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**CO-SOLVENTS AND CHELATING AGENTS CONFINED
IN COMPLEX FLUIDS FOR THE CLEANING OF
SURFACES OF WORKS OF ART**

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Alla mia famiglia,

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INTRODUCTION

In a modern society that is always more and more sensitive to the ecology, the respect and the preservation of the environments and its living beings, and where the research of sustainable resources and eco-friendly, low-environmental impact solutions/products is continuous, also in the conservation of the Cultural Heritage, in the last decades, the developing of innovative technologies has been inspired by those principles. Thus, efforts are constantly made to find conservative solutions that are as less invasive as possible, that provide the use of materials that are ecological, compatible and similar to the original ones (assuming, generally, the no reversibility of the conservation treatments).

In particular, as concern the delicate cleaning phase of surfaces of artistic and historical interest, the research is focused on finding methodologies that involve the use of low-toxicity solvents or mixtures of them and, at the same time, of thickeners/gellants, biocompatible and biodegradable themselves, to retain the cleaning agent in order to reduce its evaporation and its penetration below the surface layer, on which the treatment should be confined. In this way the cleaning would be safer for the operators, more ecological, less aggressive and better controlled.

Thus, in order to reduce the chemical risk related to the use of toxic and carcinogen solvents, in 1995 the “Istituto Superiore per la Conservazione ed il Restauro” (ISCR) of Rome, on the basis of the Teas triangle¹ and the solubility parameters, formulated different mixtures of solvents having a low toxicity and a solvating power equivalent to that of the pure and toxic organic liquids, mostly used in conservation, that they were meant to substitute. They are called “TaCo” mixtures and their composition can be modulated to selectively solubilize the different types of substances (natural and synthetic resins, oils, waxes...).

On the other hand, in the perspective of a cleaning action the less invasive as possible, “thickened” retentive systems were formulated and introduced.

¹ J.P. Teas, *Graphic analysis of Resin Solubilities*, Journal of Paint Technology, 1968, vol. 40, n° 516, pp. 19-25.

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By using hydrogels, organogels, Wolbers' *Solvent gels*² (obtained from polyacrylic acid and an ethoxylate amine) or other thickeners as cellulose ethers (methyl cellulose, carboxymethyl cellulose, hydroxypropylmethyl cellulose, hydroxypropyl cellulose, also known as *Klucel G*) or Carbopols (a series of polyacrylic acid polymers), the rate of diffusion of the fluid into the porous matrix is strongly reduced. The main drawback of these "gelled" systems as low-impact cleaning tools for works of art is that it's been verified that they leave potentially dangerous residues onto the treated surface³. This problematic is still open and it's universally known as the "residue question"⁴.

Ideally they should have adequate consistence and elasticity to be easily applied and removed from the treated surface minimizing the potential residues, so that a further clearance step with neat organic solvents or an extra mechanical action could be avoided.

It's in this context that during the past decades, in the laboratories of the chemistry department of the University of Florence and CSGI Consortium, a new family of Highly Viscous Polymeric Dispersions (HVPDs) for the cleaning of artistic, fragile surfaces was formulated and studied. They are aqueous-based systems obtained from poly(vinyl alcohol) (PVA) or poly(vinyl acetate)s (PVAc) via complexation and crosslinking between the side-chain hydroxyl groups of the polymer and borate ions (coming from the dissolution of the borax salt).

PVA and partially hydrolyzed PVAc (xPVAc, where x is the degree of hydrolysis) are biocompatible and biodegradable and are used for pharmaceutical and biomedical applications (drug delivery, tissue engineering scaffolds, contact lenses, etc...), as well as for a wide range of non-medical ones (e.g., adhesives and binders, fibers for clothes and industries, and cosmetics).

Due to the low toxicity of the basic formulations (composed of PVA/PVAc, water and borax) and considering that they are made of 95 wt% water, these HVPDs are very attractive eco-friendly cleaning tools for the conservation of painted surfaces. The only component that has a certain level of toxicity, especially when in the

² R. Wolbers, *Cleaning painted surfaces: aqueous methods*, Archetype, London, UK, 2000.

³ A. Burnstock, T. Kieslich, *Study of the clearance of solvent gels used for varnish removal from paintings*, in: ICOM Committee for Conservation, 11th Triennial Meeting in Edinburgh, James & James, London, 1996, pp. 253–262.

⁴ V. Dorge (Ed.), *Solvent gels for the cleaning of works of art: the residue question*, Getty Publications, Los Angeles, USA, 2004.

powder form, is the borax salt (the crosslinker) but its concentration within the systems is very low (0.75 wt%) and it is added in aqueous solution.

The HVPDs can incorporate large amounts of a wide range of organic solvents: selecting the hydrolysis degree of the PVAc (from 99% to 41%), it's possible to modulate the polarity of the environment and, thus, the capability of loading liquids with different dielectric constants, based on the nature of the patinas to remove. Considering this great versatility, the use of low-toxic solvents with different polarities or even the TaCo mixtures cited before is possible.

Furthermore, due to their high viscosity and thickness, the evaporation rates of the incorporated solvents and their undesirable diffusion into the inner layers of the artwork are significantly reduced, lowering in this way not only the potential damages to the original materials of the work of art but also the intoxication risk for the operators and the environmental impact.

Many tests have been carried out on easel, wood and mural paintings: the cleaning action performed by the HVPDs resulted effective, confined to the desired area, controllable and gradual, parameters that are greatly appreciated by restorers.

They have viscoelastic properties that ensure a good adhesion onto the surface (even the molded, irregular or vertical ones) and easiness of removal in one piece through lifting with tweezers; thereby, the potential for residues is minimized and the clearance step with neat solvents could be not necessary. The elasticity and, more generally, all the rheological properties of these systems can be easily tuned by changing either the ratio of PVA to borax or their total concentration.

Considering that the HVPDs formulated and studied so far were obtained from PVA or PVAc highly hydrolyzed (99% or 80-90%), a first part of the present PhD thesis consisted in a deep structural and mechanical study of HVDPs obtained from a PVAc with a lower hydrolysis degree (75% hydrolyzed and named 75PVAc).

The advantage of using polymers less hydrolyzed is that, being the polarity of the environment lowered, they could potentially incorporate solvents with smaller dielectric constants.

Then, the possibility of introducing some chelating agents into these xPVAc-borax HVPDs was also explored. Chelators are commonly used in conservation for the removal of salts efflorescences and oxidation/corrosion patinas from mural paintings and metallic surfaces. Usually they are applied in aqueous solution

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containing from 1 to 5% of additive or even more. In order to limit the penetration of the cleaning agent into the inner layers and to avoid the undesirable solubilization of the original materials constituting the piece of art, chelators aqueous solutions are usually gelled by adding thickeners (cellulose ethers, Carbopols...) that, once applied, leave residues. The necessity of a next clearance step with a neat liquid (generally water) and/or extra mechanical action can be critical in presence of fragile or hydrophilic surfaces/materials.

The loading of different chelating species into the HVPDs has been explored here in the perspective of overcoming the drawbacks of the traditional methods and of extending the application field of the xPVAc-borax HVPDs to the conservation of the metallic manufactures, frequently affected by the presence of corrosions/oxidation deposits. The chelating species selected for this study were: EDTA, ammonium carbonate, sodium and ammonium citrates, sodium/potassium tartrate.

The viscoelastic properties of the obtained stable HVPDs containing different amounts of the salts were investigated to study how the additive influence the elastic response of the HVPD.

Cleaning tests onto artificially degraded metallic and carbonatic surfaces were performed to verify the efficacy of these HVPDs embedded with chelators in the removal of salts. The effectiveness of the treatments was evaluated qualitatively (visually and with the optical microscope) and quantitatively by means of Ion Chromatography (IC) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) measurements. The quantitative analysis was possible thanks to set-up of an analytical protocol *ad hoc* for the HVPDs samples.

The study of the residues left on the treated surface after the removal of the HVPDs was also conducted, using a fluorescent probe. Fluorescein was covalently attached to the polymer and then, after studying the fluorescence behavior of free and bounded fluorescein, samples containing the fluorescent polymer were prepared, applied onto a glass surface and the residues left after their removal were analyzed through confocal microscopy.

Fluorescence emission studies were performed on samples containing different amounts of the labelled polymer and a calibration curve was constructed in the future perspective of evaluating the residues left also from a quantitative point of view.

PART I

Fundamentals

CHAPTER 1

The conservation of the Cultural Heritage: metallic and carbonatic surfaces

1.1 Introduction

“Cultural Heritage” is an expression that refers to a wide range of different kind of objects, ideated and produced by the human mind since the most ancient times, including buildings, structures and even gardens or natural environments that have been modified by the man, acquiring for that an historical and/or artistic interest.

Thus, the materials used for the art production and the conservative issues are incredibly various.

The conservation challenges which restorers and conservation scientists have to face are many because, beyond the specific and universally accepted treatments tailored for the different type of material, every case study remains unique for composition, conservation history and environmental conditions in which it's located and, thus, the set-up of new, alternative methods of intervention is often needed.

As previously mentioned, the typology of artifacts on which the present study was focused were bronze and carbonatic surfaces.

Natural and artificial stone materials and, in particular, the carbonatic ones, and the copper or its alloys are the most ancient materials used by the man for the manufacturing of all sorts of daily-life objects (weapons, working tools, recipients, graves, ornaments...) and, naturally, of the artistic ones.

The main reason for that was their plentiful supply in the environment and their pretty easy workability without the necessity of high-level technologies.

It's not surprising, therefore, that a large part of our cultural heritage is represented by these materials.

The present work focus on these two type of artistic substrates and thus, in this chapter, a brief description of them and their main degradation problems is given.

1.2 Bronze manufactures

The bronze is an alloy traditionally composed of copper and tin. It can be considered as the first alloy intentionally and widely used by man; in fact, a long period of the human history has been named “The Bronze Age”. The bronze metallurgy developed in the Middle East (IV millennium BC) and diffused in Europe in the II millennium BC, reaching a high technological level. During that period, a great quantity of weapons, ornaments and tools (i.e. axes, daggers, knives, pins...) were produced, mainly by melting, using binary copper-tin alloys with a well-defined compositions (the percentage of tin varied depending on the use to which the bronze manufacture was destined). At a certain point, due to economic and technological reasons, the ternary alloys were introduced by adding zinc or lead (up to 20-30%).

The lead, in fact, is more economic and diffused than the tin and gives better mechanical properties to the alloy, improving its castability [1].

During the Roman age the percent of lead in the bronzes used for the great statuary was very high (more than 20%), while the amount of tin usually was less than 10%. Bronzes with a high content of lead were typical in southern Italy between IX and VIII century BC [2].

As a result of alloying copper with tin or other metals, bronze is harder than copper, more fusible and easier to cast. It is also harder than pure iron and far more resistant to corrosion. The substitution of bronze with iron in tools and weapons from about 1000 BC was due to iron abundance compared to copper and tin rather than any inherent advantages of iron.¹

Since the ancient times the most common technique used to realize bronze manufactures was the “lost-wax casting”, a process by which a duplicate metal sculpture is cast from an original sculpture. In the direct method, casts are made of the wax model itself while in the indirect one they are made of a wax copy of a model that need not to be of wax. This second method was widely used for the great statuary.

Modern molding techniques are similar to the ancient ones but they contemplate the use of gummy or siliconic models [1].

¹ www.britannica.com/EBchecked/topic/81000/bronze, consulted on December 2014.

Besides its traditional use in weapons and tools, bronze has also been widely used in coinage; most “copper” coins are actually bronze, typically with about 4% tin and 1% zinc.

1.2.1 The corrosion processes of metals

From a thermodynamic point of view, a work of art or, more generally an artifact, can be considered as an open system that continuously exchanges matter and energy with its surroundings. The degradation includes all the spontaneous processes ($\Delta G < 0$, where ΔG is the variation of the Gibbs free energy that is a measure of the thermodynamic driving force that makes a reaction occur²) that, thanks to the mentioned exchanges, cause the partial or total alteration of the artifact respect to its original conformation or chemical composition.

The task of the restoration is to intervene on the kinetic and/or the thermodynamic of these processes in order to stop them or to slow them down.

Almost all the metals, except for gold, silver or copper, naturally are in the form of oxides, carbonates, sulfates, sulfurs, silicates, etc. The metallurgical processes extract them from the relative minerals and, through reduction reactions, convert them to the metallic state which is less stable than that of the natural starting compound.

The Ellingham diagram³ is fundamental for these processes because it gives the temperature values at which the metallic compounds are stable and predicts the conditions under which a mineral will be reduced to its corresponding metal.

According to the diagram, the stability of the metallic oxides decreases with increasing temperature; almost all the metals, in relation to the carbon oxidation line, in the temperatures range typical of the terrestrial atmosphere are stable in the oxidized form.

Thus, the oxidation reactions of the corrosion processes are spontaneous and tend to retransform the metals in their original compounds, thermodynamically more stable and corresponding to a desirable condition of minor free energy.

² CRC *Handbook of Chemistry and Physics*, 2009, 90th ed., Lide.

³ http://web.mit.edu/2.813/www/readings/Ellingham_diagrams.pdf, consulted on December 2014.

For this reason, metal objects unearthed during archeological excavations are completely mineralized.

There are two types of corrosion, either localized or diffuse: the dry one and the wet one. The first one determines the oxidation of metals through chemical processes in a gaseous atmosphere, at high temperature; the second one happens through electrochemical processes in presence of aqueous solutions [2].

There are many factors that are responsible for these reactions: the type of material, its structural characteristics, the presence of imperfections, the environmental conditions of conservation. Therefore, corrosion mechanisms can overlap and their analysis can be very difficult.

The chemical corrosion arises from the direct reaction of a metal with a chemical reagent, in form of a gas (O_2 , CO_2 , H_2S , SO_2 , NO_x) or a not electrolytic liquid [2].

The presence of an electrolyte, in the form of a liquid or condensate, can determine electrochemical processes and the formation of a corrosive element called galvanic and constituted by an anode (the metal part that oxidizes) and a cathode (the metal part that reduces), put in electric contact by electrolysis [2].

An example of this mechanism is the atmospheric corrosion of metals exposed to air in presence of moisture on their surface, that is accelerated by the presence of pollutants as nitrogen oxides (NO_x), sulfur oxides (SO_x) and chlorides [1].

It's the case of the gilded bronzes exposed to open air, as the *Porta del Paradiso* by Lorenzo Ghiberti in the Baptistery of Florence: the gold, in a moisturized and oxidizing environment, can behave as a cathode sacrificing, in the formed "pile", the anodic material represented by the bronze.

Thus, the anodic part is corroded, losing metallic ions in solution, while the cathodic one is preserved; the solution, which is the moisturized medium that acts as a conductor, put in contact the two parts, favoring the passage of a current (electrons) in the metal from the anodic part to the cathodic one [2].

1.2.2 The corrosion of copper/bronze artefacts

Corrosion patinas generally are constituted by concretions of exogenous substances coming from the soil or the atmosphere and by the stratification of the alteration products of the underlying metal.

In particular, as a consequence of a prolonged exposition to the external environment, the copper forms a wide range of alteration products or patinas. Since the ancient times it's been known that the corrosion of copper materials or its alloys determines the formation of thick mineralized superficial patinas called "*aurugo*". When the environmental conditions are favorable and in absence of chloride compounds, they constitute a protective shell and the metallic artefact preserve its original structure [1].

The copper corrosion products can be divided in four groups: oxides, carbonates, chlorides and sulfates.

The oxides (tenorite CuO and cuprite Cu_2O) are considered the "noble patina" of the bronzes because the aesthetical effect they produce is acceptable and for that reason they are often maintained or even intentionally induced.

The dark red cuprite is the most diffused corrosion product of copper or bronze artefacts.

It can be considered an intermediate compound because generally it's covered by superficial layers composed of other products as basic carbonates, basic sulfates [1,3].

The carbonates (azurite and malachite) form crystalline deposits that are considered "noble patina" as well, having a protective function towards the unaffected metal [3].

In moisture conditions, the azurite $[\text{2CuCO}_3 \cdot \text{Cu(OH)}_2]$ can be converted, by releasing carbon dioxide, in malachite $[\text{CuCO}_3 \cdot \text{Cu(OH)}_2]$ that is more stable [4].

Rarely the copper carbonates are found in bronzes exposed to open air while they are typical of the archeological ones; the reason is that outdoors strong acids as chloride acid, sulfuric and nitric acids attack the copper carbonates and transform them into chlorides, sulfates and nitrates [5].

The most harmful alteration products of copper are the chlorides either for their high solubility and their good ionic conductivity that favors the development of the corrosion processes. Usually the copper chlorides are present on objects buried for long periods in the sea or in desert regions with high saline content soils. Nevertheless, because of their great diffusion in nature, the chloride compounds can easily contaminate any metallic artefact [1].

The cuprous chloride (nantokite) that forms close to the substrate, is metastable; thus, it reacts with the oxygen and the atmospheric moisture producing the paratacamite or the atacamite that are highly reactive and favor the developing of the “*bronze disease*” (a detailed description of this phenomenon is given in the 1.2.3 paragraph) [6].

The sulfates (brochantite, connellite) are other corrosion products typical of copper or bronze exposed outdoors.

The sulfuric acid is responsible of their formation. This acid is present in high polluted environments as a consequence of the transformation in presence of moisture of the sulfur trioxide that previously originated from the sulfur dioxide, through a catalytic oxidation. These compounds produce bluish-green powdery patinas, easily removed mechanically.

Finally, the sulfides (chalcocite, covellite), whose presence is frequently found on the coins; they derive from the contact of the copper or its alloys with the hydrogen sulfide present in the atmosphere and in the waters, or can be produced by sulfate-reducing bacteria, which are able to reduce the sulfates into sulfides. These compounds impart to the objects a color ranging from brown to black [1,3].

Generally the outer layer of artefacts exposed outdoors is light green colored, powdered and constituted by copper hydroxychlorides and sulfides produced by the pollution, but also by copper and calcium oxalates (on monuments exposed in zones that are partially sheltered from direct rain run-off) [4].

In some cases, there can also be organic, carbonaceous or calcareous deposits and other materials of biological origin.

As concern the morphology of the alteration patinas of the bronzes, two typical structures are defined: the *type I*, identified with the “noble patina”, and the *type II* referred to as “grainy surface”.

The first type of patina (Figure 1.2.1) is a thin coating (10-100 µm) that consists of two amorphous layers: the outer layer has a lower copper content, compared to that of the alloy, and a higher content of tin and of elements such as O, Si, Al, Fe, P, Ca and Cl also, due to the environment of corrosion; the inner layer, in contact with the alloy, of irregular shape and thickness, mainly contains oxides and hydroxides and is characterized by a higher content of copper. The structure of *type I* may be, therefore, considered as the result of corrosion processes associated with the formation of “barrier” layers that prevent the dissolution of copper from the alloy [7].

The coatings belonging to the *type II* (Figure 1.2.2) result from a more intense and extended alteration and are generally made up of three overlapping zones: an innermost zone of an intense red color, characterized by the coexistence of the unaffected metal and the corrosion products (mainly cuprite, tin oxides, and chlorides finely mixed), a red layer of copper oxide (cuprite) often fragmented and destroyed, a porous outer zone, with a blue-green color, in which the oxides react with the external environment, determining the formation of carbonates, sulfides and chlorides [1,7].

When the environment is particularly rich in chlorides, a thin layer of copper chlorides may be present in direct contact with the intact metal and, in presence of moisture, it may produce the breakage of the superior layer of red cuprite giving rise to the appearance of green efflorescences composed of paratacamite or atacamite [1].

If the original metal hasn't been completely destroyed, the discontinuity represented by the interface between the inner layer and the outer one of the patina may be useful to get informations about the original surface of the artifact [8].

As concern the bronzes exhibited in museums, the corrosive phenomena present the same morphologies described above but they are generally less developed. In this case, the outermost layer of the artifacts usually presents secondary corrosion patinas⁴ containing copper sulfides, generated by the presence of very small amounts of hydrogen sulfide in the environment or arising from degradation phenomena of the protective.

