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Micelle, microemulsions, and gels for the conservation of cultural heritage

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ABSTRACT

Past restorations performed with acrylic and vinyl polymers showed detrimental effects to wall paintings that lead to the complete disfiguration of the painted surfaces. The removal of these materials performed with the traditional solvent-based methodology represents a real challenge to conservators and usually achieves very poor results. This review reports on the new palette, nowadays available to restorers, based on microemulsions, micellar systems, physical and chemical gels specifically formulated for the cleaning of cultural heritage artefacts. These systems have been developed in the last twenty years within the cultural framework of colloids and surface science.

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1. Introduction

Works of art degrade due to the natural ageing of the materials composing them. In most cases, degradation processes occur at the surface of the artefacts that is not only the locus where the artists transferred their message and emotions, but also the place where different materials, with their own specific chemical composition and mechanical properties, coexist. If we think to a work of art in a “material way” it is obvious to consider colloids and surface chemistry as the correct scientific framework to be used to understand and possibly to delay the ageing processes that depend on the particular artefact's location and exposure to the environmental factors such as the exposure to light, temperature stresses, humidity cycles, insects and microorganisms.

However, for long time Colloids and Surface Science wasn't the major player in the conservation arena and “classical” analytical and polymer chemistries were the privileged tools at the hands of conservators.

Several authors have described the principles and the approach to preserve cultural heritage, and also accounted for the efforts (and faults) in the restoration of artworks [1–4]. For example the use of polymers, such as painting consolidants and varnishes, that was and, unfortunately, is still very popular in the conservator community, produced severe degradation with detrimental effects [5] on the works of art surface that ultimately led to the disfiguration and loss of the objects.

During the years many systems belonging to the realm of colloids have been specifically tailored for conservation issues, as nanoparticulate

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inorganic sols (nanosols) [6], colloidal silica [7], and alkoxysilane [8] play an important role in wall paintings, stone, paper, and wood conservation. Some of the most important advancements in the field have been reviewed and the reader is referred to references [9–13].

In this review we will report on the application of micelles, microemulsions, and gels for the restoration of works of art. The formulation of these systems would not be possible without the scientific advancements generated in the past forty years by many scientists and in particular by Bjorn Lindman, to whom this paper is dedicated.

Complex fluids such as micelles and microemulsions are the most advanced systems used so far in the conservation field for their capability to remove soil coatings from works of art surfaces. In particular, swelling, solubilisation and selective removal of synthetic materials (acrylic and vinyl polymers), largely applied in past restorations and difficult to be removed by classical cleaning methods, can be achieved by using amphiphile-based systems.

The cleaning of wall and easel paintings presents several difficulties due to the physico-chemical properties of the substrate, which usually has a very complex stratigraphic structure, both in terms of porosity and chemical composition. Therefore, the removal of soil, dirt/grime, and altered materials requires very high selectivity, with minimal interactions with the layers beneath the dirt and coatings, i.e. the painted layer. For this reason the classical solvent technology, i.e. the use of pure (or mixed) organic liquids, is often unadvisable. In fact, the action of organic solvents is usually scarcely controllable due to their surface tension and to the common high wettability of the treated surface, leading to the solubilisation of soil material and to its spreading within the substrate porosity [14,15]. These processes are enhanced by the high evaporation rate of most of the solvents used for cleaning. An additional important issue associated with the use of neat organic solvents is represented by the toxicity of most solvents used for cleaning.

In the cleaning, selectiveness is mandatory: the basic principle ‘like dissolves like’ implies that the removal of a soiling layer is very difficult since it usually possesses physico-chemical properties similar to the surface substrate. The use of solvents, in fact, may cause the partial swelling and solubilisation of the original artwork materials. The use of blend of different solvents could perfectly fit the solubility parameters of the materials to be removed, but rarely the substrate results completely inert.

An important improvement to “classical” cleaning procedures was introduced in the conservation field with the formulation of microemulsions and micellar solutions that, for specific applications, can be confined into host systems like physical and chemical gels. The most important systems used so far in conservation will be highlighted in the following sections.

