.*

Higher wear resistance of KLIAR-CB (the new transparent e-coating) is showed in this graph where the L parameter decay against time for other passivating techniques is related to the same of KLIAR-CB.



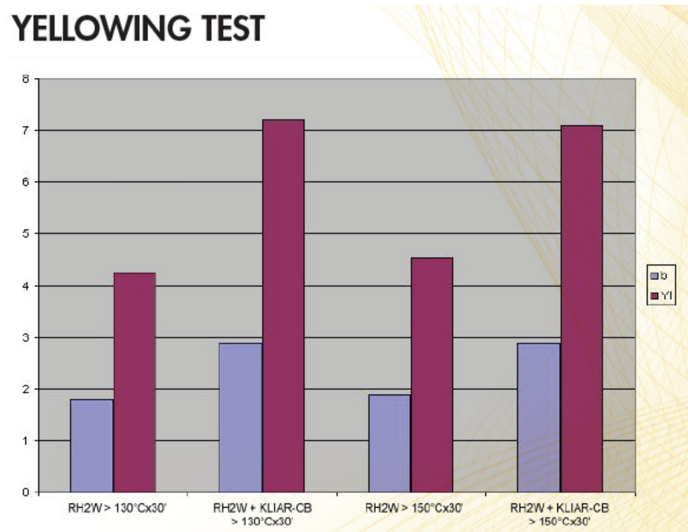

***Graph 1.*** *Relative L coordinate (CIELab system) decay of the top passivating systems available on the market with respect to that of KLIAR-CB during time.*

| **Abrasion test** | **Flash rhodium-plating** (RH2W flash, 40 sec) | **Passivating solutions** (TENARISPRO) | **ALD** (Atomic Layer Deposition) | **KLIAR-CB** (20 sec, curing: 130°C x 30 mins) |
|---|---|---|---|---|
| **Time after which loss of brighteness is observed** | 15 mins | < 15 mins | < 15 mins | No tarnishing has been observed after one hour of wearing test in tumbling machine |



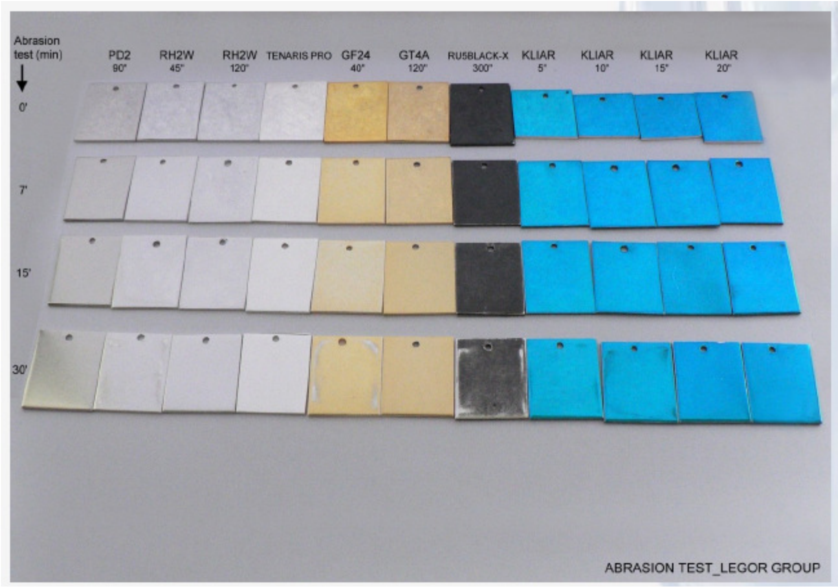

***Picture 3.*** *Samples used for abrasion test for 1 hour. The superior performance of KLIAR-CB is clearly visible compared to rhodium flash treatment and to two different types of Atomic Layer Deposition.*

Yellowing tests have also been done in order to confirm that the high temperatures at which the items are subject during the curing phase do not take too much changes on their surfaces in terms of both whiteness, brilliance and colours.
The following graph shows that the coordinate b of the CIELab system (index of colour variation from blue to yellow) and the YI datum (index of the white quality of the object) remain at values that do not cause yellowing of the samples, even after exposure of the plate to a temperature of 150°C per 30 minutes.



