

Atmospheric pressure plasma as a tool for decontamination and functionalization of wooden surfaces

Constanze Roth, Sven Gerullis, Oliver Beier, Dr. Andreas Pfuch, Dr. Annett Hartmann, Dr. Bernd Grünler

INNOVENT e.V. Technology development, Pruessingstr. 27b, 07745 Jena, Germany

cr1@innovent-jena.de

Abstract. Possible applications of plasma technology on wooden surfaces have been investigated by new research projects. There are different initial situation: The residuals of several timber preservatives, based on organo-chlorine compounds, are a high challenge for human protection, storage and wood restoration. Among the most common organo-chlorine substances that have been used as pesticides in the past are Dichlorodiphenyltrichloroethane (DDT), Lindane and Pentachlorophenol (PCP). Lindane and PCP are toxic and/or carcinogenic and all are considered to constitute several environmental hazards. The pesticides were widely used for the treatment of trusses in private homes, churches, castles as well as of furniture or wooden artefacts. This creates the necessity to develop efficient and economically viable methods for removing the harmful biocides from the contaminated timbers without damaging the original materials. For the gentle removal of biocide residuals (so-called blooming of mainly DDT crystalline forms) atmospheric pressure plasma was used as a cleaning tool for the first time. For selected working conditions the removal of up to 75% DDT contamination could be achieved on plain timber surfaces.

Using atmospheric pressure plasma jets (APPJ) it is also possible to create thin films (~ 50 – 200 nm) with different functionalities such as hydrophilicity, hydrophobicity or antimicrobial properties. To create antimicrobial effects active agents were embedded into silicon dioxide films matrices. Antimicrobial tests showed high effects of these films towards bacteria strains such as *Escherichia coli* and *Staphylococcus aureus*. An effect towards mold fungi was low using films containing only one active agent. However, significant improvements in activity were achieved by the combination of active agents. This paper will address the production of samples, analytic methods and open questions about decontamination and functionalization of wooden surfaces by using atmospheric pressure plasma.

1 Introduction

Motivation



In order to protect wooden surfaces against microbial attack preservatives based on organochlorine have been used in the past. According to a current study a high number of contaminated objects can be found in museums and collections in Germany [1]. So, there is a need to clean precious goods on the one side and to find alternative methods to protect the material on the other side.

Wood and wood-based materials as natural products are degradable by microorganism such as bacteria, fungi and/or alga. The biological degradation and the associated infestation by microorganism can be adverse, because performance characteristics such as aesthetic appearance or mechanical properties can decrease. Further critical disadvantages caused by microorganism can be health hazards such as bacterial infections [2]. Common routes to prevent microbial colonization are the insertion of active agents by impregnation procedures or the application of active agents as additive in paints or varnishes. Disadvantages of these kinds of wood treatment can be the location of the biocides over the whole cross section. Furthermore, large amounts of biocides are often need to achieve antimicrobial properties. Another point to consider is that biocide product regulations (Regulation EU No 528 2012) demand the reduction of embedded amounts of biocides. In accordance with it, a negative impact on the customer's perception can caused by embedding biocides.

This paper is based upon two research projects to decontaminate wooden surfaces and create antimicrobial films on wood by using atmospheric pressure for the first time.

Atmospheric pressure plasma

Atmospheric pressure plasma systems, especially those creating cold plasmas, are very interesting for a wide range of applications. Depending on process parameters, non-thermal plasma sources such as dielectric barrier discharges and atmospheric pressure plasma jets (APPJ) generate plasmas with temperatures down to room temperature.

Operating at atmospheric pressure, such plasmas are composed of charged species (positive ions and electrons), high-reactive species such as O^{2+} , O_3 , and NO_x as well as photons from ultraviolet to infrared [3, 4]. High-reactive species with energy up to 20 eV can cause polymer chain scission and promote the formation of free radicals and ions. This can further result in a fragmentation, isomerization, cross-linking and the introduction of functional groups to the surface of numerous kinds of materials [5, 6].

