Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

A non-invasive study of the effect of three commercial cleaning products on shellac-coated mahogany

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ARTICLE INFO	A B S T R A C T
Keywords: Wood ER-FTIR Colorimetry Varnish Norway	The Royal Palace of Norway has a large 19th century wooden furniture collection and most of it is coated with shellac-based varnishes. Since these objects are part of the royal collections, they are still in daily use at the different residences and, therefore, need to be frequently cleaned. In this work, the effect of three cleaning commercial products (Baolin, Centurio, Fulgentin) used at the royal collections on shellac-coated mahogany is investigated for the first time. A non-invasive methodology (portable ER-FTIR spectroscopy and colorimetry) was applied to assess whether the chemical composition and the color of fresh and artificially aged mahogany wood mock-ups coated with shellac were affected by the above-mentioned cleaning products. This study shows that one of them causes changes in the varnished wood, thus potentially affecting the long-term conservation of this furniture collection.

1. Introduction

The wooden furniture of the Royal Palace of Norway was manufactured throughout the 19th century according to the style of that age [1], and varnished by French polishing, a method by which shellac is applied in multiple layers and then polished to obtain a highly glossy surface [2].

Shellac is an organic resin secreted by the insect *Laccifer Lacca*, or similar insects, on trees of forests in southeastern Asia [2–4]. The secretion, scraped from the trees, washed and purified by sieving, is then typically bleached with hypochlorite and the obtained wax separated by saponification. Thereafter, shellac is shaped into dry sheets. For its application, the sheets are dissolved in alcohol, creating a varnish that dries by solvent evaporation [3,4].

The royal collections of Norway have a large amount of varnished furniture. Most of it is placed in the Royal Palace and other royal residences. These objects are still in everyday use and subjected to the related wear. Thus, the varnished furniture needs to be cleaned on a regular basis and – perhaps – in a more aggressive manner than what is usually recommended with museum objects [2,5].

In this work, the possible alteration of the shellac coating on mahogany mock-ups after cleaning with three commercial products was investigated. The effects of the use of the cleaning products on mock-ups with freshly applied shellac and artificially aged ones were evaluated. Keeping the E.C.C.O. and the AIC guidelines for practice in mind [6,7], a non-invasive methodology (handheld FTIR spectroscopy in external reflection (ER-FTIR) [8] and colorimetry) was employed. The results showed that this approach may become a valuable tool to assess cleaning routines on historical varnished furniture collections.

2. Experimental

African mahogany was used for the production of 27 (3 mock-ups/ cleaning product/experimental protocol) and 6 control mock-ups. Mock-ups were varnished with recto shellac. Randomized subsets of 9 mock-ups (3 mock-ups/cleaning product) were assigned to 3 experimental protocols: cleaning (Protocol 1), artificial aging and cleaning (Protocol 2), cleaning and artificial aging (Protocol 3). Extensive additional details are reported in the Supplementary Materials.

3. Results and discussion

The diagnostic IR bands detected in the ER-FTIR spectrum of unaged

https://doi.org/10.1016/j.matlet.2023.133963

Received 1 November 2022; Received in revised form 8 January 2023; Accepted 24 January 2023 Available online 27 January 2023

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Fig. 1. ER-FTIR spectra of aged and unaged mahogany mock-ups varnished with shellac.

shellac applied on the mahogany mock-ups (see Fig. 1) appear distorted with s-shaped signals. These bands were found at the inflection points around 2935 and 2850 cm⁻¹, assigned to CH_2 stretching modes; at 1735, 1712, 1642 cm⁻¹, indicating a complex carbonyl band; at 1467 cm⁻¹, assigned to the CH_2 bending mode; at 1255, 1173, 1112, 1043 cm⁻¹, assigned to C—O stretching modes [9–11].

The ER-FTIR spectra of the aged mock-ups (Fig. 1) presented broadening and blue-shift of the complex carbonyl band centered around 1730 cm^{-1} , as well as changes in the fingerprint region concerning the C—O bands ($1240-1040 \text{ cm}^{-1}$) [12]. Both these changes relate to the esterification that shellac undergoes with ageing. Derrick et al. corroborate this by stating that the greatest change in the spectra of aged natural resins concerns the shape and intensity of the carbonyl band [9].

Colorimetry measurements showed significant differences (increase of L^* and a^* values) in the SCE (specular-component excluded) color values of 2 out of 12 mock-ups (9 mock-ups and 3 control, Fig. 3, Protocol 2). The results in SCI (specular-component included) mode also showed a significant change, with an increase in L^* and b^* values and the corresponding ΔE^* ranged between 1.51 and 4.24. 2 of the mock-ups show ΔE^* values between 3.5 and 5, which is considered a clear difference in color [13].

