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Air Exchange Rate – the Dominant Parameter for Preventive Conservation?

Abstract
This article aims to demonstrate that air exchange rate is extremely important for the performance of display cases with regards to relative humidity buffering, dust and pollutant ingress and corrosion of metals displayed within them. The display cases built for English Heritage to house the Wernher collection of small and precious objects at Ranger's House, London are investigated. The displays were set up four years ago, and air exchange rates were measured and leakage rates reduced as far as possible at that time. The extended methods for measuring air exchange rates are discussed and the longer term performance of the cases is investigated. The importance of the capacity of the cases to maintain appropriate RH levels without using the hygroscopic objects to act as buffers is also highlighted. Maintenance of display case performance requires monitoring, actions and effort, as seals and mechanical parts age.

Introduction

Air exchange rate has been recognised as an important parameter for showcases for at least 30 years. For the majority of cases control of RH is the primary conservation concern. Ingress of dust determines cleaning rates and influences metal corrosion (Vernon 1935; Thickett and Hockey 2002) Ingressing external pollution can effect both metal corrosion and acidify and oxidise organic materials (Brimblecombe 1990; Larsen 1993). Tight showcases concentrate any emissions from construction and dressing materials and these gases have been shown to be able to cause catastrophic effects on lead, copper alloys and silver and salt laden stone and ceramics in certain instances. Numerous papers and books have been published highlighting the importance of air exchange rate, but routine measurements have been hampered by expensive equipment and the requirement for electrical mains power, which is rarely available in a showcase (Padfield 1966, Thomson 1977, Cassar and Martin 1994). The development of methodologies using relatively affordable, battery powered loggers has brought routine measurements within the reach of many institutions (Calver et al 2005, Microclimate 2005).

Many UK showcase manufacturers can now produce showcases down to 0.1 air changes per day. This is probably about the practical limit for multi geometry cases. In specific instances, cases with air exchange rates down to 0.02 per day (day-1) have been produced, but this is only feasible when using particular geometries and designs. A decade ago procuring cases to the 0.1 day-1 specification would add approximately 10-20% to the showcase cost (Cassar and Martin 1994). Advances in case design have introduced many of the design features required for good air tightness into common practise and there is no longer a price differential. However the air tightness of a case can be significantly compromised by a single hole, missed seal or misaligned joint. In order to meet even a relaxed criteria of 1 day-1, requires significant input of resources from the institution procuring the showcases. Several approaches have been tried. For major gallery projects sometimes a proportion of the cases are tested by the independent test house Building Industries Research Association, BISREA. If any of these cases fail the criteria then the remainder are tested at the manufacturer's expense. Unfortunately such testing is expensive (averaging £1000 per test), and requires mains power. Another approach reported previously in this journal is to test all of the cases as they are built internally (Stanley et al. 2003). The Wernher Collection was installed in the upper floor of Ranger's House in a major representation project during June 2002. The Collections Management Team (formerly Collections Care Team) of English Heritage collaborated with the designers, case manufacturers and lighting designers to procure 16 new display cases and renovate two original Victorian display cases. This approach is much less expensive in capital costs, the equipment needed for testing is approximately the same cost as a single BISREA test, but is much more expensive in staff time. With a significant investment of effort, 18 cases meeting the 1day-1 criteria set for the project, were developed. This process required over thirty air exchange rate tests and took twenty full staff days. However, many issues were resolved rapidly because of the on site presence.

Three years have passed since the initial instillation of the Wernher Collection display cases, and a review of their performance seemed prudent, to ensure that

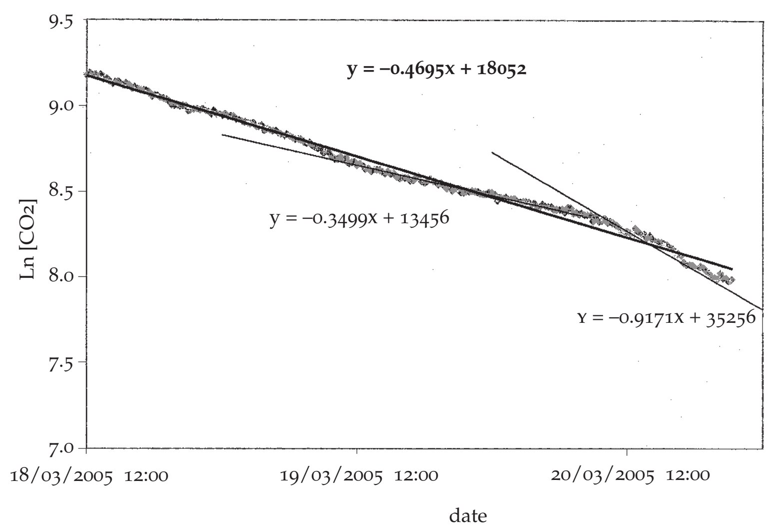

Figure 1 Carbon Dioxide Decay in Discernment Clock Case Showing Calculation of Air Exchange Rate and Diurnal Variation

they are still meeting the original design criteria. The air exchange rate of many of the cases had been measured and this allowed an assessment of several aspects of their performance against air exchange rate. Air exchange rate measurements were taken over the three year period and any increase from use or aging of sealing materials could be determined. This allowed an assessment of the benefit of investing time in procuring display cases with a defined leakage rate at the beginning of their lifetime.

The maintenance of the passive control systems used (Artsorb) and its replacement and reconditioning regime were assessed. The last three years have also allowed investigations into a number of concerns about the environment maintained within the cases.

Methods of Assessment

To evaluate the cases, a number of methods were employed.

Air exchange Rates

During the original testing of the display cases, air exchange rates, AERs were measured using a nitrous oxide tracer gas method, with the aim to ensure that all the cases met a criteria of one air exchange per day.(Stanley et al. 2003). The loggers used were all recently purchased and within the one year calibration period quoted by the manufacturer. The loggers were placed on base of the case to be tested. Between 6000 and 8000ppm of nitrous oxide was injected into the case from a dispenser. The air exchange rate was calculated from the natural logarithm of the nitrous oxide decay curve. The nitrous oxide logger used for these tests has a limited battery life (approximately 24hrs with an external battery). The large number of measurements required and the need to fit in around the busy case installation schedule led to several measurements running for as little as twelve hours overnight. This has a number of implications for air exchange rate measurements. The air exchange rate is strongly affected by temperature differences between the case and the room air. Internally lit cases or those that are in naturally lit rooms can be significantly warmer than the room. The specification for this project stated that cases should not generate temperatures in excess of 5°C of the room temperature. A careful design to vent heat generated by the lighting ensured that this was easily met. The maximum increase in case temperature was less than 1.5°C over the room air temperature. However, even this caused a very significant diurnal cycle in air exchange rate, see Figure 1. If less than 24 hours data is used for an air exchange rate measurement, then this can give unrepresentative results. Two eight hour periods are shown on Figure 1 giving AERs of 0.35 and 0.92 compared to 0.47 for the full 24 hour period. In order to make the AER measurements comparable, a twelve hour period starting at 20:00 was used, where available. If the run did not extend that far all of the available data from 20:00 was used and the time used is quoted in brackets with the results. The air exchange rate tests were repeated in 2004 to assess if there had been a change in the case performance since installation. The same logger was used for each test as had originally been used and the calibration was checked with a calibration mixture traceable to NAMAS standards. All tests were run to provide twelve hours of data after 20:00. Since temperature and RH differences between the case and room have a dramatic effect on air exchange rate this information was recorded and examined for each measurement. Two sets of measurements were repeated as visual examination of this data revealed much greater temperature differences during the second set of measurements on a particularly cold day. A final set of air exchange rate measurements were undertaken in 2005 using carbon dioxide with a Vaisala GMP70 carbon dioxide logger. This logger can run for several weeks on its internal battery and measurements are taken as an average of five twelve hour periods and also as an average of five full days after an initial injection of carbon dioxide to give 5000ppm in the case. A direct comparison of nitrous oxide and carbon dioxide for measuring showcase air exchange rates has shown no significant difference in the two methods (Calver et al 2005).

