

Cleaning of historical scientific instruments: first analytical studies

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Abstract – During the recent decades the identification of scientific instruments as a cultural heritage objects, has been drawing more attention to their preservation: a lack of knowledge is drastically evident and fill it is demanding. Varnishes from the 18th century applied as finishing of brass component in Europe are known as imitation of Chinese lacquer coming from the oriental tradition. It was considered to own the best aesthetic and mechanical properties in that period during which the manufacturing reached its apogee, and today it protects a great number of historical masterpieces' surface.

A non-invasive methodology is employed to characterize the varnish reproduced with a traditional recipe and to monitor the effect of three cleaning methods widely spread within the restorers' community.

I. INTRODUCTION

During the 18th century the manufacturing of scientific instruments reached the apogee and became subject of study also for the experimental science. Brass has always been employed in the metal components due to its malleability, ductility and to its golden aspect. Such a surface is protected and enriched by varnishes whose composition is described in different recipes and that must be preserved.

The results of the experiments were published on chemistry treatises and dictionaries, and numerous

recipes experimented over time are available. The Swedish chemist Jons Jacob Berzelius (1779-1848) [1], was the first to recommend protecting the brass scientific instruments surface. In his volume some recipes refer to a varnish made by natural resins and colorants, able to confer a shiny golden aspect to the surface. Such a varnish was described to own amazing properties very close to those typical of the precious Chinese lacquer made by the sap of the Rhus Verniciflua tree (*Toxicodendron vernicifluum*), brought to fame in Europe during the 18th century thanks to the Jesuit pilgrims' writings [2].

Nowadays, historical scientific instruments are preserved as cultural heritage objects, but in the past centuries they were used in the laboratories and their surface was exposed to soiling, aggressive cleaning and hands sweat deposition. As the preservation approach is new to this class of objects, no protocols are available for the restoration, not even for the cleaning that is commonly among the first practice to be undertaken. Experimental studies are demanding to fill this gap of knowledge towards an aware preservation practice for these objects that are part of the main collections and that in the last years are drawing more and more attention on their role and worth.

While several publications are available for the cleaning methods of polychrome surfaces [3], only a few of them are about the interaction between natural resins and cleaning methods [4], and no scientific publications

are focused on the materials of scientific instruments. Cleaning, as we know it today in the field of cultural heritage, started with systematic developing of aqueous methods carried on by Richard Wolbers in the '80s of 20th century [5]: a powerful safe and adjustable tool that is the most spread, mainly coupled with different kind of supportant like Agarose in rigid gels [6]. The range of cleaning methods and materials is also getting wider thanks to the opportunity offered by the ready-to-use products available on the market, such as silicon-based solvents [7].

In this study, some preliminary results are displayed about a monitoring of cleaning tests by means of a non-invasive methodology. Three mild cleaning methods have been selected (deionised water in Agarose gel, Tween 20 in 3% deionised water solution supported in Agarose gel and Velvesil™ Plus) and applied to artificially soiled mock-ups of a traditional finishing for brass scientific instruments.

II. MATERIAL AND METHODS

A. Mock-up and varnish preparation

The mock-ups were realized applying a varnish layer on a lamina of brass OT 63 UNI 4892 Cu63% - Zn37% (10 x 5 x 0,1 cm). Spirit-based varnish was formulated according to traditional recipes [1]: shellac (28,35g), sandarac (56,70g), mastic (28,35g), elemi gum (56,70g), dragon's blood (28,35g), gurma-gutta (21,26g), curcuma (21,26g), saffron (12 grains), crushed glass (85,10g) and ethanol 85% (57,00g). The varnish was applied to the specimen using a soft brush. A specimen named Tq was kept as a benchmark made up of metal and varnish. Three other specimens underwent to a procedure to simulate the usage condition and the soiling deposition.

