Advanced methodologies for the cleaning of works of art

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Cultural heritage assets constitute a fundamental socioeconomic resource, but the actual works of art need to be maintained, counteracting degradation processes, to transfer these benefits to future generations. In particular, the removal of soil, aged coatings, and vandalism/overpaints is one of the most needed interventions in art restoration. Traditional cleaning methodologies, based on classical solution and polymer chemistry, only grant limited control of the cleaning interventions, with the risk of affecting the original components of the artifacts, and often involving the use of toxic or non-environmentally friendly compounds. Alternatively, materials science, colloids, and soft matter have provided valuable and safe solutions in the last decades. This review provides a selection of the most recent and advanced methodologies for the wet cleaning of works of art, spanning from nanostructured cleaning fluids (microemulsions, surfactants swollen micelles) to physical and chemical gels. The new methodologies work on different physico-chemical mechanisms, such as processes for detaching/dewetting, to selectively remove the unwanted layers in sustainable and cost-effective interventions. The best performing systems, like microemulsions confined in "twin-chain" polyvinyl alcohol gels, have been assessed in the cleaning of masterpieces such as works by Pablo Picasso, Jackson Pollock and Roy Lichtenstein. Particular attention is dedicated to "green" chemistry systems, using low-toxicity solvents or bio-based/waste materials to build gel networks. Finally, current trends and future perspectives are given, showing that advanced systems for art cleaning link with transversal fields of crucial importance even beyond Cultural heritage conservation, e.g., detergency, tissue engineering, drug-delivery, food industry and cosmetics.

cleaning, conservation, cultural heritage, gels, microemulsions, surfactants, colloids, nanoscience

1 Introduction

Cultural heritage assets have crucial socioeconomic importance: they are drivers for job creation through tourism, favor inclusiveness, and social cohesion, and are carriers of aesthetical and ethical messages from diverse cultures throughout the history of mankind [1]. Yet, these benefits are hardly maintained if degradation processes, which inevitably affect the artifacts, are not counteracted with time-, cost-effective and sustainable methodologies. Degradation is typically caused by environmental factors (temperature, light, relative humidity and pollutants), natural or anthropogenic disasters and climate changes (floods, fires), microorganisms, and even poor previous restoration interventions carried out using materials with poor physico-chemical compatibility with the artifacts' original components. In response, scientific research has developed methodologies in a similar approach to medicine, where works of art stand as patients, and diagnostic analyses, preventive measures, or materials for remedial conservation are proposed against degradation [2].

Diagnostic techniques have traditionally constituted the first bulk of scientific research in conservation science with many dedicated studies, progressively moving towards

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non-invasive and portable analytical setups [3,4]. Current challenges involve the development and use of sensors with enhanced performances, to detect early degradation stages in the artifacts, and smart technologies to enable active monitoring of buildings and works of art by citizens [4–9].

Inevitably, conservation activities (i.e., remedial intervention) will be necessary to preserve the physical integrity of the artifacts; to this purpose, robust and reliable materials and methodologies are continuously required, coping with the complexity of works of art and their sensitiveness to solvents and other chemicals. In this framework, materials science, colloids, and soft matter have contributed many of the most advanced and sophisticated systems for the restoration of works of art, ranging from protection (e.g., against oxidation, corrosion, or microorganisms) to consolidation (improving cohesion and mechanical properties) and cleaning (removal of soil or aged varnishes/coatings) [10–25]. In addition, some of the generated systems and knowledge can also be used for preventive conservation (e.g., metal organic frameworks or gels as absorbers of pollutants/VOCs) and diagnostics (e.g., graphene and smart portable sensors, nanoinks and gel substrates for surface-enhanced Raman spectroscopy) [26–31]. Among all tasks in remedial conservation, cleaning is one of the most recurring and delicate operations, dealing with the removal of unwanted layers (soil, corrosion patinas, aged varnishes/coatings, overpaints, vandalism) from the surface of works of art, with the crucial requirement of avoiding any alteration of the original components such as dyes, pigments, and binders. Thus, the development of safe and reliable solutions is of uttermost importance to preserve a vast portion of iconic heritage assets like wall and canvas paintings, stone or metal objects, textiles and plastic objects. Solutions need to be time- and cost-effective given the vast number of objects in actual or potential need of cleaning, i.e., easily ranging from thousands to millions of items for a single museum or collection. In addition, recent recommendations such as the EU Green Deal, pose imperatives to devise eco-friendly and sustainable solutions in different fields, including Cultural Heritage preservation. Accordingly, the design of cleaning systems must switch from traditional synthetic polymers and petroleum-based solvents (mineral spirits) to products based on natural or bio-materials.

In the following sections, we recall the materials and methodologies employed in the traditional practice for the wet cleaning of artifacts and describe how new systems have evolved in parallel taking advantage of different physico-chemical frameworks that granted enhanced performances as opposed to classical approaches. Finally, we provide perspectives and open challenges in this field that links to transversal applications in detergency, drug-delivery, cosmetics, food industry and tissue engineering.

2   Classical approaches to cleaning works of art

Traditionally, conservators rely on classical solution chemistry for the removal of soil, grime or aged varnishes/coatings. Essentially, solubility tests or predictions via solubility parameters are used to select solvents (or solvent blends) able to swell or solubilize the unwanted layers. Ideally, the selection should be such that only the unwanted layers are affected. However, in most cases selectivity is limited, and polymers are used to thicken the solvents and gain some spatial and time control of the cleaning intervention.

Fardi et al. [32] have given an extensive discussion on the use of solubility parameters for cleaning art, while Baij et al. [33] recently reviewed the effects of solvent action on paints. We recall here the fundamental concepts to highlight the main issues and limitations in the classical solubility approach.

The total solubility parameter of a compound (δ_tot) was defined by Hildebrand as the cohesive energy density (CED):

$$\delta_\text{tot}(\text{CED}) = \sqrt{\frac{E_\text{coh}}{V}}, \tag{1}$$

where E_coh is the molar cohesion or potential energy, and V is the molar volume.

For vaporizable compounds, E_coh can be expressed as

$$E_\text{coh} = \Delta H_\text{vap} - RT, \tag{2}$$

where ΔH_vap is the molar enthalpy of vaporization of the compound at absolute temperature T, and R is the molar gas constant. In other words, solubility is expressed as the energy necessary to break intermolecular forces in the compound. Hansen then divided δ_tot into three partial components δ_d, δ_p, and δ_h, to separate the contribution of dispersive, polar, and hydrogen bonding forces, respectively:

$$\delta_\text{tot} = \sqrt{\delta_\text{d}^2 + \delta_\text{p}^2 + \delta_\text{h}^2}. \tag{3}$$

Teas eventually introduced fractional expressions using Hansen solubility parameters:

$$f_\text{d} = \frac{\delta_\text{d}}{\delta_\text{d} + \delta_\text{p} + \delta_\text{h}}, \tag{4}$$

$$f_\text{p} = \frac{\delta_\text{p}}{\delta_\text{d} + \delta_\text{p} + \delta_\text{h}}, \tag{5}$$

$$f_\text{h} = \frac{\delta_\text{h}}{\delta_\text{d} + \delta_\text{p} + \delta_\text{h}}, \tag{6}$$

$$f_\text{d} + f_\text{p} + f_\text{h} = 1. \tag{7}$$

The Teas parameters are usually plotted in two-dimensional (triangular graphs, see Figure 1) or three-dimensional plots, and compounds at close positions in the graphs are considered to have similar solvating properties in terms of hydrophilicity/hydrophobicity [35]. Materials with complex chemical compositions, such as natural varnishes or synthetic coatings, are described in the graphs by the sum of the
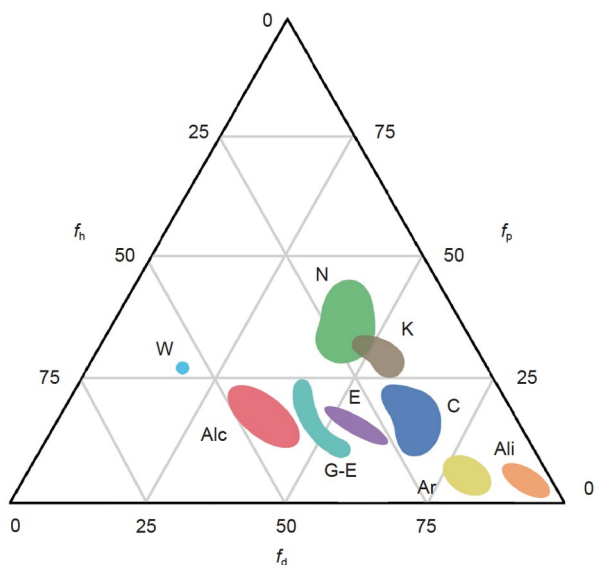
Figure 1 (Color online) Teas solubility diagram indicating the solubility parameters of common families of solvents with similar properties. W, water; N, nitrogen solvents; K, ketones; Alc, alcohols; G-E, glycol ethers and esters; E, esters; C, chlorine solvents; Ar, aromatics; Ali, aliphatics. Readapted with permission from ref. [34]. Copyright © 2013 The Royal Society of Chemistry.

points corresponding to solvents able to solubilize or swell the material. The Italian Central Institute for Restoration (ICR) has developed a program to interactively plot solvents and match them to the swelling areas of different varnishes and coatings commonly found in restoration case studies, including aged materials whose solubility is altered by changes of molecular weight or oxidative processes following exposure to light, temperature and relative humidity. The group-contribution (GC) method is a predictive computational method where the molecular structure of materials is used to calculate their partial solubility parameters [36]. Alternatively, Fardi et al. [32] proposed a Critical Solvent Selection (CSS) methodology that uses experimental data and computer-based data correlations in a multi-step flow-chart, which simulates solubility tests and optimizes the solvent selection so as to minimize risks to binding media in the paint layers underneath the coating/varnish that must be removed.

