ASSESSING THE DETRIMENTAL EFFECTS OF WOOD AND WOOD PRODUCTS ON THE ENVIRONMENT INSIDE DISPLAY CASES

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Detrimental effects of wood based construction materials used in the museum environment are discussed. Chemistry of wood and wood products is reviewed with regard to emission of formaldehyde and acetic acid, using examples of storage problems reported in the conservation literature. A method for testing wood and wood products for their detrimental effects is presented.

Introduction

Curators and conservators try to protect the objects in their care from deterioration and damage. For this purpose, objects are often stored or displayed in closed containers or otherwise enclosed spaces, in more or less controlled environments. This practice backfires when the construction material introduces substances into the environment that accelerate object deterioration.

Since most of the stored objects' surface is exposed to the surrounding atmosphere and free moisture is not available in controlled environments for transport by liquid flow, the composition of the surrounding air space will determine the detrimental effects. Such effects have been observed and reported in connection with wood and wood products (1-9). These materials are appreciated because they are inexpensive, easily workable and often look good. Their complete elimination from museum storage and display could create considerable problems. It seems desirable to screen various woods and wood products for their potential to increase object deterioration and to devise methods to reduce the ill effects. The first necessary step is to design a test for the dangers emanating from these construction materials. This paper describes experiments to develop such standardized test method.

Harmful Effects from Wood and Wood Product

The air space in contact with wood can contain large numbers of different chemicals (10). To catalogue all of them and measure their concentration would be a formidable task. For assessment of the dangers from these volatile substances, the task can be simplified by categorizing them according to their principal functional groups, which determine their reactivity. Within these categories, the members having the lowest boiling point, and hence the highest vapor pressure, will be of most concern. Volatile 'substances found in connection with wood are simple hydrocarbons, alcohols, aldehydes and acids. The first two classes are largely nonreactive at room temperature and unlikely to cause ill effects. Aldehydes and acids will be discussed in more detail. Low molecular weight esters are also found (11). These can hydrolyze into the constituent alcohol and acid.

It is long known that the atmosphere inside wooden containers can accelerate metal corrosion (12-14). The agents causing the problems have been identified as organic acids, mainly acetic acid, and formaldehyde (11-15). The museum storage problems reported in the literature are all related to the actions of acids. Acids act by dissolving metal salts, thereby catalysing metal corrosion (1-9) and relocating calcium carbonate to form efflorescence on seashells (1). They also accelerate yellowing of paper (16). Formaldehyde can be oxidized by air oxygen, e.g. on a metal surface, to formic acid which then has basically the same effects as acetic acid. By this mechanism, formaldehyde also catalyzes metal corrosion, but to a lesser extent than acetic or formic acid (17), depending on the rate of aldehyde oxidation. Form-

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aldehyde is a reductant that can discolor metal oxide pigments and bleach paper. It can make hides, wool or cotton brittle by linking two alcohol or amino groups in the polymers constituting those materials. These effects have been reviewed and discussed (7-9). More information is required to assess its actual danger at common environmental levels.

The origins of acetic acid and formaldehyde, as well as the mechanisms controlling their release rate have been reviewed (11-14). Acetic acid released from wood originates from hydrolysis of acetyl groups (esters) in the wood polyoses (hemicelluloses). The rate at which these esters hydrolyze is proportional to the concentration of esters, the availability of water, the temperature, and the acidity of the environment, since this is an acid catalyzed reaction. The rate will be inversely proportional to the concentration of the produced acid. Most condensation reactions are reversible, meaning that their direction depends on the conditions, according to Le Chatelier's principle. The acids formed by hydrolysis will at first be adsorbed to the wood substance, or dissolved in the aqueous phase on the internal wood surface. There is a limiting concentration (equilibrium) at which the rate of hydrolysis is just balanced by the rate of ester formation.