B. Artificial soiling and sweat deposition

A soiling mixture simulation made of two phases, dry and wet, was prepared according to existing protocols and experimentation [8]. The dry portion of the soiling mixture consisted of: (i) sphagnum peat moss (20.8% w/w), (ii) carbon black (1.9% w/w), (iii) iron oxide (burnt sienna pigment, 0.5% w/w), (iv) gelatine (10.4% w/w), (v) soluble starch (10.4% w/w), (vi) Portland type I cement (18.6% w/w), (vii) silica gel (1.9% w/w), (viii) lime (16.7% w/w), (ix) kaolin (18.6% w/w). The wet portion of the mixture consisted of (i) high grade mineral (paraffinic) oil, and (ii) chloroform (99% pure CHCl₃) [4]. It was applied by soft brush in two consecutive coats. The interaction between the hands and the surface was simulated by means of synthetic sweat applied by a spray in two consecutive steps. Synthetic sweat according to DIN ISO 9022-12 imitates human hand sweat with a pH of 2,3 (SYNTHETIC URINE e.K., Germany).

Every specimen displays all kind of treatments named as follows: S is the soiled area, Sw is the sweated one,

SSw is the area where both soiling and sweat are present and V is the area with only varnish.

C. Cleaning tests

Three kinds of cleaning tests were carried out on the SSw and Sw areas. They were selected among the most used: deionised water in Agarose gel (Agarose: 0,75 g, H₂O 48 ml [9]), Tween 20 (Honeywell Fluka™) 3% deionised water solution supported in Agarose gel (Agarose: 0,75 g, Tween 20 1,5 ml, H₂O 48 ml [9]) and Velvesil™ Plus added with its solvent Cyclomethicone D5. Velvesil™ Plus is purchased by Momentive Performance Materials, Inc., and consists of a silicon copolymer gel and a silicon-based surfactant in a silicon-based solvent [7]. Four application times for each cleaning method were considered (minutes): t₁=30, t₂=60, t₃=90, t₄=180.

D. Non-invasive analytical investigation

A photographic documentation using visible light was acquired with a Nikon D4 full-frame digital camera equipped with a 50 mm f.1.4 Nikkor objective using a Softbox LED lamp. Colorimetric measurements were carried out with a portable Konica Minolta CM-2600d spectrophotometer: the average of the SCE values was considered and the dataset processed in the CIELab space (CIELAB 1976). Colour difference between respectively the soiled and the Tq surfaces with the cleaned one has been calculated and L* difference was helpful to evaluate the darkening and the bleaching of the surface due to the removal of black particles in the soiling mixture. The portable ELIO XRF spectrometer (XGLab srl, Milano, Italy) with Rh anode, was employed to collect XRF maps on the specimen surface (40 kV, 15 μA, 3s per spectrum): the XRF maps highlighted the elemental distribution in Tq and SSw areas, before and after the cleaning. Ca as part of the dry fraction of the soiling mixture was considered as a marker for the presence of the soiling and Si distribution was also taken into account to determine any residue of Velvesil™ Plus. Transflection mode FTIR spectra were recorded with the Alpha portable spectrometer (Bruker) equipped with R-Alpha module. Spectra were collected between 7500 and 400 cm⁻¹ at the resolution of 4 cm⁻¹ with an acquisition time of 1 min. The data were processed in OPUS 7.2 software. Diagnostic bands were identified for the inorganic fraction of the soiling mixture, mainly consisting of Portland cement (CaO 61–67%, SiO₂ 19–23%, Al₂O₃ 2.5–6%, Fe₂O₃ 0–6%, SO₃ 1.5–4.5%) and mineral kaolin. Variation in the intensity was considered to evaluate the elimination of soiling. Moreover, diagnostic bands of the Velvesil™ Plus were identified to be considered for the detection of the cleaning residues.

The whole analytical campaign was repeated for each step of the mock-up building-up procedure, respectively before and after varnishing, soiling, sweat application and

after the cleaning tests.

III. RESULTS AND DISCUSSION

In Fig. 1, photographic documentation in the visible range of the three specimens is displayed. The presentation of the analytical results is subdivided by analytical techniques.

