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Sustainability and Tourism

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Subject: Your letter of 16 August 2019 - Austria's application for an allowance to authorise biocidal products containing nitrogen generated in-situ in Austria in accordance with Art. 55 (3) of the BPR

Dear [redacted]

Thank you for your request from 16.08.2019. Austria would like to provide more clarification and reasoning for our application for an allowance to authorise biocidal products containing nitrogen generated in-situ in Austria in accordance with Art. 55 (3) of the BPR.

Rationale behind the Austrian proposal:

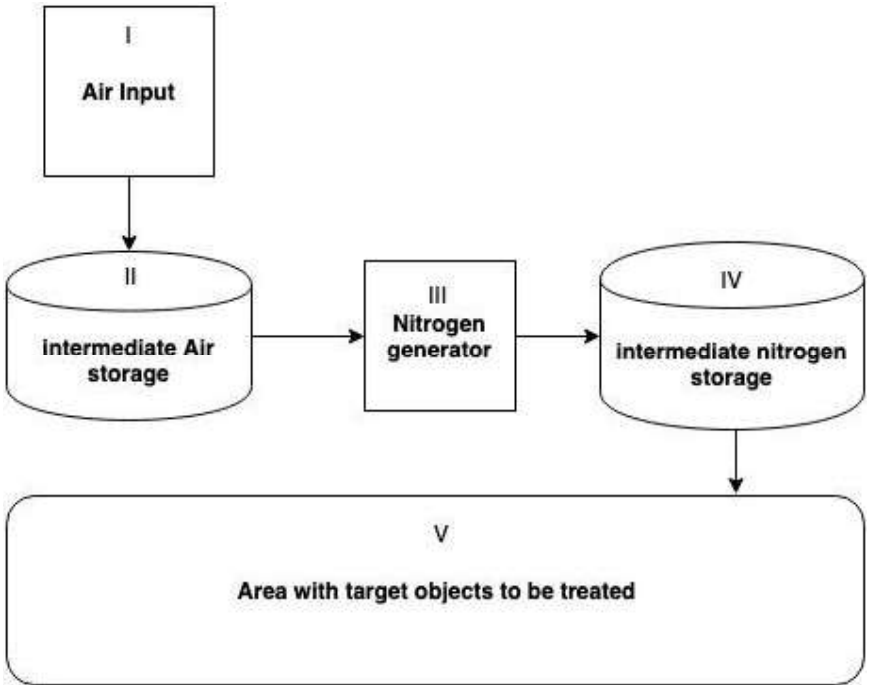
According to a long lasting experience in Austria (since 1998) and also based on literature in the field of preservation of cultural heritage the use of nitrogen **is the only technique** able to be used for **all types and mixtures of matrices** and potential **residues of pervious performed biocide treatments** to be encountered in this kind of items. The following document includes a more detailed description of the function and set-up of nitrogen systems (chapter 1), the technical parameters of the systems (chapter 1) and a further discussion on the potential effects of heat treatment on items of cultural heritage and alternative techniques (chapter 2). Furthermore, more literature has been included, however, it has to pointed out that the field

of preservation of cultural heritage represents a niche application and comprehensive publications are somewhat scarce. Most of the knowledge is based on experience of the users. After discussion with many experts in Austria on the subject of object treatment we can forward the following arguments to the discussion on the use of nitrogen, humidity regulated heat treatment, freezing and other methods of preventive treatment and treatment of objects with an active infestation:

- heat will accelerate the aging of almost all materials and objects. Objects are ideally stored in a stable environment.
- All museums follow the ICOM code of ethics to prevent any damage to the objects for the long-term preservation of cultural objects.
- Large numbers of objects are treated as a preventive measure, when objects are returned from loans or exhibitions to the storage.
- Not all incoming objects can be tested and the material composition investigated to determine the presence of incompatible materials for heat treatment

1. Details as regards the generation and use of nitrogen

To further elaborate on the use of in situ generated nitrogen for the preservation of cultural heritage a general schematic of the guiding principle of nitrogen chambers follows:



I) Following the schematic ambient air is brought into the input system. In general the ambient air has to be filtered and the humidity is reduced.

II) The processed air is then transported into a reservoir, which is necessary to allow a continuous regulated flow of processed air into the nitrogen generator.

III) After transport into the nitrogen generator it subsequently produces nitrogen on demand.

IV) The produced nitrogen is flushed into the intermediate storage reservoir "container". From the reservoir continuous regulated influx of nitrogen into the treated area occurs.

V) The treated area is flushed with a regulated stream of nitrogen on demand if the concentration of oxygen would surpass a preset threshold level.

Ad IV) It has to be emphasized that the reservoir is from a technical point of view necessary for the functionality of the system. The following points illustrate the function of the storage reservoir.

a) The storage reservoir is foremost used to allow equilibration of pressure of the treatment area which is essential due to the continuous influx of nitrogen.

b) In case of the Pressure Swing Absorption method to produce nitrogen the saturated nitrogen is periodically expunged from the generator. Furthermore, the method is based on different pressure values in the generator and the reservoir. Without the reservoir and a different pressure no oxygen depletion would occur.

c) The humidity of the nitrogen to be flushed into the treatment area has to be set according to the demand of the cultural heritage object to be preserved.