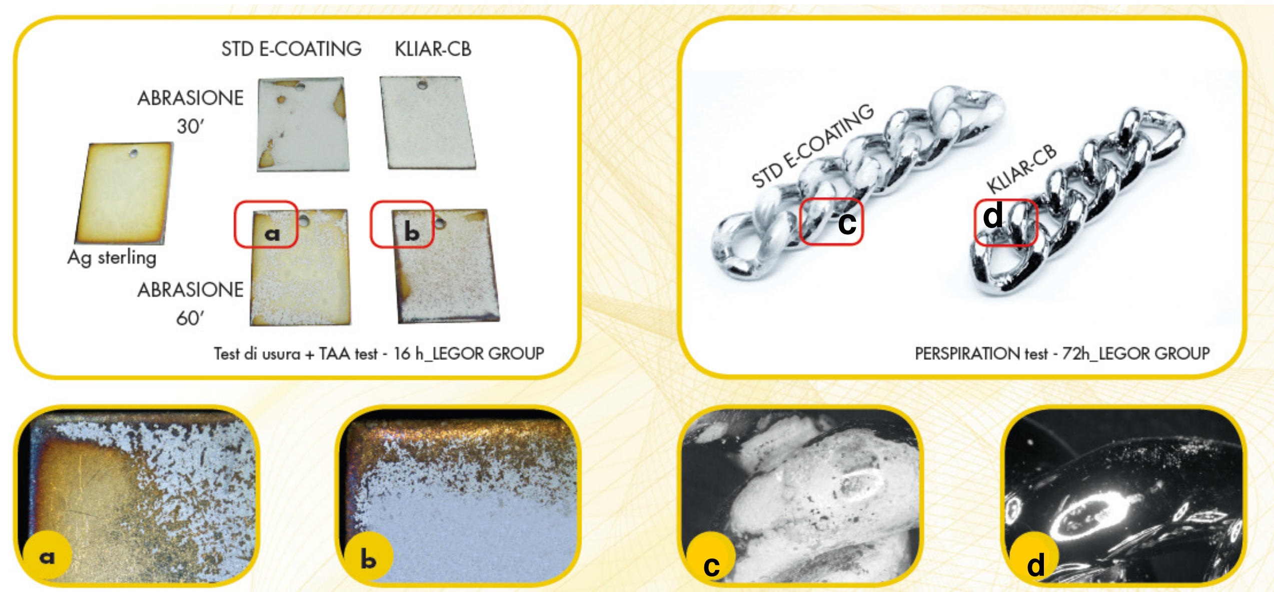

***Graph 2.*** *Yellowing test run by comparison of the **b** and **YI** parameters (CIELab system) before and after curing phase for flash rhodium plated samples and the same also treated with transparent e-coating at two different temepratures: 130 and 150°C.*

The good features in wear and tarnish resistance of such e-coatings are not provided only for the transparent one but also for the coloured products. The following picture shows the results of comparative abrasion tests in which a coloured nano-ceramic e-coating has been compared with either flash and micron traditional plating deposition in abrasion tests. Also in this case is possible to note that the samples covered with e-coating show a better resistance against abrasion.




***Picture 4.*** *Sterling silver sample-plates plated with different metals and covered with colored ceramic nano-particles thickness.*

New Kliar - e-coatings have also been tested and compared with the best cataphoretic resins present on the market today - that do not contain ceramic nano-particles as additive - to confirm their better features.
Samples treated with the nano ceramic transparent e-coating and the same samples treated with one of the today most used e-coating have been compared in the following test: abrasion, perspiration, active chlorine, UV and TAA resistance test.
Results of all these tests are very significant as show that the nano ceramic e-coating is, again, higher resistant as well as of higher deposition quality.
Among all these tests those that afforded the most important evidences were abrasion and perspiration which samples are reported on the general picture here below:



