Mechanical Adherence Analysis of Polyurethane and Polyester Commercial coatings over Alder Wood

Chanes R., M.E.[1], Chávez-García D., PhD.[1], Guzmán M., PhD.[1] and Reyes R. Eng.[1]
[1]Centro de Enseñanza Técnica y Superior (CETYS), México, dalia.chavez@cetys.mx, Mario.guzman@cetys.mx

This study is the validation for a new method to introduce a new color coating in the fabrication of electric guitars, before this, the time for the validation was 20 to 25 days. This new validation reduced the time to 15 days and improved the time and quality process. The new method consisted in the mechanical adherence analysis of polyurethane and polyester commercial coatings. First, a database was generated to identify the type of material coating using FTIR technique with ATR. Also, the thermal expansion coefficients were measured to relate them to the adhesion. As a result, two methods of adhesion measurement were correlated, the quantitative pull-off method and the qualitative cross-cut method. Finally, a validation protocol was generated with the new tools.

Keywords—Polyurethane, polyester, coating, painting, adhesion

I. Introduction

Synthetic materials (thin layers of polymers) are applied to cover and seal the wood to prevent moisture absorption and avoid changes. Wood coatings are used to protect and prevent the increase or decrease of its volume when the material is exposed to humidity and temperature change, but also to give a visually attractive finish [1-4]. Painted wooden surfaces (such as guitars) are very complex due to the multi-layer structures composed of humidity-sensitive materials. The restraint of the dimensional changes induces stresses in the wood which can cause several damages such as deformation, cracking of wood or cracking and flaking of the decorative [2].

Also, the drying process is very critical; drying is inevitable and requires a large quantity of water to be removed from the wood [5]. There are several causes that may affect the process parameters, such as relative humidity, drying medium, temperature and thickness, but also the physical, parameters are crucial as e.g. mechanical and chemical wood properties. There are important aims that need the right balance such as time (for painting and drying), cost and quality of the final product, so it is important to have a balance between them because they are not independent.

Several authors explored the multi-complex problem with the coating of wood, Goldschmidt and Streitberger [6] mentioned that coating technology is a multidisciplinary task and that paints are not a finished product, which requires skills and knowledge to reach a quality finished product. Coatings are successful when they adhere firmly to the applied surface and resist the established design factors (chemical resistance, oxidation, deterioration, among others). Also they classified the factors that can influence into having the best appearance of the coating, these factors are: process sequence (time, air conditions, number of coats), application equipment (pneumatic, airless, high rotation, etc.), application parameters (voltage, flow rate, distance of the target, climate conditions, volume of atomizing and shaping air), substrate (surface roughness, structure, surface tension, material, etc.), curing (temperature, time, oven cure, heating) and paint material (temperature, rheology, viscosity, solid content, evaporation kinetics); all the factor can affect directly in the quality and cost of the final product. Several authors explain that there are two main failures can occur if it is not correctly applied: delamination and fracture. Delamination is when the adhesion of the upper layer against a lower layer or the substrate is not enough to hold them together, and it separates; fracture is when the cohesion force between the molecules of the same coating is not strong enough, and it breaks [6-8]. In this study, we analyzed some of the factors mentioned, such as: type of coatings via FTIR analysis, thermomechanical analysis, physical tests for the adherence of the coatings for the validation of the current protocol used.

In a typical process to coat guitar bodies, uses a spray transfer technique, which consists of nebulizing the paint with compressed air to achieve a thin and uniform layer. When they want to introduce to the production line a new product, with a new type or color of paint, it is crucial to realize the validation process of the new paint to carry out the production and have no failures in the coating process (cracks or adhesion of paint).

This project aims to generate a protocol to ensure that the paint has all the elements to function correctly and perform well during the production process and another for the validation of coatings on guitars and basses to eliminate temperature cycles by analyzing the relationship between the expansion coefficient of coatings, adhesion tests and chemical identification of the compound.

The method consisted in identifying first the coating technologies that are used in the company and which of these coatings are the most produced. It was shown that by updating the validation protocol with the addition of these new tools, the color process took less time and show better results, to achieve this it was necessary to determine the IR (infrared) spectrum of each material and analyze it with the FTIR (Fourier Transform Infrared Spectroscopy) spectroscopy technique using ATR coupling (Attenuated Total Reflectance) , to identify which molecules it is composed of and determine if it is a polyurethane

Digital Object Identifier (DOI):
http://dx.doi.org/10.18687/LACCEI2021.1.1.468
ISBN: 978-958-52071-8-9 ISSN: 2414-6390

or a polyester [7,8], also by finding the correlation between the physical tests of cross-cut adherence versus those of pull-off and create a database to be able to use the pull-off as a quantitative method, and finally determine the coefficients of thermal expansion with the thermomechanical analysis (TMA) of the different materials that make up the coating to determine if there is a difference between the layers and to be able to identify if the adhesion decreases if they are different materials.

