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The Decay and Conservation of Museum Objects of Tin

INTRODUCTION

THE stability of metallic tin is such that it can be used as a protective coating for less stable metals (and, in the form of foil, as a hygienic wrapping for foodstuffs), and normally it will remain bright and untarnished. When, however, it is buried in the ground for lengthy periods it oxidises, becoming grey, and eventually almost white, as the surface film of stannous oxide is converted to the stannic condition. Museum objects made of tin, or from an alloy in which tin is a major constituent, generally display a continuous greyish patina, which may be tinged perhaps with green if copper should be present as well, and as a rule such patina is perfectly stable under museum conditions. The dull-grey patina of pewter is a case in point. Soft solders (tin plus lead) have often outlived the metals that they have been used to join together in antiquity, being protected by the growth of a compact surface-layer of oxides.

There are two types of decay, however, that merit the attention of the conservator. The first is a local kind of chemical decay (Jug, Fig. 1) in the form of disfiguring excrescences of oxide usually of an apparently spotty nature, hard to the touch. The second is the so-called 'tin pest,' superficially rather similar in appearance, save that the spots are soft and powdery and tend to spread and in time to puncture the metal. These two types of decay arise from different causes, the first by chemical or electrochemical action in the ground, and



Fig. 1. Fourteenth-century French pewter jug
(Victoria and Albert Museum, London)

TABLE I

OBJECT	ANALYSIS				
	Tin	Copper	Lead	Iron	Oxygen
Tin Scabbard End *	99.98	Trace	—		
Roman Tin 'A' †	97.70		2.73		
Roman Tin 'B' †	94.78		5.37		
Tinned Bronze ‡	99.98				
Old Vessel §	94.35	Trace	5.06	Trace	0.59

* C. O. Bannister in the *Journal of the Institute of Metals*, xxxv (1926), p. 71.

† J. A. Smythe in the *Journal of the Institute of Metals*, LXVI (1940), p. 355.

‡ C. H. Desch in a note to C. O. Bannister *op. cit.*

§ W. Gowland in *Archaeologia*, LVI (1899), p. 13, quoted by Mellor (13).

the second, which is more serious, by protracted exposure to conditions of extreme cold, which cause a change of crystal structure, to which is to be attributed the loss of lustre and weakening of the metal.

The term 'tin pest' cannot be used to cover all forms of disintegration. It is reserved specifically to describe the change to powdery grey tin that takes place at low temperatures, especially if the metal is worked in the cold and inoculated with crystals of the grey phase. From time to time we hear of museum objects suffering from 'tin pest' when in fact there are no grounds for such a diagnosis, the effect being merely one of oxidation, which may have proceeded to the limit. For the conservator, correct diagnosis is important, because, whereas oxidised metal is generally amenable to laboratory treatment, an object that has suffered the allotropic change to grey powder cannot be reconstituted.

THE CORROSION OF TIN

As the appearance and structure of the oxidised film is modified by the presence of impurities and particularly by alloying metals, it may be of interest to mention some analyses of ancient metal objects. These show lead to be the commonest minor constituent, with traces of iron and copper not unusual (see Table I).

For the corrosion-product of a tin object of 99.98% purity the following analysis has been obtained¹:

SnO (Hyd.)	43.35
SnO ₂	54.68
CuO	0.81
SO ₃	0.85
FeO etc.	0.12
CaO	0.10

It would seem therefore that there is little likelihood of confusion with the white pitting that is a feature of corroding lead; this can be shown to be a carbonate since it effervesces with acid.

A typical case of tin corrosion was presented by some 'tin-hat' money from Malaya (Fig. 2) which furnished examples of well-patinated and stable coins as well as others in an extreme condition of decay. Fig. 3 shows a section of one of the best preserved and the etched surface (Fig. 4) exhibits the dendritic structure characteristic of cast metal. This is indicative that the metal is not pure tin, although analysis of a similar piece gave a value of 99.9% (impurities iron and lead). We are indebted to the Tin Research Institute for these analyses, and for examining also the crust of corrosion products, 'which consisted mainly of stannic

¹ C. O. Bannister in the *Journal of the Institute of Metals*, xxxv (1926), p. 71.

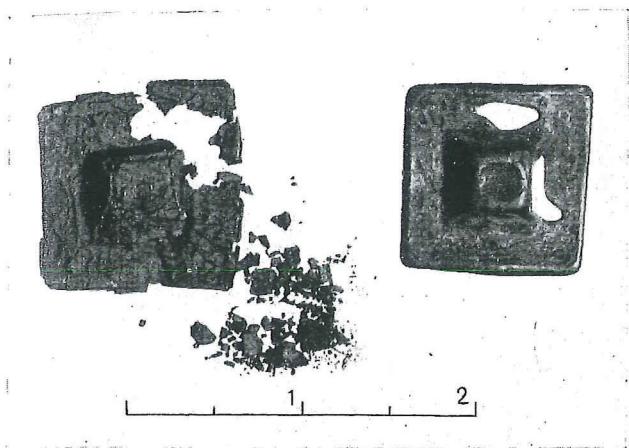


Fig. 2. Malayan tin-hat coins
Scale in inches

(Selangor Museum, Kuala Lumpur, Malaya)

