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A new approach on conservation of wooden heritage

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ABSTRACT

Biodeterioration of wooden art objects has to be treated in a more delicate manner than biodeterioration of wood. Any treatment applied to the art object should not alter the visual, structural or scientific integrity of the object. These requirements therefore restrict the use of biocides and some alternative treatment procedures like high and low temperatures and radiation. Fortunately, an alternate procedure is available, anoxic treatment using argon gas, that has so far proven to be effective at killing all insects stages of life and some fungi important in wood degradation. The argon anoxic procedure is described in this paper.

Key words: gwenmghwritmh

INTRODUCTION

One of the most potentially damaging problems that a museum collection, composed of wooden artifacts, faces is the threat of biological infestation. This may be in the form of insect and/or microbial, particularly fungal, attack. When an outbreak occurs it will have to be dealt with in a manner that is safe for the art, personnel, and environment while at the same time being effective in eradicating the infestation. Treating art objects leads to some interesting dilemmas: in general, the treatments normally used, i.e., biocides, that may be very effective in eradicating the problems have undesirable side-effects on the material that is being treated. In addition, through the course of history, and especially in modern times, artists have experimented with a wide variety of techniques to express their creative visions. Sometimes the materials used to create the vision are known or can be determined by chemical analysis, more often they are not known. The end result when a biocide(s) is applied to an art object may be an unintended alteration in the appearance and/or scientific content of the art object.

Research in recent years has focused increasingly on finding viable non-chemical alternatives to treating museum collections for biological infestations. Alternative techniques have included the use of high or low temperature, use of gamma radiation and the use of anoxic environments. The most promising of these is use of anoxic environments, generated with argon or nitrogen gas (with argon being more efficient and effective than nitrogen, especially for control of fungal infestations).

Problems with biocides

Conservation of works of art carries with it a unique set of philosophical and material considerations. The philosophical considerations revolve around prescribing treatments that have the potential to alter the original art work. The material considerations involve understanding the diverse materials of which art works may be composed, both the original material and previously introduced conservation or restoration material, and evaluating, as far as possible, what the effect of a new treatment is likely to be on those materials. Reviews of problems with biocides and cultural objects can be found in Allsopp and Seal (1985), Caneva et al., (1991), Dawson (1986), Pinniger (1994), Story (1985). In general, all biocides are reactive products and many, if not all, have caused alterations in some kinds of works of art.

Methyl bromide, for example, breaks sulfur bonds; it may weaken materials and produce noxious odors and it is not used for sulfur-containing materials anymore. This product has other serious side effects: Some reports claim it attacks the atmospheric ozone layer fifty times more effectively than CFCs do (http://www.gaiabooks.co.uk/environment/methyl.html). As a result, a worldwide phase out on methyl bromide is underway (http://mbao.org/mbrqa.html, http://www.pan-uk.org/pestnews/pn23/pn23p11a.htm).

Ethylene oxide is very effective in killing insects and fungi; it is still used extensively in hospitals. Unfortunately for art objects, though, it may be trapped in lipid-containing components of the art, e.g., parchment and leather. Ethylene oxide is also highly toxic to humans. The U.S. Environmental Protection Agency recommends no more than a time-weighted average (TWA) of 1 ppm/day. (This is a TWA over an 8-hour work day. For comparison, consider that the TWAs for methyl bromide and sulfuryl fluoride are both 5 ppm.) Ethylene oxide is further classed as a suspected human carcinogen. The U.S. Library of Congress has recently determined that it takes at least 14 cycles of outgassing before ethylene oxide residues reach low enough values to permit handling of fumigated library materials (Dr. C. Shahani, personal communications, 1994).

Sulfuryl fluoride, the fumigant most recently used by museums in the U.S., has been found to actually melt the surface of some pigment systems in tests conducted by my laboratory at the Metropolitan Museum of Art. In the study, 10 out of 11 pigment systems were altered by this fumigant. We have since banned the use of this product for any art object in our collection (Koestler et al., 1993).

Alternate approaches to control of insects or microbes in art

High temperature

Certain non-chemical methods for insect eradication have been effective in industry but have not been used in museums. Heat has been experimented with in the grain industry. It has been found that it is easier to kill insects with high temperatures rather than low temperature exposures; higher temperatures are generally lethal more rapidly and with less change in temperature than low temperatures. For instance, while the lethal temperature and exposure varies between species of insects (Arbogast, 1981; Kenaga and Fletcher, 1942), an exposure of 130F for three hours is considered sufficient to kill all stages and species (Story, 1985). Researchers have also found sub-lethal high temperatures at which reproduction ceases completely (Arbogast, 1981).

