Consiglio Nazionale delle Ricerche

Polymeric Smart Coatings for the Active Protection of Modern Bronze Artefacts

M.Salzano de Luna[1], C.Giuliani[2], G.Buonocore[1], M.Raucci[1], G.Di Carlo[2], M.Lavorgna[1], HS.Schrekker[3], GM.Ingo[2], L.Ambrosio[4]

[1] Institute for Polymers, Composites and Biomaterials, IPCB-CNR (Italy)
[2] Institute for the Study of Nanostructured Materials, ISMN-CNR (Italy)
[3] Institute of Chemistry at UFRGS (Brazil)
[4] Department of Chemical Science and Materials Technology, CNR (Italy)

NanoRestART

Nano Innovation 2016 Rome, 20-23 September

The NANORESTART project

NANOmaterials for the RESToration of works of ART

GOAL: development of nanomaterials to ensure long term protection and security of modern/contemporary cultural heritage

WP4: PROTECTION OF SURFACES

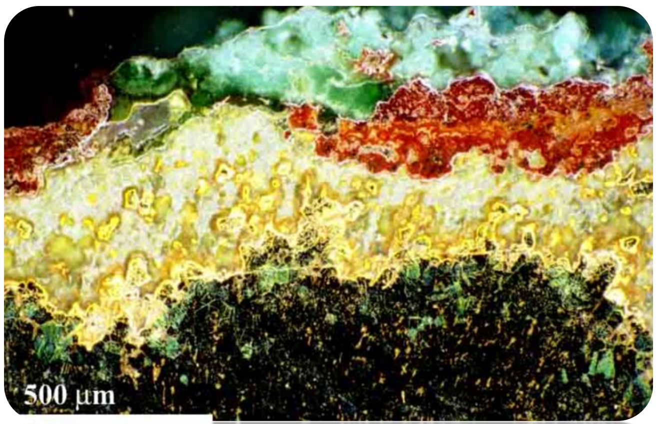
TASK: development of active, passive and multilayered coatings for metal and plastic-based artworks

CC4
Enhanced protection of artworks in museums and outdoors

Bronze: degradation mechanism

Cu-based objects

Cl^- is the most corrosive environmental agent, induces the so-called "bronze disease"

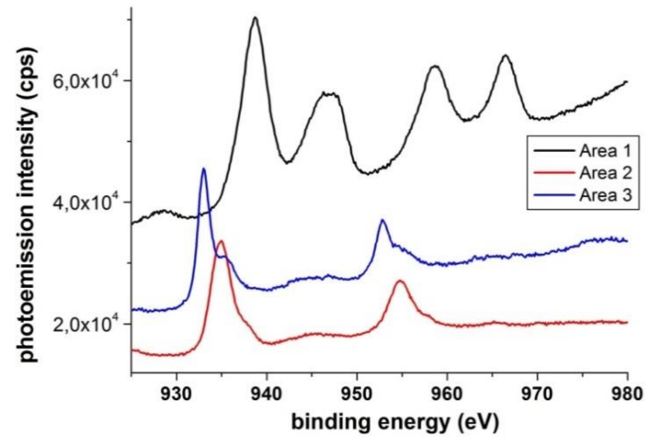


Atacamite $Cu_2(OH)_3Cl$

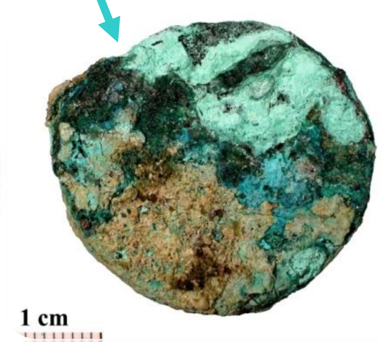
Cuprite Cu_2O

Nantokite CuCl

"bronze disease"



- $4CuCl + 4H_2O + O_2 \rightarrow CuCl_2 \cdot 3Cu(OH)_2 + 2HCl$
- $2Cu + 2HCl \rightarrow 2CuCl + H_2$

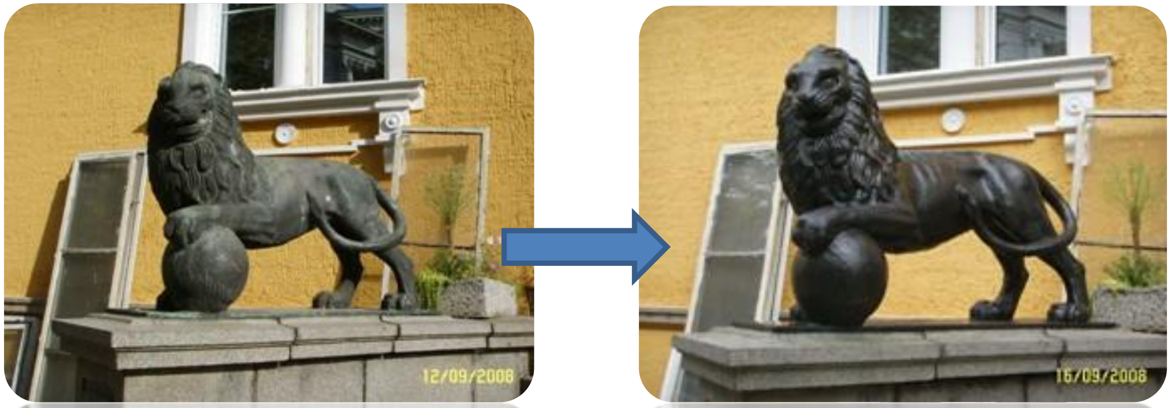


Current protective strategies

The protection of the bronze surfaces is performed in two steps:

1) Application of an acrylic solution (solvent DMSO or Toluene) with benzothiazole inhibitor (INCRALAC)

2) Application of a protective layer: wax with or without inhibitor (SOTER or RESWAX)

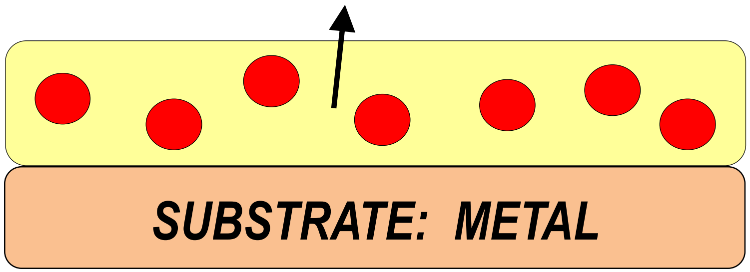


The main disadvantages of common approaches are:

- Toxic solvents
- Cracks in the protective layer (wax layer)
- Undesired reduction of the brightness of surfaces of modern bronzes

Global aims and strategies

ACTIVE LAYER able to modify the dynamics of degradation pathways by contrasting the diffusion of oxygen and water and by regulating the pH at the surface



- *Substrate protection*
- *Durability*
- *Reversibility*
- *Safety and sustainability*

Materials for coating development:

Sustainable polymers:

Chitosan-based coatings (ISMN@CNR)

HAVOH-based coatings (IPCB@CNR)

Protective Compound/Systems:
- Benzothiazole and 2-Mercaptobenzothiazole
- Ionic liquids (UFRGS-Brazil) (…less toxic!!!!)