However, as noted by some authors, Hildebrand and Hansen-based models (and the projection of solubility parameters in Teas charts) can exhibit inaccuracy in describing the solubility range of polymers and the activity coefficients of solvents at infinite dilution (often employed to define solvent-solute interactions). For instance, Baij et al. [33,37] recommended the use of alternative models to predict solvent interactions for art materials. Transport phenomena and polymer elasticity should also be taken into account to model the swelling behavior of paint layers (e.g., made by linseed oil and pigments) affected by solvents. For

instance, the Flory-Rehner model considers the equilibrium between osmotic pressure forces (entropy-driven swelling) and elastic pressure in polymers and could be in principle used to describe swelling in oil paints upon interaction with solvents [38]. Baij et al. [39] also stressed the importance to distinguish between thermodynamics and kinetics when evaluating the capacity of a solvent to affect varnishes and paint layers. Accordingly, the same authors derived a "diffusion-swelling" model that describes much better than pure Fickian diffusion the progressive solvent penetration from the top surface of an oil paint section to the bottom face (where solvent content was measured via ATR-FTIR). The model derivation starts by describing the solvent diffusion coefficient as an exponential function of the polymer volume fraction. This approach was deemed more feasible than using free-volume models, which are more comprehensive but contain several parameters that are not easily accessed experimentally. Eventually, this approach led to an accurate description of the delay times caused by polymer swelling before the solvent reaches the bottom face of the oil paint layers, and allowed obtaining diffusion coefficients at equilibrium swelling for a set of solvents in these experimental conditions. In particular, it was found that strongly swelling solvents like acetone diffuse faster than weakly swelling solvents like water or cyclohexane. The final recommendation by the authors was thus for the scientific community to develop confining systems for aqueous fluids or aliphatic hydrocarbons, or microemulsions formed by these components, fostering their use in cleaning interventions.

Confinement of the cleaning fluids in retentive matrixes is crucial, since the main limitation to the use of solvents remains their scarce selectivity, i.e., they involve the risk of swelling binding media and leaching dyes/pigments [34]. Oil paints can be affected by prolonged contact with water, for instance through hydrolysis of ester bonds or adsorption by hygroscopic clay additives, overall making the paint layer brittle [40]. Contact with acetone has been shown to leach mobile materials, producing a stiffness increase. In the cleaning of acrylic paints, extracted species can include non-ionic surfactants of the original paint formulation (e.g., polyethylene oxides, PEOs, retained in the paint film), in addition to the acrylic binder, pigments, and other additives [41,42]. PEOs aggregates at the surface of paint films, are hygroscopic and readily soluble in water released by swabs during cleaning processes [43,44]. Accordingly, changes in the long term mechanical adhesion or in the bulk film properties can occur in the treated acrylics [42,45]. In this regard, Dillon et al. [45] indicated how the conductivity and ionic strength of aqueous solutions can be adjusted to reduce the extraction of these surfactants and the swelling of acrylic paint layers. In addition, varnish molecules or soil dissolved by non-confined solvents can penetrate in the pores of an artifact, rather than being effectively removed from its

surface. Finally, most solvents used in varnish/coating removal have some toxicity issues, and their confinement reduces the impact on end-users.

Other classical approaches to cleaning formulations involve the use of surfactants, taking advantage of detergency mechanisms, and the use of polymers to thicken aqueous solutions or solvent blends.

Surface active molecules are present in natural products traditionally used for cleaning art, and examples include deoxycholic acid or abietic and aleuritic acids found in bile or in natural resins, respectively. Wolbers [46–49] developed a more systematic approach in the 1980s, covering the selection of surfactants and their combination with enzymes and chelators, or even their use combined with synthetic polymers to thicken solvent blends. Namely, non-ionic surfactants such as Triton X-100, Brij 35, or Tween 20, were indicated as optimal choices for the cleaning of oil paints, having cloud points above room temperature and hydrophilic-lipophilic balances (HLBs) in the 12–17 range, which was deemed safer for prolonged contact with oil paint layers. These non-ionic surfactants have also been used in cleaning aqueous solutions where some diluted ionic strength is included to limit the swelling of water-sensitive paint layers. Surfactants are also mixed with chelators in aqueous solutions and coupled with a microfiber cloth for soil removal [50].

The removal of greasy soil is targeted by surfactant solutions through a series of detergency mechanisms where the amphiphilic molecules adsorb at the surface of soil and art substrates in soil-artifact contact areas, or locally solubilizes the soil inside surfactant micelles. In the latter case, an oil-in-water (o/w) microemulsion can form "*in situ*", provided that the interfacial tension between soil and water is strongly decreased by the surfactant [51]. Wolbers et al. [46] also provided guidelines for the use of regular o/w emulsions that, however, are poorly stable, i.e., only kinetically stable and without the optical clarity and enhanced micelle surface area found in microemulsions. Emulsion stability was achieved by thickening the water phase with cellulose ethers, gums, and polyacrylates. Highly viscous polymer dispersions (HVPDs) were also employed by Wolbers in the so-called "solvent gels", where weakly basic non-ionic cocoamine surfactants (Ethomeen®) are used to deprotonate carboxylic groups in polyacrylic acid (PAA), whose chains unfold by electrostatic repulsion and then stack to increase viscosity. The obtained material cannot be strictly defined as a gel, as it lacks the rheological behavior exhibited by extended 3D chemical networks, e.g., elastic modulus much higher than the viscous over a wide range of frequencies under applied oscillatory stress (see the "Gels" section).

The Ethomeen® surfactants come with a range of HLBs, allowing the thickening of low- or average-polar solvents, which makes solvent-gels versatile and affordable tools.

However, the removal of these pasty HVPDs from treated surfaces involves the use of clearing solvent blends, which can be invasive to the paint layers [52]. In addition, the retentiveness of these systems is not optimal, and their use could be discouraged on highly solvent-sensitive substrates. Overall, despite the progress introduced by these approaches over traditional serendipitous experimentations, crucial improvements were still necessary in the cleaning systems, i.e., increasing their time and spatial control, lowering their environmental impact or toxicity, and improving the overall time-effectiveness of the intervention. These requirements pushed the parallel development of advanced cleaning fluids and confining networks based on different scientific frameworks, such as soft condensed matter and colloids science.

3   Complex cleaning fluids

Parallel to the development of solvent gels and systematic guidelines on surfactants or regular emulsions, an alternative approach to cleaning artifacts was pioneered by Ferroni and Baglioni starting from the 1980s, focusing on the design of microemulsions specifically tailored for the removal of soil or aged coatings from mortar, stone and painted surfaces [53,54]. Microemulsions are thermodynamically stable systems (as opposed to regular emulsions that are only kinetically stable) formed by two immiscible solvents, where the dispersed phase, e.g., an apolar solvent, is confined in nanosized droplets within a continuous phase, e.g., water, thanks to the presence of a surfactant. The dispersed oil droplets are included in self-assembled structures (e.g., spherical or elongated micelles) built by packing of the surfactant molecules that can be assisted by a co-surfactant included in the structure.

The reduced size of the droplets makes microemulsions optically clear and produces a dramatic increase in the interfacial area of the dispersed solvent as opposed to regular emulsions, or to the same mass of bulk (non-dispersed) solvent. The vast interfacial areas, along with the dynamics of the micelles that can exchange solvent and surfactant molecules to target soil/coatings, are key to explaining the boosted cleaning power of these nanostructured fluids. As indicated in a seminal work by De Gennes and Taupin [55] in 1982, to obtain stable microemulsions from a water/oil/surfactant system, the surfactant must be able to saturate the oil interface, and the resulting film must have low rigidity to allow small radii of curvature. In addition, long-range interactions among surfactant molecules must be weak, to avoid the preferential formation of extended macrocrystalline domains over local structures (micelles). This framework in colloids science and soft matter served as an inspiration for the design of an o/w microemulsion by Ferroni and Baglioni in 1986, where the cleaning task was the

removal of wax spots that were jeopardizing Italian Renaissance frescoes in the Brancacci Chapel, Florence (Italy) [53,54]. In this case, dodecane was dispersed in water using an anionic surfactant (dodecyl ammoniumsulfate) and pentanol as a co-surfactant, the overall system being ca. 87% water and only 10% solvent (w/w). The o/w microemulsion was loaded in a cellulose poultice, which acted as a sorbent to retain the fluid while wax migrated in the micelles. The application led to the removal of the wax spots, recovering the painted surfaces with high effectiveness and a strongly reduced environmental impact, overcoming the limitations of the traditional solvent blends.

This pivotal case study fathered the design of a whole class of products over the last decades, where the selection of solvents and surfactants, and thus the structure and functionality of the cleaning fluids, targeted different types of unwanted layers that needed to be removed from the surface of artifacts [34,56–58].

O/w microemulsions, as defined above, work through detergency in the removal of particulate soil and low molecular weight compounds (fatty acids and triglycerides found in greasy soil, or terpenes in natural varnishes): these layers are removed from substrates by direct inclusion of the soil/compounds in the micelles, or by gradients of osmotic pressure that, following the adsorption of ionic surfactants at the surface of substrate and soil, push water in soil-substrate contact areas [51].