Whatever its apparent effectiveness for killing insects, heat has effects on objects that probably make it unacceptable for museum applications. A common conservation science technique to artificially age materials uses heat. If the flow temperatures of adhesives and coatings fall within the range of the heat exposure, this could present major problems. A concern with wood is that with an increase in temperature there is a reversible decrease in the strength of the wood that may be permanent at high temperatures or prolonged exposure (Hoadley, 1980). Thermal expansion also occurs in wood, so grain orientation across joints and supports should be understood (Story, 1985). Even more severe than the high temperature alone is the change in relative humidity that accompanies it; the shrinking of organic materials that results from desiccation as temperatures increase is greater than the counter effect of thermal expansion (Hoadley, 1980).

Microwave energy and other radio frequency energy have also been experimented with as a method for killing insects (Nelson, 1973). Microwave energy refers to the range of radio frequency energy with frequencies between 1GHz-100GHz or wavelengths between 30 cm-3 mm. Energy in this range increases vibration along chemical bonds, and creates heat by the friction of this movement. The lethal effect in this range seems to be largely thermal, or at least studies have not been able to isolate lethal non-thermal effects of this energy on insects (Nelson, 1973). However, in surviving insects some mutations and physical injury have been noted (Nelson, 1973). As with heat treatments, sub-lethal doses will reduce reproductivity, and in general, adults are more susceptible than immature stages to this treatment (Nelson, 1973).

Setting radio frequency energy apart from other heating techniques in terms of its potential applications, it was theorized that at these energy levels the dielectric properties of the host material and insect could be exploited to yield selective heating of the insect over its host material, and thus avoid injuring the host material (Nelson, 1973), for instance wood. Along with the dielectric properties of a material or organism and the frequency of applied energy, temperature and moisture content determine the rate of energy absorption by a material. Experimentally this theory did not prove to have any consistent reliability, as might be expected from the number of variables that need to be controlled. A better degree of selective heating of insects over their host material was obtained at low radio frequency levels (10-100 MHz) rather than at microwave energy levels (Nelson, 1973). Microwave and other radio frequency energy treatments for eradicating insects do not seem, then, more promising for museum applications than any other heat treatments

Low Temperature

The use of freezing for control of insect infestations with museums or archives is quite extensive, despite the lack of scientific studies that demonstrate its safety. The procedure is effective, if done correctly, and is cost-effective for large numbers of objects. There is, however, some suggestions that mixed materials may not be appropriate for this procedure. One concern is the possibility of water freezing within the artifact. Most organic materials in museums are said to be in the 8-12% moisture content range (Florian, 1986; Strang, 1995), and this moisture is believed to be "bound" and thus not available for ice formation. Whether this is the actual case in real situations involving aged materials is unclear. Another unresolved issue is the degree, if any, of swelling that occurs in wood under the changing relative moisture content that occurs during freezing and warming of the object and if this presents a problem in the long term for the wooden object. The few published studies have assessed the effects of freezing on modern materials, e.g., paper (Björdal, 1998), wool (Jansson and Shishoo, 1998), and cotton, linen and wool (Peacock, 1999) rather than on actual museum objects so the extrapolation of the results are problematical. Even in these studies there was some indication of possible problems in paper and linen, in particular. Further, in depth, scientific research is needed in this area.

Radiation

Ultraviolet radiation has been used to kill insects, with research showing that the shorter the wavelength of the UV energy, the greater the insect mortality (Cohen et al., 1973). Since we constantly struggle to protect our museum collections from exposure to ultraviolet energy, it must be apparent that this range of energy would be an inappropriate museum biocide.

Gamma radiation has been considered as another possibility. A 30-50 krad or .03-.2 kGy (1Gray=1 J/kg) dose has been shown in at least three experiments to kill or sterilize all stages and species of insects tested (Brower and Tilton, 1972; Brower, 1973; Tilton et al., 1978) with eggs being the most vulnerable stage and adults of all species the least vulnerable to radiation. Complete sterilization implies an equally effective eradication of the insects but over a longer period of time, often several weeks; a rapid kill of all stages would require doses well over 100 krad (Brower and Tilton, 1972).

