FREEME

MAGAZINE
MAY 2023

TOXIC FREE METALLIZATION PROCESS FOR PLASTIC SURFACES

1ST ISSUE

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THE FREEME PROJECT – IN A NUTSHELL

FreeMe is a research and innovation action (RIA) project funded by the European Union's Horizon Europe programme, under the topic HORIZONCL4-2021-RESILIENCE-01-12 "Safe- and sustainable-by-design metallic coatings and engineered surfaces", with grant agreement **No. 101058699.**

The FreeMe project aims to develop safe and sustainable by design metallic coatings on plastic surfaces, based on REACH compliant chemicals, eliminating the use of Cr^{6+} and Pd from the plating on plastics process. A brief Q&A will explain the topic and present more details on the project.

WHY DO WE SELECT PLASTIC SUBSTRATE?	The industrial use of plastics has been favoured due to the lightweight, low density, flexible, strong, and low-cost attributes.
WHY IS A METALLIC COATING REQUIRED ON A PLASTIC SUBSTRATE?	To enhance the wear and corrosion resistance, as well as the aesthetic appearance of the final surface.
HOW IS THE METALLIC COATING DEPOSITED ONTO THE PLASTIC SUBSTRATE?	As most plastics are non-conductive, a series of steps is required for the coating deposition. The process is called Plating on Plastics (PoP).
WHAT ARE THE DRAWBACKS OF THE POP PROCESS?	The use of hexavalent chromium and palladium rise significant drawbacks of the process in terms of occupational safety and environmental sustainability
WHY IS HEXAVALENT CHROMIUM USED IN THE POP PROCESS?	Chromic (Cr^{6+}) acid baths are used during the plastic surface etching step to enhance metal adhesion.
WHY IS HEXAVALENT CHROMIUM USAGE CONSIDERED AS A DRAWBACK?	Cr^{6+} is included within REACH Regulation due to its toxicity. It is a carcinogenic compound affecting workers and residents of the areas around the plating plants.
WHY IS PALLADIUM USED IN THE POP PROCESS?	Sn-Pd baths are used during the surface activation step to disperse nucleation sites and ensure electroless metal deposition.
WHY IS PALLADIUM USAGE CONSIDERED A DRAWBACK?	Palladium is a critical raw material, which increases its price significantly. Russia is the world's leading Pd exporter, accounting for 40% of all mined production, followed by South Africa
WHAT DOES FREEME PROPOSE?	Epoxy polymer nanocomposite films with embedded Ni precursors will be prepared. This resin will be sprayed onto the polymer surface, formatting a thin layer, which will allow the electroless plating step, substituting entirely the use of Cr^{6+} and Pd.
	Following the same steps of surface etching and activation but substituting the Cr^{6+} and Pd solutions with safer and more sustainable bath solutions.
	The sprayable resins and the surface etching process will be supported by in silico modelling activities that will target the optimisation and allow the further analysis of suitability of processes to specific applications.
	In-line process monitoring through an optical system will allow the non-destructive inspection of the surface, measurement of the coating thickness and assessment of the deposition quality.
WHERE WILL THE FREEME TECHNOLOGIES BE APPLIED?	The FreeMe technologies will be validates in automotive, aerospace and home appliances applications.

INTERVIEW

creative nano

CEO OF CREATIVE NANO DR. ALEXANDROS ZOIKIS-KARATHANASIS

FreeMe is an EU-funded collaborative research and innovation project, where 12 partners have joined forces to accomplish the project objectives. The dissemination manager, Ms Maria Tsianti, had the opportunity to interview Dr. Alexandros Zoikis Karathanasis, CEO of Creative Nano, partner of the FreeMe project. Creative Nano is a research-intensive company, based in Greece, providing technological solutions in the field of materials' nanoscience and nanotechnology. The following interview focuses on the role of Creative Nano in the FreeMe project, their expectations, and market insights.

Dr. Zoikis Karathanasis thank you for accepting our invitation for this interview. To begin with, could you briefly present yourself, focusing on your background?

I am a Chemical Engineer, having conducted my studies in National Technical University of Athens, where I also obtained my MSc in Science and Technology of Materials, as well as my PhD in nanocomposite coatings. For the last 5 years, I am the CEO of Creative Nano. I have 20-years' experience in the field of surface treatment and approximately 15 years coordinating Research and Development projects, counting more than 30 projects in total. I have been involved in 12 publications and delivered approximately 20 presentations in relevant conferences.