In general the produced nitrogen remains only shortly in the reservoir before it is used up in a continuous flow. **Thus no storage in a common sense occurs.**

The in situ generation of nitrogen is not performed at the same location as the treatment is intended. This is in line with other in situ systems in which the mixtures of the precursors occur prior to the introduction into the system to be treated. In theory it would be possible to introduce the generator into the treatment area to produce and use the nitrogen at the same site, however, from an applicative point of view it would pose unfeasible burdens and risk for the technician (PSM) charged with the maintenance of the system during the preservation process. Additionally the treated area (in the tent or chamber) must not be opened during the treatment to ensure little to no loss of nitrogen, temperature disturbance and humidity. A large number of buildings harboring cultural heritage are limited in usable space for large treatment systems, accordingly the location of the single parts of the system are adapted to the local availability of space which lead to distribution of the system compartments over the available space. To further elaborate on this the CA AT was supported with several pictures of actual in use nitrogen systems from Austria (Annex I).

It has to be pointed out that nitrogen treatment chambers are the same in the general layout but are all at the same time unique in their final set-up. The exact layout and performance of the systems depends on biotic and abiotic factors like the demand of the cultural heritage objects to be preserved. Subsequently, a range for the nitrogen concentration and the oxygen

concentration has been compiled to provide limit values to depict the variety of the final parameters encountered on site. The concentration of nitrogen used depends on the intended time of treatment per object. Thus, for the presented range a usual time of treatment for standard size objects (3 weeks) has been chosen.

3 weeks of treatment

Range of Nitrogen	
Max	Min
99.9	99.4
Range of Oxygen	
Min	Max
0.1	0.6

Thus the nitrogen is not used at the same site as it is in situ generated which would not be technical feasible.

2. Availability of appropriate alternatives

- The provided position paper distributed for the 84th CA-Meeting contains a selected list of research papers. We want to point out that the provided list reflects only a small part of the existing literature on the subject of thermal treatment of cultural heritage objects. In our opinion a critical study comparing different preservation methods including the thermal treatment should be addressed in this context:

  M. D. Ball, C. Biscula and N. Odegaard (2011): Assessment of the Thermo-Lignum oven pest eradication treatment on natural and synthetic polymers and resins. In: Proceedings of 2011: A Pest Odyssey 2011, 10 years later. (An IPM conference at The British Museum). The paper describes how thermal treatment is tested on a number of different materials and conservation agents. In the study different changes like indication of melting, color changes, partly dissolved glue, changes of weight and examples of migration of substances and blooming on the surface of ethnographic objects were detected (Annex II).

  The authors recommend: *„From this testing it is apparent that we need to have a **full understanding of traditional manufacturing methods and the materials used in objects**, together with any historic conservation treatments, before carrying out heat treatment. …Organic materials may have deterioration products that can affect other components in the artefact (corrosion of metals, discoloration of textiles) and differences in the thermal expansion coefficients between materials can result in mechanical change".*

The study concludes that before thermal treatment is carried out a full understanding of traditional manufacturing methods and the materials used in objects, together with any historic conservation treatment is required. If full knowledge is not given or cannot be collected the application of heat treatment creates a risk to damage the artefact. In addition a decision has to be drawn if the time benefits of heat treatment outweigh the possibility of damage to materials occurring during treatment. Furthermore, it has to be pointed out that besides literature mist of the knowledge for preservation is derived from in use experience by the different institutions which harbor collections of cultural heritage. To cover a larger range of experience with different treatment approaches expert statements were collected and used. In Austria the nitrogen chamber approach is widely accepted since more than 20 years due to the mentioned arguments of risk of damage due to unknown treatments in the past of the object and often unknown build-up of the objects.

List of materials known to be a challenge in treatment with regulated warm air (see also Querner & Kjerulff 2013):

- Waxes
- Ivory
- Lacquer (Urushiol)
- Shellac
- Low melt adhesives as animal glue & paraloid B 72
- Different synthetic materials
- Modern Art objects with a unknow mix of materials
- Oiled leather
- Very little experience with old paper and books
- Photo materials
- Claws, rhino horn and other worked horn
- Tortoiseshell
- Casques (bird beaks from South East Asia)
- Mother of Pearl
- Fish skin
- New untreated wood (can change color)
- Newly restored objects
- Objects under tension (music instruments for example)
- The coefficient of expansion of copper, glass and vitreous enamel is very different from other materials and this can result in damage
- Very thin objects
- Marquetry furniture
- Machine lubricants (in technical objects)
- Chemicals (in technical museum)
- With pesticides contaminated objects (cross-contamination possible)

Querner, P., Kjerulff A.-K. (2013) Non-Chemical Methods to Control Pests in Museums: An Overview. Rogerio-Candelera, M. A. Lazzari, M. Cano, E. (Eds.) Science and Technology for the Conservation of Cultural Heritage. Taylor & Francis. 273-276"

Example pictures for damage after a regulated warm air treatment, probably due to unknown prior biocidal treatment, is presented in (Annex I).

