IPM at the Victoria and Albert Museum (V&A) and preventive treatments using Thermo Lignum™

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Abstract
Integrated pest management (IPM) and the choice of suitable treatments is an integral part of the role of the V&A's preventive conservator. IPM is now integrated into many of the Museum's objectives and has become firmly embedded within care of collections at the museum, with aspects of best practice incorporated across all collections and divisions. A group of staff representing all collections and departments are involved in trap-checking and all those involved in exhibitions and changing displays are now aware of the risks of incoming objects to the museum. With more and more organic material on open display, vigilance and pest monitoring remain crucial along with effective treatment options. Systems for risk assessment are in place and working with an object list in the planning stages of an exhibition is now standard practice so that preventive treatments can be factored in. Making the right choice of treatment for different object types is the key to the successful use of preventive measures. Also lenders may favour one treatment over another so reassurance is vital to lenders in permitting the thermal treatments available. Two thermal treatments have been in use for many years at the V&A. Treatment at low temperature of -30°C for 3-4 days goes back to the early 1990s and the more recent use of Thermo Lignum™ humidity controlled heat treatment at 52°C over a 24 hour cycle. Treatments at Thermo Lignum™ can be grouped into: treating actual infestation (which is rare), using the treatment as best practice to prevent any possible pest risk when moving museum objects from museum to store or vice versa, when sending objects on loan or for returning loans and when loans are coming in for the exhibition programme. Risk assessment and making the right choices are fundamental and thermal treatments are only part of a wider arsenal. With budget and time restraints they are often the treatment of choice as anoxia (low oxygen) treatments can take up to 6 weeks. Time between exhibitions is often restricted with only 2-3 weeks available and sometimes less. Low temperature treatment requires the objects to be bagged and so lack of time and staff means that the use of a 24 hour cycle heat treatment at 52°C with a controlled humidity is often the most appropriate choice of treatment.

Keywords: Thermal treatments; Low temperature; Heat with moisture control; Preventive conservation

1. Introduction

The Victoria and Albert Museum has an internationally recognised collection of art and design objects dating from 13th Century to the present day. This collection includes many objects which are vulnerable to pest attack, such as furniture, textiles, books, paintings and sculpture. As an accredited textile conservator for many years I worked in the textile conservation studio where my specialism was in tapestries and carpets. I became involved in the early beginnings of integrated pest management (IPM) at the V&A with David Pinniger who has acted as our pest consultant for over 20 years. David has contributed to the setting up of the IPM system, participates in training and led on the insect pest risk zones within the V&A (Fig. 1). Working with myself and staff in Furniture Textiles and Fashion Collections we established the protocols for loans and preventive treatments. Over the years, staff

training in pest awareness was established with a popular one day course on various aspects of IPM. The supporting staff training manual for IPM was written with David Pinniger and is reviewed periodically.

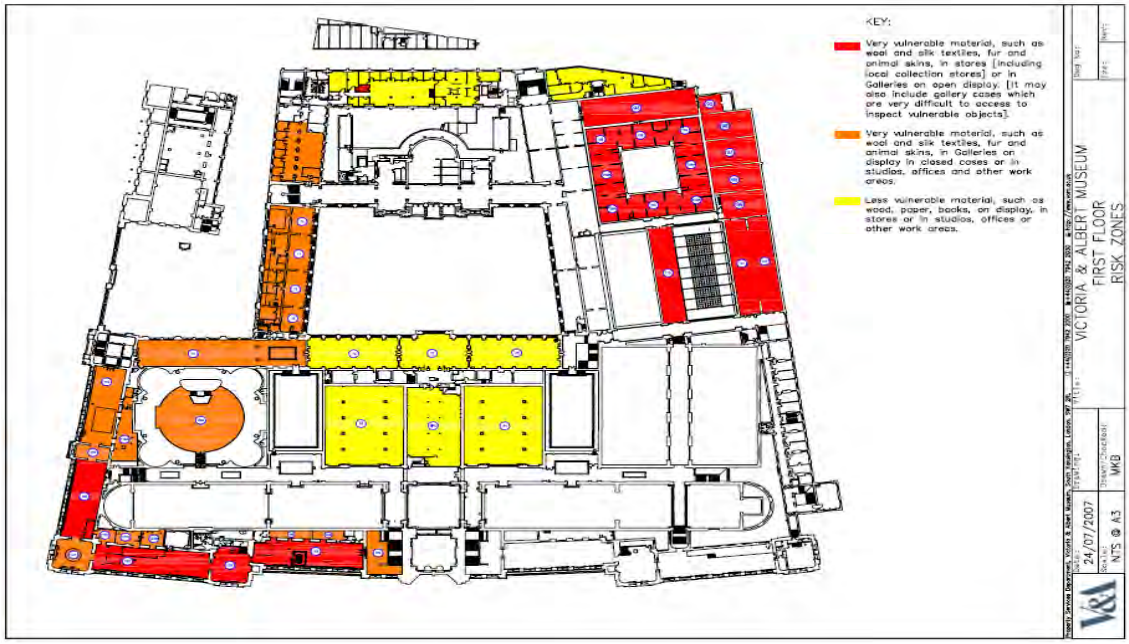

Fig. 1: Risk Zones Map of V&A ground floor showing: Zone A high risk red, Zone B moderate risk orange and Zone C lower risk yellow. © Victoria and Albert Museum.

2. History of IPM in the museum and roles and responsibilities

The V&A moved its large collection of tapestries and carpets in 1991 from the V&A site to an off-site store in West Kensington. To prevent transferring pests from our old store to the new store hundreds of large rolled textiles were treated at low temperature, over a 4 month period. This was essentially our first large preventive treatment and resulted in a collaborative publication with Linda Hillyer (Blyth and Hillyer 1992).

Over the intervening years it became part of my remit to oversee and carry out any treatments or to train and supervise others in carrying out treatments at low temperature on site or high temperature at Thermo Lignum™. Low oxygen or anoxic treatments were discounted as they were too time-consuming when compared to thermal treatments (Strang 2001).

In 2006 I was given the responsibility to reintegrate an IPM programme which had become fragmented. This coincided with the loss of the very effective vapour phase insect insecticide Dichlorvos™, one of the many insecticides to be which has been banned and discontinued from use. During this time, we had localised pest infestations from both Guernsey carpet beetles (*Anthrenus sarnicus*) and webbing clothes moth (*Tineola bisselliella*) with actual damage to museum artefacts. There were hotspots of insect activity and some examples of actual damage to textiles by insects in the Costume Courts, Dress Stores and in the British Galleries (Blyth *et al.* 2008). London has also experienced an increase in webbing clothes moth (*Tineola bisselliella*) from around the same time (Pinniger 2009).

A few of the key points of my role as Integrated Pest Manager for the V&A were to:

- Co-ordinate all aspects of pest management

- Chair the quarterly meetings of the Museum pest management group
- Review and update all of the IPM methodology
- Increase pest awareness and carry out targeted training
- Carry out preventive thermal treatments
- Instigate a point of contact for all relevant IPM documentation on the museum's staff intranet.

At the V&A as preventive conservator I work closely with my colleagues in the Science Section. IPM is included in the annual environmental report which is available to all V&A staff.

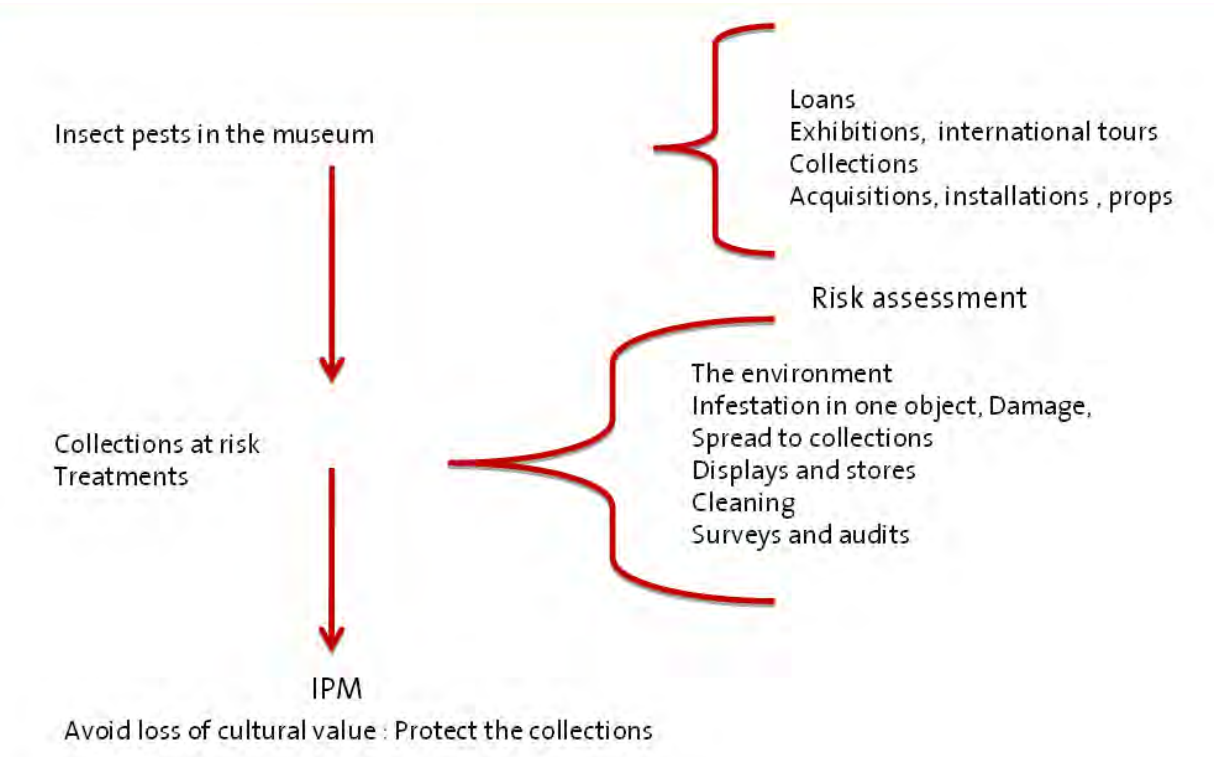

Fig. 2: IPM flow chart to show all the areas of the V&A where IPM preventive measures are used.

3. IPM Strategy

As a basis for our IPM strategy, we rely on collecting data from monitoring using sticky insect traps. There are over 1000 blunder traps distributed across the site and in all museum collections galleries and stores which are usually checked quarterly. Each department and collection has its own "Pest rep" to check their own blunder traps in their galleries and stores. They attend the pest day training workshop and are able to identify the main museum pests and present the results of the quarterly trap checks to the quarterly Pest management group meetings.

There are just under 100 webbing clothes moth lures used in the museum checked by the preventive conservator and any resident interns. The placement of these traps and the blunder traps is determined by the designated insect pest risk zones A & B (Fig. 1) (Pinniger 2011). The data collected are analysed and used to produce reports for the main sites and offsite stores. Annual reports are compiled using all the data collected. The data also informs on any hot spots, for example the increase in moth numbers in the Jameel Asian galleries in May to August 2012 (Fig. 3). These require actions and allow us to pick up on any problems early and organise any appropriate treatments.

