Chapter 1
Innovative Nanomaterials: Principles, Availability and Scopes

Abstract The collaboration between scientists and conservators is fundamental for achieving reliable and durable results in the conservation of works of art. The contribution of scientists lies in the development of both advanced diagnostic techniques and cutting-edge materials for the restoration of artifacts. Colloid and materials science have provided over the last decades a palette of tools for the cleaning, consolidation and pH control of artistic and historical substrates. Nanostructured materials such as microemulsions, micellar solutions, dispersions of alkaline nanoparticles and chemical gels, can be used to effectively counteract the degradation processes without altering the physico–chemical properties of the treated works of art, and to minimize or completely avoid drawbacks. This chapter provides an overview of the principles and scopes that underlie the use of nanomaterials in conservation science, considering the advantages with respect to traditional restoration materials, and the availability of these innovative tools.

1.1 Nanotechnology for Cultural Heritage Preservation

Cultural Heritage is an invaluable patrimony of society, embracing virtually all the artifacts, works of art, objects and intangible attributes that convey artistic, historical or anthropological values. The preservation of such patrimony is the only way to effectively transfer it to future generations, in order to continue the intellectual progress of society while conserving the ancient and modern cultural traditions that characterize our world. Besides intellectual and aesthetic aspects, the preservation of Cultural Heritage allows its valorization and exploitation, with considerable economic advantages. Given its importance, it is not surprising that Cultural Heritage has gathered in the last decades the attention of different professional characters that provided approaches to address numerous conservation issues. In fact, the variety of degradation phenomena that affect works of art

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mirrors the vast array of materials that have been used by mankind since early ages. Therefore both conservators and scientists are involved in finding effective solutions to counteract aging processes due to the action of light, temperature, relative humidity and microorganisms, chemical degradation and physical erosion, or to anthropic causes such as industrial pollution, vandalism, or the mere handling of artifacts. Moreover, restoration interventions can prove—and have often proven—detrimental in the long term whenever scientific criteria are not followed. Based on the experience acquired in the past decades, the use of products that exhibit as much as possible the same physico–chemical properties of the treated artistic or historical substrates (i.e. "compatible" materials) has been highlighted as a valid principle to grant the durability of treatments and to minimize drawbacks. For instance, the treatment of carbonate-based wall paintings with low-compatibility materials such as synthetic organic coatings and adhesives can lead to the alteration and degradation of the painted surface, and compatible inorganic materials have been successfully proposed as an alternative for the consolidation of these works of art, see for instance works by Ambrosi et al. (2001), Giorgi et al. (2010a, b), and Chelazzi et al. (2013).

A multidisciplinary approach to conservation issues is the key for a successful intervention, and the cooperation between scientists, conservators, art historians etc. is fundamental for the refinement of restoration materials and techniques.

In this framework, the role of science is comparable to that of medicine: gathering information on the "anatomy" and "physiology" of the "patient" (i.e. the composition and physico–chemical properties of the artifact) is the first task that is pursued through the use of literature, previous knowledge and both advanced diagnostic and computational techniques that are also fundamental in determining the nature of the "disease" (the degradation processes affecting the artifact) and in checking the effectiveness of restoration interventions (Bianchin et al. 2009; Fantacci et al. 2010). Finally, a "cure" must be found, meaning that tools and materials are to be developed to counteract, stop, and ideally revert the degradation process. Regarding the latter task, which is the focus of this Compendium, materials science has provided a fundamental contribution, and in particular colloids science and nanosciences have emerged in the last four decades as fields of paramount importance, being the source of concepts and tools that have improved dramatically the effectiveness, reliability and durability of restoration interventions (Baglioni and Chelazzi 2013; Baglioni et al. 2013; Baglioni and Giorgi 2006).

The aim of this chapter is to introduce the main innovative conservation materials developed by colloids and material science, namely nanoparticles, nanostructured cleaning fluids and gels. Each section will highlight the principles that underlie the use of such materials, the availability for end users, and the scopes of each class of materials. Then, Chaps. 2–5 will provide practical information on the use of nanoparticles, fluids and gels to address conservation problematics, each chapter dealing with a specific task (e.g. cleaning of easel paintings, consolidation of wall paintings, deacidification of paper, etc.).