„List of materials challenging if frozen (see Querner & Kjerulff 2013):

- Cracks in paint on wood
- Damage to paint and lacquer
- Paint and lacquer becoming opaque
- Peeling of paint on metal parts
- Smearing of paint on wooden frames
- Areas of books and paper become powdery
- Cracking of mirrors
- Increased loss of hair on fur

The Austrian expert opinion is further supported by the MuseumPests Working Group which publishes information for treatment in museum. The publication (http://museumpaet.net/) further includes a comparison of different treatment methods. For the thermal treatment as negative point it is stated that: "Not all materials may be treated this way.". Nitrogen fumigation on the other hand is accepted to be compatible with all materials and combinations. Further Literature regarding the use of thermal techniques in comparison to other used techniques in preservation of cultural heritage items showed damage on the items:

Shin Maekawa und Kerstin Elert: Oxygen-free environments in the control of museum insect pests. Los Angeles 2003. S. 3.

Beiner, G. G.. Thermal methods of pest eradication: their effect on museum objects. *The Conservator Volume 29*, (2005, 06): 5-18. (damage on bokks and leather itmes was observed)

Materials Testing: The Use of Heat and Humidity Chambers for Pest Eradication by Dr. Marieanne Davy Ball ACR, Department of Conservation, Cultural History Museum, University of Oslo, Oslo, Norway; and Christina Bisulca and Dr. Nancy Odegaard, Preservation Division, Arizona State Museum, University of Arizona presented at the American Institute for Conservation's 39th Annual Meeting in 2011 for information on what materials may or may not be considered appropriate for the Thermo-Lignum heat treatment.

Kneppel, B.. Schädlingsbekämpfung an textilem Kulturgut unter Einsatz hoher und tiefer Temperaturen. *Kölner Beiträge zur Restaurierung und Konservierung von Kunst- und Kulturgut Band 2* (1995). (German)

The AT-CA clearly wants to avoid that Museums take the risk of potential damage of artefacts and also wants to avoid the decision between time benefits (thermal treatment is faster; 24-48h) and potential damage if possible.

In the following the Austrian experts have evaluated the submitted literature to underline the thermal treatment.

- The position paper does not reflect on Standard EN 16790 (2016) „Conservation of cultural heritage – integrated pest management (IPM) for protection of cultural heritage". In contrast the Standard does reflect on the method „Elevated temperature" and describes disadvantages and side effects. Austria is of the opinion that a method claimed for the conservation of cultural heritage should be the least damaging as possible.

- The Thermo Lignum position paper lists on page 2 six non-biocidal alternatives (Low Temperature Treatment, Heat Treatment, Humidity Controlled Warm Air Treatment, Biological Treatment (e.g. parasitoid wasps), Microwave radiation and Gamma radiation) and states on page 3 that, ‚Although it may be possible, that none of the above-mentioned alternatives can stand alone to substitute all current uses of nitrogen concerning the treatment of cultural heritage objects, <u>together</u> they constitute appropriate existing alternatives to in-situ generated nitrogen. Thermo Lignum concludes that the ‚prerequisite for a derogation according to Art. 55 (3) BPR is therefore missing'.

  The AT-CA does not agree to this conclusion because Museums exhibit or store different kind of objects and it could be not proportional to oblige them to use several methods for pest management if they can use only one method for all their objects. Normally Museums change their exhibitions from time to time, have special exhibitions or lend their artefacts to other Museums. Museums may have more than one treatment possibilities but should also be able to use one suitable method of controlling insects that would serve best. Furthermore, comments on all presented alternatives may be found in the Annex III of this document.

  In the position paper it is stated that aspects of cost and labour are no valid reason for Museums for derogation unless they are absolutely out of proportion. We do not share this opinion because most of the Museums are funded by the public and the costs are socialized. Furthermore, nitrogen systems start with small tents which may be purchased at a comparable low prize (appr. 15.000-35.000 €) up to a sophisticated nitrogen chamber

which would be in correlation more expensive (appr. 100.000 €), similar to a regulated warm air chamber.

There are advantages of having a humidity regulated heat treatment facility (short time treatment, no packing needed), but it cannot be used for all objects and materials and therefor nitrogen gives a higher flexibility. The Austrian Experts provided the following argumentation:

Rentokil has the license in Austria to use nitrogen from canisters. We asked the company in October 2018 for a treatment in Carinthia (Landesmuseum Kärnten). The Museums contacted the company by phone repeated times, spoke to staff of the pest control company, but they did not visit the museum to look at the collection or send a quote for the treatment. – We did not receive a written confirmation at the time being but requested one and will provide it immediately after it was submitted to us.

We hope that we were able to clarify your request to the extent that our application according Art. 55 (3) BPR can be decided positively. If you have any further questions, please do not hesitate to contact us again.

Yours sincerely,

3. September 2019
For the Federal Minister:
[redacted]

Signed electronically
3 Annexes

ANNEX I

Nitrogen chambers in-use in Austria:

Complete chamber plus the system.

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Smaller tent and nitrogen system.