A. Colorimetric investigation

The total colour variation ΔE is shown in Fig. 2 as a function of the application time of the three cleaning methods in the SSw area. ΔE smoothly decreased ($\Delta E_{t1}=3.68$) for the water in agarose cleaning test until assuming a value close to zero to indicate that after 180 minutes there are no differences with the soiled surface. Such an ineffectiveness is supported by the drop of L^* value at t_1 that confirmed a darkening of the surface (a^* and b^* constant). As regards the Tween 20 (3%) in Agarose, it seemed to be more effective in the dark matter removal even though it was not possible to identify a trend according to the application time: ΔE in SSw area after cleaning varied from 3,50 up to 8,15 and L^* grew after cleaning ($\Delta L^*_{max}= 7$), indicating a bleaching mainly due to the black particles removal. In the Sw area, a ΔE value of 3 was recorded and remained constant over time: a variation is appreciable only in the first 30 minutes. Otherwise, concerning the Velvesil™ Plus cleaning, ΔE varied from 2.33 to 7.84 and an increasing trend could be recognised since the second application. As in the Tween 20 test, L^* resulted to be the parameter which most affected this variation (difference up to 7.54) indicating the removal of the dark layer and bleaching on the surface. About a^* and b^* , their variation was negligible. The data regarding Sw were unexpected: the value of ΔE varied from 5.20 up to 14.30, combined to a substantial reduction in the b^* value seemed to drag this trend, signifying a change in the yellow component mainly connected to the properties of the varnish.

B. XRF spectroscopy

Ca distribution obtained through XRF mapping showed that soiling was removed by the three cleaning methods with a different degree of effectiveness. Water in agarose spectra showed a slight difference in the intensity of the Ca signal among the application times, revealing the mild action carried out on the soiling. Observing the XRF maps of the mock-ups cleaned by Tween 20 (3%) and Velvesil™ Plus (Fig. 3a), Ca is not detected. Consequently, any variation trend was not appreciable. As regards exclusively the Velvesil™ Plus method, not negligible quantity of Si was detected on the cleaned surface: its distribution allowed us to monitor the cleaning residue, as shown is Fig. 3b.

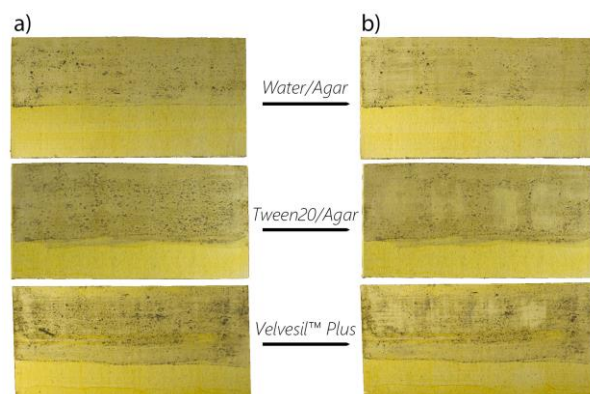


Fig. 1. Photographic documentation in the visible range of the three mock-ups, before (a) and after (b) the cleaning, respectively from the top with Water, Tween20 and Velvesil™ Plus.

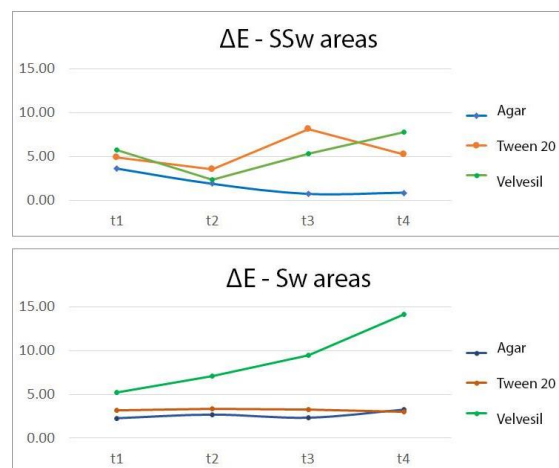


Fig. 2. ΔE as a function of the application time of the three cleaning methods for both the area SSw (top) and Sw (bottom).

C. FTIR spectroscopy

Transflection IR spectra were collected on the areas of the cleaning tests at different application times. Mainly two bands, with the absorbance maxima falling respectively at 533 and 468 cm^{-1} (Fig. 4), were identified as diagnostic of the cleaning effectiveness. In fact, the intensity reduction of these spectral features - attributed to the Portland cement and kaolin inorganic fractions - was able to provide information about the capability of the employed products to remove the soiling from the varnished surfaces. After the cleaning with water and Tween 20, the above-reported marker bands did not vary in intensity from t_0 to t_4 , suggesting the ineffectiveness of the treatment in exam.