The wood components cellulose, lignin and extractives, contain groups such as C-H, C-C, C=C, C-O and C=O. Considering the structure of biocides such as dichlorodiphenyltrichloroethane (DDT), possible groups are C-H, C-C, C=C and C-Cl. These groups have bond energies less than 20 eV and with respect to this, plasmas are intense enough to dissociate almost all chemical bonds occurring in wood and DDT and to create free radical species. These free radicals can further react with oxygen-based polar species and form hydroxyl, carbonyl and carboxyl groups. Hence, these reactive plasma environments can be apply to improve surface characteristics such as wettability and surface energy [7, 8], to clean and decontaminate material surfaces [9] or even to create functional films [10, 11]. Plasma modification effects depend on the substrate, gas flow and nature of the working gas, exposure time, electrical power and others and needs to be adjust to the desired application. These technologies could also be interesting for wood processing due to their in-line capability and therefore the possible implementation in industrial applications and scalability.

Wood preservatives

One of the most common timber preservative in the past is the liquid preservative Hylotox 59[®]. It contains chlororganic compounds: 3,5% DDT and 0,5% Lindane in a solvent mixture. Until the prohibition of fabrication in the end of the 1980s this very efficient but toxic preservative was used very often in the former German Democratic Republic and in the Federal Republic of Germany [1].

Wood preservatives usually have a long-lasting effect. Objects treated with Hylotox 59[®] are also a health risk. It is of great importance to protect employees and visitors of archives and museums by reducing the toxic components from the contaminated materials. The chlororganic residues appear as sparkling crystals on the wooden surfaces and strain the atmosphere. Hence, the removal of the unwanted crystals is desired for two reasons: first to protect the health of employees and visitors and second. to reverse the visual changes of the artefacts.

2 Experimental Methods

2.1. Materials (samples and sample preparation)

The tests for the decontamination researches were carried out by using old contaminated original samples and samples produced in laboratory scale.

The original samples were provided by the Thuringian Schlossmuseum Sondershausen. The most important piece of the museums collection is the so called “Golden Carriage” from the early 18th century. It is an artful emblazed and gilded carriage, made of beech wood, and one of the last five existing parade carriage in Europe [12]. The Golden Carriage served a several princes of Schwarzburg-Sondershausen as a representative state car.

Based on restorer’s documentations, the treatment of constructions parts of the Golden Carriage with *Hylotox-59*[®] against vermins, was firstly reported in 1969. [12]. Due to the uniqueness of this collection piece, the Schlossmuseum provided other contaminated samples of the depot like a probably fifty years old pine wood strip which served as backing protection of an easel painting (Fig. 1).



Fig. 1: The old contaminated pine wood strip, dimensions: 18 x 7 cm². Foto: Birgit Schmidt

It has to be mentioned that for these samples no reproducible depletion quantities could be determined since the original chlorine loading by the wood preservative was not documented or directly known. GC/MS (gas chromatographic-mass spectrometry) measurements revealed here from sample to sample significant differences in DDT concentrations allowing no clear statements for the different treatment conditions.

Since the construction corpus of the Golden Carriage is made of beech wood and for the statistical evaluation of the examinations, new samples were prepared from beech veneers. The specimens were about 20 x 15 mm² in size, about 0.5 mm thick and get a defined chlorine loading. After extensive analysis and comparing measurements INNOVENT prepared a liquid of DDT, mineral oil and solvent. The composition of this mixture was very similar to the aged Hylotox 59[®]. To receive a similar depletion quantity with Hylotox 59[®] treated old samples, every new beech veneer sample was loaded with a defined amount of DDT of 30 µg. More than 450 samples in total have been prepared to compare the results and to determine exactly depletion rates.

For the evaluation of the new test specimens six pieces per parameter set were plasma treated and analyzed in order to obtain a statistically reliable mean value.

2.2 atmospheric pressure plasma system

The temperature of the used cold atmospheric pressure plasma is between 30 to 250 °C. The plasma intensity can be adjusted across the entire spectrum and investigations of plasmas itself were already made in restoration projects [13]. INNOVENT compared two different sources namely the TIGRES Plasma MEF (TIGRES GmbH, Marschacht, Germany, see Fig. 2a) and kINPen 09 (neoplas tools GmbH, Greifswald, Germany, Fig. 2b). The last mentioned source is very easy to handle, has a gentle performance and is already in use for dermatological treatments [14] while the TIGRES source offers more variations in parameters due to its technical design.