What motivated you into selecting this particular sector of surface finishing?

I believe it all goes back to my studies, and the fact that I became concerned about environmental protection. Many of the processes we came across were using materials or raw materials of high environmental concern. Surface treatment was one of these processes. Moreover, the development and study of new materials seemed exciting, so I decided to dive deeper into this field through my PhD.

Could you briefly present Creative Nano? How has the company evolved throughout the years?

Creative Nano was established in 2013 in Athens, Greece, by a group of people with common interests in the field of nanotechnology. We started by setting up a small lab of approximately 80 square meters, where our passion for discovering and developing new materials has led us to expand our

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DR. ALEXANDROS ZOIKIS-KARATHANASIS

research interests covering fields such as coatings, production and use of nanoparticles in a variety of applications. In 2013, we started working on basic research related to nanocomposite coatings aiming the replacement of hard chromium. The research was based on small scale experiments, utilising baths from 1 to 40 litres capacity. Over time, Creative Nano has grown and evolved into a well-established company specialising in the field on nanotechnology and nano-based coatings in Greece. Currently, our company is hosted in a 600 meters laboratory spaces and has 12 employees, 7 of whom hold a PhD. We are providing services on the development of new materials and their characterisation, as well as small batches production.

Could you describe the role of Creative Nano in the FreeMe project?

Creative Nano is responsible for one of the two novel metallization technologies that will be developed under FreeMe project. More specifically, it will develop a hexavalent chromium and palladium free, wet metallization process. REACH compliant chemicals will be used for etching of polymeric surfaces, substituting the toxic and carcinogenic hexavalent chromium, while for the activation step of the plating on plastics process, palladium, a critical raw material, will be replaced. Different substrates will be examined, including ABS, nylon, 3D printable resins and the emerging bio-based polymer PLA. The novel hexavalent chromium and palladium free process will fulfil the requirements and specifications of FreeMe end users in the automotive, aerospace and home appliances industries.

What are your expectations from the FreeMe project? How Creative Nano aims to proceed with the expected results?

During the last 3 years, Creative Nano has invested in the plating on plastics technology, through national-funded research and innovation projects, as well as its own resources. Currently, the company is one of the few in the world that can plate 3D printed resin objects. Within the FreeMe project, Creative Nano will develop the know-how of metallization of other industrial polymers, such as ABS, nylon, as well as the rapidly attracting attention biobased polymer PLA. Based on this know-how, our company could have the opportunity to provide services to high tech applications, such as aeronautics and space exploration.

Creative Nano has been involved in other EU funded projects and many research activities in the surface finishing field. In what way were these research activities merged together into the FreeMe project?

After years of experience and the participation of Creative Nano in research projects, a variety of innovative products and processes has been developed. Many of these technologies can be combined, in order to support similar problems solving. For example, within the FreeMe project, Creative Nano is taking advantage of the experience and knowledge obtained in previous projects, such as the national-funded project "3DPlate" concerning the design, printing and plating of 3D printed resin

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DR. ALEXANDROS ZOIKIS-KARATHANASIS

moulds, or EU-funded project PureNano, which concerns the regeneration of plating baths.

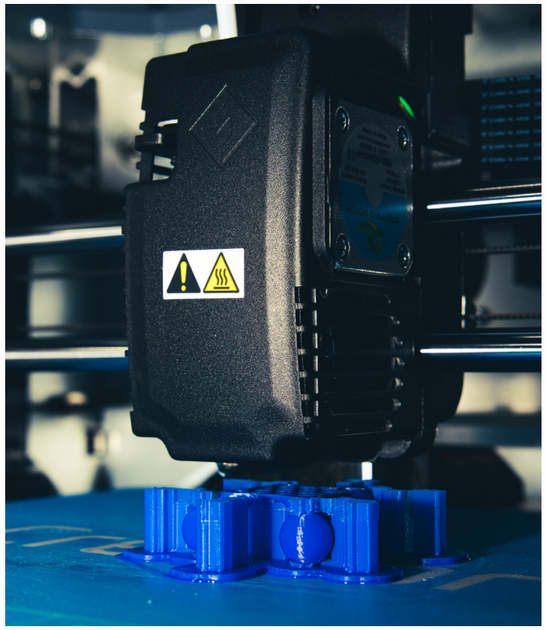
How would you describe the current status of the EU plating on plastics market? What are the main challenges, in your opinion?

