TROUBLE IN STORE

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Abstract. As air pollution in cities diminishes, or at least changes its nature, the air pollution generated within buildings becomes a relatively more serious cause of deterioration. The low rainfall indoors allows hygroscopic salts to develop and remain, without ever being washed away. Nearly airtight enclosure brings the threat of damage by modern materials outgassing into the air around museum objects, as well as chemicals given off by self-destructive objects. The commonest indoor pollutants are acid gases from the decomposition of wood, cellulose acetate and cellulose nitrate. Acid attack requires a thin watery film on the surface of the object to allow ionic processes to occur. Within showcases, there is competition between absorption on the object, absorption on a sacrificial absorber and ventilation out through imperfections in the seal.


1. INTRODUCTION

Reports dating back to the nineteenth century record damage to objects enclosed within showcases or storage cupboards. The cause is often corrosive vapours emitted by the material of the showcase or even by other stored objects. On the other hand the usefulness of enclosure for security against theft, dust, and extremes of relative humidity is undeniable. This article describes our attempt to retain the advantages and to diminish the hazards of enclosing museum objects. Our approach has been to review the nature of the damage, to investigate the patterns of air circulation within small enclosures, to review the tests that have been proposed to detect hazardous materials and finally to compile lists of those materials known to be unsafe and those thought to be safe for use within ill-ventilated enclosures.

2. TYPICAL CORROSION PRODUCTS

An excellent starting point is the review by FitzHugh and Gettens of examples of corrosion caused by acetic and formic acids emitted by wood [1]. They describe examples of corrosion of calcareous materials to form mixed anion salts such as calcium chloride acetate, and corrosion of lead and zinc metals and vitreous enamel to form formate salts. The authors touch on the probability that the reactions have been encouraged by the prior presence in the object of hygroscopic salts which deliquesce at high relative humidity to form a liquid on the surface.

We can now add to this list some more recent reports. Nockert and Wadsten [2] identified sodium formate accumulating on the glass lid of a cardboard box. They attributed this to reaction of the glass with formic
Figure 1. A cowrie shell, 4cm long. The close up on the right shows fragments of the original surface 1mm above the level of the corroded parts. This is typical of marine shells stored in wooden cabinets. The corrosion layer is calcium acetate and calcium formate.

Figure 2. A coral brooch, 4cm long, which had been stored for many years in an oak barrel, together with other ornaments made of cellulose nitrate. The white corrosion is cellulose acetate-nitrate.

acid resulting from oxidation of formaldehyde emitted from the cardboard. In this laboratory we have identified calcium acetate and calcium formate as a 1mm-thick corrosion crust on a cowrie shell (figure 1) which was originally aragonite (calcium carbonate) [3]. It had been stored for five years in a box of Douglas fir with a glass lid. We have also found a hydrated calcium acetate nitrate growing on a carved coral brooch (figure 2, 3). The corrosion had penetrated so deeply that when the salts were washed out the coral was quite porous [4]. Turning from carbonate to metallic shells, some lead bullets displayed at the National Air and Space Museum (figure 4) had acquired over a period of three years a mimic accretion of bullet-shaped crystals of lead formate over a millimetre long. A coat of varnish had provided little protection. The back of the case was painted plywood, the front was Plexiglas (polymethyl methacrylate) [5].

Lead is peculiarly susceptible to damage in ill-ventilated enclosures (figure 5). Our most dramatic example comes not from a showcase but from the interior of the roof of one of the Smithsonian Museums [6]. The lead roof
Figure 3. On the left, a close up of the brooch shown in figure 2. Notice the apparently undamaged shiny finish where there is no covering of corrosion. The middle picture shows a scanning electron micrograph of the corrosion product, calcium acetate-nitrate, in long needles often capped with flat plates (picture 200 microns across). On the right is the appearance of the surface after the brooch was washed in plain water. It dried out completely matt and bleached. The electron micrograph of the surface shows how the corrosion has etched the surface into pinacles, which scatter the light.