Nanocarriers: Functionalized Halloysite and LDHs (IPCB@CNR)

Additives: Calcium carbonate, Calcium hydroxide (CSGI)

Outline

iPCB INSTITUTE FOR POLYMERS, COMPOSITES & BIOMATERIALS

CNR ISMN ISTITUTO PER LO STUDIO DEI MATERIALI NANOSTRUTTURATI

TO DO LIST

1. Selection of the substrates - case studies
2. Optimization of the coating formulations
3. Nanocarriers: basic principles and selection
4. Protective efficacy of the coatings
5. Innovative anticorrosive compounds

Selection of case-study

Target #1: identification of real case studies

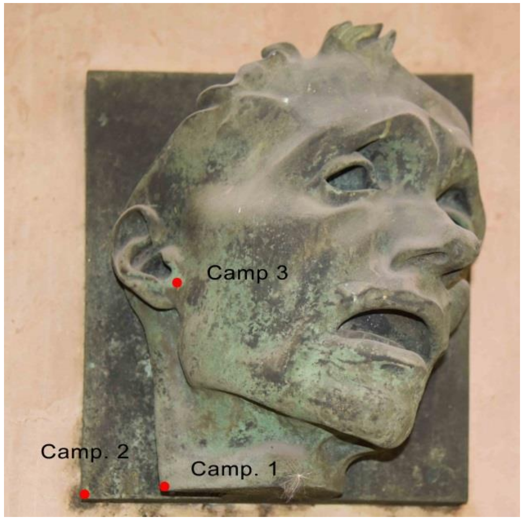
AUTHOR	---
TITLE	**Memorial plaque** dedicated to the artist Adolfo Wildt (1868-1931)
DATE	After 1931
TECNIQUE	Marble plaque with inscription and a bronze sculpture, depicting a head, probably taken from one of the works by Wildt, "*self-portrait*"
CONDITION	The surface of the marble and the bronze work presents incoherent and coherent deposits. Marble plaque: vertical percolations, related to washout and condensation. Traces of paint on the external edges. Altered adhesive residues. **Bronze: originally coated, presents on the surface, formation of green metal corrosion products. Consumption of the original patina due to percolation of water on the surface**
MEASURE	1315 (h mm) x 955 ca.
PLACING	Academy of Fine Arts of Brera, central corridor

Selection of Cu-based alloy composition

Target #2: identification of the composition of the metal alloy and surface patina of indoor works of art

The analysis reveal that the "Aldolfo Wildt" work of art consists of a **quaternary Cu-Sn-Pb-Zn alloy** with Ni and Fe as minor alloying elements (<1 wt%).

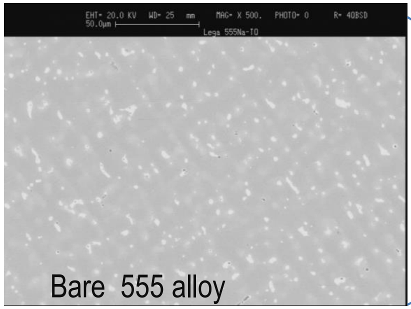
The analysis of the patina revealed the presence of **chloride and sulphate induced corrosion products**.

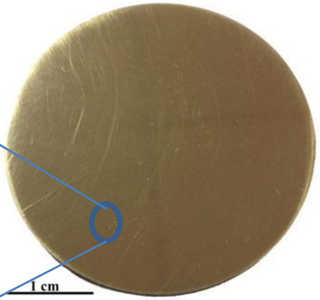


Cu	**80.1-82. wt1%**
Sn	**5.6-5.9 wt%**
Pb	**3.0-3.6 wt%**
Zn	**7.6-9-0 wt%**
Ni	**<1 wt% (0.6-0.7 wt%)**
Fe	**<1 wt% (0.5-0.9 wt%)**

Target #3: selection of a representative quaternary Cu-Sn-Pb-Zn alloy

- 555 alloy (Cu 85%, Sn 5%, Pb 5%, Zn 5%), commercially produced and used by all the partners involved in this work package





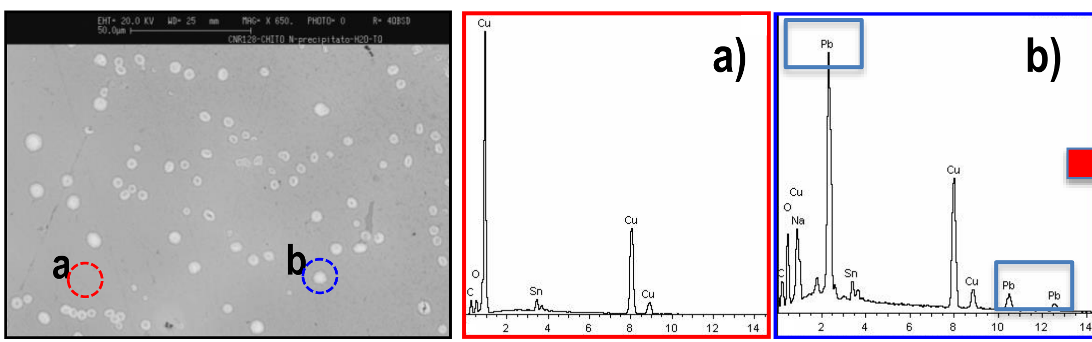
555 alloy

Chitosan-based coating formulations

Target #1: to avoid interaction of the formulation constituents with the lead from the alloy

Bare alloy **Chitosan-AcAc** **Chitosan-GDL**

✓ Comparison between the acetic acid (AcAc) and the D-(+)-gluconic acid δ-lactone (GDL)

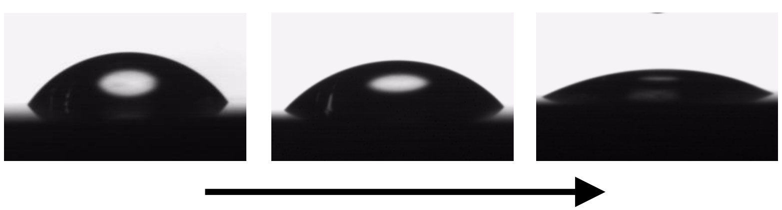


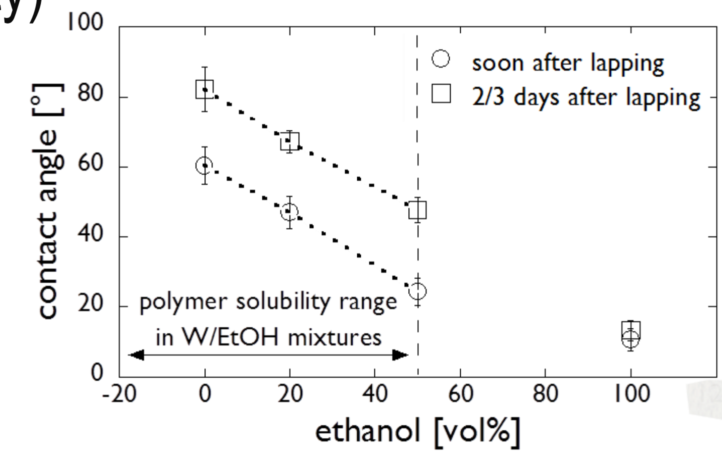
The formation of Pb-based platelets was detected by using the acetic acid

✓ **Selection of GDL as the optimal additive for chitosan dissolution**

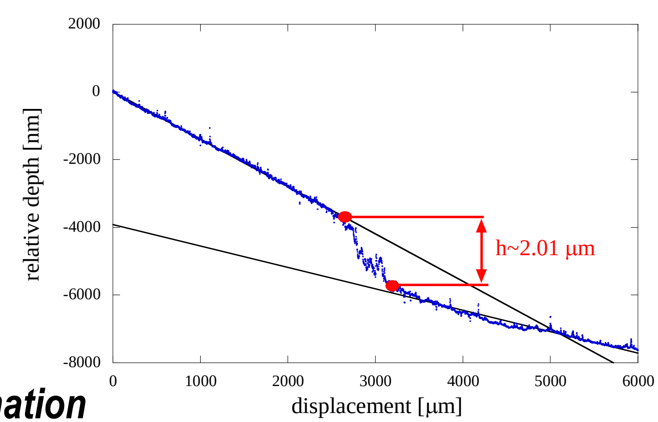
HAVOH-based coating formulations

Target #1: selection of the liquid medium to ensure good wettability with the Bronze substrate (limitation: polymer solubility)