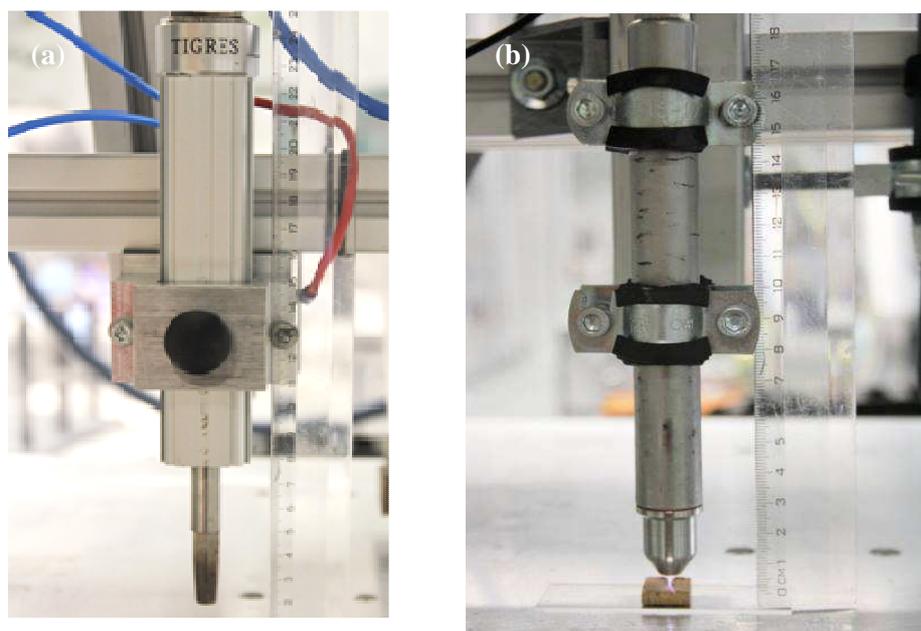


Fig. 2: The single jet plasma system by TIGRES Plasma MEF (a) and kINPen 09 by neoplasm Tools GmbH, Photo: INNOVENT e.V.

The parameters gas type, number of treatments (run), the distance between the wooden surface and the plasma as well as the distance between the treatment lines (pattern distance) were varied. The process gases during the experiments for the TIGRES plasma MEF were nitrogen, air or a nitrogen-hydrogen-mixture (5% hydrogen), for kINPen 09 argon, air and the nitrogen-hydrogen-mixture. Other parameters were kept constant; the velocity of the substrate relatively to the stationary plasma jet was set to 50 mm/s for both sources.

The results for TIGRES MEF single jet with different types of gas, a pattern distance of 1 mm or 3 mm and the number of treatment runs from 1 to 10 times are shown in Tab. 1. For every parameter six samples have been plasma treated and analyzed by GC/MS measurements. The depletion rate of DDT peaks were compared to untreated reference samples measured on the same day to minimize environmental effects.

2.3 system modifications for film deposition

In order to create active agents containing thin films the plasma system was modified in two ways. The first way contains the extension of the process gas module to introduce gaseous hexamethyldisiloxane (HMDSO). HMDSO was provided using the dosage system Pyrosil[®] STS 10.0 (SURA Instruments GmbH, Jena, Germany). The second way is based on the use of a dosing system, built to spray liquids or liquid dispersed particulate materials through a modified plasma nozzle into

the active plasma discharge. To form active agent-containing composite films besides the HMDSO secondary precursors such as silver nitrate, zinc nitrate or copper nitrate solutions were sprayed into the plasma zone, thereby generating the corresponding silver, zinc or copper (-oxide) nanoparticles *in situ*, which are embedded uniformly over the whole growing SiO_x film. The active agent-containing solutions were sprayed directly into the plasma as a nebulized aerosol using an atomizing nozzle. Moreover, by using an x-y positioning system, which realizes a computer-controlled meandering movement of the substrate holder relative to the plasma jet nozzle, it is possible to create areal coatings. A more precise description of the used plasma system can be found elsewhere [8].

2.4 Analytical methods

An evaluation of the chlorine residues was performed with headspace GC/MS for DDT peak areas. The samples were heated in headspace vials and the evaporated phase was analysed before and after the plasma treatment.

Additionally, a documentation and characterization of the sample surface is performed before and after plasma treatment using optical microscopy.

Temperature measurements during the plasma treatment have been investigated by using a type K thermocouple. The data depends on the chosen type of gas, the number and speed of plasma treatments and the chosen power of the plasma source.

