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# THE ROLE OF WATER IN THE RESTORATION OF PAINTINGS

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ABSTRACT
Cleaning old paintings has always been a major problem, because aqueous solutions may dissolve pigments. We succeeded in cleaning some precious old paintings of Siena using aqueous products. This success encourages us to clean a Lorenzetti masterpiece in the near future. The techniques used and a possible explanation of the surprising result are discussed in the light of recent insights into the physics of water.
*Keywords: cleaning with water, coherent water, interfacial water, Siena paintings.*

## 1 INTRODUCTION

In the present paper we discuss the cleaning of some old paintings of the Pinacoteca Nazionale of Siena (Museum of Sienese Paintings). The present study is part of the project 'Ricerca Applicata alle Pellicole Pittoriche delle Opere Policrome della Pinacoteca Nazionale di Siena', carried out in collaboration with Siena University and the Superintendent of Historical, Artistic and Ethnoanthropological Heritage of the Provinces of Siena and Grosseto (National Art Gallery), financed by the Monte dei Paschi (MPS) Foundation (2006–2008), having the objective of interdisciplinary study of recent noninvasive methods of cleaning surfaces painted with protein-based materials. An advantage of these methods is their low toxicity for restorers.

The first work cleaned was a tempera on wood attributed to Niccolò di Buonaccorso (Fig. 1).

It is an altar piece, probably made for private use, measuring 110 × 75 cm and depicting scenes from the New Testament around a central crucifixion. It is crowned by a lozenge showing the Assumption of the Virgin Mary, and completed by a false predella depicting various saints [1–4]. The painting was restored in the 1930s and the painted surface was in good condition, except for sporadic areas of colour sealed with beeswax. The support was also in good condition, except for a crack running the whole length on the left side. Near the main gaps in the surface and the gilt frame, there were many touch ups and patches of false gold (porporina).

## 2 CLEANING PROCEDURES AND RESULTS

Appropriately calibrated water can have many functions, even on materials with which it has little affinity, and can play different roles in the mechanism of dissolution. Water is a solvent and a method of cleaning. Its contraindications, mainly related to its retention index, have traditionally limited its use in restoration, a problem now solved with gels and supports [5–8].

*Diagnosis* – To determine a specific optimal method of cleaning the work, we used a diagnostic procedure exploiting UV, microchemical tests of fragments of material selectively removed from samples to identify proteins, saponifiable compounds and polysaccharides, stratigraphic and light microscope observation using visible and UV light, micro and histochemical tests to identify binders and SEM-EDS electron microscope analysis according to UNI-NORMAL 8/81. These studies led to a complete identification of: (a) organic binders of colours and primer; (b) mineral content of primer; (c) pigments in different samples of the painted layer; (d) the nature of paints and touch up materials. The data and the identification of traces of milk as binder in the primer (also found in previous diagnostic tests of other works of the same period) provided insights into the sophisticated painting


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Figure 1: New Testament stories by Niccolò di Buonaccorso, fourteenth century. Tempera on wood, Siena school (from Museum of Sienese Paintings), before restoration.

methods used in Siena, confirming the use of heterogeneous materials, often of high value. This first phase of the project was carried out in collaboration with the Department of Analytical Chemistry of Parma University and CESMAR7, Padova.

The data obtained from the preliminary study and the results of solvents tested on the painted surface indicated the cleaning technique to use. The results obtained in the diagnostic procedure were compared with the data of previous sampling of other works in the Museum of Sienese Paintings. Protein binders of different types, such as egg and milk derivatives, in the painting materials used by Niccolò di Buonaccorso were also found in older works of masters such as Duccio da Buoninsegna. The same was true of protein-based paints, confirming the sophisticated nature of the painting techniques used in Siena [9–11].

*Cleaning* – The cleaning method was decided on the basis of careful historical-artistic-aesthetic evaluation of the work and the diagnostic results. The aim was to clean the surface of the many deposited materials without harming the layer of paint, and also to remove touching up and heavy addition of porporina. Sampling of particles of paint made it possible to identify proteic material. A thickened aqueous solution buffered at pH 5.5 (safety range for proteic materials) with progressive addition of surfactants and chelating agents to improve cleaning power was initially tested to remove deposited dirt. The many tests on almost all colours showed the hydrophilic nature of the material to remove from a surface sensitive to water. This finding, that discouraged the possibility of cleaning with water-based preparations, was the starting point for developing a strategy by which direct contact of the surface with water was avoided, while the power of water was nevertheless exploited to remove deposited grime. A 'rich emulsion' was therefore developed: it contained 90% ligroin (an apolar solvent compatible with the colours of the painting) and 10% water, emulsified by strong shaking with a nonionic polyethoxylate surfactant (TWEEN 20, 4 ml). This preparation ensured direct contact of the surface paint with the innocuous ligroin and the cleaning action of water 'hidden' in the emulsion. The solvent gave excellent cleaning results: the patina was saved and colours retained a high grade of saturation. Tempera touching up of the surface was effectively removed by direct action of water (thickened with cellulose ether).