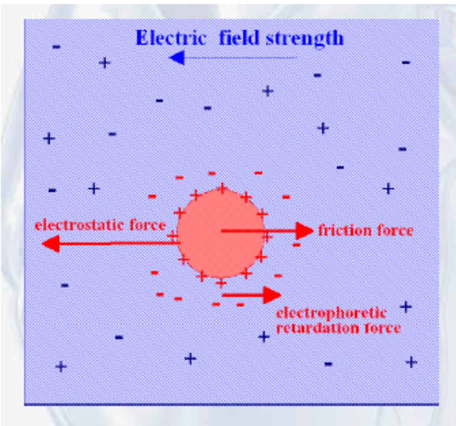

***Picture 5.*** *Comparative quality e-coating results after 1 hour abrasion test (Left) and after 72 hours of persipration test in synthetic sweat (Right).*

All these results clearly demonstrates that the advantages which nano ceramic *e* coatings takes on jewellery items should be different.
Among them it is relevant to highlight:

- An **improved wear resistance** which arose from the combination of resin and ceramic nano-particles
- **The final material is colourable** thus affording all the traditional galvanic colours (from black ruthenium to light gold) and all the colours that otherwise is difficult to achieve by traditional galvanic process or PVD.

The possibility to colour this composite material permits not only to get longer resistant coatings but also the possibility to customize the material itself by developing a specific coloration or shade according with each customer needs.
The Kliar coating is actually available in 17 shades plus the transparent one; however, it is possible to combine them and obtain new and original tones.
Among the other advantages, we can not forget that covering jewellery items with these coatings is a quite **cheap process** as covering surfaces with a higher wear resistant materials allows to considerably lowering the thickness of precious metals deposited via traditional plating process. Furthermore, for thickness less than 10 micron, **the coating does not affect the final title of precious metals** thanks to its limited specific weight.

**HOW TO APPLY**
The application of these systems is by *Cataphoresis*.
Cataphoresis means a particular way of electrophoresis which is the motion of dispersed particles relative to a fluid under the influence of a spatially uniform electric field [1,2,3,4,5,6].




**Picture 6.** Schematic representation of the motion of a particle in a fluid system under the influence of an electric field: Electrophoresis.

This electrokinetic phenomenon was observed for the first time in 1807 by Reuss (Moscow State University)[7], who noticed that the application of a constant electric field caused clay particles dispersed in water to migrate. When the particles migrate from the solution to the cathode-electrode of a rectifier, the phenomenon is thus called cathaphoresis.
As this technique is since time applied in the automotive industry to paint the main bodies of cars, the idea was finally that of translate this system to the jewellery industry.
The colouring process is relatively simple and when regards the daily production of a few hundred pieces it is relatively simples and requires no complex machinery.
Despite e-coatings are achieved by electrodeposition, as well as a traditional galvanic process, there are many technical differences that can not be neglected.

The main technical differences are here highlighted in the following Table:

| Parameters | Traditional Galvanic Process | E-Coating/Cataphoresis |
|---|---|---|
| **Applied Voltages** | 1 – 10 V | 30 – 60 V |
| **Temperatures** | From room temperature up to 70°C | Room temperature (20 – 30°C) |
| **pH** | Wide range (both acidic, neutral and alkaline) | Almost neutral |
| **Preparation of the solution** | Filtration of the solution is not necessary | A pre-filtration of solution is necessary to avoid any presence of solid particles and dust |
| **Working on flat and large surfaces** | - | A *cleanroom* is necessary |
| **Type of casting of the items surface** | The problem can be resolved by micron plating | Avoid, if possible, porousity of the surafaces to be worked |
| **Curing phase** | - | Necessary, 120-150°C for 30 minutes at least |

Among these differences, the first one that captures the attention is that of the applied voltages. In fact, in order to get the minimum amperages values to give particles migration (0.2 – 2 A), higher differences of electrical potential are necessary to apply with respect to those applied during a traditional plating process. This is because not only the process is slightly different but also because of the different chemical nature of the used solution.