As regard the gilded bronzes, the corrosion processes are located mainly at the bronze-gold interface, as in this case copper and gold represent a "couple" and a potential difference between them is established: electrochemical reactions take place in presence of rainwater or condensation, with the consequent formation of corrosion products in the form of micro pustules that disfigure the golden surface, partially detached from the underlying alloy [5].

⁴ The secondary patinas are composed by secondary corrosion products, due to the interaction of pre-existing patinas with the pollutants of the conservation environment, or to the degradation products of the protectives used in previous restorations. The primary patinas, instead, are made of primary corrosion compounds, derived by the direct interaction between the corrosive agents and the metallic substrate [4].

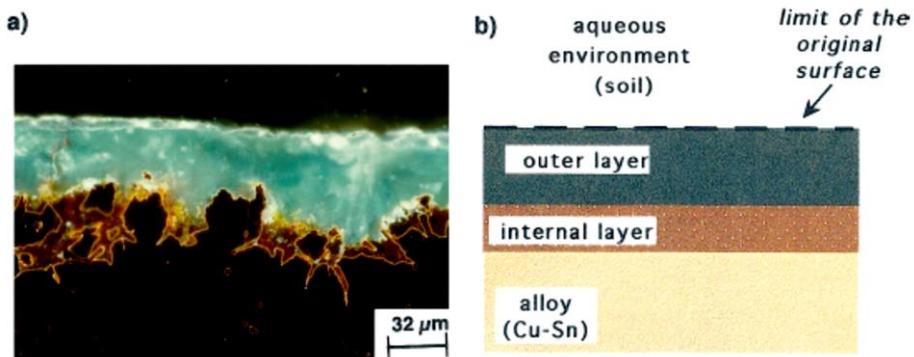


Figure 1.2.1. The *type I* patina: a) polished section of a sample from a bronze artefact; b) schematic representation of the different layers.

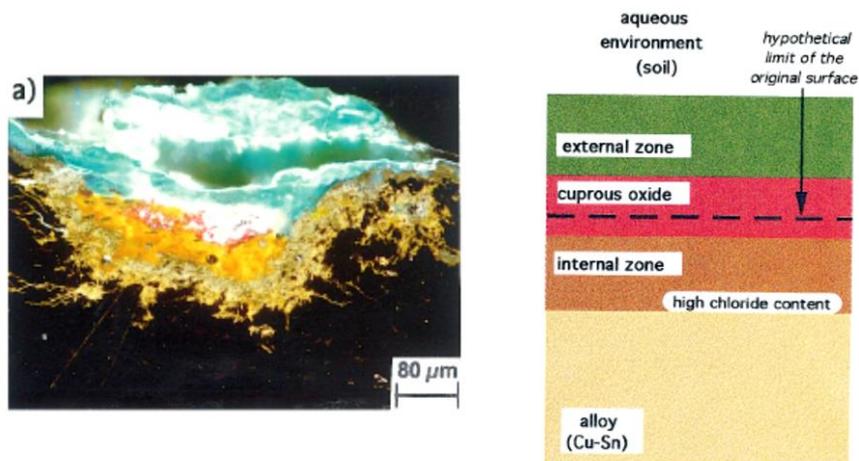


Figure 1.2.2. The *type II* patina: a) polished section of a sample from a bronze artefact; b) schematic representation of the different layers.

1.2.3 The “bronze disease”

The progressive, slow corrosion of bronze surfaces known as the “*bronze disease*” is one of the most problematic degradation phenomenon and it’s attributed to the presence of chlorides.

The chlorides generally present in the corrosion patinas of the bronzes are the *nantokite* (cuprous chloride) and the copper isomeric trihydroxychlorides: *atacamite*, *paratacamite*, *clinoatacamite* and *botallachite* (Table 1.2.1).

Table 1.2.1. Chemical-physical characteristics of the copper corrosion products responsible for the “bronze disease”.

Mineral	Formula	Crystalline system	Color	Hardness (Mohs)
Nantokite	CuCl	Cubic	Light green /white	2.5
Atacamite	Cu ₂ (OH) ₃ Cl	Orthorhombic	Glassy green	3-3.5
Paratacamite	Cu ₂ (OH) ₃ Cl	rhombohedral	Light green	3
Clinoatacamite	Cu ₂ (OH) ₃ Cl	monoclinic	Pale green	3
Botallachite	Cu ₂ (OH) ₃ Cl	monoclinic	Light green/blue	3

The “bronze disease” is a cyclic corrosion process caused by the presence of the *nantokite* that can remain latent in proximity of the metallic surface until it reacts with oxygen and moisture, forming an instable compound that then turns into one of the copper trihydroxychlorides (Reaction 1) [9]. The chloride acid produced by the Reaction 1 reacts with metallic copper, generating additional *nantokite* (Reaction 2) and giving rise to a cyclic, autocatalytic corrosion process with the formation of a green powdery layer of chlorides and the pitting of the metallic surface (Figure 1.2.3 and 1.2.4).



If this process is not properly stopped, it can disintegrate the bronze artefact up to its core, turning it to powder [10].

The Reaction 1, in fact, is spontaneous and thermodynamically favored (the free energy of formation is negative and equal to -360 Kcal/mol).

The *botallanchite* is the first to form but in high humidity conditions it recrystallizes into *atacamite* and *paratacamite* which are thermodynamically more stable [4].



Figure 1.2.3. Two small bronze nose ornaments from the site of La Compañía, Ecuador, dated to about the 10th century A.D., showing the light green, powdery eruptions typical of “*bronze disease*” [9].



Figure 1.2.4. Miniature Portrait Bust of a Woman, Roman, 25 B.C.-25 A.D., bronze with glass-paste inlays. The bust before conservation (left) shows pustular corrosion with pitting created by the bronze disease. Cuprous chloride is active within the pits after the removal of the cuprite and malachite crust that overlays the pustules. Malibu, J. Paul Getty Museum [9].

1.3 The carbonate matrices

Since ancient times, the stones have been used as construction materials because of their high availability in nature and their great properties of durability, resistance, variety in color and appearance [2].

As concern the artistic production, the limestones or the carbonatic rocks in general have been widely exploited as base material for artworks, statues, frescoes and mural paintings in general, representing the larger part of our cultural heritage for many centuries.

The carbonate matrices, which can be found in our cultural-artistic heritage, composed essentially by the calcium carbonate CaCO_3 , can be classified as “natural”, if they are obtained directly from carbonate stones as those constituting statues, sculpture or objects, or “artificial” when they are the result of physical-chemical transformation processes led by man as in the case of the mortars used to make the lime plasters for wall surfaces and mural paintings.

The carbonate stones in most of the cases are sedimentary rocks.

The sedimentary stones are initially formed as a consequence of the physical deterioration of magmatic stones (deriving from the cooling of magmas) that, along with the chemical alteration, determines the formation of solutions and sediments which can be transported by many agents as wind and water, modified during the transportation and deposited in different zones as plains, lakes, oceans, defined as sedimentation basins [11]. Once there, they can undergo chemical-physical phenomena as compaction and diagenesis (a group of complex mechanisms including redox reactions, solubilization, precipitation of salts, etc...) which lead to the “lithification”, the transformation of the incoherent sediments into coherent rocks.

The sedimentary stones are classified as:

- *clastic stones*, when they are composed essentially of sediments
- *chemical stones*, when generated by the precipitation of salts from supersaturated solutions
- *organogenic stones*, when constituted mainly by fossils.

In particular, the carbonate stones have a chemical origin, due to precipitation from supersaturated aqueous solutions and consequent sedimentation of the calcium

carbonate in marine environments and/or biological when the marine deposits of the mineral are formed by the carbonate shells of planktonic organisms [12].

They contain more than 50% of carbonate minerals. The dominant ones are the *calcite* (CaCO_3) and the *dolomite* ($\text{Mg}(\text{CaCO}_3)_2$) but there are also the *aragonite*, the *siderite* (FeCO_3) and the *magnesite* (MgCO_3). The low hardness of these minerals makes the carbonate stones easily workable and this is the reason why they are widely used for the realization of decorative elements and sculptures.

The *limestones* constituted, since the ancient times, the base material for the artificial building materials of natural origin and for the binder in the mural painting technique “*affresco*”. In fact, through calcination at 700-800°C they produce the quicklime (Reaction 4) and, for subsequent hydration, the slaked lime (Reaction 5) that then reacts with the carbon dioxide of the atmosphere originating again the calcium carbonate (Reaction 6) that welds together the inert materials (sand) of the mortar which thus hardens and acquires a discrete resistance to compression [2]. In the case of frescoes, through this 28 days-long process called “carbonation”, the calcium carbonate formed incorporates the pigments giving rise to long lasting, resistant mural paintings.



The *travertine* is another sedimentary limestone of chemical origin that was extensively used for buildings, particularly in Rome since the I millennium BC for the construction of temples and monuments. It's characterized by a porous, vacuolar structure due mainly to the holes left by the plants of lake basins which, incorporated by the calcareous deposits, later disappeared because of decomposition processes.

The most light and porous varieties are commonly named “sponge stone” and *calcareous tuff* [13].

The marble is still a carbonate stone widely used for buildings, statues and decorative elements. It forms from sedimentary carbonate stones (pure limestones) through a metamorphic process in conditions of high temperature and high pressure that determines the complete recrystallization of the calcium carbonate. The

combined action of temperature and pressure cause the progressive destruction of the textures and the sedimentary structures present in the original rock.

The low refraction index of the calcite, which allows the light to “penetrate” through the surface of the stone before being reflected, gives this material (the white variety in particular) a special brightness that made it particularly popular for sculpture.

1.3.1 The degradation of carbonate matrices

The degradation phenomena interest both the rocks in their natural site and those extracted, processed and used by man; the alteration processes are quite the same.

Not considering the damages and the degradation problems associated with the extraction techniques, the transportation, the crafting or the mistakes in the choice of the stone in relation to its use or the errors in the installation phase, here we will focus on the deterioration mechanisms that affect the stones already crafted and in use and in particular, the carbonatic matrices used as base material for artefacts of artistic and historical interest. The alteration phenomena, in fact, depend not only on external parameters as temperature, pressure, relative humidity, mechanical stresses, pollution, human intervention and so on, but also on internal parameters as porosity, mineral-chemical composition and structure-texture which are different for each typology of stone [11].

The degradation causes can be physical, chemical or biological but generally it's a combination of the three.

In polluted environments and in rainy and cold climates typical of most of the European countries, chemical and physical degradation phenomena are predominant compared to the biodeterioration. On the contrary, in hot and humid climates, where the industrial growth has not yet altered deeply the air quality, the most diffused or, at least, evident alteration processes are the biological ones.

Anyway, also in our environmental conditions, there are situations where the biodeterioration has a primary importance, for example in the archeological sites or monumental fountains [11].

The principal biodeterioration agents of stone materials are the autotrophic micro-organisms which are distinguished into: chemolithotrophic (they oxidize inorganic compounds) and photoautotrophic (they obtain energy from light radiation).

The heterotrophic microorganisms are established on the inert organic remains of the autotrophic ones, thus, they are considered secondary biodeterioration agents.

The most common biodeteriogens of the stone artefacts are the microscopic algae. Often they are implanted onto the surface of very porous or degraded materials and penetrate into the micro-fractures or underneath fragments partially detached.

Also the lichens are very much diffused, at least in slightly polluted environments, and are easily recognizable due to their typical macroscopic structures and their vivid colors (white, yellow, orange). The effects of the presence of lichens is still object of discussion and some believe they play a protective role towards the surface on which they have grown up. In some cases, anyway, it's been ascertained their corrosive action, due to their acidic metabolites, especially against the calcareous materials [11].

The role of the chemosynthetic bacteria in the alteration of stones is still object of studies. Similarly it's not easy to evaluate the damages caused by fungi, actinomycetes and heterotrophic bacteria, at least when onto the stone surface there is no presence of organic residues like the protectives applied in the past.

As concern macroscopic organisms, infesting plants and birds are two other degradation factors. The first ones mainly because of their roots which penetrate into the pre-existing cracks and produce mechanical stresses; the second ones because of the corrosive-chemical action of their *guano*, especially against the carbonatic matrices, and because the guano itself represent a good growth medium for many heterotrophic micro-organisms [11].

The physical deterioration is due mainly to freezing-thawing processes, crystallization of salts or thermal shocks (as the daytime insolation followed by the night cooling).

In the case of multi-mineral stones, the latter determine differential contractions (when the temperature decreases) or expansions (when the temperature increases) of the minerals. When the spatial disposition of the minerals is casual, internal stresses can arise from conflicting expansions between minerals with opposite orientations and very different dilatation coefficients [11].

The carbonatic ones or the marbles, which are mono-mineral stones, behave similarly as the calcite expands along the vertical axis z and contracts along the direction perpendicular to it.

If two crystals of calcite are facing each other and are both oriented along the z axis, in occasion of temperature increases, they will expand one against the other causing internal tensions into the material. On the contrary, in the direction perpendicular to it, the contractions will determine the detachment between the two crystals.

Thus, repeated thermic cycles cause decohesion, disintegration and fragmentation of the carbonatic matrices.

The porosity of the stone has a fundamental role in the physical degradation phenomena associated with the presence of water or saline solutions. In fact, the water is a “wetting agent” towards stone materials and when it comes in contact with these porous matrices, it’s immediately “sucked” within the capillaries/pores through the so-called “capillary absorption” process that is much more pronounced as smaller is the diameter of the capillaries [11].

In fact, a further disgregation action that can affect carbonatic matrices is exerted by the repeated freezing-thawing processes of the water contained into the fractures or the porosity of the stone, due to oscillations of temperature around the gelation/fusion point of water. In fact, due its particular chemical structure and contrarily to what happens usually, passing from the liquid state to the solid one the water is subjected to an increase of the specific volume (9%) that is responsible for the increase of pressure against the walls of the pores and for the consequent formation of micro-fractures [2].

A similar effect derives also from the solvent action of water that allows the transportation of soluble salts through the pores of the stone; thus, when the water evaporates because of favorable thermo-hygrometric variations or the temperature decreases (determining a lowering of the solubility of the salts) and saturation or super-saturation conditions take place, the salts crystallize with an expansion of volume, exercising pressure onto the walls of the pores (“crystallization pressure”) [11].

Periodic salts solubilization/dissolution cycles can cause the progressive disgregation of the matrix and even the loss of the molds in the case of decorative elements.

The precipitation and crystallization of salts can happen inside the porous structure or onto the external surface. The phenomenon is ruled by two concomitant mechanisms: the diffusion of water vapor through the external layers, already dried, and the migration through the capillaries of the solution from the internal zones, still wet, towards the external ones that are drying. If the velocity of diffusion of the vapor is inferior to that of migration of the solution, this one can get to the external surface and there the crystallization will take place. Otherwise, the crystallization will happen at a certain distance from the external surface.

In the first case we talk about “efflorescences”, in the second case we talk about sub-florescences [11].

The exfoliations and detachments of superficial crusts, typical of porous material affected by the presence of soluble salts, are due to the formation of sub-florescences and to the consequent concentration of mechanical stresses underneath the surface.

Generally the physical deterioration determines a decrease of the grains dimensions and a consequent increase of the specific surface and this favors the chemical alteration processes.

The chemical degradation is attributable to the high level of pollution of the conservative environment and to the interaction of the stone material with water. This type of alteration is due to the presence of aggressive gaseous substances as nitrogen oxides (NO_x), sulfur oxides (SO_x) and carbon dioxide CO_2 in the atmosphere and thus it's generally more rapid outdoors while it's less intense indoors and minimal in museums or in areas not much contaminated [2].

These compounds are produced by the combustion of engines, heating systems and industries and are responsible for the corrosion of carbonatic materials, with the alteration of the chemical-mineralogical composition and the formation of crusts and patinas, often subjected to exfoliation and detachments.

The acidic action of those pollutants is a consequence of the production of their corresponding strong acid through the reaction with meteoric rain or moisture.

The sulfuric acid H_2SO_4 derives from the oxidation of the sulfur dioxide SO_2 into the sulfur trioxide SO_3 and the following reaction of the latter with water.

The nitric acid HNO_3 forms from the nitrogen oxides NO_x which derive from the reaction between nitrogen and oxygen at high temperatures.

The carbonic acid is produced by the interaction of the carbon dioxide CO_2 with water.

Both the *calcite* and the *dolomite* are particularly susceptible to the water, especially if it contains acids as the carbonic acid (H_2CO_3), the sulfuric acid (H_2SO_4) and the sulfurous acid (H_2SO_3). The acidic pH of rain due to the atmospheric pollution and, thus, to the presence of these acids in the air gives rise the well-known phenomenon of the “*acid rains*” that is the main responsible for the chemical deterioration of carbonatic matrices.

When the carbonatic stone is subjected to the direct runoff of rain rich in carbon dioxide, a slow transformation process of the calcium carbonate into the much more soluble calcium bicarbonate occurs (Reaction 7):



The projecting areas, as cornices or ornamental elements of buildings or the noses in the case of sculptures, are the most subjected to this type of corrosion.

Another consequence of this process is the recrystallization of the *calcite* with the formation of a white superficial powder because the calcium bicarbonate is a pretty instable salt and tends to precipitate as CaCO_3 for the evaporation of water.

Repeated humidification/drying cycles determine the recrystallization, into the superficial porosity of the stone, of “secondary” *calcite* that has different form, volume and dimensions compared to the primary one of the substrate. The deposit and growth of these new crystals exert a great pressure into the pores and determine the formation of micro-cracks and decohesions between the grains, with macroscopic loss of material and increase of the porosity, making the surface more susceptible towards the corrosion processes [14].

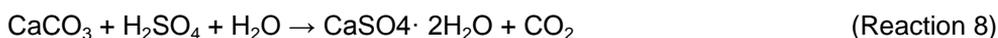
The sulphatization, that is the transformation of the calcium carbonate into the calcium sulfate bihydrate or gypsum, is the other very common alteration mechanism that affects carbonatic matrices and it can have very dramatic consequences. In fact, the formation of gypsum, which has a higher solubility in water than the calcium carbonate, can cause the formation of thick crusts known as

“black crusts”. The detailed description of this phenomenon and its consequences will be discussed in the next paragraph.

Other salts frequently present onto the carbonatic matrix of statues or frescoes or monuments are the oxalates. They form patinas which can be yellow, orange or brown colored and can have different origins: chemical transformation of organic substances used in the past as protectives or for aesthetic purposes; deposition of atmospheric particulate and metabolic activity of lichens, fungi and other microorganisms; residuals of products, extracted from plants containing oxalic acid, used for the polish of marbles [2].

1.3.2 The sulphatization and the black crusts

As anticipated in the previous paragraph, the sulphatization is the transformation of the calcium carbonate into the calcium sulfate bihydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum) through the interaction with the sulfuric acid H_2SO_4 (Reaction 8) transported by the rain or by the water vapor as a consequence of the reaction of the atmospheric sulfur dioxide SO_2 - a pollutant agent - with water (“*acid rains*” phenomenon, described previously).



In fact, the oxidation of the SO_2 occurs, in presence of catalysts (like metals - iron in particular - or their compounds, ozone, nitrogen oxides, UV radiations) and through the processes (1) or (2), within the condensation veils forming onto the stone surfaces or in the aerosol drops suspended in the air which then deposit onto the carbonatic material, rapidly triggering in both cases the sulphatization phenomenon.



The sulphatization can present intermediate hydration states of the calcium sulfate that from the anhydrous form (*anidrite*) passes to the hemihydrate one (*bassanite*) and then to the bihydrate (*gypsum*).

The elementary cell of the formed gypsum occupies almost a double volume compared to that of the calcium carbonate. In the case of carbonatic supports, when this reaction takes place and new crystals of gypsum form inside the porous structure, the consequent volume expansion determine mechanical stresses that, during repeated dissolution/crystallization cycles, cause cracking, fissuring and pulverization of the carbonatic matrix [15]. In particular, for frescoes, when the phenomenon is particularly severe, we observe lifting and detachment of the paint layer, with loss of decoration and pigments [16].

Due to the high solubility in water of the gypsum (2.4 g/L at 20°C), the presence of water increases its penetration into the material and, in conditions of high humidity, it can recrystallize in its decahydrate form with an ulterior volume expansion [2].

