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New Methodologies for the Conservation of Cultural Heritage: Micellar Solutions, Microemulsions, and Hydroxide Nanoparticles

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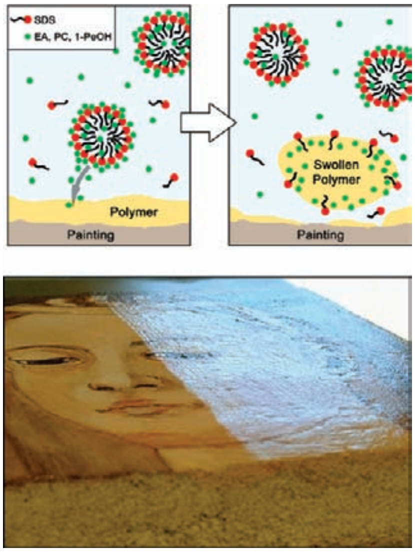
CONSPECTUS



Modern civilization's inherited artworks have a powerful impact on society, from political, sociological, and anthropological points of view, so the conservation of our Cultural Heritage is fundamental for conveying to future generations our culture, traditions, and ways of thinking and behaving. In the conservation of cultural artifacts, scientists intervene in the degradation of often unique handcrafts, resulting from a delicate balance of aging, unpredicted events, environmental conditions, and sometimes incorrect previous restoration treatments, the details of which are often not precisely known.

Nanoscience and nanotechnology are revolutionizing materials science in a pervasive way, in a manner similar to polymer chemistry's revolution of materials science over the preceding century. The continuous development of novel nanoparticle-based materials and the study of physicochemical phenomena at the nanoscale are creating new approaches to conservation science, leading to new methodologies that can "revert" the degradation processes of the works of art, in most cases "restoring" them to their original magnificent appearance.

Until recently, serendipity and experiment have been the most frequent design principles of formulations for either cleaning or consolidation of works of art. Accordingly, the past has witnessed a number of actively detrimental treatments, such as the application of acrylic and vinyl resins to wall paintings, which can irreversibly jeopardize the appearance (or even the continued existence) of irreplaceable works of art. Current research activity in conservation science is largely based on the paradigm that compatibility of materials is the most important prerequisite for obtaining excellent and durable results.

The most advanced current methodologies are (i) the use of water-based micelles and microemulsions (neat or combined with gels) for the removal of accidental contaminants and polymers used in past restorations and (ii) the application of calcium hydroxide nanoparticles for the consolidation of works of art. In this Account, we highlight how conservation science can benefit from the conceptual and the methodological background derived from both soft (microemulsions and micelles for cleaning) and hard (nanoparticles for consolidation) nanoscience.

A combination of different nanotechnologies allows today's conservators to provide, in each restoration step, interventions respectful of the physicochemical characteristics of the materials used by artists. The "palette" of methods provided by nanoscience is continuously enriching the field, and the development of novel nanomaterials and the study of nanoscale physicochemical phenomena will further improve the performance of restoration formulations and our comprehension of degradation mechanisms.

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Introduction

It is well accepted that modern Conservation Science originated from the tragic floods that devastated Florence and Venice in 1966, imposing the search for new methodologies to restore and conserve the immense Cultural Heritage heavily damaged by the flood. A scientific method for conservation of carbonatic materials was proposed for the first time by Enzo Ferroni at the International ICOM Conference in Amsterdam (1969).[1,2] This new method for the "in situ consolidation" of wall paintings was able to "restore", in a two-step series of chemical reactions, the degradation of calcium carbonate, the principal constituent of wall paintings, drastically damaged by the flood. The new Science for Conservation has developed in a fast and healthy way following two main streams: (i) the analytical characterization of the materials constituting the works of art, the characterization of the pictorial technique used by the artists, and the chemical reactions involved in their degradation; (ii) the search for new scientific methods for the restoration/conservation, allowing the transfer to future generations of our Cultural Heritage. The last point will be the object of this Account, where we will review some of the most important methodologies developed, mainly using the cultural framework of soft-condensed matter and nanoscience.

Generally speaking, the restoration of a work of art consists of two distinct aspects:

1. cleaning, which is a *transient* treatment, meant to remove the materials not originally belonging to the work of art.
2. consolidation, which is a *durable* intervention that should remediate, prevent, or slow down further degradation due to aging or external agents.

All of the current research activity in Conservation Science is mainly based on the paradigm that *compatibility* of materials is the most important prerequisite in order to obtain excellent and durable results. In view of this seemingly intuitive, yet novel, awareness, it is clear that the use of polymers for the consolidation of inorganic materials should be avoided as much as possible in the restoration of the original features of the unaltered material.

Currently this is mainly achieved thanks to the tremendous advancements witnessed by nanoscience and nanotechnology that provide theoretical and technical backgrounds to formulate innovative systems for restoration.[3,4]

We pioneered the application of nanoscience to Cultural Heritage conservation, and we devised several methods for the consolidation of wall paintings, for paper and wood deacidification, and for the removal of grime, dirt, polymers, and other organic materials soiling the original artifacts.[5−12] In this Account, we will highlight (as an example of the potential of these new "nanotools") the use of "soft" microemulsions and micelles for cleaning and "hard" nanoparticles for consolidation of works of art.

Degradation of Polymer Resins Used in Past Restoration

Reversibility of the restoration treatment has been presented for decades as a milestone in conservation.[13] This principle has supported several conservators in the usage of polymer resins, made available by the industry since 1960, which were considered the "*panacea*" for the restoration of works of art. Consolidation and protection of paintings, stone, wood, paper, glass, ceramic, and bones was made possible by simple application of organic solutions, through immersion, injection, or brushing, of acrylic, vinylic, and silicone-based polymers and (their) copolymers. Most of these polymers were considered "reversible", that is, the solvent used for the application could be later used for the removal (if desired) of the applied resins.