To determine antimicrobial effects of thin film modified wood, materials were tested applying for example the so-called agar-diffusion test (Fig. 4). In this test method the sample were embedded into a bacteria (*Staphylococcus aureus* DSM 799 and *Escherichia coli* DSM 1576)-containing nutrient agar. Following an incubation step (storage at 37 °C, 24h), agar plates were visual evaluated according to the areal growth around the wood material. Furthermore, modified materials were tested to evaluate the resistance towards fungi (mold) by applying an assay in accordance to the standard DIN EN 60068-2-10 (2005). Samples (50 x 50 mm²) were prepared with suspensions containing spores of *Aspergillus niger* DSM 1957, *Paecilomyces variotii* DSM 1961, *Penicillium funiculosum* DSM 1944 and *Trichoderma viride* DSM 1963. Samples were then stored at 95% rel. humidity and 26 °C over a time of four weeks. A visual evaluation according to the areal mold growth was conducted weekly.



Fig. 3: Wooden surface with the crystallised residues of DDT. Photo: Wikimedia Commons.

3 Results and Discussion

3.1 Decontamination

In the first series of tests, appropriate parameters for cleaning of wood surfaces were investigated. The prerequisites were: minimal loading of the surface by the plasma treatment and a significant (damage-free) cleaning effect. In general, different DDT depletion rates could be achieved by variation plasma treatment parameters. All tested types of gas did reduce DDT peak amount. Tab. 1 shows the results for TIGRES MEF single jet:

Process gas	Pattern distance	Runs	Mean value decontamination rate / total volume DDT	Standard variation of decontamination rate / total volume DDT
N ₂	3	3	50%	14%
N ₂	3	5	35%	14%
N ₂	3	7	37%	10%
N ₂	3	10	65%	8%
N ₂	1	5	60%	6%
N ₂	1	7	65%	8%
N ₂	1	10	70%	9%
N ₂ H ₂	3	1	29%	10%
N ₂ H ₂	3	2	52%	12%
N ₂ H ₂	3	3	51%	6%
Air	3	3	52%	10%
Air	1	3	56%	21%
Air	1	5	51%	14%
Air	1	7	47%	18%

Tab.1: Evaluation of the DDT peak areas of the specimens after GC / MS analysis of MEF single jet.

Using TIGRES MEF single plasma jet with nitrogen as type of gas ten times on one sample and a pattern distance of 1 mm, the highest depletion rate of DDT could be measured. With these parameters a reducing of the DDT total value about 70% is possible. Under these conditions, a maximum surface temperature of 120 °C was measured one millimeter below the substrate surface with the Type K thermocouple. These results are reproducible.

Using the gas mixture nitrogen-hydrogen, a DDT reduction of over 50% was achieved after only three runs and a pattern distance of 3 mm. So, this type of process gas is suitable for implementing a DDT reduction with a shorter treatment time. Even by using compressed air comparable DDT degradation rates can be achieved. However, the use of compressed air was not pursued because the presence of oxygen during the plasma treatment should be avoided to protect sensitive surfaces of wooden artefacts.

The second plasma source, kINPen 09, did not reached similar high depletion rates of DDT. Using a gas mixture of nitrogen / hydrogen, 1 mm distance to the samples surface and a plasma treatment of ten runs, only a depletion rate of DDT about 60% could be reached. It is positive to mention, that the maximum surface temperature 1 mm below the substrate surface did not exceeded 70 °C.

No results could be achieved about the penetration of the plasma treatment, the duration of the removal of DDT crystals from the surface and metabolites by using atmospheric pressure plasma on biocidal treated wooden surfaces. These topics have to investigate in further research projects.

3.2 Antimicrobial films

Most antibacterial modified materials (SiO_x films containing silver, copper or zinc oxide on wood) showed strong effects towards bacteria. Figure 4 demonstrates the antibacterial effect: the reference

material on the left side shows a bacterial growth all over the agar plate and around the material. However, by applying a thin active agent-containing SiO_x thin film (right part of this figure), a growth-free zone (inhibitory zone) around the material was clearly visible.

In contrast to the strong antibacterial effect, most of the surfaces were covered by mold even after short incubation times and only small mold resistance effects could be achieved. In general, copper containing films showed the highest impact. However, this film forming procedure also allows the embedment of different kinds of active agents in one films (combinations of active agents) These tests showed that an increased resistance towards mold growth can be achieved especially by combinations of active agents silver, copper and zinc oxide in one film [11].

A point needs to discuss is the applicability of the here presented methods. This technology allows the creation of thin films on nearly every material without the use of organic solvents. Hence, there is no need of curing processes such as tempering or UV-treatment and films can also be realised on materials which are incompatible with organic solvents. Another advantage of this technology is, besides the possibility to create areal coatings, the possibility to treat chosen parts of a material, for example areas frequently colonized by microorganism in sensitive sectors. Using the single-jet systems, the realisation of larger areal coatings can be time-consuming. But recent system development, using a linear array of several plasma-jets [15], allows the treatments of larger areas and consequently makes this process less time-consuming and more economical.