The damaging effects of gamma radiation on museum and archive materials have been discussed and tested. Story (1985) makes reference to the adverse effects of gamma radiation on certain plastics, including polyacetals, polypropylene, and fluorocarbons, and to possible color changes of other plastics, such as polyvinyl chlorides and acrylics, and glass. Irradiation causes cross-linking and chain scission in various organic polymers that may continue long after the dose by auto-oxidative degradation (Chappas and McCall, 1984). Physical changes associated with degradation include decreases in the elasticity, tensile strength, and solubility of cellulose- and/or lignin-containing paper (Horakova and Martinek, 1984). Non-living material can withstand a finite amount of radiation beyond which failure may occur. In addition, radiation may alter the scientific content of the material thus leading to loss of information or erroneous conclusions in future tests. Recent tests by Erhardt et al. (2003) on mixed materials that were subjected to gamma irradiation for disinfection of mail delivered to parts of the U.S.A. showed a range of damage that occurred on paper, film, glass, and gems. Some of this material is likely to be part of a wooden art or cultural heritage object and therefore may likely exhibit some of the same undesirable side-effects if gamma irradiated, as may the wood itself.

ANOXIC APPROACH TO PEST CONTROL

Research undertaken over the past 15 years has shown that the use of anoxic gases is effective in eradicating insect infestations in museum objects. An anoxic gas is one that is essentially inert; examples are helium, nitrogen, and argon. Such gases are nontoxic, nonflammable, and nonreactive. Nitrogen gas has been used for decades by agricultural services and government agencies around the world to control insects in granary silos. Helium gas had been used for more than 45 years to protect one of the most important historical documents in U.S., the Declaration of Independence; it has recently been replaced with argon gas.

Since the early 1990s, argon gas has been the technique of choice at the Metropolitan Museum of Art, it is also used at the museums of the Smithsonian Institution, the Museu d'Arte in Sao Paulo, Brazil, the Singapore Art Museum, and the Restoration Center of the Republic of Slovenia, among other art collections.

The anoxic gas method for insect control

The concept of anoxic treatment is simple, and is the same for any anoxic gas used. It consists, essentially, of the following three steps:

1) Isolate the object from the oxygen-rich environment;
2) replace the oxygen-rich air with an anoxic (oxygen-less) air; and
3) wait until the insects die and then remove the object from its anoxic environment.

While simple in concept, each step requires an understanding of environmental, physical, and biological factors that may affect the procedure. An overview of these steps is given in Koestler (1992, 2001).

Perhaps the most important of the three steps is isolation of objects. Isolating an object requires construction of a suitable barrier around the object. The anoxic environment necessary to kill all stages of insects in a reasonable amount of time (i.e., 3-4 weeks) requires an oxygen environment of less than about 500 ppm (0.05%) of O_2. This means any enclosure system must successfully maintain such a low level of oxygen for extended periods of time, ideally with a minimum of intervention and cost.

There are basically two methods of doing this: build either a solid-walled container system or a soft-walled one.

A solid-walled container system may be cost-effective if a large number of objects have to be treated, keeping the chamber in operation continuously for many years. In such a system all connections--humidity control system, oxygen monitoring system, temperature control system, gas flow system, or oxygen scrubber system--are "hard-wired" into the sides of the chamber. Each must be leak-proof, as must the door seams into the chamber. Such chambers are expensive, on the order of $100,000-200,000, and tend to leak, making oxygen levels below 0.3% difficult to maintain without constant input of new gas or constant "scrubbing" of oxygen from the air. A chamber may also require a service contract and a full-time technician, adding to the overall expense of operations.

A soft-walled enclosure system can be constructed from heat-sealable plastics, which can be made to low-oxygen leakage rate specifications that make it easy to achieve and maintain the required low-oxygen environment. In such a system, all of the control systems for temperature, humidity, and oxygen level are connected on a temporary basis, as needed. Once the internal conditions in the enclosure are set, there is usually no need to alter or readjust them. Monitoring of the bags becomes a matter of rapid visual inspection and occasional instrumental monitoring.

A soft-walled enclosure system can be easily transported to the site of the infested objects and built around those objects. This is especially important for large or odd-shaped wooden objects of cultural heritage (altars, organs, statues, credenzas…). This reduces the cost of treatment, since packaging and transporting the object become unnecessary. In addition, treatment on site reduces the risk of breakage during transport and the risk of infesting other objects during packaging, transit, and treatment.

A hard-walled enclosure system can only be started up six to seven times a year due to the long treatment times necessary to ensure insect death, and once the operation commences it cannot be interrupted to place new objects into the chamber. A separate soft-walled enclosure system, however, can be built quickly and easily around each and every object infested without interfering with objects already undergoing treatment.