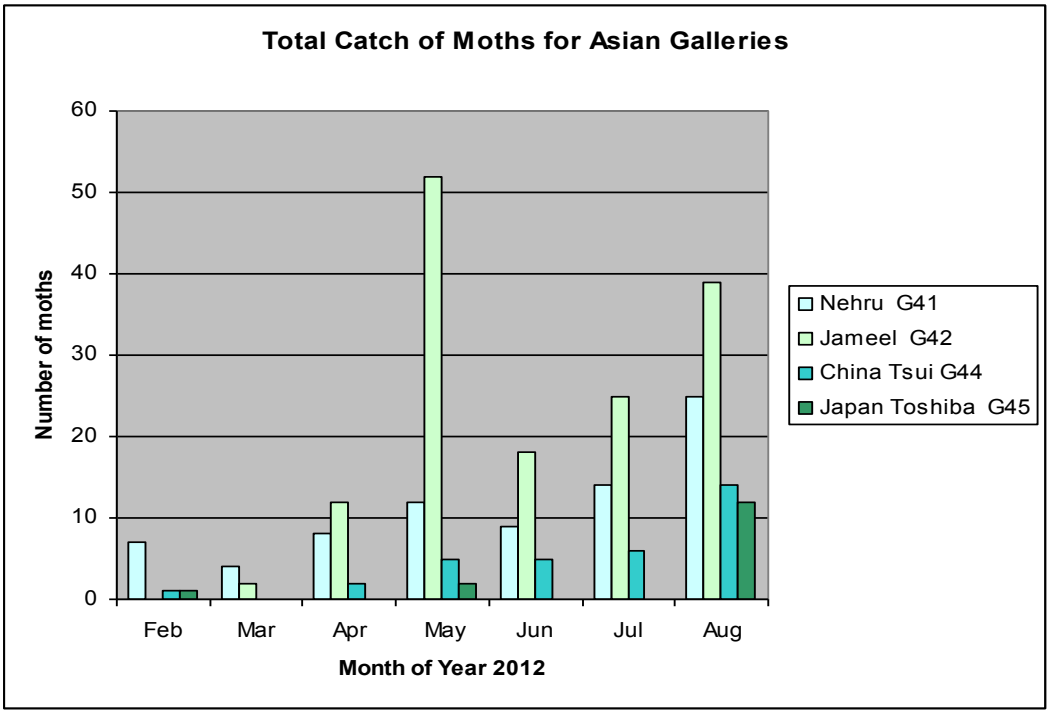

Fig. 3: Graph of number of webbing clothes moths caught in the Asian galleries (Feb. - Aug. 2012).

The V&A has many large organic collections, including textiles, which are vulnerable to insect damage on display throughout the museum galleries. They may also be displayed in "Blockbuster" exhibitions which can contain large amounts of mounted textiles and costume. Those exhibitions tour internationally for many years and this means the need for IPM has to be understood as part of the process and by all involved. Therefore, the preventive conservator has to liaise with many colleagues, advise throughout and maintain contacts with a wider circle of contacts and couriers from across the globe.

Recognising insect damage can be the key to managing any suspected infestation and to allow the correct treatment to be made. The assistant curator development programme runs over a training period of 5 years where the new staff are attached to one collection, but also gain experience in other collections. A "pest workshop" is run twice yearly to accommodate this rolling programme with a further pest identification course run annually. All assistant curators are encouraged to attend the IPM courses. Shorter specific IPM courses have also been given on risk assessment and on how to prepare items for safe treatment at low temperature. Front-of-house gallery assistants also receive a basic training in recognising the main museum insect pests and an understanding of which museum collections might be damaged. Training has also been extended to colleagues in the museum to inform those acting as couriers.

A culture of increased IPM awareness has now been established of the threats from insect pests in an old building, such as the V&A, and that we can never achieve zero levels of insect activity. We have therefore developed quarantine and local isolation techniques and protocols to new acquisitions and props as well as exhibitions and incoming loans. It is important however, to repeat training and induction as there is often a quick turn round of museum personnel and the need for these protocols may be overlooked.

4. Treatment Options

Preventive treatments are now planned and scheduled using the two thermal treatments available. Our treatment schedule for low temperature is that all objects are bagged in polythene and treatment at -30°C is carried out over 3-4 days There are now 5 chest freezers in use across all the V&A sites including the main museum and store. Hired flat-packed freezers capable of reaching -30°C have been used in the exhibition courts to minimise the movement and handling of the objects to be treated at low temperature. It is unlikely the museum would again hire a 20 foot freezer container as we did in 1991 as the costs were high and the staff resources colossal (Blyth and Hillyer 1992).

Over the years, there has been a growing use of a heat treatment with moisture control by the company Thermo Lignum™ based in London. This allows objects to be treated at 52°C in a 24 hour cycle without the need for bagging (Strang 2001). On some occasions both types of treatment may be used in any one project. For example, an infestation in a dress store resulted in objects stored in the lower portion of the store being treated by V&A staff at low temperature. However, the objects stored on the second floor were treated at Thermo Lignum™ as the technical support for the wrapping of objects was no longer available. A general lack of resources is now common place in many museums. With concurrent projects, less staff are available to prepare and bag objects for treatment at low temperature. This has resulted in an increase in the number of treatments at Thermo Lignum™ with costs of off-site treatment borne by the project or exhibition budgets. Decisions on how and when to treat can vary, but realistically choice of treatment is dependent on cost, time restraints and staff resources.

Risk assessments have to be carried out more frequently in order to decide whether a pre-treatment before display is needed. This is particularly important with incoming loans for exhibitions and display. These decisions in the V&A are made by the preventive conservator in consultation with the lead conservator for the project and an assistant curator or exhibitions assistant. It is now standard practice for this team to be incorporated as part of a project team to examine and assess the object lists and material types coming in to the museum. All proposed treatments can then be planned accordingly after permissions are obtained for treatment and any insurance details arranged.

Increasingly more textiles are on open display rather than in costly display cases and this exposes the objects to a higher risk from pest damage. It has been noted repeatedly that new wool seems to attract moths when put on open display in the museum, particularly in displays and exhibitions. It is therefore advisable that all incoming objects containing wool, and particularly red wool, are treated by one of the thermal treatments available. It is also essential that all new exhibitions and display areas are monitored with both blunder traps and moth lures throughout their exhibition run. Discussions also now take place with new venues and partner museums and art galleries where there are travelling tours to ensure monitoring is consistent at each new venue. The results of this and any comments for the couriers can mean a preventive treatment is carried out in situ or on return from a tour.

5. Case Studies

5.1 Mae West Red lips sofa

The Mae West Red lips sofa which was designed by Salvador Dali was displayed in “Surreal Things” exhibition in 2009 (Fig. 4). The sofa was made from red woollen felt and had suffered from insect damage in the past and as it was too large to be treated in our chest freezer, the sofa was treated at Thermo Lignum™ following permission from the lender.

Fig. 4: Salvador Dali Mae West Lips sofa upholstered in red woollen felt. The inset shows damage by clothes moths. © Victoria and Albert Museum.

5.2 Rolled tapestries

The use of the Thermo Lignum™ chamber was also chosen as the best way to treat 20 tapestries prior to re-display in a newly refurbished gallery. This preventive treatment was carried out because the gallery had a history of Guernsey carpet beetle (*Anthrenus sarnicus*) with larvae being regularly caught on the blunder traps. A test was carried out in the heat chamber with a data logger inside a rolled textile to ensure the warm air would penetrate the rolled tapestries throughout the treatment. This preventive treatment was primarily carried out as the gallery had a history of the Guernsey carpet beetle (*Anthrenus sarnicus*) activity caught on the blunder traps. The insect activity is usually restricted to organic debris in the parquet flooring rather than the textiles themselves. The results were satisfactory and so the rolled textiles were treated in batches of 6 in bespoke cradles and transported to the new textile study store after treatment (Fig. 5).

Fig. 5: Rolled textiles in storage at the Study Centre. Inset shows bespoke racking used for transport and treatment at Thermo Lignum™. © Victoria and Albert Museum.

5.3 The Great Bed of Ware

The Great Bed of Ware is one of the museums most iconic objects (the bed is mentioned by Shakespeare in "Twelfth Night") and is on display in the British Galleries. The bed and bed hangings went out on loan in 2011 for a period of a year to a museum in Ware where the bed was originally made in the 1590s. The decision for treatment was made because the bed has previously suffered some damage to the reproduction wool bed hangings by both carpet beetle and moth larvae. In addition, an increase in webbing clothes moth activity had been observed in the British Galleries (Blyth and Smith 2011). All elements of the bed; wool mattresses, blankets, pillows, cover and valances were treated at Thermo Lignum before the move and again on return to the V&A museum.

Objects are now routinely treated for preventive reasons for all our major exhibitions containing a mixture of textiles, wood, furniture, sculpture and upholstery. Other artefacts with differing components and /materials make the risk assessments a constant challenge. Objects containing mixed media pose particular challenges in contemporary displays. Examples of "found objects" include driftwood, seaweed, antlers sugar and spices.

The increase in the use of Thermo Lignum ™ as the treatment method of choice is also due to this wide range of materials coming in for contemporary exhibitions. Some may be suitable for treatment

at low temperature, but it is easier to have one exhibition consignment treated at the same time and more expedient to treat large numbers of objects together. The "Memory Palace" (Fig. 6) is an example; the original concept was to be constructed of contents of household rubbish. This was later modified to bales of paper only which were treated by Thermo Lignum before installation in the museum gallery (Blyth and Battison 2008).

Fig. 6: Memory Palace constructed from bales of newspaper. © Victoria and Albert Museum.

6. Conclusions and key points

Reasons to treat objects:

- actual damage and active infestation, evidence present = High risk
- perceived risk from infestation, old frass, signs of old pests = Medium risk
- preventive treatments for incoming loans = Low to medium risk

Key advantages of using heat treatments:

- Heat treatment often works out cheaper than using low temperature as more objects can be treated at one time in the heat chamber and no prior preparation and bagging is required. Staff overheads are therefore reduced.
- Larger objects can be treated in the chamber. A variety of object types made of various materials may also be treated together.

It is important to know that some objects may not be suitable for heat treatments and so further discussion and risk assessment is required before decisions can be made.

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Investigation of the use of freezing against insect pests in Danish museums and the effect of repeated freezing of 5 different surface treatments on pinewood and glass slides

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Abstract
Freezing as a method of pest eradication in museum objects is widely used in Denmark but in recent years there has been talk of damage resulting from this practice. The use and experience with freezing in Danish museums were investigated by a questionnaire which shows that 70 of the responding 99 museums use freezing as a method of pest eradication. Of the 70 museums, 15 have detected damage on objects due to freezing and many of the observed damages related to surface treatments on wood or metal. Published data suggest that the difference of the linear thermal expansion coefficients of some surface treatments and pinewood will exceed the surface treatments ability to elongate before breaking, when cooled to -38°C.

The effect of repeated freezing of 5 different surface treatments brushed on pinewood, glass and ceramic tiles is therefore examined: linseed oil varnish, shellac, cellulose nitrate lacquer and alkyd- and acrylic coatings. A special construction of 3 wood pieces glued together with the surface treatments have been made for breaking strength tests. The surface treatments on wood and glass are subjected to 5 and 20 freeze/thaw cycles and on the ceramic tiles to 1 and 15. One cycle consists of freezing at -38°C for 72 hours and thawing at room temperature for 7-16 hours. All samples have been wrapped in sheets of polyethylene during freezing and thawing.

The brushes on slides and wood are examined macro- and microscopically and by Fourier Transform-Infra Red (FT-IR) spectroscopy. Breaking strength tests have been conducted on the 3 piece wood samples and gloss measurements have been made on the surface treatments on ceramic tiles. The FT-IR spectra do not indicate any chemical changes of the surface treatments after freezing. The breaking strength measurements gave no useful results with regard to evaluating the effect of freezing. Shellac and alkyd varnish exhibit cracks after 1 freeze-thaw cycle on the ceramic tiles but the actual measurements of gloss which was the purpose of the tiles did not give an unambiguous answer and the method is not considered to be suitable for evaluating the effect of freezing. The macro- and microscopic examinations show that all 3 brushes of shellac and alkyd coating on wood, all 3 brushes of shellac on slides and 2 out of 3 brushes of alkyd coating on slides exhibit cracks after 5 freeze-thaw cycles and all brushes on wood and slides of shellac and alkyd coating exhibit cracks after 20 freeze-thaw cycles.

The questionnaire provided unique information on the use of and experience with freezing in Denmark and knowledge of damages not reported elsewhere. The freeze experiment demonstrated that freezing can result in damage on shellac and alkyd coating brushed on pinewood, slides and ceramic tiles and that the damages are of physical nature.

