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Cleaning books with light? Plasma treatment on mould infested paper

Limpar livros com luz? Tratamento com plasma em papel infestado por bolor

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Abstract

In this model-based study the effect of atmospheric pressure plasma on rag paper and mould infested paper is determined. Visual examinations with a digital microscope show the removal of mould from the surface, changes of surface properties of selected papers and micro-damages to the paper fibres occurring during the treatment process. As plasma generates highly reactive chemical components, Ozone and UVC radiation are also present and have an influence on the treated surface. Therefore, single treatments of air plasma, hydrogen-argon, oxygen-argon plasma and Ozone and UVC treatments are compared. The results show that comparing to the Ozone and UVC treatment the plasma treatments show less damage on the paper surface and the removal of the mould is more effective. But it can also be seen that the oxidizing effect of plasma has an impact on the cellulose fibres.

KEYWORDS
Paper conservation
Mould growth
Infestation
Blocked paper
Decontamination
Atmospheric cold plasma

Resumo

Neste estudo baseado em modelos, é determinado o efeito do plasma de pressão atmosférica em papel de trapos e papel infetado por fungos. Exames visuais com um microscópio digital mostram a remoção dos fungos da superfície, alterações nas propriedades da superfície de papéis selecionados e microdanos nas fibras do papel que ocorrem durante o processo de tratamento. Como o plasma gera componentes químicos altamente reativos, o ozono e a radiação UVC também estão presentes e têm influência na superfície tratada. Portanto, são comparados tratamentos únicos com plasma de ar, hidrogénio-árgon, oxigénio-árgon e tratamentos com ozono e UVC. Os resultados mostram que, em comparação com o tratamento com ozono e UVC, os tratamentos com plasma causam menos danos na superfície do papel e a remoção dos fungos é mais eficaz. Mas também se pode observar que o efeito oxidante do plasma tem um impacto nas fibras de celulose.

PALAVRAS-CHAVE
Conservação de papel
Crescimento de bolor
Infestação
Papel encravado
Descontaminação
Plasma frio atmosférico

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Introduction

In paper conservation mould is a problem that occurs frequently. In some cases, it is a recent mould outbreak due to a water damage, in other cases the infestation has happened years ago. Especially in the latter cases the mildew has had enough time to decompose the paper structure and cause a lot of damage such as degradation, stain formation and under the right circumstances blocked pages. Blocked pages or paper sheets due to mildew means that the hyphae have grown through the paper structure and thus formed a paper block from former single sheets. In most cases, the advanced degradation and weak structure of the paper leads to massive loss of stability and flexibility of the papers. The hyphae are stronger than the cellulose fibres, which form with time an even stronger block of paper. Scrolling through the pages then becomes impossible and therefore, the information is lost. In addition, it is a very difficult task to handle mould infested and highly degraded paper and perform a cleaning treatment. Cleaning the objects is always necessary to remove the mould, because of its potential health hazard. Mould-infested and blocked paper represents a very complex damage, that is still not fully understood nor successfully treated by conservators.

Depending on paper´s condition and blocking grade, conventional treatment methods such as separating pages with a spatula is mostly unsuccessful. It can cause even more damage by producing holes, tears und substantial loss. Therefore, investigations of alternative cleaning and separation methods are essential. Previous experiments show different approaches to solve the problem. In 2020 Floss tried to unblock the paper by using cyclododecane as a short time stabilizer for the degraded paper sheets. She used the sublimating effect of the chemical, which allows even in situ treatment without causing significant local tensions. In Floss' case study the blocked papers were treated in a bath of cyclododecane solved in white spirit. Her work showed that the cyclododecane was able to build a stabilizing film on the paper surface, which made it easier to separate the pages with the spatula [1]. As promising as it seems, the treatment has its limits: due to the fact that a liquid method can only be used for unbound objects not for books or documents with a binding. Thus, an in-situ treatment is not possible, nor was the mould removed by this treatment.

Between 2021 and 2023 a method to separate blocked pages based on enzymatic activity was tested by an interdisciplinary team of conservators and scientists in a two-year project at the Saxon State and University Library (SLUB) in Dresden, Germany. They developed two different approaches to treat the blocked paper: a bath treatment and the use of different gels as carriers for the Enzymes to treat the paper with less moisture. As fungi have a very complex cell wall structure they needed to find the right combination of enzymes to break down the chitin- and protein- containing cell walls without affecting the paper. Furthermore, they had to discover the effect of the enzymatic activity on the surface of the paper and a method to remove the enzymes, residues and fragments of the mildew after the treatment. The use of gel-based compresses allows a local application of enzymes, but a wet treatment afterwards to wash out any residues and avoid water stains is always necessary. The investigators demonstrated that the combination of Proteinase K, Chitinase and β-Glucanase optimizes the enzymatic degradation of the hyphae and additionally, that the bath-treatment removes the degraded components of the mildew. However, the results also showed, that the treatment – both the bath and the treatment with a gel as an enzymatic carrier- has its limits. Inks, metal and other components of historic paper can influence the enzymatic activity. Furthermore, the treatment is very complex and require a large number of analytic tests before and after implementation. In combination with the high costs the use of enzymes to unblock mould- infested paper cannot be implement in the daily work of a conservator yet [2].

In conclusion, the previous research shows that the methods are not suitable for every type of blocked paper, and furthermore, the treatments did not remove all components of the mould. Cleaning mould infested papers is essential to make them accessible to the public. The results of the existing treatments are that even if the pages can be separated, the paper is still highly instable and degraded, which makes it mostly difficult to carry out a cleaning treatment to remove the mould. Therefore, further research of alternative cleaning and separation methods are essential. Among several methods, paper conservation currently focusses on plasma treatments but it is still in the early stage of research.