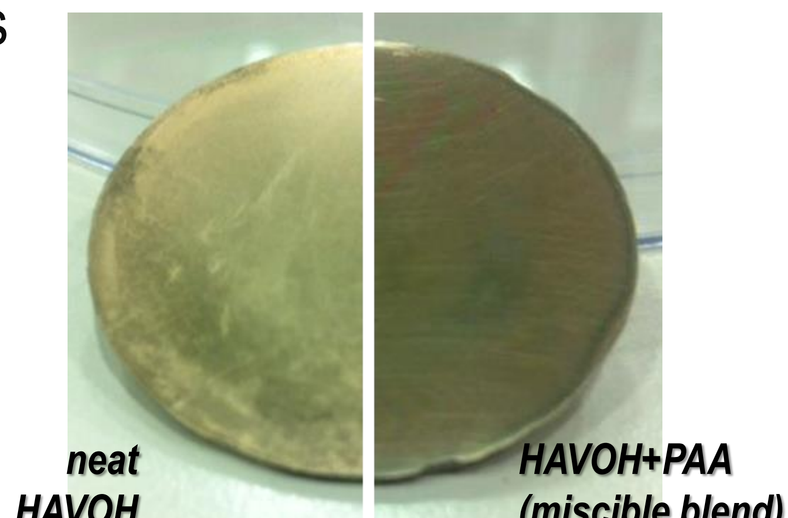




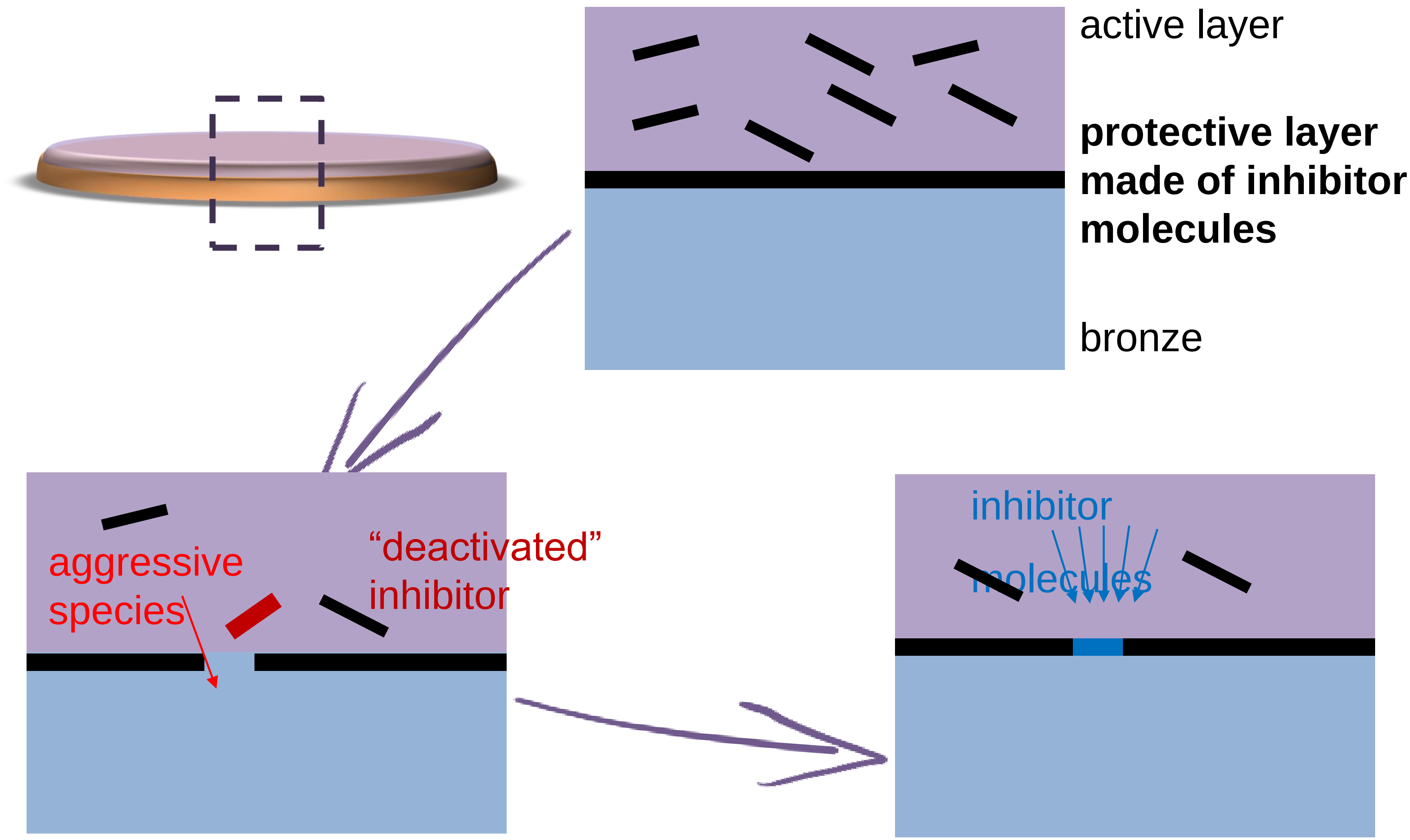
Target #2: improving adhesion between HAVOH and bronze substrate to obtain homogeneous and transparent coatings



Thickness estimation



How does the active coating work?

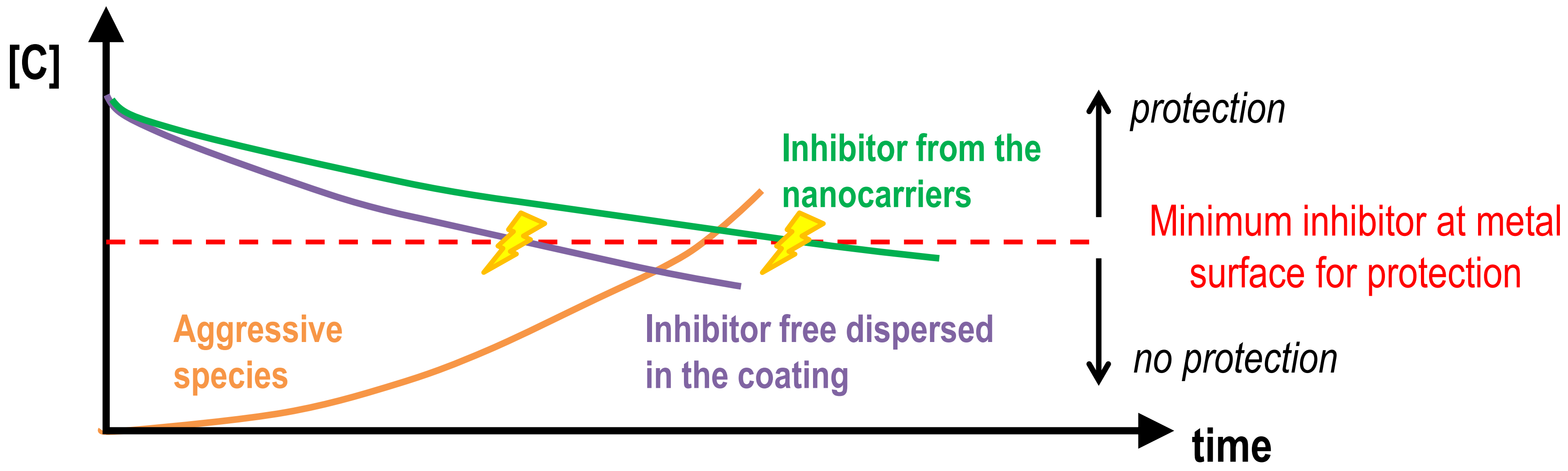


The inhibitor may be deactivated by Chloride ions or UV light

Nanocarriers: basic principles

The embedding of inhibitor molecules in nanocarriers guarantees:

- The protection of inhibitor
- The tailored release of inhibitor at the metal-coating interface to keep the concentration above the minimum threshold for effective protection.