Keywords: Freezing; pest eradication; surface treatments; questionnaire

1. Introduction

In Denmark freezing is commonly used on museum objects as a method of pest eradication. However, in recent years there has been talk among conservators about observed damages on objects resulting from the freeze treatment. There is much literature recommending freezing and reporting successful treatments and some investigations of the method used on different materials found no damages (Kite 1992, Florian 1997, Peacock 1998, Strohsneider 1998, Harvey 2001, Carrlee 2003, Pinniger 2009, Strang and Kigawa 2009). On the other hand several authors warn against freezing certain materials, such as thick paint and varnish, objects with tension like teeth and drums (Mickalski 1991, Pinniger 2003, Kelley 2005) and some find changes and damages e.g. cracking of leather on saddles and glass lids of insect boxes, deformation of insect boxes and failure of glued joints, micro-cracking of bone and matte paint on wood, change of surface structure on leather and reduced movability and deformability of new and artificially aged silk as a result of freezing (Kneppel 1995, Tanimura and Yamaguchi 1995, Ackery *et al.* 2000, Child 2003, Beiner and Ogilvie 2005). Richard *et al.* (1998) advise never to expose panel paintings on wood to temperatures under + 10°C during display, transport or storage and Mecklenburg (2007) later revises the recommendation to cover all types of paintings and the temperature limit to +12°C.

Furthermore the available data regarding linear thermal expansion coefficients and elongation before break indicate that the difference of thermal expansion of e.g. an alkyd base paint and pinewood in the longitudinal direction will exceed the paints ability to elongate before breaking when frozen to - 38°C (Wheatherwax and Stamm 1956, Browne 1960, Young and Hagen 2008):

$$\Delta L = \alpha L_0 \Delta T$$

L=length, α=linear thermal expansion coefficient, T=Temperature

Decrease of temperature +17 °C to – 38 °C = 55 °C
$3.34 \times 10^{-6}/°C^{-1} \times 1m \times 55$ °C = 0.18 mm pinewood in the longitudinal direction
$154 \times 10^{-6}/°C^{-1} \times 1m \times 55$ °C = 8.47 mm alkyd base paint

Difference in thermal contraction: 8.47 mm – 0.18 mm = 8.29 mm
The elongation before break for alkyd base paint: 4 mm at -10 °C

Browne (1969) found that 4 types of acrylic paints with titanium dioxide will contract between 2.2-4.73 mm pr. m when cooled from +17 °C to -38 °C. This gives a difference from the pinewood in the longitudinal direction of 2.02-4.55 mm. According to Young and Hagan (2008) 3 types of acrylic base paint with the same titanium dioxide and calcium carbonate will be able to elongate 0.4-7 mm and one type 17 mm at -10 °C. There is no data for the elongation before breakage at -38 °C but it will certainly be less than at -10 °C, hence some acrylic paint might be flexible enough to withstand freezing but some types probably will not.

Due to the obvious contradictive nature of the accessible information on the effect of freezing on museum object materials, it seemed relevant to investigate the use of and experience with freezing in Denmark and the effect of freezing on common surface treatments on museum objects.

2. Materials and Methods

2.1 The experience with freezing in Denmark

The use of and experience with freezing museum objects in Denmark were investigated through a questionnaire distributed to the 123 state and state recognised museums in the country. The translated questionnaire is shown in Table 1.

Table 1: Questionnaire distributed to 123 state and state recognized museums in Denmark.

Museum				
	No	Freezing	Heat treatment	Other treatment
Does the museum have a routine for preventive pest control with regards to incoming objects for storage or display?				
Has the museum taken action against an active pest infestation within the past 10 years and if so, how?				
Description of pest eradication method. Packing and equipment used (household freezer, container, walk-in freezer, heat bubble or chamber, anoxia bubble or chamber).				
Temperature (Celsius).				
Time used for treatment.				
Time used for acclimatization.				
If the museum uses freezing has any damages or changes been observed on objects after freezing and if so which type?				

2.2 Investigation of the effect of repeated freezing of 5 different surface treatments.

2.2.1 Test material and freezing routine

There were unfortunately no standards available for testing surface treatments at the very low temperatures that eradication of museum pests requires. The literature does not agree on 1 standard method for freezing. Various different procedures from 48 hours at -18-20 °C to 2 weeks at -20 °C or 1 week at -30 °C have been suggested (Florian 1997, Strang and Kigawa 2009). But all exceeds the time and temperature used in the industrial standard ASTM D 1211 that prescribes exposure to +50 °C for 1 hour followed by 1 hour at -5 °C, then a pause of 15 minutes before visual inspection for cracks. Experience from Conservation Centre Vejle even shows that *Anobium punctatum* can survive our standard freezing procedure at -38 °C for 72 hours several times and complete its life cycle, in a storage environment with seasonal variation from +7 to +18 °C and a relative humidity of approximately 50% (+/-7%). Seven days at -38 °C do however seem to eliminate the insects. The experimental design is based on the standard freezing procedure at the Conservation Centre in Vejle and a selection of materials common for surface treated museum objects, which are used to produce test pieces that make chemical and physical test methods applicable.

For the experiment 3 bases are chosen, pinewood to mimic wooden furniture or panel paintings, glass for better microscopic investigation options and ceramic tiles to allow for gloss measurements. Five different types of surface treatments are chosen to represent common ones from different time periods. There is no use of veneer, glue or base paint. The experiment and its elements are kept as simple as possible for the most conclusive results. The surface treatments used are:

- Linseed oil Varnish: 17.85 g Boiled linseed oil, 53.57 oil of turpentine.
- Shellac: 1:1 w/w Shellac Lemon 1 unbleached and ethanol 96%.
- Cellulose Nitrate Lacquer: Cellulose Glossy 441-0027 Akzo Nobel Industrial Coastings A/S.
- Alkyd coating: ES Lacquer Glossy. Akzo Nobel Industrial Coastings A/S.
- Acrylic Coating: Lignal Hydro combination Lacquer DHE 6506X PU. Lignal A7S.

The recipes for Linseed oil Varnish and Shellac are from 'Handbook for wood turners' found in Edinger *et al.* (1999).

The pinewood pieces of 50 x 22 x 5 mm are made from furniture dry wood that has been kept at a staple climate at approximately 23 °C and 55% RH for 2 months and the moisture content was hereafter measured to 6-8% with a Testo 606 moisture monitor.

All surface treatments are applied by brush in fume cupboards. The linseed oil varnish on wood has been applied 12 times over a period of 10 days. The other surface treatments and linseed oil varnish on glass and ceramic tiles are applied 3 times with drying periods of 2-4 days inbetween applications.
The test pieces for breaking strength measurements are made following the description by Daniels and Kybria (1998) as far as possible. Each test piece consists of 3 wooden pieces of 80 x 18 x 4 mm. Two pieces are placed on the surface in the fume cupboard and an area of 10 x 18 mm on each piece and in both ends of the 3rd piece are brushed with a surface treatment before the 3rd piece is placed on the 2 lying ones with an overlap of 10 mm. On the top piece, weights of 640 g are placed for 2 minutes. This gives a test piece with 2 parallel wooden pieces, held together with the 3rd piece that can be placed in the test equipment used for testing breaking strength. Daniels and Kybria (1998) used test pieces of 3 mm thickness and only 400 g weights after the gluing, though. For each surface treatment 2-3 additional test pieces were made for adjusting the apparatus that performs the breaking strength test.

After the last application all the test pieces have cured for 53 days in a climate controlled room at approximately 23°C and 55% RH. Unfortunately the curing time seemed too short for the linseed oil varnish which was still slightly tacky.

The temperature and time interval is set at the standard treatment at Conservation Centre Vejle: 72 hours at -38°C. This freezing regime is repeated 5 and 20 times for the wooden pieces and glass slides and 1 and 15 for the ceramic tiles, with a thaw period of 7-17 hours. The repeated freezing is performed since many objects are subjected to repeated freezing as part of preventive routines in connection with loans and exhibitions or in the case of reinfestation. For the wooden pieces and the glass slides there are 3 references 3 pieces frozen 5 times and 3 pieces frozen 20 times. There are 2 ceramic tiles with brushes of the 5 surface treatments for freezing first 1 cycle and then an additional 14 times. Before freezing all test material is placed in individually fitted carvings in polyethylene foam, and then wrapped in polyethylene plastic foil.

2.2.2 Test methods

Fourier Transform Infrared Spectroscopy (FT-IR spectroscopy) can provide information on possible chemical changes due to degradation. Measuring of breaking strength and gloss might give some objective values for the evaluation of possible damages after freezing. Based on the damages reported in the literature and the calculations regarding difference in thermal expansion coefficients presented in chapter 1.1, possible damages/changes are expected to be physical and visually detectable, therefore

visual inspection macro-and microscopically and digital photography are included as test and documentation methods.

2.2.2.1 FT-IR Spectroscopy

FT-IR Spectroscopy has been performed by a Perkin-Elmer 100 Spectroscope. Wooden sample pieces or off-scraped material from the glass slides have been held to the crystal with the strength of 120 and all spectra are recorded in absorbance. Wooden samples and material from glass slides frozen 20 times and the reference for all 5 surface treatments have been tested.

2.2.2.2 Breaking strength

Breaking strength measurements have been performed at an Instron 5566 with a jaw width of 110 mm and a pull of 10 mm pr. minute at 22 °C and 65% RH. Three test pieces of shellac, cellulose nitrate lacquer and alkyd and acrylic coating have been tested after 5 and 20 freeze cycles, as well as the 3 references for each surface treatment. Before testing each surface treatment, 2-3 unfrozen extra samples have been run to make sure the pull of 10 mm pr. minute was appropriate. The Instron program is set to measure breaking strength, extension at break and extension at break in percentage and calculate average and standard deviation for each test set of 3 measurements.

2.2.2.3 Gloss measurement

The gloss of each of the 5 surface treatments on the ceramic tiles has been measured 3 times before and after freezing 1 and 15 times with a Minolta multi-Gloss 268 at an angle of 60°. The instrument has been calibrated against a standard surface before the measuring of each surface treatment. All data has been processed to find the average of the 3 measurements and the standard deviation
$\frac{1}{N}$
defined as $\sigma = \sqrt{N \sum(x_1-\mu)^2}$.

2.2.2.4 Visual inspection and photo documentation

All the test pieces of wood and glass and the ceramic tiles are photographed before and after freezing together with the references with a digital camera through a macro lens and the glass slides are also photographed digitally through a polarisation microscope at 25x and 200x enlargements.

3. Results

3.1 The questionnaire

Of 99 responding museums, 56 cultural history museums, 4 natural history and 5 art museums, 70 use freezing as a preventive measure and/or in case of active infestations. Three use heat treatment and 1 has used anoxia. Twenty six museums use pesticides, mostly against wood boring insects. As seen in table 2, 15 of the 70 museums using freezing have observed damages on objects after freezing.

Table 2: shows how 70 Danish museums use freezing and at which temperatures damages have been observed. Some use both household freezers and walk-in freezers or containers at their conservation centre.

Temperature	24 hours	48 hours	72 hours	24-96 hours	More than 72 hours	Reports damages
-18-20°C	2		2	2	4	
-21-30°C		2	2	12	4	2
-31-45°C	3	8	25	3	8	13
-50-80°C		1	1			

The following damages are reported by the Danish museums:

- Cracks in paint on wood
- Peeling of both paint and lacquer
- Paint and lacquer becoming opaque
- Peeling of paint on metal parts
- Smearing of paint on wooden frames
- Glued joints become lose
- Shattering of an ink bottle
- Fusty areas of book and paper become powdery
- Cracking of mirrors
- Increased loss of hair on fur
- Drying of unpainted wood
- Water damage due to condensation on unwrapped cardboard boxes
- Wooden barrels fell apart

Many of the reported damages relate to surface treatments on wood or metal.

3.1 The freezing experiment

3.2.1 FT-IR Spectroscopy

The FT-IR spectra showed no signs of chemical changes due to degradation after repeated freezing.