Picture of a wood object treated with Humidity Controlled Warm Air (private collection, unpublished pictures):

Typical wood borer damage

Discoloration due to unknown reaction of prior used treatments (e.g.: biocides)

Annex II (see attachment)

Assessment of the Thermo-Lignum oven pest eradication treatment on natural and synthetic polymers and resins:

Thermolignum_Norway_KHM.pdf

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Assessment of the Thermo-Lignum oven pest eradication treatment on natural and synthetic polymers and resins

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Abstract

The Kulturhistorisk Museum (KHM) has recently acquired the Thermo-Lignum heat oven for pest eradication of collections. The heat treatment works by raising the temperature to above that at which insects can sustain life and at elevated relative humidity (RH) to prevent drying of materials during the treatment. While most objects appear to be stable using this treatment, conservators have noted changes that prompted more detailed investigation of the effect of this procedure. The preliminary investigation at KHM was an assessment of alteration to 34 resins, waxes and adhesive samples that are commonly used in ethnographic collections and in conservation treatments. These materials were treated with the same procedures used in the Thermo-Lignum process used for collections. Changes to samples were monitored by visual inspection, weight and dimensional changes, and chemical alteration assessed using Fourier Transform Infrared Spectroscopy (FTIR). These initial results indicate that the Thermo-Lignum procedure can have detrimental effects in proteinaceous adhesives. Acrylics were prone to slippage in joints, epoxies yellowed, and many natural resins and fats showed colour change after treatment. On actual collection materials, analysis of an efflorescence that formed on the surface of some wooden objects after treatment identified the migration of fats during heating. This information along with ongoing analyses at KHM can provide the necessary information on each material's response in order to make informed decisions about objects that can be safely treated.

Keywords

Thermo-Lignum, adhesives, resins, proteins, deterioration, pest eradication

Background

In 2009 the Kulturhistorisk Museum (KHM) at the University of Oslo built a new storage facility for its ethnographic, archaeological and antiquities collections. Concurrently, the museum also upgraded its pest eradication systems to ensure that the objects are pest-free before relocation to the new permanent storage areas. After much debate and comparative analysis of available treatment methods, it was decided to use two different systems in tandem: a walk-in freezer and a heat chamber.

The premise of heat eradication is that an object is heated to a temperature above which typical museum insect pests cannot sustain life (52–54°C), while keeping the relative humidity (RH) constant to prevent excessive drying

and distortion to the objects (Strang 1992). The heat chamber chosen was from Thermo Lignum, which has an internal capacity of 38 cubic metres allowing very large objects or multiple objects to be treated simultaneously. The RH can be set to any desired level, which at KHM is usually between 40 and 50%RH to correspond to storage conditions. The oven ramps up temperature gradually and holds at the maximum temperature for a set time (90 minutes in the KHM protocol). The primary advantage of using the Thermo-Lignum procedure is that it is highly effective in killing insects yet is more time efficient than freezing, as the entire process takes 16 hours as opposed to the week needed for freezing treatments.

Given the high susceptibility of pest infestation in ethnographic collections, these objects were the first to undergo the new pest eradication protocols. Over a two-year period, around 25,000 objects have undergone eradication, the largest proportion in the heat chamber. Initial assessment of heat treatment was made shortly after installation, and few visual changes were noted to objects after treatment. However, with the treatment of more objects, visual observations raised questions about the routine use of this method for pest eradication. Significant deformations occurred to shaped keratin artefacts, which caused concern for induced deterioration to proteinaceous materials. A white efflorescence (bloom) formed on the surface of some objects after heat treatment, particularly on wooden objects from Africa (Fig 1). Due to these experiences and others, several classes of materials were placed on to a list of those not to be put through heat eradication pending further analysis.

Fig 1
Bloom formation on wooden sculpture (UEM44130) after heat treatment.
(Courtesy of KHM: MDB)

Heat treatment protocols for pest eradication were developed for use in the food processing and lumber industries. Most of the available literature pertaining to the Thermo-Lignum system specifically for museum collections is focused on its effectiveness in insect eradication. Fewer studies have addressed the effect of heat pest eradication treatments on specific collection materials. Tscherne and Schachenhofer (2008) found minimal damage to painted and gilt surfaces, with the exception of shellac. Ackery *et al* (2004) demonstrated that Thermo-Lignum treatment did not adversely affect DNA in entomological collections, however, the potential for movement of greasy materials was observed. The findings of Hardboard (1999) showed deterioration on fish skin specimens from using heat, but not on skin/leather with shrinkage temperatures above 50°C.

In conservation it has long been known that heat and humidity are primary agents of deterioration (Feller 1967; Feller 1994). A full understanding of the effect of heat treatment requires a detailed knowledge of how each material's equilibrium moisture content (EMC) responds to changes in temperature and humidity. The size of the material and its thermal diffusivity are also important considerations in determining appropriate protocols for heat treatments (Wang 2010). However, this information is not readily available for most materials, particularly those encountered in museums that are already deteriorated from natural ageing. There are numerous accelerated ageing studies of different materials available in the literature, but the parameters used in specific studies do not often coincide with the duration, temperature and humidity used in the Thermo-Lignum treatment.