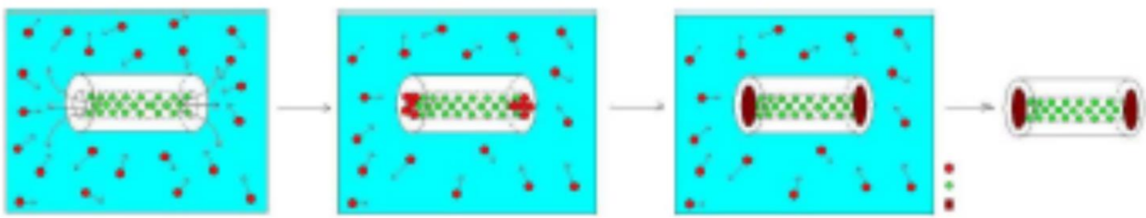


Work in progress:

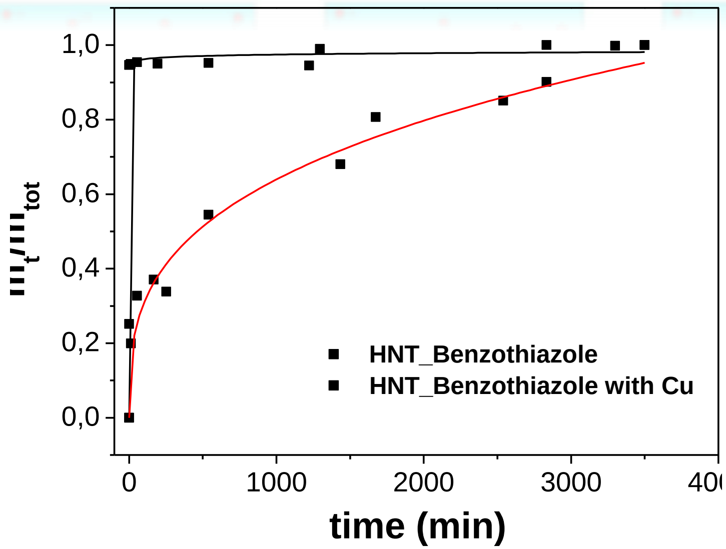
- Assessing the minimum inhibitor at metal surface for protection
- Assessing the mechanisms (kinetics, driving force, …) of the diffusion of the inhibitor molecules in the coating towards the metal surface
- Modeling the process to optimize the formulation and predict the duration of its protective action

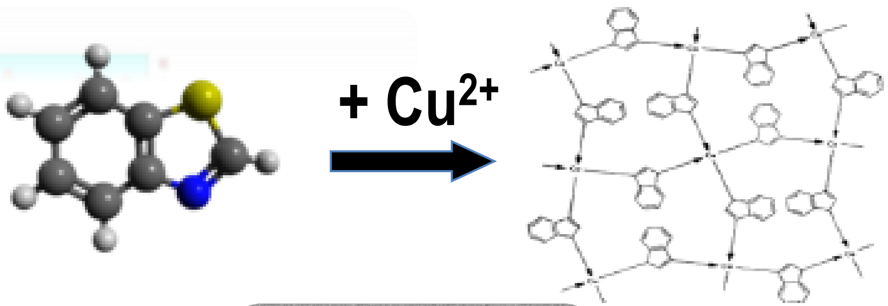
Selection of the nanocarriers

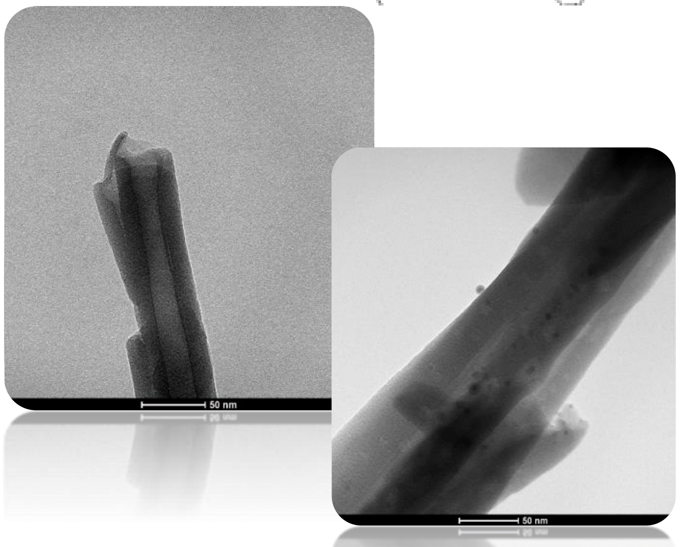
1) Halloysite nanotubes



Possible mechanisms of end tube stopper formation



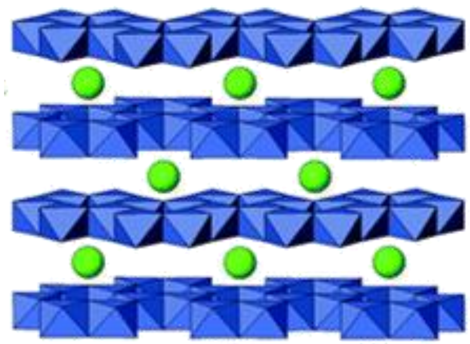




The treatment of Benzothiazole filled halloysite with Cu solution allows to slow-down the anticorrosion release

Selection of the nanocarriers

2) Layered Double Hydroxides (LDH)

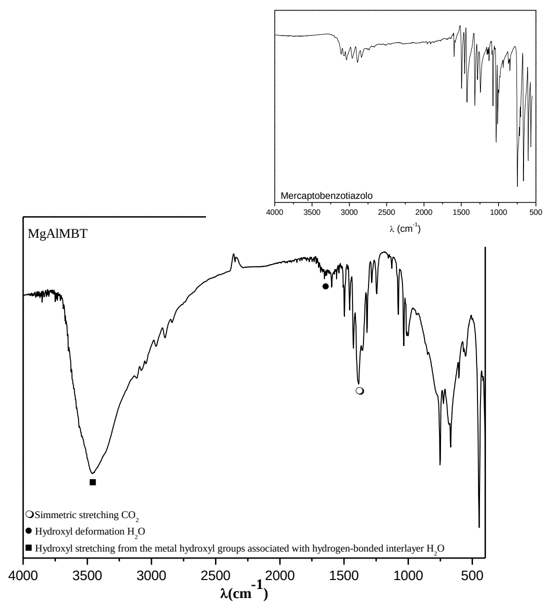


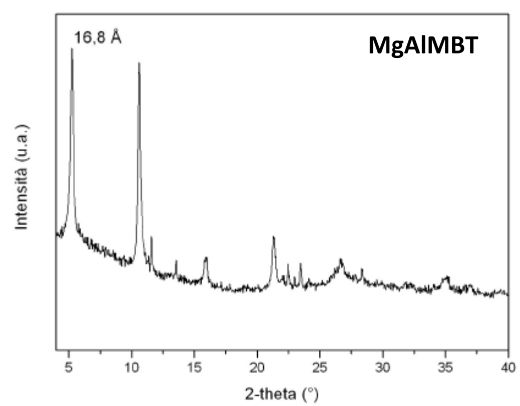
inhibitor (anionic)

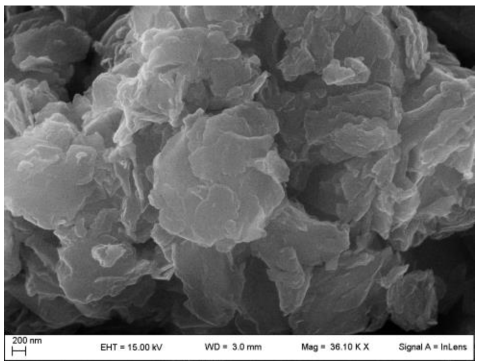
Synthesis through two steps:

- ✓ A) LDH synthesis in the nitrate form (0.2-1micron)
- ✓ B) Ionic exchange of nitrate with MBT (mercaptobenzothiazole) at pH 8.4

- The loading capacity of LDH is higher than that of Halloysite (≈30-40wt% vs. ≈10wt%)