As concern outdoor artefacts characterized by a carbonatic matrix, the sulphatization represents also the first phase of the formation of the *black crusts*. These crusts are formed through the incorporation of atmospheric particulate between the crystals of gypsum. In particular, the carbon particles are very abundant, being one of the main components of the crusts, and are responsible for the black color of the deposits.

The analyses at the Scanning Electronic Microscope (SEM) on many samples extracted from black crusts revealed that they are composed of gypsum crystals (the main component) which give coherence to the deposit, secondary microcrystalline *calcite* of recrystallization, abundant globular carbon particles and, in minor concentration, bituminous and ferrous compounds (mainly oxides), crystals of quartz (of eolic or residual origin, considering that it is frequently present as an accessory mineral in limestones and marbles) and other silicate minerals, pollens and fungal spores [11].

Sometimes it has been found also the calcium oxalates (*weddellite* and *whewellite*) derived from the metabolic activity of lichens or from ancient polish or protective treatments.

The observation at the microscope of cross sections of black crusts led to discover that they don't adhere directly to the stone but, almost always, to a layer of gypsum, pure or mixed with secondary microcrystalline *calcite* of recrystallization.

This type of encrustations is very compact and strongly anchored to the stone substrate. They are constituted by uniform layers with a thickness varying from 0.5 to 2-3 mm, which cover the stone maintaining its original morphology; sometimes in the zones protected by the water rainoff, they assume irregular dendritic shapes up to 2 cm thick or form lumps [11].

The black crusts tend to become always thicker and harder and less porous, thus emphasizing the difference in the mechanical and thermal behavior between them and the underlying stone.

For example, their black color causes a higher absorbance of the solar radiation and a consequent greater thermal expansion.

Furthermore, being slightly permeable, they block the diffusion phenomenon of the water vapor between the internal and the external parts of the stone, determining the retention of water and salts possibly present and mechanical stresses which favor the detachment of the crust itself and of the original material with loss of the modeling [17].

In conclusion, the presence of these crusts is associated with a deep and dramatic deterioration process characterized by flaking, exfoliation, swelling, cracking or fissuring, followed by the falling of the deposit and the disintegration of the underlying stone material. Onto the exposed, fragile surface the formation of a new crust takes place and all the process starts again.

Thus, the removal of the black crusts is fundamental not only to restore the artefact from an esthetical point of view but mainly to quit the degradation processes.

The problem is that if we don't remove the primary causes, that is the presence of sulfur oxides in the atmosphere due to the anthropic pollution, the formation of new crusts will be inevitable and determine, after each cleaning intervention, the erosion of the new superficial layer.

The *calcite* of recrystallization possibly present must be removed as well because it is more reactive than the well-grown one of the substrate and it's responsible for the faster formation of the black crusts.

1.4 Bibliography

- [1] M. LEONI, *Elementi di metallurgia applicata al restauro delle opere d'arte. Corrosione e conservazione dei manufatti metallici*, Opus Libri, 1984.
- [2] L. CAMPANELLA ET AL., *Chimica per l'arte*, Zanichelli Editore, 2007.
- [3] G. CARBONARA, *Trattato di Restauro Architettonico*, Torino, 1996.
- [4] P. TIANO, C. PARDINI, a cura di, *Le patine: genesi, significato, conservazione*, Kermes quaderni, Firenze, Nardini Ed., 2005.
- [5] C. LALLI ET AL., *L'inquinamento atmosferico. Danni sui monumenti esposti*, in AA.VV., *La vetrina per il museo*, Firenze, Phase, 1999, 17-32.
- [6] J. WANG ET AL., *Applied Surface Science*, 2006, 252, 6294.
- [7] L. ROBBIOLO ET AL., *Corrosion Science*, 1998, 39 (1), 2083.
- [8] A. DAVID SCOTT, *Metallography and microstructure of ancient and historic metals*, Malibu, The Getty Conservation Institute, 1991.
- [9] A. DAVID SCOTT, *Copper and bronze in art: corrosion, colorants, conservation*, Los Angeles, Getty Publications, 2002.
- [10] L. WUGAN, JIN R., *Applied Physics Research*, 2010, 2 (2).
- [11] L. LAZZARINI, M. LAURENZI TABASSO, *Il restauro della pietra*, UTET, 2010.
- [12] C. ELMI, M. DIRETTO, *“Geologia”*, Pitagora Editrice, 1996.
- [13] AA. VV., *Enciclopedia Treccani*, Istituto dell'Enciclopedia Italiana, 2009.
- [14] G. AMOROSO, *Trattato di scienza della conservazione dei monumenti*, Collana Manuali, Alinea, 2006, 58-59.
- [15] L. BORGIOLI, *Polimeri di sintesi per la conservazione della pietra*, Collana I Talenti, Il Prato, 2002.
- [16] E. FERRONI, P. BAGLIONI, *Proceedings of the Symposium on Scientific Methodologies Applied to Works of Art*, Firenze, 1984, Montedison Progetto Cultura, Milano, 1986, 108.
- [17] G. AMOROSO, *Il restauro della pietra nell'architettura monumentale*, Palermo, 1995.

CHAPTER 2

Traditional chemical methods for the cleaning of metallic and carbonatic surfaces of artistic and historical interest

2.1 Introduction

Mentioning Cesare Brandi (Teoria del Restauro, 1963), Italian art critic and art historian, specialist in the theory of restoration, founder (in 1939) and director (from 1939 to 1959) of the ICR (Central Restoration Institute) of Rome: *"restoration is the methodological moment of recognition of the work of art, in its physical consistency and its dual aesthetic and historical polarity, in view of its transmission to the future"*; moreover, *"[...] it shall be directed to the restoration of the potential unity of the work of art, insofar as this is possible without committing an artistic false or an historical false, and without erasing all traces of the past of the work of art in time"*[1].

Based on this concept the cleaning step, aimed at the removal of the degraded original materials or the extraneous ones superimposed on the surface of the artwork, represents one of the fundamental preliminary operations and the most delicate part of the restoration. The cleaning phase is critical and complex because if performed with solvents or other substances too aggressive or low compatible with the support it can trigger processes potentially harmful to the work itself (undesired softening or solubilization of original materials, bleaching effects, opacification of the colors, removal of the veils...).

Giorgio Bonsanti, Italian art historian, defined the cleaning as *"[...] an intervention aimed at the reconstruction of a decent aesthetic condition of the work, that is called, in particular, "legibility"*; he states also that *"[...] a cleaning operation is in fact the condition for the access to the surface of the artifact, without which this access is impossible or anyway strongly limited. We know, moreover, that if there is no access to the surface, generally, as a rule and with some exceptions, there aren't even the conditions for a whole series of interventions, starting with those strictly*

structural and conservative, which may include consolidations, protections and so on" [2].

For a correct cleaning operation, it is necessary to set-up specifically tailored treatments for each artifact, taking into account of its conservation condition, the stratigraphic composition of the patina, its structural response with respect to the stresses derived from the environment of conservation [3].

It's well known, in fact, that a work of art is, for definition, unique [4].

Diagnostic analyses, along with historical-artistic researches, should precede the cleaning intervention in order to individuate the most suitable, effective and less aggressive products and the best application methodology to use.

Furthermore, another aspect to consider is the desired level at which the cleaning action should be stopped, based on the definition of *patina* and the historical value and/or the protective role that it may have.

The patinas spontaneously formed onto ancient works of art are superficial layers, usually very thin, composed of different materials which deposit through time or are the result of the transformation of the original matter [5].

In some cases, for example the bronzes, an artificial patina is intentionally created by the artist to obtain a particular aesthetical effect, thus becoming an alteration that is part of the original material of the piece of art [4].

Thus, the term *patina* and its possible historical-artistic implications have been object of debates for centuries between those who sustained a drastic, integral cleaning aimed at re-establishing the original aspect of the surface with bright and vivid colors/surfaces and those who, on the other hand, defeated the authenticity of the patina.

In 1681 Filippo Baldinucci, an Italian art historian and painter, in his *Vocabolario toscano dell'Arte del disegno*, defined the "*patena*" as the term used by painters to indicate the universal, natural darkening of paintings due to the passage of time, that sometimes "favors" them in the sense that it increases their historical value [1,6].

In this definition there's the positive evaluation of the natural aging of the work of art, as a completion of its artistic value and a guarantee of its authenticity and antiquity.

On the contrary, others retained that the passage of time could not make improvements to the artefact. For example, the English painter Hogarth (mid-18th

century) had a negative conception of the patina and considered the time as a destroyer of the matter because each material responds in a different way to changes [4]. In that period the restorers of the National Gallery of London, in line with the philosophy of Hogarth, carried on integral cleanings aimed at eliminating the transformations that the paintings had suffered over time.

Nowadays, as concern the Italian concept of restoration, it's universally accepted that the cleaning methodology must be differentiate according to the material and to its conservative conditions, and that the patina hasn't to be removed completely, performing a selective, gradual and controllable cleaning action [7].

The modern guidelines for the approach to the patina are based on the theoretical principles diffused from the II World War onwards by the most important contemporary figures in the conservation field as Cesare Brandi, Umberto Baldini and Alessandro Conti.

Roberto Longhi, in 1948, defined the patina as the "skin" of a painting [4]; Cesare Brandi attributed to it an aesthetical value [1].

Conscious of the irreversibility of the cleaning step, an accurate preliminary study of the artefact and its conservation environment is fundamental and the cleaning should be the less invasive as possible, not aggressive, selective, gradual and respectful of the natural aging patinas.

Baldini and Brandi sustained, in fact, that the materials and their chromatisms should be preserved without bringing them back to their original conditions because that operation won't respect the "age" of the artwork and would be a "historical falsification" [1,8]. It's not ethically correct to restore the hypothetic primary state of an object through the cleaning action.

In this chapter an overview of the main chemical methods used for the cleaning of carbonatic substrates (stone manufacts, frescoes/mural paintings...) and metallic surfaces is given.

2.2 The removal of salts from metallic and carbonatic surfaces: the chelating agents

Chelates (from the Greek word *chele*, meaning claws) represent an important class of substances in cleaning systems. Generally they are non-toxic substances applied in an aqueous medium, traditionally used for the removal of metal ions from both carbonatic and metallic surfaces of historical-artistic interest.

Their mechanism of action is chemical, since it involves the dissociation of the molecule and the complexation of one of the resulting ions.

They are compounds that contain at least two or more functional groups that can act as electron-donor. The particular spatial distribution of the electron-donating groups let them to interact, via non covalent bonds, with individual metal ions, forming cyclic complexes called “chelates” which have quite different properties compared to those of the metal ion or the chelating agent alone in solution [9].

This mechanism of coordination is possible because the metals, having empty orbitals, are electron-acceptor and can interact with atoms rich in available electrons as nitrogen, oxygen, sulfur and phosphor.

The molecule containing the electron-donor atoms is called “ligand”; a ligand can be defined bi-, tri-, tetra-dentate and so on, if it contains two, three, four or more donor atoms. In the case of mono-dentate compounds as ammonia, the formation of a ring is not possible and thus we talk of “coordination” of metal ions rather than chelation.¹

The ligand, as well as the ligand-metal complex, can be neutral or ionic. The pH of the medium influences the ionization rate of the functional groups of the chelator and, consequently, its charge.

The metal-chelator complexation reaction is characterized by a “formation or stability constant” K_f of the chelate species. The higher is the K_f and the more stable is the complex that is formed. Generally these equilibrium constants correspond to very high or very small values and thus, the $\text{Log } K_f$ is preferred. A high value of $\text{Log } K_f$ indicates a strong tendency to the formation of the metal-ligand chelate and thus $\text{Log } K_f$ values can be used to predict the selectivity of the chelation reaction when

¹ http://www.treccani.it/enciclopedia/chelazione_%28Enciclopedia-Italiana%29/, consulted on December 2014.

many metals are present. Some Log K_f values for two chelating agents, EDTA and citric acid, referred to different metals, are reported in Table 2.2.1 [10].

Table 2.2.1. Log K_f for citric acid and tetrabasic EDTA referred to different metals.

Metal cation	Log K_f	
	Citric acid	tetrabasic EDTA
Fe ³⁺	10.9	25.1
Hg ²⁺	Nd*	21.8
Cu ²⁺	6.1	18.8
Ni ²⁺	4.8	18.6
Pb ²⁺	5.7	18.0
Zn ²⁺	4.5	16.5
Cd ²⁺	4.2	16.5
Co ²⁺	4.4	16.3
Fe ²⁺	3.2	14.3
Ca ²⁺	3.5	10.7
Mg ²⁺	2.8	8.7
Ba ²⁺	Nd*	7.8

*Nd: not determined

For example the EDTA will chelate preferentially Fe³⁺ ions (Log K_f 25.1) rather than Ca²⁺ ions (Log K_f 10.7). The same would happen in presence of the citric acid but, being the difference between the two Log K_f smaller in this case, the citric acid would be a less selective chelator than EDTA.

On the other hand, the complexing ability against a specific ion depends also on the pH value that, as already said before, influences the deprotonation rate of the ligand and, consequently, its charge and its affinity towards the different cations.

In fact for each complexing agent a characteristic diagram of species distribution is defined, which shows the curves representing the areas of prevalence of the various species differently protonated as a function of the pH (an example, for the EDTA, is given in Figure 2.2.1).

For this reason, it must be considered that the complexation of a certain metal has an optimum pH: as concern the EDTA, the optimum pH to sequester the Ca^{2+} and the Fe^{3+} ions is around 10 and around 6 respectively.

Thus, knowing the formation constants of the complexes between the ligand and the different metal cations as a function of the pH, it is possible to evaluate which is the best working pH to enhance the extraction of a specific metal.

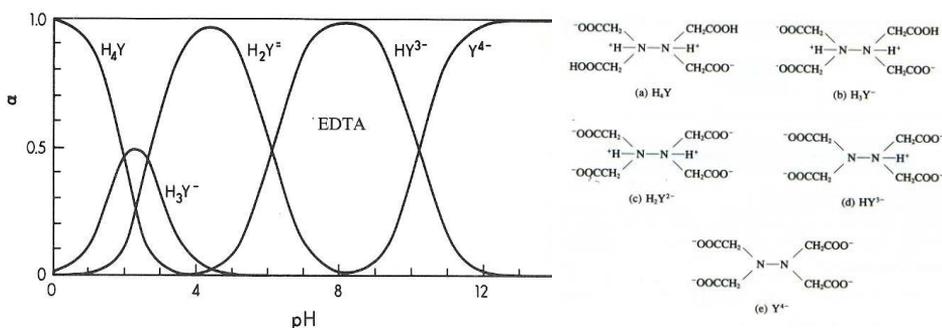


Figure 2.2.1. Left: distribution diagram of the EDTA species as a function of the pH; right: the 5 different EDTA species.

The chelating agents are frequently used in the restoration for the removal of salts (efflorescences, corrosion and oxydation layers) from carbonatic or metallic substrates because of their selectivity of action and the possibility of applying them in aqueous solution, minimizing in this way the toxicity of the cleaning method for the operator. The chelators mostly used are: EDTA, citrate salts and Rochelle salt [11-15].

The EDTA or ethylenediaminetetraacetic acid, is a white crystalline solid, slightly soluble in water (0.50 g/L), belonging to the class of aminocarboxylic acids. It's a tetra-protic acid containing four carboxylic groups ($-\text{COOH}$), which can be neutralized with a base, for example, with sodium hydroxide (NaOH), forming water soluble salts (in this case: mono-, bi-, tri- or tetra-sodium EDTA).

The disodium EDTA is the one most frequently used in the field of restoration, as the tetrasodium is less soluble in water and more harmful. EDTA forms very stable octahedral complexes with all metals, by binding either through its two nitrogen

atoms (which act as Lewis bases) and the four carboxylic oxygen atoms, once deprotonated [9].

The disodium EDTA has a pH of 4.5, while the tetrasodium has pH of 11.3 (see the speciation curves in Figure 2.2.1); these values should always be considered in relation to the support that has to be treated. The optimum pH for the extraction of the Ca^{2+} ion is around 10, while it is between 9-10 for the Cu^{2+} ion.

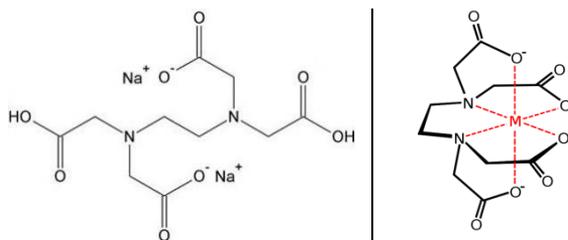


Figure 2.2.2. On the left: structure of the disodium EDTA; on the right: complex formed by an EDTA molecule and a generic metal.

The Rochelle salt (sodium potassium tartrate), is a complexing agent known since the Middle Ages (in some texts it was called "cream of tartar", as it accumulated on the walls of the barrels, falling from the must). Being weaker than the EDTA, the Rochelle salt exerts a mild action, providing a better control in the cleaning of bronze, as complex carbonates and chlorides, but to retain the red cuprite, on which acts weakly. The bland action ensured by this complexing agent makes it suitable, in particular, for the cleaning of gilded bronzes, when it is necessary to preserve the original gold leaf and simultaneously remove the surface deposits of copper salts [16].

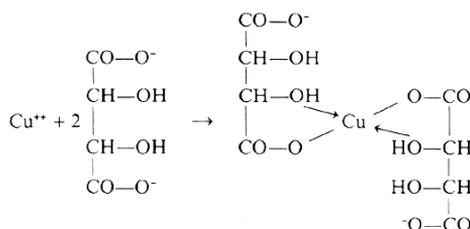


Figure 2.2.3. Chelation mechanism of the copper ion Cu^{2+} by the Rochelle salt.

Another chelator frequently used in conservation is the sodium citrate (also known as trisodium citrate), a sodium salt of the citric acid. The citric acid does not have a high complexing power but the corresponding salts, the citrates, are used for the improved effectiveness of coordination of the oxygens of the deprotonated carboxyl groups.

The sodium citrate is able, in fact, of complexing the calcium ion, Ca^{2+} , in a pH range of 2-10 and thus, it can be used in the treatment of coatings containing sulfates and oxalates. It can chelate also the copper ion, Cu^{2+} , at pH 2-9 [10].

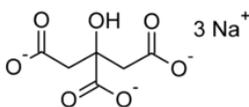


Figure 2.2.4. Structure of the trisodium citrate.

Despite the mechanical cleaning with laser [17] is by far the most widespread methodology for the treatment of metal artifacts, the use of chelating agents as cleaning tools allows to solubilize the corrosion coatings on metal objects almost without any structural risk. The chelator, in fact, acts against the metallic ions of the patina but it stops when it reaches the healthy core of the metal where only metal atoms are present and no more ions (the speed of extraction of the chelating agent on the atoms is so low that it can be considered nothing).

Of course the pH of the medium must be modulated according to the type of metal on which it must act.

For the cleaning of gilded bronzes, the chelator traditionally used is the Rochelle salt which, exerting a more bland action than the EDTA, ensures a better control of the level of cleaning, without affecting the original gold leaf. For example, a concentrated neutral aqueous solution of Rochelle salt was used for the cleaning treatments onto the so-called *Porta del Paradiso* (Figure 2.2.5), the east door of the Baptistery of Florence, gilded bronze masterpiece crafted by Lorenzo Ghiberti between 1429 and 1452. The gilding was seriously damaged, appearing weakly bound to the substrate with exfoliation and loss sites; after comparative cleaning

tests, the Rochelle salt resulted active to some extent underneath the gilding and the most selective with respect to the cuprite layer underlying the gold film [17].

The surface cleaning by optimized QS-Nd:YAG laser ablation was effective in the complete removal of the encrustation and the low concentration Rochelle salt poultice and the following rinsing, after laser cleaning, removed residual chlorides and sulfates in the proximity of the gold surface. This integrated procedure also provided an increase of specular reflectance of the gold surface in comparison with the standalone laser treatment.