At KHM there are many concerns that have been realised in the use of heat treatment. These concerns are compounded by the fact that many materials in artefacts may be under additional stresses (tension, sheer, and so on), and may be already deteriorated from natural ageing. The latter is of particular concern, as KHM some artefacts were collected about 200 years ago, and many objects may have undergone historic treatment(s) or have already been exposed to high temperature or humidity prior to acquisition. Moreover in the KHM pest

management protocols, objects may go through several heat treatments as they are removed and/or returned for exhibition, study or loan. The primary concerns addressed for initial testing are:

- inducing or accelerating ageing processes in our collection. Many polymers are subject to chain-scissioning (depolymerisation) and oxidation during heat ageing, which can lead to a loss of mechanical strength. The deterioration (hydrolysis) and/or denaturation of proteins are of particular concern, as it is caused by heat and moisture ('gelatinisation').
- damage due to softening in cases where the material's glass transition temperature (Tg) is in the range of the Thermo-Lignum oven. The maximum temperature of treatment is above the Tg of many acrylics routinely used in conservation treatments, which can result in failure of joints or distortion of surface coatings. Of greater concern is that the Tg of polymers decreases with increasing RH and thus moisture content; a phenomenon that is most pronounced for hydrophilic polymers like proteins, certain epoxies, and carbohydrates. This has a dramatic effect in proteins. In the case of gelatine, the Tg decreases from over 200°C at 0%RH to room temperature at 75%RH (McCormick-Goodhart 1996).
- alteration of water content. The EMC and sorption isotherms at elevated temperatures and humidity are not precisely known for many materials encountered in collections, particularly when considering many aged materials. The changes in water sorption with elevated temperature at 50%RH could result in dimensional changes (swelling/shrinkage) or a change in the moisture re-uptake of the material. Loss of water is a particular concern, and could result in embrittlement.

Methodology

Tests were carried out within the parameters used in the Thermo-Lignum heat chamber at KHM (core temperature of 54°C at 45%RH, 90 minute hold at maximum temperature). Ambient temperature of the chamber was also measured using a maximum/minimum thermometer placed in the chamber. The smallest sized monitoring block was chosen due to sample size (refer to Thermo-Lignum® nd for further details on this process).

Preparation

The first tests were on 20 different adhesives (Table 1). Several preparations of each were prepared: (1) as an adhesive to adhere glass slides together, (2) as an adhesive for wood tongue depressors. In both cases, the adhesive was used to create a lap joint under light tension by suspending them in the chamber, allowing measurement of slippage. The use of

Table 1 Summary of results for Thermo-Lignum treatment on 20 adhesives

		Glass	*Filter paper*			
Sample	*Adhesive*	*% Inc. length (cm)*	*% Inc. weight (g)*	*Colour change*	*Physical change*	*Change?*
Acrylics	Paraloid B72	0.87				×
	Paraloid B44		0.11			×
	Paraloid B67	1.00				×
	Plextol B500					
Vinyls	Lineco PVA		–0.20			×
	Mowital B30H	0.48				
Epoxies	Araldite rapid				×	×
(thermosets)	Akemi resin				×	×
	Hxtal NYL – 1				×	×
Proteins	Bone glue		–0.60	×	×	×
	Hide glue		–0.40	×	×	×
	Rabbitskin glue	0.86	–0.40	×	×	×
	Sturgeon glue	0.90	–0.20		×	×
	Fish glue	0.45	0.10			×
	Gelatine	0.43				×
Cellulostics	Cellulose nitrate	0.83				×
	CMC					
	Klucel G					
Other	Gum arabic		–0.41			×
	Rice starch glue		–0.50			×

Table 2 Summary of results for Thermo-Lignum treatment on 14 resins and waxes

		Weight change	*Colour/ surface changes*	*Indication of melt*					
	Adhesive		Glass	Wood	Paper	Glass	Wood	Paper	Change?
Resins	Dammar	X							X
	Gum elmi								
	Shellac				X	X			X
	Copal								
	Lacquer	X	X						X
	Colophony		X	X	X				X
Waxes	Benzoin					X			X
	Beeswax	X					X	X	X
	Paraffin wax			X		X	X	X	X
	Microcrystaline wax						X	X	X
	Renaissance wax								
	Cosmolloid H 80						X	X	X
Fat/oil	Shea butter					X	X	X	X
	Cocoa butter					X	X	X	X

different substrates allowed for comparison between absorbent and non-absorbent materials in adhesion. (3) Samples absorbed into the centre of a piece of filter paper, the edge demarked in pencil, to monitor spread, colour or dimensional change. (4) Samples prepared as films on silicon release paper, then placed in glass vials. Fourteen resins and waxes were sampled (Table 2). Each material was painted on to a glass slide and a wooden tongue depressor to see if the substrate affected the result. A sample was spread on to filter paper to observe colour change and spread; and samples of film made for later FTIR analysis. In all cases a sample was removed as a control for FTIR analysis. The samples were allowed to dry for more than a week before being photographed against a colour chart, measured, and weighed.