Edge length	4	2	1
Total surface area	96	192	384
Total volume	64	64	64
Surface-to-volume ratio	1.5	3	6

Fig. 1.1 Total surface area, volume and surface-to-volume ratio of a (model) cubic mass as it is divided into sub-units. Surface-to-volume ratio increases while total volume remains constant. (Image by Michele Baglioni)

1.2 Nanoparticles

In conservation science, the application of solid particles dispersed in a medium can be preferred to either aqueous or organic solvents solutions for different reasons. The solubility of a consolidant in water might be too low to allow its effective use as an aqueous solution, while the same material could be applied in larger quantities as a solid stably dispersed in an organic solvent. Deacidifying agents such as calcium hydroxide ($Ca(OH)_2$) nanoparticles dispersions can be deposited onto paper fibers, where they neutralize acidity (Giorgi et al. 2002). The particles excess reacts with atmospheric CO_2 and turns into calcium carbonate ($CaCO_3$) that being a milder alkaline compound is not detrimental to aged (oxidized) cellulose, and acts as a solid buffer against recurring acidity. On the other hand, the use of alkaline solutions delivers all at once a large amount of mobile hydroxide ions that could be harmful to cellulose.

In several cases, when dispersions of particles are used for conservation tasks the effectiveness of the application increases as the size of the particles is reduced down to the nanoscale.

Materials are defined as “nanostructured” if they exhibit at least one dimension in the range of 10^{-9} m. Accordingly, nanomaterials can be bidimensional (sheets with nanometric thickness), monodimensional (rods, tubes, wires or cylindrical micelles with nanometric diameter) or zerodimensional.

As the size of particles is reduced, the surface area per unit volume increases, as illustrated in Fig. 1.1. The material’s reactivity is consequently enhanced, since more active surface will be disposable for reactions and transformations to take place. In other words, the interface between the particles and the external environment becomes larger if the same mass of matter is divided into finer particles. The reactivity enhancement is important in practical applications, for instance when calcium hydroxide nanoparticles are used for the deacidification of paper as mentioned above. An increased reactivity makes the particles better deacidifying agents, and favors the transformation of $Ca(OH)_2$ into the milder alkaline buffer $CaCO_3$.

Size reduction is also important to ease the dispersion of solid particles into carrier solvents. Dispersions can then be easily brushed, sprayed or dripped onto artistic surfaces. Stable formulations do not require the use of stabilizers. For instance, reasonably stable dispersions of calcium and magnesium hydroxides nanoparticles can be prepared using short chain alcohols such as ethanol and propanol (see Fig. 1.2) without the need of surfactants that might remain as residues on the surfaces treated with the dispersions, after the evaporation of solvents.

Another advantage related to particle size decrease is to favor penetration through porous matrices, such as wall paintings, wood, surface coatings, etc. The well known Bookkeeper method (Preservation Technologies, L.P.) involves the use of particles of magnesium oxide, MgO, with a diameter slightly smaller than 1 μm, for the effective deacidification of paper, but the method is discouraged when paper porosity is low since in that case particles can not penetrate completely through the paper fibers, and deposits can be left as white hazes over the treated surfaces. Moreover several additives are present in the formulation to stabilize the dispersion. Magnesium hydroxide nanoparticles have been successfully used for paper deacidification (Poggi et al. 2010, 2011), and the small size of the particles increases penetration through the fibers, minimizing the risk of haze formation and favoring the homogeneous penetration and distribution of the deacidifying agent.

Nanosized particles are also useful to enhance the properties of organic–inorganic hybrid composites, which typically include a polymeric binding matrix and inorganic fillers (particles). Nanocomposites exhibit at least one component with nanometric size or nanostructuration, and show better performances than traditional filled polymeric matrices in terms of mechanical properties, chemical resistance, protection against UV radiation, etc. These materials can be used for conservation purposes, for instance polymer–silica nanoparticles composite films show increased hydrophobicity with respect to poly(methyl methacrylate) coatings for the water protection of stone-based monuments (Manoudis et al. 2007), and a Klucel-TiO_2 nanocomposite has been proposed for the protection of paper from UV radiation and from the formation of biofilms (Afsharpour et al. 2011).

The use of nanoparticles for the preservation of works of art will be detailed in Chap. 2 (consolidation of wall paintings and stone) and Chap. 5 (deacidification of paper, canvas, and wood), where the most recent advances and applications will be described, together with practical guidelines.