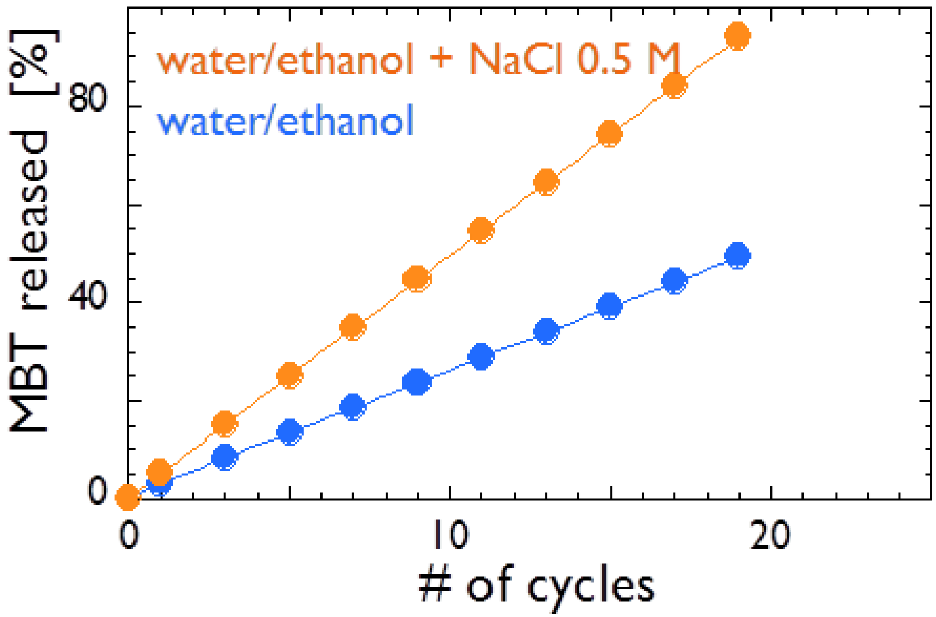


Selection of the nanocarriers

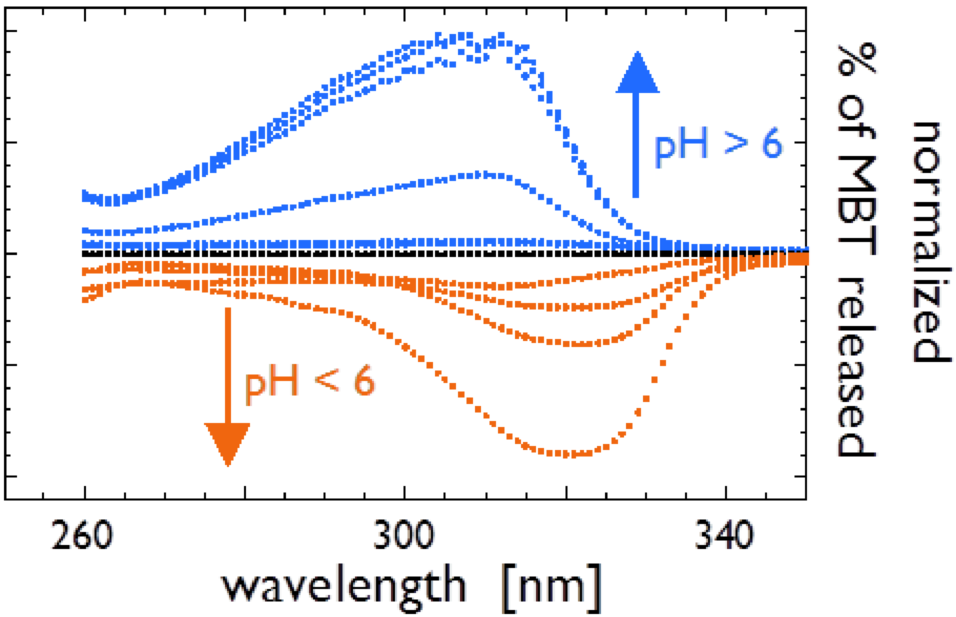
2) Layered Double Hydroxides (LDH)

- LDH nanoparticles retain most of the inhibitor during the preparation of the coating formulation because the inhibitor molecules are released only in the presence of external stimuli: presence of chloride species, pH variation

Effect of the presence of Cl^-



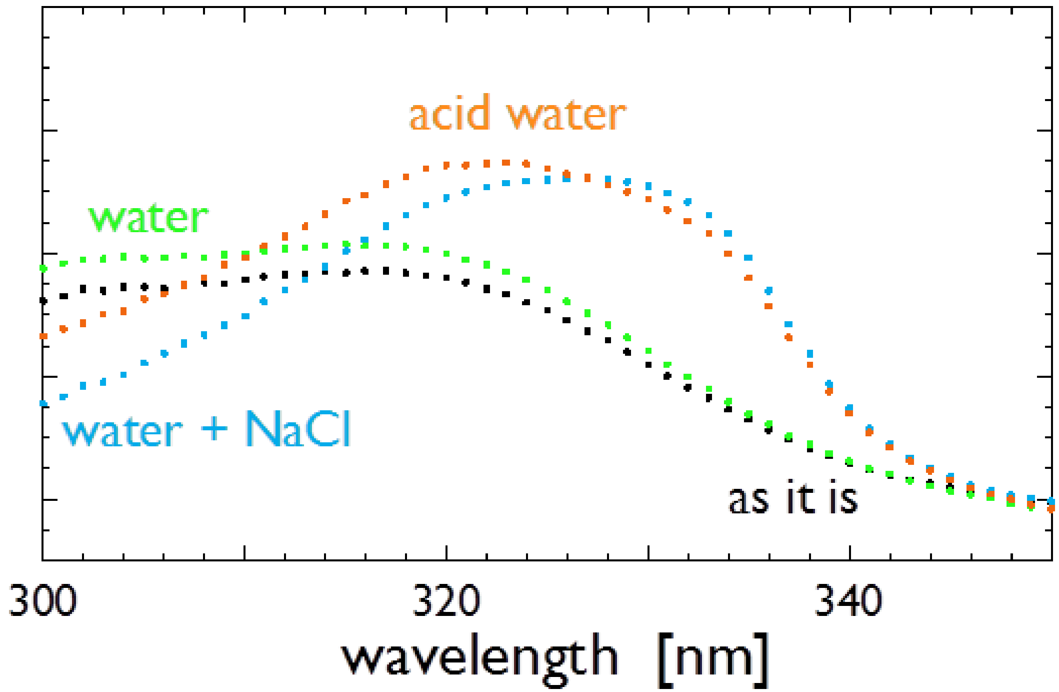
Effect of the pH variation



Selection of the nanocarriers

2) Layered Double Hydroxides (LDH)

the release of the inhibitor in the coating takes place only in the presence of corrosion-related external stimuli



Uv-vis test on coatings deposited on glass slides:

The inhibitor is released only if triggered by external stimuli (Cl^- and/or low pH)

Protective efficacy of chitosan-based coatings

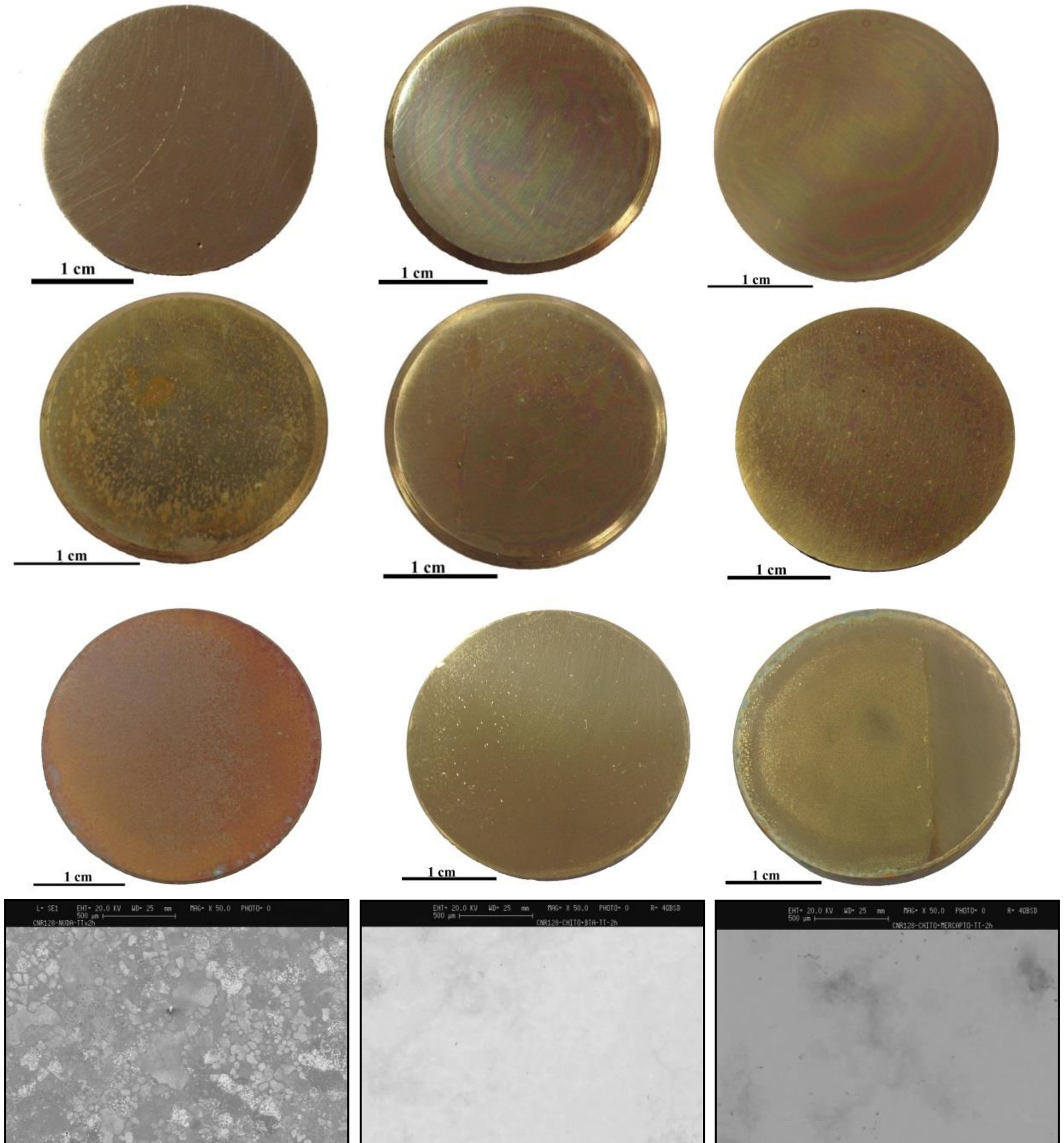
Bare alloy | Chitosan-BTA | Chitosan-MBT