Plating on plastics is without a question one of the most important segments of surface treatment industry. Its applications cover many technological fields, such as automotive, electronics, consumer goods, aerospace, medical devices and other. As a result, there is definitely great interest from the end users regarding this technology. According to market search report we have consulted, the European plating on plastics market is expected to reach 274.8 million EUR by 2027.

Nevertheless, EU and national legislation are pressing to limit or ban the use of several raw materials required for the plating on plastics process. Issues of concern are the toxic and carcinogenic hexavalent chromium, as well as palladium, which is a critical raw material, not extracted within European countries. This severe pressure is unfortunately leading a large share of the plating on plastics production to non-European countries, and mainly Turkey, India and China. If we aim to hold this production segment within the EU, new technologies shall be developed, providing an alternative to the use of hexavalent chromium, while achieving the same aesthetic result and mechanical properties.

There seems to be a great debate among the plating experts on the usage of hexavalent chromium. What are your predictions for the future of this market? Do you think hexavalent chromium will be completely banned from the surface finishing industry?

Indeed, the use of hexavalent chromium in the industry has greatly troubled this sector. As a matter of fact, everyone involved in this market admits the significant problems associated with the use of hexavalent chromium, not only from the occupational health perspective, with workers in the plating shops inhaling or have skin contact with hexavalent chromium being in severe risk, but also from the environmental perspective.



Currently, there are two main trends to solve this problem. The first trend concerns the substitution of hexavalent chromium by other methods. Unfortunately, it seems that there is no universal solution based on electroplating. Several alternative methods have been examined, such as thermal spraying, chemical vapour deposition (CVD), physical vapour deposition (PVD). However, these methods are way more expensive than electroplating and require the use of different equipment, which would lead to the end of plating shops, as far as hard plating is concerned. For this reason, the research is focused on case-by-case solutions based on the use of nickel matrix nanocomposite coatings. The advantage of this solution lays on the fact that the final properties of the coatings can be tailored based on the type of nanoparticles used. For example, ceramic nanoparticles, such as SiC, may lead to coatings of high hardness, while using 2D materials, such as graphene, may lead to low friction coefficient coatings.

The second trend is not about replacing hexavalent chromium, but rather about limiting the problems that may be associated with its use. Under this scope, research is focused on topics such as waste treatment, sophisticated ventilation systems using special filters, etc.

Creative Nano moved to brand new premises in Metamorphosis, Attica, less than a year ago. Following the interview, we had a tour around the premises and discussed with Ms Eleni Poupaki, Chemical Engineer and member of the R&D team of Creative Nano, on the different activities she is involved in, and more specifically on the progress of the FreeMe project. A wide variety of 3D printed, plastic creations, such as decorative figures, rings, etc. have been developed in the lab and plated in the plating baths of Creative Nano.

EVENTS

During the first year of the project, events organised by FreeMe partners aimed at raising awareness about the project. Under this frame, the following events were organised, where FreeMe partners presentexqd their work.

On September 2022, FreeMe's partner, Creative Nano, organised **a citizen science event in Athens, Greece,** where the FreeMe project was communicated, along with other EU-funded projects, such as cluster project:

MOZART, PureNano, NanoPAT & **SABYDOMA**

The event was focused on plating technologies and the safe and sustainable by design approach, setting the ground for future collaboration activities with cluster projects.

Figure 1: *Citizen Engagement Event on plating technologies*

Figure 2: *Dissemination materials and demos showcased during the Citizen Engagement Event in Athens.*

On the 17th to 19th of March 2023, FreeMe partner, Creative Nano, participated in **Xeirotexnika exhibition,** presenting their research on plated 3D printed items. During this event, FreeMe project and the nationally funded 3DPlate project were communicated to the public.

