MONITORING CLEANING PROCEDURES THROUGH NON-INVASIVE MEASUREMENTS: A CASE STUDY

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ABSTRACT

The removal of an altered superficial varnish layer remains a challenging problem in the restoration of XXth century oil paintings. The artist oil-based paint layers, not yet entirely polymerized, are particularly sensitive to the solvents necessary for the removal of varnish, especially those used in the case of oil based varnishes. Many cases, for which a controlled and selective intervention remains impossible, call for a different approach; acceptance of the altered layer as a fundamental part of the historic patina of the painting.

This paper presents a case study in which the problems and limitations associated with organic solvents were overcome by the use of a chelating agent in aqueous solution. To better understand the mechanism of this cleaning agent, the intervention was monitored by non-invasive in situ reflectance FTIR spectroscopy on the surface of the painting in addition to GC-MS on extracted materials from the swabbing cleaning procedure. Of particular interest was the identification of calcium oxalate, selectively and mechanically bound to the altered superficial varnish layer. Due to the chelating action of the triammonium citrate, both oxalate and altered varnish layer were removed upon cleaning.

The painting “The open door” is preserved in the Presidential Palace in Rome (the Quirinal). It is dated 1919 and signed by Venazio Zolla on the front. The painting was restored during the didactic sessions of the painting section in the Department of Contemporary Materials at the Istituto Centrale per il Restauro in Rome by the conservator Grazia De Cesare and the student Nicoletta Tomassi.

The artist (1880-1961) was considered a ‘French painter’ from Italy. A family is portrayed in a household environment: an old man is depicted in the foreground while sitting by a table; a woman and a young girl are behind, whilst in the background a figure is visible through an open door.

The paint layer is homogeneously thin, except in a few small areas, where the film is thicker and cracked, due to an excess of the drying oil-based medium and to the presence of white lead – detected through XRF – on the old man’s face and hands. It is possible to see a white underlayer along the edges. The layer is so thin that it lets the tight and fine canvas structure show through. The canvas is glued to a cardboard, slightly larger than the canvas. A wooden frame is present, but this was clearly industrially-produced and cannot be considered as original.

Before the conservation project, it was difficult to appreciate the painting in its details and colours, because of the presence of dust and grime, dark stains, and a general yellowing which was giving the painting a greenish appearance. The cleaning was the principal issue of the restoration treatment. After easily removing the dust and dark stains, first through dry cleaning and then using demineralised water applied by swab, it was noticed that a mat layer of a greasy substance, slightly green in colour, remained on the surface. Such a layer turned out to be difficult to distinguish and remove while respecting the original materials. At the

beginning it was thought that the layer could be an altered oily or oily-resin varnish or an intentional green or blue-coloured film applied as a *patinatura*. It is important to remark the total absence of this layer along the outer edges of the painting, usually covered by the frame. Here, on the contrary, the colours were brilliant and pure. This fact suggested that the layer could have been applied after mounting of the frame. No evidence of previous restorations was found, apart from the addition or replacement of the frame added in a later period.

We decided not to take samples for chemical destructive analyses, because the painted surface was extremely sound. To understand and establish the stratigraphy of the last layer and of the paint film, and to be sure that the mat layer was a distinct layer and not an alteration of the oil paint, we applied only non destructive analysis. IR Reflectography seemed to confirm that the mat layer was a distinct one, since this technique showed, in the bottom left area, a more detailed flowered decoration as a tapestry, along with a different drawing near the old man and a different position for the door through which a person is visible. We therefore concluded that the mat layer was in fact a varnish layer applied to the painted surface. XRF was carried out but did not confirm the use of any green or blue pigment responsible for the greenish colour of the varnish. On the other hand, white lead was detected in those areas showing a cracked paint film.