Formaldehyde can occur in wood, in small quantities, where it is formed by a degradation reaction of lignin. In wood products, it stems from the ubiquitous formaldehyde resins. Urea-formaldehyde (UF) resins are the most common. They also degrade at the highest rates to release formaldehyde. The major bond type in UF resins is methyleneamine (18), which is an analogue of the acetal bond (19). Formation of these bonds is a condensation reaction and reversible. They hydrolyze over time. In the manufacturing process, formaldehyde is added in excess in order to increase the yield of condensation product (Le Chatelier's principle again), which creates immediate emission problems. In phenol-formaldehyde (PF) resins, the initial bond between phenol and formaldehyde is also formed reversibly but rearrangement to a carbon-carbon bond follows (20). The rearrangement is irreversible, which accounts for the low rate of formaldehyde emission from PF resins.

Modelling the Storage Conditions

All components of the storage environment are open, dynamic systems, i.e. they allow mass transport between them and they change over time. The state at any time can be predicted from the rates of change. The rates, in turn are functions of the current state. A model of the situation, expressed in mathematical terms, requires the simultaneous solution of a set of differential equations. The necessary techniques have been developed in the engineering disciplines. Examples of their application to the calculation of relative humidity inside display cases and its moderation by silica gel (21), or the rate of emission of formaldehyde from wood products (22) have been published.

If organic acids are the major concern, moderation of environmental concentrations can be accomplished by including an acid scavenger, e.g. carbonate of soda. The effectiveness of this technique can be assessed by methods applied to humidity control (21, see above). The situation is slightly better in the case of acids, since the reservoir from which the substance is replenished is not limitless, as is the case with water vapor from the environment, but restricted to at most 10 % by weight of the wooden construction material used.

The rate at which wood and wood products add organic acids and formaldehyde to the air inside containers depends on many factors, some of which have been mentioned above. Many construction details, as well as the properties of the construction material, will influence the actually observed rate. To test construction material for its acid release potential, test conditions must be carefully controlled to ensure reproducibility and compatibility. Acceleration of the processes involved is desirable to increase the sensitivity of the test. For the processes of interest, increasing temperature and humidity are options. Wood should be tested in comminuted form so that the acid can readily diffuse out and the effect of variable wood porosity is eliminated. Care must be taken that the underlying mechanisms remain unchanged. Temperatures much above 60 °C are undesirable because thermal degradation can be significant. Humidities near saturation are unsuitable because wood can be colonized by microorganisms that produce organic acids metabolically.

Measurement of the vapors released can be accomplished by various methods, all of which have specific advantages and disadvantages. A review of the suitable methods suggested that a quantitative test based on the actual degradation process will serve the purpose best. It follows the ideas of Oddy (2,3), who incubated various metal coupons with construction material samples in water saturated atmospheres and assessed the degradation visually. The same procedure was later modified by measuring the weight change over time (5,17). The advantages of this approach are that no expensive equipment or skilled personnel are required, as would be the case with gas chromatographic techniques. Also, it is not necessary to sample large volumes of gas, as is the case with a method for determining environmental concentrations of organic acids (23). Furthermore, the method accounts for the effects of both, acids and formaldehyde, without requiring specific tests for each.

The objectives of the initial series of experiments were to establish whether (I) weight changes after reasonable incubation times are large enough to be reliably detected, (II) weight change is constant over time, and (III) results are reproducible and repeatable. The major disadvantage of this method is that actually many processes are contributing to the phenomenon measured, all of which interact. In order for this test to supply valid comparisons of the potential corrosivity of the tested materials, it is only necessary to assume that the measured weight change is proportional to the concentration of offending substances in the incubation bottle. It is planned to express the corrosivity of a tested material as a dimensionless factor, calculated by dividing the weight change observed in the presence of the test material by the weight change on incubation without the material.

Experimental Procedures

Incubation was carried out in twelve liter glass bottles for varying times up to six weeks (1080 hrs). Three lead foil coupons with equal surface area were suspended from a glass hook over 50 g of air dry wood, which had been comminuted in a Wiley mill to pass a 4 mesh screen (Fig. 1). Sample preparation and determination of corrosion rate followed ASTM standard G1 81 (24). The lead coupons were prepared by degreasing with acetone, pickling for one minute in boiling acetic acid of 1% (v/v) concentration, and washing under running water followed by drying and weighing on an analytical balance (Sartorius Selectra). Mechanical cleaning techniques were not considered because their repeatability is poor and cold working or surface contamination will alter the corrosion properties.