The large use of polymers was also favored by the "the brilliant water-white color of the polymers" that "makes it possible to secure masses of high light transmission and great optical clarity - because of the remarkable stability of the polymers to the action of heat and light, these properties are permanent" and by the "many striking and beautiful effects can be produced by the incorporation of dyes and pigments".[14]

Unfortunately, the application of polymer coatings induces severe modifications of the main physicochemical properties of artifacts, particularly for inorganic matrices as wall paintings.[15,16] Investigations performed on Paraloid B72 (or Acryloid) (EMA/MA 70:30 w/w; ethyl methacrylate/methyl acrylate; weight average molecular weight 88 000 g/mol; supplier Rohm and Haas (USA)), Elvacite 2046 (*n*BMA/*i*BMA; *n*-butyl methacrylate/*i*-butyl methacrylate), and Primal AC33 (or Rhoplex, EA/MMA 60:40 w/w; ethyl acrylate/methyl methacrylate; viscosity (Pa·s) 6, T_g (°C) 16; supplier Rohm and Haas (USA)) showed that water capillarity, water vapor permeability, and surface wettability of lime mortar change drastically. The application of polymers leads to a strong increase of surface hydrophobicity, to a decrease of about 70−85% of the capillary rise coefficients and 40−50% of the vapor permeability, and to an increase of contact angle from about 30° to 100°.[17]

When the surface is coated with a polymer, salt crystallization occurs within the pores of the wall paintings, generating strong mechanical stress beneath the painted layer (50−100 μm) and leading to the complete disruption of the pictorial layer in a period of time from about 5 to 30−40

FIGURE 1. Mural paintings in *"Templo de los Nichos Pintados"* in Mayapan (Yucatan). The pictures show the degradation that occurred to the paintings from the last restoration in 1999 due to the mowilith DM5 coating.

years, depending on the environmental conditions. The alteration of the natural "breathing" of the surface due to the presence of the polymer increases consistently the deleterious mechanical effect of salt crystallization from the interior of the wall with the complete detachment of the painting from its support, that is, the surface of the work of art. In addition to the degradation of the painted layer promoted by the drastic change of the physicochemical characteristics, polymers themselves degrade, and upon aging they are subjected to molecular weight changes due to cross-linking reactions and chain scissions. The main consequence of cross-linking is the loss of solubility, which makes the application irreversible.[18−20]

Photoaging under UV light was examined by some authors to detect the molecular weight distribution change due to chain scissions or coupling of macroradicals.[18] The overall stability of the polymers was shown to be influenced by the alkyl side groups, particularly in the case of paraloid B66 (*n*BMA; poly(methyl,*n*-butyl methacrylate)) and paraloid B67 (*i*BMA; poly(isobutyl methacrylate)), where relatively longer ester chains are present. In these compounds, the oxidation is favored by hydrogen atoms, either on the methylenes of the *n*-butyl groups in B66 or on the tertiary carbon of the isobutyl groups in B67. Polymers containing *n*-butyl ester groups undergo fast and extensive cross-linking together with some chain scissioning.

Paraloid B72 and paraloid B82 (MMA, poly(methyl methacrylate)) show a good stability toward oxidation due to the presence of the EMA and MMA methacrylic units[19] and seem to be suitable as consolidants and protective agents for applications to wall paintings and other artifacts. However, it is important to notice that the composition of commercially available products contains almost 1% *i*-BMA, formed during the polymerization reaction. Even tiny amounts of *i*-BMA may initiate radical formation leading to extensive cross-linking reactions, similarly to paraloid B66 and B67. The difference in paraloid B72 with the other member of this polymer family is mainly related to the slower degradation process but is quite common the evidence of enhanced degradation generated by paraloid B72 (as well as B66 and B67) used in past restorations. The degradation effects are particularly evident in locations where the environmental conditions are severe due to fluctuations of temperature and relative humidity or in very polluted urban areas where photochemical smog favors polymer degradation, as demonstrated in a recent paper by Favaro and co-workers.[20]

Conservation treatments based on resins have produced irreversible degradation of most of Mesoamerican paintings.[21] Recent investigations in the archeological site of Mayapan (Mexico, Post-Classic Age 1200−1450 a.C.) have demonstrated the dramatic conditions of these paintings recently submitted to consolidation and protection treatments with mowilith (vinyl acetate/*n*-butyl acrylate 65:35 w/w copolymer) resins. A photographic documentation reveals that in less than 10 years a relevant portion of the original painting was lost (see Figure 1). This was due to the combination of the mowilith film with extensive salt crystallization processes that quickly destroyed the plaster beneath the paint layer.

In addition to the mechanical degradation, the natural aging of polymer resins generates discoloration and loss of solubility, due to the increase of the polymer molecular weight. At the end of the degradation process, these polymers are very difficult or impossible to remove with conventional neat solvents. Considering the severe side effects generated by the use of polymers and the necessity of their removal, we proposed the use of nanostructured fluids; some examples are highlighted in the following.

Cleaning and Removal of Polymeric Coatings by Means of Amphiphile-Based Systems

Historically, the first application of soft matter concepts was performed in Florence at the end of the 1980s during the restoration of the Renaissance masterpiece by Masaccio, Masolino, and Lippi in the Brancacci Chapel in Florence (1984−1990).[22] Investigations under UV light of the paintings revealed the presence of a multitude of wax spots due to the extinction of votive candles kept close to the wall painting. The removal of this hydrophobic material from the *hydrophilic fresco* painting was obtained using microemulsions.[23−26]

The microemulsion used in Brancacci's paintings was very similar to the so-called "French microemulsion" and was formed by nanosized dodecane droplets, dispersed in an aqueous solution of ammonium[27] dodecylsulfate (surfactant) and 1-butanol (cosurfactant).

The oil in water microemulsion ensured low aggressiveness with respect to the original components of the painted layer, due to the presence of water as a dispersing medium that remained in direct contact with the hydrophilic surface of the wall painting.[24]

Since this pioneering example, several other surfactant-based micellar and microemulsive systems have been used by our group to clean wall paintings and canvases both from accidental contamination and from polymers that have been extensively used as consolidants and protectives in past restorations.