Plasma is a (partially) ionized gas and known for its versatile use in various fields such as medicine, technology, physics and biology. Depending on the working gas, plasma possesses various reactive components. A gas mixture containing oxygen forms for example highly reactive oxygen species (ROS) such as atomic oxygen (O), hydroxy groups (-OH), hydroperoxide (-OOH), ozone (O_3) and hydrogen peroxide (H_2O_2). A plasma generation in a nitrogenous environment forms reactive nitrogen species (RNS) like nitrogen oxides NO_x and in the simultaneous presence of oxygen, reactive oxygen-nitrogen species (RONS) can be generated such as peroxynitrite ($ONOO^-$). In presence of hydrogen, hydrogen radicals like H• can be formed. In addition to ROS, RNS, RONS and hydrogen radicals, a plasma also contains reactive molecules and atoms, ions, free electrons and photons including UV radiation. Theses reactive components can interact with the surface. The proportion of each reactive species determines the reactive properties of the plasma in relation to the surface being treated.

Plasma can be divided in two types: thermal and non-thermal plasma (NTP). Thermal plasma is not suitable to temperature sensitive surfaces like paper. However, NTP can be applied to organic materials as its temperature reaches a maximum of 50 °C and therefore only causes limited heating (and thus only limited accelerated aging) on the temperature sensitive surface. The advantage of NTP is, that it can be generated at atmospheric pressure, which makes it relatively simple to use it in a conservation laboratory, depending on the working gas. In Jiao et al. [3] a brief overview about first approaches of the use of NTP to treat different cultural heritage objects like metals, paintings and paper is given. The article summarizes for example the potential of NTP to form a protective barrier layer on corrosive metals and surface modification such as surface-cleaning of paintings or coatings of cellulose-based materials [3].

Further initial publications show that plasma treatment can be used on paper to modify the surface e.g., to change the wettability or improve the stability of acidic paper [4-5]. The reasons for these changes are the highly reactive components of the plasma. First results of a treatment with non-thermal atmospheric pressure plasma (NTAPP) on paper show that the plasma has physical and chemical influence on the surface in general and the cellulose fibre in particular depending on the working gas. Among other reactions, the physical effect is based on the abrasive effect of the first layer of the paper fibres, due to the bombardment of the surface with the components contained in the plasma [6]. This can result in formation of new hydrogen bonds and thus, increase the stability of the paper, but also leads to oxidation and then to the degradation of the cellulose fibre.

The chemical effect on the surface depends mainly on the working gas, as it determines the reactive species of the plasma. ROS, RNS and RONS are responsible for changing the chemical properties of the paper and cellulose fibres, such as increasing the functional groups or decreasing chemical bonds [4, 7]. Thus, plasma treatment in an oxygen-containing environment can create new carboxyl groups (-COOH) on the surface due to oxidation of the fibre surface, which increases the polarity of the surface and therefore, improves the water absorption capacity [8].

Literature also describes an antimicrobial effect which is used to sterilize surfaces. The sterilizing effect is based on the reactive components of the plasma like ROS, RNS, thermic reactions and UVC radiation. These components affect the stability of the cell walls and deoxyribonucleic acid and therefore, lead to degradation of the cell walls and cell death [9]. Experiments on microbial contaminated paper showed that an inactivation of bacteria is reached within a few minutes but it takes up to 30 minutes to inactivate fungi cells. The inactivating and cleaning effect depend on the used working gas and the microbial species [10-11]. Thermic reaction and UVC radiation can lead to aging and discoloration of the paper.

The combination of those plasma effects on both the paper and the microorganisms seem very promising to treat mould-infested and blocked papers. But due to the oxidizing effect on the cellulose fibre, it is necessary to find the right parameters for a successful NTAPP treatment. Therefore, the efficiency of the removal of fungal structures and the unblocking of paper sheets with plasma is measured in a model-based study. The aim of this study is to determine which optical changes in the surface properties of the selected paper and micro-damage to the paper fibres can occur during this process.

Experimental

Materials and methods

To investigate the optical changes all samples were examined macroscopically with the naked eye and under the digital microscope (Keyence VHX 7000K, 20-2500×). All test runs took place in safety cabinets isolated from indoor air and researchers.

Plasma sources and device

For conservators it is often necessary to use techniques and materials which do not need a lot of special laboratory inventory. Therefore, a commercial piezoelectric direct discharge hand device for atmospheric pressure plasma (Reylon, PiezoBrush PZ3) with the modules “Standard” (for air as working gas) and “Multigas” (for different types of working gases) was utilized. A 230 V power source and a frequency of 50 Hz was used.

As plasma-source air (indoor air) was chosen. Indoor air is easily available and contains oxygen, nitrogen and hydrogen, which means that a plasma generated of air is rich of RONS but contains ROS, RNS and hydrogen radicals as well. The plasma was applied in series for 30 seconds in direct contact to the sample surface, holding the device by hand. After every 30 seconds the treated area was observed for changes in colour or surface changes by bare eyes. The treatment was stopped when visual effects came significant, which was after 4 min. The process parameters temperature (°C), relative humidity (RH), material moisture, ozone development, and UVA and UVC radiation were also measured in order to assess possible risks to researchers and objects. A data logger (testo 610, testo SE&KGaA, Germany) was used to measure the room temperature and RH. The material moisture was measured with a moisture meter (BM 30, trotec GmbH, Germany). The ozone concentration was determined with Dräger accuro hand pump using tubes (measuring rage 0,05-0,7 ppm, Dräger Safety AG&Co. KGaA, Germany). UVA and UVC radiation were detected with a multifunctional measuring device (ALMEMO 2290-4).

