Nanomaterials for the Restoration of Works of Art

NanoRestART

June 2015 – November 2018

RESULTS AND OUTCOMES

A COMPENDIUM

THE PROJECT

The conservation of modern and contemporary works of art requires advanced solutions at the cutting edge of modern chemistry and material science. NANORESTART focused on the synthesis of novel poly-functional nanomaterials and on the development of highly innovative restoration techniques to address the conservation of a wide variety of materials.

The main conservation challenges that will be addressed in the project were:

Conservation challenge 1
Cleaning of contemporary painted and plastic surfaces (CC1)

Conservation challenge 2
Stabilization of canvases and paintings in contemporary art (CC2)

Conservation challenge 3
Removal of unwanted modern materials (CC3)

Conservation challenge 4
Enhanced protection of artworks in museums and outdoors (CC4)

The NANORESTART project was articulated into eight work-packages (WPs) that covered 42 months.

WP 2 – New tools for cleaning
Formulation of nanostructured residue-free cleaning fluids, through the use of self-degrading surfactants, new class of gels for the confinement of cleaning systems and new enzyme solutions in highly retentive gels.

WP 3 - Surface strengthening and consolidation
Restoration of the original mechanical properties of works of art using nanocellulose and cellulose derivatives in combination with nanoparticles; development of porous silica particles loaded with plasticizers for restoring the mechanical properties of plastic and paint layers.

WP 4 - Protection of surfaces
Development of polyfunctional protective systems, which combine “active” and “passive” strategies. “Active” systems are based on green polymeric matrices functionalized with nanomaterials.

WP 5 - Nanostructured substrates for highly sensitive detection
Development of nanostructured substrates and sensors for the enhanced detection of degradation products from modern and contemporary art.

WP6 - Environmental impact assessment
Environmental impact assessment of the most effective and promising technologies developed in WPs 2-5.

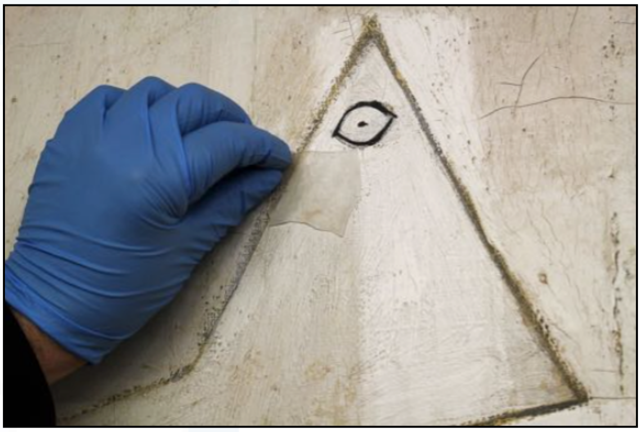
This project has received funding from the European Union’s Horizon 2020 research and innovation program under grant agreement No 646063.

Conservative challenge

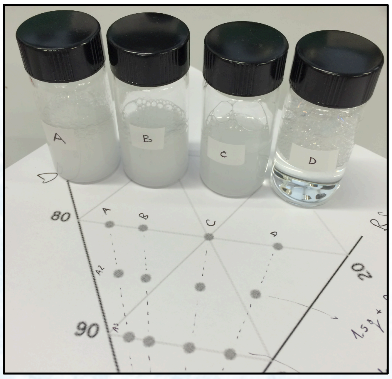
Many **contemporary art surfaces**, particularly those made of modern paints, such as **acrylic paints**, are exceptionally **difficult to clean**. In fact they possess a high tendency to incorporate dust and grime, while being **very sensitive** to the action of both **organic solvents** and **water**, i.e., the most used liquids for the cleaning of works of art. On the other hand, a recent survey of the condition of **plastic art objects** concluded that **75%** of them **require cleaning**. Also, the removal of **pressure sensitive tapes** and **adhesive residues** is equally **difficult**. To address these issues, it is important to find a solution that ensures **safe and controlled removal** with no modification of the artifact and, **no residues**. Finally, the removal of **unwanted contemporary materials** from artistic surfaces is also necessary when outdoor murals (**street art**), **sculptures**, and **monuments** are **vandalized with graffiti**. The **selective removal** of the unwanted overpaints is particularly **demanding** whenever acrylic, vinyl, and alkyd colors were used.
Thus, one of the main aims of this WP was the **development** of **novel systems** with enhanced or new properties specifically designed to address these challenges. Among the selected ways to do that, one of the most interesting was to design, formulate and test **nanostructured residue-free cleaning fluids**, through the use of **self-degrading surfactants**.

Formulations

12 nanostructured fluids: Innovative **cleavable surfactants** were synthesized, which represent a new class of **spontaneously degradable amphiphiles**. Basing on these chemicals, and some low toxicity solvents, **about 12 environmentally friendly nanostructured fluids** were developed for the removal of unwanted materials from artistic surfaces. Some of these nanostructered fluids are already **available on the market** to end-users (www.csgi.unifi.it/products/products.html).