When high air exchange rates were measured, the leakage paths were investigated with a Inficon D-Tek gas sniffer. Compressed air from a Maplin N60AN Air Duster was blown into the case. The sniffer detects the propellant from the compressed air.

Environmental Analysis (T and RH data)

Environmental data (air temperature and relative humidity) collected using a Meaco system with Rotronic Hygrostat probes over the last 3 years was assessed against criteria identified for the artefact types in the different cases. Of particular interest was any degradation of the conditions within the display cases. This could be linked to degradation of the air exchange rate or the Artsorb cassettes that have been used to control most cases.

The temperature and RH distribution in one display case was measured using four Smartreader 2 data loggers with four external SR020 probes. This allowed measurement at eight points; on the baseboard and underside of the top of the display volume, in the centre and at the side, at the front and rear of the case. This was undertaken for two, four week periods in Winter and Summer.

The weight of a wooden panel displayed in one case was continuously monitored for three months using a RDP Model 31 precision miniature tension load cell with RDP Transducer Indicator E308 transducer controller and Smartreader 7 data logger. The panel hangs from a single point and a mount was designed to ensure that it hung away from the backboard so that the whole weight was supported through the transducer. The wiring for the transducer was fed through the 'o' ring sealed hole normally used for the Rotronic probe monitoring the case. A Hanwell Humbug II data logger was placed in the case to replace the environmental data lost.

The potential for the tungsten halide case top lighting to produce thermal gradients across the length of the Limoge enamels displayed in some cases was investigated. The surface temperatures of enamels in two cases were measured with an Inframetrics ThermaCAM PM290 thermal camera. The thermal emission co-efficient for metals is much higher than for glass and the camera does not cope well with mixtures of the two materials. The temperature of the copper alloy back-plates and edges of the plaques was measured using platinum resistance thermometer attached to Smartreader 8 data loggers. The temperature of the copper alloy was assumed to be homogeneous due to copper's high thermal conductivity. The case lighting was run for two hours before being turned off for measurements with the thermal camera.

Dust

The dust deposition rate inside and outside each case was measured by exposing clean glass slides for 28 days. The outside slides were placed as close as possible to the case and as near as possible to the same height level. Microscopy and image analysis was then undertaken to characterise the amount of dust by the percentage of the area of the slide covered (Howell et al. 2002).

External and Internal Pollutants

Ingress of the external pollutants, sulphur dioxide and nitrogen dioxide, was assessed by measuring concentrations inside two display cases and the rooms they reside in with commercially available diffusion tubes. The tubes were exposed for two 28 day periods, the first in August 2004 and the second in December. The room results and showcase details were fed into the IMPACT program1. This web based program allows easy application of the equation developed by Weschler to predict the concentration of a gas in an enclosure (or building) from the external concentration (Weschler et al. 1989). The equation is;

$$C_{int} = \frac{aC_{ext}}{(\frac{dS}{V} + a)}$$

where; C_{int} is internal concentration
C_{ext} is external concentration
a is the air exchange rate
S is surface area of absorbing material in enclosure
V is volume of enclosure
d is deposition velocity of gas of interest onto absorbing material

Lead and silver metal coupons were also exposed. Lead is extremely sensitive to organic acids, the most common damaging internal pollutant in display cases. MDF and MDF coated with Dacrylate are both known to emit substantial sources of acetic acid (Eremin and Wilthew 1996; Thickett 1998). The exposed lead and silver coupons were examined both by eye and measuring the colour of the surface with a Minolta 2500D spectrometer. Tetrault has investigated the relationship between L* and the amount of corrosion for lead in an acetic acid environment (Tetrault et al. 1998). Human perception of the initial tarnishing of silver has been found to correlate well with an increase in b*. After exposure the lead coupon surfaces were analysed with Reflection/Absorption Fourier Transform infra-red spectroscopy, R/A FTIR, Perkin Elmer 2000 with Durascope. Finally the amount of oxdised lead on the coupon surfaces was determined by cathodic stripping with a Uniscan PG580 potentiostat in 0.1% sodium hydroxide solution (ASTM G1).

Case Selection for the Review

The cases that were selected for the review were those that had previous air exchange rate measurements taken. This would allow comparisons to be made with current data. A larger set of cases was used for the dust and lead and silver measurements as these are relatively quick methods. A list of those cases tested

Table 1 Cases Used for Measurement

Room	No	Display Case	Height (cm)	Width (cm)	Depth (cm)
Bath House Room	1	Central Table Case	84	117	78
	2	Victorian Case Base*	20	134	68
Private Devotion Room	3	Alcove Case	132	62	30
	4	Vitrine Near Closet	108	112	30
Discernment Room	5	Alcove Case	132	62	30
	6	Window Vitrine Case*	106	144	28
	7	Wall Case	106	62	62
Connoisseurship Room	8	Central Table Case	82	100	44

* sulfur dioxide and nitrogen dioxide measurements

1 available at http://www.ucl.ac.uk/sustainableheritage/impact/

2 repeatability is used here, but this is strictly for a number a measurements carried out over a short time frame, certainly not days, reproducibility is reserved for measurements carried out on the same material by different investigators using different sets of equipment.