As prepared

After corrosion treatments

with HCl/H_2O vapours at 50°C for 1h

with HCl/H_2O vapours at 50°C for 8h

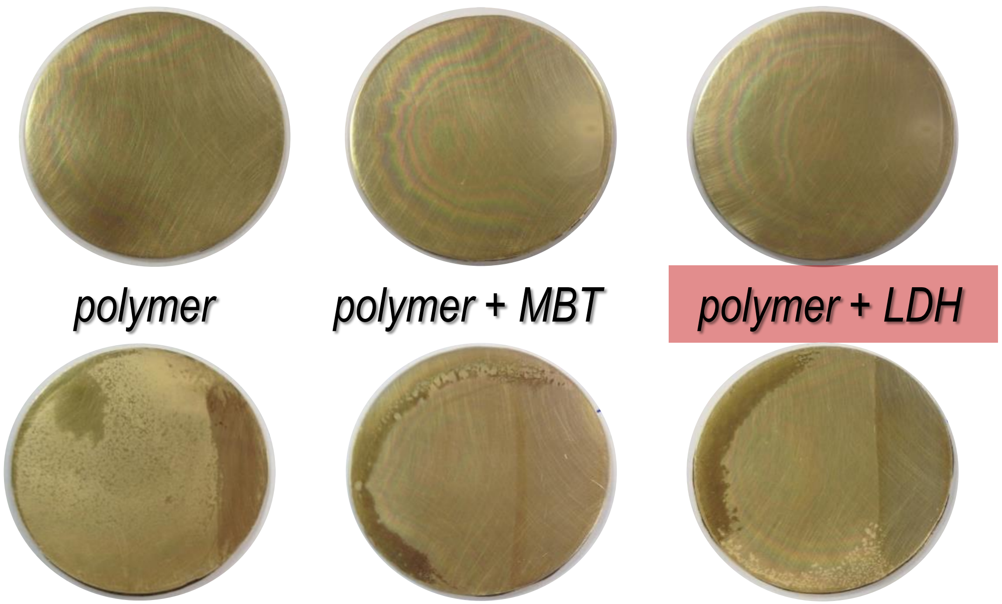


After accelerated corrosion treatments, the polymer coatings remain transparent and prevent the alloy degradation

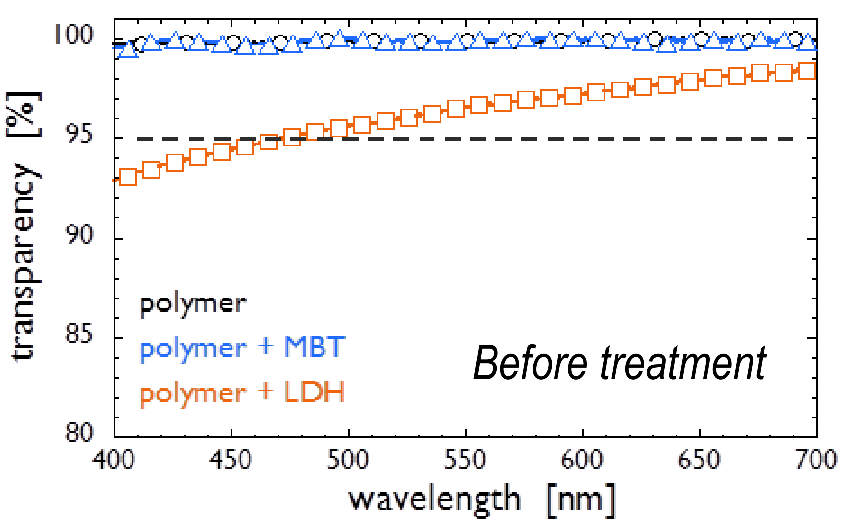
Protective efficacy of HAVOH-based coatings

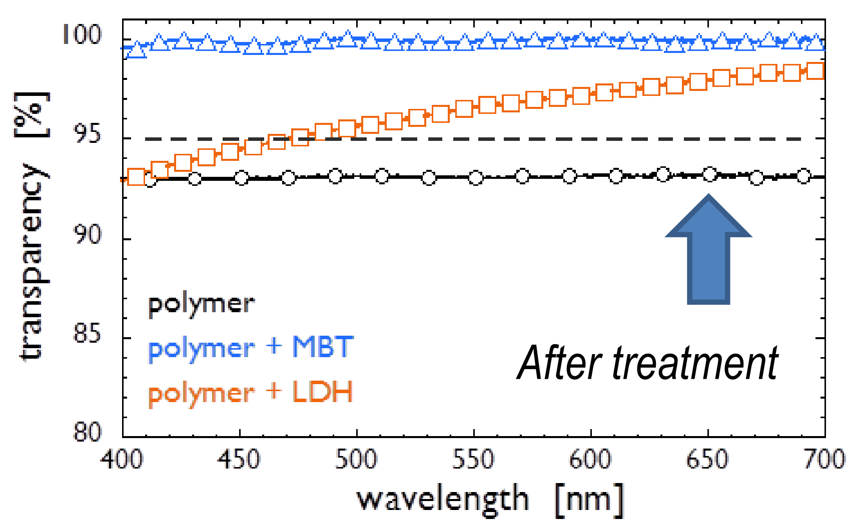
Before treatment

After treatment



All the coatings preserve the underlying substrate from corrosion but after treatment the HAVOH coating loses transparency whereas the coatings with the inhibitor (free or embedded in the LDH) remain unaltered

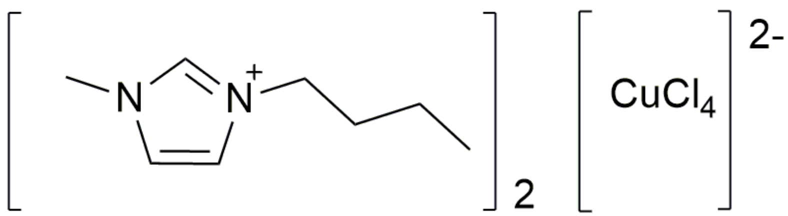




Ionic liquids

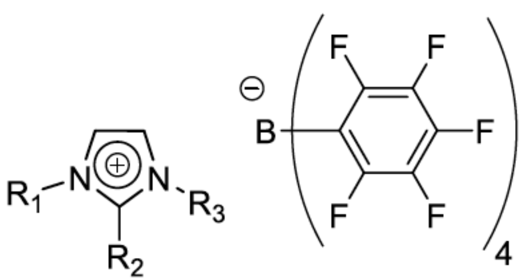
Target #1: optimimization of the chemical structure

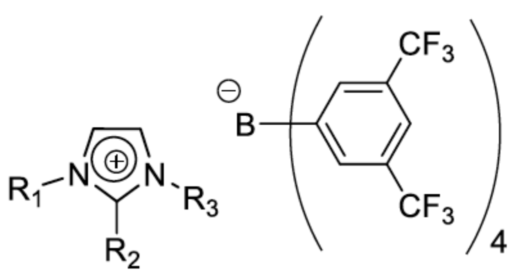
Chloride-based $CuCl_4^{2-}$ Ionic Liquid