3.2.2 Breaking strength

Test of breaking strength could not be performed on the linseed oil varnish since it did not cure enough to work as glue. However even though approximately following the experimental design as described by Daniels and Kybria (1998) it was still impossible to get interpretative results from the measuring of breaking strength of the other surface treatments. The breaking strength was determined by the uniformity of the 2 gluings and in spite of applying the surface treatments to the same areal and using the same weight after application the gluings were too uneven for the test method. In the case of the acrylic coating, the bonds of the surface treatment were so strong that it was the wood that split, not the gluing. The standard deviations are large, and all small signs of change lie within them.

3.2.3 Gloss measurement

The shellac and alkyd coating on the ceramic tiles cracked after the first freezing and the cracking increased after 15 cycles but only for those 2 surface treatments. None of the other surface treatments

exhibited any changes after freezing. The visual impression is much more explicit than the measurements.

3.2.4 The visual inspection

After 5 freeze/thaw cycles 3 of 3 pieces of shellac on glass and wood exhibit cracking and the cracking increases after 20 cycles (Photos 1-3).

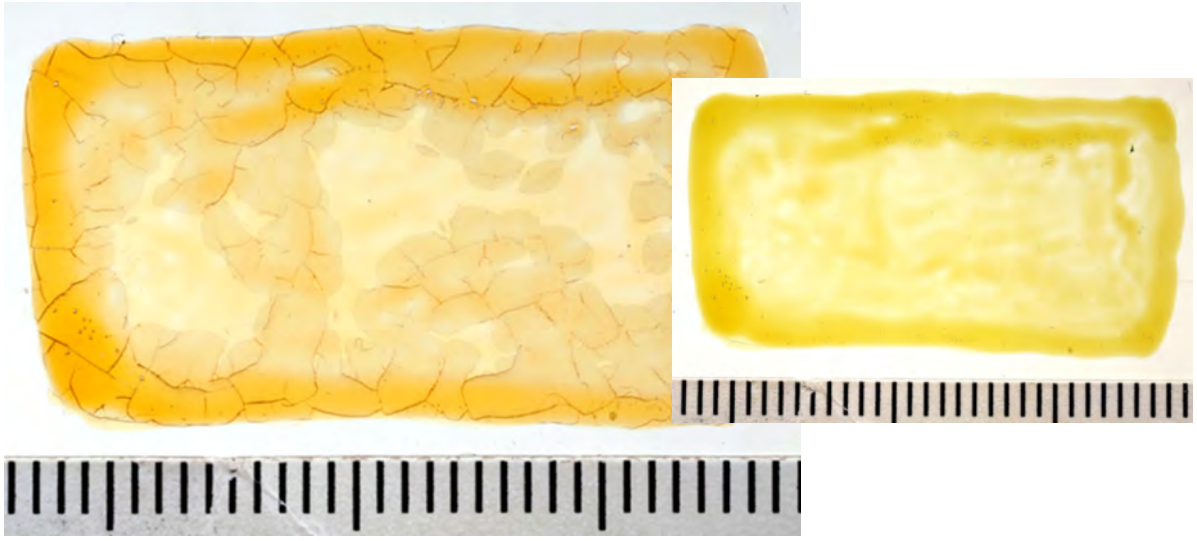

Photo 1: Shellac on glass after 20 freeze cycles. The small inserted photo shows the unfrozen reference.

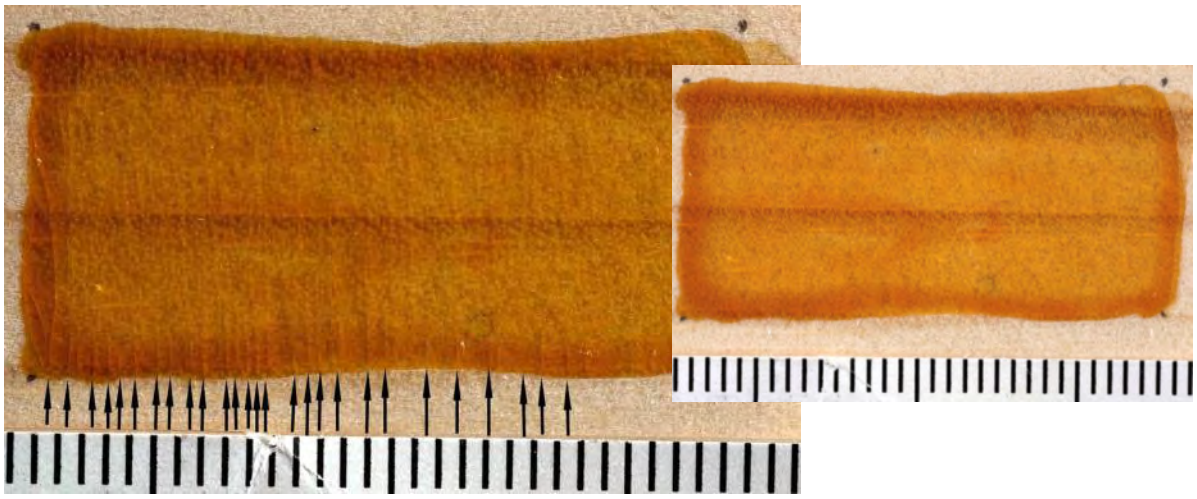

Photo 2: Shellac on wood after 20 freeze cycles. Black arrows point at cracks in the surface treatment. The small inserted photo shows the unfrozen reference.

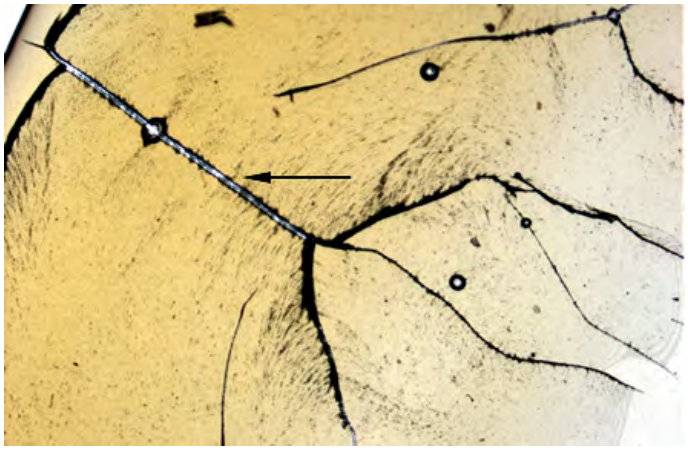

Photo 3: Shellac on glass after 5 freeze/thaw cycles seen through the microscope at 25x magnification.

Two of 3 pieces of the alkyd coating on glass and 3 of 3 on glass slides exhibit crack after 5 cycles. All 3 pieces of alkyd coating on glass and wood slides shows cracks after 20 cycles (Photos 4-6).

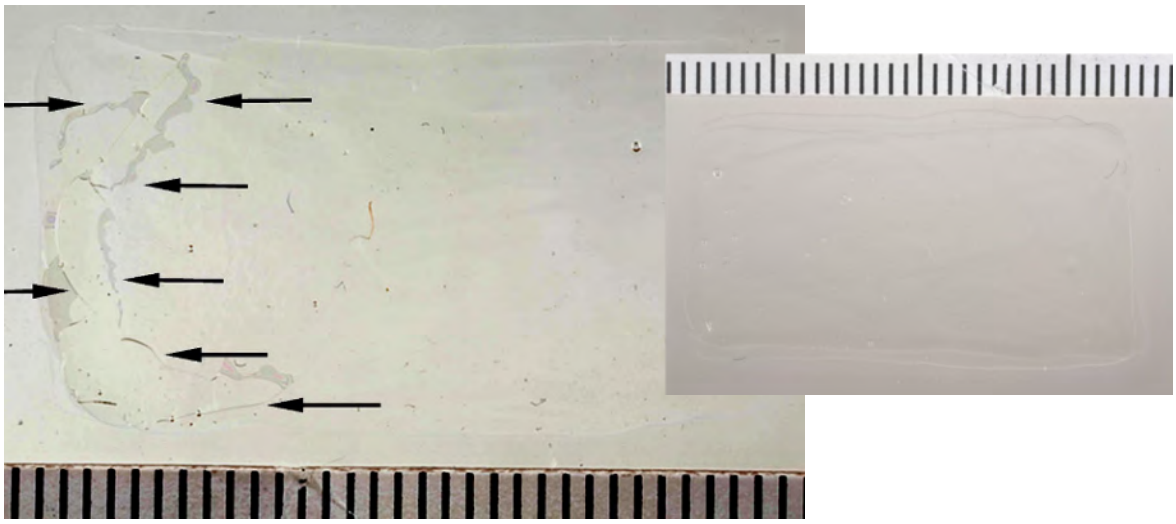

Photo 4: Alkyd on glass after 20 freeze/thaw cycles. The black arrows point at cracks in the surface. The inserted picture is the unfrozen reference.

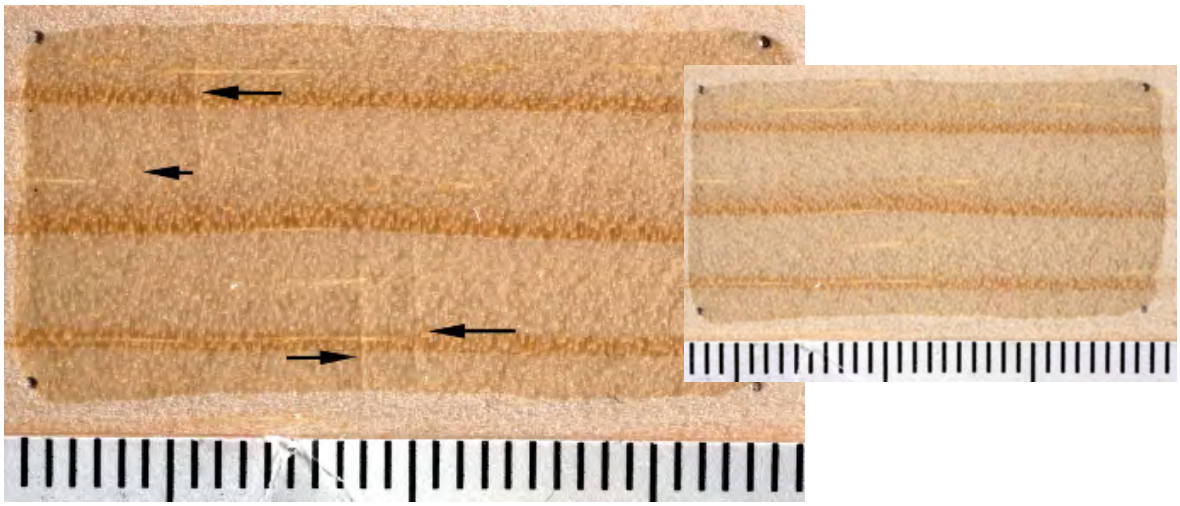

Photo 5: Alkyd on wood after 20 freeze/thaw cycles. Black arrows point at cracks in the surface. The inserted picture is the unfrozen reference.

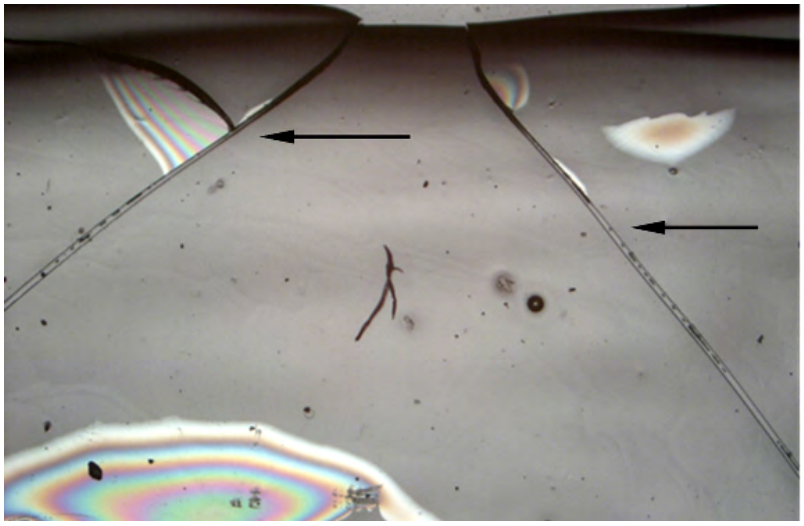

Photo 6: Microscope photo of alkyd on glass after 5 freeze/thaw cycles at 25x magnification. Cracks are shown by the black arrows.