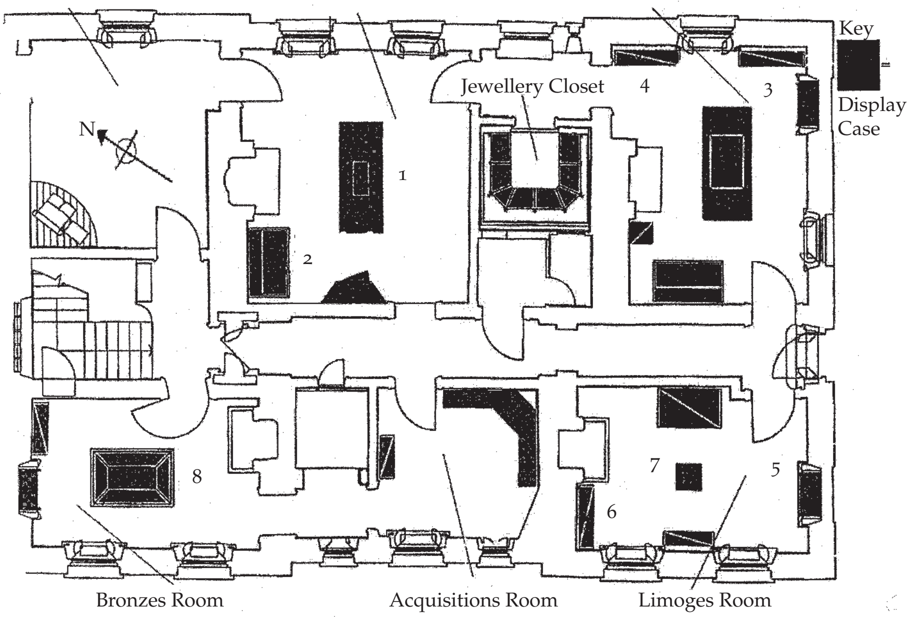

Figure 2 Floor Plan Showing Location of Cases

is below with a floor plan included as Figure 2, to show the location of the measurements.

Results

Air Exchange Rates

Table 2 shows the twelve hour normalised air exchange rates measured. The last set of carbon dioxide measurements also show the AER from five days worth of measurement. Previous work has shown that nitrous oxide and carbon dioxide measurements give comparable results and that the repeatability standard deviation of the carbon dioxide measurement is less than 5% (Calver et al. 2005). The repeatability standard deviation of the nitrous oxide method was determined to be slightly higher at 7%. Errors quoted have been determined either using the method given in ASTM E741-00 for a single measurement (first three air exchange rate columns) or root mean squares of those errors for five measurements (last two columns), and hence these second sets of errors are

Table 2 AER Measurements

		Air exchange Rate (/day)				
		Nitrous Oxide		Carbon Dioxide		
Case Number	Case Volume (m^3)	As installed Apr 2002 (times after figures)	Mar 2004 (all 12 hours)	Mar 2005 (first 12 hour measurement)	Mar 2005 (average of five 12 hour measurements)	Mar 2005 (average of five 24 hour measurements)
Case 1	0.77	0.2 ± 0.1 (12)	0.5 ± 0.1	0.4 ± 0.1	0.4 ± 0.1	0.6 ± 0.1
Case 2	0.18	1.7 ± 0.1 (12)	1.7 ± 0.1	1.9 ± 0.1	1.9 ± 0.2	2.4 ± 0.1*
Case 3	0.36	1.0 ± 0.1 (12)	2.0 ± 0.1	2.1 ± 0.1	2.2 ± 0.2	2.6 ± 0.1*
Case 4	0.29	0.4 ± 0.1 (9.5)	0.5 ± 0.1	0.6 ± 0.1	0.6 ± 0.1	1.0 ± 0.1
Case 5	0.25	0.9 ± 0.1 (12)	1.6 ± 0.1	2.0 ± 0.1	2.0 ± 0.2	2.6 ± 0.1*
Case 6	0.28	0.5 ± 0.1 (10.5)	2.0 ± 0.1	3.3 ± 0.1	3.2 ± 0.3	4.5 ± 0.1**
Case 7	0.4 0	0.3 ± 0.1 (12)	0.5 ± 0.1	0.5 ± 0.1	0.5 ± 0.1	0.8 ± 0.1
Case 8	0.36	0.5 ± 0.1 (12)	0.4 ± 0.1	0.6 ± 0.1	0.6 ± 0.2	0.8 ± 0.1

* 5 separate injections
** 5 injections to 40,000ppm

larger. Because of the complexity of the different mechanisms of air exchange between a showcase and a room and the assumptions in ASTM E471-00 these errors are probably underestimates. A figure of 20% of the measurement value is probably more realistic. Air Exchange Rate measurement errors are discussed in more detail in Appendix 1.

Considering a 20% error on the air exchange rates, generally they have increased, with cases 3, 5 and 6 substantially above the original criteria specified. Cases 3 and 5 are alcove cases which were extremely difficult to seal to the specified standard when originally installed. Significant extra silicone sealant had to be applied, particularly around the fibre optic pipes. The leakage sniffer showed significant leakage at these points indicating that this had broken down, possibly due to excessive heat build up from the fibre optic source under the cases. A small sample was removed from the edge of one of the seals and analysed with Fourier transform infra-red spectroscopy (Perkin Elmer 2000). For comparison a small sample was removed from the top of that case, an area that had not undergone heating. The spectrum indicated that the seal was a silicone rubber and that the sample from around the fibre optic fittings had lost much of the methylene normally present in its structure, with a reduction in absorption band at 2905. A strong absorption centred around 3420cm-1 may indicate formation of an hydroxyl group. These chemical changes have been linked with volume shrinkage and embrittlement of silicone rubbers (Ghanbari-Siakali et al 2005). Visual examination of the seal in situ revealed that it had not lost adhesion to the case carcass, but appeared to be cracked and perforated and have lost cohesion.

Case 6 was the prototype case for the project and has seen a very dramatic increase in AER. The sniffer indicated leaks above the top of the hinge and at the bottom opposite corner of the side hinged door. This indicates that the door has slipped on its hinges and the manufacturer was called back to rectify the problem. The door was estimated to have been opened approximately 25 times in the three years over which this had occurred.

Environmental Conditions Within the Display Cases

To help compare the performance of the display cases across the monitored rooms, an average daily RH fluctuation was calculated for both the room and the display cases. The results are shown in the Table 3 below. Whilst RH accuracy of the Rotronic HygroClip probes is 2%, the calculations give the average of over 900 daily RH fluctuations and hence are quoted to 2 decimal places. The RH control range for each case is given and the RH fluctuation measured within the room containing the cases indicated by *. The control range was selected by

Table 3: Case Performance

Room	Case∞ No	Contents	Desired RH Range	Percentage Tine Achieved during years after opening, June 2002			Average Daily Change (RH%)	Percentage Reduction
				2002–3	2003–4	2004–5		
Bath House Room	-		27–78*				6.73	-
	1	Iv, Cu	40–50	100%	95.1%	100%	1.25	82.5%
	2	Iv, En, Ag	40–50	97.4%	96.1%	94.5%	1.47	78%
Private Devotion Room	-		30–78*				7.97	-
	3	Wd	40–60	100%	100%	100%	1.58	80%
	4	Wd, St	40–60	100%	100%	100%	2.33	71%
Discernment Room	-		29–86*				11.67	-
	5	Ag, Cu, Au, Wd	40–60	76.9%	81.2%	84.7%	3.31	72%
	6	En	35–45	91.7%	81.2%	75.4%	2.48	79%
	7	En	35–45	99.3%	99.1%	98.9%	1.72	85%
Connoisseurship Room	-						11.48	
	8	Cu, Ag, Au		N/A			N/A	N/A