Figure 4. A showcase in the National Air and Space Museum, Smithsonian Institution. The bullet at the top of the fourth row is shown enlarged on the right. The millimetre long bullet shaped crystals are lead formate. The source of the corrosion is certainly the binder in the wood fibre board backing the case.
The inscribed lead plate found on exhuming Bishop Absalon from his grave in the Monastery Church at Sorø, Denmark. The plate, which is 30cm long, was conserved and encased in a brass and glass box. This inert and nearly airtight enclosure ensured corrosion of the lead by oak wood relics enclosed in the same case, though some air must have leaked in because carbon dioxide is also essential to the corrosion process. The close up of the corrosion shows a varied mineralogy, with some red lead oxide as well as abundant cerussite, lead carbonate. It is probable that a partly effective protective coating has caused the uneven corrosion. Compare a similar phenomenon in figure 8.

After three years of exposure to the Washington weather, is covered with a thin dense layer of lead sulphate but the inside surface has a felt of half millimetre long crystals of lead carbonate. We deduce that acetic acid from the plywood supporting the roof has combined with moisture from condensation and carbon dioxide from fungal activity in the damp wood to corrode the lead so vigorously. A nearby area of roof of similar construction but better ventilation has an entirely different set of lead corrosion products. Zinc-plated steel forming the ceiling has corroded to form a white powder. Zinc is susceptible to attack by formic acid which is released by wood. The rate of attack shows a maximum value at a low concentration of formic acid with a high relative humidity. Under these conditions the coherent layer of zinc formate is converted to a porous hydrated oxide with release of formic acid.

There are other reactions in which volatile products are produced which in the absence of vigorous ventilation re-attack the surface of the object.
Figure 6. David Erhardt peels back a section of the one year old lead coated copper roof of the Arts and Industries Museum of the Smithsonian Institution. The lead was corroded by the damp plywood beneath it. On the right, a scanning electron micrograph (1mm across) of columnar crystals of cerussite, lead carbonate.

Figure 7. The ceiling of the Arts and Industries Museum is zinc coated steel. Condensation in the roof, aided by fireproofing chemicals, has corroded the zinc to white oxide, accompanied by fireproofing salts, ammonium dihydrogen phosphate, borax and a reaction product koktaite (hydrated ammonium calcium sulfate).

A silver spoon (figure 8) and a pair of cufflinks on display in the Museum of American History in Washington, DC, developed a magnificent dendritic growth of silver sulphide crystals covering the surface with a glistening black fur quite unlike normal silver tarnish. A closer investigation [8] revealed that
active chloride corrosion was heaving up the laminated surface layers of the silver. It seems that hydrogen sulphide was attacking the silver chloride which was originally formed during burial. The hydrogen chloride which was released then continued to corrode the silver. A layer of varnish may have exacerbated the corrosion by preventing the released hydrogen chloride from diffusing away.

3. UNUSUAL CHARACTERISTICS OF INTERNAL POLLUTION

Showcases have, to use a fashionable metaphor, their own ecology. The combination of museum air-conditioning and the partial isolation of the air in the case excludes most of what we may grimly call normal urban pollution. Even a non air-conditioned room excludes much of the dust and gaseous pollution from outside. Buildings also inject a characteristic indoor pollution ranging from radon gas from heavy minerals in sandstone walls to organic plasticizers volatilizing from synthetic upholstery. Chlorine and ammonia are liberated from cleaning and disinfecting agents. Preservative chemicals such as formaldehyde and ethanol are important air pollutants in biological collections, as are volatile pesticides. There are always bizarre new phenomena turning up: one Canadian museum traced sodium chloride particle pollution to exhausted deionizers in the water supply for the air-conditioning equipment [9].

A characteristic feature of indoor pollution is the prevalence of hygroscopic salts [10, 11](figure 9, 16). Outdoors such salts are quickly washed away or drip away during periods of high relative humidity. Indoors they persist because of the moderate RH and also because sulphur dioxide is not sufficiently abundant to form the non-hygroscopic sulphates by displacing the other anions as volatile acids or oxides.