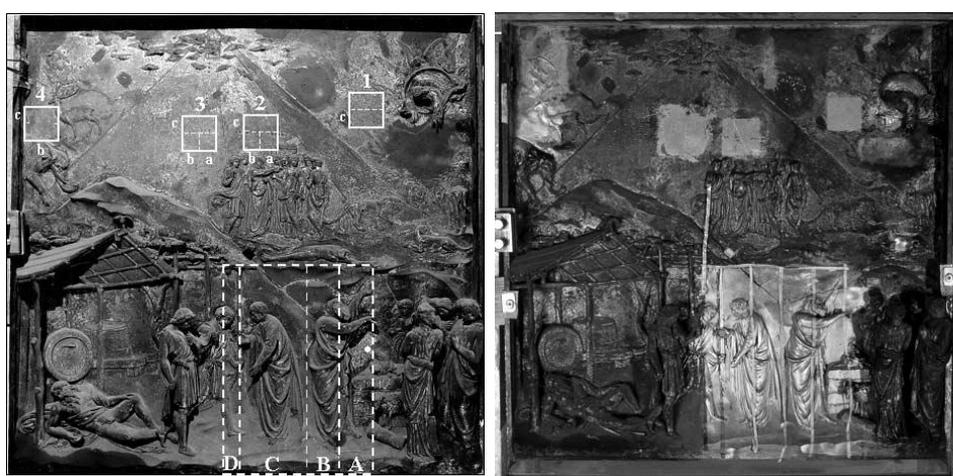


Figure 2.2.5. Left: the *Storie di Noè* panel with the indication of the cleaning test sites. Right: the *Storie di Noè* panel after the laser-based treatment followed by light sodium potassium tartrate poultice application [17].

Because of its weak chelating action, it is necessary to prepare aqueous solutions containing around 35% of the salt and make wraps of different duration, depending on the thickness of the encrustations to be removed and the final effect to be obtained. The action of the Rochelle salt can be enhanced by increasing the pH of the solution with the addition of sodium hydroxide.

As concern mural and stone supports, the use of chelators (mainly the EDTA) is aimed generally at removal of Ca^{2+} ions in form of sulfation patinas (gypsum or calcium sulfate bihydrate), calcium oxalates or calcium carbonate-based whitewashings. Particular attention must be given to avoid the solubilization of the original calcium-based material constituting the matrix (calcium carbonate in the case of lime mortar plasters or the *calcite* in the case of stone material) and the

metals constituting the pigments which can be complexed by the chelator in the right pH conditions. Thus, beyond the choice of the chelator, the pH is a fundamental parameter.

In order to know if a chelator would be effective in the solubilization of a certain salt (through the complexation of its metal ion) or not, the solubility product K_s or, better, the pK_s (logarithm of K_s with opposite sign) of the salt itself must be considered as well. The higher is the pK_s and the more stable is the salt (the less soluble).

Thus, a chelating agent is able to solubilize a salt only when the $\text{Log } K_f$ of the metal-ligand is higher than the pK_s of the salt.

In Table 2.2.2 the comparison between the pK_s of calcium sulfate and calcium carbonate and the $\text{Log } K_f$ for the Ca^{2+} chelates obtained with tribasic and tetrabasic EDTA and citric acid are reported. According to the values indicated, the citric acid can't chelate neither of the two salts; tribasic EDTA can chelate the calcium sulfate but not the calcium carbonate; the tetrabasic EDTA can chelate both [10].

Table 2.2.2. pK_s of calcium sulfate and calcium carbonate and $\text{Log } K_f$ for the Ca^{2+} chelates obtained with tribasic and tetrabasic EDTA and citric acid.

Solubility product pK_s	Formation constant for Ca^{2+} $\text{Log } K_f$
CaSO_4 4.15	Citric acid 3.15
CaCO_3 8.54	Tribasic EDTA 8.43
	Tetrabasic EDTA 11.00

This implies that, depending on the pH, extreme care must be taken to avoid the corrosion of the original limestone material through the chelation of Ca^{2+} . For example, when EDTA chelating species are used, it is necessary not to exceed a pH value of 8.

In general, for the treatment of artistic surfaces, the chelating agents are used in concentration to 1-5% in aqueous solution [10].

To limit their penetration into the inner layers and to avoid the solubilization of the original materials, chelators aqueous solutions are usually adsorbed into poultices of carboxymethylcellulose or gelled with a thickener as Klucel G or Carbopol.

The main drawback of these applicative methods is that these thickened systems release residues onto the treated surface and the necessity of a clearance step with

a neat liquid (generally water) and/or extra mechanical action can be critical in presence of fragile or hydrophilic surfaces/materials.

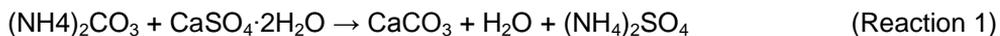
Despite the mechanical cleaning with lasers is a very diffused methodology also for the treatment of stone artefacts or architectures [18], for the removal of degradation layers from carbonate substrates, the most used chemical cleaning method is based on the use of an aqueous mixture, defined AB57, containing disodium EDTA, sodium bicarbonate, ammonium bicarbonate, alkyldimethylbenzylammonium chloride (Desogen) and carboxymethyl cellulose. The disodium EDTA exerts a chelating action towards the calcium ion, present as sulfate in the black crusts (gypsum or calcium sulfate bihydrate) or as oxalate [9].

The addition of sodium and ammonium carbonates in the cleaning solution is aimed at adjusting and maintaining the pH to about 7.5, thanks to their buffering action. The Desogen plays a bactericidal and surfactant action, while the carboxymethyl cellulose is added as thickener, allowing the application of the preparation in the form of compresses. In this way the penetration of the cleaning solution to the original material is limited, but the healthy surface of the artefact could still be affected if the procedure is not completed with the total removal of the package through washing and delicate brushing [9].

2.3 The Ferroni-Dini's method for the desulphatization and consolidation of carbonatic substrates

One of the most effective traditional treatments for the gypsum removal from carbonatic supports is the Ferroni-Dini method [7], developed in 1966 by Enzo Ferroni, chemistry professor at the University of Florence, and Dino Dini, headmaster in the restoration of frescoes of the Opificio delle Pietre Dure of Florence. It's a two-phases treatment consisting in the solubilization of gypsum with a water solution of ammonium carbonate followed by the application of barium hydroxide that ensures the consolidation of the degraded matrix and at the same time makes the sulfate unreactive and insoluble.

The first phase consists in the application of a cellulose pulp compress containing the solution with the ammonium carbonate: this compound reacts with the gypsum to form calcium carbonate, water and ammonium sulfate (Reaction 1):



The ammonium sulfate, being a soluble compound, can give rise to surface efflorescences or migrate within the carbonate matrix; furthermore, the calcium carbonate obtained from the conversion of the gypsum is in the form of microcrystalline powder, free of binding power, producing an increase of porosity in the material and promoting the disintegration of the substrate. For these reasons, the method involves the application of a second wrap of cellulose pulp and a 3 wt% solution of barium hydroxide, which reacts with the ammonium sulfate forming ammonia, water and barium sulfate, an insoluble and inert compound that partially fills the gaps created in the first phase (Reaction 2):



The excess of barium hydroxide within the porous matrix of the calcareous material, can also react with the carbon dioxide of the air (Reaction 3), undergoing carbonation and further cementing the structure [19,20]:



The characteristics of the barium carbonate are very similar to those of the calcium carbonate; furthermore, the mechanism of precipitation leads to a gradual recovery of the homogeneity of the material [9].

The calcium carbonate formed is converted from microcrystalline powder, free of binding power, in a material more similar to the original one (Reaction 4), which further reacts with the atmospheric carbon dioxide, giving rise to a new carbonation reaction (Reaction 5):



The first application of this desulphatization treatment was carried out on the *Crucifixion* by Beato Angelico, in the chapter house of the San Marco church and on other frescoes on the ground floor. The results were satisfactory and encouraging, without having to resort to drastic methods such as the detachment of the fresco or the application of adhesives for fixing the color [7].

The method has the advantage of not altering the wetting properties of the surface, whose hydrophilicity remains identical to that of the original material and is perfectly compatible with the use of other products (for cleaning, consolidating and protection); it also has high durability due to the stability of the inorganic compounds used [21]. In fact, it was discovered that many years after the treatments, the consolidating effect was higher than that obtained immediately after the restoration, due to further reactions occurred afterwards [22].

However the Ferroni-Dini's method presents also some limits as the high toxicity of the barium hydroxide and the irreversibility of the treatment [19].

2.4 Ion-exchange resins

An alternative, widely used technique for the removal of soluble salts and, in particular, of calcium sulfate from frescoes, mural paintings, plasters and stucco decorations consists in the use of ion-exchange resins [23,24].

Ion-exchangers are natural or synthetic substances which, in aqueous solutions, are able to exchange ions within their structure with equivalent amounts of other ions having the same charge. They can be cationic, anionic or mixed (cationic-anionic). Their structure is made of a matrix to which fixed ionic groups, in equilibrium with a contro-ion oppositely charged, are covalently attached. The contro-ion is the exchangeable part; it can be a cation or an anion [25].

Generally they are synthetic resins in the form of spherical granules (100-400 mesh) that swell when in contact with water and are completely insoluble in it. Due to this feature, when ion-exchangers are in contact with a work of art contaminated by salts, their action is limited to the surface up to a depth of about 70-100 μm , without penetrating into the porosity of the object, thus avoiding the interaction with

the original materials you want to preserve and the contamination with extraneous materials [26]. This is a favorable characteristic in the restoration field.

The exchange reaction, consisting in the substitution of the harmful ions with innocuous ones, is limited to the contact interface between the exchanger and the surface to be cleaned.

The reaction mechanism can be described as follows [26]:

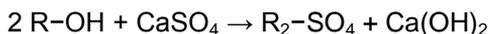


It is clear that, as the exchange action proceeds, there is a gradual increase in free acidity (H^+) for cationic resins, and alkalinity (OH^-) for anionic ones.

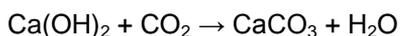
For the removal of gypsum alteration layers from mural paintings or from decorative finishes as stucco plasterworks or *marmorino* elements with lime components, anionic resins are used.

They remove selectively the sulfate ion releasing hydroxide ions; in this way, the calcium ions Ca^{2+} of the calcium carbonate of the plaster are not affected [26].

The reaction that takes place is the following:



The sulfate ion is substituted by the hydroxyl ion which, when combined with the calcium hydroxide ion (in the presence of carbon dioxide), forms calcium carbonate, according to the following reaction:



Through repeated applications of de-sulphating anionic resins, it is possible to remove the calcium sulfate from the surface and further down to a depth of about 70-100 μm . This methodology can be used as an alternative to the first step of the Ferroni-Dini's method that implies the use of ammonium carbonate that in some cases could give rise to whitening effects due to the formation of secondary calcium carbonate. Furthermore, with this treatment, the formation of barium sulfate

(characteristic of the Ferroni-Dini's method), an insoluble salt which also has a whitening effect on the surface, is avoided [26].

Due to the alkaline pH, the anionic resins are widely used because they are active even towards organic materials as oily, protein, and resinous substances.

An advantage of using exchange synthetic resins is that they can be regenerated back to their original form, allowing for long-term use and re-use of them.

Other benefits of the technique are the following: the resins are not hazardous, can be easily handled and transported; no material is lost from the reaction itself; the exchange reaction occurs only at the interphase between the resin and the substrate; the cleaning action is highly controllable due to the limited reactivity depth [27].

On the other hand, there are many disadvantages: the fact that the resins act only at the interphase implies the necessity of multiple treatments for highly concentrated substances; the reaction is slow, requiring dwell time, constant moisture and repeated applications; the resins can be quickly rendered ineffective and they can be too acidic or alkaline for sensitive painted surfaces or finishes; the exchangeable counterion has to be chosen carefully to prevent the creation of undesirable byproducts; the resins may be too costly, time-consuming and require pre-conditioning to be effective [27].

2.5 Conclusions

As will be discussed in the next Chapter, the necessity of developing new technologies for the cleaning of surfaces of artistic and historical interest comes from the limits of the traditional methods. The existing cleaning tools in fact, often provide the use of toxic substances (as most of the organic solvents or the barium hydroxide in the Ferroni-Dini's method), can be aggressive and potentially harmful for the original materials constituting the piece of art because of a too acidic or basic character or the production of undesirable products (as for the ion-exchange resins) or because of a lack of selectivity (as for the chelating agent).

Furthermore when, in order to limit the penetration of the cleaning solutions and all the related side effects (undesirable solubilizations, swelling of the binder, transport

and deposit of the removed material into the porosity of the support), gelled or thickened systems are used, the complete removal of them is not possible and thus, the presence of many residues makes necessary an extra mechanical action and a clearance step with neat liquids, both unwanted, especially in the case of fragile surfaces.

For all these reasons, during the last decades, the research in the art conservation field has focused on the development of innovative technologies the less toxic for the environment and the operators, the less invasive or aggressive as possible and, at the same time, highly retentive towards the cleaning solution, elastic in order not to leave residues, performing an effective but gradual and controllable cleaning action.

In the next Chapter, a detailed description of the innovative highly viscous polymeric dispersions for the cleaning of surfaces of artistic and historical interest that have been formulated by my research group and match all these desirable characteristics, will be given.

2.6 Bibliography

- [1] C. BRANDI, *Teoria del restauro*, Einaudi Editore, 1963.
- [2] G. BONSANTI, *Storia ed Etica della Pulitura*, in: *ibid.* 3,14-15.
- [3] AA. VV., *Enciclopedia della chimica*, Utet edizioni scientifiche, Firenze, 1997.
- [4] A. CONTI, *Manuale di restauro*, Einaudi Editore, 2001.
- [5] P. TIANO, C. PARDINI, *Le patine: genesi, significato, conservazione*, Kermes quaderni, Firenze, Nardini Ed., 2005.
- [6] F. BALDINUCCI, *Vocabolario toscano dell'Arte del disegno*, 1681, Firenze, 119.
- [7] M. CIATTI, *Appunti per un manuale di storia e di teoria del restauro. Dispense per gli studenti*, Edifir, 2009.
- [8] U. BALDINI, *Teoria del restauro e unità di metodologia*, Firenze, Nardini editore, 1981.
- [9] L. CAMPANELLA ET AL., *Chimica per l'arte*, Zanichelli Editore, 2007.
- [10] P. CREMONESI, *L'uso di tensioattivi e chelanti nella pulitura di opere policrome*, Collana i Talenti, ed. Il Prato, 2003.
- [11] H. BURGESS, *The Paper Conservator*, 1991, 15, 36-44.

- [12] A. PHENIX, A. BURNSTOCK, *The Conservator*, 1992, 16, 28-38.
- [13] J. HEUMAN, *The Conservator*, 1992, 16, 12-17.
- [14] I.D. MACLEOD, *Studies in conservation*, 1987, 32, 25-40.
- [15] L. CARLYLE, J.H. TOWNSEND, S. HACKNEY, *Triammonium citrate: An investigation into its applications for surface cleaning*, in *Dirt and Pictures Separated: papers given at a conference held jointly by UKIC and the Tate Gallery*, January 1990, United Kingdom Institute for Conservation: London, 1990, 44-48.
- [16] G. CARBONARA, *Trattato di Restauro Architettonico*, Torino, 1996.
- [17] M. MATTEINI ET AL., *Journal of Cultural Heritage*, 2003, 4, 147s-151s.
- [18] G.G. AMOROSO, *Il restauro della pietra nell'architettura monumentale*, ed. D. Flaccovio, Palermo, 1995.
- [19] L. BORGIOLO, *Polimeri di sintesi per la conservazione della pietra*, Collana I Talenti, Il Prato, 2002.
- [20] M. MATTEINI, A. MOLES, *La chimica nel restauro. I materiali dell'arte pittorica*, Firenze, Nardini Ed., 2010.
- [21] M. MATTENI, S. SCUTO, *Consolidamento di manufatti lapidei con idrossido di bario*, Arkos 1, 2001.
- [22] P. BAGLIONI ET AL., *Nanotechnology in wall painting conservation*, Self-Assembly. B.H. Robinson, Ed. IOS press, 2003.
- [23] A. GIOVAGNOLI, C. MEUCCI, M. TABASSO LAURENZI, *Ion-exchange resins employed in the cleaning of stone and plasters: research of optimal employment conditions and control of their effects*, in: *Deterioration and preservation of stones*, Proceedings of the 3rd International Congress, Venezia, October 24-27, 1979, Università degli studi—istituto di chimica industriale, Padova, 1982, 499-510.
- [24] M. MATTEINI, A. MOLES, M. OETER, I. TOSINI, *Ion exchange resins in the cleaning of stone materials and of mural paintings: experimental tests and applications*, in: *The cleaning of architectural surfaces*, Proceedings of a symposium, Bressanone, July 3-6, 1995, Libreria Progetto, Padova, 1995, 283-292.
- [25] P. FIORENTINO, M. MARABELLI, M. MATTEINI, A. MOLES, *Studies in Conservation*, 1982, 27, 145-153.
- [26] N. BERLUCCHI, R. G. CORRADINI, R. BONOMI, E. BEMPORAD, M. TISATO, *“La Fenice” theatre-foyer and Apollinee rooms – consolidation of fire-damaged stucco and marmorino decorations by means of combined applications of ion-*

exchange resins and barium hydroxide, in: Proceedings of the 9th International Congress on Deterioration and conservation of stone, Venezia, 2000, 23-31.

[27] C. SMITH, *Cleaning methods for the removal of limewash from painted plaster surfaces: utilizing ion exchange resins on the interior architectural finishes of the Capilla de Nuestra Señora del Rosario in Iglesia San José, in San Juan, Puerto Rico*, master thesis in Historic Preservation, University of Pennsylvania, 2009.

CHAPTER 3

The xPVAc-borax HVPDs

3.1 Introduction

During the last 15 years, several cleaning procedures for works of art, employing new cleaning agents, have been developed using as a guiding principle that they would be very selective. Most involve the use of highly viscous agents [1], such as gels [2], thickened or gelled solutions [3,4] or polymeric systems [5-8] in order to minimize the negative effects related to the penetration of the liquid phase into the painting matrix and the impact on both the treated work of art and the environment. However, it is not always possible to ensure complete removal of the gelling polymer after its application and this gave rise to well-known “*residue question*” [9,10]. For example, Burnstock and Kieslich demonstrated that residues of a poly(acrylic acid)-based gelator can remain after the application of its gels onto a painted surface [11].

In order to overcome this problem, during the last decades within the laboratories of the chemistry department of the University of Florence and CSGI consortium (*Consorzio interuniversitario per i Sistemi a Grande Interfase*), innovative highly retentive cleaning tools intended to minimize the residues left after their application onto artistic surfaces without the need to apply an abrasive force or neat organic solvents were developed. They are named *Highly Viscous Polymeric Dispersions* (HVPDs) and are obtained from poly(vinyl alcohol) (PVA) or partially hydrolyzed poly(vinyl acetate)s (xPVAc, where x is the hydrolysis degree) and borax salt.

As will be explained in the present chapter, due to their elasticity, they can be removed from a treated surface in one piece, without the use of a gel clearance step or a strong lateral force, thereby, minimizing the potential for residues.

Their viscoelasticity, transparency, low toxicity, ease of preparation, as well as the ability to modulate these properties by modifying the formulations, make these HVPDs very attractive cleaning tools for the conservation of painted surfaces.

Furthermore, they can incorporate large amounts of a wide range of organic solvents, being effective for the removal of different type of extraneous substances.

In this chapter a description of these HVPDs and their properties is given.

The application of them onto the surface of different artworks is also reported to demonstrate their cleaning efficacy, their selectivity and gradualness of action.

3.2 PVA/xPVAc-borax network: characteristic and mechanism of formation

Poly(vinyl acetate)s are commercially available in a broad range of hydrolysis degrees and molecular weights making possible to significantly modulate their properties to optimize the performances for specific applications. This versatility has sparked interest on the study of the physico-chemical properties of aqueous solutions of xPVAc [12], mainly on the study of the properties related to the polymer concentration [13,14], on the rheological properties [15], and on the effect of different cross-linking agents that allow the formation of chemical (i.e. using glutaraldehyde as a cross-linker) or physical gels (from hydrogen bonds or chemical reactions involving the hydroxyl groups) [16].

Gel-like systems are achievable from PVA aqueous solutions via complexation and crosslinking between the side-chain hydroxyl groups of the polymer and ions such as borate, vanadate or antimoniate [17,18].