Iv: ivory Cu: copper alloy En: enamel Ag: silver Wd: wood Au: gilding (over copper alloy) N/A: no monitoring available

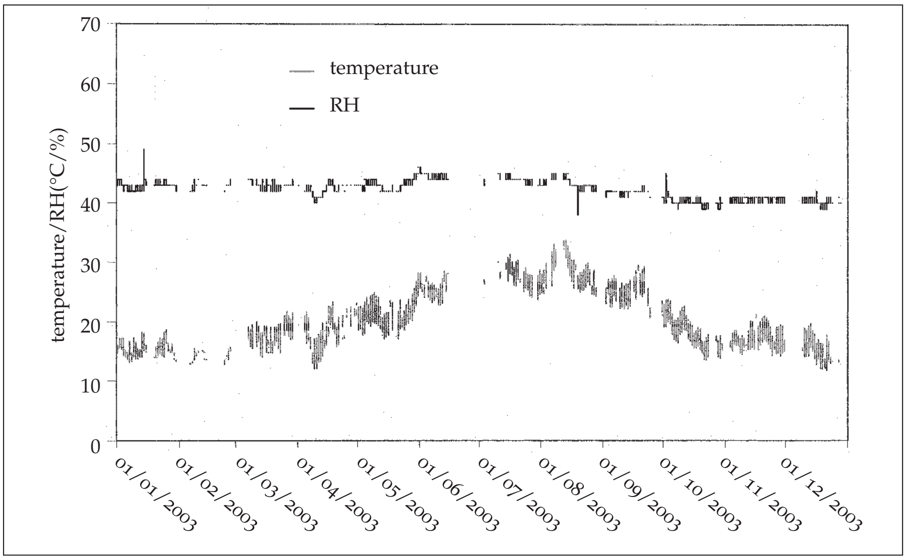

Figure 3 RH and Temperature in Table Case 1

examination of relevant literature and had to balance the needs of mixed contents in some instances. The range for the Limoge enamels was reassessed as 35–45%, 5% lower than the previous paper to incorporate the results of Ryan's investigation of glass deterioration (Ryan 1999).

RH Buffering

Decreasing RH in Table Case 1

The volume of this case is 0.77m³ with 3 Artsorb full cassettes incorporated.(3.9 kg m-3.). The manufacturer recommends between 0.5 and 1 kg m-3. Weintraub (Weintraub 2002) pointed out that this appears to be based on the work of Miura (Miura 1981). This work investigated short term RH fluctuations and as can be seen in Table 3, the Artsorb has indeed significantly reduced the daily RH variations. However a slow downward trend in RH is seen in Figure 3 which shows data for 2003. On installation in 2002 the RH was stable at around 45%. During the first winter this level dropped to a minimum of 41%, during 2003 that dropped to a minimum of 38%. The Artsorb was replaced in March 2004 and monitoring showed no change in the RH levels. Another cassette was added to see if this would have any effect. It did not, suggesting that the RH in the case is heavily influenced by buffering of hygroscopic case materials, MDF and display fabric.

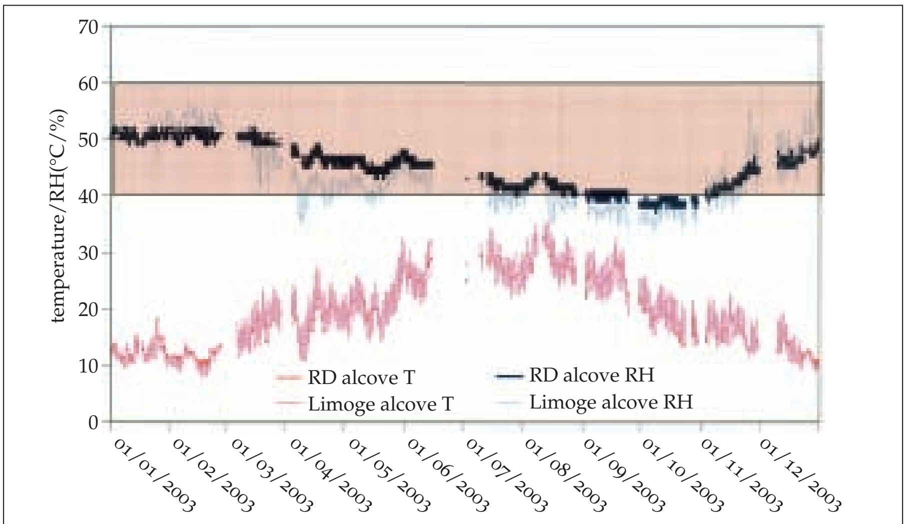

Figure 4 RH and Temperature in almost identical Alcove Cases 3 and 5 through 2003

The three Artsorb cassettes were weighed on removal and found to have an average weight of 978g (cassette weight 1020g). According to the manufacturer's information this would be equivalent to 39% RH, which is in good agreement with the case environment. The amounts of Artsorb required to maintain an RH over a year can be calculated from the formula for hygrometric half-life introduced by Thomson. Assuming a six month half life is sufficient and using the air exchange rate measured and Weintraub's modified moisture reservoir values gives a required weight of 8kg m-3. Three further Artsorb cassettes were added to the case in August 2004 to raise the ratio to the calculated amount. This raised the RH to above 49% and slowed the drop in RH over the winter sufficiently that the RH did not drop below 45% before the cassettes were replaced in March 2005.

Alcove Cases 3 and 5

A significant difference in performance was observed between the two alcove cases. Data for 2003 is shown in Figure 4. There was little difference in conditions in the two rooms containing the cases. Initially the difference was assumed to be due air exchange rate differences between the cases, but measurements in 2004 and 2005 showed that this was not so. The design and construction materials of the cases are identical, including the amount of Artsorb. The case in the Religious Devotion Room (case 3) contains four large Walnut panels and a large wooden bust, whilst that in the Discernment Room (case 5) has metal objects, with a small coconut owl as the only hygroscopic component. To test the hypothesis that the objects were providing the additional RH buffering observed, one of the wooden panels was weighed continuously over a period of three months. The weight was found to fluctuate by approximately 4.3g per day, whilst the RH fluctuation measured in the case was 4%. Measurement of the isotherm of a piece of Walnut wood of approximately the same dimension as the wooden panel using a EKG200 balance and saturated salt solutions in a Perspex chamber determined the slope of the isotherm between 20 and 60% RH to be 0.25g/%. Measurements with the actual wooden panel, in a polyethylene tent conditioned with Artsorb between 40 and 60% RH, confirmed this figure. Hence the panel is exchanging much more water than would be expected from the case RH measurements and it is contributing significantly more to the RH buffering in the case than would be expected. During the winter of 2005, the wooden objects were removed from case 3 for a week. The RHs inside case 3 were very similar to those inside case 5 over that period, confirming that the wooden objects were indeed the cause of the RH buffering observed.