Literature describes that ROS in particular have a decontaminating effect on microorganisms. Therefore, single experiments were also carried out with an 1 % oxygen-argon plasma. Argon serves as a stabilizing gas here, as it is inert and therefore, the ROS from the oxygen content are the main reactive agents. A gas flow rate of 3 slm was used for argon and 30 sccm oxygen was added. Paper fibres are susceptible to oxidation processes. For that reason, the treatment time was set at 2.5 minutes. A working distance of 4 mm between the plasma nozzle and the surface of the paper was selected, to better distribute the plasma on the surface. The plasma device was attached to a tripod.

In order to examine the reducing effect of hydrogen radicals, single experiments were also conducted with a 2 % hydrogen-argon plasma. A gas flow rate of 3 slm was used for argon and 61 sccm hydrogen was added. 2 % hydrogen was chosen because the reducing effect is described in the literature as weaker than the oxidizing reactions. Hence, a treatment time of 4 min was selected, the plasma device was attached to a tripod at a working distance of 4 mm.

Ozone and UVC radiation treatment

Air plasma treatment produces large amounts of ozone. Therefore, individual experiments with pure ozone were also conducted in order to better assess the results of air plasma treatment. A commercial ozone generator with 30.000 mg ozone per hour output was used. The samples were irradiated with ozone for 2 hours in a safety box. After 2 hours the chamber was ventilated and the samples were investigated by digital microscopy.

As mentioned before, photons, including UV radiation, are part of the reactive components of plasma. UV radiation has an aging effect and either a bleaching or a yellowing effect on the paper. UVC radiation is also used for sterilisation treatments. In order to better assess the extent of UVC radiation, a pure UVC treatment is carried out and compared with the results of the air plasma treatment. As UVC source a commercial quicksilver germicidal lamp (Light Progress CHS 40WH) with 254 nm wavelength was available. The samples were placed directly underneath the UVC tube in a distance of 30 cm and irradiated for 12 hours. After treatment the chamber was ventilated.

Test paper

For the plasma treatment of blocked papers, the blockings must be created. For this purpose, a highly absorbent filter paper (Rotilabo filter paper type 122, Carl Roth Chemie GmbH, Germany), consisting of 100 % cellulose was selected. The capillary properties of the paper can be used to provide the fungus with sufficient moisture for growth and the open-pored surface allows a good penetration for the hyphae. The paper was cut into 2 × 2 cm samples. *Penicillium* spp. was chosen as fungus, because of its rapid growth and the ability to form dense air mycelium. To initiate growth, a 1 % gelatine solution was also used as the primary nutrient source. A germ solution was prepared from the gelatine and 0.2 ml were applied to the pieces of paper. The inoculated papers were stacked and secured with a paper clip. The paper blocks were placed on malt extract agar medium and incubated at 21 °C and 50 % RH for six weeks.

Since the blocking were not yet sufficiently developed, the experiments described in this paper, were initially carried out on individual sheets. The university has historical paper objects available for testing. The advantage of using historical paper is that the cellulose has already aged naturally and the results of treatment are more similar to those on an original than when filter paper is used. Therefore, historical paper for the experiments were chosen. Papers with different characteristics were selected (Table 1) in order to examine the reactions of the surfaces, mould infestation and writing materials to the treatments.

Table 1. List of sample papers.

Source of the sample	Sample	Materials	Description (macroscopic)
Book 16th century	S1 a-c*	Rag paper (flax and hemp fibres)	Print, water edges
	S2 a-c*		Print, water edges and stains, dark coloured mould on the surface
Book 17th century	S3	Rag paper (flax and hemp fibres)	Pencil writing
Document undated	S4	Mixed paper with flax and fibres of coniferous wood	White mycelium on the surface

*Both sample paper S1 and S2 were each cut into three strips: S1 a-c and S2 a-c

The paper surfaces were characterized visually using a microscope. Sample S1 shows an even, smooth surface with long fibres and a compact fibre structure. The cross-linking of the fibres is intact and outlines of the cross-link anchors are clearly defined. The surface texture of the fibres is smooth. The fibres show an evenly gloss, which is due to the refraction of light on the smooth intact fibre surfaces. In addition, the brighter areas along the fibres could be an indication of a sizing. A minimal yellowish discolouration of some fibres and deposits between the fibres due to the water damage are visible (Figure 1a).

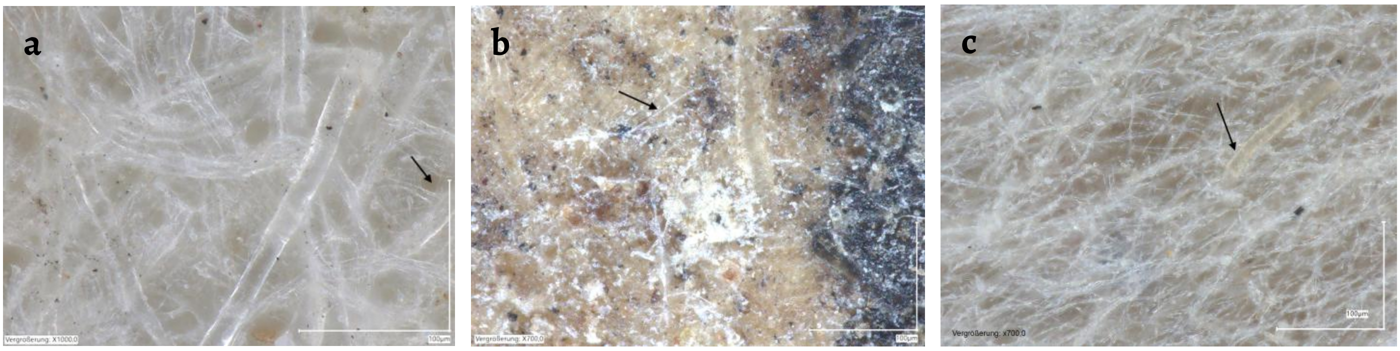

Figure 1. Samples before treatment: a). S1:the intact surface of the paper shows a compact fibre structure, with clearly defined outlines of cross-links (arrow) and an even gloss of the fibre surfaces; minimal yellowing of the fibres is visble at the left side of the picture and dark deposits between the fibres can be seen; b) S2: the uneven surface of the paper shows an irregular gloss and brownish mycelium accumulations on and between the fibres; the surface is grainy and hyphae are visible as thin transparent lines (arrow); the fibre structure is blurred; c) S4: the paper surface shows a dense mycelia growth; the thin and bright hyphae cover almost the entire surface and only individual sections of the fibres are visible (arrow).