2. Microemulsions and micellar solutions as innovative low impact cleaning tools for the conservation of wall paintings

2.1. Microemulsions

Lindman and Danielsson provided a useful definition of microemulsions described as “liquid, stable and homogeneous, optically transparent, isotropic and “spontaneously” formed systems, comprising two liquids mutually insoluble; one dispersed in the other in form of micro-spheres stabilized by at least a monolayer of amphiphilic molecules (surfactants)” [16]. The use of microemulsions in conservation dates back to the eighties and since then they are employed worldwide. Microemulsions are very versatile systems showing several advantages in the field of artwork cleaning compared to conventional systems such as neat solvents and solvent gels used by restorers:

- The continuous phase can be hydrophilic (o/w) or hydrophobic (w/o) allowing a control in the spreading of the continuous phase into the artefacts to be treated.
- The dispersed oil-in-water (o/w) or water-in-oil (w/o) nanodroplets with respect to simple emulsions develop a huge exchange surface area that enhances the interactions with soiling materials, facilitating the removal or the swelling of the materials to be removed.
- The spreading of the solubilised material into the porous matrixes may be limited, because solubilisation or swelling occurs into the core of nanodroplets and/or at the droplet interface. When dealing with hydrophilic substrates (i.e. wall paintings) the aqueous continuous phase may act as a barrier, preventing the re-deposition of the hydrophobic coatings within the substrate porosity.
- Microemulsions are thermodynamically stable systems.
- The formulation of o/w microemulsions requires small amounts of solvents with a consistent reduction of the toxicity and environmental impact.
- The cleaning process with microemulsions allows a controlled cleaning action of the works of art surface.

The restoration of the Renaissance paintings by Masaccio, Masolino, and Lippi in the Brancacci Chapel in Florence (1984–1990) [13,17] represents the first case study where microemulsions were used for conservation purposes. Diagnostics on the wall paintings revealed the presence of a large amount of wax-spots deposited over the surface. This unusual event was due to the blowing out of votive candles, kept close to the paintings over centuries. The removal of this material required the action of an apolar solvent to be applied over a hydrophilic substrate. The use of hydrocarbons (i.e. dodecane) allowed the solubilisation of wax, but the resulting solution was soaked by the wall and, after solvent evaporation, the wax was re-deposited within the pores. An oil-in-water microemulsion containing SDS/dodecane/n-butanol/H_2O was very effective in the removal of the apolar material. The positive outcome of this conservation paved the way for the use of microemulsions that become a standard method for cleaning.

Several microemulsive systems have been developed to solve conservation issues not manageable with conventional conservation methods. Examples are reported in the following paragraphs.

In 2007 some wall painting decorations in the Oratory of *San Nicola al Ceppo*, devastated by the 1966 flood of the Arno River in Florence, were restored by removing the patinas left after the flood [18]. The painted surfaces were covered by a crust of gypsum efflorescences mixed with the residuals of oil fuel from the flooding water. Sixty years after the event, the ageing of this blend of hydrocarbons and others materials resulted in an extensive cross-linking of the organic materials and further insolubilisation of the hydrophobic layer to most organic solvents. In this case, it was necessary to combine the action of a solvent capable to swell and partially solubilise the coating and, at the same time, to chemically attack the gypsum patina. This twofold purpose was successfully achieved by using an oil-in-water microemulsion based on 1% w/w xylene (for the swelling of the organic components) dispersed in a ammonium carbonate solution (for the solubilisation of gypsum) used as a continuous phase.

However, the most common use of microemulsions is represented by the removal of synthetic polymers largely used in the past to provide consolidation and protection to the works of art surfaces [19]. In fact, acrylic and vinyl polymers (or co-polymers) become, upon natural ageing, especially in urban polluted environments, insoluble or hardly soluble in solvents or solvent blends, mainly because of oxidation and cross-linking reactions [3,20–22]. Together with molecular changes due to ageing, synthetic polymers concur to the degradation of wall paintings because they change the physico-chemical properties of the surfaces (i.e. vapour permeability), dramatically increasing the effects of salt crystallization over the painted surface (see Fig. 1) [23]. Wall paintings from 16th century in San Salvador Church in Venice were restored in 1970 by applying a nitro diluent solution of 10% w/w solution of acrylic copolymer (Paraloid®; ethyl methacrylate–methyl acrylate 70:30 w/w co-polymer). At the end of 2002, a new restoration was necessary to remove the compact, yellowed, and shiny coating that