Another advantage of a soft-walled system is that it can be built to conform to the shape of the infested object(s), thus reducing the volume of gas needed. A chamber system, by contrast, requires the same volume of treatment gas whether it has one or many objects within it.

Other drawbacks of a hard-walled system are that the door seam requires maintenance or replacement with some frequency, and loading and unloading of the chamber can be time-consuming and potentially more dangerous for the objects than with a soft-walled system.

The initial cost of a soft-walled bagging system is on the order of $20,000 to $40,000, depending upon quantities of bagging material ordered.

Choice of inert gas

The inert gases that have been used in the museum field for restricting or eradicating insects are helium, nitrogen, and argon. Each has certain advantages and disadvantages. The gas with the most advantages and least disadvantages is argon. A summary of the reasons is given below:

Helium. Helium has been used for more than 45 years to preserve one of the most important historical documents in the U.S., the Declaration of Independence. The enclosure for this document was something of a minor engineering feat since helium diffuses so easily through most materials. Helium is considered to be a totally inert gas. What this means is that it does not react with anything else. Helium is the most expensive of the three gases mentioned here, but considering the valuable document it protects, cost was an insignificant factor. It was more important that the gas not be able to react with anything in the document, and that the gas does not encourage or support anaerobic life (that is, life that grows in the absence of oxygen). Despite the advantages of this gas, the helium cases have now been replaced by argon-filled cases; one reason is that there is less gas leakage with argon.

Nitrogen. Nitrogen has been used for insect control in food storage silos for decades. A superficial understanding of its use there can lead one to conclude that it will be useful in the art field, but there are some potential drawbacks that restrict its utility for art. For one thing, nitrogen is not really inert. Although at normal room conditions it is not believed to be reactive, nitrogen gas is an essential requirement for some anaerobic microbes—microbes that can survive when oxygen levels are low and when humidity levels in the material is conducive to their growth.

Argon. Argon is the gas of choice for many collections and museums, including the Metropolitan Museum of Art, which has pioneered the use of this gas in the museum community. Argon shares the inertness of helium, but it costs less. It is also easier to keep in an enclosure than is helium, since it is a larger molecule. Argon does not share any of the disadvantages of nitrogen; it is not used as a nutrient by any organism and it cannot be converted into any other product. In addition, argon is heavier than oxygen, and therefore will sink to the bottom of an enclosure, pushing any remaining oxygen to the top of that enclosure, while nitrogen will rise to the top. This has the effect of producing a lower oxygen environment at the bottom of an enclosure, where an object usually rests. In the case of wooden objects it will push the oxygen out of wood cell lumina thus reducing the length of time the object needs to be in the anoxic environment for the treatment to be effective. Valentin et al. (1992) found that argon was 25-50 % faster at killing insects than nitrogen. She attributed this difference to faster desiccation of the insects in argon. It seems more likely that the difference is due to the ability of argon to push the lighter oxygen molecules out of the object, and away from the insects. Thus producing a lower-oxygen environment faster and more effectively than occurs with nitrogen.

Length of treatment

The length of treatment (LOT) for an object is dependent upon the insect species involved, the type of infested material, and the material density and moisture content. Numerous laboratory studies of insects isolated in glass vessels have been published (Burke, 1993; Rust et al., 1993; Koestler, 2001). These studies report LOT times ranging from one to four weeks for nitrogen, depending upon temperature and humidity. Comparison studies of LOT for insects in argon versus nitrogen environments have shown that argon gas is 25-50 percent faster than nitrogen at the same temperature and humidity conditions (Valentin et al., 1992).

LOT data from the literature to date are based either upon insects isolated in laboratory containers or from newly, intentionally, infested pieces of wood. While it may seem reasonable to project LOT results from these studies to actual infested objects, there are problems with this approach. Insects in objects are well acclimated to their niche and may be physically isolated from the environment (e.g., insect frass may be packed around them) in addition to being in quite a few different physiological states (i.e., egg stage, larval stage with one to twelve distinct instars, pupal stage, or adult). Studies by Navarro (1991) and others have shown that different insect life cycle stages respond differently to inert gas treatment. It should be noted that, in practice, it is not always easy to identify the life cycle stage of the insect in an object.

Measurements of actual LOT values using an FTIR-respiration system for detection of CO_2 respired by insects hidden within art objects, before and after treatment, have provided more accurate data (Koestler, 1993; Koestler et al., 2000). As a result of these direct measurements of real art objects it was found that the literature has in some cases drastically underestimated the amount of time necessary to kill the insects. The minimum length of treatment time with argon should be 3-4 weeks and for nitrogen 25-50 % longer (or 5-6 weeks), to ensure the demise of life stages of the insects.