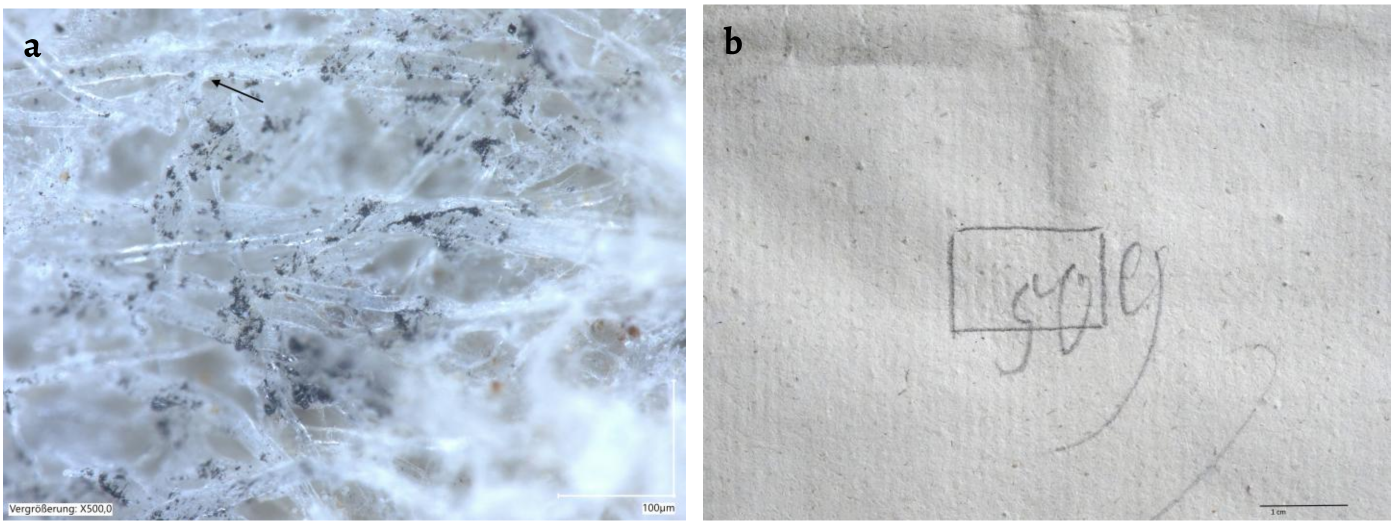

Figure 2. Sample S3, before treatment:a) the long fibres show intact fibre walls with a regular gloss in areas with no graphite. The fibre cross-linking are intact and clearly visible (arrow); the graphite is located on and between the paper fibers; b) the pencil writing is clearly legible and the typeface is even; treatment is carried out within the marked area.

Sample S2 shows a slightly degraded and roughened surface (Figure 1b), which can be recognized by the irregular gloss and uneven surface of the fibres. Dark mycelium accumulations on and between the fibres are visible. Very fine light and dark lines also show individual hyphae lying between the fibres. Overall, the paper surface is nevertheless homogeneous and the fibre interlacing of the fibre structure is largely intact.

The fibres of sample S3 are long with intact cell walls. The connection between the fibres are forming a very even surface and the cross-linking of the fibres are intact. The surface shows a regular gloss. The pencil writing adheres on the surface of the paper fibres and between the fibres. It is typical that the graphite does not adhere evenly to the fibres, but is distributed in irregular accumulations (Figure 2a). Macroscopically, it can be seen that the writing is clearly legible and shows an even typeface (Figure 2b).

Sample S4 shows dense mycelial growth on the surface. The thin and bright transparent hyphae are located on and between the fibres. Compared to the hyphae, the paper fibres are thicker and they are only partially visible under the mycelium (Figure 1c).

Treatments

Table 2 provides an overview of the experiments carried out.

Table 2. Overview of the experiments and related number of figures, describing the results in the following text

Sample paper	Experiment	Image
S1a	UVC radiation treatment	Figure 5a
S1b	Plasma treatment with air plasma	Figure 3b
S1c	Ozone treatment	Figure 4b
S2a	UVC radiation treatment	Figure 5b
S2b	Plasma treatment with air plasma	Figure 3a
S2c	Ozone treatment	Figure 4a
S3	Plasma treatment with hydrogen-argon plasma	Figure 7
S4	Plasma treatment with oxygen-argon plasma	Figure 6

In order to investigate the effect of air plasma treatment on the surface of the paper fibres sample S1b and to evaluate the decontaminating effect sample S2b were treated first. During these treatments, the development of temperature and relative humidity, ozone production, UVC and UVA radiation development were measured.

A pure ozone treatment of samples S1c and S2c was then carried out for comparison with the air plasma treatments, in order to better evaluate the results of the air plasma treatment. Samples S1a and S2a were treated with pure UVC radiation for the same reason with focus on the surface decontamination.

Subsequently, sample S4 was treated with oxygen-argon plasma, with a focus on reducing of the mould infestation and examining the fibre surface.

Sample S3 was then treated with hydrogen-argon plasma, where the reaction of the fibre surfaces to the treatment was of interest, but the focus was on a possible reduction of the pencil writing through the treatment.

