Cleaning of Wall Paintings and Architectural Surfaces by Plasma

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Coating surfaces with a protective layer is a common method to protect artwork from deterioration. These layers consist often of organic substances such as acrylic resins. Due to weathering and ageing polymers usually suffer changes in optical properties and these organic coats also reduce the water-permeability of porous systems which can cause an accelerated decay. Therefore, we need a method to remove organic matter without harming the substance. In the present study, cleaning procedures with different types of artificially soiled surfaces were carried out. Two different atmospheric pressure plasma jets that permit an economic application were investigated to get the optimal plasma parameters for cleaning.

Introduction

The present study has dealt with the application of atmospheric pressure plasma in the field of the restoration and conservation of mural paintings and architectural surfaces.

In this end, substances which belong chemically to the group of acrylic resins are often used. These are applied in the form of dispersions with water or non-polar solvents on mineral surfaces to protect them against ageing processes. However, for many surfaces, such a treatment is inexpedient and involves considerable damage, as for example on lime plaster or sandstone.[1]

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These porous materials have a complicated water exchange with the environment. The water enters due to high humidity, rain or bottom dampness into the structure of plaster or stone and condenses there. It is important that this water should leave faster the inside of lime plaster or sandstone.[2] Otherwise, the water-soluble components of the plaster layer, or of the stone, such as some salts (sulphates, chlorides and nitrates) are washed out and deposit near under the surface. If the surface is covered with a water-repellent substance as acrylic resin, the enclosed water evaporates only very slowly and leaves a high concentration of salts. The salts crystallise and are sprinkled partly on the plaster layer or sandstone structure by the large increase in volume.[3]

Contaminations like soot, exhaust gases, abrasion of car tyre and graffiti belong to the undesirable organic matters on facades and memorials. These deposits clog the surfaces and make them badly permeable to water. Further, the aesthetic aspect is important, too.[4]

Current methods for the removal of organic foulings and undesirable matters are striping the paint with aggressive solvents and abrasive technologies like sandblasting. Nevertheless, chemical and mechanical cleaning processes have their disadvantages. Chemical methods contaminate the building fabric with toxic solvents and sandblasting damages the original surface.[5] The destination of the research project is to find out how to remove these

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different undesirable layers by a single process. Atmospheric pressure plasma was used as an affordable and practicable alternative process to chemical and mechanical cleaning methods.

Experimental Part

We attempted to remove synthetic resin layers, varnishes and soot deposit by plasma etching from different surfaces.

Specimen

A hydrophobic coating always consists of a binding agent, involves a dispersion of solid synthetic resins by a solvent, and some colour pigments. Twelve typically hydrophobic customary binding agents were selected for the study and the specimens were preserved (see the list of binding agents in Appendix).

These pure binding agents were applied on object slides, strips from cardboard or canvas, with lime plaster-coated slabs and panels from sandstone. Besides these pure binding agents, some cheap paint-sprays from the market meant for tiles and red brick were also used. Furthermore, some pigmented lime plaster slabs were sooted artificially and later the sooted layer was coated with one of the afore-mentioned binding agents to obtain the close to the real conditions.

The main point of the investigations is the questions in which way the combination of a certain protective layer with a certain substrate reacts to plasma treatment and whether an ablation of the coating happens. The results of the plasma treatment were evaluated and compared with the help of light microscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), laser scanning microscopy (LSM) and macrophotography.

The specimens should approximate the real conditions most often and they should be measurable.

Plasma Sources

Two plasma sources were used to determine the best plasma parameters for the removal of the available protective layers. One of the used plasma sources is a customary plasma jet Plasma-BLASTER of the company Tigres Dr. Gerstenberg GmbH which works with a corona discharge.[6] According to the function principle of a jet (to blow the plasma filaments out through a nozzle with a gas flow), the plasma source works with atmospheric pressure and is suitable for the treatment of rough and also relief-shaped surfaces. Furthermore, it is possible to supply the Plasma-BLASTER of Tigres with compressed air as a process gas by a mobile compressor. This enables a flexible application outdoor.

