

A NEW TECHNOLOGY WITH POTENTIAL INTEREST FOR CONSERVATION OF CULTURAL HERITAGE: VAPORIZED HYDROGEN PEROXIDE STERILISATION (VHPS)

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1. Introduction

Deterioration of cultural assets, is strictly related to the characteristics of constitutive materials and to both environmental parameters (U.R., temperature, light) and presence of macro-micro biological systems. Microbial colonization (fungi, bacteria) induce deep alteration of materials up to molecular level, modifying the structure also under the macroscopic plane. Moreover, many microbial species are able to growth in different habitat, colonize inorganic/organic material, easily adapting to the changes of environmental conditions. At present the procedures utilized to block or control the biodeterioration of materials, are in relationship to the microbial species and to biocide chemical compounds, but frequently inadequate. In addition, sterilization procedures are usually impracticable in the indoor environments where the collections are stored, such as museum, library, archives, since it is impossible avoid contamination events that could be dangerous for the operators and the environment.

2. Sterilization by Vaporised Hydrogen Peroxide (VHPS)

The vaporised hydrogen peroxide represents a safe and repeatable sterilisation method, useful for the healthcare and life sciences sectors. The effectiveness of this methodology was showed by KIDA *et al.* (2007) using five kinds of carriers, contaminated with *Geobacillus stearothermophilus* spores, utilised as biological indicator [1]. Actually, this method useful for microorganisms (bacteria, fungi, virus) and spores is performed following different protocols, where efficiency and promptness of action is strictly

related to concentration and exposure time. Moreover, one peculiarity is the low degree of toxicity but, in contrast, negative aspects are the effectiveness during the time, the reactivity with metals (iron) and related corrosion phenomena. In this work we combine scientific information coming from the application of sterilization procedure in different fields such as medicine, pharmacology, nanotechnology, in order to develop a new applicative protocol focused on conservation/restoration of cultural heritage. The application of this technology allowed that:

- a) the procedure has to be performed on site; the procedure can be repeated in several runs;
- b) the procedure performs microbial biocide and sporocide activity;
- c) the human toxicity has to be controllable (safe working environment);
- d) the gaseous mixture has to avoid creating a cumulative chemical toxic burden;
- e) the validation and reproducibility of the decontamination process.

Utilizing this new ultrasonic technology, a multiple mixtures of gaseous solutions of hydrogen peroxide is produced, that: start to work at a very low humidity level already; avoid the condensation on cold surface spots (e.g. wall anchors); show a quick distribution within the treated compartment, reaching also the countless tiny sub-compartments. Particular interesting is the application of this technique for delicate works of art, and for microstructure of paper or textiles, which have to be handled very careful because of their mechanical instability. The development of treatment boxes (clean-rooms, airflows, etc.) and related sluice systems, allows the application of the method in a wide range of situations and works of art, avoiding contact with decontaminating gaseous substances during the manipulation.

The following example showed the reduction of spots, produced by fungi activity on cellulose and lignin molecules [2-3], identified on paper surface of ancient book page.

The documents (dated back to 1710 to 1790) involved in this study, belong to the bibliotheca of the Castle of Bärnegg¹ in der Elsenau in eastern Styria (Austria), forgotten and mistreated for a long time, were found and returned to Bärnegg by Mr. Di Romirer (Tech. Dir. Castle Laxenburg, Lower Austria).

Most of them were in bad conservation conditions and the restoration will take a long time and, in order to guarantee the success keeping the cost at a bearable level as well, in 2006 it was decided to utilize this new sterilisation technology to stop, or inhibit, the destructive processes in wood, paper and walls by employing, on site, the VPHS procedure.

A protocol was designed in order to perform the VHPS using a clean-room with specific characteristics, such as the possibility to operate an inspection of the whole room

system, of the wall, of the pipes that going into and out of the room, in order to put in evidence other possible leaks or cold spots.

The protocol followed these steps:

- Pre-designed and described DECONTAMINATION CYCLE, defining the Critical Control Point (CCPs)
 - Pre-phase of the DCC (De-Contamination Cycle)
 - Rising the concentration of the gaseous mixture to the best working concentration as fast as possible;
 - Avoid condensation (by measurement of the humidity at CCPs).
 - Decontamination – Sterilisation phase (De-Steri phase)
 - Avoid a lowering of the designed and calculated best working concentration by measurements at the defined CCPs;
 - Avoid a deviation of the temperature by measurements at CCPs.
 - Post-Steri phase. Desorption
 - Replacement of the gaseous atmosphere by fresh and not contaminated (spores or microbes) air.