Innovation



These **aqueous cleaning systems** are particularly **effective** in the **removal** of **organic unwanted materials**, without redeposition into the pores of artwork substrate. They grant performances not achievable with traditional solvent cleaning, as their action is **more controlled**, **selective**, and **safe**. In nanostructured cleaning fluids (i.e., water-in-oil microemulsions, micellar solutions) organic **solvents** content is **minimized**, thus **reducing** their **environmental impact** and **increasing** the operators' **safety**. With respect to previously developed formulations, the systems proposed in NANORESTART include nonionic, **cleavable surfactants** and mild surfactants that are **biodegradable**. The solvents included in the liquids are all "**green**", **low-toxicity** solvents, with different polarities and good solving power towards different kinds of substances. Therefore, their **application** is virtually **residue-free**, while their cleaning effectiveness is increased when compared to previous formulations. In fact, these systems represented a **significant step forward** for the field of cleaning of works of art.

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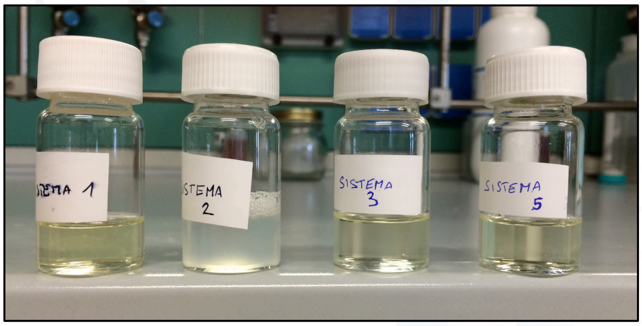
WP2 – ENVIRONMENTALLY FRIENDLY INNOVATIVE CLEANING FLUIDS

How do they work?

These **water-based formulations** allow the removal of soil, aged varnishes/adhesives, and grime from the surface of works of art. Being water-based, they are **safer to operators** and the environment than traditional solvents used in the restoration practice. Their **excellent cleaning properties** are due to the **combined** and **sinergic** action of **organic solvents** and **surfactants**. Microemulsions induce the **swelling** and **detachment** of unwanted **organic coatings** from artistic surfaces, possibly through a **dewetting** mechanism, which is **different** and much more controlled than the **solubilization** processes involved in the use of **neat solvents** or **solvents blends**.

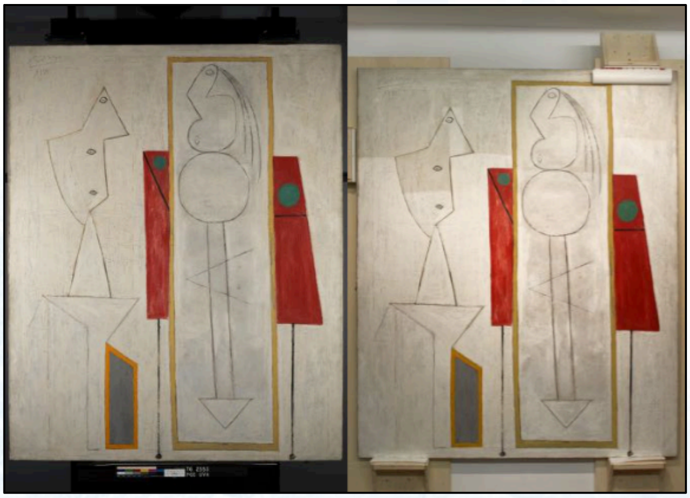
How are they applied?

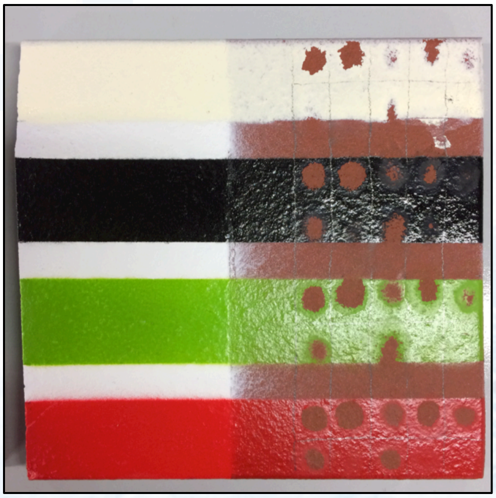
Aqueous nanostructured fluids can be simply **loaded** into a common **cellulose pulp poultice** and applied on the **surface** to be cleaned, provided that it is **not water sensitive**. However, being the majority of contemporary and modern art objects' surfaces very sensitive to solving/swelling action of water, the **most suitable way** to apply these newly developed cleaning fluids is to **confine them** into the **innovative gels** developed in NANORESTART (see next section), in order to limit the undesired diffusion of liquids and greatly **enhance the control** on the cleaning process.