The system generates a non-thermal short-lived corona discharge. The equipment consists of a power pack and a treatment-head in which the plasma is generated (Figure 1). The corona discharge is initiated between the internal pin-shaped electrode and the external cylinder-shaped or truncated cone-shaped external electrode (nozzle). Both are made of stainless steel and are replaceable. The coronal filaments are brought out with a gas flow (pressure from 0.55 MPa) after the nozzle opening. The leaving plasma flows freely. The discharge is initiated with a sine-shaped high voltage of about 12 kV, with a working frequency in the range of 18 to 50 kHz. The power output is regulated with an automatic impedance adaptation through the variation of the frequency in the studied range.[7] The plasma jet's temperature depends on the flow speed of the process gas and is between 70 and 250 °C. The thermal load of the substrate can be influenced by the distance between the specimen and the opening of the nozzle.

The DBD jet is a patented development of HAWK and a prototype.[8] It is also free of potential. A dielectric barrier discharge is generated in a cylindrical system at the atmospheric pressure. The system consists of two electrodes, of which one electrode is insulated with a dielectric material in the form of a tube. The ground electrode in the form of a rod is placed in the middle of this tube, which drives the plasma to the environmental air. The high voltage electrode is a ring placed over the tube. The electrodes are made of brass and the dielectric material is fused silica. By forcing gas through the tube between these two electrodes, the plasma is caused by a Fourier synthesis pulse generator with a pulse width of 600 ns and a frequency of about 25 kHz. The high voltage is in the range of 12–20 kV. Two watts electric power was injected in this system. The beam temperature was about 80 °C at a distance of 2 mm.[9]

Parameter

The ablation by Plasma-BLASTER was investigated as a function of the following parameters: input power, pressure of the working gas, diameters of the nozzle opening and distance to the specimen.

Figure 1. Plasma source: "Plasma-BLASTER MEF"; 1, power supply unit; 2, gas supply; 3, treatment head.

Table 1. Ablation of Paraloid B72, cleaned area in comparison to output power and temperature of plasma beam.

Ablated area	Output power	Temperature
mm^2	W	°C
1	40	80
10	85	115
26	145	160

First of all, all the specimens were rejected in which the substrate was destroyed or the binding agent was cracked thermally but not removed. Nozzles with 8 mm of diameter or more reached too high temperatures for the substrate, even with low powers and high working gas pressures. Nozzles with 4, 2 and 1 mm opening diameters were used. Further, a new nozzle was developed which has 1 mm opening diameter and generates lower turbulence.

The optimum working distance is between 2 and 5 mm. The substrate is destroyed below this distance by filaments, the ablation effect becomes rapidly weak above it. For working gas pressure, two values were selected: 0.55 and 0.75 MPa. The output power was set at three values between 45 and 145 W.

The parameters of the DBD-Jet are still the same: the input power was about 2 W; the high voltage was 15 kV and the frequency was 25 kHz.

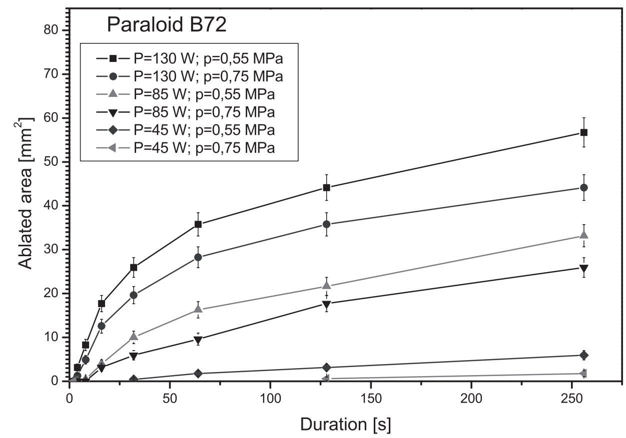

Figure 2. Ablated area of Paraloid B72 as a function of duration at the defined pressure and input power.

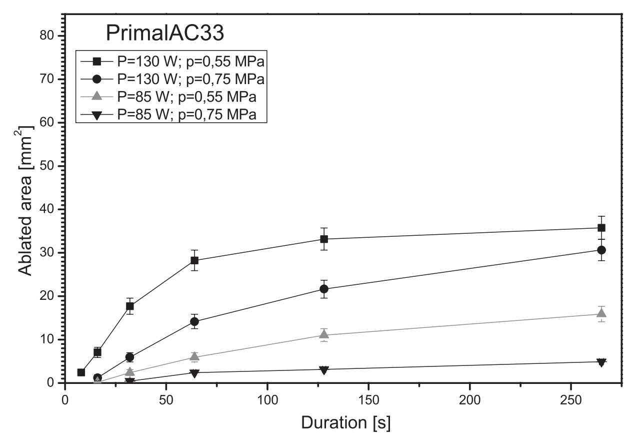

Figure 3. Ablated area of Primal AC-33 as a function of duration at the defined pressure and input power.