Nanocompartmentalized systems specifically tailored for the removal of paraloid B72, primal AC33, and mowilith DM5 (vinyl acetate/*n*-butyl acrylate 65:35 w/w copolymer; viscosity (Pa·s) 3.5, T_g (°C) 2; supplier Hoechst, Germany) resins have been recently formulated by some of us. Both micelles and swollen micelles work as nanocontainers of solvents that can dissolve polymers to obtain their complete removal from the surface and from the porous texture of the work of art. The detergency capability mainly depends on the very large surface area of micelles and nanodroplets available for interaction with the polymer coating. The water-based system reduces the penetration into the artifact porous matrix that occurs with organic solvents and the associated polymer redissolution into the artifact but also reduces the toxicity of the formulation, offering better and faster performance than pure organic solvents. Table 1 reports the composition of some of the most successful formulations used for cleaning.

Oil in water microemulsion made with sodium dodecyl sulfate (SDS), 1-pentanol (PeOH) as a cosurfactant, and a small amount of a mixture of *p*-xylene and nitro diluent (a mixture of 62% toluene, 15% butyl acetate, 15% ethyl acetate, 6% *n*-butyl alcohol, 2% cellosolve acetate) was shown to be effective for paraloid B72 removal (Classical system; see Table 1). Polar polymer resins such as poly(vinyl acetate), not soluble in the oil mixture above-reported, were successfully removed by using a four-component micellar solution with a high amount of propylene carbonate (PC), which replaced the nonpolar mixture of xylene and nitro diluent (Conegliano system). Previous investigations have shown that PC acts as a cosurfactant inducing a rod-to-sphere micelle transition reducing the size and aggregation number of SDS micelles by increasing the headgroup area.[28,29]

TABLE 1. Composition (% w/w) of Systems Used for Polymer Removal from Wall Paintings[a]

Classical		Conegliano		Mayapan	
component	composition	component	composition	component	composition
water	86.2	water	69	water	73.3
SDS	3.9	SDS	5.1	SDS	3.7
1-PeOH	6.5	1-PeOH	3.9	1-PeOH	7
p-xylene	1.8	PC	22	PC	8
nitro diluent (ND)	1.6			ethyl acetate (EA)	8

[a] *Classical* refers to the first o/w microemulsion formulated for paraloid B72 removal; the other formulations are named after the places where they were used for the first time.

The Conegliano system could also be used for paraloid B72 removal since it favors the swelling of paraloid B72 films, which can be then removed by mechanical action for a complete cleaning of the surface.

Very often paraloid B72 and mowilith DM5 have been used in mixtures or sequentially applied to wall paintings. An ideal system should remove simultaneously both resins. A major improvement in this direction has been recently obtained by adding ethyl acetate (EA) to the Conegliano formulation to obtain the Mayapan micelles, whose composition is reported in Table 1. The aromatic and aliphatic solvents of the Classical formulation are replaced by less toxic solvents. Pure ethyl acetate and propylene carbonate are known to solubilize paraloid B72. They are partially water-soluble (EA 8% w/w, PC 20% w/w), but a saturated aqueous solution of EA and PC provides only partial swelling of the polymer. The addition of SDS and 1-PeOH either to the EA or PC aqueous solutions provides a drastic improvement in the efficiency of the removal process, due to the presence of micelles that provide the large interfacial area necessary for polymer uptake. It is important to stress here that micellar solutions formed by SDS or SDS/PeOH alone are practically ineffective in polymer removal; therefore it is the synergistic action of the presence of micelles and PC that causes the polymer removal. Even better performance was obtained by adding simultaneously 8% EA and 8% PC to aqueous SDS/1-PeOH micelles (Mayapan system). This system allowed a complete cleaning of the surfaces treated with paraloid B72 in a few minutes. The Classical system is very efficient in removing acrylic polymers, but the polymer removal is quite slow compared with the Mayapan micelles. This is probably due to the lower amount of

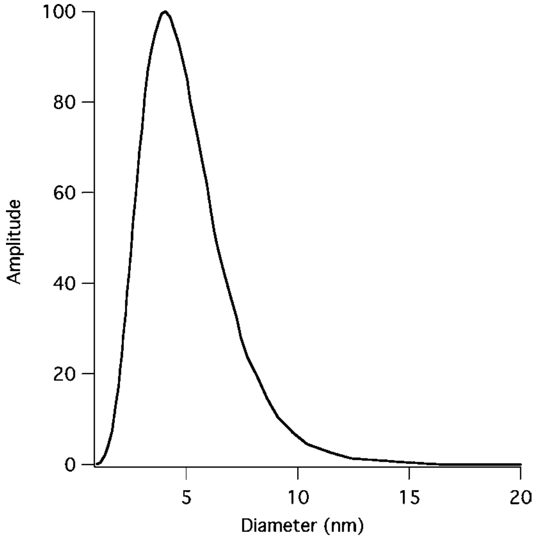

FIGURE 2. Size distribution of the *Mayapan* micellar system obtained from QELS.

organic solvents contained in the former leading to different microstructural features of the system.

It is clear from the above examples that the design of efficient formulations for the tailored removal of polymers requires a deep comprehension of the solubilization mechanisms, which can be more complex than traditional detergency, due to the presence of partially water-soluble organic solvents (cosolvents). To better understand the polymer removal process, we performed swelling tests of polymer films deposited in glass vials and detergency tests on paraloid films on models of wall paintings.

Quasi-elastic light scattering (QELS) is an efficient and noninvasive tool to characterize size and size distribution of complex systems in the nanometer domain. Figure 2 shows that the intensity weighted size distribution of Mayapan micelles is centered around 4 nm with a relatively broad size distribution, while the average droplet diameter of the Classical sys-