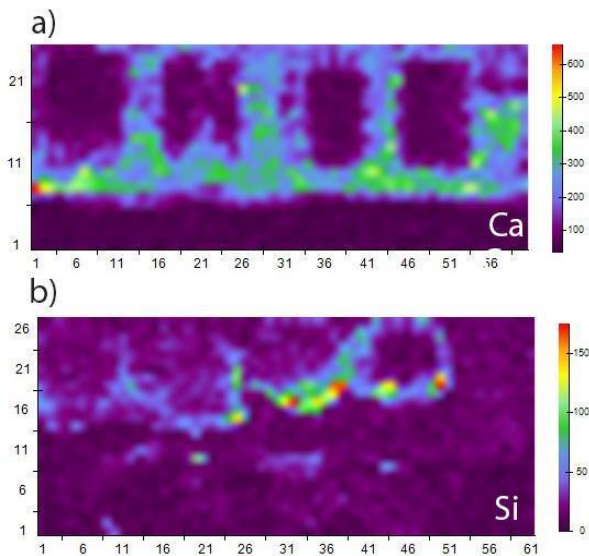


Fig. 3. XRF maps: Ca distribution highlights the areas (from t_1 to t_4 , from the left to the right) cleaned with Tween 20 (a), and Si distribution reveals Velvesil™ Plus residue - heat map colours represent the minimum (blue-violet) and the maximum (red) values.

Conversely, on the areas where the Velvesil™ Plus was tested the IR spectra clearly showed a significant intensity decrease from t_0 to t_4 proving the positive cleaning effect of this application (Fig. 4). However, the use of Velvesil™ Plus would exhibit some disadvantages to be taken into consideration in the art conservation field: after cleaning, indeed, residues of the product were detected on the surface as the silicon bands in the 1500-1000 cm^{-1} range and 800 cm^{-1} proved.

IV. CONCLUSION

The study investigates the removal of soiling from varnished surfaces using aqueous methods in gel and a silicon-based material. Their action efficiency was shown by identifying specific IR absorbance bands related to the inorganic fraction of the soiling mixture and defining Ca as a marker of the same mixture by the XRF spectroscopy distribution maps: while deionized water in agarose was proven to be weakly efficient, Tween 20 (3%) in agarose and Velvesil™ Plus produced more remarkable responses. In fact, Tween 20 (3%) in agarose resulted effective in removing the dark matter also in the shorter time, even though it was observed that not all the soiling was removed after the longest one. As regard the Velvesil™ Plus, it is more efficacious and it depends on the application time: a significant removal was observed starting from 90 minutes of application. A practical outstanding result for the conservators and the restorers was related to post-cleaning residues of Velvesil™ Plus as demonstrated by the FTIR spectroscopy that it could be used as a test.

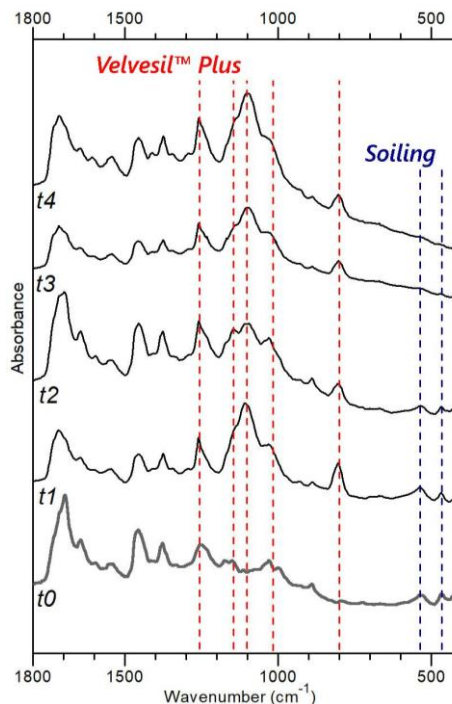


Fig. 4. FTIR spectra of the Velvesil™ Plus test from t_0 (bottom) to t_4 (top) - Velvesil™ Plus (red) and soiling mixture (blue) diagnostics bands are highlighted.

V. REFERENCES

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