Weighing after incubation gave the weight gain. Removal of corrosion product in order to measure weight loss was done by pickling as in the preparation. Since this cleaning method may attack the base metal of the specimen, ASTM suggests that cleaning for short periods of time should be repeated and the mass loss plotted against the total cleaning time. The plot should reveal two different, approximately linear, rates of mass loss. Straight lines are then fitted by hand to the weight loss data. The intersection of the lines will give the weight loss caused by removal of corrosion product alone.

The wood used was black oak that had been stored at 70 OF and 66 % r.h. for five years. The nominal equilibrium moisture content (emc) at these conditions is 12 %. Corrosion runs were carried out at 80 % r.h. and 70, 50 and 30 °C. Incubation bottles were kept in an AMINCO controlled environment chamber set to the desired conditions, for five days in order to allow equilibration of moisture content and temperature of the bottle contents. Preliminary experiments showed that this time was sufficient for the wood to reach moisture equilibrium. After five days, the bottles were fitted with the stoppers as shown in Fig. 1. For the experiments at 50 and 30 °C, incubation in empty bottles was included for comparison. The first two runs at 70 and 50 °C were carried out with an old stock of lead foil of unknown purity and with high surface roughness. After the feasibility of the method had been established, chemically pure lead foil of 0.006 inch thickness with clean and smooth surface was used. In the first two experiments, two incubation bottles were withdrawn for every incubation time in order to establish the variability of corrosion rates between bottles. The third experiment was aimed at testing for linearity of the corrosion rate over time and only one bottle was withdrawn after every incubation period to give more data points.

Results

Weight gain of the incubated lead coupons as a function of time is shown in Figs. 2-4. It can be seen that the weight gain varies considerably between the coupons. Bottle averages vary much less, indicating potentially good reproducibility. Fig. 4 shows that in the same bottle, the middle coupons (no.'s 2) consistently had the lowest weight gain. Visual inspection showed that tarnishing was uneven on the surfaces between two strips, decreasing from the periphery to the center. This indicates a concentration gradient of acid and/or water vapor in the narrow space between the coupons, due to insufficient mixing at these conditions. In future corrosion runs, the gap between coupons will be enlarged by using only two per bottle. The experiment at 30 °C clearly shows a decrease in the rate of weight gain with time. At 50 °C, the decrease is still noticeable but less pronounced than at the lower temperature. At 70 °C, no change was noticeable over the incubation period. There was measurable weight change on incubation without wood at 50 °C (Fig. 3). At 30 °C, weight change was so small that reliable determination was impossible.

A sample of the plots prepared for weight loss determination is shown in Fig. 5. The example demonstrates the large random error inherent in this method. Another problem with measuring weight loss is the disposal of the removed lead salt. The local Municipal Utility District allows aqueous solutions containing up to 2 mg/l of lead to be poured down the drain. The concentration of lead in the effluent was estimated as 14.3 mg/l, assuming worst circumstances. Dilution of the collected effluent to allowable concentrations would be considered by the EPA as treatment of hazardous waste and is illegal. Weight loss determination was discontinued after the environmental problem was realized.

In the experiment at 50 °C, the weight loss/weight gain ratio was between 5.0 and 5.7 after 311 hrs. It decreased to between 4.4 and 4.8 after 648 hrs, and to between 3.8 and 4.2 after 1080.5 hrs. The weight loss/weight gain ratio is determined by the salt composition. The ratios for some lead salts are PbO:

12.9, $2PbCO_3 \cdot Pb(OH)_2$: 4.02, $PbCO_3$: 3.45, $Pb(HCOO)_2$: 2.3, $Pb(CH_3COO)_2$: 1.75. The measured ratios indicate a salt composition similar to basic lead carbonate. Loss of corrosion product would reduce the measured weight gain and increase the loss/gain ratio. It should be expected that loss of corrosion product increases with incubation time. The changes in loss/gain ratio, as well as visual examination of the corrosion product, indicate that no corrosion product is lost. It must be concluded that the salt composition changes over the incubation time.