Reconditioning Artsorb

The Artsorb is presently reconditioned by weight. Two sets of Artsorb were purchased for the project. The cassettes are weighed when they are swapped for reconditioned cassettes. If they hold less water than desired (by consultation with the manufacturers isotherm literature), then they are sprayed with water and weighed until the desired weight is reached. The wet cassettes are sealed in Moistop bags to equilibrate, and the RH checked before use. If the Artsorb is too wet, it is placed in the boiler room at approximately 30% RH for a period of two weeks to dry, before wetting. As Artsorb ages, the isotherm changes and the cassettes have almost reached the stage where reconditioning by weight requires more extensive checking of the RH.

Weintraub cautions against direct wetting of Artsorb as this causes excess heating and deterioration of the silica gel. Experiments with a cut open cassette indicated that no liquid water ingressed the cassette and that the temperature of the gel rose by no more than 10°C. Examination of Artsorb beads from within the cassettes showed no visible signs of powdering or cracking. Similar examination of beads from cassettes used to condition a case for over ten years, with reconditioning of the Artsorb approximately every six months, similarly showed no visible signs of deterioration. Now the amount of Artsorb in the cases has

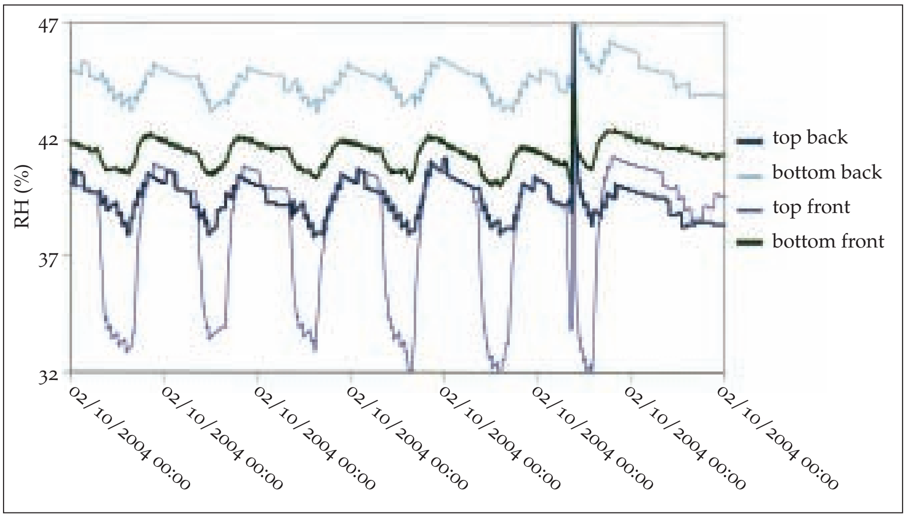

Figure 5 RH variation at different positions within display case

been reassessed, long term RH monitoring, coupled with AER measurements when necessary, should determine any reduction in performance of the Artsorb.

Environmental Variations within the Display Cases

The results of the monitoring of RH and temperature at points within a display case are shown in Figures 5 and 6.There was little difference between the centre and side readings at any given position in the case and only one of each has been included in Figures 5 and 6 for clarity.

The RH is generally higher and less variable at the base of the case. The highest daily variations are at the top front of the case in close proximity to the tungsten halogen lighting. These positions show RH drops of almost 8%. Fortunately the objects at the high level in this case are close to the backboard and experience a lower 4% RH drop. Since the case is running towards the top of its desired RH range, this is acceptable. Generally the RH variations are higher at the front of case when compared to the same position at the back and considering absolute humidity, there are also greater variations in the front than at the back of the case. This is most likely due to air ingress through the seals of the door in the front of the case.

The temperatures at the top of the case are warmer than at the baseboard, with the front being 2.5ºC higher than the majority of the sensors due to the close proximity to the tungsten halogen lighting. Objects are displayed high up on the backboard and could be subject to temperature profiles.

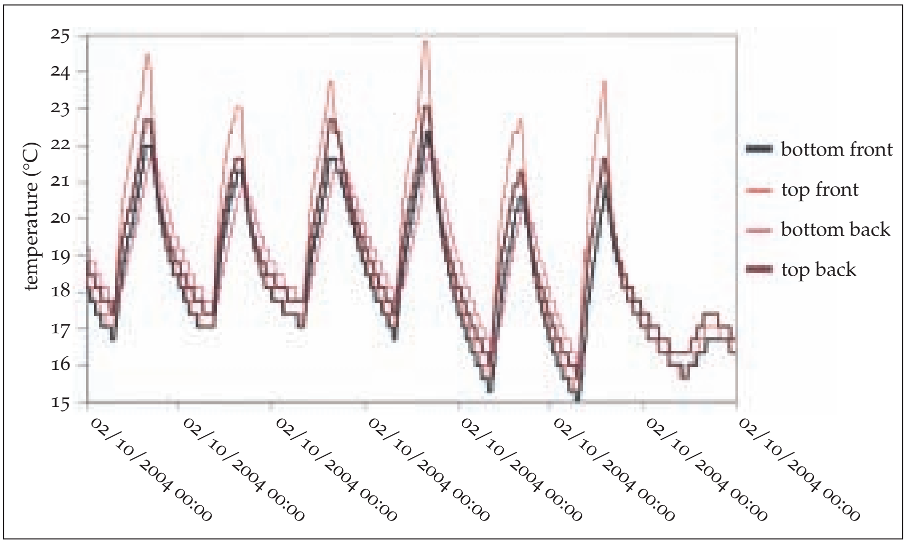

Figure 6 Temperature variation at different positions within display case

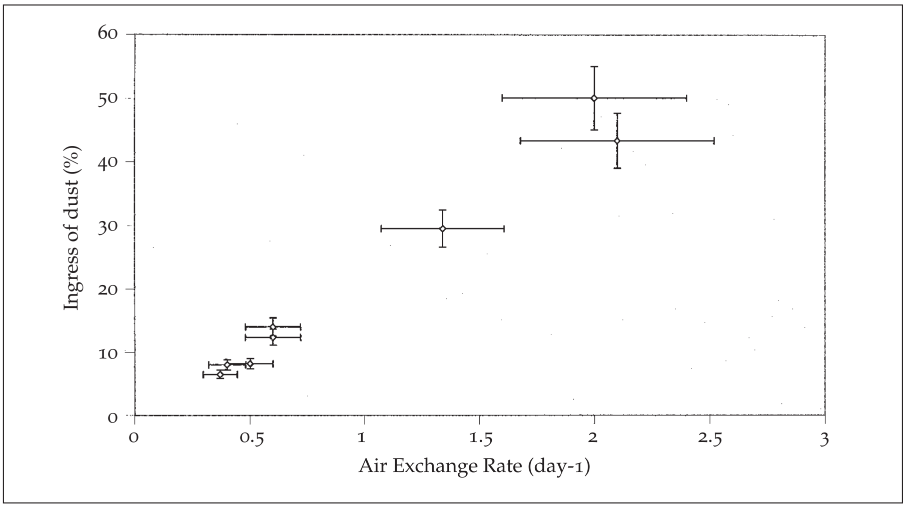

Figure 7 Dust ingress into cases showing relationship to air exchange rate

This has important implications for placing temperature and RH sensors in showcases. The Rotronic HygroClip sensors in this exhibition are placed approximately 5cm above the baseboards of the cases, which is probably the most common sensor position in showcases. They are fed through from below with a sealing system and this allows them to be relatively unobtrusive within the case, in keeping with the displays evocation of Julius Wernher's turn of the century display of these objects.