Mixtures of salts, and mixtures of salts with organic water-soluble substances, deliquesce below the relative humidity needed for either component alone. Hygroscopic salts in microporous materials such as textiles and paper absorb water at an RH below the value for the salt alone (figure 11)[12].
Figure 9. A Daguerreotype, disassembled to show the typical method of presenting and protecting the delicate silver image. The centre of the image is protected by the edge of the silver plate which absorbs hydrogen sulfide diffusing past the edge of the glass. In this example, from the Museum of American History in Washington D.C., the interior surface of the glass has become contaminated. The droplets contain sodium, sulphate and formate ions, with crystals of sodium sulphate and sodium formate. The mixture is deliquescent at the 50% RH of the museum environment.

The presence of such liquid films may be at least as important in promoting chemical attack as the high concentration of corrosive vapour built up in a closed container. These hygroscopic salts may be present in the object before enclosure (figure 10) or they may be formed by chemical reaction afterwards and then serve to accelerate further reaction. The susceptibility of carbonates to attack by acid gases formed within museum cases suggests that carbonate-loaded papers are probably excellent pollutant absorbers for confined spaces. To decide if such a measure is practical we must look next at the way air and pollutants circulate in enclosures.

4. AIR CIRCULATION WITHIN SHOWCASES AND AIR LEAKAGE RATE

Showcases and storage cabinets are typically a hundred times less well ventilated than the rooms around them. The variation between different designs and even different examples of one design is obviously very great since leakage rate is seldom defined in specifications for museum containers. Perhaps it should be, but what should we require? A perfect seal ensures the build-up of an unpredictable array of volatile chemicals, fierce ventilation draws in dust and transmits variations in relative humidity, risking physical damage infinitely faster than chemical damage.

A rational compromise can only be reached if we know how air circulates within a container. So far attention has been concentrated on leakage rates. Ramer [13] gives a leakage rate of about one air exchange in a day or two. This was based on the rate of loss of carbon dioxide and the rate of gain of oxygen in a case initially filled with nitrogen and carbon dioxide. Thomson
Figure 10. A Jacquard woven silk picture of Joan of Arc, 35cm high. The lower image in the centre is the ghostly image on the glass which was in contact with the picture. Above it is a raking light picture of the silk weave. Close comparison of the images revealed that the salt is on the glass precisely where the cloth did not touch it. The mechanism is shown on the right: salt left in the picture from its weaving has migrated as a water solution to the glass. It has spread out over the glass where the water has evaporated and been re-absorbed by the silk fibres. The driving force for the process is the lower RH at which salts in absorbent polymers become liquid, compared with the deliquescence point of the salt in isolation. Even at moderate, museum RH, the salt is partly in solution within the fibres. This fascinating process is described in more detail in [T.Padfield and D.Erhardt,'The Spontaneous Transfer to Glass of an Image of Joan of Arc'. Preprints of the Sydney Conference of the ICOM Conservation Committee, September 1987, pp 909-913]

[14] gives a rate of about a day. We agree with these results. Our case was made of Plexiglas sides and top cemented together to form a box which rests on a gasket laid on the metal base-plate. We used changes of water vapour concentration to measure the leakage rate (figure 12)[15].

A leak rate of one air change per day in a case of one cubic metre is produced by a 30mm diameter hole through a thin wall leading to a draught-free room. We measured this by putting the hole in the lid of a smaller box containing a large area of desiccant. This box was put inside the larger case to act as a sort of 'black hole' for water vapour.

