Non-toxic methods and systems to control biodeterioration in historic objects of large size

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Summary

The novel Veloxy® system has been produced as a non-toxic insect elimination procedure. This apparatus, which creates a low-oxygen environment, has been validated for the de-infestation of objets d'art. Veloxy® is a portable piece of equipment which works in situ, producing large volumes of nitrogen. It enables the treatment of delicate ancient objects in large enclosures in which an artificial environment is maintained. The machine is designed to generate specific conditions that improve the efficacy of the de-infestation treatments. It is safe and easy to handle in museums, archives, libraries and other cultural institutions. Moreover, a nitrogen atmosphere at low relative humidity has been found to be an effective method of stopping or decreasing microbial contamination of historic materials.

Bio-deterioration control using portable nitrogen-producing equipment

A low-oxygen environment can be used to eliminate insects in museum objects, a method which provides an alternative to toxic chemicals. In fact, since 1989 nitrogen atmospheres have been utilised to control bio-deterioration in Egyptian mummies (VALENTIN, 1989), library collections, furniture and many other historic objects (GILBERT, 1991; MAEKAWA, 1996; SELWITZ, 1998). The artefacts are placed in a gas-proof plastic bag, and the air is replaced by an inert gas, achieving the complete extermination of insects by anoxia. The inert gas, usually nitrogen, is provided by cylinders. This method has been found to be effective and inexpensive. However, the de-infestation of single large objects using low-oxygen environments presents problems which are difficult to solve and increase costs significantly. For these purposes, a novel and environmentally-friendly tool called Veloxy® has been investigated as an alternative procedure for the large-scale de-infestation of historic artefacts.

The Veloxy® equipment separates nitrogen from the other air components by means of a membrane system. The separation system is made up of bundles of tiny hollow polymeric fibres, which are attached to a manifold. An air compressor is connected to Veloxy® to provide pressurised air. Thus, oxygen and minor compounds of air permeate through the walls of the fibres, producing a nitrogen flow of high purity. The Veloxy® equipment has been validated as part of the EU 'Save Art' project (ENV4-CT98-0711) for the de-infestation of furniture, polychrome sculpture, natural history and large book collections.

Objectives

The main objective was to develop an effective and easy procedure to eliminate bio-deterioration of art collections on a large scale. Thus, we focused our work on the validation of a portable piece of equipment to treat infested art objects made of wood *in situ*. Other goals included:

- Assessment of the system for eliminating resistant insects in objects of large size.
- Design of a protocol to treat art collections using different low oxygen concentrations and various environmental conditions.
- Evaluation of the efficacy of the apparatus in controlling microbial activity.
- Protection of the health of the users and the environment.

Method and Protocol

Spain has different climatic regions that contribute to the development of many species of bio-deteriorating insects. Consequently, a survey was carried out during 1999-2001 in museums, archives, libraries, monasteries and convents to detect the presence of active larval or adult insects infesting cellulose objects, such as furniture, polychrome sculptures, altar pieces, wood paintings, books, frames and textiles. This work allowed us:

- To identify the communities of insect species developing in different environments and materials.
- To study the distribution and frequency of species involved in the deterioration of specific objects.
- To determine the risk of infestation in museums.
- To study the relationship between type of wood and insect species.
- To use the most appropriate insect species as a model for experimental research into anoxia treatment.

This search indicated the progressive infestation of art collections by *Anobium punctatum*, *Lyctus brunneus*, *Hylotrupes bajulus*, *Nicobium castaneun, Oligomerus ptilinoides, Anthrenus flavipes, Anthrenus verbasci,* *Attagenus unicolor, Attagenus pelio, Tineola biselliella* and especially by the termite *Reticulitermes lucifugus*. The last of these was detected on the Mediterranean coast and in the southern, north-western and central regions of Spain. Species of the *Anobiidae* family were found in works of art made of pine, oak, walnut, cedar, cherry, holm-oak, cork and chestnut. *Cerambycidae* insects were isolated from pine, cherry, oak, holm-oak, cork and walnut wood. *Dermestidae* species were mainly isolated from textiles made of silk and wool and from wooden objects made with the help of organic adhesives.