Instead, different kinds of nanostructured fluids and cleaning mechanisms were used to target aged synthetic polymer coatings, such as acrylate and vinyl acetate copolymers, which have been widely employed by conservators as protectives or adhesives on mural and easel paintings, wood, paper, textiles, parchment, leather, and even metals. These coatings are typically yellow and crack upon aging, producing strong aesthetical alterations on artistic surfaces [54,58–61]. In addition, they can produce extensive damage on stone and wall paintings, where the coatings fill and block the substrate porosity; this enhances the pressure induced in the pores by salts contaminants (usually present in these artifacts) as the salt crystals form in narrowed and constrained spaces at the coating-substrate interface [62].

The polymeric chains, globules, and beads, are too large to fit in the nano-sized micelles, but can be removed by taking advantage of different, non-classical cleaning mechanisms promoted by the dynamic exchange of solvent and surfactant molecules from the cleaning fluids to the polymer coatings [56,63–67]. To boost these processes, multi-component fluids were designed where partially water-soluble solvents populate both the continuous water phase and the dispersed micelles. For instance, Baglioni et al. [56,63,68] designed an o/w fluid where ethyl acetate and propylene carbonate (8% w/w each) are partitioned between the continuous phase and the micelles formed by SDS and pentanol (ca. 4% and 7% w/w),

with partition coefficients of 0.7 and 0.3, respectively. This class of cleaning systems, defined more correctly as nanostructured fluids rather than standard microemulsions, has been explored owing to its versatility and effectiveness in the removal of polymeric coatings [69]. Some partially water-soluble molecules are good solvents for the typical synthetic polymers encountered in art conservation, and it was shown that the polymer layer can uptake solvent, surfactant and co-surfactant in proportions dictated by its chemical nature. The solvent/surfactant/molecule migration causes shrinkage and structural re-arrangement in the micelles, and swells polymer beads that soften up and detach from the substrate (see Figure 2) [56,63,70]. The polymer swelling and detachment can be coupled with gentle mechanical cleaning to achieve complete removal of films and coatings from painted surfaces, as was demonstrated in numerous case studies where traditional approaches had previously failed. This novel class of nanostructured fluids was employed with great effectiveness and versatility to address the conservation of cultural heritage assets ranging from Mesoamerican historical sites to the Renaissance and modern/contemporary art production [19,53,56]. In addition to the ethyl acetate and propylene carbonate formulation, current o/w swollen micelle systems feature non-ionic surfactants (alcohol ethoxylates or methoxy-pentadeca(oxyethylene) dodecanoate) and a variety of solvents (see also next section) [57,66]. The non-ionics have a lower critical micellar concentration (CMC, concentration threshold for the formation of surfactant self-assemblies) than ionic surfactants, thus their use reduces the amounts of non-volatile residues in the cleaning systems.

Extensive assessment and validation by end-users worldwide eventually culminated in the market uptake of these cleaning fluids as new benchmarks in art cleaning tools [62].

Recent studies have further elucidated the interaction of these fluids with polymer coatings, highlighting the role of dewetting processes to obtain polymer removal [64–67]. Dewetting is defined as the inverse process of a fluid's spreading on a surface: owing to some instability, thin fluid films can break and withdraw spontaneously from a substrate forming spinodal patterns that evolve in patterns of holes with characteristic correlation lengths related to capillary waves and the film thickness [71–74]. It is well known that thin polymer films (<100 nm) dewet from surfaces upon thermal annealing or exposure to solvent vapors, bulk poor solvents, water-solvent blends, and even non-solvents. However, the inclusion of surfactants in water/good-solvent mixtures, as in the cleaning fluids, was shown to induce dewetting even in films with a thickness of few microns, representative of coatings found on works of art, where the process is thermodynamically favored but kinetically inhibited by an energy barrier. Good solvents, along with surfactants, swell the polymer chains, increasing their mobility which is a necessary requisite for dewetting to occur
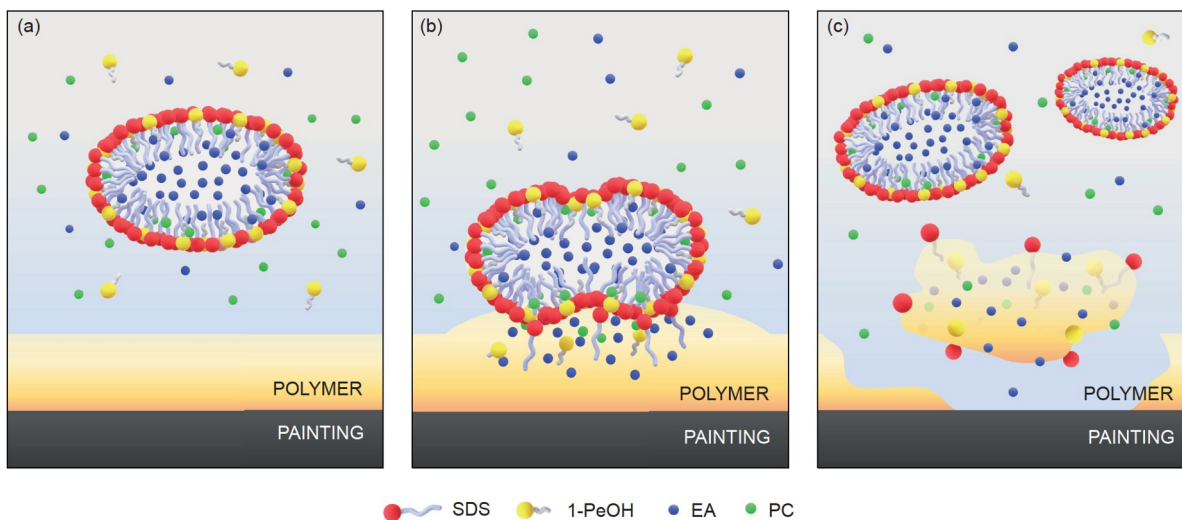
Figure 2 (Color online) Interaction of the continuous phase and swollen micelles of an o/w nanostructured cleaning fluid with a polymer coating on the surface of a painting. (a) The partially water-soluble solvents (also good-solvents for the polymer) are found both in the aqueous continuous phase and in the micelles built by the surfactant and co-surfactant molecules. (b) The aqueous phase and the micelles dynamically exchange solvents, surfactant and co-surfactant molecules with the polymer layer, which uptakes them and swells/softens up, while the micelles shrink and rearrange in smaller aggregates. (c) Beads of the swollen/softened polymer detach from the surface and are removed in the aqueous phase of the fluid. Readapted with permission from ref. [56]. Copyright © 2010 The Royal Society of Chemistry.

[65,67]. Depending on the nature of the solvent and surfactant, micelles can also extract chains with low molecular weight from the swollen polymer [66]. In addition, surfactants also lower the interfacial energy of all the interfaces involved in the dewetting process, decreasing its activation energy. The process is initiated by isolated holes that evolve in the film through nucleation and growth, leading to Voronoi patterns and finally to isolated polymer droplets that detach from the surface (see Figure 3). In other words, surfactants with high surface activity enhance polymer swelling and boost the kinetics of polymer dewetting from substrates, even though they make the polymer-substrate interface less thermodynamically unstable [65,67]. Accordingly, non-ionic surfactants like alcohol ethoxylates with 9–11 carbon chains showed better efficacy than SDS in dewetting coatings cast from polymer solutions [75]. In the case of coatings cast from aqueous polymer emulsions/latexes, the swelling was preferentially observed rather than dewetting, likely due to the presence in the polymer latex of surfactants, which makes dewetting from hydrophilic surfaces less thermodynamically favored [76,77].

Water-in-oil systems (w/o) have also been designed for the removal of hydrophilic soil from water-sensitive surfaces like modern oil or acrylic latex paints [78,79]. The rationale behind this choice is that an apolar continuous phase (paraffin and naphthenes, ethers such as DOWANOL[TM], CELLOSOLVE[TM], and CARBITOL[TM]) can limit the swelling/leaching of the paints, while the dispersed aqueous phase can contain chelators to achieve soil removal [80]. Linear alkylbenzene sulfonate or nonionic ethoxylated/propoxylated branched alcohols (ECOSURF[TM]) were used, along with short chain alcohols as co-surfactants. Further attention and investigation need to be dedicated to these potential tools, possible concerns involving the surfactants amounts needed to obtain stable w/o microemulsions, which can range from 5%–10% to more than 25% (w/w) or even up to >50%. Working with surfactant content >10% might imply extensive rinsing steps after cleaning interventions, which must be carefully evaluated.

Overall, it is crucial to adopt, whenever possible, readily biodegradable or self-cleavable surfactants in nanostructured cleaning fluids, with the goal of reducing their environmental impact as well as lower the amounts of non-volatile residues left on the treated artifacts [57,66,81,82]. Possible candidates include recently proposed gemini surfactants with a carbonate bond in the spacer [83].

Finally, other approaches such as Pickering emulsions have been recently explored to formulate nanostructured fluids for art cleaning tasks. Namely, halloysite nanotubes have been modified with SDS to obtain micelles that encapsulate tetradecane in o/w microemulsions, and are used to clean historical marble surfaces [84,85]. These Pickering emulsions were also thickened with pectin to gain more control in the cleaning action [86].