In this investigation is proposed a methodology to validate the paintings and coatings in the fabrication process of guitars. In this company, all the guitars are made from wood; it is a natural polymer and has peculiar characteristics because it can change depending on the given conditions of humidity and temperature [1–4].

The new method developed consisted in ensuring good adherence and quality, and the time to validate the painting was reduced from 25 to 15 days by identification of the coating first to make the correct recipe, use of the quantitative adherence method to study the samples (or dummies) and using the TMA for the analysis of the coefficients of thermal expansion to avoid wrong combinations of coatings.

MATERIALS AND METHODS

Tests were conducted on Alder wood (Alnus) the raw material for the guitars; we used dummy specimens for all the procedures (6-inch by 8-inch rectangles of Alder wood). The coatings and substrates used were: Red Urethane Party, Party Net Polyester, Lime Green Urethane, Lime Green Polyester, Snow White Urethane, Snow White Polyester. The topcoats used were: Polyester and Urethane. The undercoat was polyester.

A. Coatings and actual methods

We searched for the most used coatings and paintings; they were selected to validate in the protocol. The inventory of the factory paint warehouse was used to identify which colors of the currently used were available and in which types of technology, polyurethane or polyester based. Subsequently, the application history was searched to select three colors with the highest production that will be available in the two different technologies. The current protocol was evaluated, and an improvement was sought to reduce testing times. The validation procedure currently used was analyzed, and the tasks to be carried out were adjusted to be executed in parallel. Dummies were made using all possible combinations from the three selected colors on a polyester and polyurethane basis.

B. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectrum measurement equipment used was Frontier Perkin-Elmer Infrared FTIR Spectrometer, using the ATR method. The objective of this method was to find and characterize the most important absorbance peaks that occur in a polyester and a polyurethane, the peak identification tables were searched in the literature representative of these materials, later the spectra generated were subsequently analyzed for each material studied and with this, a template was generated with which it will be possible to identify what material it is. One of the disadvantages of the ATR is that it can only analyze the surface of the sample; there are also some materials that cannot be analyzed by this technique if their internal friction is very close to that of diamond. This technique is very versatile for analyzing polymers since it is able to read the spectrum of uncatalyzed coatings, in liquid state and catalyst in solid state [9]

C. Cross-cut and Pull-off tests

In the previous procedure, for the validation of coatings, a method called cross-cut is used as an adhesion test (ISO 2409 y ASTM D3359), a cut in the shape of a cross is generated over the substrate being analyzed and the level of laminate generated from a reference table is evaluated, which is a qualitative method of verification of adhesion that goes from 1 as the worst-case to 5 as best, the tool used was TQC Sheen CC3000 Cross Cut. The disadvantage of this method is that despite being a quick test, it does not show continuous values, which hide much information on the behavior of the coating, which is why the new quantitative Pull-off method (ASTM D4541) was employed, which is a very useful tool to perform validations since it returns continuous strength values in pounds per square inch (PSI), which can be used to perform more specific studies like the ones from this research, the tester used was Defelsko posi-test pull-off method AT-A automatic adhesion Tester S / N AT11398 [10].

To make the transition from the qualitative to the quantitative method, a data correlation was first generated, where 24 test elements (dummies) were carried out using the different combinations apart from the selected materials with the colors Fiesta Red, Lime Green and Snow White, based on polyester and polyurethane, and two types of Topcoat made from the same materials were used. Using these test dummies, adherence tests were performed with both methods and the results were recorded. Subsequently, a correlation analysis was performed using Minitab software to analyze the results.

D. Thermomechanical analysis

To study the relationship between the expansion coefficient and adherence, a Perkin Elmer thermomechanical analyzer was used (model TMA 4000) with the expansion probe. To perform this measurement, a sample of each material from the test dummies previously manufactured was extracted using a precision knife, square sheets of approximately 1 cm by 1 cm were cut, with an average thickness of 250 μm. The test tube was used for expansion measurement, with a null force, which allows identifying the dimensional changes of the sample concerning the temperature change.

