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INVESTIGATION ON A LOW ENVIRONMENTAL IMPACT SOLVENT MIXTURE APPLIED TO A WOODEN PAINTED SLAB

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Abstract

Cleaning is one of the most complex and delicate step in a restoration project, often due to the manufacturing techniques of the artifacts and their advanced state of decay. Eco-friendly solvents can permit to execute the cleaning operations with a reduced health impact for the restorers and for the environment. In this work, the performance of the 1,3-dioxolane/methylal (DIOX-MET) solvent mixture is evaluated over a wooden painted slab that had been covered with a thin layer of a protective varnish, probably during a previous conservation work performed in the Sixties. Removal of this varnish has been considered on behalf of its yellowing degradation process, which caused chromatic changes over the pictorial layer. The study was performed by comparing DIOX-MET performance to that of a traditional solvent mixture. The effectiveness of the cleaning process was followed in situ by using a portable FT-IR total reflectance spectrometer.

Keywords: *Eco-friendly solvent; Varnish; Portable Infrared Spectroscopy; Wooden ceiling; Steri.*

Introduction

The operation of cleaning has always been a difficult task to perform on artworks. The need to use both controlled and selective cleaning methods, in order to minimize the impact of the treatment over the artistic surface, has guided many of the researches in the conservation field. In this field, a great part of the most recent researches are concentrated on finding new application methods that make use of traditional organic solvents trapped in retentive systems thus reducing their diffusion rate into the inner pictorial layer (also called "solvent gels"[1]). Despite being effective in performing with efficiency the cleaning task, these systems carry with themselves all the safety issues related to the use of some of those traditional organic solvents, potentially hazardous to the user's health. Taking this into account, an attempt to use solvents with lower environmental impact and increased health safety should be carried out in order to preserve the health of the restorers.

In this work, two of these "green" solvents have been considered, 1,3-dioxolane (DIOX) and methylal (MET).

Methylal, also called dimethoxymethane, is a colorless, highly volatile solvent with a low boiling point, low viscosity and an excellent dissolving power. It has a good toxicological profile and it is biodegradable. Thanks to an exceptional solvent power, its amphiphilic character (methylal is both hydrophilic and lipophilic), an extremely low viscosity, a low surface tension, a particularly high evaporation rate, methylal is useful in several fields [2].

1,3-Dioxolane is a powerful aprotic solvent for use in formulations, in production processes or even as a reactant itself. It has a very good toxicity profile. It is increasingly used in the formulation of waterborne coatings. It is not carcinogenic, toxic, explosive or auto-flammable, with no unpleasant odor and low peroxide formation tendency. It is also miscible in water and in most organic solvents. With its strong solvent power and favorable toxicity profile, dioxolane is rapidly finding acceptance as a replacement for halogenated, aromatic, and problematic solvents such as methyl ethyl ketone [3]. In spite of their use in cosmetics and personal care formulations [4], at the moment, they aren't commonly employed by restorers for cleaning. The cleaning performance of a 1:1 mixture of these two solvents was evaluated over a real case study, a wooden painted slab covered with a thin layer of a protective varnish applied during a previous conservation intervention. DIOX-MET mixture performance was compared to a traditional solvent mixture, both in terms of cleaning efficiency and residues lingering through FT-IR total reflectance measurements, realized directly in situ using a portable spectrometer.

FT-IR Total Reflectance measurements permit to evaluate the molecular composition of the sample surface. The penetration of the IR beam varies depending on the composition of the pictorial layer. In principle, the IR reflected beam can vehicle information up to the preparation layer. Nevertheless, in many cases, the presence of an organic varnish layer can reduce the penetration of the infrared radiation, maximizing the signal reflected from the surface and inhibiting the response from the deeper parts of the artwork. In this case, the reflectance IR analysis permitted us to determine the kind of substances present over the pictorial layer and to evaluate the effectiveness of cleaning treatments. This assessment allowed us to establish whether DIOX-MET mixture has proved to be a good alternative to the use of a traditional system.