Within the case, air mixes by convection [16]. This happens even in a cluttered case in a room whose temperature is constant within two degrees Celsius over 24 hours. The rate of mixing is quite fast. We have used water vapour as a tracer to study the rate of equilibration at various places within
Figure 11. The sorption curve of water on silk containing two concentrations of sodium chloride contamination. There is excess water absorption at a relative humidity well below the deliquescence point of the pure salt, at 76%RH. The electrical conductivity is also detectable at very low RH in salt contaminated silk. This result indicates that invisible contamination of absorbent materials with hygroscopic substances is likely to be a potent accelerator of reactions which proceed through ionisation in water.

an enclosure. The air in one corner of a metre cube moderately stuffed with objects will come half way to equilibrium with air in the opposite corner within about 20 minutes. We have detected no stratification of air in the case; dry air does not stay at the bottom nor moist air rise to the top. We confirmed that the small density difference between dry and damp air is not the cause of the air circulation by using trace gases in air of uniform RH to show that convection was still proceeding. We generated hydrogen sulphide at the base of the case by slow hydrolysis of barium sulphide. Small discs of silver chloride were suspended in the case. The hydrogen sulphide liberated hydrogen chloride from the disc. This formed a plume whose direction was made visible by its reaction with particles of magnesium oxide smoked onto glass plates. Magnesium chloride is deliquescent so a pattern of tiny liquid droplets marked the path of the contaminated air.

Such rapid circulation should allow collection of pollutant gases on a reactive absorber placed anywhere inside the case. The problem here is that a pollutant absorber is often no faster to react than the cherished object it is intended to protect. The distribution of the pollutant between victim and protector will be more or less the ratio of their surface areas. The only certain protection is to interpose the absorber between the source and the object to be protected, which means wrapping it up (in a safe wrapper!).
Figure 12. Tim Padfield crouching behind an experimental showcase partly filled with bent wax walls to make a labyrinth. The purpose is to investigate the air circulation within a showcase under a constant indoor climate. The persistence of convective circulation was demonstrated by mounting tubes containing plates dusted with hygroscopic salt at various places and orientations. A dish of water was placed in the bottom of the case and the pattern of deliquescence of the salt crystals was inspected after ten minutes. The small circles on the drawings of the plates indicate a liquid drop, the dots indicate unreacted powder. The pattern shows clear evidence of convective movement, as shown by the heavy arrows. It could be argued that the less dense moist air would rise from the dish and provoke convection, so a similar experiment was performed where the hygroscopic process was caused by a trace gas, without any change in the moisture content of the air within the case. This is described in the text.

Daguerreotypes (figure 9) operate on this principle, showing a tarnish on the silver around the edge where the hydrogen sulphide has forced an entry between metal and glass. The central part of the image is well protected for many years.

Even if reaction with the object is slow, a large area of absorbent is needed to reduce significantly the time during which a pollutant molecule remains at liberty. If we want to intercept a slow acting pollutant molecule we must aim to reduce its residence time in the case to about half an hour to produce a real reduction in the rate of attack. A large surface area is needed. If the absorber is totally efficient so that the molecules never bounce off it, then about 1000 square centimetres is needed for a cubic metre of case. In
The Apollo 11 capsule of the moon landing adventure is exhibited in the main concourse of the National Air and Space Museum in Washington D.C. It is protected by a close fitting acrylic plastic case. At some times of year it is illuminated by direct sunlight, which causes both evaporation of adsorbed water and fierce convective air movement, which causes water to condense within the heat shield, which is always shaded. The condensed water dissolves sea salt within the porous structure of the heat shield, causing corrosion of the steel parts and an ooze of brown ferric chloride solution. The Russian manned space program brought its astronauts down on land, thus avoiding this threat to the durability of their relics.

In practice the absorber efficiency will be much less, particularly in a closed case with rather sluggish air movement. Probably a square metre, say the whole base of the case, must be covered with absorber. Our experience with RH-controlling materials supports this argument; the rate of transfer of water vapour through the surface of the buffer is the process controlling RH change in sealed showcases; subsequent dispersion of the water molecules is much faster.