No cracking or other visual changes are detected on the other surface coatings.

4. Discussion

4.1 Discussion of the freeze method based on published data and experience

In Denmark and elsewhere freezing has been introduced as an easy and safe alternative to pesticides in the battle against pest insects in museum objects (Tanimura and Yamaguchi 1995). When in the 1970s and 1980s it became apparent that pesticides were a threat to both humans and objects, the search and development of methods of eradicating pest insects in museum objects became inevitable. This continues to be an important task as freezing might not be the best solution for all pest problems related to museum objects. However in Denmark so far only 3 museums have tried using heat and just 1 an anoxia treatment. Other methods as already mentioned here or in detail in Querner and Kjerulff (2013) are rarely entering the Danish museum world, where freezing is still predominantly applied.

Freezing museum object differs in great parts from household freezing of food.

Ideally a method for eradication of pest insects in museum object should meet 3 criteria:

(1) Efficacy:
The product or method should be sufficiently effective to be worth the workload and cost.

(2) Safety:
The product or method should not be harmful for the personnel working with the objects or the public that visits the museum to look at them.

(3) Effect on the museum objects:
The product or method should not physically damage the object nor react with the object materials which may complicate or hinder future analysis as well as change the physical appearance or stability. Nor should the object's natural aging be accelerated.

Freezing easily meets the 2nd criterion. However to assess the suitability of this method on a given museum object, it is essential to know the lower lethal time-temperature relation for the insects to be

eliminated and understand basic mechanisms of the reaction to changes in temperature of the materials involved. First of all the freezing procedure used must be effective against the insect species infesting the object. Much work has been done to establish lower lethal time-temperature relations for many common museum pests, but recommendations in the literature still vary (see chapter 1). Moreover experience from Conservation Centre Vejle shows that some species might require even lower temperatures and longer time periods than suggested anywhere in the literature in order to eliminate the pest in all stages. Around 30 years after the method was implemented there is still a need for more knowledge on the time-temperature relation on museum pest species in order to use freezing effectively.

With regard to the effect of freezing on objects several reactions might be considered. When wooden objects are kept in an environment of around 50% RH, the equilibrium water content should be around 9.5-10.5% (Bengtson and Selck 2006). When bagged and cooled the wood will begin to take up moisture since the RH in the bag will rise during cooling. At the same time, water in small capillaries within the wood, along with the newly absorbed, can begin defusing to cell lumens and the outer surface and start freezing there at -30-40°C causing drying of the wood (Horne 1969, Kaufmann 2004, Kärenlampi *et al.* 2005, Nanassy 1978, Padfield 1999).

For composite objects the important factors are the different thermal expansion coefficients and the ability of elongation before break for the materials constituting the object. Although hygroscopic materials as described above take up water during cooling this reaction is slow compared to the thermal contraction and will therefore not be able to compensate for this (Michaelski 1991). In the calculation on thermal expansion coefficients for pinewood and alkyd base paint compared with the ability to elongation before break for the paint seen in chapter 1, it is obvious that the paint will expand much more than the wood and that the difference exceeds the paints flexibility at -10 °C. It will be even less flexible at - 38 °C.

According to the above there is a risk to freezing objects: wood will become dry even when bagged, composite objects might crack and the surface structure of leather might change (Beiner and Ogilvie 2005).

4.2 Discussion of results

The questionnaire has provided unique information on the use of the freeze method on 99 Danish state and state recognised museums, the types of damages observed as well as knowledge of other pest control methods that are used. These data are not accessible anywhere else and have probably only been obtainable since the museums have been guaranteed anonymity. It shows that freezing times and temperatures vary from 24 hours at -18-20°C to more than 3 days at -31-45°C and 2 museums even use temperatures between -50 and -80°C for 48 to 72 hours. Even though lower lethal time-temperature relations vary between different species of museum pests the considerable differences in freeze methods demonstrate the need for more knowledge on how to use the freeze treatment effectively. It is important not to freeze at temperatures lower and in periods longer than necessary as this poses a greater risk of damage to the objects and wastes valuable resources. Moreover freezing procedures will be ineffective at high temperatures and short treatment times. Though the risk of damaging the objects is smaller at higher temperatures and shorter treatment times there is still always a risk of damaging objects during the handling connected to wrapping, loading, unloading and unwrapping, all beeing part of the freeze treatment. In case of ineffective freeze procedures the man-hours and the power used to cool is still wasted. The examples of the reported damage to an ink bottle and unwrapped cardboard boxes suggest that the use of the freeze treatment is not always based on a critical and scientific approach to handling cultural heritage objects. Since freezing is already implemented on 70 of 99 responding museums, it should at least be used in a way that provides reasonable efficacy and poses the least possible risk to the treated objects.

The types of damage reported by the Danish museums through the questionnaire correlates well with the type of damages that can be expected to result from freezing based on already published literature. Much of the damage observed at the Danish museums is related to surface treatments on wood or metal. Drying of wood could be an explanation for the barrels that fell apart and the loosening of joints on wooden furniture. A change in the surface structure of leather related to the size and shape of the hair holes (Beiner and Ogilvie 2005) might be the mechanism behind the increased loss of hair on reindeer skins after freezing observed by one museum.

The freezing experiment clearly demonstrated the potential for damages on shellac and alkyd coating as a result of freezing. Damage to objects with oil paints was reported by the Danish museums, but the linseed oil varnish did not fully cure. Browne (1969) gives data on the thermal contraction coefficients of oil paints but it has not been possible to obtain data on elongation before break to make a calculation of the risk of damage. Therefore further investigations with fully cured oil varnishes and paints should be performed to better understand this type of surface treatments reaction to freezing when applied to wood or other materials.

The damages observed after the freezing experiment are physical and best detected as well as documented by simple visual tests. The measuring of gloss is not applicable to the freeze damaged surface treatment nor to the surface treatments that do not exhibit visible cracks. The method is too inaccurate for this purpose. Measuring breaking strength with the method described by Daniels and Kybria (1995) can neither be recommended. If this method should be used for testing in future freeze experiments a test piece with only one gluing and a way to make the gluings completely homogenous must be found.

4.3 Freezing in the future

A promissing result is that the cellulose nitrate lacquer and the acrylic coating did not exhibit any damages after freezing. The acrylic coating used also contained polyurethane that might have made the coating more flexible during cooling than a pure acrylic coating would be. More freezing experiments with different types of acrylic coating are necessary before it is possible to say that freezing acrylic coatings on wood or canvas is safe.

Millions of objects have been frozen and published data on damages experienced by museums might be limited to the Japanese survey from 1995 (Tanimura and Yamaguchi 1995). There have been projects where the objects have been examined before and after freezing as the large freezing campaign in connection with the collection move of the National Museum of American Indians to new storage facilities (Carrlee 2002). This is not standard procedure in Danish museums. The results advocate that there are objects and materials where freezing can be used but also that there is not much important knowledge on the potential dangers and the limitations of the freeze method.

The damages reported through the questionnaire and the ones seen on shellac and alkyd coating in the freeze experiment provide material for consideration upon the future use of the freeze treatment especially on surface treated objects and as a preventive method. Clearly an infestation is potentially very damaging for an object and if freezing is the only available option it may be a good solution. But it is relevant to recognise and evaluate the potential risk of damage that preventive freezing pose to a large amount of surface treated objects that may not be infested. It may be worthwhile to think of replacing some of the routine freezing of vulnerable objects with other non-toxic methods like anoxia treatments, or focus on inspection, cleaning and quarantine procedures.

Conclusion

A questionnaire where the museums have been guaranteed anonymity has given an exclusive insight into how freezing is used in Danish museums and information on damages on objects, resulting from freeze treatments. Reports of damage on objects are also seen in a questionnaire from 1995 with 34 responding museums from across the world. Museums do not seem keen on publishing reports of damages on objects caused by freeze treatments. However when offered anonymity there are museums willing to also share their less successful experiences with freezing, the predominant method of pest eradication in Danish museums.

The freezing experiment demonstrated that shellac and alkyd on pinewood, glass and ceramic tiles can exhibit cracks and that the cracking increases with repeated freeze/thaw cycles. The damages that can be expected to occur on composite objects after a freezing treatment are physical and can be examined and documented with visual methods such as visual inspection, microscopy and photography. Test methods that examine chemical changes are not suitable to detect these damages.

Results of the questionnaire and freeze experiments question the extensive use of preventive freezing especially on surface treated objects. Other non-toxic eradication methods should be considered as well as increased priority of inspection, cleaning and quarantine procedures.

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Biodegradation of cultural heritage made of cellulose and protein based materials

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Abstract
Textile material degradation by microorganisms depends on their wear rate, type and origin, organic composition, temperature and humidity conditions, degree of aeration, the amount of impurities of the fibres etc. Gamma irradiation may be one of the unconventional decontamination methods for the cultural heritage within the Integrated Pest Management. This paper aims to study the effect of gamma irradiation on the behaviour of textiles in the TEXLECONS project 'Improvement of occupational environment quality in cultural heritage deposits. Validation of gamma radiations treatment of textile and leather cultural goods'. This research shows that an Irradiation Dose of 10 kGy in the textile conservation does not affect the structure and the properties of the textiles.

Keywords: textiles; microorganisms; insects; gamma irradiation; thermal analysis

1. Introduction

The storage of cultural heritage goods in accordance with the conservation standards creates the conditions for their preservation and prolongs their life as long as possible. Ethnographic textile goods are fragile items, made of vegetal (cotton, flax, hemp), animal (silk, wool, leather) or artificial fibres. The degradations are determined by their sensitivity to the environmental factors, but especially by the biological agents: bacteria, fungi, rodents and insects. The most active agents of the textiles deterioration are fungi. Among *Deuteromycetes*, we find several species of *Alternaria*, *Aspergillus*, *Fusarium*, *Memnoniella*, *Myrothecium*, *Neurospora*, *Penicillium*, *Scopulariopsis*, *Stachybotrys* and *Stemphylium*, etc. Quite frequent and particularly harmful because of its high cellulolytic activity is the genus *Chaetomium* of Ascomycetes. Zygomycetes, such as *Mucor* and *Rhizopus* sometimes occur on textiles (Tiano 2002, Brokerhof 2007, Abdel-Kareem 2010, Pekhtasheva *et al.* 2012).

Fungi have a great destructive capacity in wet atmosphere and can cause chromatic modifications, colour changes; some of them even attack the intimate structure of the materials. Microorganisms which deteriorate the cellulosic fibres develop at air humidity over 80% and temperatures between 20-25^{0}C (Malcomete *et al.* 2000, Kavkler 2011, Pekhtasheva *et al.* 2012).

Microorganisms cause important damages through their attack on the surface and by weakening their mechanical strength. They feed on the cellulosic fibres, which represent a source of carbon or energy released due to the enzymatic action, while the intermediary or excretion metabolic products can deteriorate, colour or destroy the textiles (Oprea 2006, Pekhtasheva *et al.* 2012). Protein textiles are less susceptible to fungal deterioration than the cellulosic ones (Kavkler 2011).

Cellulosic textiles are also susceptible to attack by insects such as silverfish (*Lepisma saccharina*) and cockroaches (Blattelidae). The probability of attack is increased when this material contains glues made of starch or dextrin. The main insect families involved in textile biodeterioration are *Blattidae*, *Lepismatidae* and *Mastotermitidae*, *Hodotermitidae*, *Rhinotermitida*e (termites), but many others may occur occasionally (Tiano 2002, Kavkler 2011). In general, their attack ranges from surface erosion to destruction of parts of the object.