The expansion coefficient of all the materials investigated in this work was measured using a temperature gradient of 5°C/min. Temperature range was from -10°C to 90°C, reproducing the temperatures that are being used in the temperature cycle in the previous method. This cycle has performed a total of 10 times. Subsequently, the results were analyzed to obtain the expansion coefficient; the data was taken from the region where the slope of the graph produced by the equipment is linear.

RESULTS AND DISCUSSION

A. FTIR Analysis

In this article section, it is shown the analysis of the Perkin Elmer FTIR with an ATR complement, the measures show the spectrum of the coatings based on urethanes and esters to identify the peaks that characterize these materials. After the measure of the spectroscopy, the results are graphic, and the peaks are analyzed based on reference tables.

Figure 1 shows the peaks of the spectroscopy of the FTIR for urethanes. The region of N-H and O-H bonding groups stretching mode are shown around 3400 and 3500 cm^{-1} respectively. This groups are associated with the addition of the isocyanate (R-N=C=O) and the polyol (R-OH), which are commonly used to obtain de polyurethane R'-O-C=O-NH-R'. Defeyt et al. [11] reported an analysis of ATR for FTIR spectroscopy of different polymer samples, in their work is proposed that the peaks centered around 2273 $cm^{-1}$and 3300 cm^{-1} corresponds to the isocyanurate and N-H groups stretching modes. Additional peaks were identified based on the reported by Kaminsky et al. [12, 13], as it follows: peaks at 2954 cm^{-1} and 2857 cm^{-1} corresponds to the asymmetric and symmetric stretch vibration mode for the CH_2 group; peak around 1735 cm^{-1} is related with the hydrogen free carbonyl group. On the other hand, the sample Fiesta red presented a shoulder around ~3400 cm^{-1}, which is usually associated to aromatic -CH groups. Finally, the samples Fiesta red and Lime green also presented a peak centered at ~1525 cm^{-1}, this peak was not observed in the snow-white sample and corresponds to the deformation of the N-H bond and the asymmetrical stretching of the C-N bonding, some other peaks were also identified for wavenumbers under 1000 cm^{-1}, these were connected to the C-C (967 cm^{-1}) and C-N skeleton modes [12]. The same analysis was realized for every color of materials based on Polyurethanes. I was found that the Polyurethanes share three important regions, it is important to mention that the region that goes from 1200 cm^{-1} to the 400 cm^{-1} will show peaks with variations even in the same type of material, for this reason, this zone is known as the fingerprint, and it is difficult to distinguish any peak. This region is characteristic of every coating.

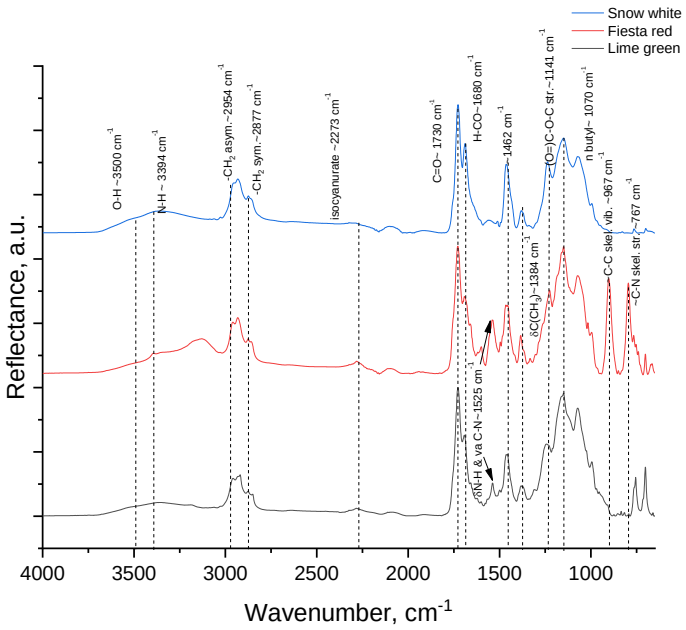

Figure 1. FTIR- ATR spectra of polyurethane coatings

In Figure 2 it is shown the spectra generated by the polyester-based samples, the most significant peaks are in the regions 1718 (C=O stretching), 1231 and 1126 cm^{-1} (C-O asymmetric and symmetric stretching) [14]. Additionally, in the region between 3000 and 2800 cm^{-1} there are peaks associated to the C-H bonds in the -CH_2 and -CH_3 functional groups. First, C-H bond in the CH_3, stretching symmetrical and asymmetrical modes are located at 2890 and 2962 cm^{-1} respectively; and secondly there is, some shoulders around 2934 and 2876 cm^{-1} related to the asymmetrical and symmetrical stretching bonds of the C-H in the -CH_2 groups. It can be seen the vibration of the charcoal and the vibration of the oxygen from the ester. The stretches from the joints C-O, in the region 1077 cm^{-1} and 970 cm^{-1} confirm the presence of this joint in the ester molecule. The alpha carbon has a presence in the 1047 cm^{-1} region.