Anobium punctatum, Lyctus brunneus, and *Hylotrupes bajulus* were the most common insects found in wooden works of art. Objects made of coniferous wood were very susceptible to infestation. They were selected from furniture, polychrome sculpture, frames and altarpieces. The full range of developmental stages of these beetles were used as an experimental model to investigate the effect of low-oxygen environments on mortality.

Experimental

According to the methods used by VALENTIN, 1993, various groups of insects at different developmental stages were placed in pine wood samples provided with a central gallery in which the insects were housed. The external hole was covered with a wooden layer to simulate insect infestation in a real object.

Three samples were used for testing each stage of the life cycle of *A. punctatum, L. brunneus* and *H. bajulus*. These analyses were performed using 20 insects per sample. The eggs were transferred with a soft brush to the wooden test samples. After exposure, the number of treated insects surviving was counted at approximately 24-hour intervals for 3 weeks. Insects which showed any sign of movement were considered to be alive. Treated eggs and pupae which did not hatch after three weeks post-treatment exposure to the air were taken to be dead. In the case of pupae and eggs of *Hylotrupes*, the treated insects were counted at an interval of about 2 days for a duration of nine weeks.

Groups of infested wood samples were placed in low-permeability plastic bags and purged with humidified nitrogen. Art-sorb, equilibrated at the appropriate relative humidity (RH), was used to maintain the selected RH in each bag throughout the treatment. The bags were then kept in an incubator at a constant temperature for 1 to 3 weeks. Different combinations of RH, temperature and oxygen concentrations were used to eliminate infestation. Insect monitoring was maintained in a normal-air atmosphere under otherwise identical environmental conditions for 3 weeks.

Protocol

Based on our practical results, a protocol has been designed to carry out de-infestation treatments. It is summarised in the following points:

- Identify the type of insect.
- Using gas-proof plastic, construct a hermetic enclosure containing the infested object.
- Replace the atmospheric air in the enclosure with high purity nitrogen with an adequate flow, temperature and relative humidity, until the oxygen concentration has been reduced to lower than 0.2%. This is called the dynamic phase.
- Disconnect the nitrogen flow and maintain a low-oxygen environment for 2–8 weeks, depending on the size and material of the object and type of insect. This is called non-dynamic treatment.
- To eliminate insects in objects installed in enclosures of large size, exceeding $10 m^3$, a dynamic system maintaining a continuous low nitrogen flow for the whole of the treatment is necessary (Figures 1 and 2).

Figure 1. Objects of large size in a hermetic enclosure.

Figure 2. Veloxy equipment maintaining a nitrogen flow in the enclosure.

Table 1. Parameters used for the de-infestation of non-polychrome wood artefacts utilising the Veloxy® system.

Type of treatment	Bag size (m^3)	T (°C)	RH (%)	Maximum oxygen accepted (%)	Insect family	Exposure (days)
Semi-dynamic*	0.5–2	18–22 23–25	50–60 45–50	0.1 0.2	Anobiidae Lyctidae Dermestidae	15
Semi-dynamic	0.5–2	23–25	60–80	0.1	Anobiidae Lyctidae Dermestidae	25
Semi-dynamic	0.5–2	23–25 z	80–90	0.002	Anobiidae Lyctidae Cerambicidae	>30**
Semi-dynamic	2–10	18–22 23–25	50–60 45–50	0.1	Anobiidae Lyctidae Dermestidae	25
Dynamic	2–10	18–22 23–25	60–80	0.1	Anobiidae Lyctidae Dermestidae	30
Dynamic	10–50	18–22 23–25	50–60 45–50	0.1	Anobiidae Lyctidae Dermestidae	40
Dynamic	50–100	20–25	45–60	0.2	Anobiidae Dermestidae	50
Semi-dynamic	0.5–2	23–25	45–60	0.005	Cerambycidae	20
Dynamic	2–10	23–25	45–60	0.005	Cerambycidae	25

*A semi-dynamic treatment corresponds to a continuous nitrogen flow until low oxygen levels have been achieved. The system is then continued for various time periods without using the gas flow.