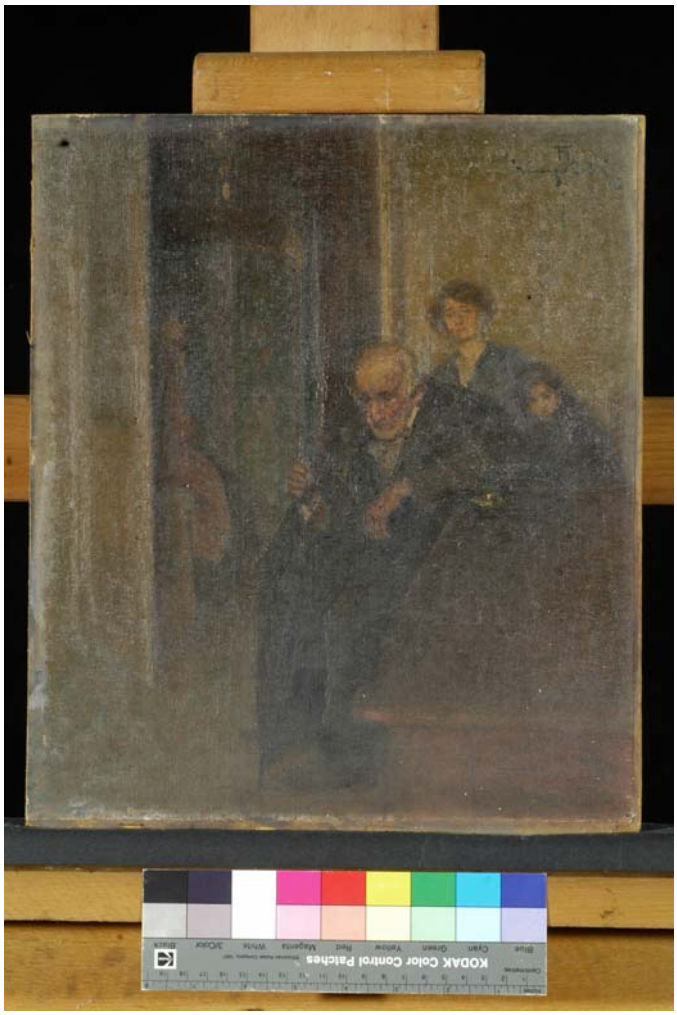
In order to complete the cleaning, different tests with organic solvents were undertaken using the Teas chart. The tests are presented in the table below. None of them yielded satisfactory results. As a substitute for organic solvents the triammonium citrate was finally and successfully used. A 1% triammonium citrate solution was applied by brush and subsequently rinsed with demineralised water. In order to understand the effects of the cleaning procedure, collaboration with the Department of Chemistry of the University of Perugia was sought and set up. Cleaning was monitored using non-invasive in situ reflectance FTIR spectroscopy on the surface of the painting. GC-MS was carried out on the extracted material collected from the swabs employed in the cleaning process. The reflectance FTIR spectroscopy was used to examine the painted surface after the first superficial cleaning with demineralised water, after the cleaning with triammonium citrate, and after rinsing the surface with demineralised water.

The results of the reflectance FTIR spectroscopy showed, during all the phases of the cleaning, the presence on the painted surface of lipidic material, calcium oxalate, calcium sulphate, along with Prussian blue. Only after the final rinsing with demineralised water, calcium oxalate was not detected. GC-MS carried out on the swabs collected after rinsing, treated with water confirmed the presence of oxalate, sulphate, and citrate and treatment with a basic solution also the traces of terpenic resin and aged drying oil.

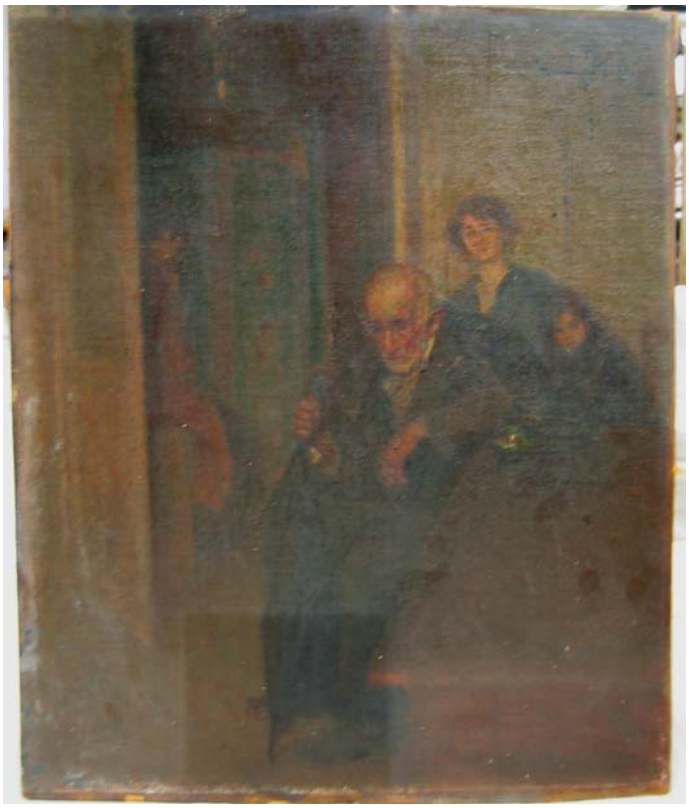
Of particular interest is the identification of calcium oxalate, selectively and mechanically bound to the altered superficial varnish layer. Due to the chelating action of the triammonium citrate, both oxalate and altered varnish layer were removed upon cleaning.