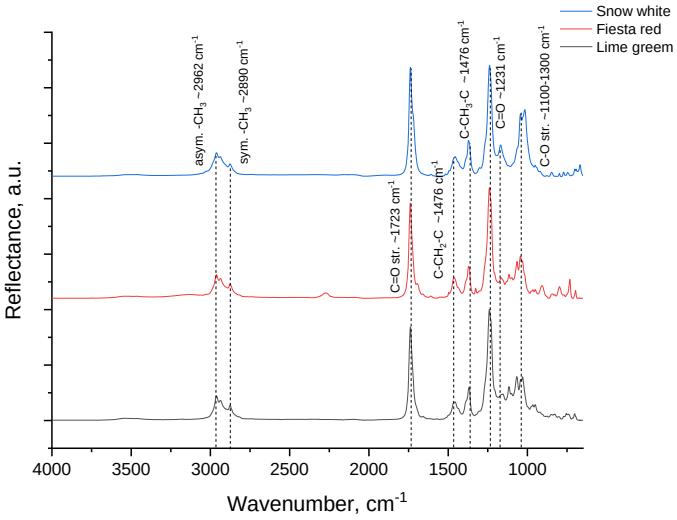

Figure 2. FTIR-ATR spectra of polyesters coatings

B. Cross-cut and Pull-off tests

The relationship between the Cross-Cut and Pull-off was obtained, with this evaluation of the levels of adherence was evaluated for correlating with the necessary force to retire the Dolly from the pull-off test. The program Minitab was used for the generation of the correlation and verification of the variation model study, in figure 3, it is shown this study with a result of a variation of 92.8%.

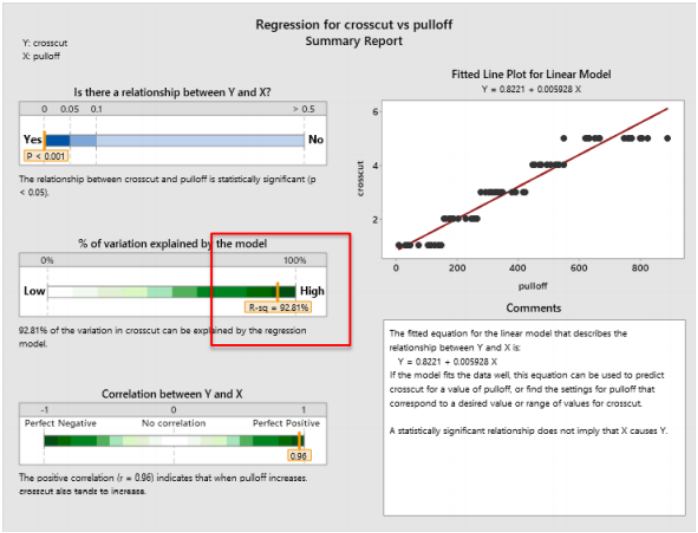

Figure 3. Results obtained from the correlation between the cross-cut and pull-off tests

In this study, the results from the qualitative test from the cross-cut, this with the minimum level of adherence 1 and the maximum value is 5. In table 1 the existing correlation is shown.

TABLE 1. CORRELATION BETWEEN CROSS-CUT AND PULL-OFF METHODS

Cross-cut/Pull-off ratio	
Cross-cut (level)	Pull-off (psi)
5	550-900
4	549-445
3	444-266
2	265-151
1	150-0

In figure 4 are shown the results of the cross-cut and pull-off after the realization. In both methods it is necessary to reach the substrate to evaluate the adherence.