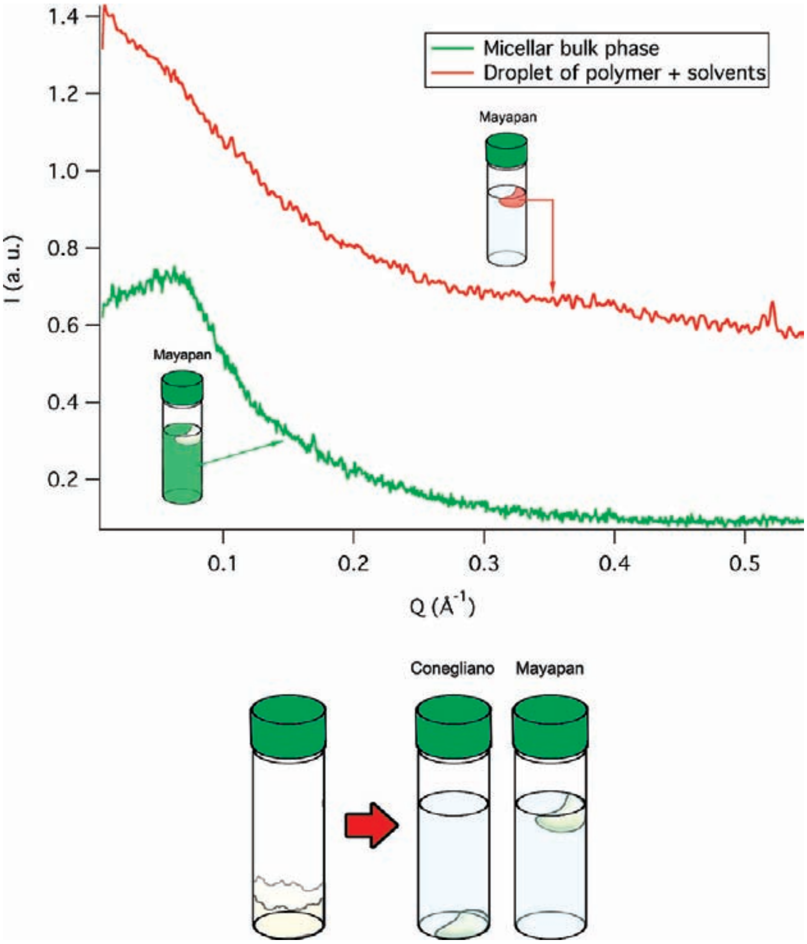

FIGURE 3. Schematic representation (bottom panel) of the differences in the removal mechanisms of paraloid B72 performed by Conegliano and Mayapan formulations. Conegliano system only swells the polymer layer, while the application of Mayapan micelles to a paraloid B72-coated surface results in a liquid−liquid phase separation. SAXS spectra (upper panel) obtained after the application of Mayapan micelles to a paraloid B72-coated surface. The more dense phase (green line) still contains micelles, while the upper phase (red line) contains the polymer dissolved in a blend of EA/PC/PeOH.

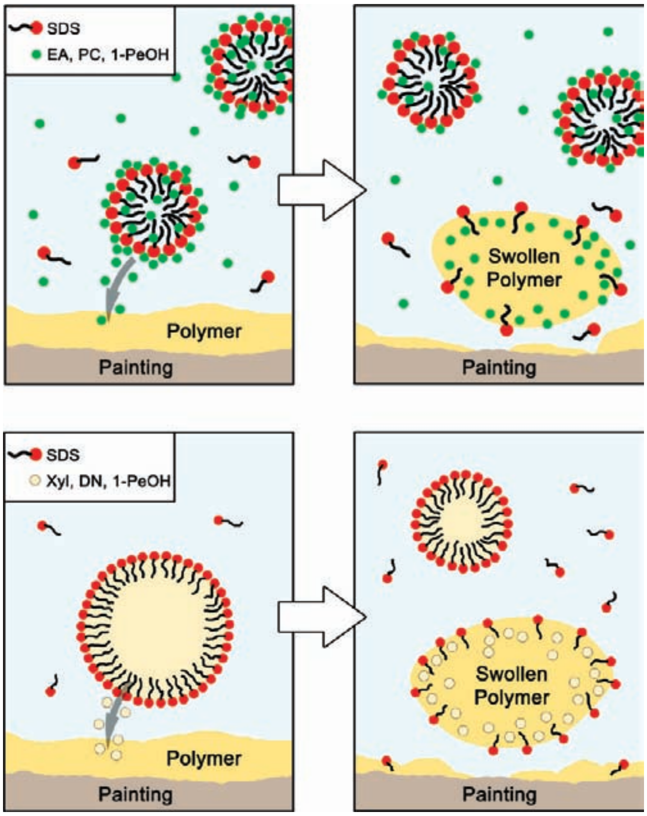

FIGURE 4. Schematic representation of the hypothesized detergency mechanism of the Mayapan (upper panel) and Classical (lower panel) systems. While in the first case the partially water-soluble solvents (EA and PC) partition among the aqueous and the micellar phase, in the second case, we have a "traditional" microemulsion where the water-insoluble oil core is dispersed in water by the presence of a surfactant film. The "naked" micelles (SDS/PeOH) do not detatch paraloid B72 from the surfaces. In this cartoon, the Mayapan micelles act as solvent carriers and quickly mediate their interaction with the polymer, which "chooses" the right amounts of solvents to undergo a swelling process. It is worth noticing that the micelles of the Mayapan system, after the interaction with paraloid B72, change about 10% in size, while the microdroplets of the Classical system get sensibly smaller; for microemulsions, the kinetics is slower, due to the oil confinement in the micellar core. After the interaction, the micelles decrease in size because of the solvent release.

tem is about 17 nm with polydispersity of 25%, typical of a common o/w microemulsion. The smaller micellar size, together with the presence of specific organic solvents, results, for a given surfactant content in a very high interfacial area that is correlated to the kinetics of the cleaning process.

The Conegliano "micelles" are characterized by very small aggregates with a hydrodynamic diameter of about 2 nm[28,29] and refer to clusters formed by 7−10 SDS monomers and not to conventional micelles. For the sake of clarity, we indicated these clusters as "micelles". Mayapan "micelles" are similar but present a higher effectiveness toward polymer removal that is nicely illustrated by the results of a semiquantitative test on model systems that we used to compare the removal efficiency of these two systems. Coating the bottom of two vials with a known amount of paraloid B72 (whose thickness is comparable to that spread on art handcraft) and putting the film in contact with Conegliano and Mayapan micellar solutions (see Figure 3, bottom), we found that the Conegliano micelles are able to swell the polymer, but the swollen polymer remains at the bottom of the vial. Mayapan micelles were also able to swell the polymer but in addition a spontaneous detaching of the polymer from the glass was observed with a liquid−liquid phase separation in the micellar phase. This behavior is ideal for polymer removal from artifacts.