All ER-FTIR spectra of the mock-ups cleaned with Centurio showed

changes in the fingerprint region (Fig. 4), suggesting physico-chemical changes and/or the presence of residues of the product. After cleaning (Protocols 2 and 3), a weak band at about 2963 cm⁻¹ and a narrow doublet appeared at around 1035 and 1013 cm⁻¹. Two additional bands become visible at around 918 and 803 cm⁻¹.

According to colorimetry results, 8 out of the 9 mock-ups aged and cleaned with Centurio showed significant changes in their color values (Fig. 3, Protocol 2). As for the ΔE^* , 7 mock-ups feature values around 5, indicating that the colors of the mockups after aging and cleaning with Centurio are different [13]. The trends observed by the colorimetry measurements are in line with the results obtained from the FTIR measurements.

No changes in the ER-FTIR spectra of the mock-ups cleaned with Baolin and Fulgentin can be observed (Fig. 2). On the basis of the results from the tested mock-ups, this is a good indicator that these cleaning products have not chemically affected the shellac in a way that it is detectable by ER-FTIR.

According to colorimetry measurements, 2 out of the 9 mock-ups cleaned with Baolin showed significant changes in their color values (Fig. 3, Protocol 1). The ΔE^* values of the mock-ups cleaned with Baolin span between 0.89 and 4.99. The latter is considered a significant color change. For the mock-ups cleaned with Fulgentin, 3 out of the 9 mock-ups showed significant color changes (Fig. 3, Protocol 3). Indeed, the

Fulgentin



Fig. 2. ER-FTIR spectra of the wooden mock-ups that underwent experimental Protocol 1 (cleaning), ATR-, and ER-FTIR spectra of the pure products.



Fig. 3. Colorimetric results in SCE mode for the three tested products with the three experimental protocols (cleaning, aging and cleaning, cleaning and aging). The upper part of the black box indicates the first quartile, the solid black line in the middle of the box is the median of the data. The whiskers indicate the range of the data.



Fig. 4. ER-FTIR spectra of the mock-ups treated with the three tested products that underwent experimental Protocols 2 and 3 (aging and cleaning, cleaning and aging). The main spectral changes related to the application of Centurio are marked with *.

 ΔE^* values span from 0.26 to 5.45. The latter is a value indicating that the mock-up has a different color after cleaning [13]. The results showed that 2 mock-ups treated with Baolin and 2 with Fulgentin had a significant color change in SCE mode (darker and bluer, respectively). For the mock-ups cleaned with Fulgentin, the significant changes occurred in the mock-ups with fresh shellac, indicating that this is more vulnerable to color changes than the ones submitted to the other experimental protocols.

4. Conclusions

The cleaning test with Baolin and Fulgentin indicate that there are no changes in the ER-FTIR spectra of the shellac coating. This is in line with the colorimetry results, where the shellac surface of these mock-ups did not have a significant color change. There were some mock-ups that had significant color change but these were not of such an extent to indicate a change caused by the cleaning. These results indicate that, in the limited timeline tested and with the technique employed for the study, these products do not seem to react with shellac. In the future, long-term study should be conducted to study possible changes caused in the shellac coatings using these two products.

The spectra of varnished mock-ups cleaned with Centurio showed instead changes mainly in the fingerprint region. These may be due to either a physico-chemical alteration of shellac, or to the presence of invisible residues of Centurio on the cleaned mock-ups. The findings from the ER-FTIR results were supported by the colorimetry ones.

One of the aims of the study was to investigate whether there were any differences in the effect of the cleaning products when applying on fresh shellac and aged one. When looking at the mock-ups cleaned with Centurio and Baolin, fresh and aged shellac react in the same way. For Fulgentin, only the color of fresh mock-ups changed after cleaning. Otherwise, no difference in the interaction with the cleaning products was observed for the mock-ups with freshly applied shellac and artificially aged ones.

This non-invasive approach paves the way for future investigations on coatings on historical furniture and the detection of physico-chemical changes after cleaning procedures without interfering with the original materials and without the need of sampling. Therefore, this methodology could be used as a viable tool to evaluate the safety of a cleaning agent used on varnished wooden furniture.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

The following people are kindly acknowledged: Silje Nome Schiander (The Royal Collections of Norway), for insightful discussions; Anne Cathrine Hagen and Hanne Bjørk (Møbelverkstedet), for their help with coating the mock-ups and for information regarding the cleaning of furniture; Ulrich Hundhausen (Norsk Treteknisk institutt), for the use of the ageing chamber; Susan Braovac (KHM-UiO), for the use of the colorimeter. Francesco Caruso acknowledges his Maria Zambrano fellowship from UPV/EHU, funded by the Spanish Ministry of Universities and the European Union NextGenerationEU/PRTR. Open access funding provided by UPV/EHU. This work has been supported by grant TED2021-129299A-I00, funded by MCIN/AEI/10.13039/ 501100011033 and by the European Union NextGenerationEU/PRTR.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2023.133963.

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