Temperature Profiles on Enamel Surfaces

The thermal camera and surface temperature measurements undertaken on Limoge enamels did show a slight vertical thermal gradient. This was greater nearer the tops of the tungsten halide lit cases, but never exceeded 1°C across a single plaque. Since copper has a moderate thermal expansion co-efficient and the enamels are in good condition, this is unlikely to pose a threat to the enamel plaques displayed.

Dust Levels

To allow a comparison to be made between different rooms, dust slides were placed both outside and inside the display cases. The percentage of dust ingress, into the case, compared to the room was calculated. Figure 7 shows this plotted against AER for the cases.

The results above indicate that those cases with higher air exchange rates do allow more dust ingress, so objects displayed in them, will require more frequent cleaning.

Although many studies of dust deposition on open display or during building projects have been published, little work is available on deposition levels inside showcases (Ford and Adams 1999; Watts and Berry 2002). This may be due to the limited sensitivity of the glass slide reflectance method (Adams, Brimblecombe et al. 2001). In many instances exposure times in excess of eight weeks would be required to produce a statistically significant result inside a showcase and it is likely that slides exposed in the room would have passed beyond the linear reflectance versus coverage regime due to overloading (Adams, Kibrya et al. 2002).

External and Internal Pollutants

Sulphur dioxide and nitrogen dioxide

The concentrations measured inside cases 2 and 6 and in the Bath House and Discernment Rooms in summer are shown in Table 4 along with the calculated concentrations from the IMPACT1 program.

The cases provide significant protection against nitrogen dioxide ingress. The

Location	Sulphur dioxide concentration (ppb)		Nitrogen dioxide concentration (ppb)	
	measured	IMPACT	measured	IMPACT
Bath House Room	0.9 ± 0.05	-	30 ± 1.5	-
Case 2	< 0.06		1.1 ± 0.2	1.0
Discernment Room	0.7 ± 0.05	-	35 ± 1.5	-
Case 6	< 0.06		2.4 ± 0.4	2.2

- IMPACT calculation for internal case concentrations only

Table 4 Pollution results for summer exposure

sulphur dioxide concentrations inside the cases were too low to detect with diffusion tubes, but a significant reduction in concentrations had occurred. The IMPACT predictions are within the experimental error of the diffusion tubes used and the pollution results appeared to fit the Weschler equation for both sets of seasonal exposures. This is an important result for showcase design, as it allows cases to be specified and designed to yield a certain level of reduction in pollutant concentration.

Unfortunately there is still little information available about likely reaction rates of artefacts towards external pollutants in indoor atmospheres. For example both nitrogen dioxide and ozone are known to accelerate the tarnishing of silver as the formation of silver oxide is the first stage of this process (Costa 2001, Dubois 2004). The concentrations at which this occurs have not been fully elucidated.

Lead Coupon Analysis

Figure 8 shows the decrease in L* values for the lead coupons. Delta E values followed the same trend, as L* dominated the colour changes. As can be seen there is a strong negative correlation between AER and the darkening of the lead. Those cases with activated charcoal felt incorporated, reduced the darkening significantly. The amount of oxidised lead is also included in Figure 8. These results correlated well with the L* and colour changes. The A/R FTIR analysis of the coupons detected only plumbanacronite on their surfaces. No lead acetate oxide hydrate or hydrocerrusite were detected, which would have indicated acetic acid initiated corrosion (Tetrault *et al.* 1998).

Silver Coupon Analysis

Whilst a* and b* are not independent variables and can not normally be considered separately, the stability of a* (Δa was less than 0.02 in all instances)

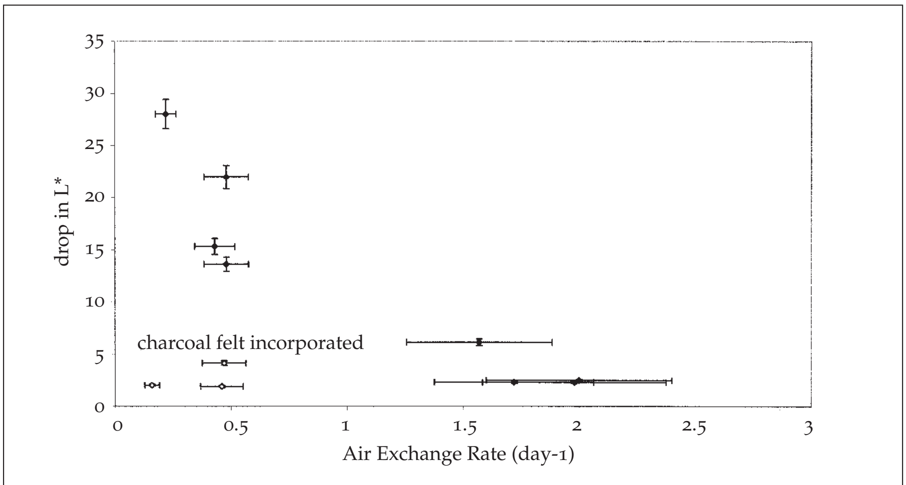

Figure 8 Lead colour and oxidation in cases showing relationship to air exchange rate