Cleaning Tests

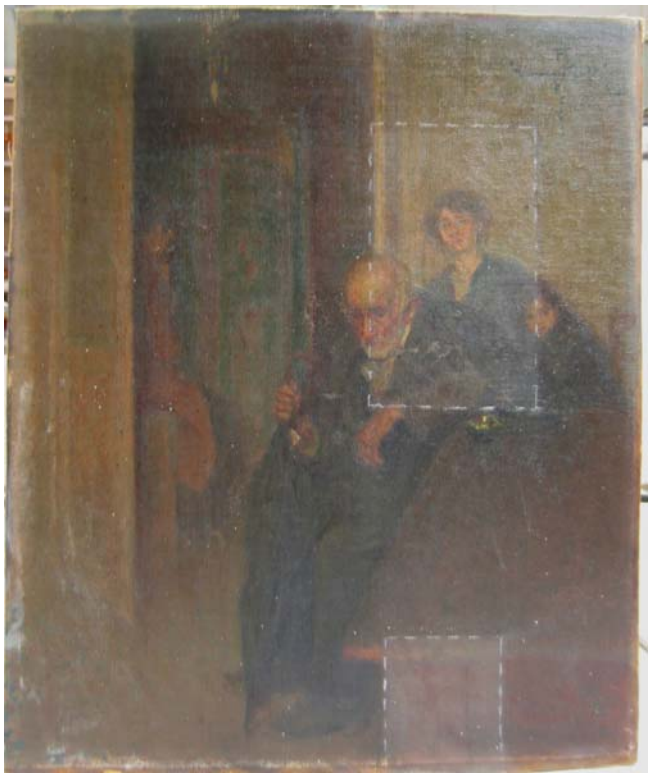
Solvents	**Solubility areas**	**Result**
Demineralised water by swab	Proteins Polysaccharides	It removes superficial dust and the dark stains
Petroleum ether (40-60°C) by swab	Greasy substances	No effect
Isopropyl alcohol by swab	Proteins and polysaccharides	No effect
MEK 50% ethylic alcohol 50% by swab	Proteins and polysaccharides Synthetic resins natural resins and fresh oils	Light cleaning of a green substance, non homogeneous, mixed with the original colour
Ethylic alcohol 13%, acetone 61%, isooctane 26% by swab and Japanese paper for two minutes	Proteins and polysaccharides Natural and synthetic resins Fresh and aged oils	It removes the superficial layer, but not completely, too much volatile
Isopropyl alcohol 30% Mek 56% Isoctane14% by swab and Japanese paper for two minutes	Proteins and polysaccharides Natural and synthetic resins Fresh and aged oils	It removes the superficial layer, but not completely, less volatile, but not sufficient
isopropyl alcohol 19% Acetone 21% Isooctane 60% By swab	oils wax	Light cleaning, but non sufficient
Triammonium citrate 1% in water	Chelating action	It removes a greenish - yellowish material: the cleaning respect the original paint film that appears without alteration and more clear.