**Larvae were found alive.

The de-infestation of large polychrome sculptures has proven to be quite difficult. To optimise the application of the system, a long exposure time may be necessary, depending on the materials involved and the size of the object.

The results obtained are shown in Tables 1 and 2. The parameters established indicated complete insect extermination in wooden objects treated in enclosures in a range of 1 to 100m^3. The environmental conditions depended on the type of wood, insect and art technique.

For the de-infestation of art pieces in plastic enclosures of a volume lower than 2m^3, the following parameters have been established:

Objects: Books, textiles, furniture infested by: *Anobiidae, Lyctidae, Dermestidae, Tineidae.*

– Temperature: in a range from 23–25°C.

– Relative humidity: in a range from 50–55%.

– Oxygen concentration: 0–0.1%.

– Exposure time: 2 weeks.

Objects: Furniture and wooden objects infested by *Cerambycidae.*

– Temperature: in a range from 23–25°C.

– Relative humidity: in a range from 50–60%.

– Oxygen concentration: 0–0.05%.

– Exposure time: 3 weeks.

Objects: Delicate museum artefacts including silk textiles, leathers, parchments, paintings, mummies, which have been infested by *Anobiidae, Lyctidae, Dermestidae, Cerambycidae*.

– Temperature: in a range from 21–23°C.

– RH: identical to the RH in the exhibition room.

– Oxygen %: 0–0.05% depending on the insect.

– Exposure time: 3–4 weeks depending on the RH, materials and insect.

Table 2. Parameters used for the de-infestation of polychrome wood artefacts utilising the Veloxy® system.

Type of treatment	Bag size (m^3)	T (°C)	RH (%)	Maximum oxygen accepted (%)	Insect family	Exposure (days)
Semi-dynamic	0.5–2	18–22 23–25	50–60 45–50	0.10.2	Anobiidae Lyctidae Dermestidae	20
Semi-dynamic	0.5–2	23–25	60–80	0.1	Anobiidae Lyctidae Dermestidae	30
Semi-dynamic	0.5–2	23–25	80–90	0. 002	Anobiidae Lyctidae Cerambycidae	>30*
Dynamic	2 – 10	18–22 23–25	50–60 45–50	0.1	Anobiidae Lyctidae Dermestidae	25
Dynamic	2 – 10	18–22 23–25	60–80	0.1	Anobiidae Lyctidae Dermestidae	35
Dynamic	10 – 50	18–22 23–25	50–60 45–50	0.1	Anobiidae Dermestidae	45
Dynamic	50 – 100	20–25	45–60	0.2	Anobiidae Dermestidae	55
Dynamic	0.5–2	23–25	45–60	0.005	Cerambycidae	25
Dynamic	2–10	23–25	45–60	0.005	Cerambycidae	30

*Larvae were found alive.