The case-study

The slab belongs to the wooden ceiling of “Hall of Barons” of “Steri”, in Palermo, Italy. In the past, the ceiling has been restored several times: the first restoration was done in 1438, few decades after its construction. One of the most important restorations was conducted by Giuseppe Patricolo at the end of the XIX century [5]. The last one was conducted by Soprintendenza of Cultural Heritages of Palermo between 1970 and 1972. Due to the poor state of conservation of the decorative furnishing and to a xylophage agents attack, a restoration work on the entire ceiling is to be expected. In view of this work, a pilot restoration on two slabs has been carried out.

The slab *“Fregio con doppio intreccio di fettucce”* (figure 1), used as case-study in this work, was in a bad conservation state. The wooden support had a slight cupping and some injuries due to the natural movement of the wood. The painted surface was affected by numerous deep gaps and abrasions. Several forms of alteration, ascribable to the natural aging of the original materials and to the environmental setting, were present. The natural movements of the wooden support, together with the nature and the morphology of the preparatory layer, caused the cohesion loss and the subsequent detachment of adjacent layers. Therefore, these conditions lead to the lifting and peeling of the very thin preparation layer and of the painting film. Furthermore, crimps, caused by the movements of the support, were recognizable in the

pictorial film, particularly on the white areas. The original colors were affected by the presence of surface dirt and by the alteration of some pigments. A very thick layer of aged brown varnish was present on the emplaced slabs of the ceiling. The presence of the varnish seemed to be stronger in some areas of the slab.

Fig. 1. Photo of the slab "Fregio con doppio intreccio di fettucce": upper) in visible light; lower) in ultraviolet light.

In order to perform the restoration, considering the fragility of the pictorial layer, some areas of the slab were pre-consolidated before the detachment from the ceiling, using Japanese tissue paper and Paraloid B72 dissolved in acetone. After the detachment, the Japanese paper was removed by using acetone, applied using cotton swabs. After removing the Japanese paper, the slab was observed using UV illumination [6] (figure 1). Despite the fact that the pictorial layer was realized in tempera [7, 8], which does not give a strong fluorescence when UV irradiated, the presence of a bluish and not homogeneous fluorescence was witnessed. This can be attributed to the presence of a substance overlaid on the pictorial layer.

Experimental

Preliminary cleaning tests

To evaluate the most suitable solvent systems for the removal of the substance located on the paint layer, the restorers executed some preliminary cleaning tests. The application of the cleaning systems was done using cotton swabs.

Among available systems buffer solutions have been chosen because they do not change the pH of the surface, and, being aqueous-based, are not harmful for the restorers and for the painting [1]. This test has not been effective in trying to remove the varnish layer. Solubility tests were thus performed using mixtures of organic solvents (Wolbers-Cremonesi) [9], i.e. mixtures at various composition of Ligroin-Acetone and Ligroin-Ethanol. The results obtained from these tests indicated that the substance to be removed had a polarity similar to some of these mixtures. The best one was the LA6 (Ligroin-Acetone 1:6) and it was selected by the restorers in order to clean the entire slab.

As mentioned before, a 1:1 mixture of 1,3-dioxolane and methylal (DIOX-MET) was proposed as a more eco-friendly and new alternative to the traditional LA6 system. Ligroin, acetone, ethanol and the DIOX-MET mixture were supplied by C.T.S. s.r.l. and used as received.