Important remark

Each run has to be documented and controlled by measurements and bio-checks previously defined, in order to obtain information on about:

- ✓ streaming conditions and their influence in room system utilized;
- ✓ stability of concentrations and exposure conditions;
- ✓ physical-chemical interactions with material;
- ✓ effectivity and efficiency of the whole procedure.

This documentation guarantees the consequence of treatment, and is the most effective quality management tool to prevent mistreatment of rare and worthy pieces of art. Moreover, it is the only way to register unexpected events and to learn about the application of this method, in relationship with the cultural assets.

3. Results

The first picture showed the original surface of grey and dirty first page of an old (Arzney-buch, 1710-1730) paper manuscript, where small dark or dark brown spots, related to microbial activity, were spread over the whole page section, (fig. 1/A). The microbial growth was, for sure, induced by changes in humidity and temperature val-

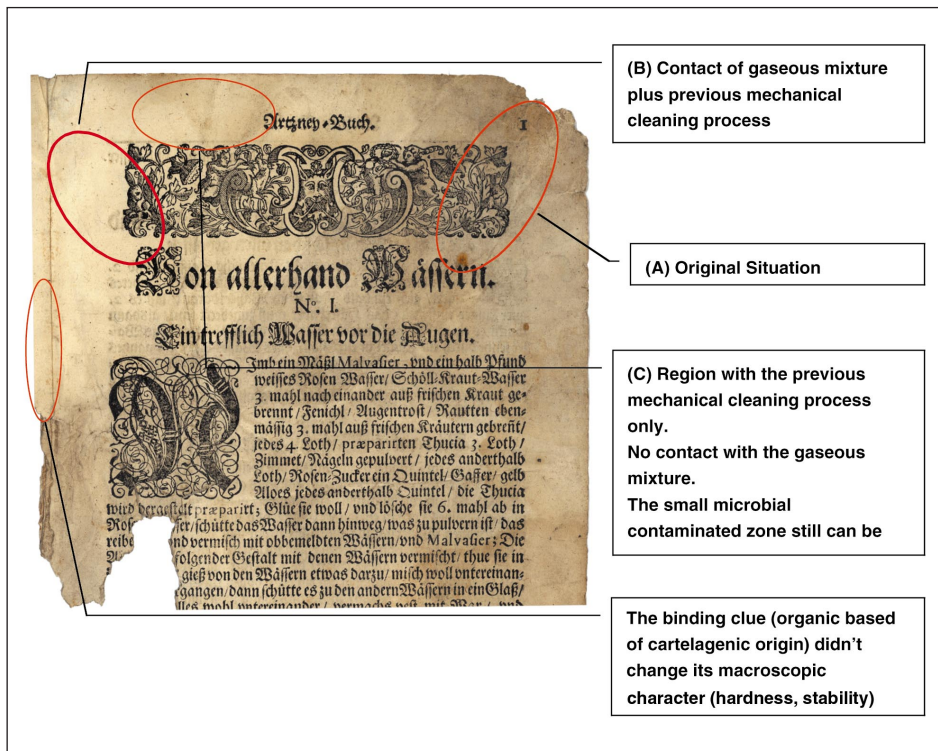


Figure 1. VPHS treatment of a degraded manuscript page.

ues, during the time of the bad documents conservation. In those conditions, even spores could be reactivated by temperature variations (22°C-28°C), changing their vegetative phase, performing, again, their destructive activity on the contaminated surfaces [2, 4].

The results of the pre-check step, showed that:

- there is not a reactive bleaching effect,
- the brightness of the background is related to the mechanical cleaning (fig. 1/B);
- print colour and intensity didn't changed after the contact with the gas (fig. 1/C).