The synthesis of nanoparticles and the preparation of stable particles dispersions are normally carried out at scientific and specialized facilities, since both the required skills and equipment rule out the possibility of preparing homemade formulations in ateliers, restoration laboratories etc. However, several products for restoration are presently sold on the market.

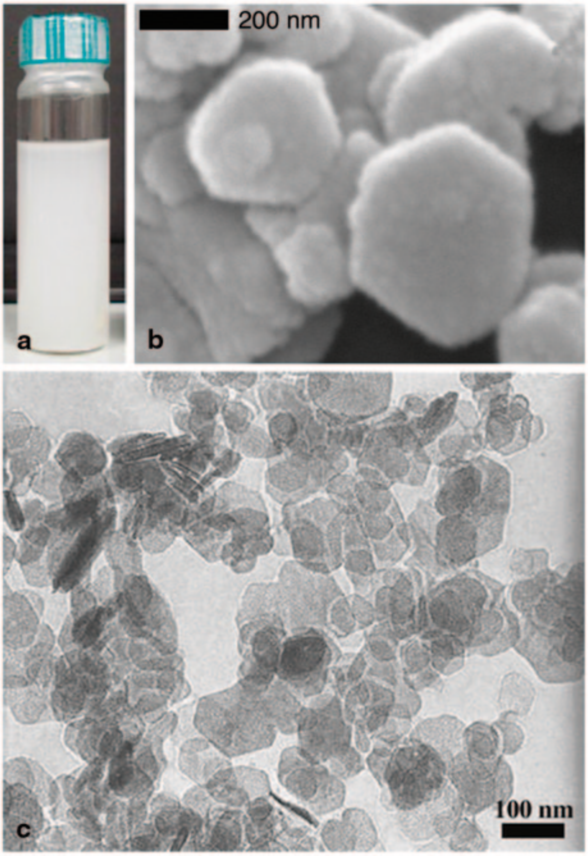

Fig. 1.2 **a** A dispersion of calcium hydroxide nanoparticles in 2-propanol. Reprinted with permission from Carretti et al (2013) Interactions between nanostructured calcium hydroxide and acrylate copolymers: implications in Cultural Heritage conservation. Langmuir 29:9881. Copyright 2013 American Chemical Society. **b** Scanning electronic microscopy (SEM) image of calcium hydroxide ($Ca(OH)_2$) nanoparticles. Reproduced from Baglioni and Giorgi (2006) Soft and hard nanomaterials for restoration and conservation of Cultural Heritage. Soft Matter 2:293, with permission from The Royal Society of Chemistry. **c** Transmission electronic microscopy (TEM) image of magnesium hydroxide ($Mg(OH)_2$) nanoparticles. Reprinted with permission from Giorgi et al (2005) Nanoparticles of $Mg(OH)_2$: synthesis and application to paper conservation. Langmuir 21:8495. Copyright 2005 American Chemical Society.

The application of nanoparticles dispersions for the consolidation of stone and wall paintings, or for the deacidification of cellulose, can be relatively easy once the fundamental properties of the artistic substrate are known, as well as the environmental conditions experienced by the artifact during and after treatment. Years of experience and collaboration with conservators on real case studies have led the authors of this Compendium to formulate practical guidelines for the use of the nanomaterials that they have designed. For what concerns the application of nanoparticles, such guidelines will be described in Sects. 2.4 and 5.4. However, it is important to highlight that each case study exhibits specific features and issues, which must be considered carefully before selecting the best intervention protocol. Therefore, it is imperative that these guidelines be considered critically case-by-case, rather than applied mechanically. Throughout any restoration intervention that involves the use of advanced materials, it is the constant information and expertise exchange between scientists and conservators that allows maximizing the effectiveness of protocols while limiting, or avoiding, drawbacks.

1.3 Nanostructured Cleaning Fluids

Cleaning of a work of art can be a very delicate task. In its wider meaning, cleaning involves the removal of any undesired material from artistic or historical surfaces. In practice, the intervention must be carried out in a controlled way without damaging the original artifact due to mechanical stress or any other process such as swelling, leaching of components, discoloration, etc.

Materials to be removed come in great variety and range from dirt, grime and soil to natural and synthetic coatings, adhesives and varnishes, which can darken and degrade over time so that they produce aesthetic alteration or even physico–chemical degradation of the artistic substrate. As a matter of fact the application of synthetic hydrophobic coatings, for instance poly acrylates and vinyl-acetates, strongly alter the physico–chemical properties of substrates such as carbonate-based wall paintings and stone, resulting in medium or long-term damage of the artistic surface (Carretti and Dei 2004; Giorgi et al. 2010a, b).

