The Decay and Conservation of Museum Objects of Tin

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It is twenty-five years since I first read 'The Decay and Conservation of Museum Objects of Tin' by Harold Plenderleith and Robert Organ, which appeared in the first volume of *Studies in Conservation* [1]. On reading the paper once more I was overwhelmed by a sense of awe and total admiration for the quality of the applied conservation research shown in this pioneering paper. The concern over 'tin-pest', the drastically deleterious effect of tin undergoing an allotropic phase transformation from the stable white tetragonal metallic (β) structure to the grey powdery cubic (α) form of tin (Sn), has achieved an almost legendary status. Courses in metal conservation often refer to this signal paper in *Studies in Conservation* as the reference to the problems of 'tin-pest' but it would appear that few presenters have read or comprehended the final paragraph of the paper where the authors state "For these reasons we feel that its possible existence may well be ignored by the museum laboratory, and all manifestations of decay regarded as corrosion phenomena amenable to treatment by the usual methods of electro-chemical reduction."

The structure of the paper was well crafted, as the authors took us on a tour of museum objects that had previously been thought to be subject to 'tin-pest' but were all shown to be suffering from varying forms of localised corrosion. Having spent a quarter of a century analysing corroded metals, principally from archaeological sites in a marine environment, I have become acutely aware of the need to conduct corrosion studies on real objects, full of their differences in microstructure, impurity distribution and stresses associated with their manufacture, use and deposition. In one way, the two great men of the British Museum had done it all long ago. Tin objects are rarely found with tin contents much greater than 95%, though many of the 'pewter' plates on the wreck of the *Mary Rose* (1545) were essentially 99% tin. The authors listed a range of artefacts from a sword scabbard end with a tin content of 99.93% to Roman tin objects that were essentially leaded pewters with lead contents of 2.7–5.4%, and trace amounts of iron and copper. In attempting to clarify if the surface growth was the grey tin-pest, the corrosion products on a 'pure' tin object were analysed and found to be a characteristic mixed Sn(II) and Sn(IV) patina, which accounted for 98% of the weight of the pustule. Thus they demonstrated that even on an object of remarkably high purity, there was no sign of allotropic phase transition.

The remarkable 'tin-hat' coins from Malaysia, so named because their cross-section resembled a flat topped hat, had 99.9% purity and could have been expected to be a candidate for tin-pest. The authors demonstrated the advantage of taking sections from corroded objects. From the metallographic analysis and from the corroded matrix it was clear that a series of changes in the burial environment had caused a banded structure to form in the layers of oxidised metal. The examination of the matrix showed that the object had been subjected to periodic changes in the burial microenvironment, as seen in the banded layers and in the different colours of the corrosion products. This structure also revealed another characteristic of tin, that it is very prone to pitting corrosion. Subsequent work has shown that the presence of minor impurity or alloying elements in an otherwise essentially pure metal will have a dramatic effect on corrosion rate, through processes of internal galvanic corrosion along grain boundaries where the impurities tend to concentrate. Once again the authors were able to establish that the degradation processes were clearly forms of localised corrosion rather than a form of physical change associated with the transition from β to α tin.

As an adopted cousin of Western Australia there could be little greater joy than reading of the analysis of our earliest recorded historical item, the Hartog 'pewter' plate that was left at Cape Inscription by the Dutch ship the *Eendracht* in 1616. The plate was found by the Dutch explorer Willem de Vlamingh in 1697 and taken to the Netherlands where it eventually entered the collection of the Rijksmuseum. Analysis showed that the plate degradation had nothing to do with tin-pest but was the result of intergranular corrosion and the stresses associated with mechanical deformation in producing a flat surface from a dinner plate and the stress associated with the large volume expansion of corrosion products between the grains. The authors had recommended a stabilisation process involving some form of impregnation and although this appears to have been effective, subsequent damage during a remounting exercise caused the plate to collapse into many pieces. Happily the broken elements have been relocated and are on exhibition in an appropriate showcase environment back in the restored Rijksmuseum in Amsterdam.

One of the primary reasons for writing the paper was that the physical chemical literature had reported that the phase transition from the metallic β form of tin to the powdery α form takes place at around 13°C, which is perilously close to the temperatures often encountered in European museum storage environments, or in the exhibition areas in the winter months, particularly during the then-prevalent power crises. Experiments with β tin were conducted at −78°C and it took 10–11 days to get unworked cast metal to start the transition to the powdery α form. Clearly it is not a process that begins easily. Other workers found that the transition was facilitated by the presence of an ammonium tin (IV) chloride, $(NH_4)_2SnCl_6$, or by having samples of the grey α form present on the surface, but even then it could take up to ten days in the temperature range of −10 to 0°C. The presence of as little as 0.02% silver in 99.98% pure tin will prevent the initiation of the transition even after cold working or in the presence of grey tin.

Plenderleith and Organ reported results from a study that involved inoculation of pure plates of Kahlbaum-tin and Banka-tin with grey (α) tin particles and monitored the process at −10 ±2°C over many weeks. Analysis showed that the rate of change was a maximum at −30°C and that the linear velocity of transformation of β to α tin was greatest for the smallest grain sizes. The authors noted the implication of grain size and warned that non-annealed and extensively cold worked objects, which have the smallest grain size, would be the most at risk. Before all readers suddenly wonder if their tin organ pipes or other objects are going to crumble, it is important to read on and learn how the natural mineralogy of tin ore bodies can save the objects from this unusual form of decay. Bismuth (Bi) is a naturally occurring impurity in tin and the presence of as little 0.01 wt % Bi will dramatically retard the transition process. Even 'chemically pure' tin will often contain 0.0035 wt% Bi, which alters the microstructure of the tin, producing a cored eutectoid which leaves the metal subject to tin-pest after the bismuth has been removed electrochemically. However, if the microstructure has a uniform distribution of bismuth, the impurity largely inhibits the physical process of phase transformation. Other workers had noted that solid solutions of tin with traces of cadmium, antimony and bismuth prevented the transition even after 3–4 weeks at −78°C in the absence of any electrolyte.

Plenderleith and Organ conclude this monumental work by summarising the factors that could lead to the presence of tin-pest in museum collections. Factors include the degree of cold and the length of time the objects were held below the equilibrium temperature versus the time stored above the transition point. Clearly the presence of the grey form of tin has an accelerating effect, as the presence of inoculated spots of grey tin seeds the transition from the white metallic form. Previous history of cold working and annealing has an effect and the purity of the metal is perhaps the dominant factor. If small warty growths of tin-pest are noted, attempts to reverse the transition by gently heating the metal are problematic as heat and moisture initiate the natural oxidation of metallic tin to form a stable mixed tin oxide patina. The authors conclude that in all events they have not been able to identify a "single illustration known with certainty to represent authentic tin pest of natural occurrence".

Only one example of tin-pest has been detected in the last fifty years; Paulitsch and Wittmer reported this singular event in 1987 [2]. Thus, the original findings of the Plenderleith and Organ have stood the test of time, the paper's quality is undiminished, and reputations remain untarnished.

References

1 Plenderleith., H.J., and Organ, R.M., 'The Decay and Conservation of Museum Objects of Tin', *Studies in Conservation* 1 (1952–1954) 63–72.

2 Paulitsch, P., and Wittmer, S., 'Tin corrosion products on objects of art', in *Recent Advances in the Conservation and Analysis of Artifacts*, Summer Schools Press London (1987) 163–164.