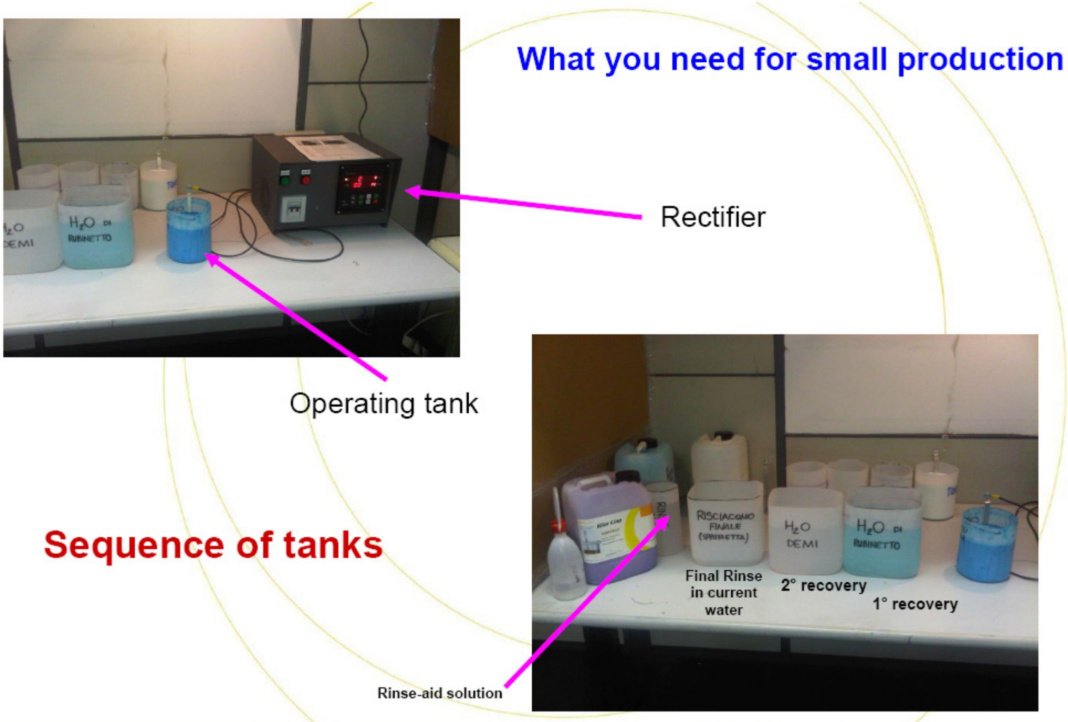
While the galvanic system is a salt based aqueous solution with high conductivity, the nano-ceramic e-coating solution is a composite material in which both organic, inorganic and pigments are dissolved at the same time affording different physical-chemical behaviour.
In order to achieve the best results, practice is necessary, as well as the preparation of the items to be covered.

If these precautions are not well followed, it will be easy to get some defects like not uniform coatings or orange peel like effects rather than iridescence and or clots.

As consequence, to evaluate an investment involving the use of e-coating solutions for jewellery purposes it is very important to:

- Avoid any solid particles pollution either in the solution and in the working-laboratory room: so that the solution needs often to be filtered;
- Avoid any salts-based residues in the e-coating solution;
- For big daily productions which can involve bats higher than 150 liters, is even necessary an ultrafiltration system in the industrial plant.

All devices that are, on the contrary, not so far indispensable in a traditional galvanic system.