Of particular interest in this study is the *di-diol complexation* [19] in which PVA (or xPVAc) aqueous solutions form thermally-reversible, highly-viscous polymeric dispersions (HVPDs) in the presence of borax.

The nature of the cross-links proposed by Deuel and Neukom [20] in eq.1 (Figure 3.2.1) has been confirmed by ^{11}B NMR investigations [20-22].

In the first step of cross-link formation, a borate ion (commonly obtained by dissolving borax $[\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}]$ in water to form boric acid $[\text{B}(\text{OH})_3]$ and borate ions $[\text{B}(\text{OH})_4^-]$ that interchange rapidly under mildly basic solutions) condenses with a vicinal diol of one polymer chain to yield a monoborate ester and two molecules of water. Subsequent intra- or inter-chain reaction with another vicinal diol results in the formation of a di-diol cross-link [18].

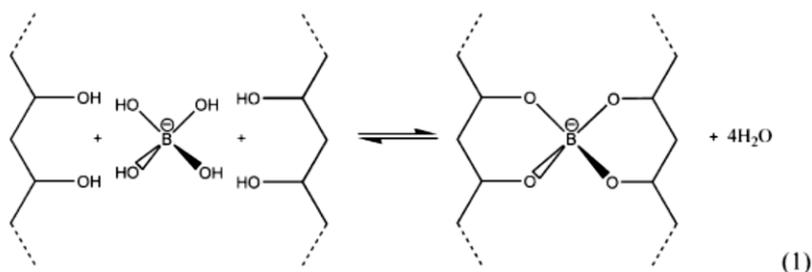


Figure 3.2.1. Di-diol complexation mechanism (Angelova et al., Langmuir, 2011, 27, 11671-11682).

Because several borate ions may attach to one chain, the polymers act as polyelectrolytes and separate from each other because of charge repulsion [23]. Although electrostatic shielding effects from sodium counterions may allow some chains to contract and form cross-links by the esterification of a borate ion with pairs of vicinal diol units on different polymer chains [23], the contraction of the polymer chains destabilizes the cross-linked network. In effect, the conformation of the polymer chains in these HVPDs is the result of a balance among electrostatic repulsions, charge-shielding effects, and the polymer-chain excluded volume [24].

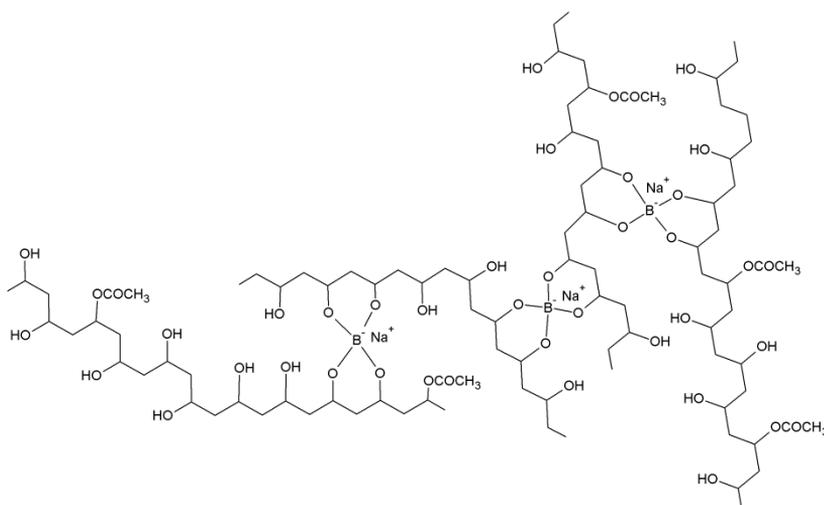


Figure 3.2.2. Representation of the structure of the PVAc network induced by borate cross-links (Natali et al., Langmuir, 2011, 27, 13226-13235).

The cross-links, made through interchain esterification reactions between pairs of vicinal diols [25], are dynamic because ester formation is reversible and a steady-state concentration of them is established under isothermal conditions [18].

The threshold polymer/borax weight ratio (or the $\text{OH}/\text{B}(\text{OH})_4^-$ functional group ratio) needed to obtain the 3D network and have the formation of the HVPDs, according to melting range studies (falling drop tests) and to intrinsic viscosity η_0 measurements, was found to depend on the molecular weight of the xPVAc as well as the value of x. Polymers with fewer hydroxyl groups (i.e., smaller x values) require larger concentrations for network formation. However, high molecular weights can compensate in part for low hydrolysis fractions [18].

As shown in Table 3.2.1 the limit concentrations obtained from intrinsic viscosity studies are much lower than those suggested by melting-range. The two types of experiments measure different aspects of the system; the melting range tests determine the thermal stability of the networks, and the intrinsic viscosity indicates the lowest necessary amounts of the two components for network formation. The two different polymer and borax concentrations reported in Table 3.2.1 obtained from the two experimental methods can be viewed as the minimum concentrations required to form a network in water (from η_0 values) and the minimum required to make a stable HVPD system at room temperature that is also thermally stable to at least 50°C (melting-range value) [18].

Table 3.2.1. Parameters describing the concentrations of polymer and borax found in the most thermally stable HVPDs formed with 30/70 (w/w) 1-propanol/water mixtures (melting range values) or with the largest observed increase in η_0 in HVPDs prepared in pure water (intrinsic viscosity values) [18].

			PVA	80PVAc	75PVAc	45PVAc	40PVAc
HVPD parameters	From melting ranges	[xPVAc]	4 wt%	4 wt%	6 wt%	14 wt%	11 wt%
		[borax]	1.1 wt%	1 wt%	1.4 wt%	1.3 wt%	2 wt%
	From η_0	[xPVAc]	0.9 wt%	1.3 wt%	3.5 wt%	8 wt%	5 wt%
		[borax]	0.25 wt%	0.3 wt%	0.8 wt%	0.7 wt%	0.9 wt%
		$\text{OH}/\text{B}(\text{OH})_4^-$ functional group ratio	16/1	12/1	11/1	20/1	5/1

By integrating the peaks of cross-linked and free boron species in ^{11}B NMR spectra (this technique is used to quantify the fraction of borax-derived species participating in xPVAc cross-links and thus, the absolute concentration of those cross-links) [22,26] it was found out that, although the molar concentration of hydroxyl groups in the polymer solutions is much higher than the concentration of borate ions in the studied HVPDs, only a fraction of the borates participate in cross-link formation [15,27]. For example, only 6% of the borates present in a 4 wt% 75PVAc/1 wt% borax in D_2O sample participate in cross-links [18]. If the concentrations of the polymer and borax are increased incrementally while keeping the w/w ratios constant, then the quantity of borate species that are cross-linked remains relatively constant with only a small increase in the absolute concentration of cross-linked borate ions [18,28].

^{11}B NMR spectroscopy revealed also that a high molecular weight in the polymers contributes greatly to the dispersion strength but not through increased cross-linking. In fact, increasing molecular weight results in a reduction of the cross-linked boron species in these systems. The high thermal stability and elasticity of HVPDs prepared from high-Mw polymers is therefore a result of increased hydrogen bonding and chain entanglements [18].

Melting-range experiments, as well, showed that the thermal stability of the HVPD systems increases more drastically when the polymer concentration is increased while it doesn't change appreciably with the cross-linker concentration.

It must be considered that a factor that plays a fundamental role in the cross-links density is the fraction of hydroxyl groups that exists as vicinal diols because they are the only ones that can effectively participate in cross-links. Nevertheless, even when the availability of hydroxyl groups is decreased because of a lower degree of hydrolysis, the polymer concentration still seems to be the dominant factor in determining the thermal stability of the borax cross-linked system [18].

All these results were in agreement with neutron spin-echo results obtained for PVA/borax systems by Kanaya et al. showing that cross-linking is not necessary for HVPD formation whereas chain entanglements are crucial [27].

From a further ^{11}B NMR study it resulted that the number of borate ions participating in cross-links with the PVAc chains increases when increasing amounts of an organic solvent are added to the system. In fact, the environment created by large

concentrations of organic liquids is less attractive to borate ions, forcing them either to become complexed with PVAc chains or to convert to boric acid [28].

Furthermore, according to DSC measurements [18], it was found out that the organic solvent acts as a water-structure maker (a kosmotropic effect) [29] and reinforces the water/polymer gel network. In fact, as the organic liquid content in the HVPDs is increased, the amount of free and freezable bound water (*Free Water Index* or FWI¹) [30] decreases dramatically in favor of the bound water, unable to freeze and strongly retained within the PVA-borate gel network [31]. This effect is very desirable for gels used to clean the surfaces of easel paintings because more water is expected to reside at the gel painting interface and the swelling of underlayers should be reduced [31].

3.3 HVPDs viscoelastic properties: ease of application/removal and minimization of the residues

As anticipated in the introduction, the complete removal of the cleaning agent is the main problem associated to the relatively recent technologies that imply the use of gels or gelled/thickened systems [9,10].

If, on one hand and according to the Washburn equation [32], their high viscosity prevents the solvent to penetrate into the internal layers of the piece of art, on the other hand it makes the complete removal of gelator residues difficult. An abrasive mechanical action or a clearance step with a neat liquid, each of which is undesirable, is usually performed to remove as much polymeric gelator as possible [33].

Thus, unremoved residues and their potential damages to works of art are often a serious limitation to the use of gels as cleaning tools for painted surfaces of historical and artistic interest.

¹ The FWI was calculated with the following formula: $FWI = \Delta H_{exp} / A \cdot \Delta H_{init}$ where ΔH_{exp} is the enthalpy change (in $J g^{-1}$ of HVPD) of the water melting determined by the DSC experimental curve, A is the average weight fraction of water in the HVPD, and ΔH_{init} is the theoretical value of the specific fusion enthalpy of water at 0°C in the HVPD determined by assuming that all water in an HVPD can be frozen.

The xPVAc-borax HVPDs formulated at the chemistry department of the University of Florence and CSGI consortium demonstrated to have very interesting mechanical properties, suitable for cleaning purposes.

Their very high elasticity allows them to be peeled from a surface without introducing a strong lateral force (Figure 3.3.1). Thus, residues left on the painted surface are expected to be minimized and the mechanical action and repeated washings usually necessary for the complete removal of traditional gels can be avoided [31].



Figure 3.3.1. Image of the painting (oil on canvas) “Les Voiles” by Marcel Burtin (1902-1979) with the magnification of the region where the HVPD (3 wt% 80PVAc/0.75 wt% borax in water) was peeled off from the surface by means of tweezers [28].

Moreover, this elasticity can be easily modulated by changing the ratio of PVA to borate or the hydrolysis degree/molecular weight/concentration of the polymer (that is varying the entanglements density of the network[34,35]) and/or the polarity of the continuous phase by incorporating different organic solvents [18].

Therefore just by modifying their composition they can assume the right consistency in order to be sufficiently soft and viscous to have a good adhesion to the surface to be treated (even the vertical or the molded, irregular ones) and at the same time sufficiently elastic to maintain its ability to be easily removed from the surface in one piece with a peeling action. This is a very attractive attribute of the xPVAc-borax systems because it allows a conservator to tune the mechanical properties to fit a specific cleaning task best [28].

Rheologically, xPVAc-borax HVPDs exhibit both self-healing and flow over extended periods of time [18]. The finite chemical relaxation time (i.e., the time required for an applied stress to decay to $1/e$ of its original value) at room temperature, 0.1-0.3 s [15,36], indicates that these dispersions are not solid like or ideal dispersions whose relaxation time approaches infinity [18]. In fact, the finite relaxation times of xPVAc-borax HVPDs indicate that they are viscoelastic dispersions but not true gels [36,37].

The short relaxation time and small amount of energy required to break and reform the cross-links account for the “slime” consistency of these complex fluids.

The crossover point between the shear elastic modulus G' and the shear viscous modulus G'' in the flow curves of the HVPDs (Figure 3.3.2) indicates the viscoelastic behavior typical of polymeric dispersions, characterized by two different regimes: for $\omega > \omega_c$ (ω_c is the crossover frequency between the G' and G'' curves) $G' > G''$, indicating a predominantly elastic behavior; for $\omega < \omega_c$ the viscous character prevails ($G' < G''$).

Thus, these systems behave like elastic solids at short observation times (high frequencies) and like viscous liquids at long observation times (low frequencies).

In agreement with earlier results on PVA-borate-based hydrogel systems [36], the flow curves of the HVPDs cannot be fitted to a single Maxwell element [31].

The G' modulus at high frequencies is asymptotic, approaching a value that is almost independent of the applied perturbation and that corresponds to the intrinsic elastic shear modulus G_0 [31,38]. This modulus is associated with the entanglement density ρ_e [39]: $G_0 = \rho_e K_B T$ (K_B is the Boltzmann constant and T is the absolute temperature in K) [31].

Furthermore, rheologically, the G_0 modulus is the most important parameter that indicates peelability [28]. The soft mechanical perturbation during peeling relies

upon frequency components in the range from several to hundreds of Hertz. For poly(acrylic acid)-based gels traditionally used in conservation, peelability is not possible because the corresponding G_0 values are ca. 200 Pa; for xPVAc systems that are peelable, G_0 values are always larger than 400 Pa [28,40]. Therefore, we assert that the threshold value for peelability is ca. 400 Pa at frequencies typical of the perturbations commonly induced during the removal of the dispersions from a painted surface (i.e., somewhat more than a few Hz).

As shown in Figure 3.3.3, there is an almost linear increase in both the intrinsic shear elastic modulus (G_0) and the apparent relaxation time, τ_c (defined as $1/\omega_c$, where ω_c is the crossover frequency of the G' and G'' curves [37]), with increasing polymer concentration and consequently borax (keeping their ratio constant) [28]. The dispersions become stiffer as the polymer concentration increases. Both G_0 and τ_c suggest increasingly elastic behavior characterized by more cross-links but, as demonstrated by the ^{11}B NMR data and as already mentioned before, the percentage of complexed boron remains constant as long as the polymer/crosslinker ratio is kept constant.

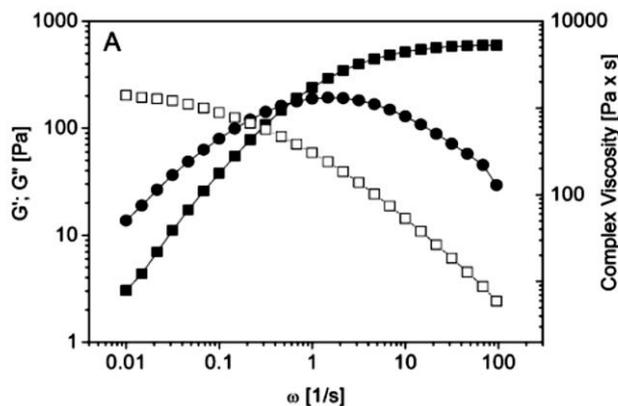


Figure 3.3.2. Example of a typical flow curve of the xPVAc-borax HVPDs characterized by the cross-over point between the G' and the G'' moduli, index of a viscoelastic behavior [31].

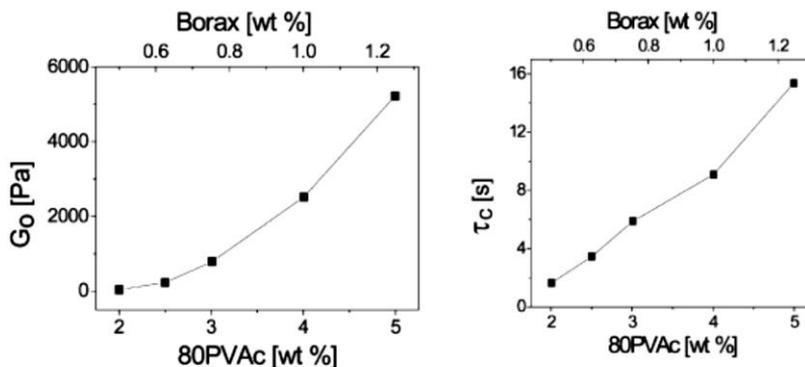


Figure 3.3.3. Intrinsic elastic shear modulus and apparent relaxation time as a function of the 80PVAc concentration in water [28].

Furthermore, it was found out that the addition of an organic solvent to the HVPD influences its intrinsic elastic modulus. As shown in Figure 3.3.4, the G_0 moduli increase — leading to stiffer materials— for up to 30 wt% acetone and NMP, 20 wt% MEK, and 40 wt% 1-propanol [28]. Extensional rheology, as well, shows an increase in the strength of the networks as the amount of organic solvent is increased (Figure 3.3.5). In fact, the maximum force necessary to pull the dispersions apart, a quantitative measure of their “stiffness”, increases.

Thus, the organic solvents result to strengthen and stabilize the cross-links of the polymeric networks [28].

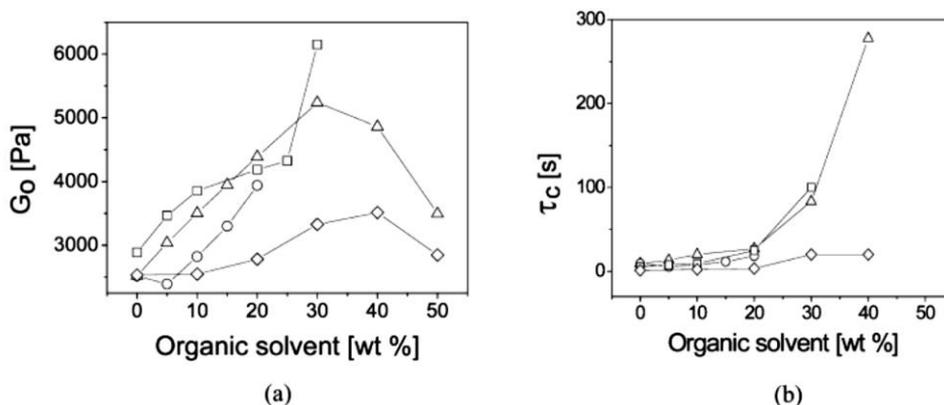


Figure 3.3.4. (a) Intrinsic shear elastic modulus and (b) apparent relaxation time as a function of the amount of added (\diamond) 1-propanol, (Δ) NMP, (\square) acetone, or (\circ) MEK in dispersions containing 4 wt% 80PVAc and 1 wt% borax [28].

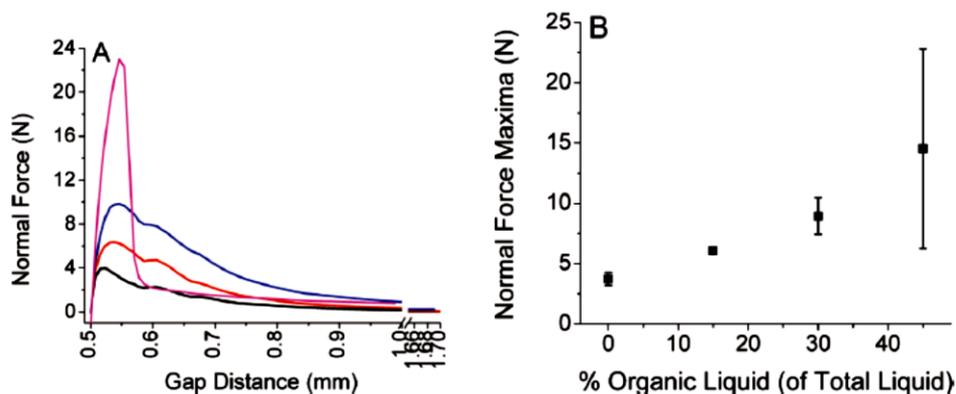


Figure 3.3.5. (A) Extensional rheological curves and (B) values of and maximum force for dispersions prepared from 4 wt% 80PVAc, 1 wt% borax, and different fractions of 1-propanol in the liquid: (black) 0 wt%, (red) 15 wt%, (blue) 30 wt%, and (purple) 45 wt% [28].

3.4 Versatility of the HVPDs: the possibility of incorporating a wide range of organic solvents

The versatility of the xPVAc-borax dispersions due to the possibility of changing their properties of viscosity and elasticity by simply tuning the concentrations of the components was already discussed in the previous paragraphs.