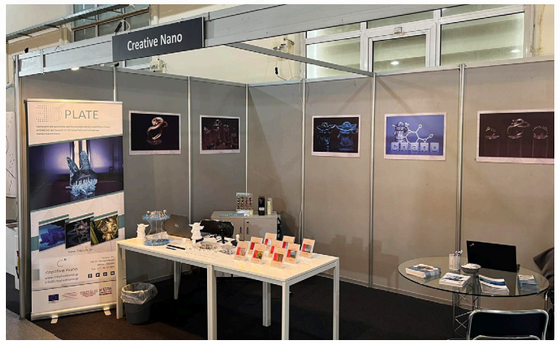


Figure 3: *Creative Nano at Xeirotexnika Exhibition, Peristeri, Greece*

Figure 4: *Demonstration of 3D printed & plated elements at the booth of Creative Nano at Xeirotexnika Exhibition, Peristeri, Greece*

CLUSTERING ACTIVITIES

FreeMe project has already taken steps to establish a strong collaboration with the three cluster projects funded under the same topic on safe and sustainable by design metallic coatings and engineered surfaces, namely **MOZART, NICKEFFECT** and **NOUVEAU** projects. Cluster projects aim to enhance their dissemination and communication activities, supporting each other, while also considering the possibility of organising joint events. But mainly, the goal is to identify common ground and share experiences.

Clustering activities will be initiated with an event co-organised by FreeMe and MOZART under the scope of EU Green Week 2023 on the skills guiding the green transition of the plating industry. The workshop will be organised online on the 7th of June 2023. Participation will be free; however, registration is required. All four cluster projects will be presented during this event.

REGISTRATION LINK HERE!

THE MOZART PROJECT

In this first issue of the FreeMagazine, the MOZART project is briefly presenting its scope and main goals.

METAL MATRIX NANO-COMPOSITE COATINGS UTILIZATION AS ALTERNATIVE TO HARD CHROMIUM (MOZART) is a project funded by the European Union's Horizon research and innovation program (HORIZON-RIA) under the same topic as FreeMe: "HORIZON-CL4-2021-RESILIENCE-01-12 – "Safe- and sustainable-by-design metallic coatings and engineered surfaces". It follows a multidisciplinary approach involving 15 stakeholders from 8 countries, including universities, research institutes, large enterprises, and SMEs.

To better understand the concept of the project, it is important to consider the substance that has been dominating the surface finishing industry for almost 100 years: hard chromium (HC). HC coatings have been extremely attractive for a series of applications in automotive, aerospace, and other industries due to their excellent hardness, as well as wear and corrosion resistance.

However, the process of acquiring these types of coatings presents significant environmental and occupational health issues as it is based on the use of Chromium Trioxide (CrO3) also known as hexavalent chromium (Cr^{6+}), a recognized toxic, carcinogenic, and mutagenic compound. For these reasons, chromium trioxide is already listed in Annex XIV of REACH (European Regulation No. 1907/2006). In 2019, the European Commission (EC) approved a proposal that obliges companies who use HC to implement strict risk management procedures for various uses of the substance in the automotive, aerospace, and other sectors. The decision also gives these companies a maximum of 7 years to reassess the availability of safer alternatives or substitute the substance earlier when possible.

In this context, the main goal of the MOZART project is to develop high-quality durable composite coatings as a replacement for hard chromium under the principles of the Sustainable and Safe by Design (SSbD) concept based on nickel matrix nano-composite electroplating processes.

These types of coatings will cover a wide range of applications and sectors, will be free of toxic chemicals, based on abundant raw materials, and their mechanical properties have already been experimentally proven to be comparable or even higher in relation to the hard chromium coatings. In particular, the novel nano-composite coatings will be tested in demonstrators introduced by companies in the field of manufacturing, automotive, and machinery.

Besides the alternative coatings, MOZART will have two more important outcomes: a web-based decision support tool that will support the integration of its technologies and advancement into the industry, facilitating the adoption of the SSbD frameworks; and an AI-based tool for coating properties prediction to establish correlations between electrolyte compositions and coating properties considering computational hydrodynamic models of the plating process and integrating SSbD approaches.

Overall, the MOZART project provides scientific, technological, and societal impact aligned with the twin transformation targets of the EC: "Green" – based on the REACH compliance materials that will be utilised, the increased energy efficiency of the process, modifications of plating lines for decreasing wastes and increased occupational safety; and "Digital" – based on the utilisation of AI models and simulation for the identification of optimum parameters of plating in relation to the geometry of the objects that will be plated, leading to savings in raw materials and time.