Results

Ablation of Binding Media by Plasma-BLASTER

For most of the synthetic resins, the best results were reached with a nozzle diameter of 1 mm and a pressure of 0.55 MPa. Within this range, it may be expected that the higher the output power, the bigger is the ablated area. Besides, the temperature of the beam plays an important role, and it rises with the power. All the tested binding agents, except cellulose lacquer, are thermoplastics; they have a melting point of about 120 °C.[5] If the polymers are at their glass temperature, the ablation effect rises significantly. Therefore, the ideal beam temperature is from 80 to 130 °C. The substances are softened by temperature which means that the long carbon chains disassembled in smaller segments such that the plasma can delete the smaller molecules. The ablated area cleaned from Paraloid B72 is a function of temperature and is formed after 30 s of treatment at 0.55 MPa gas pressure and is shown in Table 1.

However, the output power of 145 W is too high; the film becomes brown and is left to remain on the substrate. Primal AC-33 cannot be removed by the output power which generates temperatures below 100 °C on the substrate. The reason being the higher softening point of Primal AC-33 (125 °C) in comparison to Paraloid B72 (95 °C).[10] The

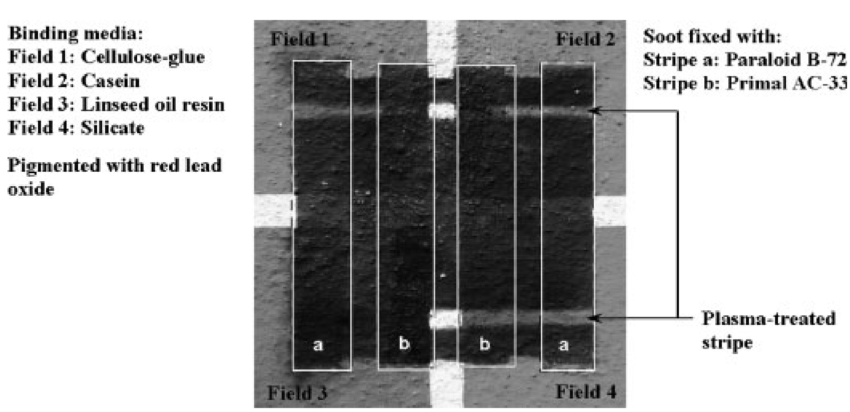

Figure 4. Cleaning of soot on pigmented lime plaster by plasma jet.

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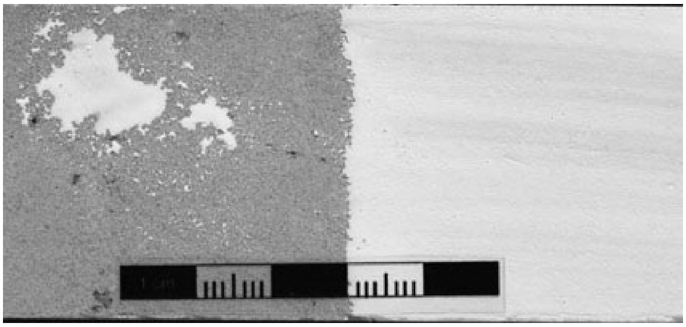

Figure 5. Comparison of dispersal of lime milk on impregnated sandstone between treated (right) and untreated (left) sides.

treatment results of both selected substances, Paraloid B72 and Primal AC-33 are shown in Figure 2 and 3.

Almost all of the 12 binding media show ablation effect on treatment by plasma. The kind of surface is a very important factor for the cleaning results. Low temperature conductivity or a big nozzle prohibits high output powers, e.g. for paper or wood. Treatment with 145 W generates surface temperatures above the temperature of decomposition of lignin and cellulose. Also in some historical pigments like metal salts or oxides (Ochre, Massicot, all lead oxides, Cinnobar, etc.) weak colour changes occur under the influence of plasma beam of the Plasma-BLASTER by high input power. This group of pigments is very sensitive to temperatures higher than 200 °C.[11] Specimens like canvas reach this temperature during the treatment.