4 Gels

Most iconic objects in the historical and artistic heritage can show high sensitiveness to solvents or aqueous solutions.
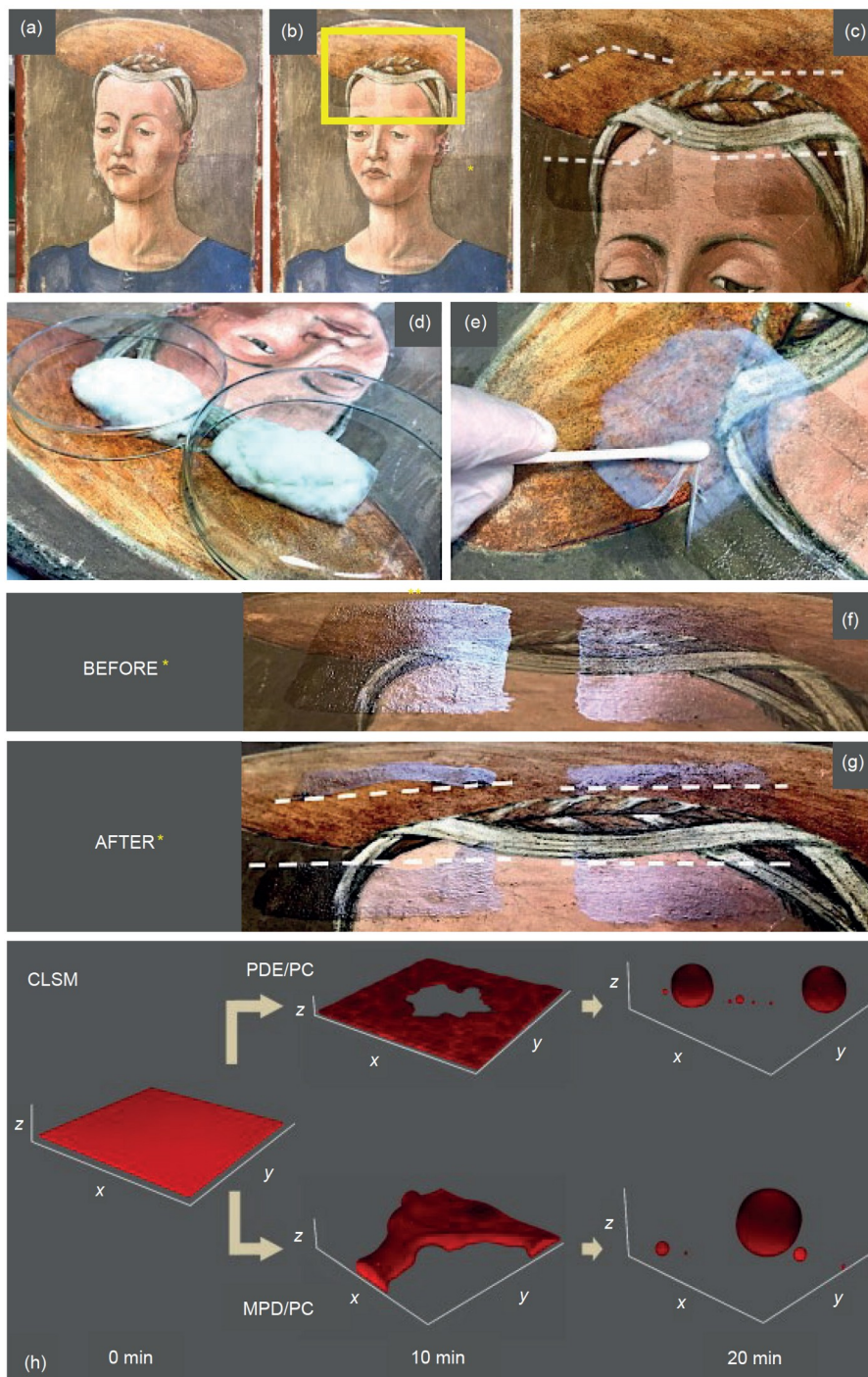
Figure 3 (Color online) Dewetting and detachment of a synthetic polymer coating from the surface of a fresco painting, using an o/w nanostructured cleaning fluid. (a) Visible light image of the fresco painting. (b) The yellow box marked with "*" indicates the area where the fluid was used to remove the polymer coating. (c) The dashed lines highlight the areas where the polymer was removed. (d) Detail of the application of the fluid uploaded in cellulose poultices. (e) A gentle mechanical action is applied to remove the swollen and detached polymer coating after the action of the cleaning fluids. (f)–(g) Grazing light comparison of the painting before (f) and after (g) the removal of the coating. (h) The combined action of good solvents and surfactants dewet the polymer (labeled in red in the confocal laser scanning microscopy images), which forms ripples and eventually isolated droplets on the surface, leading to the removal of the coating simply by using a fluid-loaded cellulose poultice and some gentle mechanical action (swab roll). PDE: pentadecaoxyethylene dodecyl ether; MPD: methyoxy pentadecaoxyethylene dodecanoate; PC: propylene carbonate. Readapted with permission from ref. [67]. Copyright © 2022 with permission from Elsevier.

Examples include ancient and modern ink manuscripts, inked/dyed paper artworks, modern oil and acrylic paintings, plastic materials, parchment, and leather [80,87–89]. When it comes to removing soil, contaminants, or aged adhesives/ coatings from these objects, spatial and time control of solvent-substrate interfacial processes are crucial. This also

applies to cases where only partial removal of varnishes and patinas is required to leave some historical patinas on the surface of the art objects [90]. Poorly retentive and mechanically weak confining networks, like traditional HVPDs and cellulose poultices, can hardly cope with these challenging tasks. Alternatively, gels and molecular scaffolds with enhanced properties have been designed in the last decade in the framework of colloids science and soft matter [34].

Gels are materials of uttermost importance in several transversal scientific and technological fields, spanning from detergency to cosmetics, the food industry, pharmaceutics, and drug delivery. Indeed, several classes of gel or gel-like materials have been traditionally borrowed from these fields by restorers and conservation scientists; examples include gellan and agar gels which will be mentioned further in this section. Then, starting from the early 2000s, gel systems specifically designed for use in conservation science have been progressively designed, physico-chemically characterized, and assessed in art cleaning case studies worldwide.

Gels are distinguished by HVPDs in that they feature a full 3D network of bonds spanning the whole system, which in polymer gels is permeated with finite branched polymers. The gelation process can have diverse physico-chemical drivers that eventually lead from a solution (sol) to the emergence of macroscopic rigidity [91]. The presence of a 3D fully extended bond network translates in structural and dynamic properties that set gels apart from mere polymeric dispersions. The first fundamental classification regards the type of bonds holding the network, which can be distinguished between physical and chemical, as illustrated in Table 1 [91].

Taking advantage of different types of cross-links can lead to gel systems with various mechanical and rheological behaviors, which are broadly classified as strong vs. weak gels. In the standard rheological characterization, gel materials are perturbed with small oscillatory deformation, measuring their stress response over a range of oscillation frequencies.

Typically, the elastic (or storage) modulus, G', and the viscous (or loss) modulus, G'', are obtained by the Fourier transform of the shear relaxation function, and used to evaluate the viscoelastic behavior of the material (see Figure 4). Strong gels have $G'>G''$ and both moduli are nearly frequency-independent over a large frequency range, owing to the presence of localized particles or molecular structures able to store deformation energies over long timescales [91]. Several materials commonly termed "gel-like" have strongly frequency-dependent storage and loss moduli, and fill in the class of weak gels. HVPDs can even exhibit crossover points frequencies above which $G''>G'$ [92].

Another fundamental distinction is between hydrogels, which confine aqueous media or blends of water with polar solvents, and organogels, used to confine average- or low-polarity solvents.

As anticipated in the previous sections, traditional thickeners like cellulose ethers (Klucel®, Tylose, HPMC) and PAA HVPDs have been largely employed in art cleaning, but they only offer limited control on the action of the poorly confined solvents/fluids and are known to leave residues.

Polysaccharides (see Figure 5) have been widely explored to formulate bio-based hydrogels for the cleaning of art, and a comprehensive review was recently given by Passaretti et al. [93,94]. For instance, gellan or agarose have been formulated as rigid (physical) gel sheets that reduce or avoid residues, but are too rigid to adapt to the rough surfaces typically encountered in modern/contemporary paints [18,95].

However, they have been successfully used on flat surfaces such as paper artworks. Upon heating, the gellan polymer is dispersed in water as coils, which partially form double helices when cooling; the helices are alternated with coils, and calcium ions are used to stabilize the structure, e.g., by adding calcium acetate. Concentrations from 1%–2% to 3%–4% are typically used to obtain rigid gel sheets. Applications include the removal of degradation products from paper, the

Table 1 The main types of cross-links building chemical and physical gel networks, with representative examples[a]

Type of cross-link	Procedure	Example
Chemical gels	Cross-linking of existing polymer chains in random (vulcanization) or end-linking process	rubber, poly(vinyl alchol) gel
	Cross-linking polymerization	poly(acryl amide) gel
	Addition polymerization	silicone gel (addition cure)
	Condensation polymerization	silicone gel (condensation cure)
Physical gels	Formed by physical (e.g., hydrogen) bonds	'jello', agarose gel
	Formed by crystallization	cellulose gel
	Formed by ionic bond	gelatin gel
	Formed by self-assembly of small molecules (e.g., organogelators)	steroid gel
	Formed by mechanical dispersion of carbon nanotubes in polypropylene	carbon nanotube, entanglement network

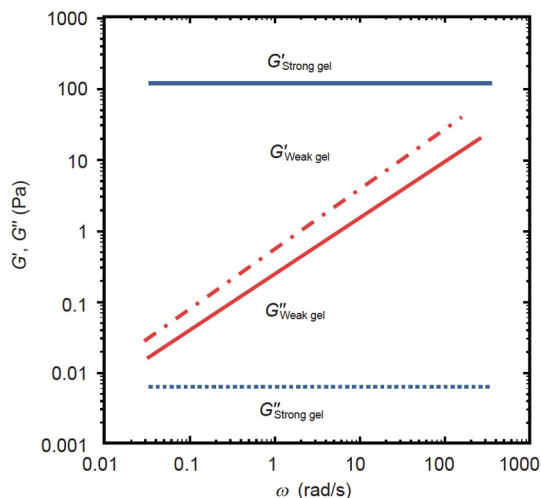a) Readapted with permission from ref. [91]. Copyright © 2018 American Chemical Society.