To know more about MOZART Project, visit **WEBSITE** and follow on social media!

FREEME CONSORTIUM MEETINGS

The kick-off meeting of the FreeMe project was held remotely on 20th of June 2022. During the meeting, which was hosted by the project coordinator GASER, partners presented their role and next actions within the project.

Figure 1: *FreeMe kick off meeting – online*

The first physical consortium meeting of the FreeMe project took place on the 5th-6th of October 2022, in Milan, Italy. On October 5th, the meeting was hosted by Politecnico di Milano, while on October 6th partners visited GASER premises in Caravaggio BG and received a tour in the production lines.

Figure 2: *FreeMe 2nd Consortium Meeting in Milan, Italy*

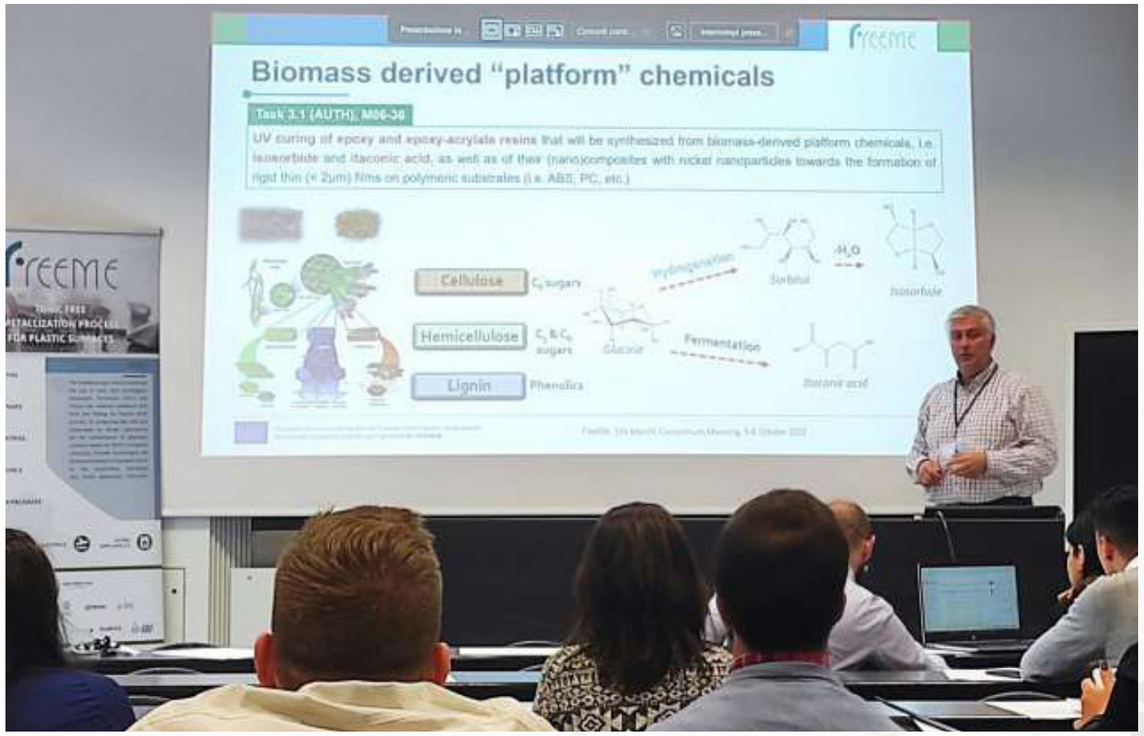


Figure 3: *FreeMe 2nd Consortium Meeting in Milan, Italy*

Figure 4: *Partners visit to GASER's premises during the 2nd consortium meeting*

PROJECT PROGRESS

DELIVERABLES SUBMITTED

D1.1 - Report on specifications - GASER, M06
D8.1 - First PEDRC - EXELISIS, M06
D8.2 - Data management Plan - POLIMI, M06

MILESTONES ACHIEVED

MS1 - “Kick off meeting” - GASER, M01
MS2 - “Definition of REACH compliance baths chemistries” - GASER, M05
MS3 - “Integrated safe- and sustainable-by-design approach” - UBU, M10

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