One final note on pollutant absorbers: such materials should react with pollutants, not merely absorb them reversibly as active carbon does. The reason for this is that some objects will react with such low concentrations of pollutants that the carbon will desorb pollutant to replace that removed from the air by the object. We have succeeded in tarnishing silver by exposing it to a carbon loaded paper previously exposed to hydrogen sulphide [17]. On the other hand, active carbon will compete effectively for pollutants, such as solvent vapours, which act by physical disruption after absorption rather than by reaction.
Figure 14. The lid of this silver topped decanter provides sacrificial protection of the silver within the neck. Even though the lid is a simple drop fit, the silver reacts so completely with hydrogen sulfide gas that none penetrates to the interior.

5. WHAT ARE THE POLLUTANTS?

A sensible choice of reactive absorber can only be made after compiling a catalogue of the chemicals likely to vaporize into the case. The list will be long. Wood, for example, releases many of the lower molecular weight carboxylic acids, particularly acetic and formic acids. It also emits alcohols such as methanol, and esters such as methyl acetate [18-21]. The rate of release is very variable, depending on the species of wood and how it was seasoned, the moisture content and the concentration of free acid in the wood. Among woods that have been tested [18] the least acetic acid came from Sitka spruce, Picea sitchensis (Bong.) Carr, Douglas fir, Pseudotsuga menziesii (Mirb.) Franco, and Parana pine, Araucaria angustifolia. Hardwood species such as birch, Betula, and beech, Fagus, gave intermediate amounts and oaks, Quercus, the most.

Organic surface coatings will slow down the rate of emission and by doing so will increase the acidity of the wood and increase the rate of production of acid. The only sound treatment for wood exposed within showcases is to cover it with metal foil or a vapour barrier paint loaded with flakes of metal or mica. The end grain should ideally be exposed outside the case and all outward facing wood should have a rather permeable coating.

Modern synthetic materials also cause trouble by giving off solvents, unreacted monomers, decomposition products, low molecular weight plasticizers,
This book had only been exhibited for a few weeks in a temporary exhibition before the strong yellowing of the paper was revealed by the paler paper preserved under transparent polyester strips which restrained the pages. The damage cannot have been caused by light but must be due to chemicals in the air. The reactivity of the gas is emphasised by the greater yellowing immediately adjacent to the strips and at the edges of the pages. A pollutant absorber discretely placed in a remote part of the case would not have given protection.

oxides of nitrogen, etc. The list of damaging volatile products is long. Attempts to reduce the quantity of volatile residues may back-fire: stoved drying oil based paints have been observed to cause more corrosion than the unbaked paint [7](figure 20).

6. CHOICE OF MATERIALS FOR SHOWCASES

Several authors have published simple tests to screen modern materials destined to support or to decorate museum displays.

Weyde [22] proposed a test for oxidizing gases which relied on the colour change of a film of colloidal silver.

Oddy [23] and Blackshaw and Daniels [24] devised a test for gases corrosive to silver, copper and lead in which metal foils and a little water are sealed up with the suspect material and heated to 60°C for a few weeks.

Hopwood [25] used buffered pH indicator paper instead of metal foil to detect acid gases emitted from materials and to give some indication of their quantity.

Collings and Young [26] give a test for contact corrosion of silver that will also detect attack by vapours.