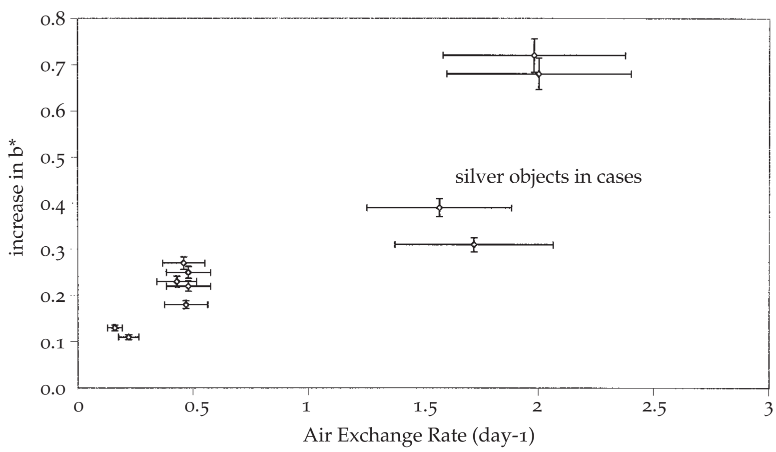

Figure 9 Silver tarnishing in cases showing relationship to air exchange rate

allowed changes in b* to be considered separately. Figure 9 shows the increase in b* plotted against AER. There appears to be a reasonable correlation between the two sets of values, showing the benefit of reducing the air exchange rate in relationship to silver tarnish rate. Improvements to air exchanges rates to cases can sometimes be effected quite cheaply depending on where the leakage is occurring. It is in this situation that leak detectors become invaluable. If the leakage is predominantly through gaps around doors then replacing compression seals and ensuring that the seals fully extend to cover the whole door edge or mating surface can have pronounced benefits. Refitting self adhesive seals to an older showcase at Brodsworth House, reduced its air exchange rate from 128.3/day to 1.1/day and reduced the silver tarnish rate by a factor of 31. However leakage from some areas of a case can be extremely expensive to refit and it can be extremely difficult to determine where leakage is occurring is certain designs of cases or for cases in certain locations.

Cases with large areas of silver included (cases 2 and 5) tend to show lower tarnishing rates. The tarnish is spread between the objects and the tokens, hence the tokens show a lower increase in b*. There is no obvious evidence that the inclusion of activated charcoal felt reduces the tarnishing rate. The gases causing silver tarnish ingress the case through gaps concentrated around the edges of the cases and have to pass near the silver before coming into contact with the felt. The silver surface is extremely reactive (the collision factor for hydrogen sulphide on silver is 0.99) and it is likely that the surface tarnishes before the activated carbon can remove any of these gases.

Several authors have studied absorbents to reduce silver tarnishing in controlled laboratory studies (Bradley 1989; Ankersmit, Noble et al. 2000; Bradley 2005). Only two trials have been reported translating those trials into the more complex real showcase situation. Although the two measurements reported in this work are too few to draw firm conclusions from they do agree with experience from the British Museum were absorbents deployed passively have had only very limited effect on silver tarnish (Bradley 2005).

Conclusions

Air exchange rate has been confirmed to be extremely important for the performance of display cases with regards to RH buffering, dust and pollutant ingress and corrosion of metals displayed within them. Indeed cases slipping above the original air exchange rate criteria were unable to meet the RH specifications in the rooms at Ranger's House. The use of hinged doors for the large cases for the project has been problematic for their air exchange rates. There is evidence of the glass weight causing deformation even when the case is only infrequently opened. Secondary sealing with silicone has also been problematic, where adequate seals were not designed into the case. The sealing for the fibre optic cables into the cases was compromised by the high temperatures generated by the fibre optic light boxes. Although the case design successfully bled the heat away from the object display volume, the high temperatures generated underneath the case aged the silicone applied retrospectively to improve the sealing. As the silicone became brittle it could no longer provide an adequate seal and the case air exchange rates increased to their original values before the silicone was applied.

The balance of risk of the other factors will depend on the objects housed inside showcases. Whilst the ivory objects are of course sensitive to low RHs, soiling of their fragile surfaces by dust is probably the second major conservation risk from display, as light is adequately controlled. The Limoge enamels are sensitive to middling and high RHs. The concentration of internally generated formaldehyde from the MDF could pose a risk to the long term preservation of some of them, depending on glass composition. Silver objects are most at risk from external sulphur containing gases and would benefit from tighter showcases. The activated charcoal felt does not appear to be having an effect on the silver tarnish rate inside the showcases. Some evidence of a potential effect from the case atmosphere on the leaded bronzes was determined. Activated charcoal appeared to mitigate this, but more work is required to determine a replacement regime.

Experience with the Wernher project has shown that achieving a given air exchange rate for display cases requires a significant amount of effort. Maintaining a satisfactory solution also requires monitoring and actions to redress the display case performance if it begins to slip.

The results have raised the important issue of objects buffering their own environment and that RH monitoring data within cases can be falsely reassuring. RH is controlled to control the moisture content of organic objects and in case the moisture content appears to show much more dramatic variations than would be indicated by monitoring the RH. This effect is probably determined by the air volume of the showcase and its air exchange rate. In very small volumes with low air exchange rates the RH is controlled by the moisture content of hygroscopic materials inside the enclosure (Padfield 2002). The boundary conditions when this transfers to the RH inside the case controlling the moisture contents of hygroscopic materials is obviously of great import for conservation and would benefit from further research.

Case lighting can lead to significant distributions of temperature and RH within a case and may need to be seriously considered, depending on the geometry of the display. The issue of positioning of RH and temperature monitors within display cases has also been highlighted. Presentation considerations often severely limit sensor placement, but this work has shown large temperature and RH variations within showcases and indicates that the issue of how representative a sensor's readings are of the showcase environment requires serious consideration.

Appendix – Errors in Air exchange Rate Measurements

There are a number of different sources of error in a tracer gas air exchange rate measurement. There is an error in the concentrations determined by the measurement devices. Medigas the manufacturer of the nitrous oxide loggers used quote 10% of the reading. Vaisala quote 20ppm plus 2% of the reading for the GMP222 carbon dioxide probe. These are figures for accuracy. The air exchange rate is calculated from these figures using the equation;

$$N = [\ln(C_{intt0} - C_{ext}) - \ln(C_{intt1} - C_{ext})]/(t_1 - t_0)$$

where
N = number of air changes
C_{intt0} = internal concentration of tracer gas in enclosure at start
C_{ext} = external concentration of tracer gas in room
C_{intt1} = internal concentration of tracer gas in enclosure at end

t_0 = time at start (days)
t_1 = time at end (days)
ln = natural logarithm.

Since it is the slope of the natural logarithm of the concentration against time that is of interest then it is the precision of the instrument and not it's accuracy that determines the error in the air exchange rate measured. Experiments reported in Calver et al 2005, ran carbon dioxide air exchange rate measurements over thirty consecutive days in an enclosure. From these a repeatability2 standard deviation of 7% of the air exchange rates measured was determined, provided the initial injection concentration did not exceed 10,000ppm. Similar tests with the nitrous oxide logger determined a slightly higher repeatability standard deviation of 9%.

ASTM E741-00 recommends that the confidence intervals of the air exchange rate measurement are determined from a standard statistical procedure that used eth deviations of the measured data from a straight line and assumes that these deviations are the random error in the measurement. Since the instantaneous air exchange rate is highly dependant on the temperature difference between the case and the room, with internal lighting a diurnal sigmasoidal curve is generally observed in the natural logarithm concentration against time graph, as seen in Figure 1. This variation from a straight line is not random error, but a function of the physics of the air exchange rate mechanisms operating, hence the errors calculated to ASTM E741-00 are almost always over estimates.

The previous paragraph refers to errors for a single measurement on a certain day. Meteorological conditions, atmospheric pressure and sunlight will also alter the air exchange rate on a day to day basis. The repeatability standard deviations take this into account.