The anoxic gas method for fungal control

Eradicating a fungal infestation is more difficult than eliminating insects. Like insect control there are also suggestions of differences in efficacy of argon vs. nitrogen gas for fungal control (Tavzes et al., 2001, 2002, 2003). There is still a significant degree of uncertainty regarding length of exposition and minimal concentration of oxygen required for control of fungal attack (mold, wood-decay) on art objects. Although most wood-decay fungi require free oxygen for several metabolic reactions involving energy release or synthesis (Zabel and Morell, 1992), some of the fungi are able to survive in sealed vessels for more than two years (Scheffer, 1986). Oxygen is also a direct reactant in reactions catalysed by oxidative lignin degradation enzymes (Kirk and Cullen, 1997). Therefore methods using continuous measurements of oxygen consumption and carbon dioxide production were developed to detect the presence and activity of wood-decay fungi in wood (Ternifi, 1999; Cepin, 1999).

While there have been a few physiological studies on the effect of different oxygen concentrations on growth and survival of fungi and the extent of decay that they cause, none have specifically addressed using low-oxygen environments to kill them. Jensen (1967) reported that fungal biomass production was significantly lower at an oxygen concentration of 15% and that it ceased in the absence of oxygen. Otherwise, if the oxygen concentration was kept at a fixed level and the carbon dioxide concentration was varied, the amount of dry weight produced decreased as carbon dioxide concentrations increased. The ability of several fungal species to degrade wooden blocks was severely retarded when oxygen content was as low as 1% or CO_2 levels were raised to 10% (Highley et al., 1983). On the other hand, delignification was not affected by an atmospheric CO_2 content of 14%, and was only slightly retarded at 7% of O_2 in the bulk gas phase, concentration of oxygen inside the wood particles could be lower (Reid, 1985). The ability of fungi to survive in an environment with a low oxygen concentration is best described by Scheffer (1986). There it was shown that the fungi that survived the longest were more often heart-rot rather than the sap- and products-decay fungi. Some of the fungi were even able to survive in sealed vessels for more than two years. However, most of the fungal species studied died within three months, and cultures of two of the species died within a week.

None of the above-cited authors used pure argon or nitrogen gas to replace the oxygen and carbon dioxide atmosphere in experimental vessels. Tavzes et al. (2001) have shown that some species of brown rot fungi lost significant viability when grown in pure culture medium (PDA) under extremely low oxygen concentrations generated with argon or nitrogen gas.

Placing the fungi directly in a low oxygen environment shortened the time needed for eradication of fungi on growth medium compared to Scheffer's data (1986), obtained with a gradual "self-asphyxiation" of fungi. However, when gown on culture plates there was no significant difference in effectiveness between the two gases (Ar or N2). The reason was believed to be that the fungi could readily absorb accessible nutrients from the PDA medium without having to secrete oxygen-requiring enzymes as would be necessary when fungi are gown in wood blocks. The fungi grown on wood blocks asphyxiated faster than those grown on culture plates, and those put under argon died faster than those under nitrogen, on wood blocks (Tavzes et al., 2002).

Another series of tests, asphyxiation of fungal-infested wood blocks in plastic enclosures, was run to approximate as closely as possible practical conservation procedures for insect control. Since argon had proven to have higher efficiency than nitrogen in lowering the viability of fungal cultures infesting wood blocks, only this gas was used for this test. Five fungal species, well-known destroyers of wooden art and historic objects, known to differ in their sensitivity to anoxia (Scheffer, 1986), were chosen. The results showed that asphyxiation was a time-speciesspecific response in general, however, it was shorter in these tests than in Scheffer's study (Tavzes et al., 2003).

To ensure the effective use of argon-induced anoxia in eradicating fungi it is necessary to identify the species infesting the object. Molecular techniques of DNA identification offer the promise of doing this (Adair, 2002; Di Bonaventura et al., 2003). Rapid identification of infesting fungal species combined with the argon anoxic procedure would be important to speed up the conservation effort on an art object and reduce possible fungal damage.

These studies demonstrate that the argon anoxic procedure can be successfully employed to eradicate (within a timeframe suitable for practical conservation procedures) at least some of the most dangerous wood-destroying fungi that infest not only lumber but also art objects. Future studies will continue to expand the list of species that can be treated in this manner.

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