Another aspect that makes these systems very versatile is that they can incorporate large amounts of a wide range of organic solvents, significantly reducing their evaporation rates and slowing their undesirable diffusion into the inner layers of the artwork [5,28] and allowing to solubilize most of the different type of extraneous or degraded substances that can be present onto the surface of an artwork (natural or synthetic resins, oils, polysaccharides, proteins, fats...).

The possibility for PVAc's with reduced (i.e., incomplete) hydrolysis fractions (xPVAc) to be cross-linked with borate ions as well as the PVA or the 80PVAc and to form stable, elastic HVPDs was a noticeable improvement in that direction. In fact, the presence of some acetate groups on the polymer chains increased the ability of larger fractions of organic liquids with different polarities to be incorporated into xPVAc-borax HVPDs as compared to the PVA-borax systems [18].

Table 3.4.1. Maximum amounts of the organic liquid component that yield a stable HVPD (i.e., without hysteresis or flow for at least 10 s when a sample was inverted) for PVAc with different hydrolysis degree [18].

		PVA	80PVAc	75PVAc	45PVAc	40PVAc
Liquid components	water	100 %	100%	100%	100%	100%
	methanol	30	50	70	75	75
	ethanol	30	50	70	75	75
	1-propanol	30	50	70	75	75
	2-propanol	30	50	70	75	75
	acetone	30	50	50	75	75
	Methyl acetate	^d	^d	50	50	75
	N-Methylpyrrolidone	30	50	70	75	75

^dthese systems are unstable and undergo syneresis shortly after the preparation.

Although some water is necessary to solubilize the borax component as the HVPDs are being formed, the maximum volume fraction of organic liquid possible is roughly inversely proportional to the degree of hydrolysis of the polymers (Table 3.4.1).

The obtained dispersions are transparent or translucent and are stable over the course of weeks in closed containers. Some of the less polar liquids, such as 1-pentanol and ethyl acetate, can be incorporated, but the resulting HVPDs undergo syneresis within minutes to hours [18].

Examples of the different nature of degradation layers that can be thinned using these xPVAc-borax systems will be given in the next paragraph.

3.5 HVPDs cleaning performance: gradualness, control, efficacy, ease of application/removal

Applicative tests carried out on different type of artworks [40,41], demonstrated that xPVAc-borate HVPDs are effective low impact cleaning agents for delicate surfaces of artistic and historical interest.

The cleaning action performed by the PVA-borax dispersions can be visually controlled due to the transparency of the systems; the appropriate level of thinning of the patina can be achieved by modulating the contact times or by executing two or more consecutive applications onto the same surface area.

From the applicative point of view, their peculiarities are mainly the gradualness of the cleaning action (that makes these HVPDs suitable for delicate and precious

surfaces) and their ease of removal that can be achieved simply by a peeling action, without leaving any detectable residue onto the treated surface. Both these features are strictly related to the rheological properties of the HVPDs.

In particular, we showed that a value of $G^0 > 400$ Pa allows the peeling of the cleaning system from the treated surface by a onestep not invasive mechanical action realized by tweezers (see Figure 3.3.1 in the 3.3 paragraph) [28].

The first test on the surface of an oil-based painting was performed in cooperation with the International University of Art Foundation of Florence (Fondazione Università Internazionale dell'Arte (UIA)) on a portion of a wood panel by Ludovico Cardi called "il Cigoli" (1559-1613) that is part of the collection of the Curia Museum and on exhibition at the Santo Stefano al Ponte Church in Florence. The painted surface had been altered by a thin brown patina composed of oxidized varnishes used in past conservation treatments (Figure 3.5.1) [31].



Figure 3.5.1. Left: wood panel by Ludovico Cardi called "il Cigoli" (1559-1613). The box indicates the region where a very small cleaning test was carried out (the picture was collected after the cleaning test). Right: magnified view of the boxed region (A) before application of the HVPD and (B) after two applications of the HVPD as described in the text. The area where the gel was applied is indicated by the red dashed line [31].

The HVPD selected for the tests contained 20 wt% 1-propanol. The system was applied with a spatula, kept in contact with the surface for 4 min, and then, thanks to its elasticity, removed in one piece without leaving any detectable residue. The remaining brown patina was removed after a second application of the HVPD. Thus, the dispersion carried out a selective, gradual cleaning of the surface. To the best of our knowledge, this was the first test in which an easel painting had been cleaned without using any additional solvent as an after-treatment [31].

Another satisfying cleaning test with the HVPDs was carried on the “Coronation of the Virgin with Saints” (Figure 3.5.2), an egg tempera wood panel (15th century, 150×150 cm) by Neri di Bicci, housed at the Galleria degli Uffizi in Florence and presently on loan to the Civic Museum in Pescia (Pistoia), Italy [40].

The original appearance of the work of art was modified by a highly degraded and yellowed brown varnish (Figure 3.5.3). In the regions where the red vermilion pigment is present (for example the mantle of Saint-Caterina and Saint-Girolamo in the lower part of the painting), the aging effects were particularly pronounced.

As shown in the two images of Figure 3.5.3 shrinkage induced by the oxidation of the varnish layer (made of shellac resin, according to FTIR analyses) as a consequence of its aging was inhomogeneous, manifested in two superimposed layers. The first was characterized by the presence of brown, rough clots, while the second one, underneath, by a dark texture bound strongly to the paint layer and very difficult to eliminate [40].

The cleaning action had to remove selectively both the varnish coatings without damaging the red pigment layer underneath.

A previous cleaning attempt by means of cotton swabs impregnated with conventional organic solvents (acetone, benzyl alcohol, or mixtures of them) led to loss of stability of the red pigment layer due to the high sensitivity of vermilion-containing paints to aqueous and polar organic liquids.

The HVPD system selected for the tests contained from 5 to 15 wt% of acetone (acetone was chosen as the co-solvent because it was able to soften the hard, highly degraded coating).

After a first application of the PVA/borax system containing 15 wt% of acetone for ca. 5 minutes, the clots were softened (see Figure 3.5.3 A left side and B) and a weak mechanical action, carried out with a spatula, was sufficient to remove them completely. However, the lower inhomogeneous texture of dark residual resin (see

Figure 3.5.3 A right side) was not removed by an aliquot of the same dispersion in some regions of the painting. In these cases, complete cleaning was possible only after the application of a second aliquot of the dispersion.



Figure 3.5.2. “Coronation of the Virgin with Saints”, a 15th century egg tempera wood panel by Neri di Bicci, Galleria degli Uffizi, Florence, Italy. The black box indicates the region where the cleaning tests using PVA-based dispersions were carried out [40].

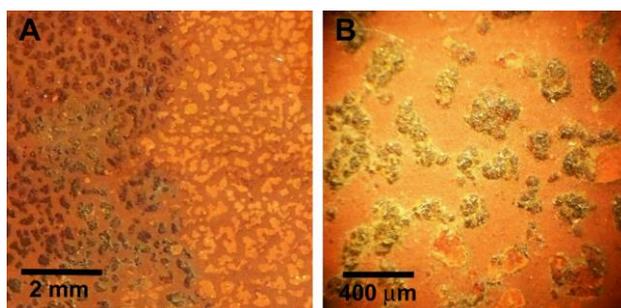


Figure 3.5.3. Optical micrographs at two different magnifications of the region of the “Coronation of the Virgin with Saints” showing the morphology of the degraded varnish coatings to be removed. In A, the two features of the coatings are seen as brown clots (on the left) and a dark texture underneath (right). B shows the clots at higher magnification [40].

Figure 3.5.4 A shows a region with the dark texture beneath the clots removed by the first application; the dark coating is visible because the polymeric dispersion is transparent, allowing the cleaning action to be followed visually by a conservator. The additional cleaning action by the second application is apparent in Figure 3.5.4 B – there is a very large reduction in the amount of dark brown coating only in the treated area.

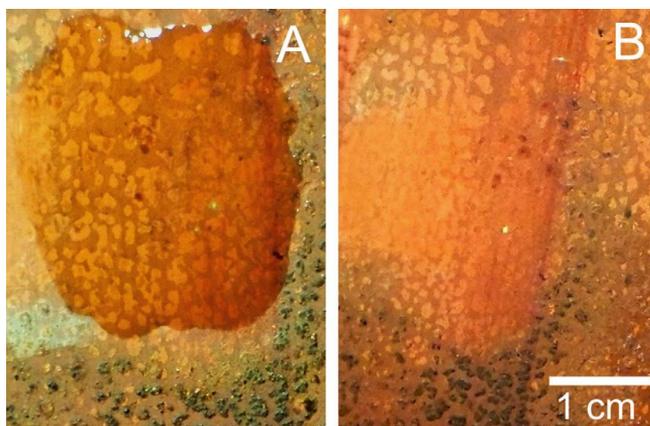


Figure 3.5.4. Images of the surface area of the “Coronation of the Virgin with Saints” subjected to a cleaning test (see box in Fig. 3.5.2): A. Transparent dispersion of PVA-borax with 15 wt% acetone, applied on the painting surface where the clots had been already removed and only the dark undercoating layer that strongly adhered to the red pigment layer remained. B. The surface after the removal of the dispersion. The distance bar applies to both images [40].

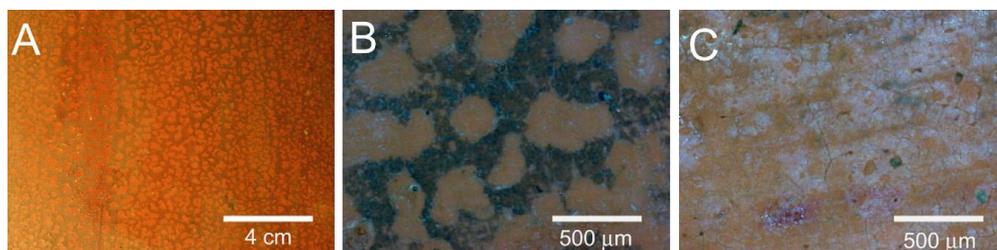


Figure 3.5.5. True color image of the texture of the residual resin after removal of the clots (A) and USB false color micrographs before (B) and after (C) a second application of the cleaning dispersion [40].

A real color image of the texture of the surface after the removal of the clots is reported in Figure 3.5.5 A.

Figure 3.5.5 B shows false color micrograph (obtained with a USB microscope interfaced with a computer) of the same region after the first application: no traces of the dark clots constituting the degraded organic surface materials were present.

USB micrograph of the complete softening of the lower undercoating layer achieved after an additional application of the dispersion is reported in Figure 3.5.5 C.

Importantly and unlike the results from cleaning procedures using traditional methods with conventional liquids (i.e., ungelled or unthickened solvents), softening of the coating here was achieved without any apparent damage to the red pigment layer. These results are the proof that the xPVA-borax systems containing co-solvents allow both excellent control of the cleaning and a gradual but effective removal action even against thick and strongly adherent materials, while minimizing the risk of altering or damaging the painted layers underneath. Furthermore, the cleaning action can be monitored visually or in situ with a microscope [40].

The ability of the 80PVAc-borax dispersions to remove a layer of an aged acrylic resin, applied almost 30 years ago to the surfaces of wall paintings by Il Vecchietta in the Old Sacristy of the S. Maria della Scala church in Siena (Figure 3.5.6), was also tested [28].

In this case, the main challenge was to determine whether the 80PVAc-borax dispersions could clean a vertical surface well, while adhering to it with sufficient strength for the period required.

The area tested in the box in Figure 3.5.6 had a glossy surface indicative of an organic coating. The polymeric dispersion, containing 40/60 1-propanol/water, was applied for 25 min to a portion of the hat of the man portrayed with his arms crossed and then removed with metal tweezers. The grazing light image after the cleaning procedure (Figure 3.5.7) clearly shows the absence of the organic coating in the area where the 80PVAc-borax dispersion was applied [28].



Figure 3.5.6. Wall paintings by Il Vecchietta in Santa Maria della Scala in Siena. The boxed area at left shows where the 4 wt% 80PVAc/1 wt% borax dispersions with 40/60 1-propanol/water were applied [28].

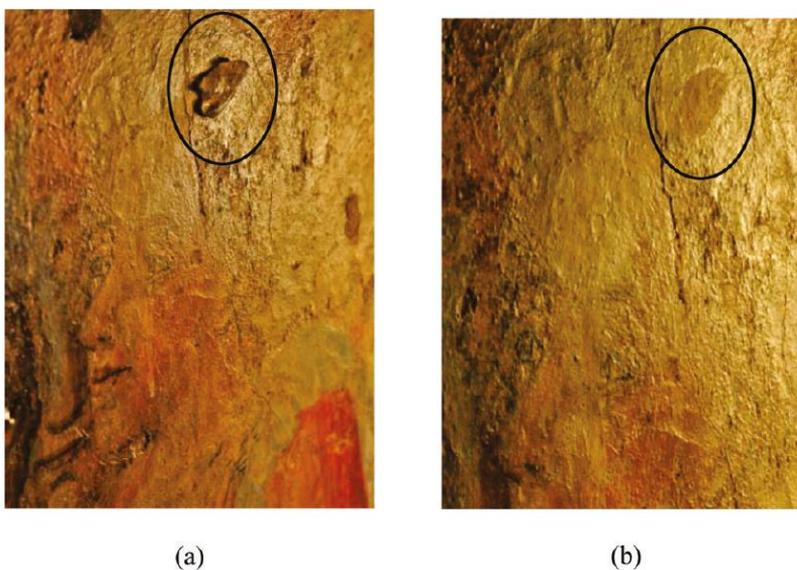


Figure 3.5.7. Grazing light images obtained (a) during and (b) after the cleaning test. The black ovals highlight the area where the cleaning dispersion was applied and from which it was removed [28].

3.6 Bibliography

- [1] S. BERTOLUCCI, E. BIANCHINI, C. BIAVE, F. CALIARI, P. CREMONESI, S. GRAVINA, M. ZAMMATTARO, B. ZANGANI, *Preparazione e utilizzo di soluzioni acquose addensate, reagenti per la pulitura di opere policrome*, Progetto Restauro, 2001, 8,11–21.
- [2] R. WOLBERS, *Cleaning painted surfaces: aqueous methods*, Archetype, London, UK, 2000.
- [3] *Materiali tradizionali ed innovativi nella pulitura dei dipinti e delle opere policrome mobili*, in: Proceedings of Primo Congresso Internazionale - Colore e conservazione: materiali e metodi nel restauro delle opere policrome mobili, Piazzola sul Brenta, October 25-26, 2002, Il prato, 2003.
- [4] A. ONESTI, CAB newsletter, 1993, 2, 10-13.
- [5] E. CARRETTI, E. FRATINI, D. BERTI; L. DEI, P. BAGLIONI, *Angew. Chem.* 2009, 48, 8966.
- [6] E. CARRETTI, M. BONINI, L. DEI, B.H. BERRIE, L.V. ANGELOVA, P. BAGLIONI, R. G. WEISS, *Acc. Chem. Res.*, 2010, 43, 751.
- [7] M. BONINI, S. LENZ; R. GIORGI, P. BAGLIONI, *Langmuir*, 2007, 23, 8681.
- [8] M. BONINI, S. LENZ, E. FALLETTA, F. RIDI, E. CARRETTI, E. FRATINI, W. ALBRECHT, P. BAGLIONI, *Langmuir*, 2008, 24, 12644.
- [9] D. STULIK, H. KHANJIAN, V. DORGE, A. de TAGLE, J. MAISH, B. CONSIDINE, D. MILLER, N. KHANDEKAR, *Scientific investigation of surface cleaning processes: quantitative study of gel residue on porous and topographically complex surfaces*, in: ICOM Committee for Conservation, ICOM-CC: 13th Triennial Meeting, Rio de Janeiro, 22–27 September 2002: James & James, London, 2002, 245–251.
- [10] V. DORGE (Ed.), *Solvent gels for the cleaning of works of art: the residue question*, Getty Publications, Los Angeles, USA, 2004.
- [11] A. BURNSTOCK, T. KIESLICH, *A study of the clearance of solvent gels used for varnish removal from paintings*, in: ICOM Committee for Conservation, 11th Triennial Meeting in Edinburgh, James & James, London, 1996, 253–262.
- [12] H. GAO, R. YANG, J. HE, L. YANG, *J. Appl. Polym. Sci.*, 2010, 116, 1459.
- [13] W.S. LYOO, S.J. LEE and J.H. KIM, *J. Appl. Polym. Sci.*, 2004, 93, 1638.

- [14] J.H. CHOI, S.W. KO, B.C. KIM, J. BLACKWELL, W.S. LYOO, *Macromolecules*, 2001, 34, 2964.
- [15] R.K. SCHULTZ, R.R. MYERS, *Macromolecules*, 1969, 2, 281.
- [16] E.V. BASIUK, A. ANIS, S. BANDYOPADHYAY, E. ALVAREZ-ZAUCO, S.L.I. CHAN, V.A. BASIUK, *Superlattices Microstruct.*, 2009, 46, 937.
- [17] A.L. KJØNIKSEN, B. NYSTRÖM, *Macromolecules*, 1996, 29, 5215.
- [18] L.V. ANGELOVA, P. TERECH, I. NATALI, L. DEI, E. CARRETTI, R.G. WEISS, *Langmuir*, 2011, 27, 11671.
- [19] H.L. LIN, W.H. LIU, Y.F. LIU, C.H. CHENG, *Journal of Polymer Research*, 2002, 9, 233.
- [20] H. DEUEL, H. NEUKOM, *Makromol. Chem.*, 1949, 3, 13.
- [21] K.T. NIJENHUIS, In *Thermoreversible Networks: Viscoelastic Properties and of Gels*; Springer: New York, 1997, 267.
- [22] S.W. SINTON, *Macromolecules*, 1987, 20, 2430.
- [23] H.L. LIN, T.L. YU, C.H. CHENG, *Colloid Polym. Sci.*, 2000, 278, 187.
- [24] H.L. LIN, Y.F. LIU, T.L. YU, W.H. LIU, S.P. RWEI, *Polymer*, 2005, 46, 5541.
- [25] C.Y. CHEN, J.Y. GUO, T.L. YU and S.C. WU, *J. Polym. Res.*, 1998, 5, 67.
- [26] J. M. MAERKER, S.W. SINTON, *J. Rheol.*, 1986, 30, 77.
- [27] T. KANAYA, N. TAKAHASHI, K. NISHIDA, H. SETO, M. NAGAO, Y. TAKEBA, *Physica B*, 2006, 385-386, 676.
- [28] I. NATALI, E. CARRETTI, L.V. ANGELOVA, P. BAGLIONI, R.G. WEISS, L. DEI, *Langmuir*, 2011, 27, 13226.
- [29] D. JERUZALMI, T.A. STEITZ, *J. Mol. Biol.*, 1997, 274, 748.
- [30] S. GRASSI, L. DEI, *J. Phys. Chem. B*, 2006, 110, 12191.
- [31] E. CARRETTI, S. GRASSI, M. COSSALTER, I. NATALI, G. CAMINATI, R.G. WEISS, P. BAGLIONI, L. DEI, *Langmuir*, 2009, 25, 8656.
- [32] E.W. WASHBURN, *Physical Review*, 1921, 17, 273.
- [33] E. CARRETTI, L. DEI, R.G. WEISS, P. BAGLIONI, *Journal of Cultural Heritage*, 2008, 9, 386.
- [34] C.Y. CHEN, T.L. YU, *Polymer* 38, 1997, 2019.
- [35] A. KOIKE, N. NEMOTO, T. INOUE, K. OSAKI, *Macromolecules*, 1995, 28, 2339.
- [36] I.D. ROBB, J.B. SMEULDERS, *Polymer*, 1997, 38, 2165.
- [37] L. PICULELL, M. EGERMAYER, J. SJOSTROM, *Langmuir*, 2003, 19, 3643.

[38] R. SRINIVASA, S.R. RAGHAVAN, E.W. KALER, *Langmuir* 2001, 17, 300.

[39] B.A. SCHUBERT, E.W. KALER, N.J. WAGNER, *Langmuir*, 2003, 19, 4079.

[40] E. CARRETTI, I. NATALI, C. MATARRESE, P. BRACCO, R.G. WEISS, P. BAGLIONI, L. DEI, *Journal of Cultural Heritage*, 2010, 11, 373.

[41] P. BAGLIONI, D. BERTI, M. BONINI, E. CARRETTI, L. DEI, E. FRATINI, R. GIORGI, *Advances in colloid and interface science*, 2014, 205, 361.