4. Relationship between gas mixture-temperature-contacts time

During the process, the constant needs of fluid mixture is directly related with:

- temperature;
- the volume of the micro spaces consuming the gas in the structure;

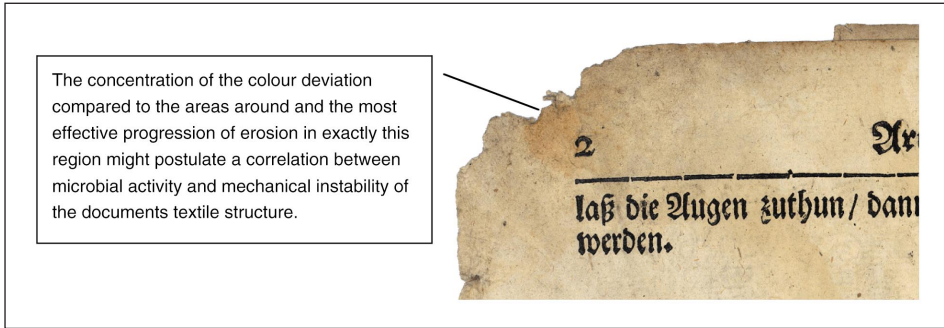


Figure 2

- adhesion and adsorbing ratio of the gas at the accessible surfaces and
- binding rate by the components of the layers (e.g. painting).

Moreover, a standard can be defined by using technical structures with a well defined surface area. Because of the changed behaviour of those particles with a diameter far below $2.5 \mu\text{m}$, the control and test area can be packed within a spongiform material. A test bodies can be loaded with biological test organisms and a count of the redetected active organisms gives us the limit of this method. In parallel, for safety reasons too – the measurements of various physical and chemical parameters have to be done.

The binding / desorption ratio is the leading parameter to calculate the total exposure time and even more important to estimate the $(\text{WPC}_{\text{max}})$ workplace² concentration you have to expect over the time.

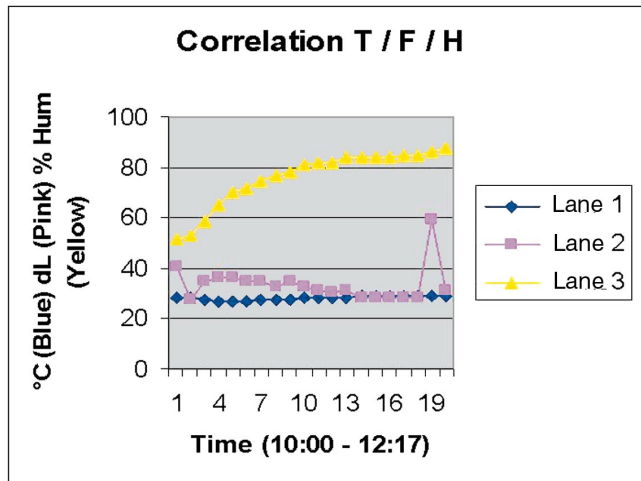


Figure 3. This graph reflects the needs for fluid in an artificial test environment with wood and plastic surface (1:1) and can be modified ad hoc.

5. Conclusions

As demonstrated on two samples the VHPS-Method is a sophisticated method to decontaminate pieces of art and to stop further destruction by microbial activity.

The application of this method can be performed:

- a) in an isolated workplace, with an high protective effect for the working expert and handcraft;
- b) in an total network of rooms as in an archive system;
- c) that firstly occurs the decontamination of assessments, under isolated conditions, followed by the decontamination of the storage rooms. After this two steps it guarantees a refilling of the archive with the already decontaminated sealed pieces;
- d) in these conditions a recontamination can be excluded.

Despite a toxic burden, an adequate personal protection (mask, avoiding direct contact to epidermal and mucodermal tissues) is required. The decontamination process can be adjusted to the needs on site and it is reproducible, controllable and validated and it fulfils the requirements of a safe working area.

Notes

- ¹ Old way of writing: Perneckh; therefore you have two interpretations of the name Bärnegg deducted from the name of the Perner or the bear also a figure in the nearby villages symbol.
- ² Maximal Concentration of toxic substance in the air on site = MAK (Maximale Arbeitsplatz Konzentration).

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Summary

The VHPS technology can be considered as a safer and more environmentally friendly method for decontamination of works of art, and environments, colonized by microorganisms (fungi, bacteria). The application of this technology allowed that:

- the procedure has to be performed *on site*;
- the procedure has to be repeated in several runs;
- the procedure has to perform microbial biocide and sporocide;
- the human toxicity has to be controllable (safe working environment);
- the gaseous mixture has to avoid creating a cumulative chemical toxic burden;
- the validation and reproducibility of the decontamination process.

In the present work we put together the information coming from the application of sterilization procedure from different field such as medicine, pharmacology, nanotechnology, in order to develop new applicative protocols, particularly for cultural heritage field.