Case studies and application

These innovative systems have been successfully used to remove soil and other unwanted layers from masterpieces by **Pablo Picasso, Jackson Pollock, Roy Lichtenstein, Eva Hesse, Giorgio De Chirico, Albert Gleizes**, **Jean Dubuffet,** and others.





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Conservative challenge

Many **contemporary art surfaces**, particularly those made of modern paints, such as **acrylic paints**, are exceptionally **difficult to clean**. In fact they possess a high tendency to incorporate dust and grime, while being **very sensitive** to the action of both **organic solvents** and **water**, i.e., the most used liquids for the cleaning of works of art. On the other hand, a recent survey of the condition of **plastic art objects** concluded that **75%** of them **require cleaning**. Also, the removal of **pressure sensitive tapes** and **adhesive residues** is equally **difficult**. To address these issues, it is important to find a solution that ensures **safe and controlled removal** with no modification of the artefact and, **no residues**. Finally, the removal of **unwanted contemporary materials** from artistic surfaces is also necessary when outdoor murals (**street art**), **sculptures**, and **monuments** are **vandalized with graffiti**. The **selective removal** of the unwanted overpaintings is particularly **demanding** whenever acrylic, vinyl, and alkyd colours were used.
Thus, one of the main aims of this WP was the **development of innovative gels** for the **confinement of cleaning fluids**, specifically designed to address these challenges. In order to provide conservators with a **wide palette** of available solutions, we developed **elastic and flexible hydrogels**, and tunable **organogels** which can be **safely used on artistic surfaces** to be cleaned, even if **rough, irregular, or sensitive to water and organic solvents**.

Formulations

- **20 hydrogels:** Responsive hydrogels for the **safe and controlled cleaning** of water- and solvent-sensitive surfaces. About 20 hydrogels formulations (with tunable mechanical properties and retentiveness) were developed for the removal of unwanted materials from artistic surfaces (acrylic paint, oil paint, watercolor, metal, plastic, canvas, paper, stone, wood, etc.). Some of these hydrogels are already **available on the market** to end-users (www.csgi.unifi.it/products/products.html).

- **12 organogels**: Responsive organogels for the **safe and controlled cleaning** of surfaces that can not tolerate even minimal contact with water. About **12 organogels formulations** were developed, loadable with different solvents (apolar ---- polar). Some of these organogels will be soon **available on the market** to end-users.

Innovation

Innovative hydrogels and organogels developed in NANORESTART leave **no residues** on the surface of the painting and **release** the cleaning fluids in a **controlled way**. In particular, the developed hydrogels are **highly flexibile** and **elastic**, allowing for the **application on rough and/or irregular surfaces**. **Organogels** are designed to be used on **highly water-sensitive** works of art. Depending on the formulation, they can be used **once loaded with different solvents** or without any solvent, to **remove dust** from artistic surfaces, thanks to their **stickiness**.

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WP2 – INNOVATIVE HYDROGELS FOR SURFACE CLEANING

How do they work?

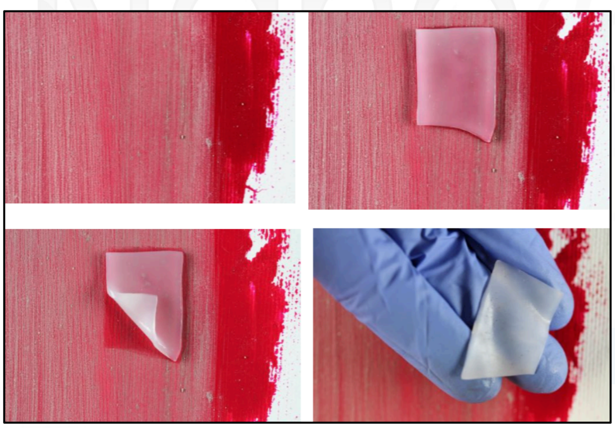
Gels developed in NANORESTART are used as **vehicle** (containers) for **cleaning fluids**. They can be loaded with different solvents and cleaning fluids, as the **12 nanostructured fluids** featuring cleavable surfactant developed in NANORESTART (see previous section). Innovative gels **prevent the cleaning agent from fast evaporation** and **uncontrolled penetration** into porous materials making the cleaning safer. Moreover, thanks to their formulation **they do not leave residues** on the treated surface. Sticky organogels do not contain any solvent, and can be used to remove dust from highly solvent-sensitive artistic surfaces.