We welcome the publication of such useful tests but look forward to the development of more comprehensive screening tests. The foil and indicator
tests detect only the more dramatic problems - corrosion by acid gases which cause visible, identifiable and therefore publishable types of damage. Other gases such as solvent vapours may cause subtler damage just as serious in the long run but not readily identified. The other problem with these tests is that many organic materials such as plastics, fibres and paints are formulated with inhibitors that protect the polymers for a time, giving a spuriously comforting result in short tests [27]. Wilson [28] shows the course of the deterioration of plasticized cellulose acetate film which starts slowly then suddenly accelerates. Cellulose acetate also illustrates another hazard in testing modern materials the enormous variation in stability from batch to batch. We recently examined a roll of film [29] which was emitting acetic acid at a rate which needed no more sensitive analytical technique than a nose at ten paces and which was encrusted with crystals of the plasticizer triphenyl phosphate. It seems that residual acid in the film was hydrolyzing the cellulose acetate, reforming cellulose which was incompatible with the plasticizer. Curiously, the metal can was in quite good condition.
Figure 17. Microfilm in a steel can. The needle shaped crystals growing under the gelatin layer are triphenylphosphosphate, a plasticiserdiffusing out from the cellulose acetate film base. The separation rate is increased by hydrolysis of the cellulose acetate to cellulose. There was a strong smell of acetic acid when the can was opened. Triphenylphosphatelowalsohydrolyses to produce phosphoric acid, which further accelerates degradation of the film. The decomposition of triphenylphosphate is also catalysed by acetic acid, so this is an example of a doubly autocatalytic reaction which proceeds ever faster with time.

Figure 18. An unusual source of indoor air pollution. This is a scanning electron micrograph of the tin-mercury amalgam backing of a mirror, viewed from the side which was adhering to the glass. The rounded depressions were once mercury drops, trapped between amalgam and glass. These have slowly evaporated, leaving air filled voids. It is these that give the characteristic tiny pricks of light which make amalgam mirrors so attractive as they gradually decay. The white bar is 100 microns. Photo: Per Hadsund.
Figure 19. The image (right) transferred to the glass protecting this poster is tiny drops of dibutyl phthalate. It must come from the oil based ink of the print. The curious thing is that the glass was several millimetres away from the paper, yet the image is quite sharp.

Figure 20. The lock of this new storage cabinet corroded on the inside during a few weeks of storage before use. It is likely that the paint had been over-baked in an attempt to remove solvents, generating low molecular weight decomposition products.

7. CONCLUSIONS

This brief review leads us to put forward some recommendations for museum display that will minimize internal corrosion.

A leakage rate that gives about one air change a day is about the fastest that is compatible with effective damping of the daily cycle in relative humidity but it is also slow enough to allow chemical damage to objects by internal pollution. Exhibition designers should therefore limit themselves to a short and inevitably constricting list of techniques and materials which
Not all contamination in enclosed spaces is caused by diffusion and convection. This acrylic glazing (left, about 1m square) protected a confederate flag in the Battlefield Museum at Fredricksburg, Virginia. The strange feathery deposits along the edge are gypsum. The source is the wall behind the picture. The gypsum moved in solution in water penetrating the outer wall and migrated into the board supporting the flag. It would have stayed there, but for the enthusiasm of the cleaner, whose cloth generated an enormous electrostatic field where the acrylic glazing met the metal frame (we have reproduced this process in the laboratory).

are probably safe (see section 9). Until a general purpose, wide range, showcase pollutant absorber is developed we recommend, as an acid gas absorber, carbonate-buffered paper, laid in cases but not in contact with objects. Such paper is, of course, not only commercially available but made in the conservation departments of museums and libraries! Paper impregnated with active charcoal and molecular sieves is also available and useful, but it needs to be changed occasionally. The exposed surface area of absorber must be large – a discreetly small container nesting in one corner is less effective than natural ventilation, which in turn is demonstrably inadequate. Finally, keep the temperature down!

8. SOME MATERIALS KNOWN TO RELEASE HARMFUL VAPOURS AT ROOM TEMPERATURE

Wood, particularly hardwood, releases organic acids, alcohols, aldehydes, esters and hydrocarbons. Protein-based glues and wool can release volatile sulphides (refined, photographic quality gelatin is sulphur-free). Cellulose nitrate releases oxides of nitrogen. Cellulose diacetate can release acetic acid (see text). Polyvinyl chloride releases hydrogen chloride. Polyvinyl alcohol is made by hydrolyzing polyvinyl acetate and may continue to release traces of acetic acid. Polyvinyl acetate and its copolymers are generally regarded as forming very stable films but it certainly releases acetic acid.

9. MATERIALS THAT ARE SAFER


10. REFERENCES

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