Test procedures

All samples were subject to five cycles of heat treatment according to the procedures used at KHM. All samples were placed on metal trolleys placed centrally within the chamber (Fig 2). Adhesive tests were suspended from the wire grid to give a light tension. All the resin and wax samples were laid on to tissue paper on the metal shelving. FTIR analysis on samples before and after five cycles of treatment was done to assess whether Thermo-Lignum treatment could cause chemical deterioration

Fig 2
Test samples in the Thermo-Lignum chamber.

(oxidation, hydrolysis, and so on). FTIR was performed using an Avatar 360 ATR-FTIR spectrometer, spectra were recorded in reflection mode, from 4000 to 800cm^{-1}, 256 scans at 4cm^{-1} resolution, using OMNIC ESP 6.1a software. Recorded spectra of blooms were compared with various commercial libraries and the Infrared and Raman Users Group (IRUG).

Results for the adhesives

Using the readings on the maximum, minimum thermometer these were found to range between 54.5°C and 60.8°C, with the first three runs recording the highest temperatures.

Visual result

On glass samples, the acrylic adhesives were prone to dimensional changes/movement indicating partial melt during heat treatment (Figs 3 and 4). Both Paraloid B72 and Paraloid B44 had spread and formed a more tendril-like dispersal, with Paraloid B44 also taking on a petrol-like hue. Paraloid B67 had spread beyond the joint, but showed no other changes. In protein-based materials there was also some indication of movement due to softening: the dispersal of the bubbles in bone glue changed, and the fish glue became tacky along the edges of the glass. In the epoxies, more bubbles appeared in the Akemi Marmokitt 1000 samples. The polyvinyl acetate became clearer, which appeared to be due to further drying of the sample. Similar changes were not observed for acrylic adhesives on wooden samples, which showed minimal changes in length or tackiness with the exception of Hxtal NYL–1 which failed during the third run. In the adhesive films on paper, there were colour changes noted to the HMG cellulose nitrate, all of the epoxies, as well as most of the hide glues (Table 1). For many of the hide glues on paper (bone, hide and rabbit skin) the filter paper also buckled significantly with movement of the adhesive.

Length change results

For the glass samples, length increases (slippage) were observed primarily with the acrylics and hide glues (Table 1) as well as with Mowital B30H. In most cases the change in length was observed only on a single cycle, with the exception of Paraloid B72, which continued to show slippage on repeated heating. The movement of Paraloid B72 and Paraloid B67 is expected, as the temperatures reached are over 10°C higher than their Tg (approximately 40°C and 50°C respectively). Even though there was some movement with temperatures well above the Tg of many adhesives, the joints did not fail. Higher Tg acrylics showed no movement, as is the case for Paraloid B44 and Plextol (Tg 60°C and 90°C, respectively). In samples prepared on wood, no changes to the length were found, but Hxtal NYL–1 failed as the joint broke down on the first test run. The lack of slippage in wood joints is most likely due to mechanical adhesion, and indicates that failure joints with heat treatment must also consider the substrate, even if temperatures are above the Tg of the adhesive.

Weight results

All hide glues showed a decrease in weight, which is most likely a loss of water after heat cycling. Loss of water and shrinkage is also likely to be the reason that paper samples distorted. The amount of water loss in protein glues is relatively large considering that the

Fig 3 (far left)
Glass sample for Paraloid B72 before testing.

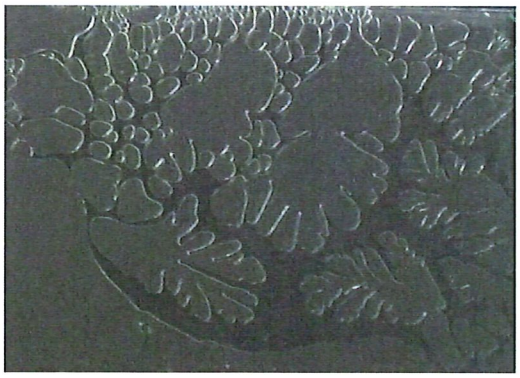

Fig 4 (left)
Glass sample for Paraloid B72 after testing.

percentage weight change recorded includes the weight of the glass slides. Water loss may be due to continued drying of the adhesive during heat treatment, but does indicate that damage due to water loss and dimensional change can be considerable for proteinaceous materials. Loss of water can lead to embrittlement and eventually failure of hide glue adhesives. Cellulose-based adhesives like CMC and Klucel G showed no changes due to heat treatment, so are likely not a concern when using heat treatments for pest eradication.

Samples prepared on wood and paper cannot be compared in terms of changes to the adhesive, due to the sorption of water by the substrate during heat treatment. However, in most cases the wood samples showed on average a two per cent increase in weight, with the exception of bone, hide, rabbit skin and rice starch adhered samples, which still showed a decrease in weight.

FTIR

No significant changes were noted based on ATR-FTIR analysis. However, any chemical deterioration incurred during these relatively short temperature increases are likely to be confined to the surface and not significant enough for detection on bulk samples. In some cases changes in FTIR spectra were noted, but they were not reproducible and variation within the prepared films could not be excluded.