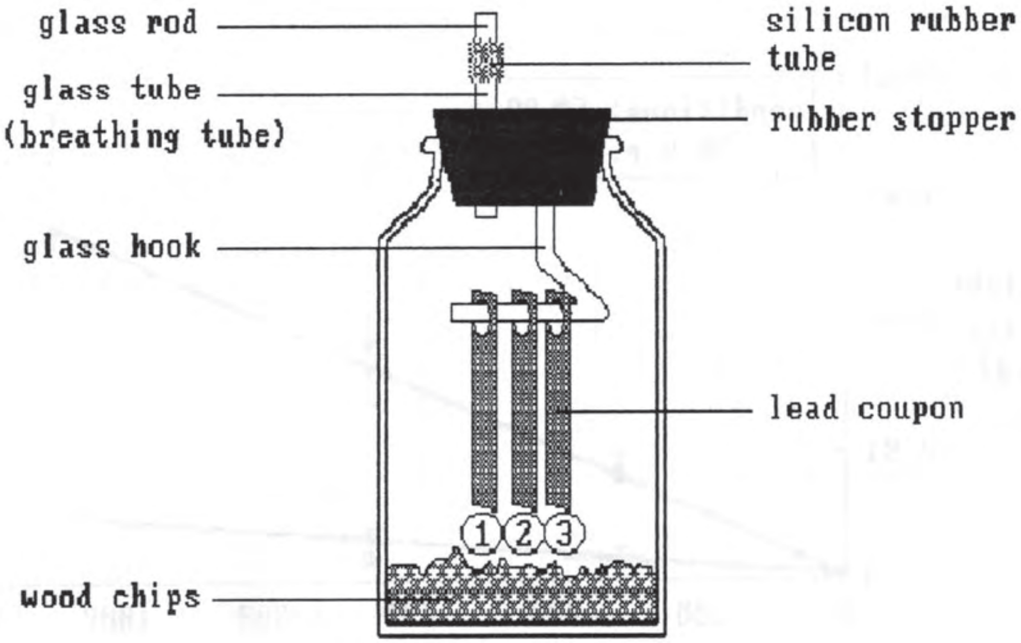

Fig. 1: Schematic representation of incubation bottles

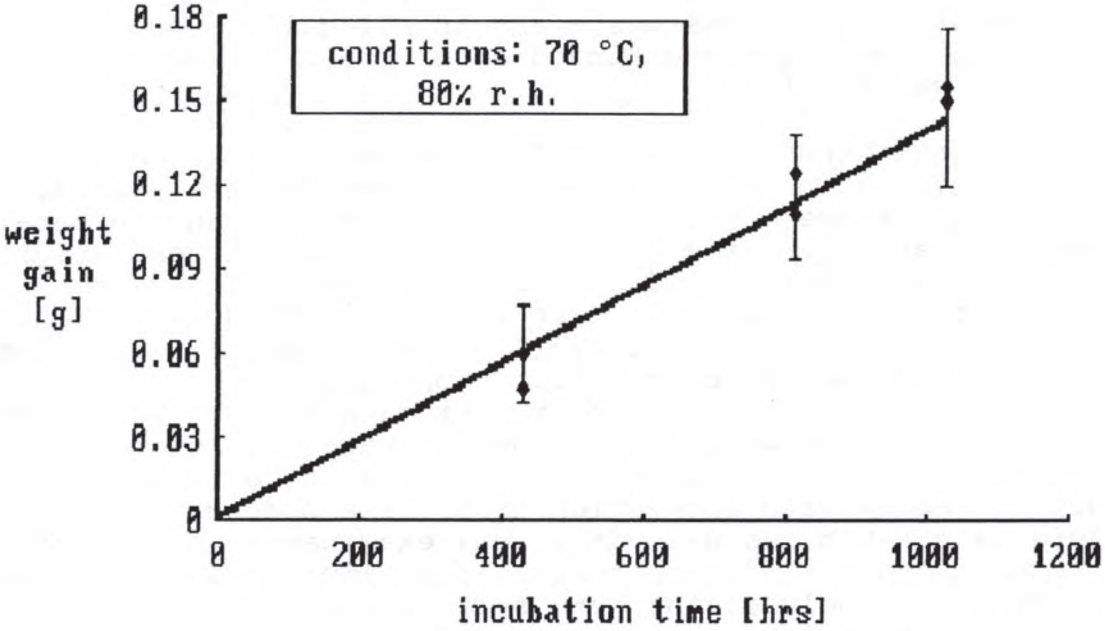

Fig. 2: Weight gain on incubation over wood, lead coupons with 80.5 cm2 surface area.