The visual changes and possible decontamination of the paper surface through hydrogen-argon respectively oxygen-argon plasma treatment were compared with the changes to the surface after treatment with plasma using air as working gas.

Results

Treatment with air plasma

As mentioned before, the plasma was applied in series for 30 seconds in direct contact to the sample surface. Every 30 seconds, the treated area was examined with the naked eye for colour changes, reduction of the microbial contamination and changes of the surface texture. After a 4-minute treatment, a significant reduction in mould growth was observed in sample S2b, whereupon the treatment was discontinued. Dark mycelium was removed from the surface (Figure 3a), which is now lighter in colour. However, black mould residues are still visible between the fibres. The plasma only decontaminated the top layer of the surface. The paper's surface has a grainy structure and light-coloured, glossy hyphae fragments are visible. This makes it difficult to assess the surface gloss of the fibres, but in less grainy areas, it is less pronounced.

After a 4-minute treatment, sample S1b continues to exhibit a homogeneous surface of the paper and the fibre interlacing is largely intact. However, a loss of gloss is visible on the fibre surfaces, which is particularly noticeable in areas with altered fibre cross-linking anchors. The fibre cross-links now have blurred outlines and exhibit a stronger surface structure in areas with loss of gloss. The fibres are roughened here (Figure 3b).

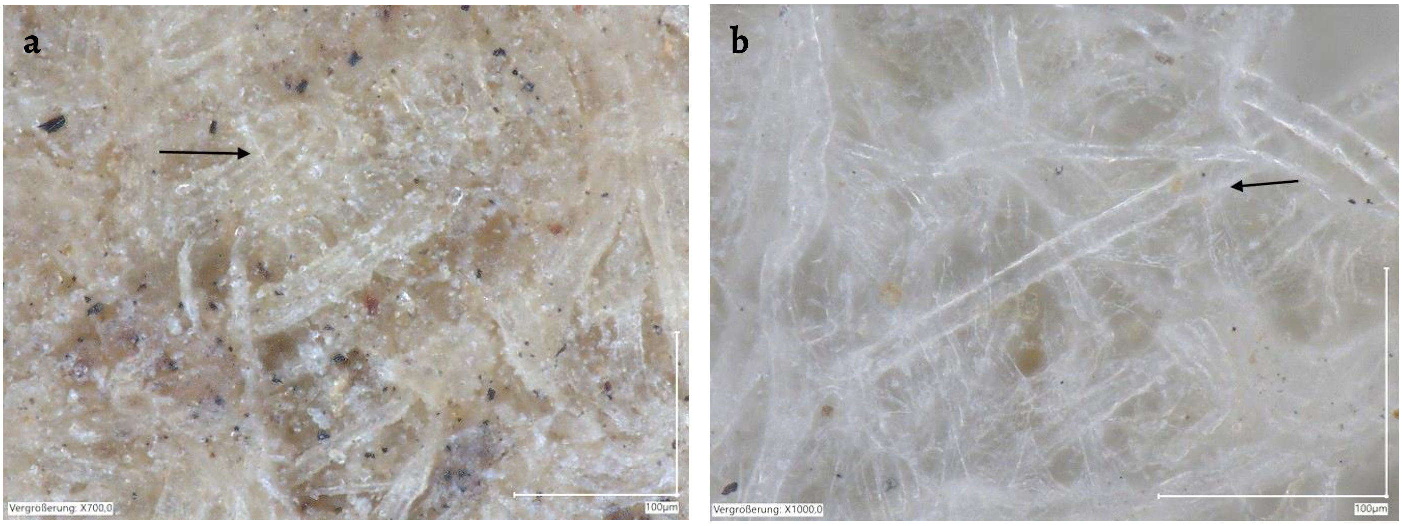

Figure 3. Samples after treatment with air plasma: a) S2b: a significant reduction of mycelium can be observed; the paper surface appears lighter, although it has a grainy texture; shiny hyphae fragments are visible (arrow) and dark mycelium residues can be seen between the fibres; as can be seen in the upper right part of the image, the surface gloss of the fibres is reduced; b) S1b: the surface of the paper appears homogeneous, and the fibre interlacing is intact; a loss of gloss is particularly noticeable in areas with altered fibre cross-linking anchors (arrow); in areas where gloss has been lost, the outlines are blurred and a structure is visible on the fibre surface.

Heat and moisture development

Heat development of the surface of the paper can have an aging effect on the paper and was therefore measured during and after the plasma treatment. The results of the measurement for sample S1b are listed as an example: the temperature on the surface of the paper reaches 41.7 °C during and 27.4 °C after the treatment. The time for the paper sample to cool down took 8 min. Due to the short duration, the heating remains within tolerable limits and should not force any significant and persistent aging processes. An increase or decrease of material moisture was not detected. The measurement of the relative moisture and temperature of the room is shown in Table 3. As expected, the room temperature rises by a few degrees and the relative humidity drops accordingly.

Table 3. Measurement room temperature and relative humidity.

Measurement	Parameter	Result
Before treatment	Temperature	22.1 °C
	Relative humidity	51.5 %
During treatment	Temperature	24.2 °C
	Relative humidity	45.7 %

Ozone, UVA and UVC radiation development

To evaluate the ozone development, a measurement was taken using Dräger tubes in a box with a volume of 66 cm^3. Ozone development was outside the measurable range and could already be detected by smell without measurement.

While no UVC radiation could be detected, UVA radiation fluctuated up to a maximum of 1 W/m^2. For comparison a disinfection hand lamp (herolab NU-8 UV hand lamp, 8 W tube, Carl Roth Chemie GmbH, Germany) in a working distance of 20 mm was used, containing a UVC source with 254 nm and a wavelength of 365 nm for UVA. For example, a value of 6.02 W/m^2 was measured for the UVA radiation value.