Results for resin and waxes

Visual results

In glass samples, the shellac had become slightly granular in appearance and the benzoin more globular; the surface of the paraffin wax had become totally crizzled; whereas both shea and cocoa butters had a much more uniform appearance. These surface changes are attributed to movement due to melt. The benzoin and colophony had both darkened and the lacquer greyed in patches. On wood samples, a slight darkening had occurred to colophony and a shadowing to the lacquer. Paraffin, microcrystalline and Cosmolloid 80H waxes and shea butter all appeared to have partially melted and been absorbed into the wood. On paper samples, benzoin and colophony again showed darkening, as well as shellac, and the surface appearance of lacquer again was altered (shadowing). Most of the waxes showed some movement, and both the shea and cocoa butters had become transparent and spread to various degrees.

FTIR

Notable change was only observed for shea butter (Fig 5). Alteration appears to be due to ester formation based on the shift in the carbonyl from free fatty acid (1709cm^{-1}) to 1730cm^{-1} (ester) and the shift in C–O to the ester stretch

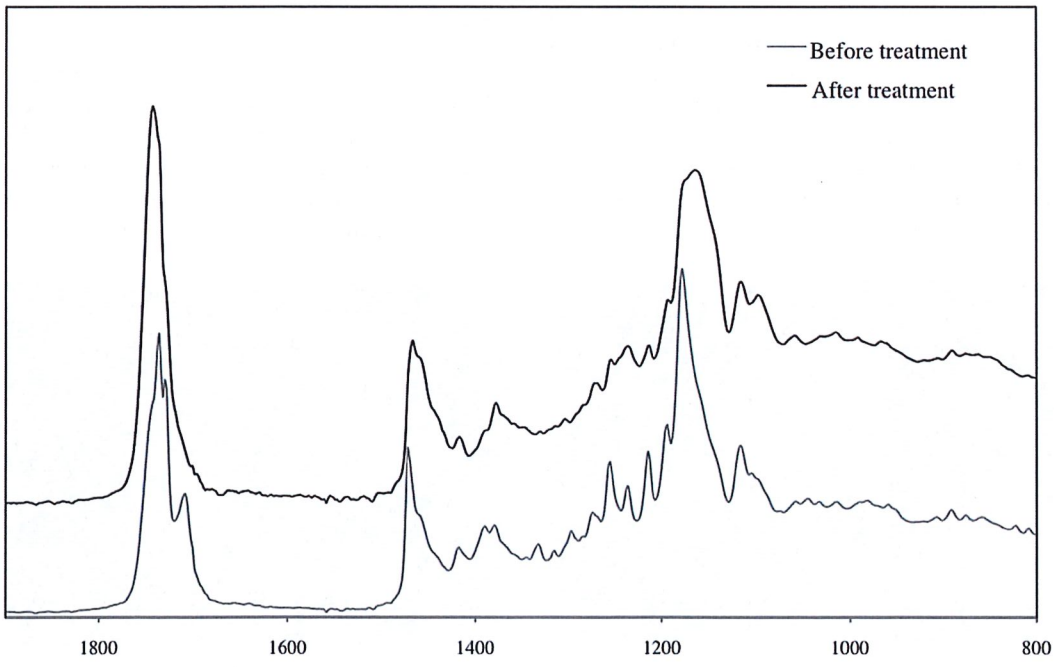

Fig 5
Fingerprint region of FTIR spectra of shea butter before and after Thermo-Lignum heat treatment.

at ~1300cm^{-1}. There were slight changes also noted in dammar and gum arabic in the OH stretching region that may indicate a gain and loss of water, respectively.

Identification of blooms

For two of the blooms, the best correlation based on FTIR is long chain free fatty acids such as stearic or palmitic acid, possibly from an emollient or oil applied to the surface (Fig 6). The band 1692cm^{-1} is assigned to the carbonyl bonds in free fatty acids, the less intense shoulder at 1723cm^{-1} to fatty esters (triglycerides). These blooms appear to be consistent with those studied by Pearlstein (1986), identified as fats. In the other two cases, the bloom was not identified. FTIR spectra correlated best with an unidentified conjugated aromatic, which may be a natural component of the wood.

Conclusion

In this preliminary investigation, most of the adhesives and resins showed some change due to heat treatment, including weight loss, dimensional changes, and discoloration. This raises the point that while gross visual changes to objects may not be routinely observed with the use of Thermo-Lignum heat treatment, our results indicate that there are likely changes that may be apparent upon closer visual examination and analysis. The primary concern identified is damage to proteinaceous materials, and a moratorium on the Thermo-Lignum treatment is recommended for skins and leathers pending more detailed analyses. In common acrylics used in conservation, there was slippage, but not failure, of adhesive joints. Examination prior to treatment is needed to ensure that potential failure or distortion of these acrylics is deemed acceptable. Bloom formation on wooden objects was found to be due to migration of fats during heating. These coatings were not visible before treatment. This raises concerns for the heat treatment of objects where fats and oils may have been traditionally applied, which is the case for certain wooden sculptures and many leather artefacts. From this testing it is apparent that we need to have a full understanding of traditional manufacturing methods and the materials used in objects, together with any historic conservation treatments, before carrying out heat treatment. This preliminary investigation did not address synergistic effects, which are expected in the treatment of museum objects. Organic materials may have deterioration products that can affect other components in the artefact (corrosion of metals, discoloration of textiles) and differences in the thermal expansion coefficients between materials can result in mechanical damage.