***Pictures 7. and 8.*** *Example of a typical equipment for small productions. A kiln is also necessary for curing phase after leaving the pieces dry to air for 5-30 minutes.*

## MAIN DRAWBACKS

There is no doubts that if this technique takes some advantages in the decorative and protective finishing, there are also some drawbacks that must not be neglected.
In fact, each colour foresees its own tank or a dedicated plant in order to avoid any pollution coming from other coloured solution. It has already been mentioned the requirement of a *cleanroom* for particular items or surfaces and, for sure, the brighteness of the surfaces so worked is lower with respect to those plated with galvanic alloys or pure metals deposition. Also the design can influence the quality of such deposition and in this sense is preferable to avoid any edges or corners ton the items surfaces.
Thickness achieved are always higher than 2 micron and, despite the presence of ceramic nano-particles acts in order to minimize this phenomenum, the e-coatings always take a sort of barrier against either electric and thermic conductivity so that the feeling in touch will not never be like the same of a pure metal or alloy.
Last but not least the constant in the quality of the used solutions to get the nano ceramic e-coatings on metal surfaces: as their chemical nature is organic, also in their pigments, the ready to use solution has got an expiry date of six months since the production date.

## CONCLUSIONS

With this paper a new line of products for either protective and decorative purposes on metal surfaces has been presented aside experimental results achieved on different items covered with these new hybrid coatings.
The experimental results confirm the excellent protection against the wearing effect of time and metal tarnishing, being four times more resistant than the treatment with a flash rhodium coating.
Kliar coatings helps make jewels more durable, regardless of the metal they are made of and enrich them with a high-quality colour: all this provides the manufacturer with a greater opportunity to get away from traditional precious metals, which are now reaching prohibitive costs and use alternative materials with high appeal on customer.
Just this mix of advantages convinced the judges of the Thinking Ahead Award (MJSA organization in the USA), to award a prize to Kliar nano ceramic e-coating as the most strategic product of the season, able to reconcile the needs of manufacturers with those of an increasingly demanding and sensitive clientele.

## APPENDIX I – Experimental part

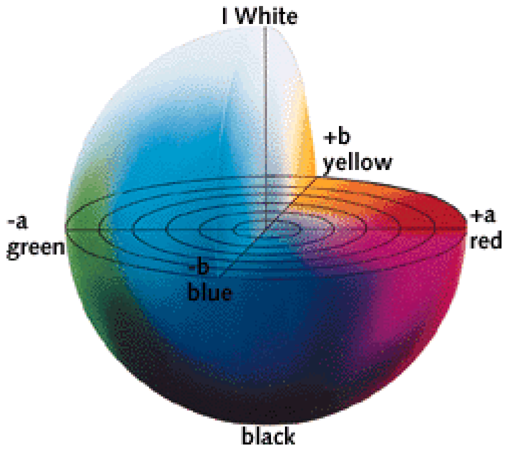
**Perspiration test (Artificial sweat test):** carried out according to an internal procedure that derives from the ISO12870:2004 perspiration test standard for spectacles industry. Pieces are exposed to concentrated sweat vapours for not less than 16 hours.

**TAA (Thioacetammide test):** it is an internal procedure for tarnishing resistance evaluation. It follows partially the ISO4538 standard for corrosion testing. Pieces are exposed for a fixed time (16 hours for uncoated samples, 60-80 hours for coated samples) to a hydrogen sulphide atmosphere in a closed environment at room temperature (20°C). The occurrence of a browning discoloration indicates the tarnish sensitivity of the exposed item.

**Wearing test:** is an internal procedure. Pieces are submitted to mechanical abrasion in a tumbling machine with abrasive media and detergent for 1 hour. Afterwards, the integrity of the coating is assessed by submitting pieces to a TAA test. The areas from where the coating has been worn-off will highlight a browning discoloration.

## APPENDIX II

**CIELAB reference system [8] [9]:** it is a colorimetric space in which every point (corresponding to a vector that starts from Cartesian coordinate axes origin) represent unambiguously a colour. The elements that define each of these points are the three coordinates **a**, **b** and **L** each of them has a value between -100 and + 100.




To have a practical reading of the model, consider that:

- **a coordinate moves from green to red,**
- **b coordinate moves from blue to yellow,**
- **L coordinate represents luminosity,** that can be defined as an indication on the quantity of reflected light from sample surface.

Luminosity is strongly dependant on the surface finishing of the piece; a polished piece has obviously a higher luminosity than a matte surface.

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