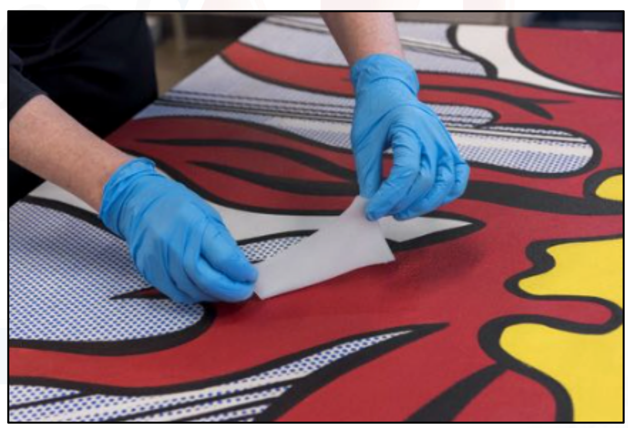
How are they applied?

Innovative gels **can be easily cut down** and shaped in the **desired size** and form prior to application. The application is carried out by laying the gel over the surface to be cleaned. Depending on the type of material to be removed and on the type of cleaning fluid used, the **unwanted material** can be either **solubilized** or **swollen**. In the latter case, a gentle mechanical action should be carried out to remove the swollen and soften unwanted materials. Hydrogels or sticky organogels can be also used as **ultra-delicate eraser** for the removal of surface dirt.

Case studies and application

These innovative systems have been successfully used to remove soil and other unwanted layers from masterpieces by **Jackson Pollock, Roy Lichtenstein, Eva Hesse, Giorgio De Chirico, Albert Gleizes**, **Jean Dubuffet,** and others.





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WP3 – HYBRID FUNCTIONAL NANOSYSTEMS FOR THE STRENGHTENING OF FIBERS

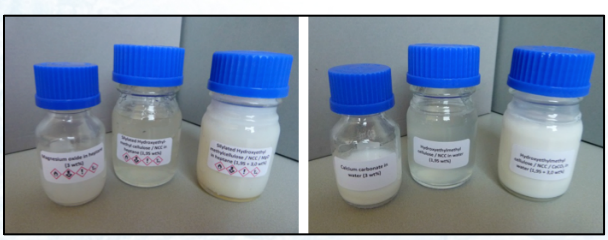
Conservative challenge

This WP addresses a crucial aspect of **interventive conservation**, the restoration of **mechanical properties** of a work of art. Examples are (i) **painting canvases** that are **degraded** and severely endanger the conservation of the paint layer; (ii) the **paint layer** itself; (iii) **degraded polymeric surfaces** where plasticizers have migrated out rendering the material brittle.
Canvas degradation results in deterioration of its **mechanical properties** and may ultimately affect the integrity of the paint layer. A common method for canvas consolidation is a **lining** operation in which the painted canvas is attached upon a new one. However, such a method possesses a range of **drawbacks**. Improving the **mechanical properties** of the existing canvas is a more attractive alternative. To this end, NANORESTART formulated **systems** capable of **treating** the material at **different levels**, i.e. **yarn**, **thread**, **plain fabric**, and provide **reinforcement** and **deacidification** to arrest the degradation and stabilize the artifact.

Formulations

- **25 polar systems:** Dispersions of **nanoparticles**, **polyelectrolytes**, and **cellulose fibers/crystals** in water or ethanol (or blends). **25 formulations** were developed, for the strengthening and deacidification of canvases. These formulatiosn were sorted in **3 families**, each of them aiming at provided one or several functionnalities.

- **3 apolar systems**: Dispersions of nanoparticles, and silylated cellulose fibers/crystals in apolar solvents. **3 formulations** were developed, for the strengthening and deacidification of water-sensitive canvases.



Innovation

Two complementary **strategies** were used: the development of **inorganic nanoparticles** formulations for **deacidificying canvases**, and the application of **cellulose based materials**. The inorganic nanoparticles systems aim at arresting the degradation process while providing some mechanical reinforcement at the yarn/thread/fiber level. The application of **nanocellulose** on the canvas will **strengthen the canvas** in its whole by forming a film at the surface that can be seen as a nanolining. Polyelectrolyte-treated silica nanoparticles (**SNP**) and cellulose nanofibrils (**CNF**) can be **combined to obtain canvas consolidation**. The approach is innovative, as it used colloidal **systems** that are **physico-chemically compatible** to the original canvas cellulose, as opposed to traditional lining adhesives based on glues or synthetic polymers. This means that the **long-term stability** of the treated canvas will be **enhanced**. It also implies that the amount of material used to reach a sufficient strengthening is significantly reduced.