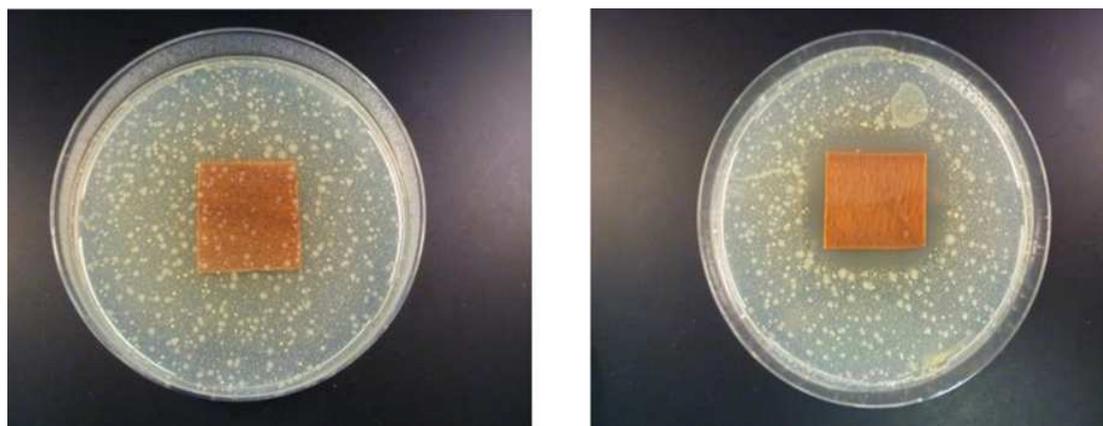


Fig. 4: Antibacterial effect on *Escherichia coli* using agar-diffusion test: uncoated wood slide (left), active agent-containing SiO_x film on wood slide (right) [16]. Photo: INNOVENT.

4 Conclusion:

The removal of DDT crystals from wooden artworks as a result of a biocidal treatment with cold atmospheric plasma was demonstrated. Using the TIGRES plasma MEF with nitrogen as working gas on new contaminated samples depletion rates of 70% could be achieved with a relatively high number of treatment runs. Using nitrogen-hydrogen gas mix a depletion rate of 70% could be achieved with half of treatment runs. The low energy plasma source kINPen09[®] achieved similar results as TIGRES plasma MEF by using nitrogen as working gas (ca. 60% depletion of DDT).

Open questions about decontamination of wooden surfaces are left about the penetration of the plasma treatment, the duration of the removal of DDT crystals from the surface and metabolites by using atmospheric pressure plasma on biocidal treated wooden surfaces. Also the matter of “patina”, an aged surface of a wooden artefact, has to be interdisciplinary discussed between restorers and scientists to improve the technical development of plasma sources. Suitable applications for cultural heritage should be considered in further plasma systems.

By the modification of plasma jet systems, the introduction of precursors into the active plasma zone is possible. Using this approach, the formation of thin, active agent (silver, copper, zinc oxide) containing films on wood materials was achieved. Furthermore, this technology is a suitable and economical way to create antimicrobial properties, especially in comparison to conventional methods, which incorporate much larger amounts of biologically active components in the whole bulk material. Applying the agar-diffusion test, a strong antibacterial effect was observed. More challenging to achieve was the creation of an effect towards mold fungi. Here, films containing only one active agent showed poor antimycotic properties and samples were strongly covered by mold even after short incubation times. Significant improvements were obtained by using combinations of active agents.

Acknowledgement:

The authors would like to thank restorer Birgit A. Schmidt, Dr. Jörg Krüger, Simone Pentzien and Andrea Conradi (BAM Berlin) for open minded discussions and Karolina Barnikol (INNOVENT) for GCMS measurements. Thanks to the Schlossmuseum Sondershausen for providing old contaminated samples.

This work was financed by the Deutsche Bundesstiftung Umwelt DBU (AZ 32953) and The German Federal Ministry of Economic Affairs and Energy, ZIM "PlaCoW".