FT-IR Total Reflectance spectroscopy

Infrared Total Reflectance spectra were directly recorded on the artwork, in a totally non-invasive manner (figure 2), using the Bruker ALPHA FT-IR Spectrometer, equipped with a Total Reflectance module (ALPHA-R configuration). Each measurement was acquired in the spectral range of 7500-400cm^{-1}, with an average spectral resolution of 4cm^{-1}, for duration of 3 minutes. The Kramer-Kronig Transformation (KKT) [10], which takes into account reflectance indexes and absorption indexes of the constituent materials, has been applied to the spectra in order to convert the reflectance spectrum in an absorption index spectrum, which is comparable to an absorption spectra measured in transmission mode. KKT-corrected spectra, after a baseline correction, were compared with a database of transmittance IR spectra in the range 3400-400cm^{-1} registered on reference materials. Both operations were performed using the data treatment software OPUS 7.5. Measurements were performed both on some unprotected points and on some points which had been previously protected with Japanese paper and Paraloid B72. For the evaluation of the performances of the cleaning systems, reflectance spectra were recorded on the same point, before and 15 minutes after the cleaning treatment.

Fig 2. Instrumental setting for the Total Reflectance IR measurements.

Results and Discussion

Identification of the overlaid substance

Unprotected points. The negative logarithm of a representative reflectance spectrum acquired on an unprotected point is reported in figure 3.

The KKT algorithm and baseline correction were applied to the spectra in figure 3, and the result is reported in figure 4A.

In the absorbance index spectrum of figure 4A, the ketone carbonyl (C=O) stretching present at 1707cm^{-1} can be observed. Other signals at 3200cm^{-1} (wide O-H stretching), 2921cm^{-1} and 2849cm^{-1} (-CH_2 and -CH_3 stretching), 1448cm^{-1} (C-H asymmetric bending), 1253cm^{-1} (O-H bending), 1110cm^{-1} (C-H bending), 1044cm^{-1} (C-O hydroxyl stretching) [11] have been identified. This recognition allowed us to establish that the substance observed by UV imaging as superimposed to the pictorial layer was a ketone resin, in particular a cyclohexanone polycondensation resin, which general formula is reported in the inset. As it is well known, the

cyclohexanone polycondensation resin is contained in the Laropal® K80 or in the Ketone Resin N, commonly used in the coating of paintings.

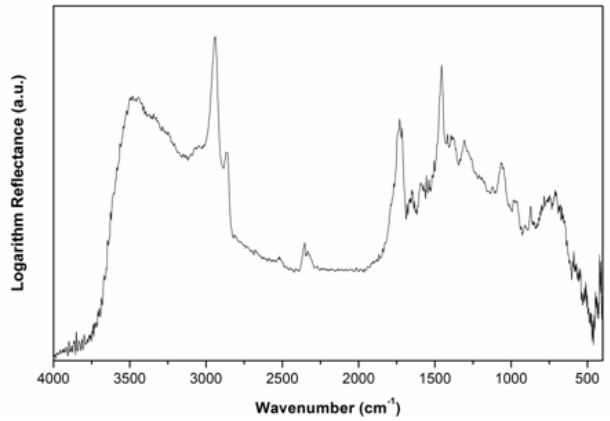

Fig. 3. Negative logarithmic reflectance IR representative spectrum of an unprotected point.