PART II

Experimental

CHAPTER 4

HVPDs obtained from 75PVAc

4.1 Introduction

In the present chapter the structural, mechanical and calorimetric properties of the Highly Viscous Polymeric Dispersions obtained from 75PVAc (where 75 is the hydrolysis degree of the poly (vinyl acetate)) and borate as the cross-linker are presented while maintaining a constant molar ratio between the OH groups and borax.

In fact, the structural and mechanical properties of aqueous PVA–borate HVPDs, as described in Chapter 3, have been extensively studied while only a few studies were devoted to the study of the properties of PVAc with lower hydrolysis degrees cross-linked with borate. The possible modulation of their mechanical behavior induced the exploration of their use in the removal of extraneous materials from surfaces of works of art [1]. In the past few years, some studies dealt with the use of peelable aqueous highly viscous systems [2,3] as innovative tools for cleaning painted and decorative surfaces. For cleaning purposes [4] HVPD should be sufficiently soft to have a good contact with the surface to be treated and its elasticity and viscosity should be sufficiently high to maintain its ability to be easily removed from the surface after cleaning.

Here, the 75PVAc-borax systems were analyzed by a detailed rheology investigation (in particular, trends between the viscoelastic parameters like the storage modulus (G') and loss modulus (G'') and HVPD compositions). The free water indices (FWI) were determined from differential scanning calorimetry (DSC) measurements and their structural properties were established through Small Angle X-ray Scattering (SAXS) measurements.

Some application tests on wall paintings were also reported to assess their possible use in the field of works of art conservation.

4.2 Falling drop tests

The falling drop tests [5] normally give the sol–gel transition, whereas in the case of HVPDs the method was used to establish the temperature at which the HVPD's network starts to loose strength (T_{Is}).

A 0.5 g portion of each HVPD, prepared as described above, was sealed in a glass tube and cooled to 5 °C. Then, the tube was inverted and placed in a water bath at 0 °C; the temperature of the bath was raised by 2 °C min⁻¹. The temperature ranges over which each HVPD first showed signs of flow and fell completely were recorded. Before the tests, all the glass tubes were washed with piranha solution and demineralized water.

The falling drop test [6,7] indicated that the T_{Is} of the investigated HVPDs significantly increases upon increasing the 75PVA concentration (Figure 4.2.1 (A)), while the effect of the crosslinker concentration was much less pronounced. The data indicated that the T_{Is} was mainly determined by the number of the hydroxyl groups that are the only ones able to form crosslinking. As indicated by Kanaya et al. [8] and by Kjoniksen et al. [9], this behavior can be interpreted considering that the driving factor for the HVPD formation is the entanglement between polymer chains rather than the borax-modulated cross-linking (Figure 4.2.1 (B)).

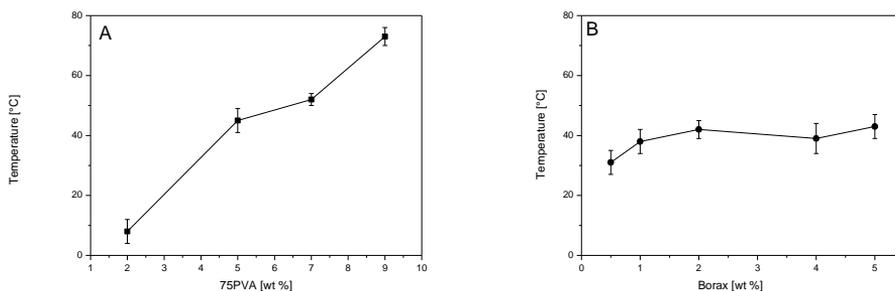


Figure 4.2.1. (A) Variation of the T_{Is} for HVPDs maintaining constant the molar ratio between the -OH groups and $B(OH)_4$ ions equal to 20.4; (B) T_{Is} of HVPDs containing 5 wt% of 75PVA. Bars indicate the melting ranges.

4.3 Mechanical characterization

The threshold 75PVA concentrations (indicated as C^*) necessary for the formation of an extended three-dimensional network were determined rheologically from the trends of the changes in the zero shear viscosity η_0 as a function of the polymer concentrations: the amounts of both 75PVA and borax were varied incrementally while keeping the $(\text{OH}/\text{B}(\text{OH})_4^-)$ ratio constantly equal to 20.4. The obtained C^* value is 3.0.

Furthermore, Figure 4.3.1 indicated that upon increasing the $(\text{OH}/\text{B}(\text{OH})_4^-)$ ratio an increase of the C^* value is observed.

In order to understand the effect of the polymer concentration on the mechanical properties of the 75PVA HVPDs and to obtain information about their relaxation dynamics, oscillatory frequency sweep tests were carried out in the linear viscoelastic regime in order to obtain the dependence of the complex moduli G' and G'' on the frequency of the applied shear perturbation. As 75PVA concentration was increased, the decrease of $\tan\delta$, indicated enhanced elasticity (Figure 4.3.2) due to the increased number of interchain interactions and entanglements between the 75PVA molecules resulting from the decreased chain flexibility and increase of the molecular size.

As shown in Figure 4.3.3 (A), the 75PVA-borax systems showed a behavior typical of viscoelastic polymeric dispersions; two different regimes can be individuated: for $\omega > \omega_c$ (ω_c is the crossover frequency between the G' and G'' curves) $G' > G''$, indicating a predominantly elastic behavior; for $\omega < \omega_c$ the viscous character prevails ($G' < G''$).

The value of the intrinsic elastic modulus G^0 , given by the asymptote of G' curves of the HVPDs, is correlated with the density of the borate-modulated cross-linking (ρ_e) between the 75PVA chains (eq. 1):

$$G^0 = \rho_e k_B T \quad (\text{eq. 1})$$

where k_B is the Boltzmann constant and T (K) is the temperature [10].

The increased ρ_e , upon increasing the 75PVA content (Figure 4.3.4) indicated an increase of the complexity of the HVPD structures and an increase of the strength of the 3D network confirming that the driving factor for the formation of the 3D

network is the number of OH groups available for the formation of covalent cross-links.

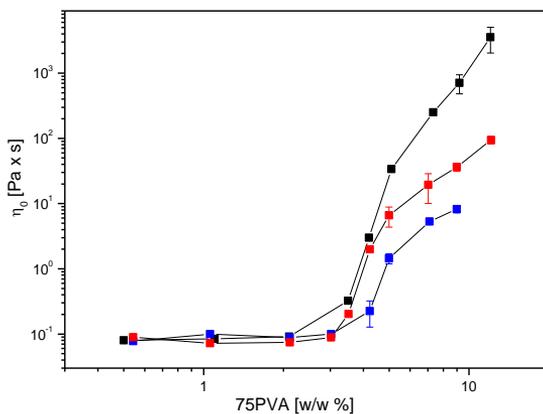


Figure 4.3.1. Plots of η_0 versus xPVAc concentration in H₂O for HVPDs obtained with 75PVA at 20:1 (black curves), 34:1 (red curves) and 51:1 (blue curves) [75PVAc]/[Borax] ratios.

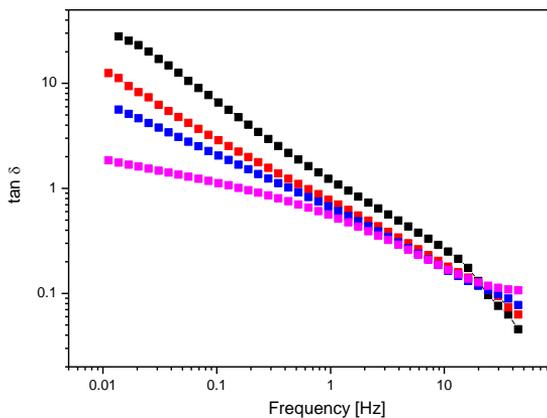


Figure 4.3.2. Complex viscosity of 75PVA-borax based HVPDs at 5 (black), 7 (red), 9 (blue) and 12 (purple) wt% 75PVA concentration.

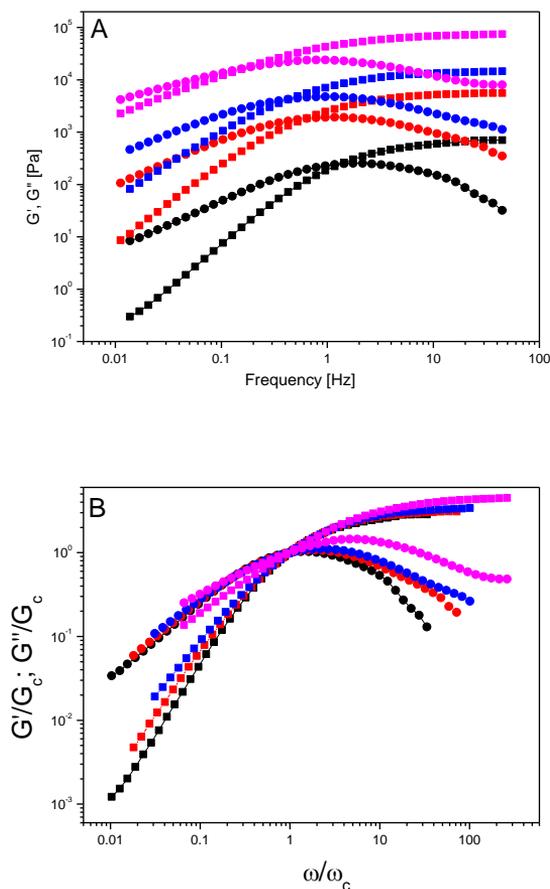


Figure 4.3.3. (A) Frequency sweep curves at 5 (black), 7 (red), 9 (blue) and 12 (purple) wt% 75PVA concentration. Squared symbols indicate the elastic modulus G' , circles indicate the loss modulus G'' . (B) Normalized mechanical spectra at 2 (black), 5 (red), 7 (blue) and 9 (purple) wt% 75PVA concentrations. Closed symbols indicate the G'/G_c ratio, open symbols indicate the G''/G_c ratio. G_c and ω_c are the crossover modulus and the crossover frequency respectively.

Normalized frequency sweeps are reported in Figure 4.3.3 (B) and indicate that increasing 75PVA and borax concentrations had little effect on the rheological behavior of the HVPDs: the normalized curves overlapped, indicating that, even if the global time scale of the relaxation phenomena slightly changes, the mechanism were almost the same at all concentrations.

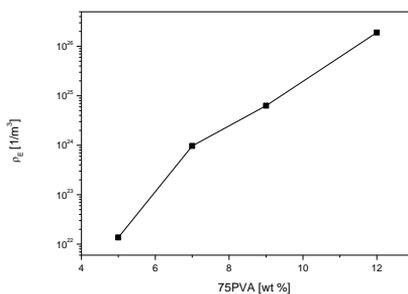


Figure 4.3.4. Effect of 75PVA concentration on the density of the borate-modulated cross-linking ρ_e on the HVPDs.

Since the dynamic of the 75PVA based HVPDs cannot be described by a single-element Maxwell model (Figure 4.3.5), both G' and G'' were used to calculate the time-weighted relaxation spectrum $H(\tau)$ [11]. In Figure 4.3.6 the $H(\tau)$ spectra are normalized with respect to the zero shear viscosity in order to compare them on similar scales.

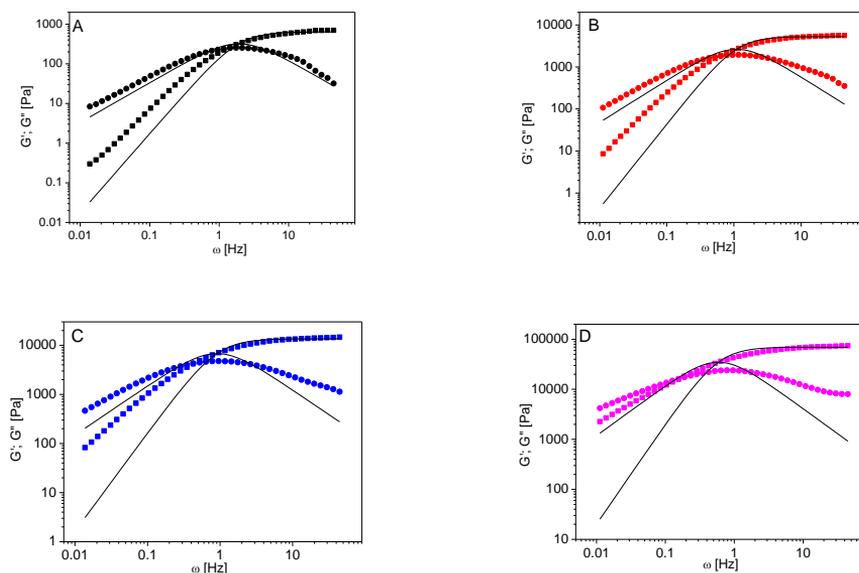


Figure 4.3.5. Frequency sweep curves of the 75PVA-borax based aqueous HVPDs at 5 (A) 7 (B) 9 (C) and 12 (D) wt% 75PVA concentration. Squared symbols indicate the elastic modulus G' , circles indicate the loss modulus G'' . Continuous lines indicate the best fitting curves obtained with the single-element Maxwell model. The $(\text{OH}/\text{B}(\text{OH})_4^-)$ ratio was kept equal to 20.4:1 for all the investigated samples.

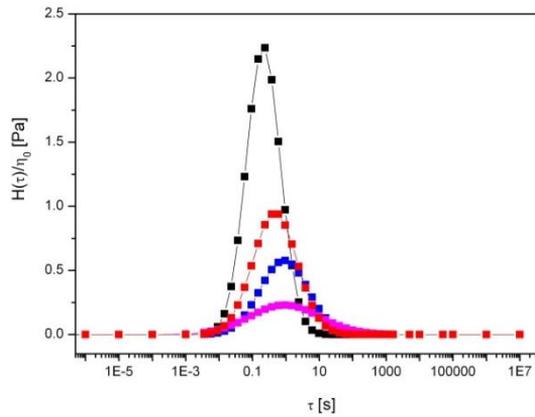


Figure 4.3.6. η_0 normalised stress relaxation spectra ($H(\tau)$) at 5 (black), 7 (red), 9 (blue) and 12 (purple) wt% 75PVA concentration.

All the spectra showed only one peak, confirming that the main relaxation mechanism was unchanged upon increasing 75PVA concentration. However, the observed increase in the width of the spectra indicated that additional modes of relaxation resulting from increasing entanglements among the polymer chains (i.e., enhancement of polymer–polymer interactions), were operating.

Figure 4.3.7 shows a nearly quadratic dependence of the mean relaxation time τ_H , given by the peak of the relaxation spectra, on the 75PVA concentrations (i.e., $\tau_H \sim C^a$, in the linearized form $\log(\tau_H) = a \log C + b$). The slope a of the plot $\log(\tau_H)$ vs $\log C$ is equal to 1.9).

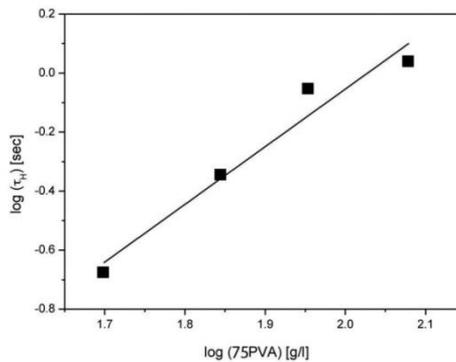


Figure 4.3.7. Effect of the concentration of 75PVA on the mean relaxation times (τ_H) of their HVPDs.

In order to identify the main relaxation mechanism $G(t)$, the trend of the stress relaxation modulus has been investigated. The Doi-Edwards model [12] (eq. 2) for a pure reptation process indicates that $G(t)$ is given by:

$$G(t) = \frac{8}{\pi^2} G^0 \sum_{\text{odd } k} \frac{1}{k^2} \exp\left(-\frac{k^2 t}{\tau_{rep}}\right) \quad (\text{eq. 2})$$

where G^0 is the asymptote of G' curve and τ_{rep} was taken as the mean relaxation time τ_H of Figure 4.3.6. The comparison between the experimental trend of the stress relaxation modulus and the Doi-Edwards equation indicated that the 75PVA based HVPDs didn't relax following a pure reptation mechanism (Figure 4.3.8).

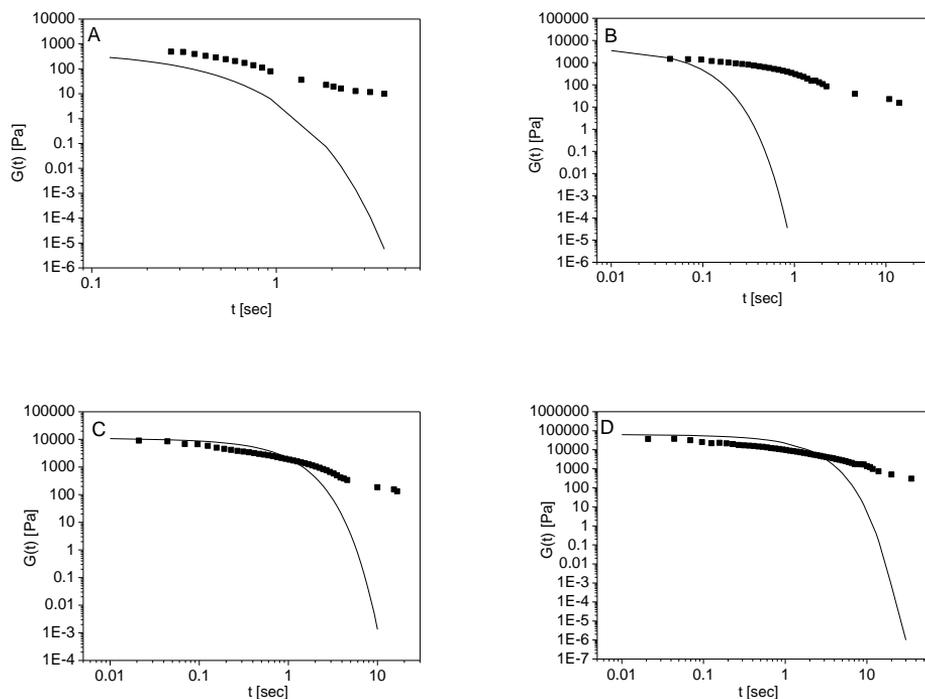


Figure 4.3.8. Experimental stress relaxation modulus $G(t)$ of the 75PVA-borax based aqueous HVPDs at 5 (A) 7 (B) 9 (C) and 12 (D) wt% 75PVA concentration. Squared symbols indicate the experimental data; continuous lines correspond to the best fitting curves obtained with the Doi-Edwards model (see eq.3 in the main text).

This was probably due to the interchain interactions that slowdown the relaxation process. Rubinstein and Semenov [13] studied the dynamic of entangled solution of associating polymers and demonstrated that their dynamic in good solvents is controlled by the associating groups (stickers). They explained this behaviour in terms of sticky reptation. The corresponding reptation time strongly depends upon concentration as follows: $\tau_{rep} \sim C_a$ with a ranging from 1.44 to 4.5 as a function of the length of the strands between 'sticking points'. Our data supported that for all the HVPDs investigated:

- water is a good solvent as demonstrated also by SAXS data (paragraph 4.4);
- the mean relaxation process is controlled by a sticky reptation mechanism.

4.4 Structural characterization: SAXS and DSC analyses

Small angle X-ray scattering (SAXS) experiments were conducted to investigate the polymer structure at the nanometer level and to visualize the changes imposed by the presence of borax. Figure 4.4.1 shows the SAXS intensity distribution in the case of 75PVA (see panel A) and 75PVA/borax (Panel B) systems from 5 to 12 wt% polymer. All the SAXS curves were modeled according to a functional form [14] that can be interpreted as a generalized version of the Debye-Bueche (DB) approach [3]. The generalized DB model in its original form presents a low- q clustering and high- q solvation contribution plus a flat background, and it has been used to fit small angle neutron scattering curves obtained in the case of both neutral and charged polymeric solutions consisting of synthetic and biological macromolecules [14]. In our case, the low- q clustering term is omitted because no intensity increase was evidenced in the low- q region of the SAXS curves (see both panels of Figure 4.4.1). A previous SANS investigation confirms that the clusters in similar systems are evident only below 0.01 \AA^{-1} [15]. For this reason, the SAXS curves were modeled according to a solvation term plus a flat background (Eq. 3):

$$I(q) = \frac{I_0}{[1 + (|q - q_0| \xi)^m]} + bkg \quad (\text{Eq. 3})$$

where I_0 is the scattering intensity at $q=0$, q_0 is the peak position, ξ is the correlation length which corresponds in a semi-diluted solution to the average distance

between neighbouring entanglement points [16], m is the Porod exponent associated with the solvation term and bkg is a q -independent instrumental background term. All these parameters were allowed to vary during the least-square fitting procedure.