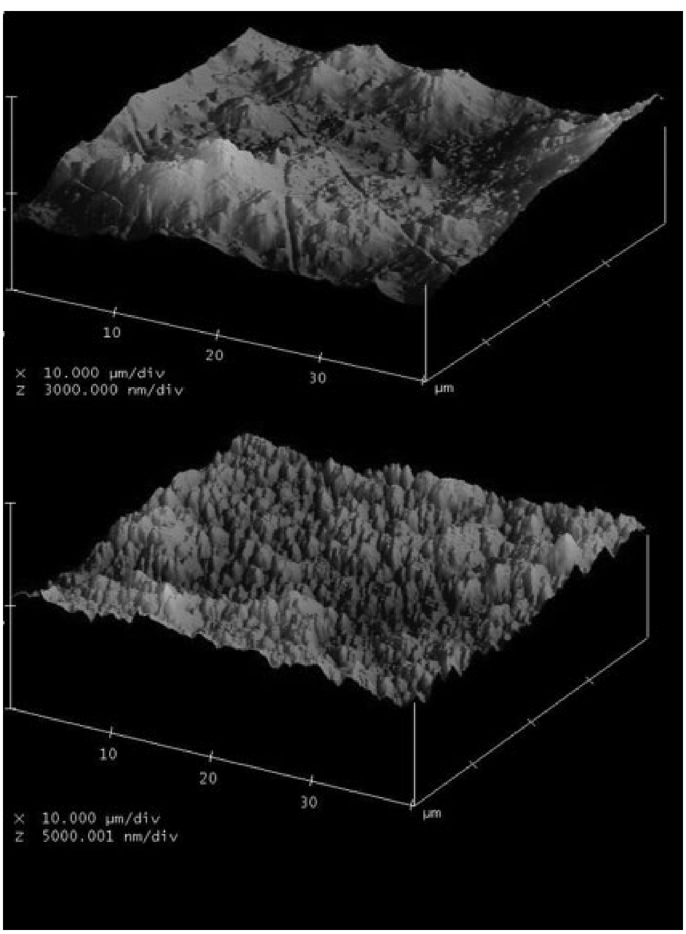

Figure 6. Surface topography pictured by atomic force microscopy of alkyd resin layer before (upper) and after (lower) plasma treatment.

Soot Removal by Plasma-BLASTER

To eliminate soot from the pigmented lime plaster, subsoil has shown us that the complicated interactions of subsoil, fouling and fixation layer have a great influence on the cleaning results. In Figure 4, four sooted fields are shown. Every field has a different binding agent but the same pigment (red lead oxide). This pigment binding agent mixture (paint) was applied on lime plaster slabs and then was sooted artificially with a torch. The sooted layer was subsequently attached trajectorywise with two clear acrylic resins, ensuring a problem of formulation close to reality: a fresco which got dirty by candle soot and evaporated wax, was substituted with the acrylic resins.

All the four fields, with both fixations, were treated stripwise with the plasma beam of the Plasma-BLASTER. In field 1 which has water-soluble cellulose glue as a subsoil, the attached soot and the Paraloid B72 are partially removed (stripe a), whereas with Primal AC-33 the attached soot remains almost completely (stripe b). In field 2, a similar figure appears, Paraloid B72 and under it the soot can be deleted almost completely from casein pigment layer, Primal AC-33 and the soot remains well preserved completely. Field 3 is again covered with soot after plasma cleaning, neither Paraloid B72 nor Primal AC-33 can be deleted from the plaster coated with resinous linseed oil. In the fourth field, a silicate has been used as the subsoil and the best cleaning results were achieved for both fixations.

The plasma beam of Plasma-BLASTER was able to make the hydrophobic surfaces, coated with linseed oil, permeable to water again. An uncoated clean face carries water fast. A drop of 50 µl needs approximately 5 min to penetrate. If one saturates this face with linseed oil, the drop of water needs 150 min to disappear and also a part of the water simply evaporates in this time. After a plasma treatment, the drop permeates within 30 min. Indeed, one does not reach the injection time before the hydrophobic coating is applied, but the water stays clearly for a short time in the structure and can be carried faster.