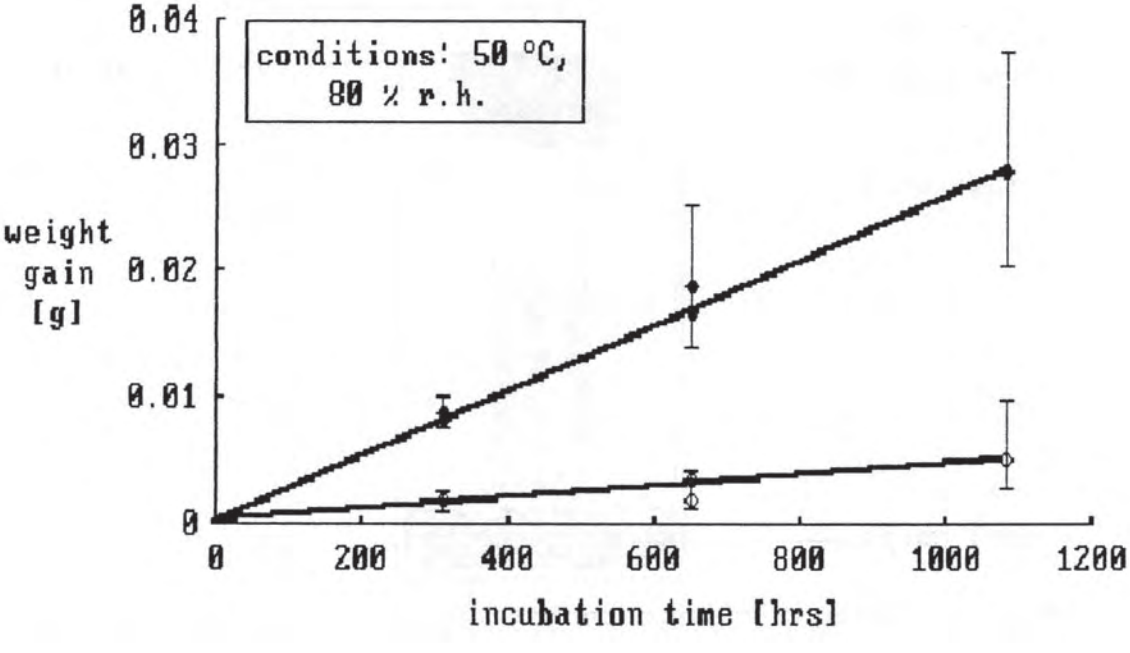

Fig. 3: Weight gain in presence and absence of oak wood, lead coupons of 80.5 cm^2 surface area.