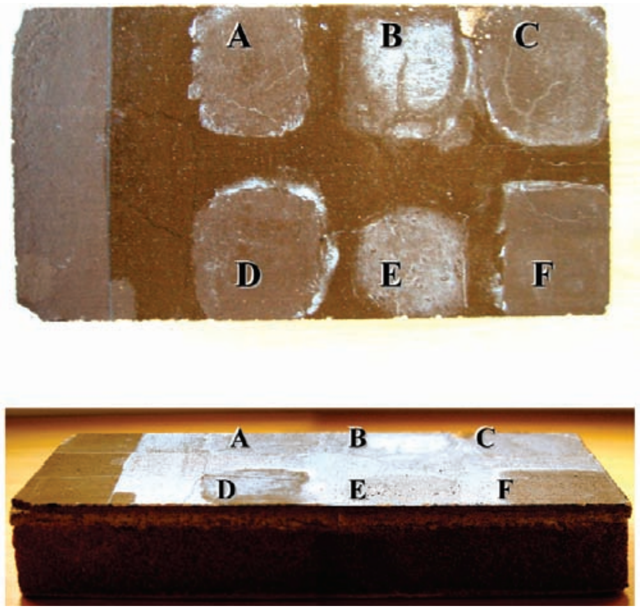

FIGURE 5. Experimental cleaning test on model fresco paintings treated with paraloid B72: (A) water/SDS/1-PeOH/(8%)EA; (B) water/PC; (C) Classical system; (D) Conegliano system; (E) water/EA/PC; (F) Mayapan system.

In order to understand this mechanism, both phases have been investigated with static and dynamic scattering techiniques. Figure 3 reports the SAXS spectra obtained from the polymer-rich and the surfactant-rich phases. The less dense phase contains the polymer and a mixture of H_2O, PeOH, PC, and EA solvents, enriched in the less polar components. The more dense and abundant phase is still a micellar solution but is depleted of the organic phase.

It is clear that the mixture of organic solvents, dispersed in the aqueous medium thanks to the presence of micelles, guarantees specific interactions with the polymer (see Figure 4) suggesting a mechanism where the Mayapan micelles work as a carrier of solvents during the phase separation process that is the final step of the cleaning procedure.

Figure 5 shows a brick with a 1 cm thick lime plaster layer, painted with fresco technique, treated with paraloid B72. Visual

FIGURE 6. Mural painting sample treated, on the right side, with mowilith DM5 under glazing light (center), and SEM pictures of the uncoated (left) and coated (right) surface.

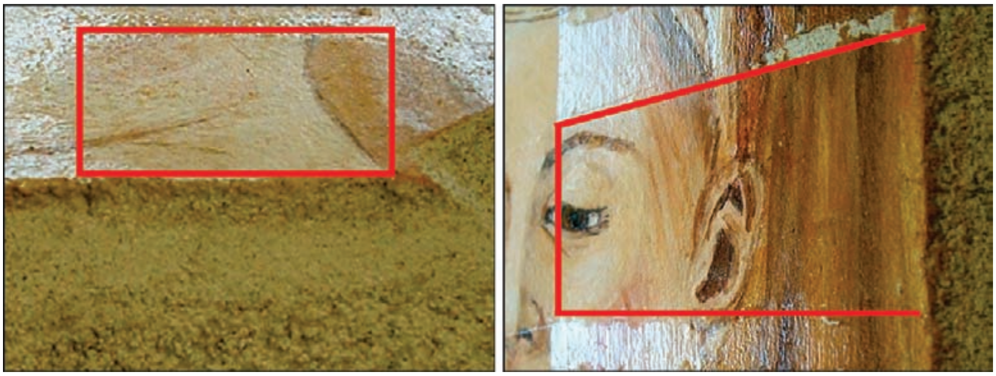

FIGURE 7. Details of the painting surface after removal of mowilith DM5 coating by using micellar solution (Mayapan system).

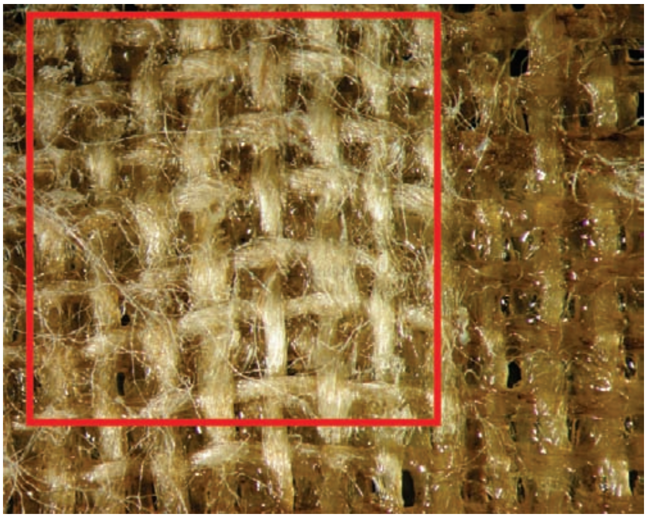

FIGURE 8. Linen canvas glued with mowilith DMC2 for a relining treatment. In the red box, the appearance of the treated area after micellar solution application.

analysis of this model painting after cleaning showed a complete recovery of the optical features of the surface in the area treated with the Mayapan system (see Figure 5F). The Classical and Conegliano systems gave slightly worse results, as is clearly observable from the polymer residues still present in the treated areas as shown in Figure 5, areas C and D, respectively.

As already mentioned, the Mayapan micelles are also active for mowilith DM5 removal. Figures 6 and 7 report illustrative examples of a fresco painting treated with the Mayapan system.

Confinement of Micellar Solutions and Microemulsions in Chemical Gels

Microemulsions and micellar solutions are usually applied over a painted surface by using cellulose-pulp compresses or physical gels soaked with them.[30] In many cases, as in the case of canvas or wood painting cleaning, a more controlled release of the microemulsion is required to avoid the swelling of inorganic and organic binding materials by water, that is, the most abundant component in an oil in water microemulsion.