Hydrophilising, Matting and Weak Ablation Effects

The DBD-jet has a much lower ablation rate, but it is better suited for increasing the surface energy from hydrophobic impregnated agents. This effect is necessary to apply polar liquids and colour systems on such impregnated surfaces. Modern methods of conservation contain coating with lime-milk or other mineral substances to refresh aged facades. These coatings are water-based dispersions and do not adhere on hydrophobic surfaces. Figure 5 shows the dispersals of lime-milk on a treated surface (right side) in comparison to an untreated surface (left side) on impregnated sandstone. The specimen surface remained vertical and most of the lime-milk drained off on the untreated side. The lime-milk on the plasma-treated side adhered to the unchanged surface.

Another domain for the preferred application of the "colder" DBD-jet is the matting of lucent shiny varnishes which are applied preferentially as a protective coating on paintings. For different historical artefacts like paintings, documents and books, varnishes are needed with different gloss levels. The plasma treatment allows the use of one substance which can be set at different gloss levels. The matting effect is caused by the change in the surface roughness which is shown in Figure 6.

Ink and felt-tip lines can be removed from paper by Plasma-BLASTER at low temperatures and by DBD-Jet.

Conclusion

In recapitulation, we can say that the cleaning method by plasma is partly successful. With both sources, an ablation takes place, different substances react very differently to the DBD jet and the Plasma-BLASTER. It can be deleted faster and a bigger number of protective layers are formed by Plasma-BLASTER than by the DBD jet. The use of reactive gas provides the highest ablation rate. The mixture of argon and hydrogen (95 and 5%) ensures an ablation rate of more than 100 $\mu m \cdot min^{-1}$. Some substances like cellulose lacquer are very hard and resistant. We detected the weakest ablation effect (<1 $\mu m \cdot min^{-1}$) on cellulose lacquer after treatment by DBD-Jet. Cellulose lacquer resists the treatment by Plasma-BLASTER. Only the highest output power produces thermal damage of the coat in the form of burned-in black spots.

For temperature-sensitive materials, it is better to use the DBD-jet. Cleaning of documents and books is an important field in conservation and offers a new challenge. Water-based dispersions adhere on plasma-treated hydrophobic surfaces. This effect is very useful for the refreshing of conserved lime plaster facades. It is imaginable to use Plasma-BLASTER to remove graffiti. We have planned in collaboration with the University of Hanover, a cleaning of graffiti by different methods: abrasive and chemical cleaning, laser ablation and plasma treatment. This action will give a chance to compare the cleaning results of different technologies.

Appendix-List of applied binding media.[10,11]

Customary name	Components
Primal AC-33	100% Acrylic dispersion, PMMA in solution with aromatic hydrocarbons (benzene, toluene, xylol)
Plextol	Water dispersion of acrylate vinyl acetate copolymers on the basis of ethyl acrylate and methyl methacrylate.
Cellulose lacquer	Nitrocellulose in a mixture of ethyl alcohol, ethyl glycol and ethyl acetate.
Paraloid B72	Copolymer from ethyl methacrylate (EMA) and methyl acrylate (MA). Paraloid B72 is especially well dissolvable in toluene, ethyl acetate, acetone and MEK. Solution (15%) of B 72 in ethyl acetate can be diluted with anhydrous ethyl alcohol.
Retouch-varnish	Ketone resin (polycyclohexanone resin) in solution with alcohol.
Mowilith DML-2	Water dispersion of a copolymer of vinyl acetate and maleic acid dibutylester.
Mowilith M-77	Dispersion of copolymers of vinyl acetate and maleic acid dibutyl ester in ethyl acetate.
Plexisol B500	Dispersion of butyl methacrylate (BMA) in esters, ketones and chlorinated hydrocarbons
Mastic gum	Water-indissoluble resin of the Mastic (*Pistacia lentiscus*, an evergreen shrub or small tree), relaxed in ether, benzene or 80%th chloral hydrate solution.
Shellac	Shellac is a brittle or flaky resin gathered from the lac insect, Laccifer lacca, found in the forests of Assam and Thailand. Solution in ethanol.
Dammar	Resin of Malay-Indian broad-leaved trees in solution with spirits of turpentine.
Alkyd resin	= Alcohol + acid, the saturated polyester which originates, e.g., from conversion of bicarbon acid with polyvalent alcohols like glycerol or ethylene glycol.

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