Final activity report

CONTRACT N° : **COOP-CT-2005-18031**

ACRONYM : **Hyponick**

TITLE : **Hypoallergenic nickel-free (imitation) jewellery by employing nano-structured galvanic coatings**

PROJECT CO-ORDINATOR: **Dr. Mauro Gajo**

PARTNERS :

Elsy Research	I
AZ Bigiotterie	I
Liw Lewant	PL
MSO	F
Venrooy	NL
University of Trento	I
TNO	NL

PROJECT START DATE : 01-09-2005 **DURATION : 27 MONTHS**

Reporting period : 01-09-2005 to 30-11-2007

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Project introduction and objectives
The HYPONICK project has obtained the support of the EC thanks to funding in its SME-targetted scheme for Collective Research and Co-operative Research ("CRAFT"). The project started Sep1st 2005 with a duration of 27 months.

Main objective of the 2-year CRAFT-project 'Hyponick' was to develop innovative nickel-free undercoats for hypoallergenic precious and semi-precious plated jewellery articles by electrodeposition of nanostructured coatings, thereby reducing the levels of exposure of (European) citizens to nickel towards zero. Although alternative undercoats exist, most of these are still on nickel basis (e.g. Pd-Ni) and these still give rise to allergic reactions on sensitive skin, despite the fact that these conform to European Union Directive 76/769/EEC-12th Amendment (94/27/EC).

The main technical objective of the proposed research was to develop innovative completely nickel-free undercoats for hypoallergenic precious and semi-precious plated jewellery articles by electrodeposition of nanostructured coatings. These coatings can solve the issues that remain unsolved by present-day technology. Targets were:

- 100% complete absence of nickel and therefore fully hypoallergenic character
- Reduction of diffusion speed of Cu from the undercoat to the Au surface with >90% compared to conventional white bronze, thereby reducing gold surface tarnishing
- increased durability of the gold plated article due to improved abrasion resistance and corrosion resistant properties. Target is improvement > factor 2 compared to conventional white bronze
- reduced costs, 30% for total coating stack

Consortium
The SME contractors involved in the project were:
- Elsy Research (I) – coordinator
- AZ Bigiotteria (I)
- Liw Lewant (PL)
- M.S.O. (F)
- Venrooy Goud- en Zilverindustrie (NL)
- Galvafin (SK)

RTD partners involved were:
- University of Trento (I)
- TNO Science & Industry (NL)

Description of work
First, materials and configuration requirements established on the basis of input of all participating SMEs. Base materials were defined and coating specifications were determined. Tests and standard for characterisation were selected and requirements concerning costs of the process were established.

By RTDs TNO Science & Industry together with University of Trento, progress was made in development of nickel-, cyanide and lead-free undercoats for jewellery applications. A nanocrystalline white bronze alloy bath (Cu-Sn-Zn) was studied based on boric acid/gluconate. Moreover, work was done to develop a bath based on methanesulphonic acid (MSA). Smooth films are obtained when high concentrations of specific non-ionic wetting agents are used. The targeted alloy composition of 60-70% Cu, 30-40% Sn and 0-5% Zn was achieved. Pulse reverse plating was investigated as an

alternative to use of wetting agents to get rid of foaming effects. Further work was carried out on pulse reverse plating with Elsy's nickel-and lead free white bronze bath. A compositional change was clearly seen as function of plating frequency. Sample material was made and tested for performance (WP3). The results were characterised as very promising the by SMEs.

Figure 1: MSA-based white bronze coating on ring with Au topcating

The SMEs expressed serious doubts about further researching the inclusion of nanoparticles in bronze layers as a technical direction for the project. Both based on experiments and experience in handling nanoparticle containing baths, the chance of industrial success is rated low. After 9 months in the project, all participants agreed to reduce the effort on this and instead focus on the other routes (nanocrystalline bath and pulse reverse plating).

The technologies developed were tested on jewellery items supplied by SMEs M.S.O., Elsy, Liw Lewant, AZ Bigiotterie and Venrooy (dial plates, eye-glass frames, belts, buttons etc). The items were coated with different undercoats (Elsy's white bronze, MSA white bronze, nickel) followed by a gold topcoat. Samples were evaluated on corrosion performance and Au tarnishing due to Cu diffusion.

The optimal CuSn composition was determined as 50 wt Cu / 50 wt% Sn giving bright white coatings with attractive appearence. The hardness of the amorphous bronze coatings, 500 HV, is higher than that of Ni, but also that of single Cu or Sn coatings. The corrosion and tarnishing resistance (< 200h NSS) of the white bronze coating outperforms Ni and even white bronze coatings from traditional cyanide based baths (Table 1). Upscaling at an industrial facility shows promising results for application.

Table 1: Comparison of the corrosion and tarnishing resistance of the MSA-based CuSn to standard nickel and cyanide based CuSn. (5 µm coatings on brass as undercoat to 1 µm gold finish)

Test / Coatings	*Nickel*	*MSA white bronze CuSn*	*Conventional white bronze CuSn (cyanide)*
Neutral salt spray test	4	200	110
Thioacetamide (tarnishing)	> 200	> 200	4

The MSA white bronze bath clearly showed most potential and was scaled-up by Elsy Research. In a following phase, industrial validation of the process was done by all SMEs at the locations of Elsy Research and Venrooy Goud- en Zilverindustrie where pilot production was set up.

Cost evaluation

The Table below compares the relative costs of the developed MSA bronze bath to the targeted nickel electroplating and the alternative cyanide copper. It can be seen that the bath make-up of costs of the MSA bronze bath are around 70% of that of a nickel plating bath.

Table 2: Relative bath make-up and maintenance costs

	Nickel	Cyanide bronze	MSA Bronze
Bath make-up	1	0.4	0.7
Bath maintenance	1	5	2.5

The bath maintenance costs of the MSA bath are higher than that for nickel. As can also be seen from the maintenance costs of the cyanide bronze bath, alloy plating generally involves higher maintenance costs because the metals are replenished as salt and not by anode dissolution. In the project and pilot trails a copper anode was used to replenish the consumed copper. When using a copper anode the bath maintenance costs for the bath are reduced to 0.9 of that of nickel.

The relative contribution of bath make-up and bath maintenance costs can not yet be estimated. It strongly depends on the amount of products treated and the bath life-time. With the current short life-time of the MSA bath the bath make-up costs will be the main cost of coating that is obviously undesired. However, if the life-time of the MSA bronze bath can be extended to the typical life time of a nickel plated bath, approximately 2 years, its bath make-up costs compare favourably to that of nickel.

Conclusion

Most, but not all objectives of the project were met.

- The process is entirely nickel free, and moreover free from cyanides and lead which are important assets and makes operation straightforward
- The objectives with respect to the functional behaviour of the films deposited, both tarnishing and corrosion resistance were met, see table 1
- Esthetically, both gloss and colour of the deposits are however not fully satisfactory for the high demands that are set in jewelry industry and need further optimization
- Pricewise, using nickel is still a better option. One of the main reasons for this is the relatively short life of the bath. Although much progress was made, the lifetime of the process bath is limited to several weeks due to oxidation of Sn(II). The bath is therefore best run under continuous load.
- Despite EU legislation the drive for industry to shift to nickel-free processing is unfortunately only small yet.