The advantage of using gels resides in the "easy" manipulation, the possibility of microemulsion and micellar solution confinement into the gel network, and the possibility to make them responsive to external stimuli (i.e., pH, magnetic fields, temperature, light).[31−35]

Gel structure may result from formation of relatively weak physical bonds (i.e., hydrogen bonds or van der Waals interactions) or covalent chemical bonds; both can be responsible for the cross-linking of particles or polymer chains to create the gelled state. In the first case, we refer to a physical gel, in the second to a chemical gel.

FIGURE 9. Wall paintings from Mayan Classic period in Calakmul (Mexico). Calcium hydroxide nanoparticles were used for consolidation.

Among the large number of polymers that can be used for gelation, cellulose derivatives, polyacrylic acids, and polyamines are the most used in the field of conservation science. Unfortunately, these physical gels present some difficulties in their removal and may release residues on the surface of the work of art after the application. Besides, the gels' mesh size is difficult to control during gelation.[36,37]

Chemical gels are characterized by stronger interactions in the gel molecular network. This type of gel behaves like a soft solid, and the mesh size is tunable by controlling the crosslinking during the polymerization reaction.

Chemical gels, based on an acrylamide/bis-acrylamide network and PEG or silane cross-linkers, loaded with the detergent solutions have been recently synthesized and applied to Conservation.[11,38]

The microemulsion release or uptake can be modulated by controlling the gel mesh size or applying a stimulus. In a previous paper,[38] it was shown by SAXS that a microemulsion retains its structure when loaded into the gel. The uptake/release capability of the gel was quantified by analysis of hydration/dehydration curves. Microemulsion-loaded gel was shown to be effective for the removal of paraloid B72 from limestone and wall paintings.

Cleaning tests on canvases, previously treated with adhesives (i.e., mowilith DMC2 (vinylacetate/dibutylmaleate copolymers) and acrylate/methacrylate copolymers) that are normally used for the relining of canvas paintings, have been performed with a chemical gel, tailored in order to have good water retention. The gel was loaded with the Mayapan system specifically developed for the swelling and the removal of acrylate/methacrylate and vinylacetate/butylacrylate copolymers. After a 2-hour application, the capillary sorption of water through the ground and paint layer was restricted to the contact area of gel over the canvas. The swollen polymers were partly removed by the gel, and the complete cleaning was accomplished by gentle mechanical action with a blade (see Figure 8).[39]

Inorganic Nanoparticles for the Consolidation of Wall Paintings

Very often the cleaning process (particularly for wall paintings) cannot be completely performed without a concomitant consolidation of the painted layer. Consolidation is often forced by the degradation of the painted layer enhanced by the polymer, as occurs in Mexico where the unfavorable climate conditions[40,41] increase the rates of polymer degradation generating severe flaking of surfaces and paint detachments in a very short time.

Consolidation of wall paintings and limestone by using compatible material is now achieved by using calcium hydroxide nanoparticle dispersions that are completely compatible with the original material constituting the works of art. They present increased reactivity and dramatically different transport properties in porous media.[42] The high surface area of nanoparticles influences their chemical reactivity, producing just few days after the application a consistent consolidation of the treated surfaces, due to the reaction of hydroxide with CO_2 from the air to give crystalline calcium carbonate (calcite). These positive effects are particularly important in archeological sites where the conservation *in situ* usually requires an immediate intervention after discovery.

Nanoparticles have been used in several restoration workshops in Europe and are extensively used in Mexico for the *in situ* consolidation of paintings (see Figure 9) and limestone in "La Antigua Ciudad Maya de Calakmul", a UNESCO World Heritage Site since 2002 (Campeche, Mexico).[43,44] Nanoparticles of calcium and barium hydroxide have been used in Calakmul for *in situ* consolidation of the wall paintings (from the Classic period (600−700 AD)) discovered during the excavations from 2004 to 2008 in the Structure I of the *Acrópolis Chik Naab*. Figure 9 reports an image of one of the main buildings in the Calakmul area, and some parts of the mural paintings were consolidated by using calcium hydroxide nanoparticles.

The use of hydroxide nanoparticles is not restricted to consolidation of wall paintings but can be used to control the pH in cellulosic material (paper) or wood to avoid the catalytic cleavage of the β-glycosidic bond or the Fenton reaction usually occurring in the presence of transition metal ions, opening new perspective in the conservation of an enormous number of documents and artifacts.[6,7]

Conclusions and Outlook

Conservation science has matured using plenty of methodological tools borrowed from nanoscience. Soft matter, surface science, detergency, and polymer and organic chemistry contribute to this new branch of science. Micelles, microemulsions, and nanoparticle systems are valuable systems for the optimal conservation of artifacts. These systems have many avenues for additional improvements at the hands of researchers.

Improvements of these technologies will be possible through accurate investigations aiming at the knowledge of the following:

- extraction capability and transport mechanisms in microemulsions and micellar solutions
- transport mechanisms and structure of the physical and chemical gels
- extraction capability and transport mechanisms of confined microemulsion and micellar systems
- synthesis of new organic and inorganic nanoparticles and nano- or microcontainers for repairing or self-repairing

These new smart materials add a new palette to the "classical" methodologies for the "cleaning" of works of art. Paraphrasing a well-known sentence we could say that "there is plenty of room" for nanoscience in Conservation.

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BIOGRAPHICAL INFORMATION

Rodorico Giorgi, Ph.D. in Science for Cultural Heritage Conservation at the University of Florence and master in Chemistry in 1996, is currently research fellow at the Department of Chemistry and CSGI. Giorgi's main research activity is in physicochemical characterization of materials, investigation of degradation processes and the development of methodologies for the conservation of works of art materials (wall and canvas paintings, stone, paper, photographs, and wood). Giorgi is author of about 60 publications.

Michele Baglioni is a doctoral candidate in Science for Cultural Heritage Conservation at the University of Florence and holds a Master in Technology for the Conservation of Cultural Heritage. He is currently working in the development of soft matter systems for conservation.

Debora Berti obtained her Laurea Degree in Chemistry in 1993 and a Ph.D. in Physical Chemistry in 1997. She has been Visiting Scientist at the ETH (Zurich) during 1994−1995 and postdoctoral fellow at CSGI until 2000. In 2000, she joined the University of Florence, where she coordinates a research group working on phospholipid and nucleolipid self-assembly. She is the author of more than 60 publications and has presented more than 100 invited and contributed lectures to international conferences. Her background in physical chemistry of surfactant self-assembly has gradually shifted throughout the years to self-assembly of bioinspired and biorelevant functional amphiphiles, using scattering techniques.