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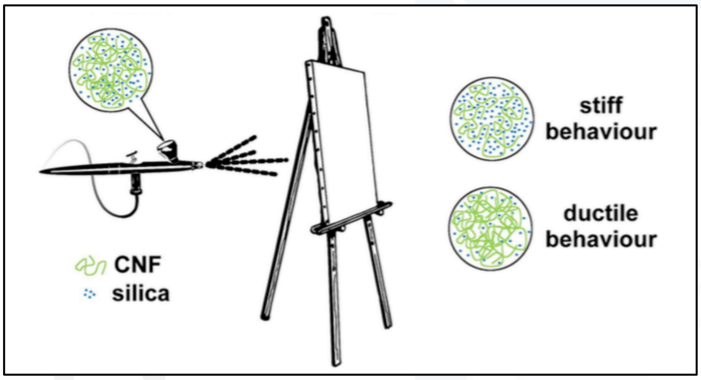
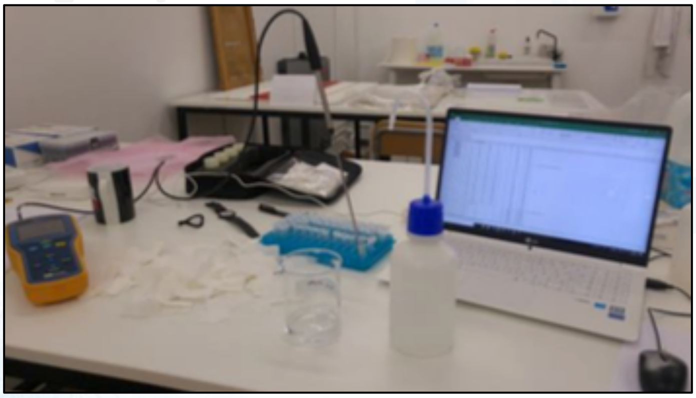
How do they work?

CNF forms a **film** at the canvas surface that increases ductility, while **SNP penetrates** deeper and reinforce at the fiber scale, yielding higher stiffness. These two effects can be balanced to reach a suitable reinforcement. The **inorganic nanoparticles** (e.g. calcium hydroxide, calcium carbonate) are able to **neutralize** the **pH** of acidic canvases, hindering the acid-based degradation of cellulose.
Besides aqueous and water-alcohol dispersions of particles, **silylated cellulose** was used to prepare **dispersions** of consolidants in **organic solvents**: this allows the treatment of highly water-sensitive canvases that cannot tolerate the contact with aqueous systems.

How are they applied?

These systems can be applied by **brushing** or **spraying**, which enables controling the solvent exposure of the canvas.





Case studies and application

These systems have been used to **consolidate**, **strengthen** and **deacidify** canvases from the 19th and 20th century.

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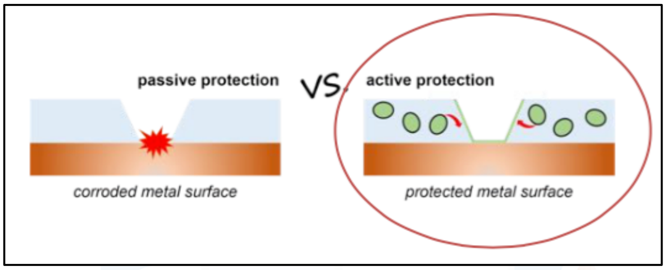
Conservative challenge

Metal objects are affected by atmospheric **aggressive agents** that induce **corrosion** processes (e.g. "bronze disease" of copper-based objects) and **deactivation** of traditional **anticorrosion agents**. Many **plastic materials**, found in art collections, show **instability**, e.g. **yellowing** and **embrittlement**. Thus, regardless the nature of materials, **artworks** require **protective treatments** in order to avoid rapid degradation, which is often due to autocatalytic processes whose early stages are not easily perceivable by curators.
Up to now the most widespread approach for corrosion protection of metallic artefacts is the application of **protective polymeric coatings**. However, extra functionalities have to be imparted to the polymeric coating in order to provide long-term protection to the substrate. The **aim** of **WP4** "Protection of surfaces" was to **develop**, **optimize** and **validate** a **new generation** of **multifunctional coatings**, by exploiting the concept of nanoparticle and nanocarriers which possess also **ACTIVE feedback** in response to changes in the local environment, so that they are capable of hampering the degradation process in addition to the merely **passive protection** provided by traditional approaches.



Formulations

8 protective coatings: multifunctional protective systems, both **active** (able to delay the degradation mechanisms by interfering with the chemical degradation pathways), **passive** (able to delay the diffusion of gases pollutants towards the substrate), and multilayer (active+passive) were developed for the preservation of **metal artifacts** and polymer-based **rapid prototyping objects**. Active/passive/multilayer **systems (6 formulations) for metal surfaces overcome commercial benchmarks** from the restoration practice, in terms of long-lasting durability, safety and sustainability. The active and passive **coatings for plastics (2 formulations) introduced a knowledge advancement** in the field, as no benchmark currently exists for the protection of polymers.