The insects most frequently found on protein textiles are some species within the families Dermestidae, Oecophoridae (brown house moth) and Tineidae (clothes moth). The better-known species of moths are *Tinea pellionella*, *Tineola bisselliella* and *Hofmannophila pseudospretella*, which degrade wool extensively and on a rare occasion, unscoured silk. Larvae, which use wool to feed and to build a protective sheath, are also a cause of damage. Carpet beetles, too, cause damage to textiles. Among most frequent species of *Dermestidae* are *Anthrenus verbasci*, *Anthrenus museorum*, *Attagenus pellio*, which cause damage only through their larvae because the adults usually spend their life elsewhere. The resistance of textiles to a biological attack depends on the chemical nature of the composing fibres. The most frequent microbiological damages can be seen in textile materials based on natural fibres: cotton, flax, hemp etc. (Gutarowska and Michalski 2012, Pekhtasheva *et al.* 2012).

Various studies focus on finding unconventional treatments for the decontamination of infested artefacts and for the preservation within museums (Pinniger 2011, Querner 2012). Radiations, which have a wide range of applicability in various fields, can be applied in order to decontaminate organic textile materials. The irradiation doses for the destruction of microorganisms are offered by the specialized literature. The low irradiation doses (5 and 10 kGy) simulate the conditions of the disinfection of textile objects performed to obtain bactericidal and fungicidal effects (Norberg and Serra-Freire 1993, Machnowski 2013). In this research work on the Iasa Ethnographic textile collections, (1) infestation types with their specific degradations, (2) resistance to fungi infestation of textile materials and (3) their behaviour to aging and gamma irradiation are presented. The effect of aging and gamma radiation on the properties of textiles was investigated by thermal analysis (Grigoriu *et al.* 2009, Abdullah *et al.* 2010, Bilkova 2012).

2. Materials and methods

2.1 Identifying the infestation types of the Ethnographic Museum and History Museum collections

Ethnographic textiles in these collections are made of vegetal (cotton, hemp, flax) and/or animal (wool, animal hair, silk) fibres. Most of the objects were made by traditional handicraftsmen in their own households, between 50 and 150 years ago. In the History Museum, there are textiles made of cellulose, protein or artificial based fibres (19th-20th centuries).

2.2 Sampling the model materials

This study was carried out based on model samples using woven fabrics made of 100% cotton, 100% flax and 100% hemp. The samples were marked as follows: initial (B0, I0, C0), artificially aged at 120 h (B3, I3, C3), gamma irradiated at 10 and 25 kGy.

2.3 Weathering Procedure

The cotton, flax and hemp model samples were subjected to the following hygrothermal aging atmosphere under a controlled atmosphere: the temperature was set at 80°C and the relative humidity was set at 65 %. All samples were kept in this atmosphere for 120 hours in a laboratory chamber

(Angelantoni Ind., Italy).

2.4 Fungal inoculation of model textile materials

In order to evaluate the incidence of microorganisms on the cultural heritage textiles, the procedure was carried out with cotton, flax and hemp model samples which were inoculated with microorganisms. The initial textile model samples and those hygrothermally aged at 80^0C and 65% RH were submitted to a biological attack. Fungi isolated from the cultural heritage textiles were grown on Sabouraud agar medium. According to SR-EN 1275/2006 growing standard procedure, the method of successive dilutions was used in order to prepare the suspension of microorganisms. After preparing the plates with Sabouraud agar medium, they are inoculated with a suspension of microorganisms (1 ml/10^{-4}).

The suspension contains the following species: *Aspergillus niger*, *Aspergillus flavus, Penicillium chrysogenum*, *Penicillium frequentans*, *Alternaria alternata*. Tests were performed according to STAS 20645/2005. Textile model samples with a diameter of 25 mm were used. They were kept between 12 and 24 hours in sterilized Petri boxes at ambient temperature. The inoculation was done according to the standard methodologies. The Petri plates are incubated for 24 h at 37^0C, followed by a first reading and then continued to 48 hours. The plates are left in an ambient temperature for 24 days and then, final evaluations are done.

2.5 Gamma irradiation procedure

Samples were irradiated at the Technological Irradiation Center IRASM / IFIN-HH using an Irradiator, SVST Co-60/B type with 10 and 25 kGy and were marked with B0_10, B0_25, B3_10, B3_25, I0_10, I0_25, I3_10, I3_25 and C0_10, C0_25, C3_10, C3_25 according to aging times and Irradiation Doses.

2.6 Thermal analysis

To analyse the thermal stability of cellulose fabrics, in order to evaluate the effect of the fibre type on the sample degradation process, we used thermogravimetric analysis which involves recording the thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermal (DTA) curves in an inert (N2) atmosphere using a Mettler Toledo Derivatograph. TG, DTA and DTG curves were recorded in nitrogen, at a flow rate of 20 ml/min, the heating rate of 10°C / min. within the temperature range of 25-600°C. The mass of samples subjected to the thermal degradation was between 2-6 mg. The checking of the reproducibility of the obtained characteristics was performed by repeating the recordings for the same atmosphere. The processing of the curves in order to obtain the thermal characteristics was performed using the STAR software from Mettler Toledo.

3. Results and discussion

3.1 Identifying the infestation types of the Ethnographic Museum and History Museum collections

Within the Ethnographic Museum collections, 104 infested objects were identified, out of a total of 1796 items made of protein based materials. The following types of insects were identified: Lepidoptera Order, Tineidae family, genre *Tineola bisselliella*, *Tricophaga tapetzella* and *Tinea pellionella*, as larvae or adults (Fig. 1).

Within the History Museum, 27 objects were identified out of a total of 281 infested parts (197 items from protein based materials, 62 items from cellulose based materials, 22 items from artificial fibres), of which 26 items from protein based materials and 1 item from cellulose based material. The following types of insects were identified: Phylum Arthropoda, Class Insecta, Order Coleoptera, Family Dermestidae *(Anthrenus verbasci*, *Dermestes maculatus)*, Tenebrionidae *(Trilobium destructor)* and Anobiidae *(Anobium punctatum)*.

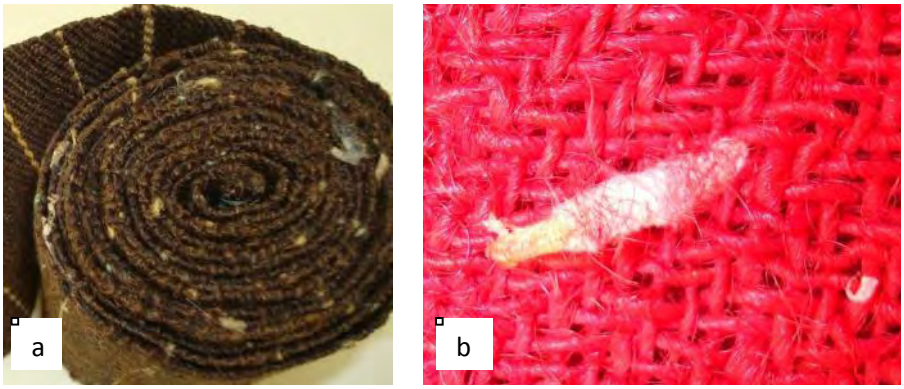

Fig. 1: Wool belts – pupal sleeves of *Tineola bisselliella* (a) and *Tricophaga tapetzella* (b)

3.2 Fungal inoculation of model textile materials

Each side of the textile model samples was macro and microscopically evaluated. The following results were obtained after 48 hours of incubation (Table 1). It is found that the cotton and flax model samples are comparable in sensitivity to fungal attack with the inoculated contaminants. After assessing the fungal attack macro and microscopically, the results show that the hemp model samples are the most sensitive ones; the mycelial hyphae develop almost on the entire Sabouraud agar medium (Fig. 2).

Table 1: Assessment of the fungal attack on cotton (B), flax (I) and hemp (C) model samples (see Fig. 2)

Sample type	**Development of spores and mycelium**	**Development level**
B0	A small number of colonies of microorganisms were microscopically observed on the samples.	0
B3	As seen on the microscope, only 10% of the surface of the samples was occupied by colonies of microorganisms.	1
I0	Only an area of 2 mm from the surface of the sample was contaminated.	0
I3	As seen on the microscope, only 12% of the surface of the samples was occupied by colonies of microorganisms.	1
C0	As seen on the microscope, only 15% of the surface of the samples was occupied by colonies of microorganisms.	1
C3	The entire surface of the sample is covered with mycelial hyphae.	2

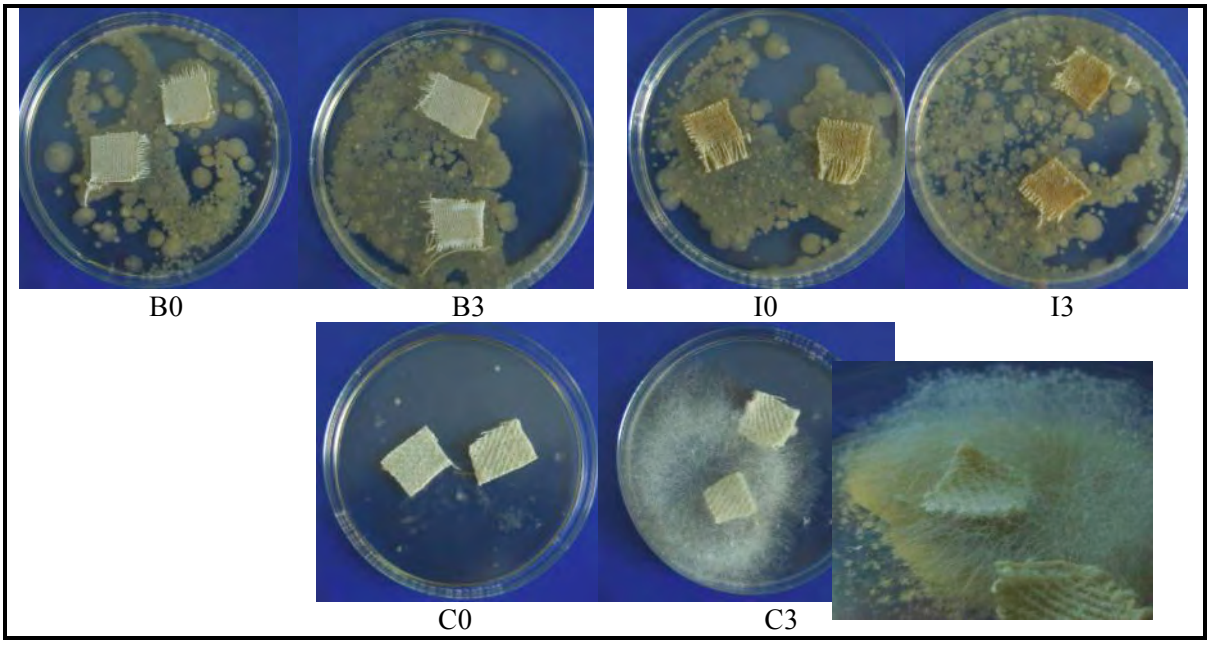

Fig. 2: Fungal attack on textile model samples cotton (B), flax (I) and hemp (C) (see Table 1).

3.3 Thermal analysis

The TG, DTG and DTA curves recorded in the nitrogen atmosphere for the initial, artificially aged, irradiated model samples led to establishing the main thermogravimetric characteristics which are presented in Table 2. The degradation takes place for all samples in two stages in nitrogen. The first stage which takes place within the range of 40-110°C, whatever the working atmosphere consists in the removal of moisture from the samples. The percentage mass loss (W, %) at this stage varies between 2 and 8%. In nitrogen it is found that the thermal decomposition ends for all samples in around the temperature of 400°C. This stage which takes place in the temperature range 300-400°C is due to the release of the volatile hydrocarbons by the thermal decomposition of cellulose, hemicellulose and a part of lignin from the composition of cellulosic materials; volatile products have an important role in the pyrolysis of these materials.

Table 2: Thermogravimetric characteristics for cellulosic textile samples.