Piero Baglioni is a Full Professor of Physical Chemistry at the Department of Chemistry and CSGI of the University of Florence. He is the author of about 300 publications in the field of colloids and interfaces and a pioneer in the application of soft matter to the conservation of Cultural Heritage. He has produced several innovative methods applied worldwide.

FOOTNOTES

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REFERENCES

1 Ferroni, E.; Malaguzzi, V.; Rovida, G. Experimental Study by Diffraction of Heterogeneous Systems as a Preliminary to the Proposal of a Technique for the Restoration of Gypsum Polluted Murals. ICOM-CC Plenary Meeting - The International Council of Museums-Committee for Conservation, Amsterdam, Netherlands, 1969 [Paper read at the Amsterdam ICOM meeting in 1969; copy in ICCROM library, Rome].

2 Ferroni, E.; Baglioni, P. Experiments About the Method for the Restoration of Sulfated Frescoes. In *Proceedings of the Symposium 'Scientific Methodologies Applied to works of Art', Florence, May 2−5, 1984*; Parrini, P. L., Ed.; Montedison Progetto Cultura: Milan, 1986, pp 108−109.

3 Baglioni, P.; Giorgi, R. Soft and Hard Nanomaterials for Restoration and Conservation of Cultural Heritage. *Soft Matter* **2006**, *2*, 293–303.

4 Baglioni, P.; Giorgi, R.; Dei, L. Soft Condensed Matter for the Conservation of Cultural Heritage. *C. R. Chim.* **2008**, *12*, 61–69.

5 Ambrosi, M.; Dei, L.; Giorgi, R.; Neto, C.; Baglioni, P. Colloidal Particles of $Ca(OH)_2$: Properties and Application to Restoration of Frescoes. *Langmuir* **2001**, *17*, 4251–4255.

6 Giorgi, R.; Dei, L.; Ceccato, M.; Schettino, C. V.; Baglioni, P. Nanotechnologies for Conservation of Cultural Heritage: Paper and Canvas Deacidification. *Langmuir* **2002**, *18*, 8198–8203.

7 Giorgi, R.; Bozzi, C.; Dei, L.; Gabbiani, C.; Ninham, B. W.; Baglioni, P. Nanoparticles of $Mg(OH)_2$: Synthesis and Application to Paper Conservation. *Langmuir* **2005**, *21*, 8495–8501.

8 Giorgi, R.; Chelazzi, D.; Baglioni, P. Nanoparticles of Calcium Hydroxide for Wood Conservation. The Deacidification of the Vasa Warship. *Langmuir* **2005**, *21*, 10743–10748.

9 Carretti, E.; Dei, L.; Baglioni, P. Solubilization of Acrylic and Vinyl Polymers in Nanocontainer Solutions. Application of Microemulsions and Micelles to Cultural Heritage. *Langmuir* **2003**, *19*, 7867–7872.

10 Carretti, E.; Giorgi, R.; Berti, D.; Baglioni, P. Oil-in-Water Nanocontainers as Low Environmental Impact Cleaning Tools for Works of Art: Two Case Studies. *Langmuir* **2007**, *23*, 6396–6403.

11 Bonini, M.; Lenz, S.; Giorgi, R.; Baglioni, P. Nanomagnetic Sponges for the Cleaning of Works of Art. *Langmuir* **2007**, *23*, 8681–8685.

12 Carretti, E.; Grassi, S.; Cossalter, M.; Natali, I.; Caminati, G.; Weiss, R. C.; Baglioni, P.; Dei, L. Poly(vinyl alcohol)-Borate Hydro/Cosolvent Gels: Viscoelastic Properties, Solubilizing Power, and Application to Art Conservation. *Langmuir* **2009**, *25*, 8656–8662.

13 Mora, P.; Mora, L.; Philipot, P. *Conservation of Wall Painting*; Butterworths: London, 1984.

14 Neher, H. T. Acrylic Resins. *Ind. Eng. Chem.* **1936**, *28*, 267–271.

15 Resins in Conservation, *Proceedings of the Symposium, Edinburgh, 21 and 22 May, 1982*; Tate, J. O., Tennent, N. H., Eds.; Scottish Society for Conservation and Restoration: Edinburgh, 1983.

16 Horie, C. V. *Materials for Conservation*; Butterworths: London, 1987.

17 Carretti, E.; Dei, L.; Baglioni, P. Aqueous Polyacrylic Acid Based Gels: Physicochemical Properties and Applications in Cultural Heritage Conservation. *Prog. Org. Coat.* **2004**, *49*, 282–289.

18 Lazzari, M.; Chiantore, O. Thermal-Ageing of Paraloid Acrylic Protective Polymers. *Polymer* **2000**, *41*, 6447–6455.

19 Chiantore, O.; Lazzari, M. Photo-Oxidative Stability of Paraloid Acrylic Protective Polymers. *Polymer* **2001**, *42*, 17–27.

20 Favaro, M.; Mendichi, R.; Ossola, F.; Rosso, U.; Simon, S.; Tomasin, P.; Vigato, P. A. Evaluation of Polymers for Conservation Treatments of Outdoor Exposed Stone Monuments. Part I: Photo-Oxidative Weathering. *Polym. Degrad. Stab.* **2006**, *91*, 3083–3096.

21 Orea, H.; Magar, V. A Brief Review of the Conservation of Wall Paintings in Mexico. In *Preprints of the 13th Triennial Meeting ICOM Committee for Conservation, ICOM-CC, Rio de Janeiro, 22−27 September 2002*; Vontobel, R., Ed.; James and James (Science Publishers): London, 2002; p 176.

22 Borgioli, L.; Caminati, G.; Gabrielli, G.; Baglioni, P. Removal of Hydrophobic Impurities from Pictorial Surfaces by Means of Heterogeneous Systems. *Sci. Tech. Cult. Herit.* **1995**, *4*, 67–74.

23 De Gennes, P. G.; Taupin, C. Microemulsions and the Flexibility of Oil/Water Interfaces. *J. Phys. Chem.* **1982**, *86*, 2294–2304.