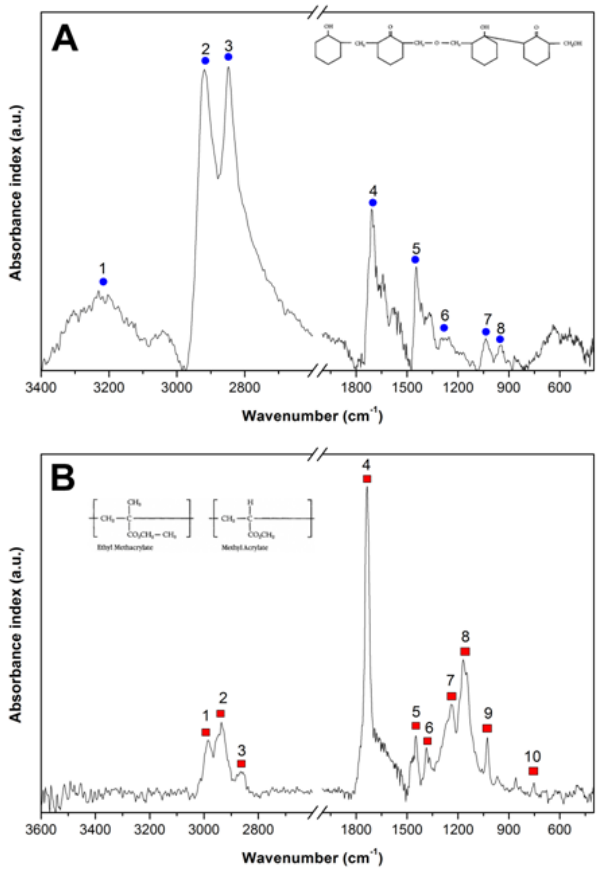

Fig. 4. Reflectance IR spectra KKT-converted representative spectrum of (A) an unprotected point and of (B) a previously treated point. The dotted signals are due to the ketone varnish presence. The squared signals are due to the Paraloid B72 presence. General formula of a polycyclohexanone resin [12] and of monomers of the Paraloid B72 acrylic resin are reported in the insets.

Previously protected points. IR measurements were also performed on some points previously treated with Japanese paper and Paraloid B72, after the detachment operations executed using acetone. A representative spectrum, after application of the KKT algorithm and baseline correction, is reported in figure 4B. In the absorbance index spectrum, an ester carbonyl stretching band centered at 1735cm^{-1} can be observed. Other signals at 2986cm^{-1}, 2935cm^{-1} and 2860cm^{-1} (-CH_2 and -CH_3 stretching), 1453cm^{-1} and 1381cm^{-1} (C-H asymmetric and symmetric bending), 1240cm^{-1} and 1027cm^{-1} (C-O ester bending), 1168cm^{-1} (C-H bending), 755cm^{-1} (CH_2 rocking) [11] have been identified. Residues of Paraloid B72 used for the preconsolidation are still present. The chemical structures of the two Paraloid B72 monomers are reported in the inset.

Furthermore, the ketone resin identified in the unprotected points is not observed in this spectrum. This lead us to think that the varnish has been removed from the surface during the removal of the Japanese paper with acetone (according to its solubility parameters, it should remove ketone resins).

Controlling the cleaning effectiveness

Total reflectance FT-IR was used also to evaluate the cleaning performance of the solvent systems. The two cleaning mixtures compared were Ligroin/Acetone 1:6 mixture (LA6) and 1,3-dioxolane/methylal 1:1 mixture (DIOX-MET). According to the Teas Triangle [13], reported in figure 5, both solvents are ideal for removing acrylic resins like Paraloid B72.

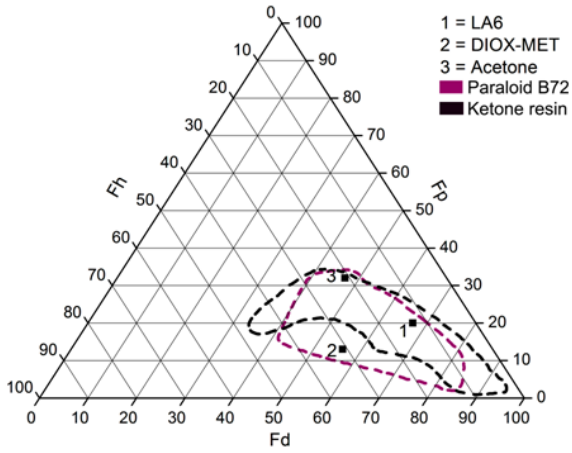

Fig. 5. Teas Triangle. Violet dashed line = Paraloid B72 solubility zone, black dashed line = Keton resin solubility zone. The following solvent systems are reported: 1 = LA6, 2 = DIOX-MET, 3 = Acetone.

The mixtures were directly applied on two points of the slab where Paraloid residuals have been found, gently massaging the surface with a cotton swab. Measurements were taken 15 minutes after the treatment.

LA6 mixture. The KKT-corrected spectra acquired on the cleaned area are reported in figure 6A.