The extent to which undesired layers are removed can be a matter of debate and depends from case to case based on historic, aesthetic or ethic factors. For instance, sometimes a "patina" is left on top of artistic surfaces since it is considered as a historical part itself. Recently, an "overcleaning" issue arose concerning the restoration of Leonardo's painting "The Virgin and Child With Saint Anne" (Alberge 2011).

Through the ages, a vast array of cleaning materials has been used, such as soaps (from fats and oils), alimentary products (vinegar, wine, lemon juice), inorganic materials (potash solutions) and even biofluids like urine, bile or saliva, which is nowadays synthetically prepared and used by conservators (Wolbers 2000). Some of these fluids (bile, saliva, soaps) contain surfactants, which have been used since ancient times and have been widely studied and diffused by synthetic industry starting from the twentieth century. Nowadays surfactants are involved in everyday life ranging from detergency to food chemistry, pharmaceuticals, etc., Branches of modern advanced chemistry and physical chemistry such as materials, colloid and nanosciences have carried out intense research on both theoretical and applicative aspects related to soft matter, such as binary or ternary systems composed of water, surfactants and other additives (e.g. solvents).

The end of the 1980s saw the first application of nanostructured fluid systems based on surfactants for the removal of wax spots from the painted surface of Italian Renaissance wall paintings in Florence (Borgioli et al. 1995; Baglioni et al. 2013).

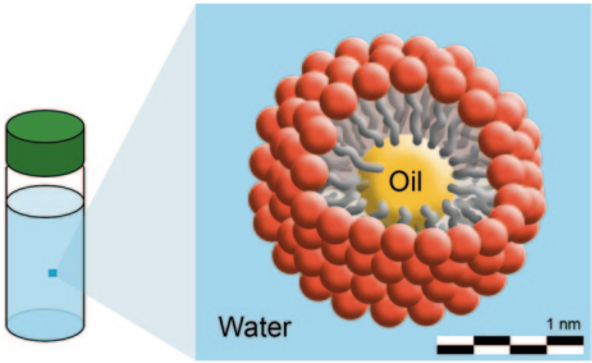

Fig. 1.3 An oil-in-water (o/w) microemulsion, where organic solvents are dispersed into nano-sized surfactant micelles surrounded by a continuous water phase. (Image by Michele Baglioni)

Starting from that pioneering study, several systems have been prepared characterized and successfully applied for the removal of undesired materials from artistic surfaces. Numerous examples are reported by the literature, see for instance Baglioni et al. (2011) and Carretti et al. (2003, 2007), making nanostructured fluids one of the most appealing advanced cleaning tools for Cultural Heritage conservation, together with gels (see Sect. 1.4), laser technology (Nevin et al. 2007; Siano and Salimbeni 2010; Pouli et al. 2010), and the promising "biocleaning" based on the use of microorganisms (Cappitelli et al. 2006; Alfano et al. 2011).

One typical class of nanostructured fluids used for artifacts cleaning are oil-in-water (o/w) microemulsions, where an organic solvent is dispersed into nano-sized surfactant micelles surrounded by a continuous water phase (see Fig. 1.3). These systems are thermodynamically stable and optically transparent; they exhibit a high water content (75–99 %) and a reduced organic content (from less than 0.5 % to about 15 % including both solvents and surfactants), nonetheless they have proven highly effective in swelling and removing detrimental coatings from works of art. In fact microemulsions and other surfactant-based fluids have emerged as a valid alternative to the use of organic solvents, which involves several drawbacks: first, the action of free solvents is not completely controllable and might lead to the swelling and solubilization of the artifact's organic components (e.g. binders, organic additives); secondly, coatings and grime dissolved by solvents are then transported through porous matrices and deposited in the artifact's pores; finally, but most importantly, many solvents are toxic and conservators often work in scarcely aerated environments. The use of gelled solvents can limit these drawbacks (see Sect. 1.4).

Compared to these limitations, the use of nanostructured cleaning fluids involves the following advantages:

- The processes that lead to the swelling (and/or solubilization) and removal of substances (polymers, wax, etc.) include interaction and matter exchange at the interface between the nano-sized containers (micelles), the aqueous continuous phase and the surface of the layer to be removed. The micelles exhibit a large surface area; therefore the extended interface maximizes the interaction with the detrimental layer and its swelling/solubilization.