Figures 2 and 3 show the differences before and after cleaning. In particular, Fig. 3 shows the differences in the colour of Madonna's mantle.

Porporina was also removed from the gilded parts by the 'water method', where the whole range of organic solvents in various mixtures and dimethylsulfoxide (DMSO) solvent gel, an aproteic dipolar molecule that also has a partly chemical solvent action, proved ineffective. The problem of cleaning a surface gilded with gold-leaf, sensitive to water, again prompted us to use the rich emulsion, varying its pH (8.5 against oily binders) with small quantities of chelating agent (0.1 g EDTA) towards the metallic component of porporina. Decisive selective action on one of the components of porporina removed the material completely.

Figure 2: Detail: the upper part has been cleaned.

Figure 3: Details: (a) left part, after cleaning; (b) right part, only the upper part is cleaned.

## 3 DISCUSSION

Successful cleaning using an aqueous product, without any damage to the painting, defies the usual intuition. An average expert would be afraid of using water, fearing that it would dissolve pigments and other components and wash them away. The empirical evidence does not support those fears. Why not? It is apparent from the success of this procedure that the water involved in the products used somehow lost its solvent properties. We know that interfacial water on a hydrophilic surface is no longer a solvent, and can be termed *EZ-water*. EZ stands for *exclusion zone* and was coined by G. Pollack [12, 13]. Solutes are excluded from interfacial water and strong gradients of electric potential can be expected at the surface between EZ-water and other media, so that EZ-water should attract polar particles to its surface. In conclusion, EZ-water trapped the dirt particles and did not dissolve soluble painting components, such as pigments and proteic ligands. These anomalous properties of EZ-water have also been explained in terms of quantum field theory (QFT) and of formation of coherence domain (coherent water) [14–16].

In order to exploit the properties of EZ-water for cleaning, bulk water must be absent, since bulk water is a solvent and would damage the paintings. This requirement is met by a gel of suitable chemicals that provide 'surfaces' and have a veil of water on them that becomes entirely EZ-water. Of course only a small amount of water can be used since any excess would act as a solvent.

The problem of designing a suitable cleaning product is undoubtedly complex, and as stressed in Wolbers [5], has so far been solved empirically. The composition of each product depends on the particular painting to be cleaned, since the amount of EZ-water is a function of the nature of the gel components, which in turn depend on the chemical structure of the painting.

Moreover as soon as surface of paintings on which particles of dust and other debris have been adsorbed has been contacting air and was illuminated with ambient light these particles are slowly, but incompletely oxidized. This process of slow oxidation could transform dust into supramolecular free radicals and peroxides that could fix on the surface of paintings not only by electrostatic and Van-der-Waals forces, but also by quasi-covalent bonds. That is why the problem of cleaning original paintings from external 'dust' is so complicated.

Water hydrating ligroin has evidently the properties of interfacial water (exclusion zone water). There is evidence that EZ-water has reducing properties, that is, it is able to donate electrons to appropriate electron acceptors. One of the most abundant of such acceptors in the environment is oxygen; carbon dioxide and other carbonates promote such electron transfer. Thus EZ-water interacting with air can promote, through electrons it is able to release, oxygen activation and mild oxidation (burning) of external layer of debris on the surface of paintings. Simple substances that arise in the course of oxidation easily detach from the original painting. On the other hand this oxidation is not intense enough to damage the original paints because they were chosen by the artists not only for their pure and bright colours, but also for their chemical inertness and hence they do not fade and discolour even after many years and even centuries of exposure to ambient light in the presence of oxygen-containing air.

We expect that the conceptual framework suggested here will be helpful in choosing solutions to use for cleaning particular paintings.

## 4 OUTLOOK

Research underway in the framework of the present project concerns two other important works in the Museum of Sienese Paintings: a tempera on wood predella of 'Christ stumbling under the Cross with Saint Peter, Saint Michael Archangel, infant Tobias, angel and Saint Paul' by an unknown popular artist of the mid-sixteenth century and 'Virgin and Child' by Pietro Lorenzetti (fourteenth century).

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