This investigation raises the question of the optimal protocols for heat treatment when

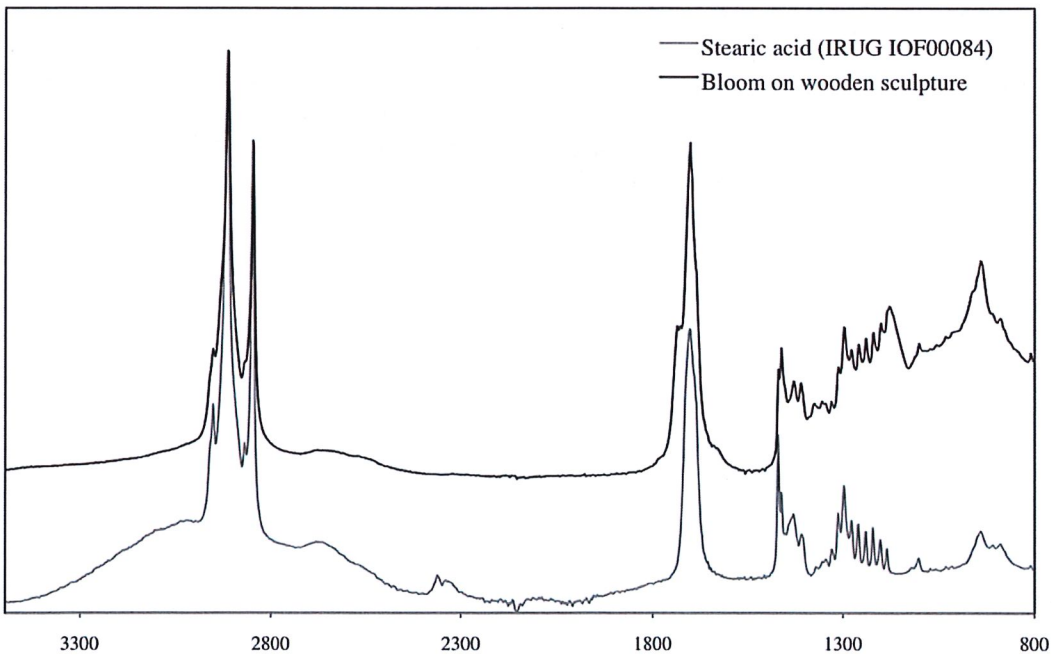

Fig 6
FTIR of bloom sampled from the surface of a wooden sculpture after heat treatment. The spectra correlate best with a long chain fatty acid such as stearic acid.

used on museum collections. The existing protocols were largely developed through the analyses of commercial lumber, and are not necessarily directly transferable to ethnographic collections where materials are often less dense or more porous than wood, and likely have different moisture sorption and thermal properties. It would be beneficial to re-examine temperature gradients and hold times needed for pest eradication in different collection materials, as current protocols may be harsher than necessary for museum applications. Collection management policies need to be addressed to determine if the time benefits outweigh the potential damage to materials occurred during treatment.

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Annex III

Comments to the stated alternatives:

Non-biocidal alternatives:	Use in Austria
+ Low Temperature Treatment	widely used in many museums in Austria: for example in the Natural History Museum Vienna, Weltmuseum Vienna, Technical Museum Vienna, War Museum (HGM), etc.; but delicate objects can get damaged by packing or treatment
- Heat Treatment	heat treatment with uncontrolled humidity is not used for museum objects, only for wood pallets or attics for example
- / + Humidity Controlled Warm Air Treatment	used from time to time, not for waxes and other materials (see information above); for example Salzburg Museum, War Museum (HGM), open-air Museums Niedersulz; chamber only in Salzburg – transportation needed
+ Biological Treatment (e.g. parasitoid wasps)	used from time to time in different museums, but very limited method; for a few museum pests only available
- / + Microwave radiation	very specific method for infested wood that cannot be transported (wood flooring); used from time to time in different museums: Schönbrunn palace, Hermesvilla, Wagenburg KHM
- Gamma radiation	very damaging to the materials; not used for museum objects
Biocidal alternatives:	
- Ethylene Oxide	highly toxic; easily inflammable; cancerogenic; not used for museum objects
- / + Sulfuryl fluoride	highly toxic, cannot be used in densely inhabited cities; mainly used for churches and open-air museums, used rarely in museums: Schönbrunn palace, Wagenburg KHM
- Hydrogen cyanide	Damage of museum objects possible, not used for museum objects; highly toxic; easily inflammable
- Phosphine	highly toxic; corrosion for gold and silver (and other metals), not used for museum objects
- Carbon dioxide (Annex I - Approval for use in ready-for-use gas canisters functioning	this is used against rodents in traps, not insects

together with a trapping device)	

[redacted]