Whenever a case door is opened and closed the seals will not necessarily meet in exactly the same way, although case manufacturers have spent much time devising systems to overcome this. For carbon dioxide the repeatability standard deviation rose to 11% when the enclosure door was opened for each gas injection.

Errors based on ASTM E741-00 are quoted in table 2, as this is an existing standard. Although ASTM E741-00 overestimates the random concentration measurement error, additional errors due to changing meteorological conditions and door seal seating exist and these are almost certainly much larger than that overestimate. A figure of 20% would be a safe estimate, compensating for different designs and geometries of cases used and this has been used in Figures 7, 8 and 9. Air exchange rates are quoted only to one decimal place in Table 2 to indicate this uncertainty. A 20% error does not effect the major conclusions of this work.

This is obviously an area that requires further work to accurately determine the inter-measurement errors for air exchange rates of cases of different designs.

References

Adams, S., P. Brimblecombe, et al. 2001. 'Comparison of two methods for measuring the deposition of indoor dust. The Conservator 25: 90–94.

Adams, S. J., R. Kibrya, et al. 2002. A particle accumulation study during the reconstruction of The Great Court, British Museum, Journal of Cultural Heritage 3(4): 283–287

Ankersmit, H. A., G. W. Noble, et al. 2000. The protection of silver collections from tarnishing. Tradition and Innovation, Contributions to the IIC Melbourne Congress, Melbourne. 7–13

ASTM G1-90. 1999. Standard practice for preparing, cleaning and evaluating corrosion test specimens. American Society for the Testing of Materials, Conshohocken, PA, US

ASTM E741–00, 2000, Standard Test Method for Determining Air Change in a Single Zone by Means of Tracer Gas Dilution, ASTM E741–00, ASTM International

Bradley, S. M. 1989. Hydrogen sulfide scavengers for the prevention of silver tarnishing. Environmental monitoring and control, Dundee, Scottish Society for Conservation and Restoration and Museums Association. 65–67

Bradley, S. M. 2005. Preventive conservation research and practice at the British Museum. Journal of the American Institute of Conservation: forthcoming.

Brimblecombe, P. 1990. The composition of museum atmospheres. Atmospheric Environment 24B(1): 1–8.

Cassar, M. and G. Martin 1994. The environmental performance of museum display cases. Preventive conservation: practice, theory and research. Contributions to the IIC Ottawa Congress 1994

Calver A., Holbrooke, A., Thickett, D. and Weintraub, S. 2005. Simple methods to measure air exchange rates and detect leaks in display and storage containers. In: I.Verger, ed. Pre-prints of ICOM-CC 14th Triennial Meeting Hague. London. 597–609

Costa, V. 2001, The deterioration of silver alloys and some aspects of their conservation, Reviews in conservation 2, 18–34

Dubus, M., Moulherat, C., Robinet, L. and Spencer, H., Influence of the 2003 heatwave on the corrosion of Silver in museums, available at http://www.isac.cnr.it/iaq2004/accessed on 11/11/2005

Eremin, K., and Wilthew, P. 1996. The effectiveness of barrier materials in reducing emissions of organic gases from fibreboard: results of preliminary tests. Pre-prints of ICOM-CC, 11th triennial meeting Edinburgh 1–6 September 1996: James & James (Science Publishers) Ltd.

Ford, D., and Adams, S.1999. Deposition rates of particulate matter in the internal environment of two London museums. Atmospheric Environment 33(29): 4901–4907

Ghanbari-Siahkali, A., Mitra, S., Kingshott, P., Almdal, K., Bloch, Kem Rehmeier C and H 2005. Investigation of the hydrothermal stabililty of cross-linked liquid silicone rubber, Polymer Degradation and Stability, 90, 471–480

Howell, D., Brimblecombe, P. Lloyd, H. Frame, K. and Knight, B. 2002. Monitoring dust in historic houses. In: J.H. Townsend, K. Eremin and A. Adriaens, eds. Conservation Science 2002. London. pp8–11

Larsen, R. 1993. Evaluation of the Correlation between Natural and Artificial Ageing of Vegetable Tanned Leather and Determination of Parameters for Standardization of an Artificial Ageing Method: STEP Leather Project. European Cultural Heritage Newsletter on Research 7(1–4): 19–26.

Microclimate at http://www.microclimate.ca/productdata/caseleakage.htm Accessed 11/11/2005

Miura, S. 1981. Studies on the behavior of RH within an exhibition case. Part II: The static and dynamic characteristics of sorbents to control the RH of a showcase. In Preprints of ICOM-CC 6th Triennial Meeting, Ottawa: 1981/18/5:1–10.

Padfield, T. 1966, The control of relative humidity and air pollution in show-cases and picture frames, Studies in Conservation 11, 8–30.

Padfield, T., Berg, H., Dahlstrøm, N. 2002 How to protect glazed pictures from climatic insult, in Preprints of ICOM-CC 13th Triennial Meeting , Rio de Janeiro, R. Vontobel (ed.), 80–85. London: James and James.

Ryan, J. L. 1995. The Atmospheric Deterioration of Glass. Unpublished PhD dissertation, Imperial College of Science, Technology and Medicine, University of London.

Stanley, B., Xavier-Rowe, A. and Knight, B. 2003. Displaying the Wernher collection: a practical approach to display cases. The Conservator 27, pp34–47

Tetrault, J., Sirois, J. and Stamatopoulou, E. 1998. Studies of lead corrosion in acetic acid environments. Studies in Conservation 43, 13–32.

Thomson, G.1977, Stabilisation of RH in exhibition cases: hygrometric half time, Studies in Conservation 22, 85–102.

Thickett, D. 1998. Sealing MDF to Prevent Corrosive Emissions, The Conservator 22: 49–56.

Thickett, D. and Hockey, M. 2002. The Effects of Conservation Treatments on the Subsequent Tarnishing of Silver. Post-prints of Conservation Science 2002, Edinburgh, 155–161

Vernon, W. H. J. 1935. A Laboratory study of the atmospheric corrosion of metals: Part II, iron: the primary oxide film; Part III, the secondary product or rust (influence of sulphur dioxide, carbon dioxide, and suspended particles on the rusting of iron). Transactions of the Faraday Society 31: 1668–1700.

Watts, S. and Berry, J. 2002. In control or simply monitoring? The protection of museum collections from dust and vibration during building works. Preprints of ICOM-CC 13th Triennial Meeting, Rio de Janeiro, R. Vontobel (ed.),. London: James and James.

Weintraub, S. 2002. Demystifying silica gel. In Object Specialty Group Postprints. 9, Washington, D.C.: American Institute for Conservation., available at http://www.apsnyc.com/pdf/silica_gel_SW_2003.pdf

Weschler, C.J, Shields, H. C. and Naik, D.V. 1989. Indoor ozone exposures. Journal of the Air Pollution Control Association 39, pp 1562–1568

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