Working atmosphere		**nitrogen**				
Sample	Stage	T_{onset} (°C)	T_{peak} (°C)	T_{endset} (°C)	W (%)	Residue (%)
B0	I	58	74	105	4.62	14.92
	II	327	361	382	80.46	
B3	I	54	67	102	5.00	15.15
	II	305	362	381	79.85	
B0_10	I	46	63	102	6.20	13.57
	II	311	361	377	80.23	
B0_25	I	57	65	94	2.30	16.97
	II	310	358	374	80.73	
B3_10	I	52	62	101	2.02	16.52
	II	304	360	377	81.46	
B3_25	I	54	58	99	2.15	15.95
	II	302	358	373	81.90	
I0	I	53	59	98	3.84	19.11

	II	305	361	377	77.05	
I3	I	47	60	118	4.98	18.44
	II	301	359	377	76.58	
I0_10	I	46	63	94	7.89	14.39
	II	299	358	374	77.72	
I0_25	I	55	72	99	7.43	16.87
	II	318	354	372	75.70	
I3_10	I	47	63	109	3.60	18.95
	II	315	357	374	77.45	
I3_25	I	43	55	96	6.47	14.89
	II	312	357	370	78.64	
C 0	I	44	55	105	4.00	17.12
	II	320	359	384	78.88	
C3	I	52	68	95	6.34	18.30
	II	317	355	370	75.36	
C0_10	I	44	56	105	5.26	20.31
	II	321	357	371	77.43	
C0_25	I	54	69	103	5.13	21.71
	II	307	354	369	73.16	
C3_10	I	54	65	114	4.09	21.62
	II	318	358	373	74.46	
C3_25	I	51	67	111	3.44	22.10
	II	315	356	373	74.46	

T_{onset} – the initial temperature at which the thermal degradation begins in each stage;
T_{peak} – the temperature at which the degradation rate is maximal in each stage;
T_{endset} – the temperature at which the thermal degradation ends in each stage;
W(%) – the percentage mass loss in each stage;
Residue – the amount of deteriorated sample remaining at the temperature of 600°C.

To point out the influence of the hygrothermal aging and irradiation process on the flax samples Fig. 3 shows comparatively. One can notice also in the case of the flax model samples that a 10 kGy intensity of the irradiation process does not cause significant changes of the main thermogravimetric characteristics.

For the hemp model samples, the thermogravimetric curves are presented in Fig. 4. Both in the case of the initial model sample as well as in the case of the artificially aged sample, significant changes of the main thermogravimetric characteristics are noticed if the intensity of the irradiation reaches 25 kGy.

Thermal analysis of silk model samples indicates a reduction of the thermal stability after 120 h aging treatment and gamma irradiation (Fig. 5).

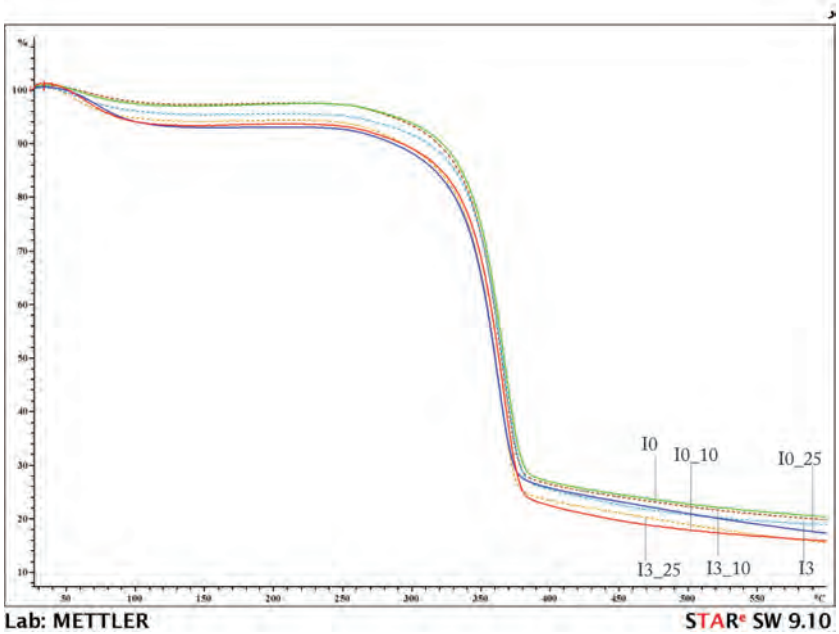

Fig. 3: TG curves for flax model samples.

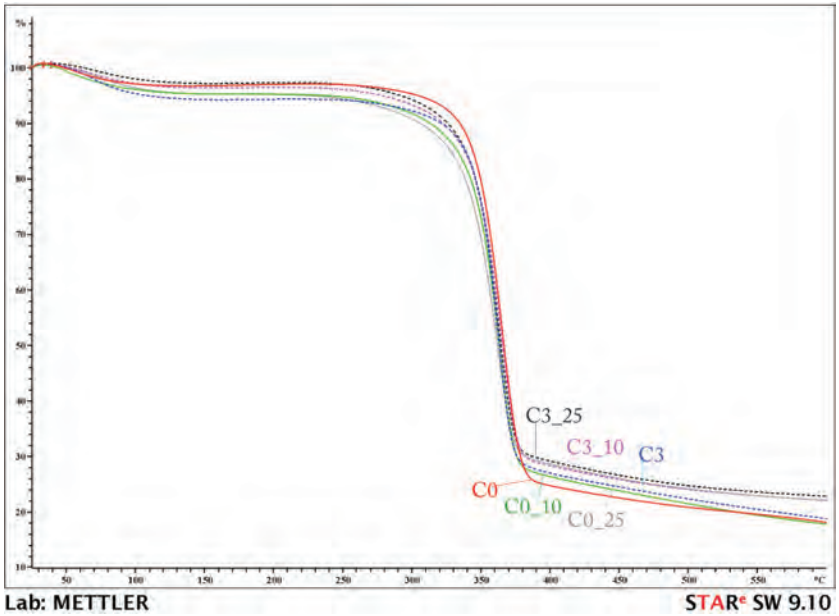

Fig. 4: TG curves for hemp model samples.

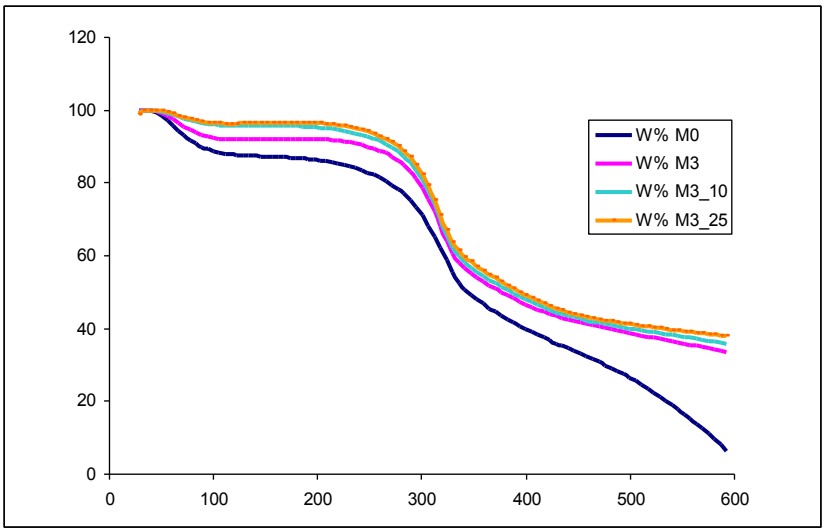

Fig. 5: TG curves for silk samples.

The results for thermal analysis for wool model sample in the inert atmosphere showed around 30% residue at 600ºC and a loss of water by evaporation of 7-11 %. The temperature initiation point for degradation (value of T_{onset} in the second degradation step) is not significantly changed by aging and irradiation conditions (Fig. 6).

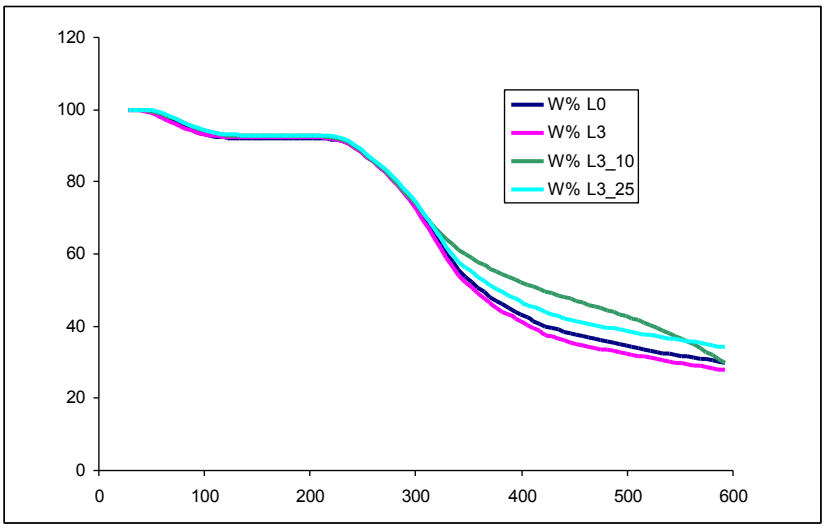

Fig. 6: TG curves for wool samples.

Conclusions

On the textile artefacts belonging to the two museums, the following species of insects were identified: Lepidoptera Order, Tineidae family (*Tineola bisselliella*, *Tricophaga tapetzella* and *Tinea pellionela*, Phylum Arthropoda), Coleoptera Order, Dermestidae Family *(Anthrenus verbasci*, *Dermestes maculatus)*, Tenebrionidae Family *(Trilobium destructor)* and Anobiidae Family *(Anobium punctatum)* as larvae or adults.

After assessing the fungal attack macro and microscopically, the results show that the hemp model samples are more sensitive than the cotton and flax ones. The thermal stability study of the different cellulosic textile material types has pointed out the influence of the following factors: working

atmosphere, the duration of the accelerated aging process and the intensity of the irradiation treatment. Thus, it has been found that, for all samples, degradation takes place in two stages in nitrogen. The changes of the main thermogravimetric characteristics are more obvious for the samples subjected to 120 hours accelerated aging. Their thermal stability slightly decreases compared to the one of the initial model samples. In the case of all cellulosic textile materials it is also noted that a 10 kGy intensity of the irradiation treatment does not change significantly the main thermogravimetric characteristics. Smaller 60Co doses up to 10 kGy do not cause significant changes in the levels of degradation for the artificially and naturally aged protein-based fibres, compared with the unirradiated fibres. The results of tests and the analysis are suggesting a level of gamma irradiation below 10 kGy for the conservation of the textiles from the cultural heritage.

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The gamma-ray disinfection of historical collections

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Abstract
This review gives an overview on the current applications and limitations of gamma irradiation in the conservation practices. Studies performed to assess the impact of gamma-ray treatments on historical materials method are discussed. The available data indicate that inactivation of micro-organisms and insect pests is essentially complete at the gamma radiation doses usually employed (up to a maximum of 10 kGy), while the efficacy of the method appear to be dependent upon the radiation dose, the dose rate for the process, the type of the targeted biological attack, and should be selected according to the chemical and physical properties of the materials.

Keywords: gamma irradiation; pest control; heritage collections; natural polymers; radiation effects

1. Introduction

The long-term conservation policies applied to museums or archives proves to be difficult in the case of the historical collections containing organic materials. The mixed collections are imposing quite various levels of environmental parameters considered to be optimal, due to their diverse effects on the chemical response of different objects, and there are many factors that can assist the development of bio-deterioration processes in case of organic materials (Strang *et al.* 1991, Rose 1994, Flieder 1999, Pinniger 2004, ASHRAE Handbook 2007). Fungicides and bactericides have long been used in various applications within the conservation practice. Often recorded as hazards to humans but also detrimental to the treated objects, applying chemicals in museums is currently avoided. In this context, pest control plans are now involving non-toxic procedures such as air ventilation, low temperature and low oxygen environments (Burke 1996, Rust *et al.* 1996, Carter *et al.* 1999, Pinniger 2001, 2004, Winsor *et al.* 2011).