Figure 4 (Color online) Schematic representation of the dependence on the perturbation frequency of the elastic modulus G' and viscous modulus G'' for strong and weak gels subjected to an oscillatory mechanical perturbation. Readapted with permission from ref. [91]. Copyright © 2018 American Chemical Society.

reduction of oxidized groups, or even targeting biopollution and aged glues by uploading in the gellan, respectively, hydrolats from botanical species or enzymes [96–103]. Agar is composed of agaropectin and agarose, extracted from red seaweeds, and forms coils in water at 80°C, which rearrange upon cooling into a thermo-reversible 3D gel structure built by the coils linked through hydrogen bonds. An extensive review of the use of agar gels for cleaning art was recently provided by Sansonetti et al. [104], covering important applicative aspects. Agar gels have been used as loaded with chelating agents, enzymes, surfactants, or o/w microemul-

sions, and have been formulated as poultices, grated particles, or rigid gels [46,105–108]. Agar can even coordinate copper centers, especially in cooperation with chelating agents, and can thus be used for removing stains from copper or stone [109]. Overall, agar gels are versatile and sustainable tools, but the possible presence of gel residues left on treated surfaces still needs thorough investigation. Hydrogels or viscous dispersions of xanthan gum have been used to remove polyacrylate coatings from paintings or to clean archaeological metals, while chitosan has been mostly used to realize protective coatings in art conservation applications [94,110].

Regarding synthetic polymer hydrogel networks, a plethora of different compounds has been explored over the years for art cleaning tasks, including polyacrylamide, poly (2-hydroxyethyl methacrylate) (p(HEMA)), poly(vinylpyrrolidone) (PVP), and polyvinyl alcohol (PVA) [34].

Chemical networks formed by radical crosslinking of acrylamide were used to remove lining adhesives from canva [111]. The application provided one of the first examples in art cleaning where the meso/nano and microporosity of a hydrogel network were controlled to tailor its water retentiveness and mechanical properties for specific applicative purposes. Successively, pHEMA/PVP semi-interpenetrated networks (SIPNs) were formulated to achieve highly retentive gels and remove particulate soil from poorly bound, powdering and highly water-sensitive paintings, such as the Tibetan *Tang-ka* [112]. These SIPNs were formed by crosslinking HEMA in the presence of linear PVP, which does not participate in the crosslinked network but remains embedded in it. The resulting SIPN gathers the optimal
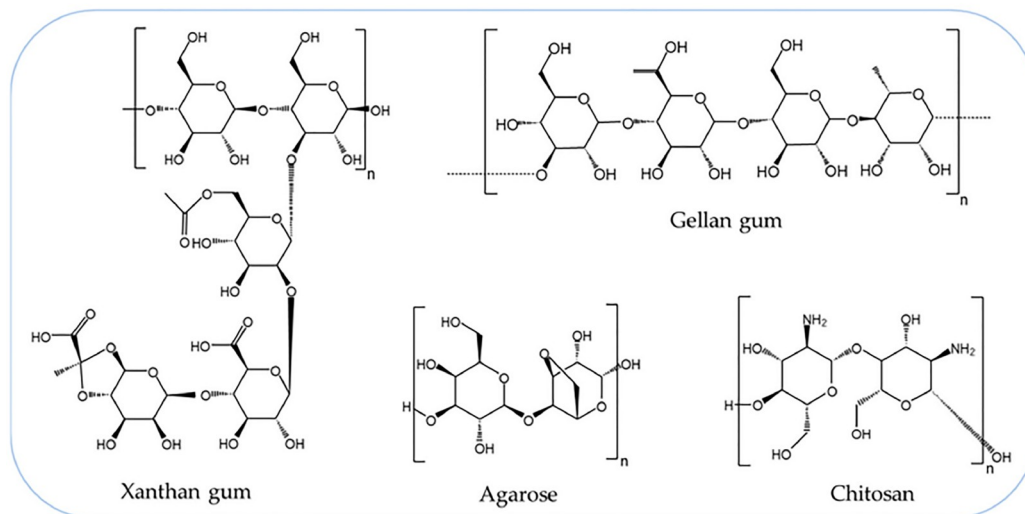

Figure 5 Bio-polymers used for hydrogel formulations in cultural heritage: structural formula of xanthan gum, gellan gum, agarose and chitosan. Reproduced with permission from ref. [94].

mechanical properties of pHEMA and the high hydrophilicity and water retention of PVP. Indeed, these gels marked a significant step forward in art cleaning formulations and were assessed in numerous case studies. On paper artworks, they proved to be more retentive, mechanically resistant and safe than gellan gels, and were uploaded also with enzymes to remove glues and cellulose degradation products [112,113].

These positive results culminated in the publication of applicative guidelines and in the formulation of commercial products based on the pHEMA/PVP systems [114]. In addition, the pHEMA/PVP gels were loaded with o/w microemulsions to produce one of the most advanced cleaning tools, able to target the selective detachment or dewetting of unwanted surface layers, leaving unaltered the original artistic surface underneath. The gels behave as sponges able to upload different nanostructured fluids with only minimal alteration of the SIPN 3D structure (see Figure 6) [115]. The fluids' micelles can undergo slight size reduction. Overall, the combination of non-classical cleaning mechanisms by the fluids with their confinement in the gels' networks allowed the safe removal of aged coatings/adhesives from highly sensitive surfaces (watercolors, wood icons, leather, paper artworks), and of vandalism/graffiti from murals and painted surfaces [17,89,115]. The latter case was particularly

challenging as the chemical composition of the graffiti often matches that of the original paint layer of the artifact, making the safe removal of the vandalism time-consuming with traditional solvent chemistry [17,116,117]. In the case of paper artworks, a frequent challenge is to remove scotch tape adhesives, used as repairs in past restorations, from inked/dyed areas that are highly water- and solvent-sensitive. A recent study showed how the combined gel+fluid system was quickly effective in transferring the fluid through the scotch plastic backing into the adhesive layer, swelling the adhesive and allowing its safe and feasible detachment from inked areas [17]. The fluids composition can be tuned to address different types of backings, e.g., cellulose or plastics.

As effective as pHEMA/PVP SIPNs are, they have one main limitation in that they typically have high elastic moduli, which hinders complete adhesion to the rough painted surfaces commonly found in modern/contemporary paintings. To overcome this limitation, a completely new class of gels was formulated based on polyvinyl alcohol [18,118]. PVA is an optimal candidate for building gel networks, being an almost non-toxic, affordable, and water-soluble synthetic polymer able to produce physical gel networks with optimal properties simply by freeze-thawing (FT) PVA aqueous solutions, without the need of cross-linkers or other additives [18,19]. Upon freezing of PVA
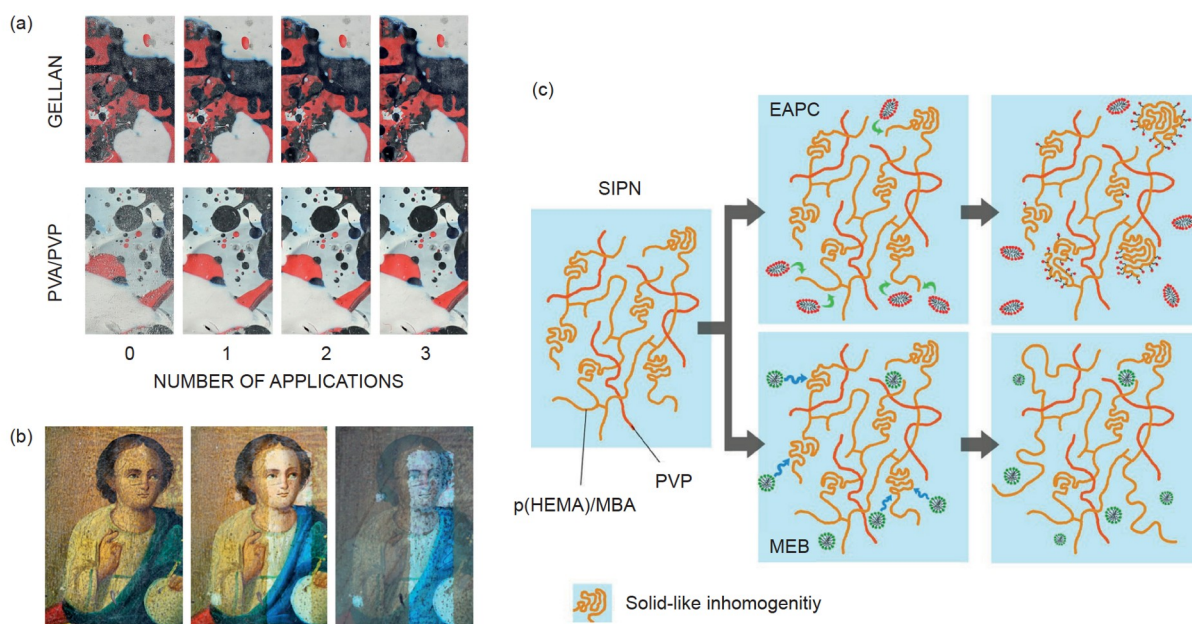