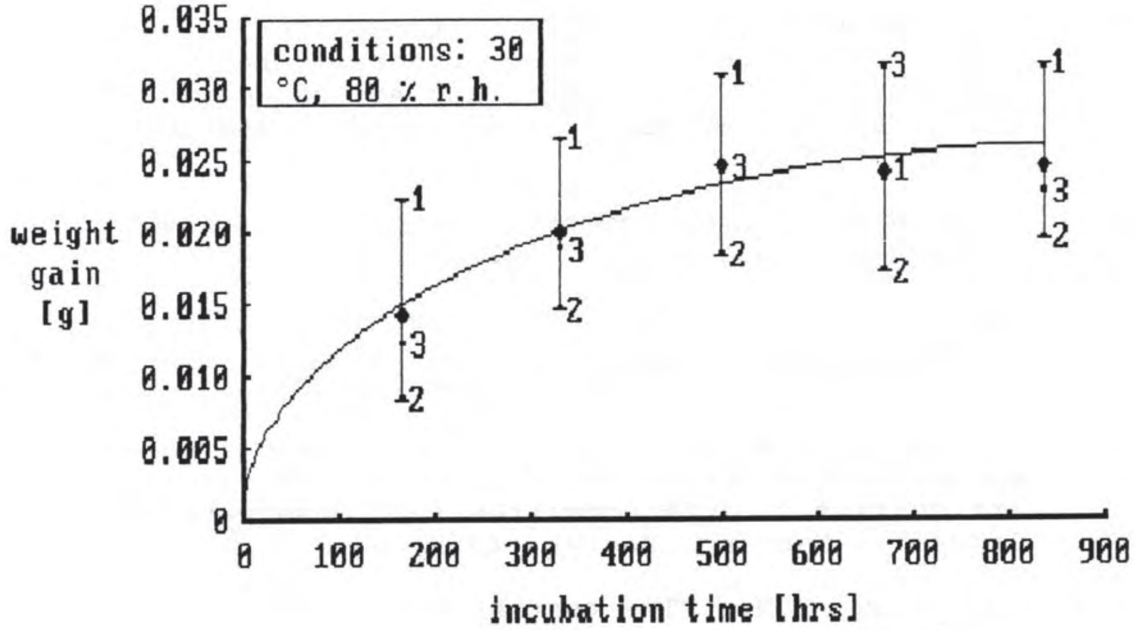

Fig. 4: Weight gain on incubation over oak wood, lead coupons with 60.1 cm² surface area. (NOTE: the circles in Figs. 2 to 4 are bottle averages)

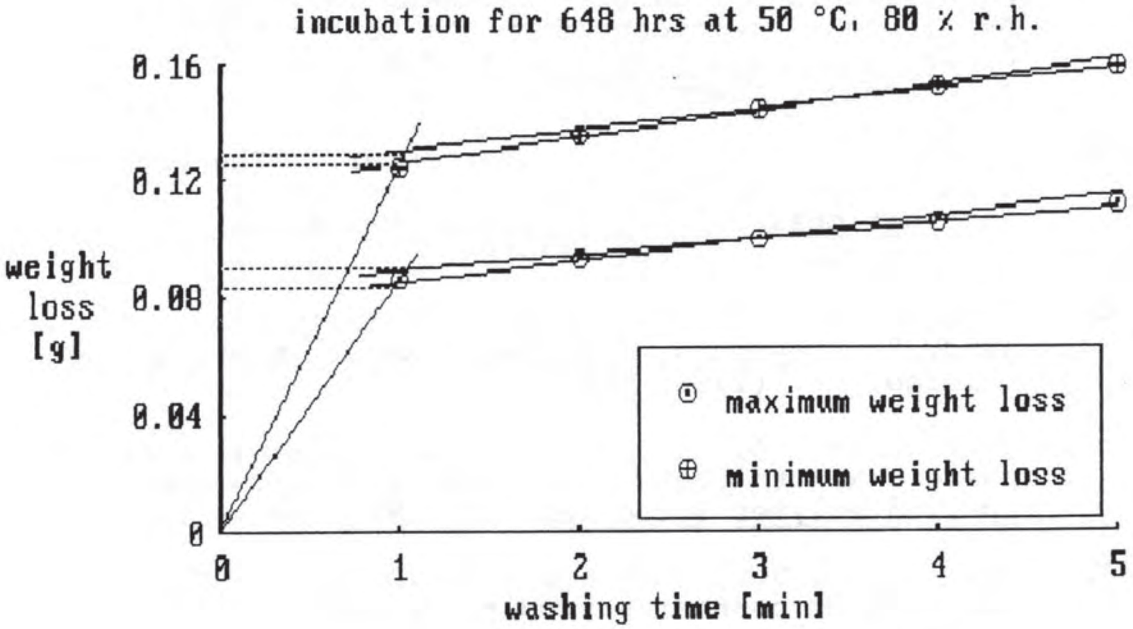

Fig. 5: Sample plot for weight loss determination.

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