Treatment with pure ozone

During the ozone treatment, an increase of temperature up to 5 degrees was observed. The ozone treatment led to the fragmentation of the mycelium on the surface of sample S2c, whereby the hyphae and mycelium residues were not removed from the surface. The surface now appears grainy and irregular due to the fragments lying on it (Figure 4a). A lightening of the paper surface was detected with the naked eye.

As sample S1c shows, ozone treatment has led to a loss of gloss on the fibre surfaces. The fibres are roughened and the fibre composite is less defined. The fibre cross-links show blurred edges but clear structuring on the surface. Breaks in the fibre bond anchors can also be seen (Figure 4b).

Treatment with pure UVC radiation

UV-C radiation treatment has caused significant changes to the paper surface of sample S1a: the fibre edges show isolated damage and the fibre surface is roughened, which has led to a loss of gloss. The fibre cross-linking shows blurring at the fibre edges and structural formations on the surface. Fibre fragments are present on the surface as bright reflective particles (Figure 5a).

Sample S2a shows that the mycelium has been fragmented by the treatment. Dark mould residues are distributed on the surface but not removed (Figure 5b). The paper surface has a grainy structure and the gloss of the fibres is not very pronounced overall. The fibre edges are weakly defined and the surface is rough.

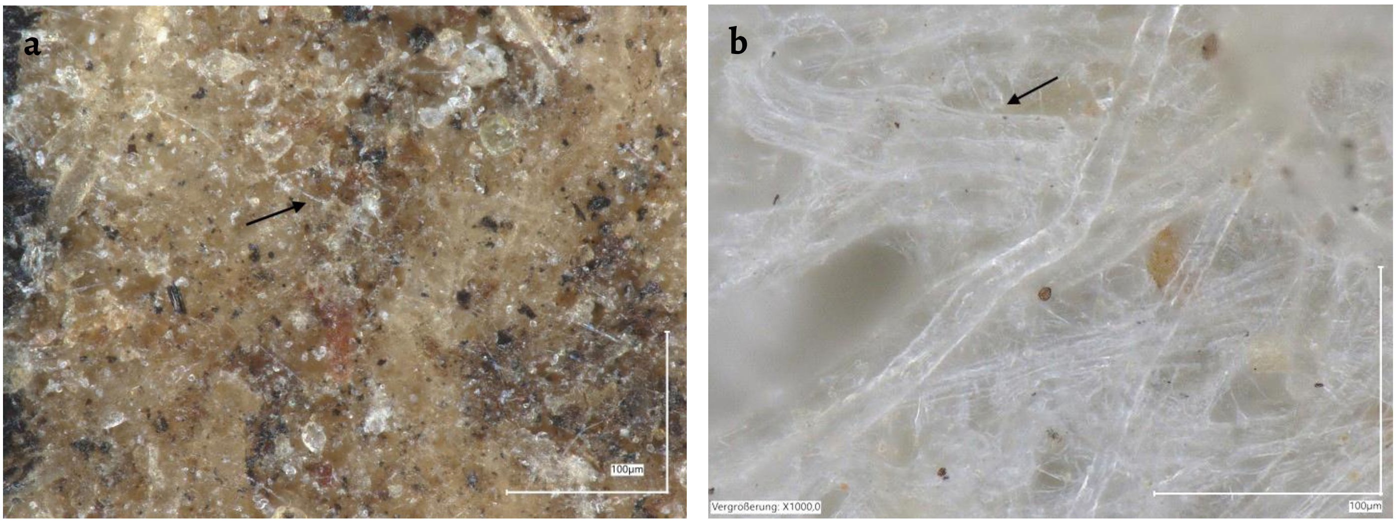

Figure 4. Samples after treatment with pure ozone: a) S2c: the mycelium lies fragmented on the paper surface; hyphae and hyphae residues are visible on and between the fibres as shiny particles and filaments (arrow); the surface has a grainy structure and microbial contamination has not been removed from the surface; b) S1c: the fibers show a significant loss of gloss and the fibre composition is weakly defined; the fibre cross-links are blurred at the edges, but there is a clear structure on the fiber surfaces; breaks in the fibre cross-link anchors are visible (arrow).