CNR-128 alloy: Chloride corrosion processes

Chloride-free IL with "non-coordinating" anions

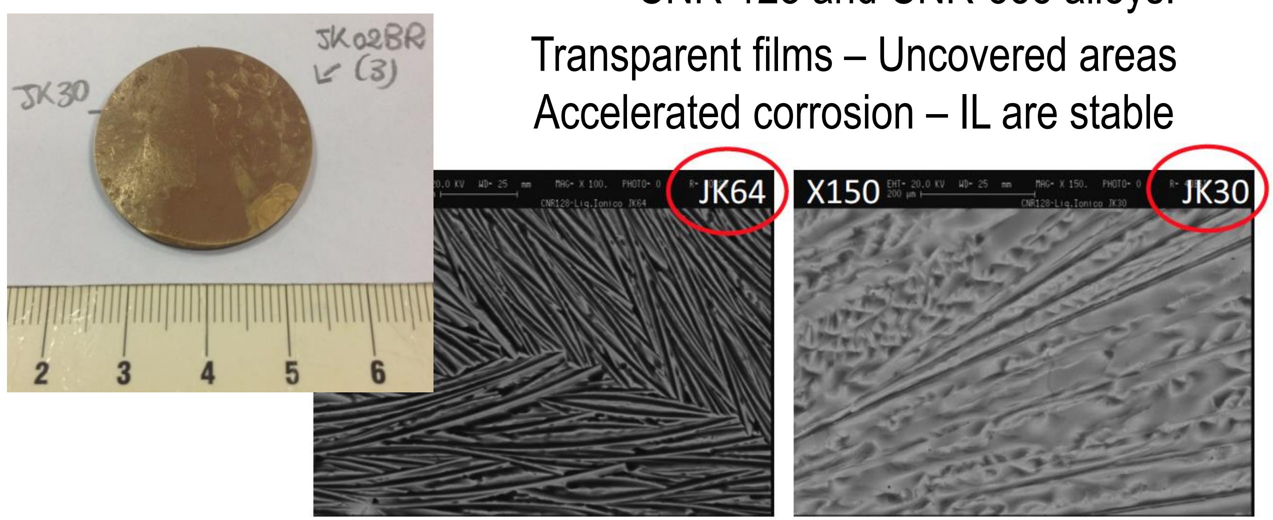




CNR-128 and CNR-555 alloys:

Transparent films – Uncovered areas

Accelerated corrosion – IL are stable

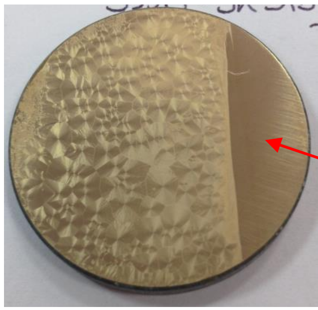


Alloy unchanged after IL removal – Chitosan films

Protective efficacy of IL-based coatings

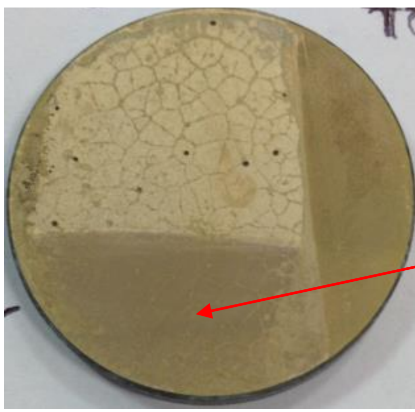
Chloride-free benzotriazole-functionalized ILs

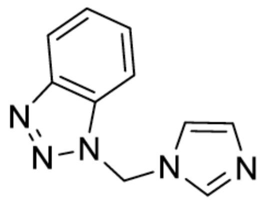
<u>ILs directly applied on bronze substrate</u>



Insoluble in water/ethanol solutions

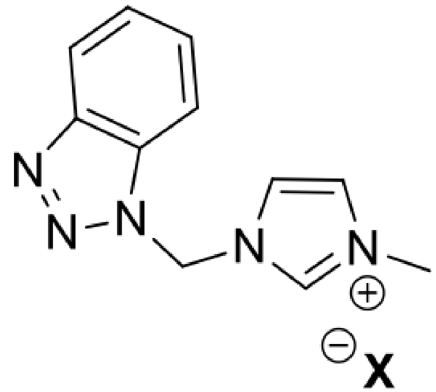
Film removed before the corrosion test





Film removed after the corrosion test: the bronze surface is not affected

(3 h, HCl 1 M, 50° C)



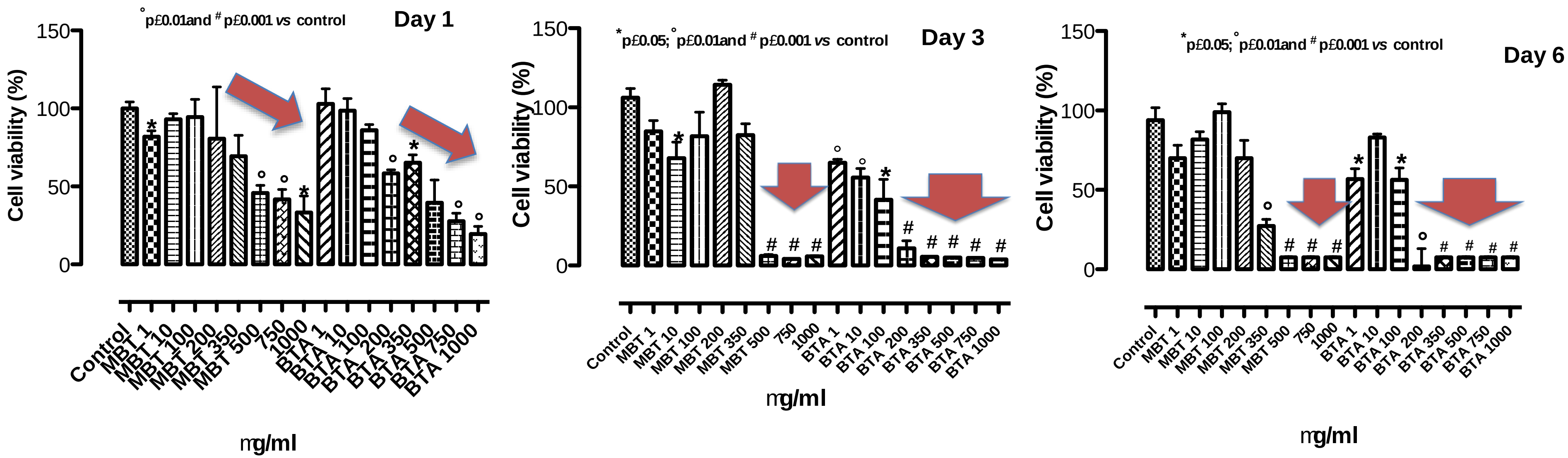
Special attention will be given to improving the IL solubility in water-ethanol mixtures and to enhance the removability of the coating

The IL are promising candidates for the protection of copper-based alloys.

Ionic liquids

Target #2: assessment of the toxicity with respect to commercial inhibitors

Cytotoxicity tests by using murine fibroblasts L929 (10,000 cells/well) in presence of commercial anticorrosive compunds



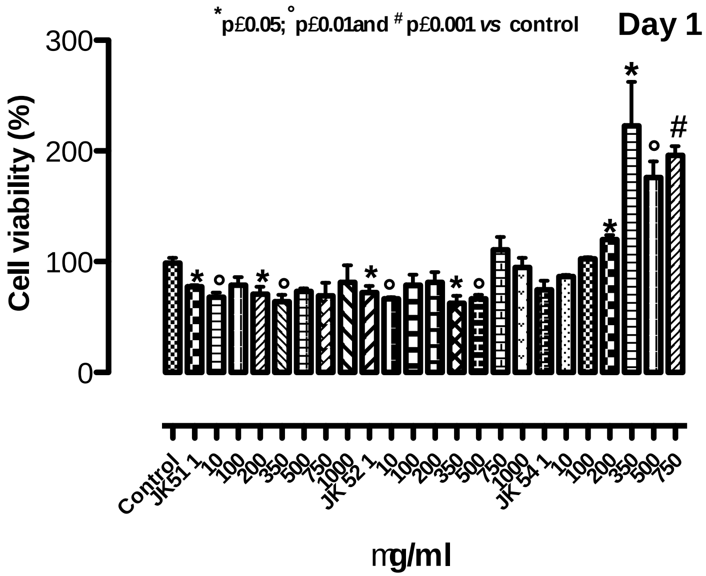
MBT @day1 shows a **decreasing of cell viability** by increasing the concentrations [500-1000ug/ml]