- In several practical applications, nanostructured fluids can remove effectively detrimental coatings that can not be dissolved by conventional solvents (e.g. acetone, benzyl alcohols and xylenes), or that would require the use of aggressive and toxic solvents (Carretti et al. 2007; Baglioni et al 2012). This is due to the structure and chemical composition of the surfactant-based fluids, and to the mechanisms through which they interact with organic coatings (the interaction will be further described in Sect. 3.1).
- Once swollen and detached, the removed hydrophobic material (organic coatings, wax, etc.) is surrounded by a hydrophilic phase (aqueous phase) that limits the re-deposition of the coating within the porous matrix of the substrate (e.g. wall painting).
- The low organic content of water-based nanostructured cleaning fluids depresses the health risk and the environmental impact involved in the cleaning intervention.
- Microemulsions are thermodynamically stable systems, which means that they can be used in different environmental conditions without causing the formation of two separated macroscopic phases (organic and aqueous). In stable systems, the organic content is dispersed in water (see Fig. 1.3), and the system is macroscopically monophasic (optically clear).

As mentioned above, microemulsions were initially designed for the cleaning of wall paintings. However, the application of water-based cleaning fluids on water-sensitive substrates (e.g. paper and canvas) is not only possible but also very effective when the fluids are confined in hydrogels, which allow controlling the fluid release and the cleaning action so that no detrimental effects, such as fiber swelling, is induced on the treated surface (see Sect. 1.4).

The literature reports several case studies where specific formulations of microemulsions and micellar solutions have been used for the removal of some of the main classes of synthetic coatings that have been applied on artifacts starting from the second half of the twentieth century. Sections 3.2, 4.2, 3.4 and 4.4 describe formulations and application procedures for the cleaning of wall paintings, stone and easel paintings. As previously mentioned for nanoparticles, it is important to notice that such guidelines must be adopted critically, and the cooperation between the nanostructured fluids designers (scientists) and end users (conservators) is essential to achieve the best results.

1.4 Gels

As described in Sect. 1.3, the use of solvents involves several drawbacks mainly related to safety risks and to the possibility of altering the artifact during cleaning. The ideal intervention should be fully selective, which means that removal of undesired layers must be carried out without affecting the original artistic materials either chemically or physically. One of the best methods to achieve such task is to confine solvents in a matrix that releases them gradually onto the substrate.

Over the last few decades, conservators have adopted different tools, including modified natural products such as cellulose ethers (e.g. Kucel®, Tylose), or synthetic polymers such as polyacrylic acids (e.g. Carbopol®). These materials can be used to thicken solvents, so to limit uncontrolled penetration through porous substrates.

In the late 1980s and early 1990s Richard Wolbers developed the so-called “solvent gels”, which are obtained dispersing polyacrylic acid in a solvent and then adding weakly basic non-ionic surfactants like Ethomeen C12® and C25®. The bases cause deprotonation of carboxylic functions in the acid chains that unfold and form an extended 3D network, which confines the solvent (Wolbers et al. 1988; Wolbers 2000). Solvent gels are still one of the most used cleaning tools due to their effectiveness and versatility; in fact they can also be used to control the action of detergents and enzymes.

Both cellulose ethers and polyacrylic acid-based gel-like networks are built by molecules cross-linked through non-covalent interactions, such as dipole–dipole interactions and hydrogen bonding; therefore they are classified as “physical gels” as opposed to networks where cross-links are covalent bonds (“chemical gels”). The main drawback associated with physical gels is that they leave solid residues on the treated surfaces (Stulik et al. 2004). The long-term effects of these residues have not been completely clarified yet, and the common procedure to remove them is to use cotton swabs and solvents, which eventually brings back the aforementioned issues. Moreover, residual degradation products of Ethomeen (especially C25®) evaporate only partially from the painted layer, and their effects on the long-term are still to be fully characterized. A study by Burnstock and White (2000) indicated that, in regard to the effects of aging of combined samples of di- and triterpenoid resins, Ethomeen C12® has a synergetic influence on degradation processes, and the surfactant degradation products include amine N-oxides, which gave rise to concern about long-term contact with the resin or painted media.

Owing to these issues, scientific research has focused in the last decade on the formulation of alternative systems that can be easily and fully removed from the painted layer, minimizing or completely avoiding the presence of solid residues.