Figure 6 (Color online) (a) The optimal adhesion of PVA-based gels to rough painted surfaces favors the homogeneous removal of soil in a few short applications (5 min each), while only poor removal could be obtained using a rigid gellan sheet. Reproduced with permission from ref. [118]. Copyright © 2022 with permission from Elsevier. (b) Selective removal of an aged, yellowed varnish from the surface of a wood icon, using a pHEMA/PVP SIPN hydrogel loaded with an o/w nanostructured cleaning fluid (Left: before cleaning; Center: cleaned, visible light; Right: cleaned, UV light). (c) Slight alterations were induced on the pHEMA/PVP SIPN by different o/w nanostructured cleaning fluids ("EAPC", containing ethyl acetate and propylene carbonate as solvents, vs. "MEB" containing methyl ethyl ketone and butanol). The size of solid-like inhomogeneities in the SIPN network can be slightly increased or decreased, but the mechanical properties and retentiveness of the gel are not essentially altered. Reproduced with permission from ref. [115]. Copyright © 2018 American Chemical Society.

solutions, the polymer phase separates from water, and is pushed by ice into polymer-crowded regions that become crystallites held by tightly ordered hydrogen bonds [119]. The crystallites act as joints in the forming 3D network that produces hydrogels with high viscoelasticity and tunable flexibility. While FT PVA gels have been vastly explored in several technological fields, a new class of "twin-chain" (TC) PVA gels was recently devised for applications in art cleaning [18]. The key concept in these new materials is the use, in the same pre-gel sol mix, of two types of PVA, differing in their molecular weight and hydrolysis degree. The different hydrophilicity and molecular weight cause the de-mixing of the two polymers in the aqueous medium, to produce micrometric blobs of the lower molecular weight PVA (L-PVA) in the continuous sol formed by its high molecular weight counterpart (H-PVA). When the sol undergoes FT cycles, the L-PVA blobs are elongated while the H-PVA is mainly involved in the formation of gel walls. Upon washing, some of the L-PVA is removed, leaving a spongy, disordered and interconnected porous network in the PVA gel. The difference from single-component FT PVA gels is striking, as the latter feature cylindrical and hexagonally packed pores. The spongy interconnected network of the TC PVA gels likely offers an advantage in soil uptake from treated surfaces through the gel matrix, pulled by evaporation at the gel's upper face. In addition, some of the L-PVA remains blocked in the gel walls during FT, where it provides improved compliance of mechanic stress and flexibility that is unparalleled by either the pHEMA/PVP SIPNs or by rigid gellan sheets (see also Figure 6) [115,118]. These features have made the TC PVA gels the preferred choice in the cleaning of masterpieces such as paintings by Pablo Picasso, Jackson Pollock, Roy Lichtenstein and others, and these tools are now being adopted by the conservation community along with the pHEMA/PVP gels [18,19,120–122]. The TC gels can be uploaded with o/w nanostructured fluids, and it was shown that, when the gel is in contact with a surface, the cleaning process is driven by the osmotic equilibrium inside the gel network: the fluid diffuses freely in the outer pores and interacts with the painted surface, while fresh fluid is continuously recalled at the gel-paint interface thanks to the interconnected porosity and to the equilibrium between free and bound micelles [19]. Thus, the diffusion dynamics of the micelles are optimized by confinement in the TC polymer network, while uncontrolled spreading of the cleaning fluid is avoided, granting time- and space-controlled cleaning action not achievable with the non-confined fluids. These features make the TC gels combined with the o/w fluids the most sophisticated and advanced aqueous systems currently available to conservators.

In addition to the TC gels, PVA was also used in semi-IPNS along with linear PVP: PVA is crosslinked via FT cycles, while PVP acts as a hydrophilic porogen to yield large equilibrium water contents [118].

PVA has also been adopted in gel formulations where the polymer is crosslinked with telechelic PVA (*tel*-PVA, i.e., PVA with an aldehyde at each chain end). The ratio between the two components can be adjusted to tune the porosity/retentiveness and mechanical properties of the gels, which have proven optimal tools for cleaning photographs and paper items [123–125].

Previously to the PVA gels, the polymer had been largely explored to form HVPDs cross-linked through the esterification of the vinyl hydroxyl groups by anions like borate, vanadate or antimonite [126]. The resulting covalent cross-links are dynamic and their density is affected by temperature and other factors including electrostatic interactions and charge-shielding effects, as well as PVA chain excluded volume [127–129]. Also, importantly for art cleaning applications, these HVPDs can upload significant amounts of high- and medium-polarity organic solvents. The type/amount of loaded solvents and the molecular weight of PVA affect the mechanical behavior of the HVPDs, which can have enough viscoelasticity to allow their easy removal from treated surfaces in one piece. The mechanical properties can also be improved by blending PVA with agarose in double polymer networks [130]. The PVA-borax HVPDs can be loaded with o/w microemulsions, and it was shown that, while SDS has a de-structuring effect, the co-surfactant 1-pentanol and the solvent xylene provide an overall structuring effect and increase the mechanical strength of the polymer network, whose relaxation process follows a sticky reptation mechanism where reversible bond breaking and making between associating groups (stickers) controls the dynamics of the associating polymers [131,132]. According to the model, viscosity has a very strong concentration dependence.

Finally, PVA has also been employed to upload chelating agents in polymer dispersions that can film on metallic surfaces and extract metallic ions from corrosion patinas. These systems have been successfully used to clean bronze sculptures with finely carved surfaces, since the dispersions can penetrate small cavities [133]. However, they can only be used on artifacts whose original surface is not mechanically fragile, to avoid the risk of inducing damage when the dry films are peeled off the surface. In the case of sensitive metallic surfaces, interpenetrated networks of pHEMA and PAA can be uploaded with chelators in an aqueous solution, to remove the corrosion products [134]. These pHEMA/PAA IPNs are pH-responsive, and have proved more effective than pHEMA/PVP SIPNs in the cleaning of bronze, owing to the improved chelating power of PAA over PVP. In particular, when the gels are uploaded with highly alkaline solutions of tetraethylenepentamine (TEPA), ternary complexes are formed by carboxylate groups (from PAA) chelating copper ions in cooperation with TEPA.

The other large class of gels, organogels, is being growingly explored owing to the need of complementary tools when artistic surfaces cannot sustain even minimal contact with aqueous solutions, even if confined in retentive matrices. Research in this applicative field has started from synthetic polymers and is now progressing to bio-derived and waste materials [94,135]. Organogels based on the cross-linking of methyl methacrylate (MMA) were prepared as gummy cylinders or sheets loaded with different organic solvents (ethyl acetate, butyl acetate, and ketones), and used for the controlled removal of aged varnishes from the surface of canvas paintings [135]. The uptake of solvents in the polyacrylate network follows different combinations of Fickian diffusion and Case-II transport, i.e., where the relaxation of the polymer chains upon solvent imbibition is the rate-controlling step. Solvent contents ranging from ca. 65% to >90% were obtained; confinement reduces the solvents' volatility and hence their toxicity to the operators. Successively, a PMMA gel loaded with methyl ethyl ketone was formulated with improved retentiveness for use on paper artworks. This gel was used to remove wax spots from 19th century inked manuscripts, and the controlled solvent release avoided damage to the sensitive inked portions of the artifact. Alkyl carbonates, a class of "green" solvents with good activity to several materials, were also uploaded in the PMMA networks, tailoring the systems to the removal of pressure-sensitive tapes from paper artworks [116,136,137]. When the gel is in contact with the tape, the solvent gradually penetrates-through the tape plastic backing layer (as shown by laser scanning confocal microscopy) and swells the underlying adhesive. The swollen/detached adhesive can then be removed by gentle mechanical action, as nicely demonstrated in the cleaning of artworks such as drawings by Keith Haring, which could be safely restored despite the presence of highly sensitive inks.

PVA-borax HVPDs were extended to upload organic solvents by employing benzene-1,4-diboronic acid (BDBA) as a crosslinker [138]. BDBA is soluble and stable in many organic liquids, and allows uploading dimethyl sulfoxide, dimethylformamide, tetrahydrofuran, and 2-ethoxyethanol in the HVPDs. Aged varnishes were feasibly removed from 16th to 18th century oil paintings using these systems.

Moving to bio-based systems, organogels for cleaning art were synthesized using polyhydroxy butyrate (PHB). PHB was used with alginic acid to synthesize a functionalized organogel loaded with chelators for the removal of iron compounds from archaeological wood [139]. However, the authors used chloroform to obtain lower molecular weight PHB in the synthetic route, which could be not sustainable in upscaled productions. PHB was then used to formulate organogels, along with γ-valerolactone (GVL), ethyl lactate (EL), and dimethyl carbonate (DMC, also coupled with biodiesel) as organic solvents. These systems were ex-tensively characterized and effectively used to clean water-sensitive tempera paintings and remove aged terpene varnishes, as well as to clean historical metal heritage [94,140–143]. One limitation in the inclusion of biodiesel is that, being non-volatile, its use implies the need of rinsing steps to remove solvent residues from treated surfaces. To improve the cleaning efficiency, retentiveness, and mechanical properties of the PHB gels, they have been successively combined in sandwich-like composites with nonwoven fabrics of micrometric fibers made by electrospinning technology [144]. Besides providing mechanical improvement, the fabrics participate in the cleaning process, likely by slowing down solvent diffusion and conferring surface micro-roughness to the composites.