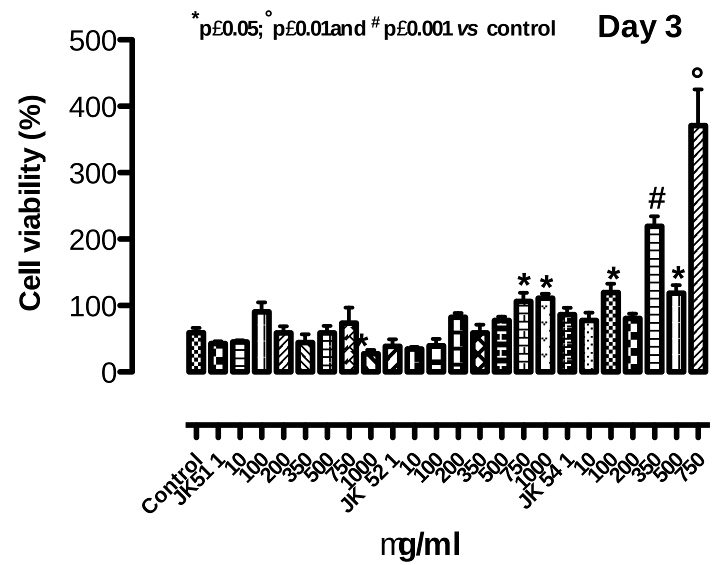
Cytotoxic effects are evident @ 3 and 6days for concentrations [500-1000ug/ml].

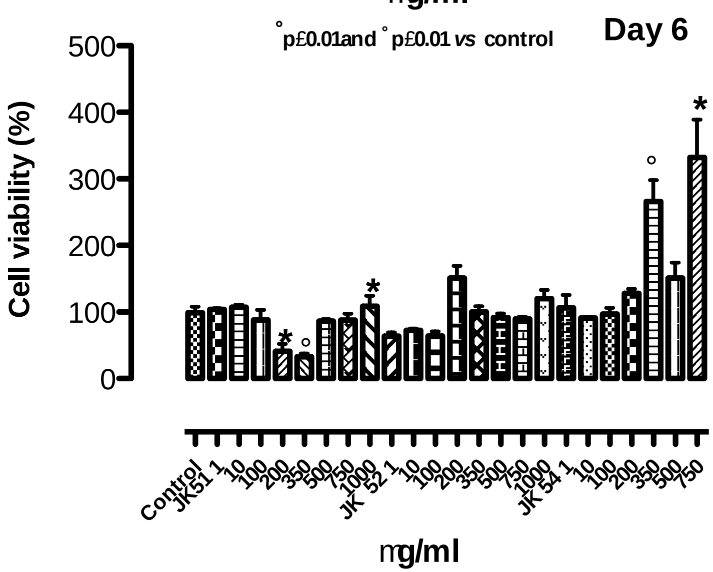
BTA @day1 shows a **decreasing of cell viability** by increasing the concentrations [500-1000ug/ml]

Cytotoxic effects are evident @ 3 and 6days for concentrations [200-1000ug/ml].

Ionic liquids







JK51-52 show **no negative effect** on **cell viability** @1 - 3 and 6days

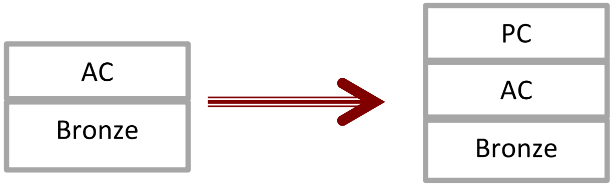
JK54 shows an improvement of cell viability at higher concentrations [350-750ug/ml] over culture time.

<u>Additional citotoxicity tests by using Human dermal fibroblast and inflammatory response tests are in-progress</u>

Protective performances of the multilayered coatings

<u>Active coating (AC):</u>

1. Cithosan from (ISMN-CNR)
2. HAVOH/PAA (IPCB-CNR)



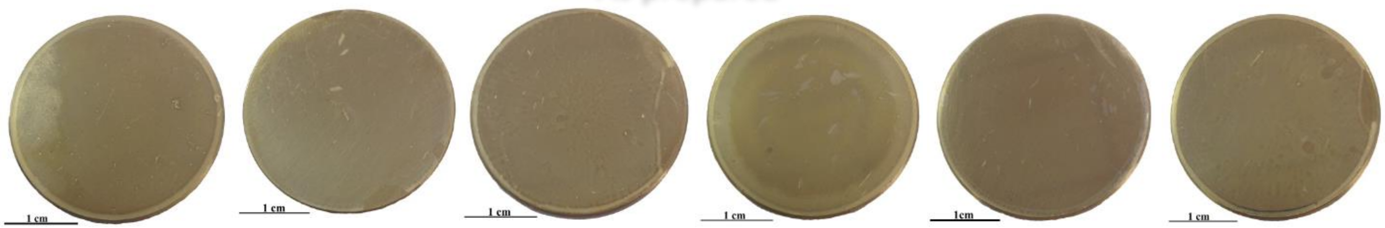
<u>Passive coatings (PC) – Solvent-borne:</u>

	Thickness
N-91-1 (fluoropolymer/BuAc/POSS/additives) R	3.4 μm
N-91-2 (fluoropolymer/BuAc/POSS/additives) nR	2.1 μm
N-91-3 (acrylate resin/BuAc/POSS/additives)	3.0 μm

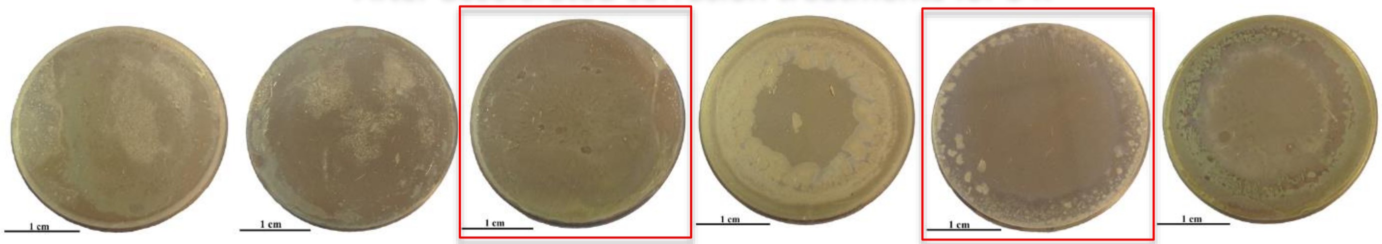
Spin coating deposition of 3 SB formulations (NIC)
(N-91-1, N-91-2, N-91-3)

Chit-1 Chit-2 Chit-3 HAVOH-1 HAVOH-2 HAVOH-3

As prepared



After accelerated corrosion treatments for 3 h



- ✓ Some formulations are able to prevent alloy modifications
- ✓ The compatibility between <u>active and passive coatings has to be improved</u>
- ✓ The coating thickness has to be optimized

Conclusions

New ecofriendly formulations based on sustainable polymers as chitosan and HAVOH

Porous nanocarriers which exhibit a stimuli-responsive release of the embedded anticorrosion inhibitor

New ecofriendly inhibitors based on ILs less toxic than traditional benzothiazole and mercaptobenzothiazole

Acknowledgements

iPCB INSTITUTE FOR POLYMERS, COMPOSITES & BIOMATERIALS

Dr Giovanna Buonocore
Dr Letizia Verdolotti
Dr Fabiana Tescione
Dr Mariamelia Stanzione
Dr Martina Salzano de Luna
Dr Tianliang Zhai
Dr WangLei
A.Aldi, M.Marcedula, M.de Angioletti, F.Docimo…e tutti gli altri che ho dimenticato!!!

CNR ISMN ISTITUTO PER LO STUDIO DEI MATERIALI NANOSTRUTTURATI

Dr Gabriel Ingo
Dr Gabriella Di Carlo
Dr Chiara Giuliana

THANK YOU!