Film-forming gels for the removal of corrosion products from copper-based artifacts

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An innovative polyvinyl alcohol-based film forming system was specifically devised for a controllable and selective cleaning of copper-based artifacts, with enhanced performances in terms of both applicability and efficacy. The main advantage of this cleaning system consists in the simultaneous chemical and mechanical action, guaranteed respectively by the presence of a confined complexing agent specific for selected ions (Cu^{2+}), such as EDTA and/or polyethyleneamines.

Metallic artifacts are affected by corrosion phenomena that induce the formation of complex *patina* on their surface. Degradation causes the formation of overlapping structures, characterized by a layer of Cu(I) oxide (cuprite Cu_2O) at the interface with the metal, and by an external layer of Cu(II) carbonates, sulphates, chlorides, etc. The presence of copper oxychlorides (atacamite and its polymorphs) is usually considered as a symptom of the 'bronze disease', a cyclic phenomenon that leads to the progressive deterioration of ancient copper alloys. Cleaning procedures of these materials are traditionally performed by mechanical (vibrating or abrasive tools, micro-peening with vegetal granulates, ultra-high-pressure water, laser) and/or chemical methods (complexing agents, bases, acids). Mechanical cleaning presents some limits related to the scarce selectivity and invasiveness of this procedure, while the chemical action is generally affected by an insufficient control over the reactions involved.

The film forming cleaning system, based on polyvinyl alcohol as a polymer and loaded with a complexing agent (EDTA and polyethyleneamines), is a promising tool for the selective removal of corrosion products from copper-based artifacts, by respecting the cuprite layer. In fact, this innovative approach permits to achieve: i) improved chemical control, step-by-step, of the cleaning process, thanks to the high selectivity of the chosen complexing agent and to its confinement in the polymeric system; ii) simultaneous chemical (complexation) and mechanical action (favored by the gentle *peeling* of the final film); iii) adjustability of the physico-mechanical properties (consistency, adhesiveness, transparency, etc.), by tuning the additives content to adapt to different substrates (non-horizontal, rough and irregular surfaces).

Two main aspects were studied over both complexing agent-loaded and not loaded systems: i) the kinetics of film formation, by investigating the evolution of the systems from polymeric dispersions towards the formation of elastic films and ii) the evaluation of the formed films properties, through the parameter of crystallinity degree. The techniques used to obtain information over the evolution of the system through time, involved the use of gravimetry, thermogravimetry (both scanning and isothermal), and rheology (both dynamic and rotational experiments). The evaluation of the mechanical properties and of the degree of crystallinity of the dried films was obtained, instead, from differential scanning calorimetry (DSC) and ATR-FTIR spectroscopy experiments.

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