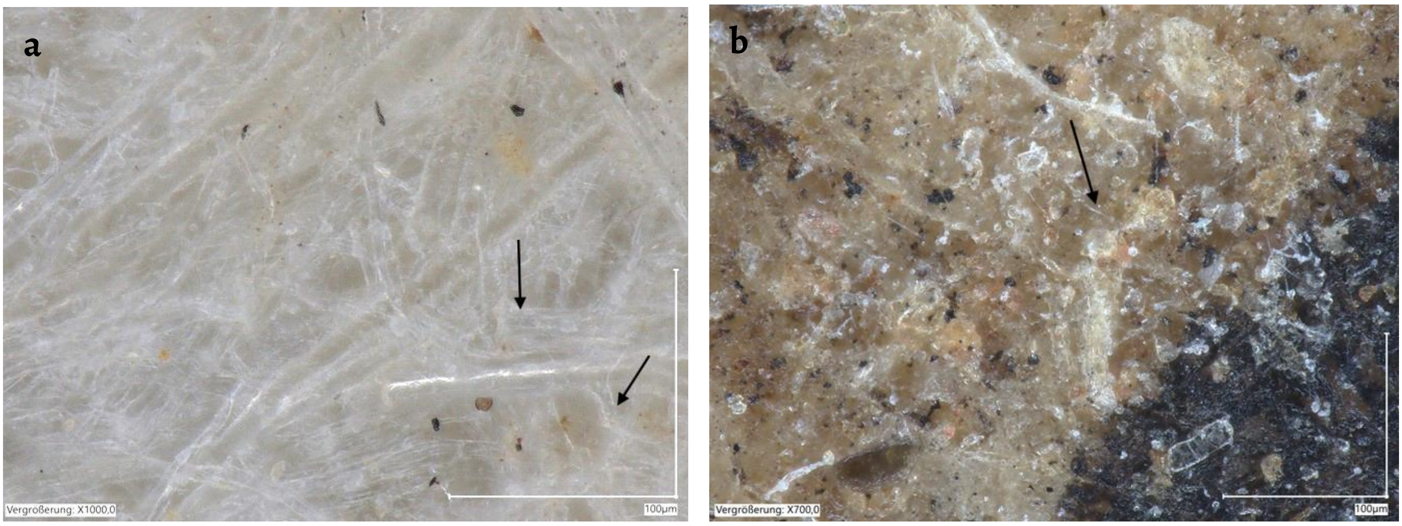

Figure 5. Samples after treatment with pure UVC radiation: a) S1a: the fibres show a massive loss of gloss at the fiber edges and the fiber cross-links appear blurred (arrows): structures are visible on the fibre surfaces; b) S2a: fragmented mycelial residues and hyphae are scattered across the surface (arrow) but have not been removed; the paper surface has a grainy texture and shows only a loss of gloss and the fibre edges are weakly defined.

Treatment with 1 % oxygen-argon plasma

The oxidizing effect of the treatment has a significant effect on the surface of sample S4: the hyphae were partial removed from the surface of the paper. Figure 6 shows that mycelium has been removed from the surface, but hyphae and hyphae residues remain between the fibres. The hyphae can be seen as thin, shiny lines. The fibre cross-linking in the deeper layers of the paper structure are intact, but the surface fibre cross-linking shows partial breaks and a loss of gloss on the fibre surface. The paper fibre is roughened at the edges of the affected area.

Treatment with 2 % hydrogen-argon plasma

After macroscopic examination of the surface of sample S3 with the naked eye, it was determined that the intensity of the pencil writing had been reduced by the treatment (Figure 7a). Under the microscope it can be seen that the pencil has been removed from the top of the surface of the uppermost fibres of the paper web (Figure 7b). Otherwise, the paper fibres show no significant change in surface gloss. A break in the fibre cross-link can be seen in the area where the pencil has been removed from the upper layer of the fibre.

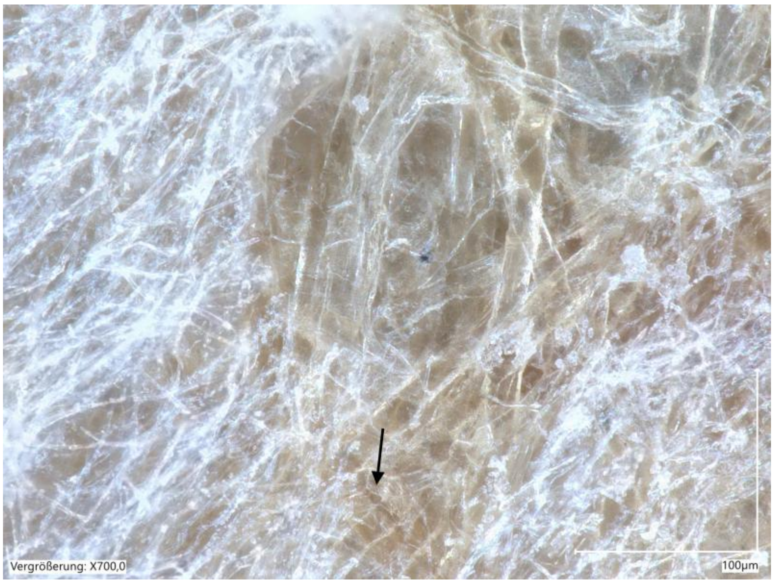

Figure 6. Sample S4, after treatment with 1% oxygen-argon plasma. The mycelium has been partial removed from the surface and the fibres are visible. Hyphae fragments can be seen between the fibres. The fibre cross-linking in deeper layers appears intact, while the surface cross-linking shows a loss of gloss and the edges are blurred (arrow).