24 Ferroni, E.; Gabrielli, G.; Caminati, G. Asportazione di Materiali Idrofobi da Superfici Pittoriche Murali Mediante Solubilizzazione in Sistemi Dispersi. In *La Cappella Brancacci, la scienza per Masaccio, Masolino e Filippino Lippi, Quaderni del restauro*; Olivetti: Milan, 1992; pp 162−171.

25 Friberg, S. E.; Flaim, T. Surfactant Association Structures. In *Inorganic Reactions In Organized Media*; Holt, S. L., Ed.; ACS Symposium Series 177; American Chemical Society: Washington, DC, 1982; pp 1−17.

26 Fontell, K.; Ceglie, A.; Lindman, B.; Ninham, B. W. Some Observations on Phase Diagrams and Structure in Binary and Ternary Systems of Didodecyldimethylammonium Bromide. *Acta Chem. Scand.* **1986**, *A40*, 247–256.

27 The ammonium counterion was chosen because the painting, after the cleaning from the wax, was consolidated using the Ferroni−Dini method, which uses the ammonium carbonate in the first step of the consolidation process.

28 Palazzo, G.; Fiorentino, D.; Colafemmina, G.; Ceglie, A.; Carretti, E.; Dei, L.; Baglioni, P. Nanostructured Fluids Based on Propylene Carbonate/Water Mixtures. *Langmuir* **2005**, *21*, 6717–6725.

29 Colafemmina, G.; Fiorentino, D.; Ceglie, A.; Carretti, E.; Fratini, E.; Dei, L.; Baglioni, P.; Palazzo, G. Structure of SDS Micelles with Propylene Carbonate as Cosolvent: A PGSE-NMR and SAXS Study. *J. Phys. Chem. B* **2007**, *111*, 7184–7193.

30 Carretti, E.; Fratini, E.; Berti, D.; Dei, L.; Baglioni, P. Nanoscience for Art Conservation: Oil-in-Water Microemulsions Embedded in a Polymeric Network for the Cleaning of Works of Art. *Angew. Chem., Int. Ed.* **2009**, *48*, 8966–8969.

31 Baglioni, P.; Dei, L.; Carretti, E.; Giorgi, R. Gels for the Conservation of Cultural Heritage. *Langmuir* **2009**, *25*, 8373–8374, and references therein.

32 Carretti, E.; Dei, L.; Weiss, R. G. Soft Matter and Art Conservation: Rheoreversible Gels and Beyond. *Soft Matter* **2005**, *1*, 17–22.

33 Peng, F.; Li, G.; Liu, X.; Wu, S.; Tong, Z. Redox-Responsive Gel−Sol/Sol−Gel Transition in Poly(acrylic acid) Aqueous Solution Containing Fe(III) Ions Switched by Light. *J. Am. Chem. Soc.* **2008**, *130*, 16166–16167.

34 Liu, Q.; Wang, Y.; Li, W.; Wu, L. Structural Characterization and Chemical Response of a Ag-Coordinated Supramolecular Gel. *Langmuir* **2007**, *23*, 8217–8223.

35 Carretti, E.; Dei, L.; Baglioni, P.; Weiss, R. G. Synthesis and Characterization of Gels from Polyallylamine and Carbon Dioxide as Gellant. *J. Am. Chem. Soc.* **2003**, *125*, 5121–5129.

36 Wolbers, R. C. *Cleaning Painted Surfaces: Aqueous Methods*; Archetype Publications: London, 2000.

37 Stulik, S.; Miller, D.; Khanjian, H.; Khandekar, N.; Wolbers, R.; Carlson, J.; Petersen, W. C. In *Solvent Gels for the Cleaning of Works of Art: The Residue Question*; Dorge, V., Ed.; The Getty Conservation Institute: Los Angeles, 2004; pp 18−83 and references therein.

38 Bonini, M.; Lenz, S.; Falletta, E.; Ridi, F.; Carretti, E.; Fratini, E.; Wiedenmann, A.; Baglioni, P. Acrylamide-Based Magnetic Nanosponges: A New Smart Nanocomposite Material. *Langmuir* **2008**, *24*, 12644–12650.

39 Chevalier, A.; Chelazzi, D.; Baglioni, P.; Giorgi, R.; Carretti, E.; Stuke, M.; Menu, M.; Duchamp, R. Extraction d'Adhésifs de Rentoilage en Peinture de Chevalet: Nouvelle Approche. In *Proceedings of the 15th Triennal Conference ICOM Committee for Conservation, New Delhi, September 22−26*; Bridgland, J., Ed.; Allied Publishers Pvt. Ltd: New Delhi, 2008; Vol. II, pp 581−589.

40 Riederer, J. The Restoration of Archaeological Monuments in the Tropical Climate. In *Proceedings of 7th Triennial ICOM Meeting, Copenhagen, 10−14 September 1984*; De Froment, D., Ed.; ICOM Committee for Conservation: Paris, 1984; pp 21−22.

41 Espinosa, A. Conservation and Restoration of the Murals of the Temple of the Paintings in Bonampak. In *Proceedings of in situ Archaeological Conservation, 6−13 April 1986, Mexico City*; Hodges, H. W. M., Ed.; INAH: Mexico City, 1987; pp 84−89.

42 Odom, T. W.; Pileni, M.-P. Nanoscience (guest editorial). *Acc. Chem. Res.* **2008**, *41*, 1565 and articles collected in this special issue.

43 Giorgi, R.; Chelazzi D.; Carrasco, R.; Colon, M.; Desprat, A.; Baglioni, P. The Maya Site of Calakmul: In situ Preservation of Wall Paintings and Limestone by Using Nanotechnologies. *Proceedings of the IIC Congress 2006, Munich - The Object in Context: Crossing Conservation Boundaries*; Saunders, D., Townsend, J. H., Woodcock, S., Eds.; James and James: London, 2006; pp 162−169.

44 Giorgi, R.; Dei, L.; Baglioni, P. A New Method for Consolidating Wall Paintings Based on Dispersions of Lime in Alcohol. *Stud. Conserv.* **2000**, *45*, 154–161.