References

- [1] H. Tello, B. Paz, Über den Einsatz von Bioziden in naturkundlichen, botanischen und musealen Sammlungen – Rückblick und Ausblick, in: P. Zalewski (Ed.), Biozidbelastete Kulturgüter- Grundsätzliche Hinweise und Texte zur Einführung in die Problematik. Bericht über das EU-/ ESF-Projekt „Kleine und Mittlere Unternehmen und Wissenschaft im Dialog. Dekontamination von Kulturgütern“, Frankfurt (Oder), 2014, pp. 107 – 124.
- [2] Hankammer, Gunter, and Wolfgang Lorenz, "Schimmelpilze und Bakterien in Gebäuden." Erkennen und Beurteilung von Symptomen und Ursachen. Rudolf Müller, Köln (2003), Regulation (EU) No 528/2012 of the European Parliament and of the Council of 22 May 2012 concerning the making available on the market and use of biocidal products Text with EEA relevance
- [3] A. Schutze, J.Y. Jeong, S.E. Babayan, J. Park, G.S. Selwyn, R.F. Hicks, The atmospheric-pressure plasma jet: a review and comparison to other plasma sources, *IEEE transactions on plasma science* 26 (1998): 1685-1694.
- [4] Jamali, A., and P. D. Evans. "Etching of wood surfaces by glow discharge plasma." *Wood science and technology* 45.1 (2011): 169-182.
- [5] Denes, Ferencz S., L. Emilio Cruz-Barba, and Sorin Manolache. "16 Plasma Treatment of Wood." *Handbook of wood chemistry and wood composites* (2005): 447.
- [6] Zhou, Xiaoyan, et al. "Glass transition of oxygen plasma treated enzymatic hydrolysis lignin." *BioResources* 7.4 (2012): 4776-4785.
- [7] Noeske, Michael, et al. "Plasma jet treatment of five polymers at atmospheric pressure: surface modifications and the relevance for adhesion." *International Journal of Adhesion and Adhesives* 24.2 (2004): 171-177.

- [8] Cheng, Zhang Liye, and Ru-Juan Zhan. "Surface modification of polymer fibre by the new atmospheric pressure cold plasma jet." *Surface and Coatings Technology* 200.24 (2006): 6659-6665.
- [9] Iwasaki, Masahiro, et al. "Nonequilibrium atmospheric pressure plasma with ultrahigh electron density and high performance for glass surface cleaning." *Applied Physics Letters* 92.8 (2008): 081503
- [10] Beier O, Pfuch A, Horn K, Weisser J, Schnabelrauch M, Schimanski A (2013) Low temperature deposition of antibacterially active silicon oxide layers containing silver nanoparticles, prepared by atmospheric pressure plasma chemical vapor deposition. *Plasma Processes and Polymers* 10: 77-87. doi: 10.1002/ppap.201200059.
- [11] Gerullis, Sven, et al. "Thin antimicrobial silver, copper or zinc containing SiO_x films on wood polymer composites (WPC) applied by atmospheric pressure plasma chemical vapour deposition (APCVD) and sol-gel technology." *European Journal of Wood and Wood Products* (2017): 1-13.
- [12] B. Bärnighausen, H. Bärnighausen, *Die Goldene Kutsche von Schloß Sondershausen. Amtlicher Führer Special*, Deutscher Kunstverlag GmbH München, Berlin 2001, p. 7.
- B. Bärnighausen, H. Bärnighausen, *Die Goldene Kutsche von Schloß Sondershausen. Amtlicher Führer Special*, Deutscher Kunstverlag GmbH München, Berlin 2001, pp. 37.
- [13] Alessandro Patelli, Monica Favaro, et al., PANNA Project – Plasma and Nano for New Age Soft Conservation. Development of a Full-Life Protocol for the Conservation of Cultural Heritage, in: *Progress in Cultural Heritage Preservation, 4th International Conference, EuroMed 2012, Limassol, Cyprus, October 29 – November 3, 2012. Proceedings*, 793-800.
- [14] T. von Woedtke, K.-D. Weltmann, *Grundlagen der Plasmamedizin, MKG-Chirurg 10-2016*, Springer-Verlag Berlin-Heidelberg, 2016. Published online.
- [15] Ramm M, Pfuch A, Beier O, Spange S, Schimanski A, Taylor-made surfaces by means of inline plasma coating at atmospheric pressure. *Melliand International* 4, 2013, 232-234.
- [16] Gerullis, Sven et al. "Antimikrobielle Beschichtungen auf Holz mittels Atmospheric Pressure Plasma Chemical Vapour Deposition (APCVD)" *Holztechnologie* 57.5 (2016): 16 – 25.