Riassunto

L'innovativa tecnica basata sulla sterilizzazione con perossido di idrogeno vaporizzato (VHPS) permette la rimozione di alterazioni cromatiche, oltre ad inibire il degrado dei materiali costituenti manufatti scrittori ad opera di microrganismi. La tecnologia VHPS presenta le seguenti caratteristiche:

- possibilità di un controllo preliminare delle interazioni;
- applicazione *in situ*;
- assenza di ricontaminazione di materiali già sterilizzati in archivi, biblioteche e/o unità culturali, includendo anche l'ambiente di deposito nella procedura di decontaminazione;
- processo convalidato e ripetibile che, dopo l'avvio, procede automaticamente;
- nessun effetto tossico a lunga durata;

Inoltre, migliora le condizioni negli ambienti di lavoro per coloro che operano nel campo della conservazione e del restauro dei beni culturali.

Résumé

L'innovante technique basée sur la stérilisation avec peroxyde d'hydrogène vaporisé (VHPS) permet l'enlèvement d'altérations chromatiques, outre à interdire la détérioration des matériaux constituant des ouvrages écrits grâce à des microorganismes. La technologie VHPS présente les caractéristiques suivantes:

- possibilité d'un contrôle préliminaire des interactions;
- application *en situ*;
- absence de recontamination de matériaux déjà stérilisés dans des archives, bibliothèques et/ou unités culturelles, incluant aussi le milieu de dépôt dans la procédure de décontamination;
- processus validé et répétable qui, après le démarrage, procède automatiquement;
- aucun effet toxique de longue durée.

En outre, elle améliore les conditions dans les milieux de travail pour ceux qui opèrent dans le domaine de la conservation et de la restauration des biens culturels.

Zusammenfassung

Durch die innovative Sterilisationstechnik mit dampfförmigem Wasserstoffperoxid (VHPS) kann man Verfärbungen entfernen und dem von Mikroorganismen verursachten Verfall der Materialien von schriftlichen Artefakten entgegenwirken. Die VHPS- Technologie hat folgende Merkmale:

- die Möglichkeit, eine Vorkontrolle der Interaktionen durchzuführen;
- Anwendung *in situ*;
- keine Wiederkontamination von sterilisierten Materialien in Archiven, Bibliotheken und /oder kul-

turellen Anstalten, weil der Aufbewahrungsort in der Dekontaminationsprozedur eingeschlossen wird;

- es ist ein mehrmals bestätigter und wiederholbarer Prozess, der nach dem Starten automatisch läuft;
- keine giftige Wirkung langfristig;

Außerdem verbessert diese Technik den Zustand der Arbeitsplatzes für die Leute, die im Bereich der Konservierung und der Restauration von Kulturgütern tätig sind.

Resumen

La innovadora técnica basada en la esterilización con peróxido de hidrógeno vaporizado (VHPS) permite la eliminación de alteraciones cromáticas, además de inhibir la degradación de los materiales que constituyen piezas escritas por obra de microorganismos. La tecnología VHPS presenta las siguientes características:

- posibilidad de un control preliminar de las interacciones;
- aplicación *in situ*;
- ausencia de recontaminación de materiales ya esterilizados en archivos, bibliotecas y/o unidades culturales, incluyendo también el ambiente de depósito en el procedimiento de descontaminación;
- proceso convalidado y repetible que, después de la puesta en marcha, procede automáticamente;
- ningún efecto tóxico de larga duración;

Además, mejora las condiciones en los lugares de trabajo para quienes operan en el campo de la conservación y restauración de bienes culturales.

Резюме

Иновационная техника стерилизации при помощи испарений пероксида водорода (VHPS) позволяет устранить хроматические видоизменения, помимо того, что замедлить разрушение рукописных материалов, вызванное микроорганизмами. Техника VHPS имеет следующие характеристики:

- возможность предварительного контроля взаимодействия материалов;
- применение *in situ*;
- отсутствие повторного загрязнения уже простерилизованных материалов в архивах, библиотеках, культурных центрах, включая также место нахождения материалов в процессе стерилизации;
- процесс проверенный и проведенный неоднократно, который после его запуска в действие все делает сам;
- никакого длительного токсического эффекта.

Кроме того, улучшает условия труда тех, кто работает в сфере сохранения и реставрации предметов культурной ценности.