Standing at the spectrum reported in figure 6A, the main absorption peak due to the ester carbonyl bond (C=O) stretching, at 1735cm^{-1}, is not identifiable after the treatment, as well as other peculiar signals attributed to the Paraloid (the resin signals are indicated with an arrow). LA6 mixture perfectly acts in removing the acrylic resin. In addition, no solvent retention on the surface of the artwork is observed 15 minutes after the treatment: the applied solvent completely evaporated.

DIOX-MET mixture. The KKT-corrected spectra acquired on the cleaned area are reported in figure 6B. The main absorption peak due to the ester carbonyl bond (C=O) stretching of the acrylic resin, at 1735cm^{-1}, is not identifiable after the treatment, as well as its

other peculiar signals (the resin signals are indicated with an arrow). DIOX-MET mixture worked well in removing the acrylic resin. In addition, no retention of the solvent on the surface of the artwork was observed 15 minutes after the treatment. Differences between LA6 and DIOX-MET treated spectrum can be ascribed to the different background on which the solvent system were tested, in fact LA6 was tried on some white areas, while DIOX-MET on some red areas.

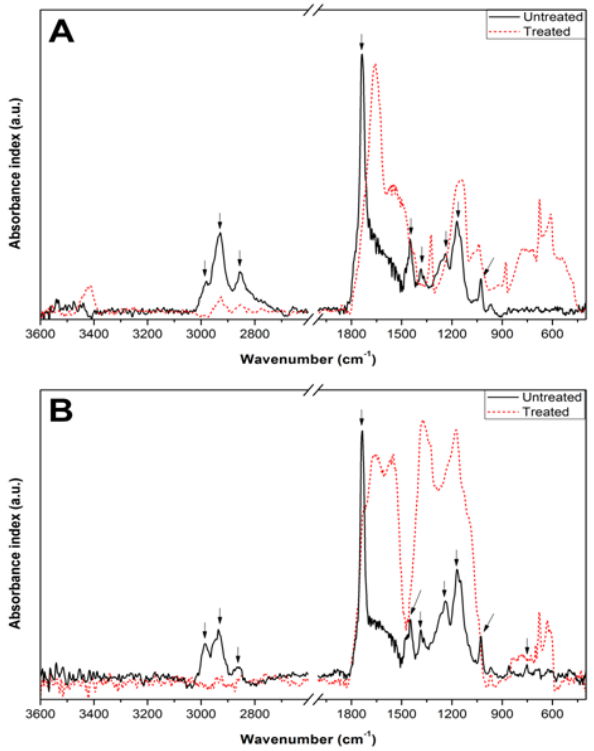

Fig 6. Comparison of the KKT-corrected spectra recorded before and after 15 minutes from cleaning with (A) LA6 and (B) DIOX-MET.

Conclusions

In this work, the cleaning performance of a mixture of eco-friendly solvents has been evaluated. The slab taken in account as case-study belongs to the wooden ceiling of "Hall of Barons" of "Steri", in Palermo. Total reflectance FT-IR measurements have been carried out in order to identify the substances on its surface and to evaluate the cleaning treatment using a totally non-invasive approach.

The pictorial layer of the slab was covered by ketone resin and in some area by Paraloid B72, due to a pre-consolidation made during the removing of the slab from the ceiling.

The restorer performed different cleaning tests in order to determine which traditional solvent mixture worked better for the removal, obtaining the best results with the LA6 mixture.

The performance of the DIOX-MET mixture was compared to the traditional solvent mixture, both in terms of cleaning efficiency and lingering residues of the cleaning material in an attempt to use solvents with lower environmental impact and increased health safety for the end user.

In both cases, analysis of the spectra registered after the cleaning indicated the removal of Paraloid B72 residues. An equal low retention of the used solvent mixture has been observed. Nevertheless, DIOX-MET can be considered an excellent alternative to the traditional LA6

solvent mixture and a low impact solvent mixture not only for the artwork, due to its low retention, but also for the safety of end user and of the environment.

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