Recently, Çakmak et al. [145] proposed bio-based organogels using thiol-ene photopolymerization (TEP) starting from three different bio-based building blocks. In particular, limonene and isosorbide were selected as they have an affinity to terpene-based natural varnishes, while pyrogallol (which in principle has some toxicity since it can form free radicals) introduces aromatic units to promote the removal of aromatic compounds. DMC was used as the solvent. This approach has potential for green gel formulations, but one current limitation involves the low polymerization tendency of some of these systems.

5 "Green" solvents and surfactants in cleaning formulations

The continuing trend toward an ever-improving quality of life is boosting the need for the consumption of vast amounts of chemicals and increasingly sophisticated goods. By now, chemistry has taken on a key role in practically all facets of modernity. The manufacture of industrial chemicals has not always been welcomed by society or seen favorably [146,147]. Even though the chemical industry was formerly viewed as the answer to many of society's demands, concerning skepticism toward it has grown in recent years because of an increase in disasters, spilled materials, or the presence of undesirable substances in commonly used products [148,149]. As the civil community becomes more conscious of environmental challenges, there is an increasing interest in designing new goods, procedures, and services to meet specific economic and environmental objectives [150]. As a result, "green" methodologies are deeply permeating today's modern society, developing chemical reactions and processes to ensure improved efficiency, safety, and cleanliness in terms of decreased waste [151]. In this framework, "Green chemistry" emerges as a core pillar that represents a fundamental application of sustainable development and industrial ecology to reduce the usage and handling of hazardous compounds. It follows that minimizing the raw

materials employed, and reducing the buildup of hazardous products and wastes, are indeed complementary to the use of renewable resources aimed to maximize the recycling of materials, towards a more cost-effective chemistry [152,153]. Recently, the path to eco-sustainability was implemented as a major strategy for achieving climate neutrality on a European level. According to this principle, the "Green Deal" was proposed by the European Commission in late 2019 as a European transition plan which focuses on halving carbon emissions by 2030 and achieving carbon neutrality by 2050. As a matter of fact, Europe seeks mitigation of the global warming rate by implementing an all-encompassing approach that, through intermediate phases, allows concurrent regulation activities in a multitude of sectors, such as industrial manufacturing, energetic production, transportation, finance, and agriculture [150,154,155].

Because the huge European cultural heritage constitutes a significant part of the social-cultural landscape of Europe, its preservation must confront the growing awareness of the Green Deal imperatives. Despite certain developments backed by research over the last years, the traditional materials and procedures employed in current remedial and preventative conservation practices do not always fulfill the criteria for durability, sustainability, or cost-effectiveness. Indeed, while conservators are globally adopting aqueous systems in wet cleaning, conservation practice typically relies on time-consuming or energy-intensive processes. In addition, there is the need to replace unfriendly materials that remain in the traditional approach, including silicones and petroleum-based solvents such as mineral spirits, with "Green chemistry" solutions. It has become crucial to suggest new eco-friendly and sustainable materials and strategies to protect, maintain, and restore cultural heritage to solve these issues.

In this sense, some large industrial enterprises have produced so far multiple solvent selection recommendations in a variety of formats during the last ten years, contributing to the continuous evolution of regulations. These selections are generally based on Safety, Health, and Environment (SH&E) criteria, and on energy consumption. Specifically, importance is given to the energy production requirements and the available options to recover some of these energetic demands. The energy recovery depends on the solvent type and can be achieved by incineration or by solvent recycling *via* distillation. Additionally, solvent classification is also dependent on hazard and risk codes, as well as legal exposure limits [156–158]. Major pharmaceutical companies such as Sanofi, AstraZeneca, GlaxoSmithKline (GSK), and Phizer, between 2010 and 2016, made strong contributions in providing and updating this bulk of recommendations. However, the classifications introduced so far cover only in part the vast pool of industrially employed solvents. Academia and industrial enterprises established together, in 2005, the

American Chemical Society's Green Chemistry Institute Pharmaceutical Roundtable (ACS GCI GCI-PR), which has recently created a solvent reference open access database collecting recommendations and information supplied by Pfizer and AstraZeneca. In addition, further classifications and assessment updates were recently provided by several researchers [156–164].

In this section, we provide an updated summarizing classification that includes the final scores currently available for solvents used in the traditional conservation practice and in the current state-of-the-art methodologies for the cleaning of works of art. These final scores are expressed by institutions using a color assignment, where a red flag indicates a highly hazardous solvent (major issues), a yellow flag a problematic solvent (some issues), and a green flag a recommended solvent (few/no issues).

We added color scores for traditional and recently used cleaning solvents that were missing from the industrial/academic surveys. The added solvents were scored according to the Innovative Medicines Initiative (IMI)-CHEM21indications, which use the most recent and stringent combination of SH&E criteria (taken from REACh and SDS sheets available from producers) [156].

The same approach was used to score surfactants currently used in the cleaning of works of art.

Finally, we also calculated a global color score for each chemical that weighs all the final scores given to it by different institutions. First, we assigned a numerical value of 1 to red flags, 2 to yellow flags, and 3 to green flags. The sum was then divided by the total number of score entries given to each chemical by all the considered institutions, using two decimal digits for the result. We chose to ignore "unclassified" entries in the global score evaluation. For instance, 1-propanol has 0 red flags, 1 yellow flag, 2 green flags, and 5 "unclassified" entries, yielding a global score of 2.67. The global scores were also translated in colors, from deep red (lower end) to yellow (average values) up to deep green (high end). The full tables with the final and global scores for solvents/surfactants are reported in the Supporting Information file.

In Figures 7 and 8 we show a visual synthetic representation of the global scores (color scale) for the solvents and surfactants that we evaluated.

Overall, among the classes of solvents used in art cleaning interventions, the highest global "green" metrics scores are exhibited by alcohols, ketones, and alkyl carbonate esters.

Regarding surfactants, most of the used compounds have good scores, except cocoamines. Alcohol ethoxylates are generally classified as potentially able to accumulate in the environment, and thus classified as toxic to aquatic life. However, the alcohol ethoxylate surfactants proposed so far in art cleaning formulations are considered as readily cleavable or biodegradable [57,82,83].
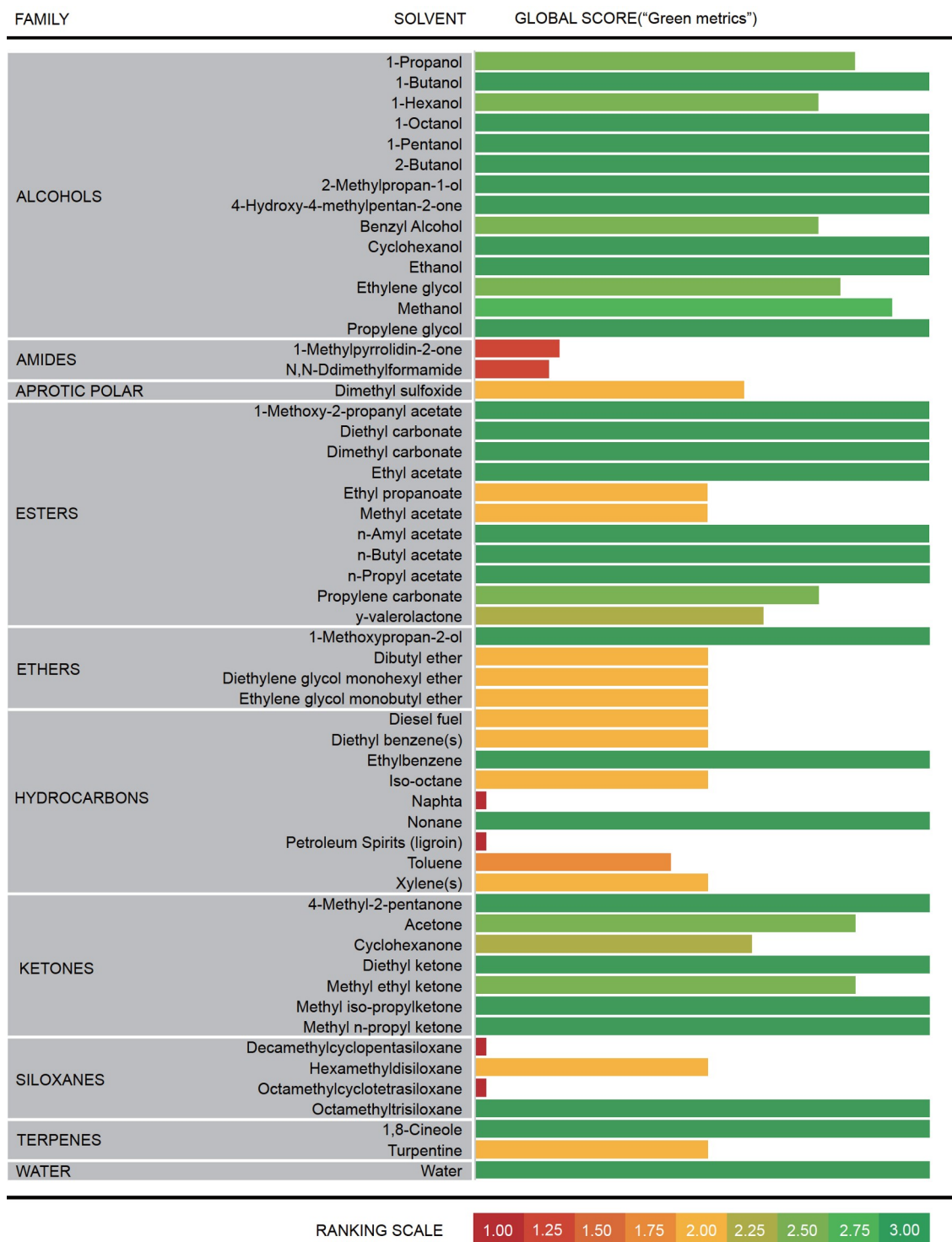
Figure 7 (Color online) Graphical representation of the global score that averages, for each solvent, the "green" metrics scores provided by industrial and academic institutions [156–160,162,163]. The figure includes the solvents used in the traditional conservation practice and in the current state-of-the-art methodologies for the cleaning of works of art. For the main references to the use of these solvents in cleaning formulations see refs. [34,46,47,54,57,62,78,79,114,144].