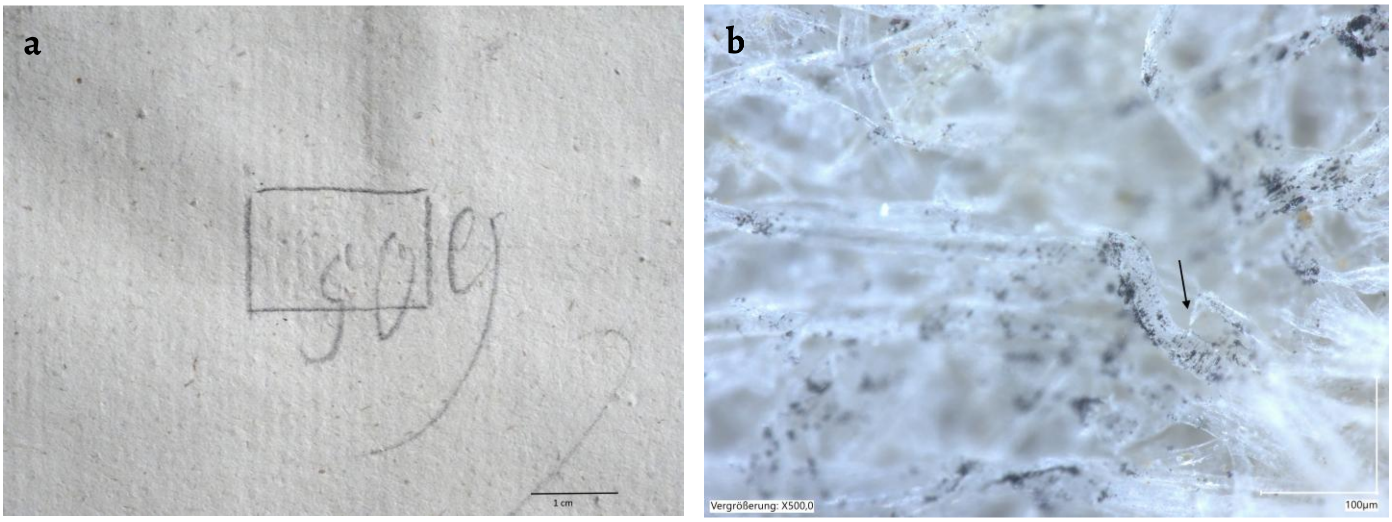

Figure 7. Sample S3, after treatment with 2 % hydrogen-argon plasma: a) The pencil writing faded in the upper area after treatment; the markings on the treatment area were covered during treatment; b) The pencil was removed from the top layer of the fibers and a break in the fibre cross-link in the area where the graphite has been removed, was observed; the fibre interlacing and surface structure of the fibres show no significant changes in the surface gloss.

Discussion

The Measurement of heat development under the selected test parameters shows only moderate heating of the paper and since no capacitive change in material moisture could be detected, it can be concluded that the paper can be treated with the plasma handheld device and NTAPP without the paper being permanently damaged by heat-induced degradation processes. The measured RH of the room shows a short-term decrease, which is due to the heating of the air. However, it should be noted that the paper can also emit moisture when heated. The duration of treatment affects this factor.

Oxygen-containing plasma forms ozone, which can be a threat to the user and the treated paper. The exact ozone content of the air plasma could not be determined because the measuring range was exceeded. However, it can be concluded that ozone is a strong component in the reactive species formed.

UVC radiation could not be detected, which may be related to the selected energy source. Since the plasma device is a handheld device, the UVC component must also be highly regulated for occupational safety reasons. In contrast, a significant amount of UVA radiation was measured. UVA radiation is not used for decontamination but can have a damaging effect on paper.

Treatment with air plasma versus pure ozone respectively pure UVC radiation treatment

Treatment of sample S2b with air plasma shows, in comparison to treatment with pure ozone (S2a) and pure UVC (S2b), that only plasma removes the mycelium from the surface. Ozone and UVC radiation treatment have degraded and partially pulverized the mould structures, but leave behind fragmented hyphae and mycelium residues. With all methods, mycelium residues remain between the fibres. The grainy structure of the surface of the paper is more pronounced after treatment with pure ozone and pure UVC radiation than after air plasma treatment.

A comparison of the samples S1 a-c shows that the oxidizing effect of the reactive parameters from the plasma leads to less loss of gloss on the paper surface compared to pure ozone and pure UVC radiation treatment. The loss of gloss is due to the roughening of the fibre surfaces, which affects the refraction of light under the microscope. After each treatment, the fibre cross-links show similar signs of oxidation, namely a slight blurring of the fibre walls, loss of gloss, and structuring of the fibre surface. In comparison, these signs are more pronounced with treatment with pure ozone and UVC radiation than with treatment with air plasma.

Treatment with air plasma versus oxygen-argon and hydrogen-argon plasma

Both the air plasma and the 1 % oxygen plasma reduce the mycelium on the paper surface. As can be seen in sample S4, the oxygen plasma has not yet removed the mycelium as effectively as the air plasma in sample S2b. In both cases, hyphae and hyphae fragments can still be seen on and between the paper fibres. The different depth effects may be related to the selected distances and the chemically reactive plasma components. In addition to ROS, air contains other reactive compounds and therefore appears to have a stronger decontamination effect than oxygen plasma at the selected working distance. This is also confirmed by a comparative examination of the fibre surfaces in S1b and S4.

Sample S4 shows a loss of gloss and structural changes only at the edge of the treatment area and at superficial fibre connection anchors. This effect is already more pronounced in sample S1b. At the selected distance and treatment duration, the oxygen plasma removed the mycelium, but the surface change of the paper is only minor.

While air plasma and oxygen plasma treatment did not cause any visually noticeable changes to the printed text, the 2 % hydrogen plasma visibly reduced the amount of pencil lead on the paper surface. This can be explained by the porosity of the pencil and the duration of treatment. Compared to oxygen-containing plasmas, hydrogen plasma has hardly caused any loss of gloss on the fibre surface. Only in the areas where pencil lead was also removed is damage to the fibre cross-linking visible. Overall, the changes to the fibre surfaces are less pronounced with hydrogen plasma than with oxygen-containing plasma.

Conclusion

Overall, the use of NTAPP for the decontamination treatment of historical papers is a promising method. As the here presented experiments have shown, mould growth can be reduced by the reactive components and physical effects of plasma treatment. However, it has also been found that the effect of these reactive components causes a change in the paper fibres, which manifests itself in the form of roughening of the fibre surfaces and changes in the fibre cross-links. Comparative studies with pure ozone and pure UVC radiation show that this change is significantly more pronounced than when plasma is used. A comparison of the used working gases shows that air produces a highly reactive plasma that delivers good cleaning results but also alters the paper surface. Hydrogen plasma also showed an abrasive effect, although the influence on the fibre surface appears to be less than with oxygen-containing plasma. Further research is needed to find the right parameters for removing mould without altering the paper surface or affecting the writing material.

Further perspectives

This paper focuses on the visual results after treatment with ozone, UVC radiation and NTAPP plasma with three working gases. In order to verify how these treatments chemically change the cellulose fibres and how these changes affect the stability of the paper and writing materials, further investigations and tests are needed to examine how these treatments chemically alter the cellulose fibres and how these changes affect the stability of the paper and writing materials. This includes, for example, FTIR- analyses of the paper and examining the composition of the reactive components of the working gases used for the plasma and investigating the depth effectiveness of the plasma with regard to the possible separation behaviour of blocked papers.

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