Microbial control

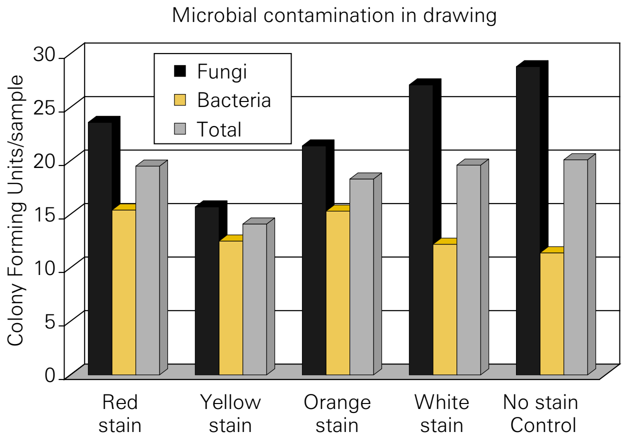
As an extension of this work, developed in the 'Save Art' project, a nitrogen atmosphere was used to control microbial contamination in historic materials. In previous research, a low-oxygen environment was found to be an effective method of stopping or decreasing fungal and bacterial growth (VALENTIN, 1990). In fact, most of the fungi involved in the deterioration of cellulose and proteinaceous materials are aerobic. Anaerobic bacteria can develop at low oxygen levels, however they need very high water activity for their development (higher than 0.98). Consequently, we carried out our experimental work using a dynamic nitrogen flow at RH of 50 ±5% to arrest the growth of cellulose micro-organisms.

Practical applications were performed using Veloxy® to treat a drawing on paper (400 × 380cm) contaminated by *Aspergillus, niger, Penicillium sp., Cladosporium herbarum, Thrichoderma viride, Actinomyces sp* and *Bacillus subtilis*, which had produced different stains on the support. The equipment was working in a dynamic system producing a very low flow of nitrogen (1 l/minute). The conditions were stabilised at 50% RH, 22°C temperature, and 0.002 oxygen concentration for 3 weeks. Microbial analyses were carried out to evaluate the contamination in the treated drawing. The results showed a drastic decrease of micro-organisms in all the samples tested as shown in Figure 3.

Using low oxygen environments for microbial control, it is essential to apply a dynamic system producing a low flow of nitrogen during the whole treatment. Thus, the moisture content in art supports should be properly decreased – in relation to the composition of materials – to avoid risk of drying damage. After the treatment, it is important to keep the objects in a ventilated environment to avoid the increase of moisture content, or water condensation on the materials. Maintenance and microclimate control through measurement of environmental parameters (CAMUFFO, 1998) is the best method for guaranteeing the preservation of cultural heritage

Conclusions

A new type of portable equipment, Veloxy®, has been developed for the de-infestation of historic objects, in-



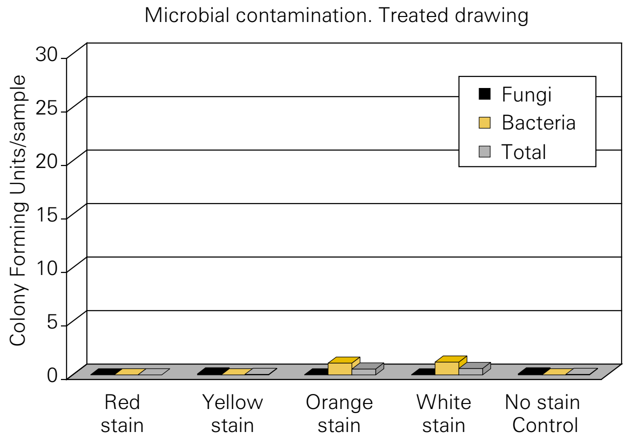


Figure 3. De-infestation of stained paper using dynamic nitrogen flow at RH of 50%.

cluding artefacts of large size. This dynamic system works *in situ,* without necessitating the transport of art, and thus avoiding risk of damage. In addition, instruments have been designed to monitor the process.

The efficiency of the treatment can be enhanced using a low RH (50–55%) and a temperature in the range of 23–25°C. These conditions favour insect desiccation. A high relative humidity (over 85%) protects insects against anoxia.

The equipment is easy to use and safe for the public in museums and archives. Staff members will not need to handle toxic and dangerous products. Moreover, the system avoids risk to the environment. The cost per treatment on a large scale is reduced by 60%, excluding the initial expense of the apparatus. This is due to the low cost of gas production and the reduction of time and personnel required to control the whole process.

This system has been found to be effective in stopping or decreasing microbial activity in historic collections. The moisture content of the material should be monitored to guarantee the efficacy of the treatment.

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