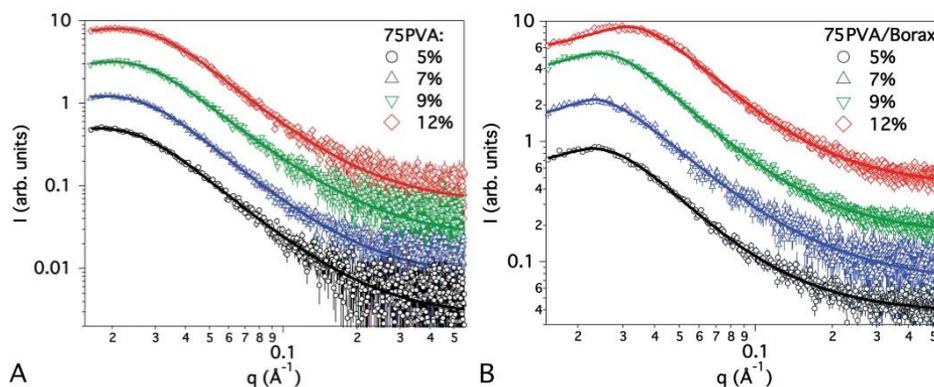


Figure 4.4.1. Double-logarithmic representation of the SAXS intensity distribution for: (A) 75PVA and (B) 75PVA/borax dispersions. The solid lines are the best fits to the scattering points according to eq. 1. The curves are offset vertically by an arbitrary factor to avoid overlap.

Table 4.4.1 lists the parameters according to the best fits of the SAXS curves in Figure 4.4.1. While for 75PVA concentrations between 5 wt% and 7 wt% ξ remains constant, a further increase of the amount of the polymer in its dispersions decreased the correlation length from 55.1 to 49.3 nm. The presence of a finite q_0 can be questionable in this 75PVA series because this polymer is expected to be uncharged. However, it must be noted that the q_0 values are very close to the lowest q accessed by the SAXS experiment and, moreover, the curves could also be fitted by constraining q_0 to zero with only a very small increase of the overall χ^2 . This result clearly indicated that the charge present on the 75PVA polymer (perhaps as a result of its partial hydrolysis during sample preparation or storage) is almost negligible. q_0 shifted slightly towards high- q as a consequence of increase in concentration. The average distance between the charges, estimated as $2\pi/q_0$, varied from 37 to 30 nm as the concentration was raised from 5 to 12 wt%. The parameter m has a constant value of 2, corresponding to a Gaussian coil conformation arising from monomer–solvent and monomer–monomer interactions

being equal in strength. In the systems in which borax was present, similar considerations hold. However, the correlation lengths decreased by 0.5 - 1 nm in all cases as a consequence of the cross-links made by the borate ions. The inclusion of these ions in the polymeric network rendered the chains negatively charged, and the interaction peak became more evident and shifted to higher q -values. The associated average distances $2\pi/q_0$ decrease to 27.5-20.1 nm (following the shifts to higher q values imposed in the more concentrated dispersions). In the 75PVA/borax series, the Porod exponent m passed from 2 to about 1.67 as a consequence of the borax addition, which changed the complexity of the network topology and, more importantly, increased the solvent-polymer compatibility. A value of 5/3 (= 1.67) describes the behavior of a polymer coil in a 'good' solvent (i.e., when the monomer-solvent interaction is more favorable than monomer-monomer interaction).[9]

Table 4.4.1. Parameters associated to the best fits to the SAXS curves of the 75PVA (column A) and 75PVA/Borax systems (column B). The (OH/B(OH)₄) ratio was kept equal to 20.4:1 for all the investigated samples.

A	75PVA			
	5%	7%	9%	12%
I_0	4.96 ± 0.05	6.02 ± 0.04	5.25 ± 0.07	7.19 ± 0.06
ξ (Å)	55.1 ± 0.04	55.0 ± 0.05	50.7 ± 0.04	49.3 ± 0.04
q_0 (Å ⁻¹)	0.0168 ± 0.07	0.0188 ± 0.07	0.0189 ± 0.06	0.0208 ± 0.04
m	2.02 ± 0.08	1.98 ± 0.07	1.97 ± 0.08	1.96 ± 0.06
bkg	0.0268 ± 0.02	0.0396 ± 0.02	0.0487 ± 0.03	0.0572 ± 0.03
B	75PVA/Borax			
	5%	7%	9%	12%
I_0	3.34 ± 0.08	5.53 ± 0.02	6.56 ± 0.03	6.14 ± 0.06
ξ (Å)	51.8 ± 0.03	51.1 ± 0.07	50.5 ± 0.06	39.0 ± 0.05
q_0 (Å ⁻¹)	0.0231 ± 0.08	0.0227 ± 0.09	0.0241 ± 0.04	0.0312(3)
m	1.69 ± 0.06	1.67 ± 0.06	1.67 ± 0.05	1.64 ± 0.03
bkg	0.150 ± 0.02	0.157 ± 0.03	0.210 ± 0.05	0.300 ± 0.04

In order to estimate the level of interaction of water with the 75PVA-borax network, and relate it to the elastic properties of the polymeric dispersions, the Free Water Index (FWI) [17,18], a parameter that represents the percent of free and freezing bound water contained in the samples, was determined from DSC measurements.

It was calculated using the following formula [19]:

$$FWI = \Delta H_{\text{sample}} / \Delta H_{\text{purewater}} * 100 \quad (\text{Eq. 4})$$

where ΔH_{sample} is the enthalpy change due to the fusion of the ice contained in the HVPD sample ($J g^{-1}_{\text{water}}$), experimentally determined from the DSC curve; $\Delta H_{\text{freewater}}$ ($=333.6 J/g$) is the theoretical value of the specific fusion enthalpy of pure ice at 0°C .

As seen in Figure 4.4.2, for 75PVA concentrations between 2 wt% and 5 wt%, the FWI values are almost constant. By further increasing the polymer concentration, the percent of non-frozen, bound water at temperatures below 0°C (i.e., water that interacts strongly with the polymer chains and borate ions) strongly increases up to the 45% for a concentration equal to 12 wt%.

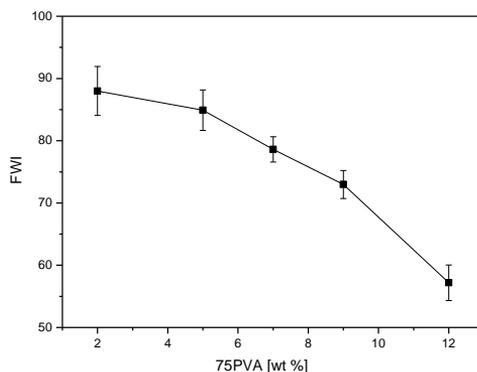


Figure 4.4.2. FWI values of the HVPDs as a function of 75PVA concentration. The (OH/B(OH)₄⁻) ratio was kept equal to 20:1 for all the investigated samples.

4.5 Cleaning tests onto the Carlo Carrà's wall painting "Giudizio Universale" in the Palazzo di Giustizia, Milano, Italy

On the basis of both the rheological results obtained with the PVA-borate HVPDs and the test already carried out, the efficacy of these aqueous systems as cleaning tools was tested on a surface of a wall paint. The experimentation was made in cooperation with the restorer Barbara Ferriani on a portion of the *Giudizio*

Universale (Figure 4.5.1, A), a fresco by Carlo Carrà (1881-1966) in the *Palazzo di Giustizia* in Milan.

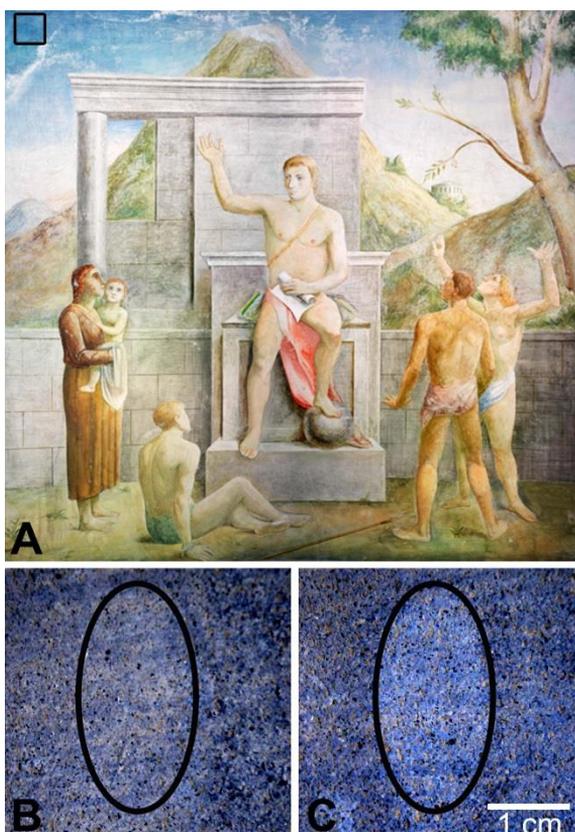


Figure 4.5.1. (A) “*Giudizio Universale*” a XX century wall painting by Carlo Carrà (1881-1966), Palazzo di Giustizia, Milano, Italy. The black box indicates the region where the cleaning test was carried out by means of the 75PVA-borax based HVPD. Magnification of the area interested by the cleaning test before (B) and after (C) the application of the HVPD. The application procedure is described in the Materials and Methods section.

The painted surface had been altered by a uniform thin dark grey layer present all over the surface and constituted by carbonaceous particles mainly deriving from atmospheric pollution (Figure 4.5.1, B). For the realization of the paint Carrà used substances highly sensitive to aqueous media like white egg as binding medium and gypsum in order to obtain effect of different colour saturation. A first attempt for the removal of the surface dirt layer showed that deionized water was able to solubilize the surface dark layer but its penetration into the mortar’s porous

structure caused the swelling of the binder with consequent local surface whitening. In order to avoid all these drawbacks, the cleaning was carried out by means of the 75PVA/Borax/H₂O based HVPD (cleaning tests were carried out by means of the systems containing the 7 wt% of 75PVA) that, due to its high viscosity, minimized the penetration of the water into the porous support. The system was applied with a spatula and maintained in contact with the surface for 4 min; thanks to its elasticity, the gel was completely removed in one step without residues left on the painting surface. After the gel application some dark layers were still present on the surface and were completely removed with a second application of the gel (Figure 4.5.1, C). It is worth nothing that an important advantage in using these gel-like systems, beside the lack of residues, is related to the selective, controllable and progressive cleaning of the surface.

4.6 Experimental section

4.6.1 Materials

75% hydrolyzed poly(vinyl acetate)s (75PVAs), as random copolymer, was supplied by Kuraray Co., Ltd. It was copiously washed with ice-cold water and dried under vacuum in order to eliminate by-products and residual free acetate. Sodium tetraborate decahydrate (>99.5%, Fluka) was used as received. Water was purified by a Millipore Elix3 apparatus ($R \geq 15 \text{ M}\Omega \text{ cm}$).

4.6.2 Molecular weight distribution

The molecular weight (M) distribution of 75PVA was obtained by means of a Size-Exclusion Chromatography (SEC) apparatus equipped with a column calibration based on dextran standards. The mobile phase was aqueous phosphate-buffered saline (PBS). The molecular weight distribution was obtained by linearly fitting the $\log M$ vs elution volume and then generating the M-value using the Empower software from Waters. Analyses were performed using 2 TSKGM PWXL columns (in series) from Tosoh Biosciences and a Waters SEC-LS chromatograph consisting of a Waters Alliance 2690 (solvent delivery and auto-injector) component, a temperature-controlled column compartment, and a Waters 410

differential refractive index detector. The M_w -value determined in this way of 75PVA was 7300.

4.6.3 Preparation of the HVPDs

For the preparation of the HVPDs the polymer was placed in a vial and was dissolved in water by heating under stirring at 85 °C for 2 h. Then, an aliquot of an aqueous 4 wt% borax solution was added drop-wise by stirring (vortex apparatus). The sample became rigid after a few minutes.

All the characterization studies were carried out 24 h after sample preparation to ensure the reaching of equilibrium of the HVPDs. The ratio between the amount of polymer hydroxyl groups and the borate ions ($\text{OH}/\text{B}(\text{OH})_4^-$) was kept equal to 20.4:1 throughout.

4.6.4 Rheological measurements

Mechanical equilibration of all the investigated samples was monitored by means of rheology. Frequency Sweeps (*vide infra* for the measurements set up) were carried out 1, 2, 5 and 10 hours after the sample preparation. It was observed that after 2 hours the trend of both the elastic (G') and the loss (G'') moduli remained constant. On the other hand, chemical equilibrium detected by the invariance of pH was anticipated, since pH remained equal to 7.30 ± 0.20 1 hour after the sample preparation. pH measurements were performed with a digital pH-meter CrisonBasic 20.

Oscillatory shear measurements were carried out on a Paar Physica UDS200 rheometer at 25 ± 0.1 °C (Peltier temperature control system) using a cone-plate geometry (25 mm diameter and 1° cone angle). The minimum gap between the plates at zero radial position was 0.5 mm. The cone was lowered up to the measuring position in the z axis force controlled mode; the maximum squeezing force was 3.0 N. After being loaded, the samples were allowed to equilibrate for 30 min at 25 °C prior to start the experiments. Frequency sweep measurements were carried out within the linear viscoelastic range (4% strain), determined by means of an amplitude sweep test. The storage and loss moduli (G' and G'' , respectively) were measured over the frequency range of 0.01 to 100 Hz. The intrinsic viscosity, η_0 , values were deduced from the plateau of the flow curves in the low Newtonian

region (low-shear-rate regime). This value was plotted as a function of the polymer concentration in order to determine the threshold 75PVA concentrations C^* above which the drastic increase of the η_0 value indicates the formation of the extended 3D polymer networks at different $(\text{OH}/\text{B}(\text{OH})_4^-)$ ratios. In order to minimize the handling of the HVPDs, immediately after the addition of the borax solution, the vials were turned upside down to favour the accumulation of the sample on the cap side. Then, all the HVPDs were easily directly transferred onto the measurement plate.

4.6.5 SAXS measurements

SAXS measurements were carried out with a HECUS S3-MICRO camera (Kratky-type) equipped with a position-sensitive detector (OED 50M) containing 1024 channels of width 54 μm . Cu K α radiation ($\lambda = 1.542 \text{ \AA}$) was provided by an ultra-brilliant point micro-focus X-ray source (GENIX-Fox 3D, Xenocs, Grenoble), operating at a maximum power of 50 W (50 kV and 1 mA). The sample-to-detector distance was 269 mm. The space between the sample and the detector was kept under vacuum during the measurements to minimize scattering from the air. The Kratky camera was calibrated in the small angle region using silver behenate ($d = 58.34 \text{ \AA}$) [20]. Scattering curves were obtained in the q -range between 0.01 and 0.54 \AA^{-1} , assuming that $q = 4\pi/\lambda \sin \theta$, where 2θ the scattering angle. Gel samples were placed into 1 mm demountable cells having Mylar films as windows. Liquid samples were filled into a 1 mm borosilicate Mark-Tube (Hilgenberg GmbH, Germany) using a syringe. The borosilicate capillaries were sealed to avoid solvent evaporation. The temperature was maintained at $25 \pm 0.1 \text{ }^\circ\text{C}$ by a Peltier controller. All scattering curves were corrected for the empty cell contribution considering the relative transmission factor.

4.6.6 DSC measurements

DSC measurements were performed with a Q1000TA Instruments apparatus. The samples, sealed in aluminum pans, were equilibrated at $25 \text{ }^\circ\text{C}$, cooled to $-90 \text{ }^\circ\text{C}$ at a cooling rate of $5 \text{ }^\circ\text{C}/\text{min}$, kept at $-90 \text{ }^\circ\text{C}$ for 8 min, and then heated to $30 \text{ }^\circ\text{C}$ at $5 \text{ }^\circ\text{C}/\text{min}$, under a 50 mL/min stream of nitrogen. An empty sealed aluminum pan was used as the reference. For each system, three different samples were prepared and scanned. The enthalpy of fusion of the water was calculated by integrating the heat flow curves.

4.6.7 Cleaning tests onto a fresco by Carlo Carrà

The HVPD was applied onto the surface of a wall painting by Carlo Carrà 48 hours after its preparation. It was applied directly onto the wall painting surface by means of a spatula and left there for about 5 minutes. The HVPD was peeled from the surface by means of a pincer, without adding any additional liquid component to the remaining polymeric dispersion or on the painting surface after the peeling process. The procedure was repeated twice.

4.7 Bibliography

- [1] E. CARRETTI, M. BONINI, L. DEI, B.H. BERRIE, L.V. ANGELOVA, P. BAGLIONI, R.G. WEISS, *Acc. Chem. Res.*, 2010, 43, 751.
- [2] P.D. HONG, C.M. CHOU, H.T. HUANG, *Eur. Polym. J.*, 2000, 36, 2193.
- [3] J. DOMINGUES, N. BONELLI, R. GIORGI, E. FRATINI, F. GOREL, P. BAGLIONI, *Langmuir*, 2013, 29, 2746.
- [4] I. NATALI, E. CARRETTI, L. ANGELOVA, P. BAGLIONI, R.G. WEISS, L. DEI, *Langmuir*, 2011, 27, 13226.
- [5] A.A. SOBCZUK, S. TAMARU, S. SHINKAI, *Chem. Commun.*, 2011, 47, 3093.
- [6] D.J. ABDALLAH, L. Lu, R. G. WEISS, *Chem. Mater.*, 1999, 11, 2907.
- [7] T. SEO, S. TAKE, K. MIWA, J. K. HAMADA, T. IJIMAR, *Macromolecules*, 1991, 24, 4255.
- [8] T. KANAYA, N. TAKAHASHI, K. NISHIDA, H. SETO, M. NAGAO, Y. TAKEBA, *Phys. B*, 2006, 385–386, 676.
- [9] A.L. KJONIKSEN, B. NYSTROM, *Macromolecules*, 1996, 29, 5215.
- [10] B.A. SCHUBERT, E.W. KALER, N.J. WAGNER, *Langmuir*, 2003, 19, 4079.
- [11] J. HONERKAMP, J. WEESE, *Rheologica Acta*, 1993, 32, 65.
- [12] M. DOI, S. F. EDWARDS, *J. Chem Soc. Faraday Trans.*, 1978, 74, 1818.
- [13] M. RUBINSTEIN, A.N. SEMENOV, *Macromolecules*, 2001, 34, 1058.
- [14] F. HORKAY, B. HAMMOUDA, *Colloid Polym Sci.*, 2008, 286, 611.
- [15] L.V. ANGELOVA, P. TERECH, I. NATALI, I., L. DEI, E. CARRETTI, R.G. WEISS, *Langmuir*, 2011, 27, 11671.

- [16] P.G. DE GENNES, *Scaling concepts in polymer physics*, Cornell University Press, Ithaca, New York, 1979.
- [17] S.J. KIM, C.K. LEE, S.I. KIM, *Journal of Applied Polymer Science*, 2004, 92, 1467.
- [18] H. HATAKEYAMA and T. HATAKEYAMA, *Thermochimica Acta*, 1998, 308, 3.
- [19] M. SHIBUKAWA, K. AOYAGI, R. SAKAMOTO and K.J. OGUMA, *Chromatogr., A*, 1999, 832, 17.
- [20] T.N. BLANTON, M. RAJESWARAN, P.W. STEPHENS, D.R. WHITCOMB, S.T. MISTURE, J.A. KADUK, *Powder Diffraction*, 2011, 26, 313.