Along with other eco-friendly pest management techniques, the disinfection with ionizing radiation is nowadays more and more used, as a method which is based on physical principles (Gonzalez *et al.* 2002, Magaudda *et al.* 2004, da Silva *et al.* 2006, Bratu *et al.* 2009, Katušin-Ražem *et al.* 2009, Manea *et al.* 2012). Despite its advantages, there is still a limited implementation of this technique. Occasionally, concern has been expressed over the potential damage to historical objects by exposure to radiation of short wavelengths from the electromagnetic spectrum (γ-rays) and electron beams (β-rays), and there is still some lack of knowledge on the specific responses to irradiation of certain biological attacks in museums or archives (Maggauda 2004, Adamo 2007, Moise *et al.* 2012, Negut *et al.* 2012). This review gives an overview on the principles of the method, and its current applications and limitations in conservation practices.

2. Radiation processing

Commercial gamma ray irradiation facilities working on the service basis or installed on-line are used mostly in the sterilization of medical devices and for industrial application (e.g. pharmaceutical, food, cosmetic industries, etc.) (Muranno *et al.* 1995, Katušin-Ražem 2001, Kamat *et al.* 2003, Rimnac *et al.* 2005, Farkas 2006, Nguyen *et al.* 2007, Gomes *et al.* 2009). These facilities are using standard sealed

sources of ^{60}Co isotopes, strictly related to the international and national regulation (ISO 11137, Parts 1-3, ISO-14937(E)). The radioactive decay leads to high energy photons: γ-rays. The energy carried by the gamma radiation is transferred to the irradiated material, by collisions between the radiation and the atoms of the material. The potential application in decontamination is based upon the fact that high penetrating ionising radiation damages the DNA so that cells in microorganisms or insects become inactivated (Farkas 2006).

The sterilization dose for a treated material can be expressed as the absorbed energy per unit mass [J x Kg^{-1}] = [Gy]. Doses for sterilization should be chosen according to the required or desired sterility assurance level (SAL), the natural bioburden, and the resistance to ionizing radiation of microorganisms. The radiation resistance of a microorganism is measured by the irradiation *decimal reduction dose* (D-10 value), which is defined as the radiation dose (in kGy) required to kill 90% of the total number (Whitby and Gelda 1979). The reported results on the inactivation of microbial populations were observed to be environmentally dependent - e.g. drying or freezing, aerobic or anaerobic conditions - (Grecz *et al.* 1965, Saleh *et al.* 1988, Thayer *et al.* 2001, Jo *et al.* 2012). For instance, the radiation response of vegetative bacteria lies within the limits of 0.04 – 1.0, while the average D_{10} value for bacterial spores and for fungi is higher: 1 – 2.2 kGy. Approximate D_{10} values of heat resistant moulds *is:* 1.08±0.08 kGy (Farkas 2006, Yun *et al.* 2007, Gumus *et al.* 2008).

Gamma rays of the radionuclide ^{60}Co can deliver the necessary dose of ionizing radiation required for preventing the reproduction of microorganisms and insect gametes that might be present in the treated objects, on an industrial scale. The duration of exposure can be from minutes to hours, depending on the thickness and the volume of the product, on the resistance of the particular species and according to the number of the organisms in question. While 25 kGy is commonly used for sterilization, elimination of pathogenic microorganisms (other than viruses) in fresh and frozen food would require 1.0 to 7.0 kGy, and the usual doses for the reduction or elimination of microbial population in dry food ingredients lies within doses of 3.0 to 10 kGy. Relatively low doses from 0.2 to 0.8 kGy are reported when using irradiation to kill and sterilise insect pests, as an alternative treatment to pesticides (Farkas 2006).

3. Gamma irradiation in the preservation of cultural heritage

The first studies using gamma radiation in the early 60's were concerning the need of finding an effective disinfection method, due to a reported fungal attack in an archive from Russia (Belyakova 1960). From that point on, the technique was applied for the disinfection of Ramses II mummy (de Tassigny *et al.* 1978) and has been most successful in emergency circumstances (e.g. flood-damaged books or archeological waterlogged wood) (Bonetti *et al.* 1979, Pointing *et al.* 1998, Maggauda *et al.* 2004). Irradiation proved to be a safer method because it does not leave behind any harmful residue and the ionizing radiation does not generate radio-activation in the historical materials (Adamo *et al.* 2001, Rochetti *et al.* 2002, Smith *et al.* 2003, Bratu *et al.* 2009, Katušin-Ražem *et al.* 2009, Moise *et al.* 2012). According to Maggauda, in case of heritage applications the target should be not the sterilization, but the 'reduction of the amount of biodeteriorating agents below the danger threshold' (Magaudda 2003).

Preventive and curative irradiation treatments also included celluloid film rolls collection (Mitran *et al.* 2002), wooden objects (Cutrubinis 2008, Katušin-Ražem *et al.* 2009), paintings (Rizzo *et al.* 2002) and paper-based collections (Adamo *et al.* 2001, Gonzales *et al.* 2002, Maggauda 2004, da Silva *et al.* 2006, Bratu *et al.* 2009).

Because the biological attack on organic materials within the collections have different degradation patterns, it is quite difficult to establish a standard dose. In order to ensures a significant decrease of bioburden or insects and minimize the negative effects on materials, the proposed dose ranges vary up

to 20 kGy. Some studies have recommended doses of 0.5 kGy as an insecticide and of 10 kGy as fungicide (Maggauda 2003, Cutrubinis 2008, Bratu *et al.* 2009), but reported results on gamma radiation dose/inactivation response are varying from 2 to 25 kGy. For instance 14.4 kGy were needed for mold inactivation (Gonzalez *et al.* 2002), 16 kGy against fungal attack on archives (da Silva *et al.* 2006) and 25 kGy to inhibit microbial growth on Egyptian paintings and stone surfaces (Abdel-Haliem *et al.* 2013).

4. Effects of gamma irradiation on organic materials

Depending upon the chemical structure of the polymer but also upon the conditions under which irradiation is performed (ex. absorbed dose, dose rate, environment, temperature, etc.) ionizing radiation affects material properties, so the compatibility of all of the components in an object has to be considered (Moise *et al.* 2012). When the natural polymers within the cultural heritage materials are irradiated by ionizing radiation, radiation degradation chemistry involves changes in the molecular structures, mainly as a result of chain scission and crosslinking processes.

The high-energy photons, such as gamma rays can generate time-dependent free-radical reaction mechanism in polymers (Bratu *et al.* 2007), the free-radicals being able to undergo chemical reactions -especially in the presence of oxygen- long after the exposure to radiation treatments. The extent of chemical changes induced by radiolysis in macromolecules is usually associated with the changes in crystallinity and morphology of a certain organic material (Geba *et al.* 2008).

The correlations of the changes in morphology and crystallinity with other properties during irradiation are important to explain the pattern of the further evolution of aging in the irradiated historical objects. The published studies relate the crystallinity and morphological changes to the corresponding changes in other properties such as mechanical (Bratu *et al.* 2009), structural (Geba *et al.* 2008) and optical properties (Adamo *et al.* 2007) or thermal stability (Bratu *et al.* 2009, Severiano *et al.* 2011). Table 1 is including data from the available literature on the reported effects of gamma irradiation treatments on the materials that are frequently found within museums or archive collections.

Table 1: Reported effects of gamma irradiation on organic materials

Absorbed dose (kGy)	**Dose rate (kGy/h)**	**Material**	**Reported effects**	**Author**
0.2–0.5 for insects	-	Paper (pure cellulose)	- no significant harmful effect on the mechanical and physical properties of paper or printing inks bellow 5 kGy	Magaudda 2003
3–8 for micro-fungi				
25 and 50		High quality printing paper; low quality recycled paper (newspaper)	-significant changes in paper resistance at a 50 kGy dose -the presence of free radicals in newspaper - reduction of thermal stability for the low quality paper	Bratu *et al.* 2009

2;3;5	14.700	Commercial paper	- depolymerising effect at the lower dose/ rate - minimum colour changes -no substantial structural changes	Adamo *et al.* 2001
3–30	1.7	Whatman paper, copy paper	-decrease in mechanical (<20%) and thermal stability for doses bellow 10 kGy	Moise *et al.* 2012
14.4	0.15	Cardboard, permanent paper, photo print paper	no significant changes in the mechanical properties	Gonzalez *et al.* 2002
3 -15	0.817	Paper (bleached eucalyptus pulp)	-no significant effects on the paper resistance -brightness decrease after 9kGy -yellowing	D'Almeida *et al.* 2009
21; 29; 57; 74	-	Raw cotton fibres	-affected physical fibre properties (strength, elongation, length uniformity) decrease of molecular weight -no significant structural changes -increase in colour difference after dyeing	van der Sluijs *et al.* 2013
1-2	-	Jute yarn	-decreased tensile strength -free radical sites formation -relatively unchanged crystallinity -no significant structural changes	Saha *et al.* 2000
0, 100, 500, and 1000	-	Degummed silk fibres	-destruction of the hydrogen linkage of secondary structure -no degradation of the polypeptide chain	Kojthung *et al.* 2008
25,50,100	10	4 wood species	-no meaningful changes of thermal stability	Severiano *et al.* 2011
24		Samples from wooden churches	-decrease in lightness -free radicals persistence	Cutrubinis 2008
20-9.000	-	Pine wood	Reduction of the degree of crystallinity: -at 120 kGy slightly decreased -at 500-4500 kGy dropped rapidly -at 9000 kGy occures a total degradation of cellulose	Kasprzyk *et al.* 2004
11 and 24.5	-	Oil painting	-No significant colour alterations -No change in appearance of yolk egg (binding medium in	Manea *et al.* 2012

			paintings)	

Many of the observed variations for the studied properties (see Table 1) can be considered significant, and data suggest that in order to minimize undesirable effects of free radicals in natural polymers, an ideal absorbed dose and the dose-rate should be established. Also, from experimental data it cannot be concluded that γ-rays are evenly absorbed in objects having different shapes (Choi *et al.* 2012). In this case, attempts to use Monte Carlo computer models may significantly improve the accuracy of radiation treatment setup for historical objects. Monte Carlo calculations gained an exponential growth in Medical Physics since the 80's and give the advantage of simulating the passage of gamma photons beam from different models of gamma sources, in a finite geometry (ex. the shape of a composite historical object). At the same time, the mathematical models serve as a good estimate for the attenuation and scatter of radioactive contaminants inside different objects and lead to determining the dose-distributions in the artefacts.

Up to now, the only published result (Choi *et al.* 2012) of a simulation of irradiation treatments in cultural heritage is using the Monte Carlo N Particle Transport Code. The study was comparing the experimental data from gamma radiation inactivation of fungi on agricultural tools (wood and iron) at 20 kGy with simulated calculations, and concluded that simulated and measured dose showed good agreement (the difference was less than 1 kGy). At the same time, all data showed that gamma rays penetrated heterogeneously the organic materials: in a 80 cm cylinder - from 19.3 kGy to 4.7 kGy, in a box-shaped wooden part- from 19.3 kGy to 15.8 kGy and in a comb-shaped iron part the absorbed does was 19.3 kGy. The model proved to be reliable for a broad range of cultural heritage artefacts subjected to irradiation treatments.

Conclusions

The goal of the review was to acquire a consensus value of the efficacy of gamma irradiation for inactivation of various contaminants in heritage collections. In the case of certain bio-contaminants and specific organic materials, the results have been very similar, but it is hard to assess a perfect inactivation treatment. The effectiveness of the method is dependent upon factors like the radiation dose, the dose rate for the process, the type of present insects or microorganism. The process should also be selected according to the chemical and physical properties of the materials to be exposed to gamma rays irradiation. Therefore, the simulation of irradiation treatments using mathematical models may significantly improve the accuracy of radiation treatment setup for historical objects.

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