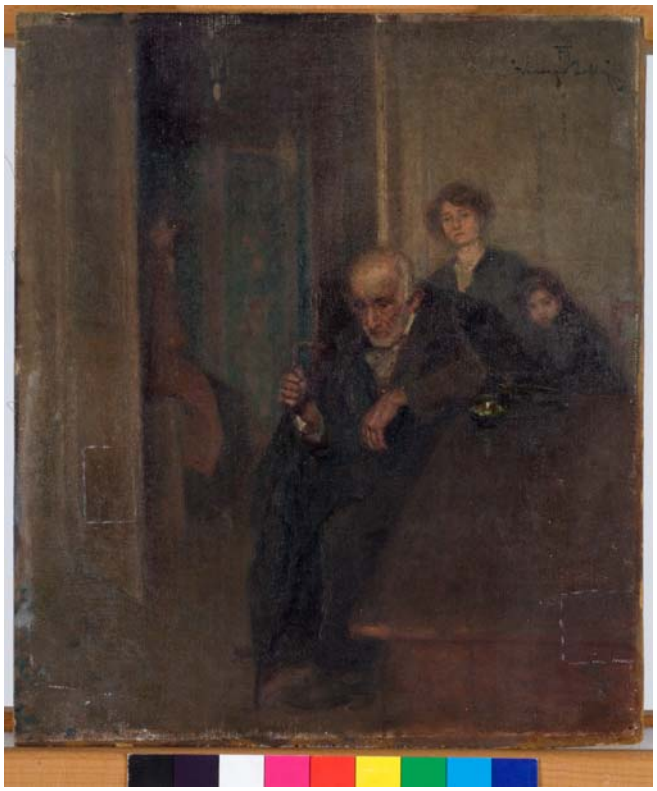
1. Before Restoration



2. First dry cleaning test

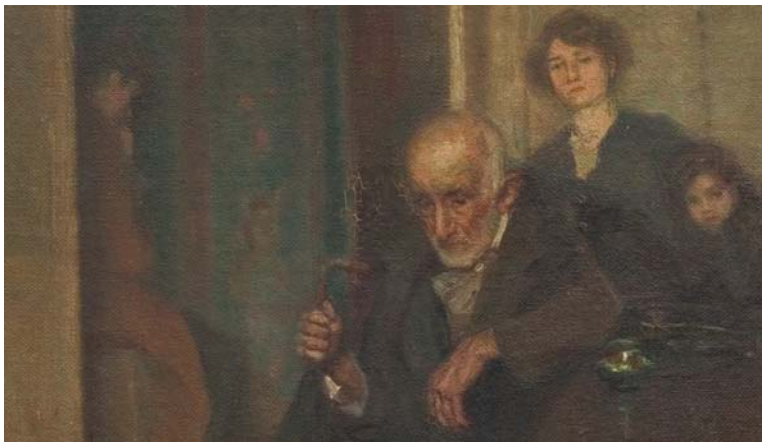


3. After the first superficial cleaning, leaving two windows of dust

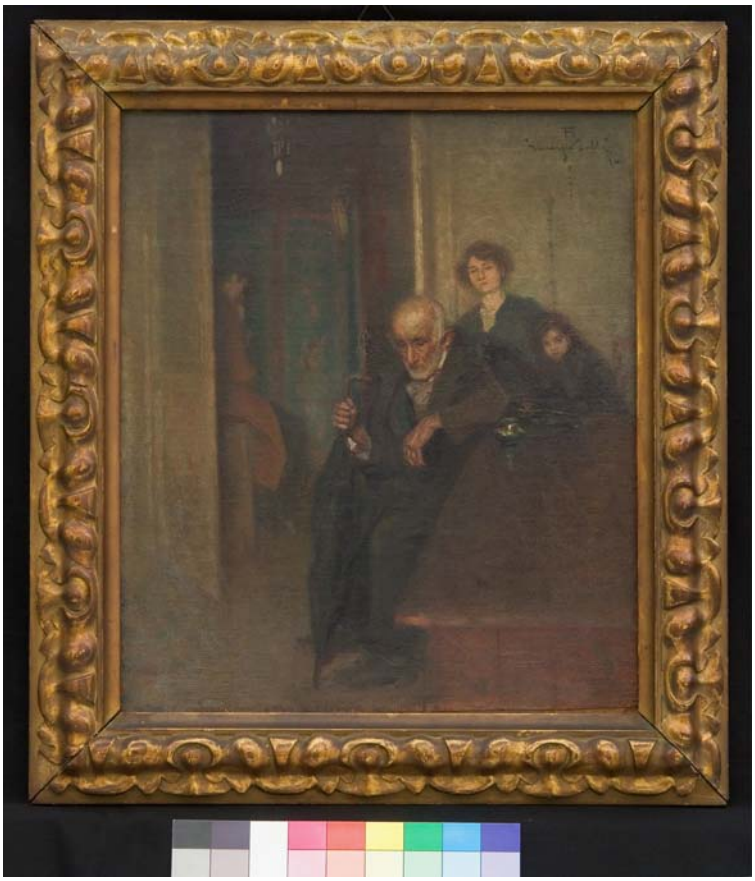


4. After cleaning with triammonium citrate, before the last analysis

5. Detail before cleaning



6. Detail after restoration



7.After the restoration

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