Polysaccharide-based gums have been recently considered for the cleaning of artistic and historical surfaces. For instance, agar (or agar–agar) is a mixture of agarose and agaropectin, and it is sold as powder that can be mixed with water, obtaining a gel whose porosity depends on the concentration of agarose. This gel can support solutions or water-based systems such as microemulsions for the treatment of porous substrates (Campani et al. 2007; Gorel 2010). Another example is gellan gum (Phytagel®), a microbial exopolysaccharide that can be gelled and used for the controlled cleaning of water-sensitive substrates such as works of art on paper (Iannuccelli and Sotgiu 2010).

Chemical hydrogels are another class of materials that have recently found application in the cleaning of artifacts, owing to characteristic features that make them advantageous with respect to other formulations. Domingues et al. (2013) developed semi-interpenetrating p(HEMA)/PVP networks where free chains of poly(vinylpyrrolidone)—PVP—are embedded into a network formed by poly(2-hydroxyethyl methacrylate)—p(HEMA). These systems exhibit the mechanical

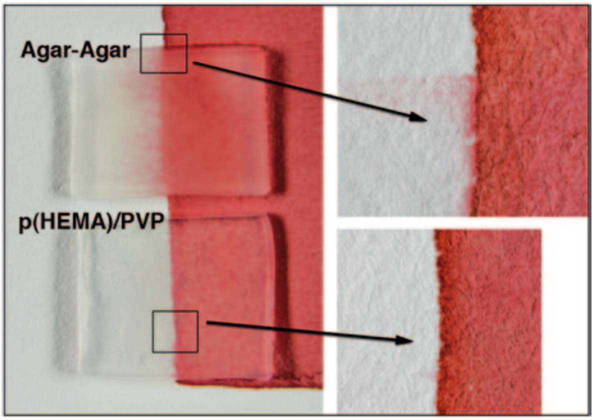

Fig. 1.4 Five minutes application of agar–agar (2 % w/w) and semi-IPN p(HEMA)/PVP hydrogels on paper painted with brazilwood ink. (Reprinted with permission from Domingues et al. (2013) Innovative hydrogels based on semi-interpenetrating p(HEMA)/PVP networks for the cleaning of water-sensitive cultural heritage artifacts. Langmuir 29:2746. Copyright 2013 American Chemical Society)

strength of p(HEMA) combined with the hydrophilicity of PVP. In particular, both the p(HEMA)/PVP ratio and the amount of water used during the preparation steps affect the final properties of the gels, which can be tuned to obtain the desired properties, i.e. good adhesion to the substrate, ideal retention/release of the detergent system (water, o/w microemulsions, micellar solutions etc.), confinement of the cleaning action to the contact area between the gel and the artistic substrate.

Literature reports the size of both the macropores and of the mesh of p(HEMA)/PVP gels (Domingues et al. 2013). The mesh size intrinsically provides a measure of the average microporosity of the gel network, i.e. of the nano-sized pores. The average porosity values depend on the gel formulation, for instance a particular formulation (named H50) has macropores of 5–15 μm and a mesh of 2.5 nm.

The p(HEMA)/PVP gels are highly water-retentive, which is a crucial feature for granting controlled cleaning. In fact, the water release of these systems is strongly reduced with respect to AgarArt® (agar–agar gel) and Kelcogel® (gellan gel) prepared by dispersion of dry powders in water (3 % w/w), as shown by Domingues et al. (2014).

p(HEMA)/PVP hydrogels have been tested on highly water-sensitive and scarcely cohered painted surfaces, such as *tempera magra* paintings on canvas, where pigments and colorants are mixed with the minimal amount of binder (animal glue) necessary to wet the pigment particles. The gels, loaded with water, proved effective in the gradual and controlled removal of grime trapped into the substrate surface pores, without any alteration of the painted layer (swelling, leaching). The p(HEMA)/PVP gels were also tested on paper samples painted with a water-soluble ink (see Fig. 1.4). As a matter of fact, the application of the highly retentive chemical hydrogel did not alter the surface and no diffusion of the colorant through the paper substrate was observed, indicating that the use of the gel avoided excessive wetting. The same work demonstrated that, owing to their mechanic properties, the p(HEMA)/PVP gels can be easily handled and applied as sheets on the artistic surface. The gels network is more cohesive than physical gels because it is formed by covalent bonds that link polymer chains. As a consequence, after the application

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