Innovation

Traditional protectives (e.g. acrylics or wax films) exhibit the following critical issues: they can **induce changes** in the appearance of the **treated surfaces**, use **toxic** corrosion inhibitors or harmful organic solvents, or **lack safe** application and removal protocols. The **new "active" coatings** are based on **environmentally friendly** polymeric **transparent** matrices that embed **nanomaterials** (.ie. Layered double hydroxide and alkaline nanoparticles as calcium carbonate and calcium hydroxide), to **protect** the surface of **metal** artifacts. The **active coatings** developed for **plastic-based** artworks are based on **silver clusters** (i.e. aggregates of 5 silver atoms) which are **safely** deposited on the **polymeric substrates**. The "passive" protective systems have better gas barrier properties than the current best practice. The new "active" and "passive" protective layers can be **combined** in protective **multilayer structures** to provide reliable and long-lasting protection.
For plastic artifacts, no benchmark exhisted before NANORESTART, where the exploration of innovative active and passive coatings was carried out.

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How do they work?

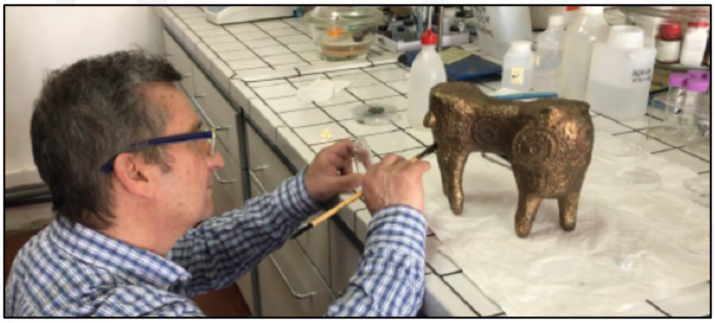
Active coatings for metal substrates are **based** on **green-chemicals**, such as **chitosan** and High Amouprhous PolyVinyl Alcohol (**HAVOH**), and contain nanoparticles consisting of Layer Double Hydroxide modified with anionic anticorrosion additive able to be released upon external corrosion-related stimuli (e.g. increase of acidity and presence of chloride ions) alongside with alkaline ananoparticles. **Silylated cellulose** ether-based formulations were used to grant hydrophobic properties along with active protection.
Active coatings for polymeric substrates are based on waterborne dispersion of **silver clusters** able to substract radicals which generate on the surface of plastic artworks when exposed in aggressive environment.
Improved passive protective coatings based on **polyurethane** as well as high dense inorganic matrix can **work** as high **barrier** against **water**, **oxygen**, **heat**, and **UV** light.

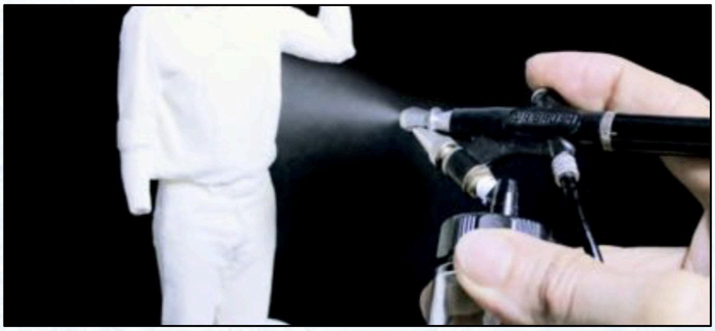
How are they applied?

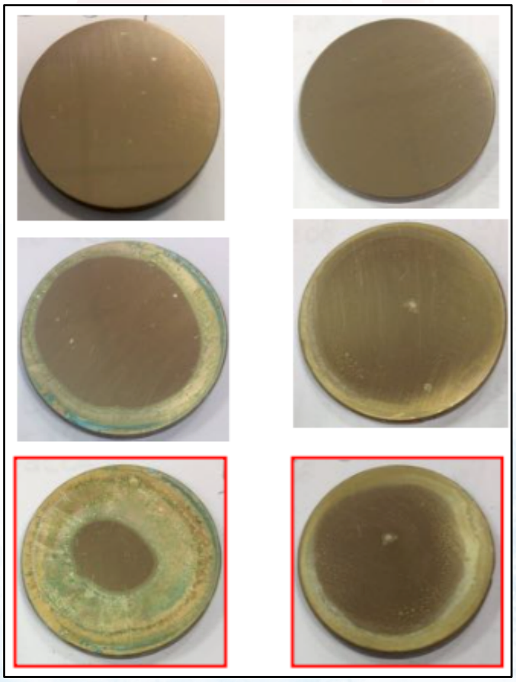
The coatings can be applied by **brushing** or **spraying**.

Case studies and application

These systems have been used on **modern and contemporary metal and plastic** surfaces. The multilayer coating (consisting of an active layer covered by a passive layer) prevents interactions of Cu-based alloy artifacts with the atmospheric aggressive agents that induce corrosion processes (e.g. “bronze disease”) and protects the anticorrosion additives through a stimuli-responsive mechanism involving its realese when chloride ions migrate in the coating. The developed multilayer coatings applied on plastics are able to reduce the amount of oxidation induced by light aging.