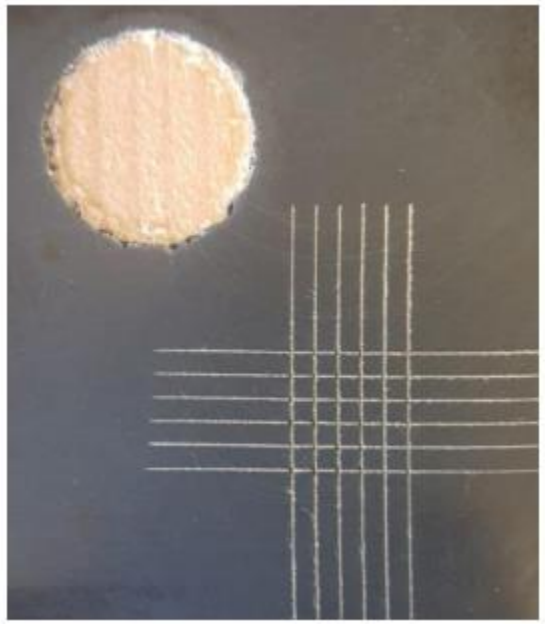

Figure 4. Test pull-off up and cross-cut down

In table 2 are shown the results of the adherence tests, this data was obtained from different realized dummies. When merging of different materials, it is shown that the adherence is reduced, in comparison to the merge of the same materials. The merge of Polyurethane in color and the topcoat of polyester have the lowest result, for example: polyurethane-fiesta red-polyester had fewer adherences with 450 psi in comparison with the same color with polyurethane-polyurethane with 861 psi.

TABLE 2. RESULTS ADHESION TESTS IN DUMMIES

Combination			Adherence	
Material	**Color**	**TOPCOAT**	**Pull-off (psi)**	**Cross-cut**
Polyurethane	Lime Green	Polyurethane	894	5
Polyurethane	Lime Green	Polyester	533	5
Polyurethane	Fiesta Red	Polyurethane	861	5
Polyurethane	Fiesta Red	Polyester	450	4
Polyurethane	Snow White	Polyurethane	900	5
Polyurethane	Snow White	Polyester	590	5
Polyester	Lime Green	Polyurethane	702	5
Polyester	Lime Green	Polyester	850	5
Polyester	Fiesta Red	Polyurethane	657	5
Polyester	Fiesta Red	Polyester	852	5
Polyester	Snow White	Polyurethane	686	5
Polyester	Snow White	Polyester	849	5

C. TMA analysis

Using the mechanical thermal analyser was found the polyester and polyurethane expansion coefficients, in table 3, it is shown the results. The polyurethane shows expansion coefficients of 57µ K^{-1} to 73.3µ K^{-1}, in comparison to the polyester that is between 102µ K^{-1} and 118.3µ K^{-1}, this indicates that both materials have different coefficients. After the realization of the thermal cycle, the difference between the coefficients is not significant, so it is not necessary to apply this test to the verification. Analysing tables 2 and 3, the results confirm the differences between coefficients lower the adherence force.

TABLE 3. RESULTS OF THE THERMOMECHANICAL ANALYSIS

Material type	**Name**	**Expansion coefficient ($x10^{-6}$ k^{-1})**	**After temperature cycles (-20 °C a -80°C)**
Polyurethane	Lime Green	68.20	68.8
Polyurethane	Snow white	64.5	64.8
Polyurethane	Fiesta Red	57.8	58.2
Polyurethane	Topcoat	73.3	73.4
Polyester	Lime Green	112.5	112.4
Polyester	Snow White	115.3	114.6
Polyester	Fiesta Red	108.7	109.4
Polyester	Topcoat	118.2	119.1
Polyester	Undercoat	102.3	103.4

Analyzing the results of the adherence tests and those of the TMA is possible to observe that the lowest adherence result was found with the combination of polyester TOPCOAT and party Red urethane and it is also where the biggest difference of coefficient of expansion, 57.8 x10-6 k^{-1} against 118.2 x10-6 k^{-1} indicating that a coefficient difference decreases adherence.

D. Comparison and Discussion of both methods

Before we conducted this research, there was no registered protocol. For the validation of colors, some tests were performed on the paint, which consisted mainly of creating dummies for adherence verification, they performed hot and cold tests and were released. In the table 4, you can find the validation protocol that was generated from this research.

TABLE 4. RELATIONSHIP OF THE PROPOSED METHOD AGAINST THE CURRENT ONE TO OBSERVE THE ADVANTAGES

Old method
The Advanced Manufacture department, make a performance test that measures the thickness for every register dummy in this measure. Therefore, the samples are sent to initiate a temperature cycle where they are put in a furnace with an 85°C temperature for an hour, later on, the samples stay outside at room temperature for another hour, finally, the samples are put in a freezer with a temperature of -20°C for the last hour. After the temperature cycle, it is applied to a cross-cut test and the color is freed.
Proposed method
The new method follows the procedures carried out in this research to identify the characteristics of materials before they enter production. Ensuring good adherence, maintaining quality. 1. Coating identifying, (polyurethane or polyester) to realize the recipe. 2. Use the quantitative adherence method to study dummies. 3. To prevent a bad combination and find the expansion coefficient the use of the TMA is recommended. The time has been reduced from 25-20 to 15 days.