6 Conclusions and future perspectives

Materials science, colloids, and soft condensed matter have provided (and are providing) the most sophisticated and effective solutions for the safe and selective removal of soil, degradation products, aged coatings, and vandalism from the surface of works of art. Nanostructured cleaning fluids, such as microemulsions or swollen micelles, have improved over
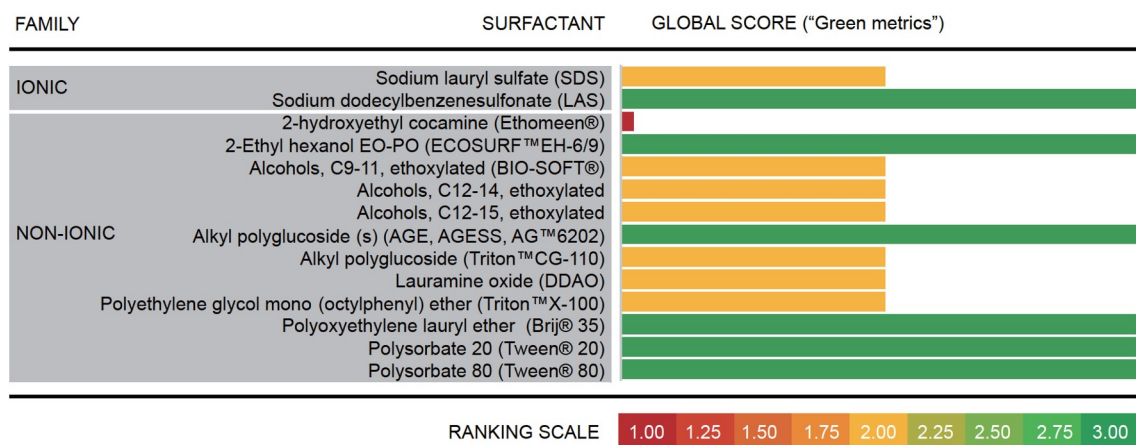
Figure 8 (Color online) Graphical representation of the global score that averages, for each surfactant, the "green" metrics scores provided by industrial and academic institutions [156]. The figure includes the surfactants used in the traditional conservation practice and in the current state-of-the-art methodologies for the cleaning of works of art. Other common names for the surfactants in the figure are as follows: Sodium lauryl sulfate (Sodium Dodecyl Sulfate, SDS); Lauramine oxide (dodecyldimethylamine oxide, DDAO); Polyethylene glycol mono(octylphenyl) ether (Triton™ X-100); Polysorbate 20/80 (Tween™ 20/80); Alkyl polyglucosides (AGE, AGESS, AGTM 6202); Polyoxyethylene lauryl ether (Brij™ 35); 2-hydroxyethyl cocoamine (ETHOMEEN®). For the main references to the use of these surfactants in cleaning formulations see refs. [34,46,47,54,57,62,78,79,114,144].

traditional solvent blends, taking advantage of non-classical cleaning mechanisms that work on dewetting or swelling/detachment processes. In addition, novel confining systems have been designed to overcome the limitations of solvent thickeners. Polymer gels have shown excellent performances in cleaning operations on masterpieces spanning from classic art to the Renaissance and modern/contemporary production, where requirements such as optimal mechanical properties and high retentiveness are imperatives to all cleaning systems. The current benchmark for the wet cleaning of art is constituted by the combined gels and nanostructured fluids, which are the most efficient and advanced tools currently available to conservators for this kind of restoration tasks. Synthetic polymers like polyvinyl alcohol and polyvinyl pyrrolidone are optimal choices for formulating physical gels with good mechanical properties, adhesivity to surfaces, and retentiveness, such as the recent "twin-chain" PVA gels.

Current and future trends in the design of gelled systems for cultural heritage preservation, involve the development of synthetic materials that mimic natural tissues, or the direct employment of bio-based and waste polymers to build the gel networks. In the first case, an approach that has been growingly adopted is to vary the architecture of network strands such as graft polymers [165,166]. Parameters like the degree of polymerization of the side chains and their grafting density can be controlled to tune the structures and physicochemical properties of the network.

Figure 9 shows a state diagram where different graft architectures are obtained as a function of their chemical structure and composition. For instance, in the "Comb" regime, both side chains and backbones of graft polymers interpenetrate and remain ideal, while in the "Bottlebrush"

regime excluded volume interactions between densely grafted side chains can cause the backbones or side chains to stretch to maintain a constant monomer density. Architectures such as extended backbones (Stretched Backbone, SBB), stretched side chains (Stretched Side Chain, SSC), and fully stretched side chains (Rod-like Side Chain, RSC) can
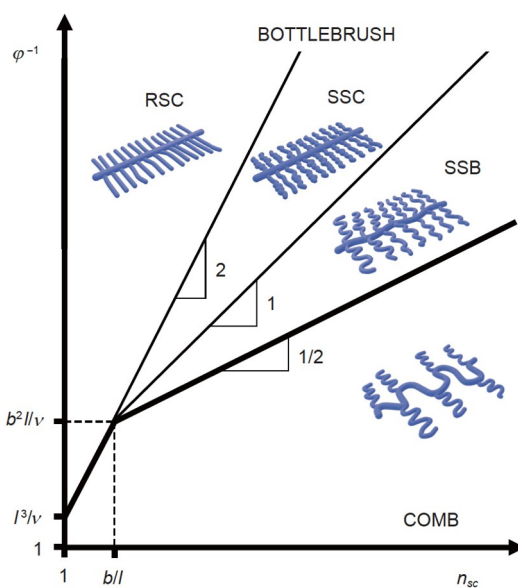

Figure 9 (Color online) Diagram of states of graft polymers in a melt, with bond length l, Kuhn length of the backbone b (i.e., the length of a segment in a chain treated as made up of freely jointed segments), degree of polymerization of the side chains n_{sc}, and monomer excluded volume v (i.e., inaccessible to other molecules in the system). φ is the monomers partitioning between a side chain and backbone spacer between two neighboring side chains ("dilution" of the backbone). SBB, stretched backbone regime; SSC, stretched side chain regime; RSC, rod-like side chain regime. Logarithmic scales. Adapted with permission from ref. [166]. Copyright © 2017 American Chemical Society.

thus be obtained.

Regarding the use of bio-derived polymers, current trends and future perspectives involve mixed structures where low-toxicity polymers (e.g., PVA) interact with bio-materials (e. g., starch) to build gel and scaffolds, or the complete replacement of synthetic polymers with materials derived from agricultural waste or vegetable sources as opposed to petroleum-based products [167,168]. In the second case, current examples include the polyhydroxy butyrate gels, as well as scaffolds of bio-based polyurethanes from castor oil, which have already found application as pollutants absorbers in the preventive conservation of artifacts [169–172]. Chemically crosslinked networks of chitosan, L-cysteine, and itaconic anhydride have been proposed by Lai et al., demonstrating metallic ions' uptake capacity [173]. Other promising networks could be realized via the so-called Michael addition reaction, yielding hydrogels from renewable and biodegradable sources [173–175].

"Green" solvents, such as alkyl carbonates, are progressively replacing the traditional solvents used in the conservation practice, and we provided here a summarizing overview of the "green" chemistry scores for solvents and surfactants currently used in the cleaning of works of art. Future perspectives in this sense regard the use of deep eutectic solvents, an emerging class of mixtures with significantly depressed melting points compared to their neat parental solvents. These materials have great potential in several applicative fields, being affordable, "green" and characterized by many tunable physicochemical properties. Hansen et al. [176] recently provided an exhaustive review on these highly promising fluids, and their use in the cleaning of artifacts is still an open field where only a few attempts have been tried. Ionic liquids constitute another class of fluids that has a promising impact in art cleaning, for instance, for fungi and bacteria removal, building on the knowledge gathered on the use of these materials as protectives against biofouling or corrosion [177–182].

Finally, other important perspectives regard the use of microorganisms (and enzymes) as tools for removing organic or inorganic unwanted layers. Biocleaning is a topic of interest where several methodologies have been proposed, but these are not yet established nor standardized, and involve several requirements, e.g., the safety and effectiveness of the microorganisms employed, and the need for monitoring the treated surfaces before and after treatments to avoid contamination/proliferation [183–190]. The need to tailor the cleaning action on a case-by-case scenario is one of the main limitations to this approach, which is also a crucial concern to conservation scientists developing optical cleaning methods like laser ablation [191–193].

Overall, these perspectives make the preservation of cultural heritage an exciting field where new systems can (and must) be developed. The new solutions designed in this field have a great potential socioeconomic impact, and foster the possibility of transferring new tools also to other transversal industrial and pharmaceutical sectors of fundamental importance.

Supporting Information

The supporting information is available online at tech.scichina.com and link.springer.com. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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