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Conservative challenge

WP5 addressed the **development** of **nanostructured** substrates and **sensors** for the enhanced **detection** of **diagnostic degradation products** from modern and contemporary cultural heritage artifacts, and for the identification of components present in very small quantities e.g. **faded inks** and **dyes**. This is crucial for understanding the early stages of rapid and irreversible deterioration processes of artifacts, which is the case for modern and contemporary cultural heritage. Examples include the **detection** of **degradation products** of modern painting techniques based on synthetic binders (acrylics, vinyl, alkyds) and of the volatile organic compounds (**VOC**) emitted from plastics and other contemporary art materials (including rapid prototyping materials) either during storage or exposition.

Formulations

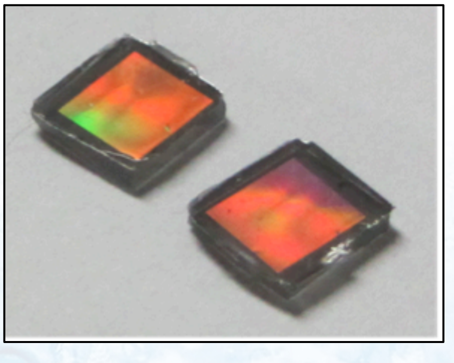
- **4 nanoinks and nanopastes for performing Surface-Enhanced Raman Spectroscopy (SERS):** these were developed for the detection of dyes, which is challenging with conventional tools.

- **3 SERS substrates**: substrates for SERS were developed, including elastomers, hydrogels, and glass. These allow the non-invasive sampling of minimal amounts of matter from works of art, to be analyzed by SERS

- **3 VOCs sensors**: electrochemical sensors were developed for convenient detection of gaseous formaldehyde, ketones, and phenols, i.e. the most important indoor pollutants. They can be used as marker molecules for material degradation.

Innovation

The **diagnostic tools** developed by the project (**SERS**, **sensors** for **VOCs** detection) exhibit **enhanced detection limits** and more **specificity/sensitivity** than traditional detection techniques. SERS was found to be a more effective way to identify components in inks than normal Raman. The sampling methods for SERS were validated and optimized so as to guarantee non-invasiveness and non-destructiveness.
Electrochemical sensors provide a very useful approach to **VOC analysis**. They represent a **simple**, **robust** and **inexpensive tool** that can be used for a wide variety of target analyses and have scope for miniaturization and rapid analytical responses. However, their use for analysis of VOCs from heritage artifacts had not been explored before NANORESTART; in the project, the detection of specific volatile degradation markers from plastic museum artifacts was accomplished.



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WP5 – NEW DISPOSEABLE SENSORS

How do they work?

The two approaches proposed consist of: 1) **in situ detection** of artistic materials and degradation products using the novel SERS substrates; 2) **environmental detection** of degradation products using novel electrochemical sensors. The newly developed sensors have been shown to successfully detect selected gaseous aldehydes such as formaldehyde and benzaldehyde and gaseous ketones such as acetone and butanone. Besides, sensors were developed to detect volatile emissions from plastic objects, i.e. gaseous phenol(s).

How are they applied?

For SERS substrates, a **non-invasive approach** using silver nanoparticles deposited on a glass substrate is used to effectively analyze inks while leaving no residue on the analyzed surface. The second approach is to use silicone sampling strips in contact with the artwork surface, so as to pick up minimal amount of matter that is then transferred to the SERS substrate and analyzed. VOCs sensors can be placed in different positions around plastic objects.

Case studies and application

These systems have been used to **non-invasively analyze modern and contemporary artifacts**, such as drawings by **Federico Fellini**, and **plastic sculptures**.

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WP6 – CLP AND TOXICITY ASSESSMENT

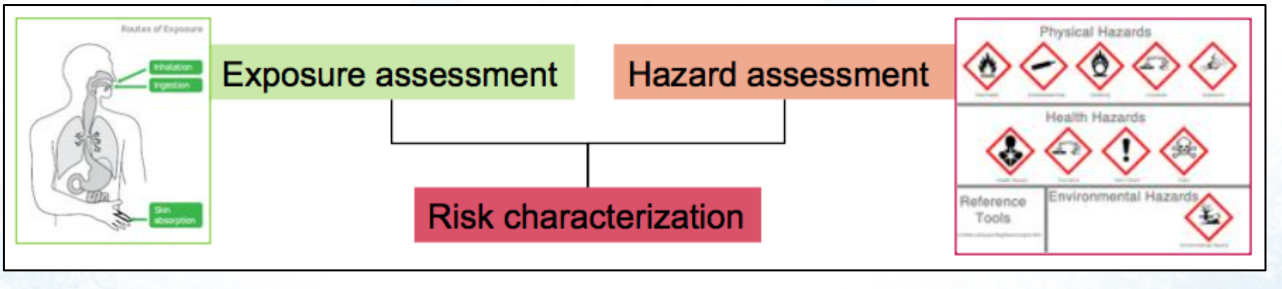
Objectives

WP6 aimed to:

• Perform **environmental impact assessment** of the most effective and promising **technologies** developed in **WPs 2-5**;
• **Identify** a set of **indicators** for evaluating the **sustainability** of such technologies and (related operations) including environmental, economic, social and technical aspects;
• **Develop** a **Weight of Evidence** (**WoE**) methodology integrating the identified indicators into a technology-specific (semi-)quantitative **sustainability judgment** (i.e. the Sustainability Assessment methodology);
• **Incorporate** the proposed **Sustainability Assessment** indicators and methodology in an ad hoc guidance document to support manufacturers towards the certification of their nano-enabled technologies.

Main results

WP6 completed the **Environmental impact assessment**, and then developed the WoE sustainability assessment methodology and a guidance document for sustainability assessment. For the first task, WP6 updated the **CLP self-classification**, additional **ecotoxicological** and **colloidal characterization**, as well as leaching testing and the safety assessment of the new formulations. For the second and third task, suitable criteria were selected according to the three pillars of sustainability (i.e. environment, economy and society) as well as technical criteria, and a **MultiCriteria Decision Analysis** (MCDA) methodology for criteria normalization, integration and visualisation was developed. This application allowed to refine the sustainability assessment methodology by adding a new criterion and by further specifying criteria's definitions and thresholds. The **developed protocol** can be used as a **guideline** for the **assessment** of **innovative products** for conservation of artworks.
Overall, the **new products** developed in the project **show excellent to very good environmental performance**.



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AT A GLANCE

Title: NANOmaterials for the REStoration of works of ART

Project reference: 646063

Topic: NMP-21-2014 - Materials-based solutions for protection or preservation of European cultural heritage

Call for Proposal: H2020-NMP-2014-two-stage

Total cost: EUR 9 178 647,25

EU Contribution: EUR 7 918 397

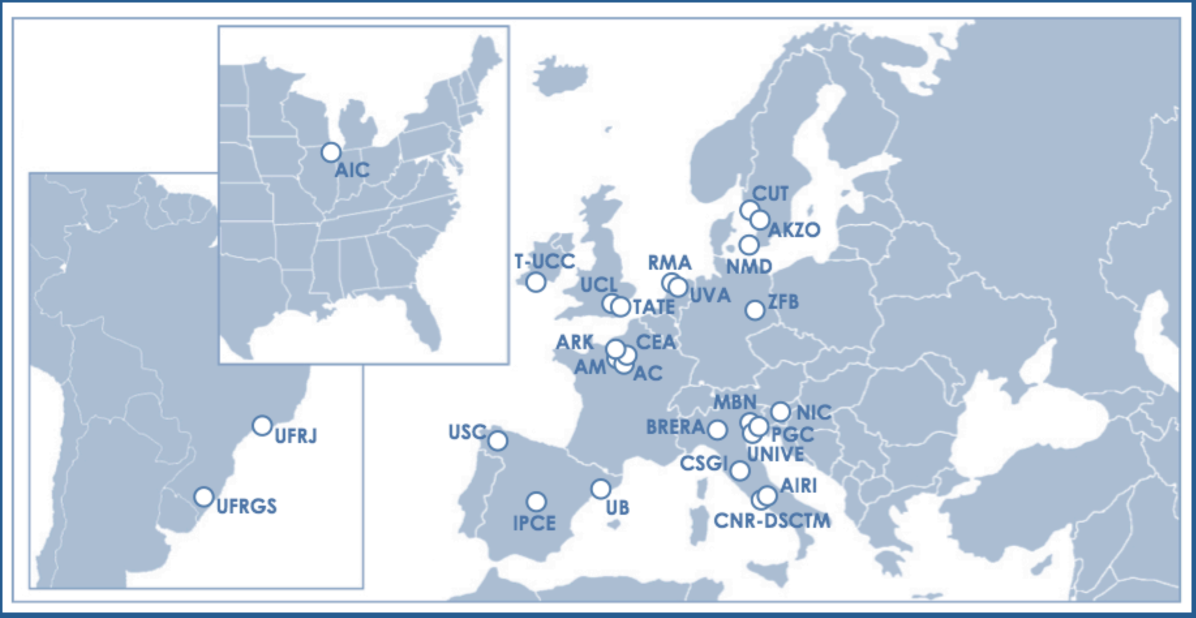
Duration: 42 months

Start Date: 01-06-2015

End Date: 30-11-2018

Consortium: 27 partners from 12 countries

Project Coordinator: CSGI - Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase (Firenze, IT)



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