From these improvements, it was possible to reduce the validation time of the coatings from 10 to 5 days. This was achieved by modifying the previous protocol and performing tasks at the same time.

CONCLUSIONS

The development of a new method to validate coatings and panting over alder wood for the fabrication of electric guitars was performed. Before of this method, the validation consisted in the measurement the hardness of the sample, no identification of the type of material was done, so the FTIR-ATR technique was introduced to validate better combination of coatings, resulting in polyurethane-colour-polyurethane and polyester-colour-polyester. The older method only validated a temperature cycle, from 85°C to -20°C, with the finalization of the cross-cut test. We established that the addition of a quantitative adherence method to study the samples/dummies was necessary and also, we added the TMA study to analyse the expansion coefficient to validate the materials. The time to validate the coating and painting was reduced from 25 to 15 days.

ACKNOWLEDGMENTS

The authors wish to acknowledge the support of CETYS University, the company in where the tests were performed and the Consejo Nacional de Ciencia y Tecnologia (CONACYT).

REFERENCES

[1] P.D. Vici, P. Mazzanti, L. Uzielli, Mechanical response of wooden boards subjected to humidity step variations: Climatic chamber measurements and fitted mathematical models, J. Cult. Herit. 7 (2006) 37–48. doi:10.1016/j.culher.2005.10.005.

[2] M. Łukomski, Painted wood. What makes the paint crack?, J. Cult. Herit. 13 (2012) S90–S93. doi:10.1016/j.culher.2012.01.007.

[3] E. Mecklenburg, Tumosa, Structural response of painted wood surfaces to changes in ambient relative humidity, (1998) 464–483.

[4] W. and Raymond, Make your own Electric Guitar & Bass, Sterling Publishing Co., New York, 2001.

[5] P. Perré, Fundamentals of wood drying, A.R.BO.LOR ENGREF, Nancy, France, 2007.

[6] H.-J. Streitberger, A. Goldschmidt, BASF Handbook Basics of Coating Technology: 3rd Revised Edition, Vincentz Network, Hannover, n.d. doi:https://doi.org/10.1515/9783748600251.

[7] M. Anghelone, V. Stoytschew, D. Jembrih-Simbürger, M. Schreiner, Spectroscopic methods for the identification and photostability study of red synthetic organic pigments in alkyd and acrylic paints, Microchem. J. 139 (2018) 155–163. doi:10.1016/j.microc.2018.02.029.

[8] A.M.B.I.N.M. MUSTAFE, FTIR studies on 2K polyurethane paint, (2005).

[9] T.R. Crompton, Book details thermal methods of polymer analysis, 2013. doi:10.1016/s1350-4789(13)70095-3.

[10] A. Goldschmidt, H.-J. Streitberger, Basics of Coating Technology, BASF Handb. (2007) 1–791.

[11] Defeyt, C., Langenbacher, J., & Rivenc, R. (2017). Polyurethane coatings used in twentieth century outdoor painted sculptures. Part I: Comparative study of various systems by means of ATR-FTIR spectroscopy. *Heritage Science*, *5*(1), 11.https://doi.org/10.1186/s40494-017-0124-7

[12] Fockaert, L. I., Pletincx, S., Ganzinga-Jurg, D., Boelen, B., Hauffman, T., Terryn, H., & Mol, J. M. C. (2020). Chemisorption of polyester coatings on zirconium-based conversion coated multi-metal substrates and their stability in aqueous environment. *Applied Surface Science*, *508*, 144771. https://doi.org/10.1016/j.apsusc.2019.144771

[13] Kaminski, A. M., & Urban, M. W. (1997). Interfacial studies of crosslinked polyurethanes; Part I. Quantitative and structural aspects of crosslinking near film-air and film-substrate interfaces in solvent-borne polyurethanes. *Journal of Coatings Technology*, *69*(872), 55–66. https://doi.org/10.1007/BF02696244

[14] Kaminski, A. M., & Urban, M. W. (1997). Interfacial studies of crosslinked urethanes: Part II. The effect of humidity on waterborne polyurethanes; a spectroscopic study. Journal of Coatings Technology, 69(873), 113–121. https://doi.org/10.1007/BF02697762