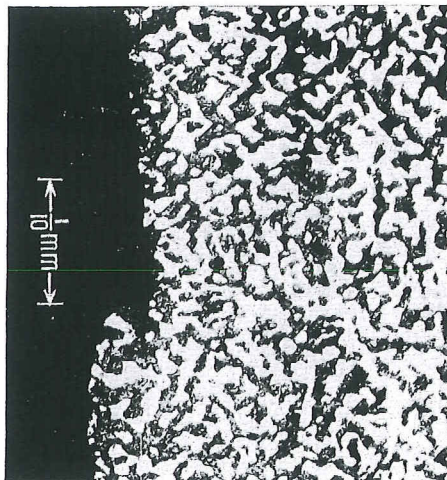


Fig. 4. Etched portion from Fig. 3
(250 x)

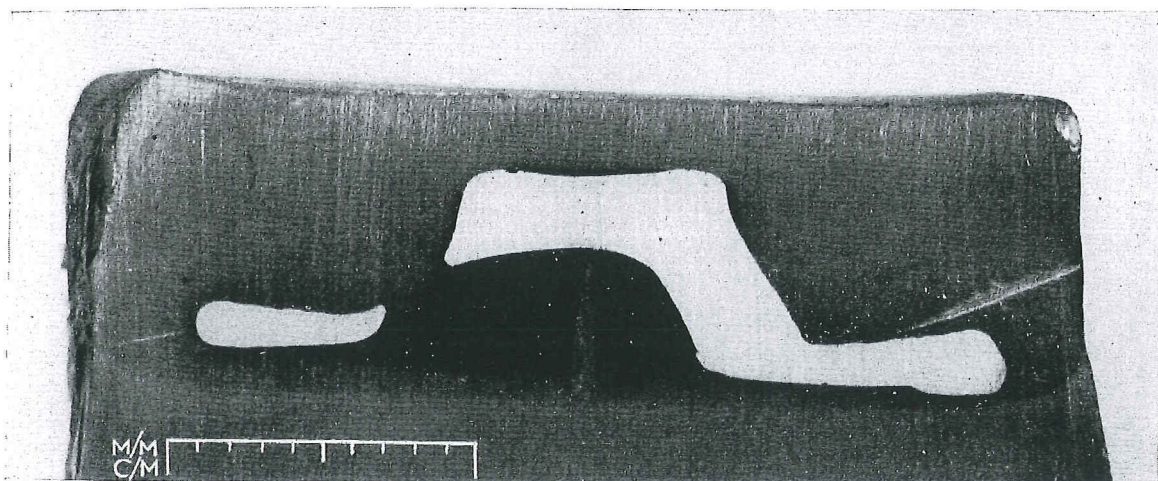


Fig. 3. Section of tin-hat coin
(Selangor Museum, Kuala Lumpur, Malaya)

oxide containing only traces of impurity (iron, silica, etc.) and about 7% of a stannous compound which may be stannous oxide. Sulphate was detected in appreciable quantity, but little chloride.

Even when impurities are present in small amount it is possible, as Fig. 5 shows, to trace the progress of the oxidation immediately beneath the surface and extending in to the metal core, by suitable etching, magnification and illumination. The cross-section exhibits

a banded structure in greys and browns composed of dozens of layers. The strain on expansion to oxide must be considerable and the skin can be shown to split away very easily from the metallic core, in which case, of course, it must cease to be protective. A coin in this condition is nevertheless amenable to treatment by reduction so long as a metallic core remains. Fig. 6 shows how reduction with zinc and caustic soda revealed hidden ornament on a 'tin-hat' coin; and equally

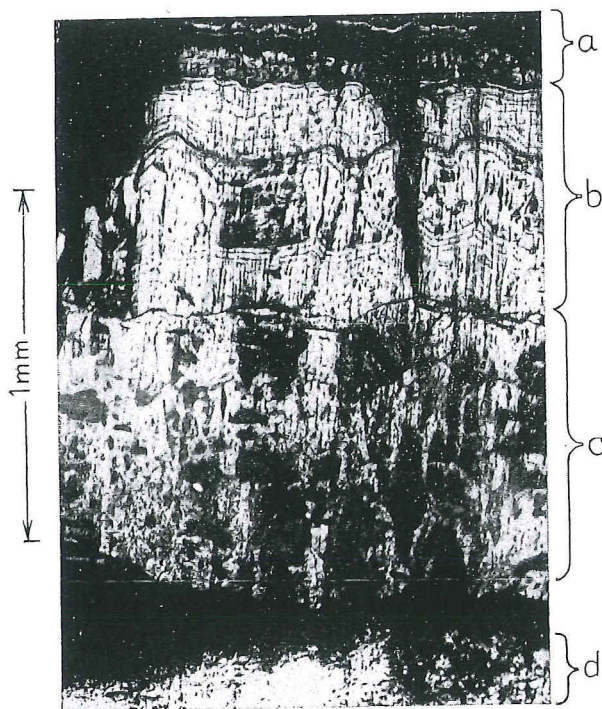


Fig. 5. Section of the patina on tin-hat coin
Layers (a) gray, (b) brown, (c) gray, (d) metallic tin.
The unbanded dark areas in (c) are pits.

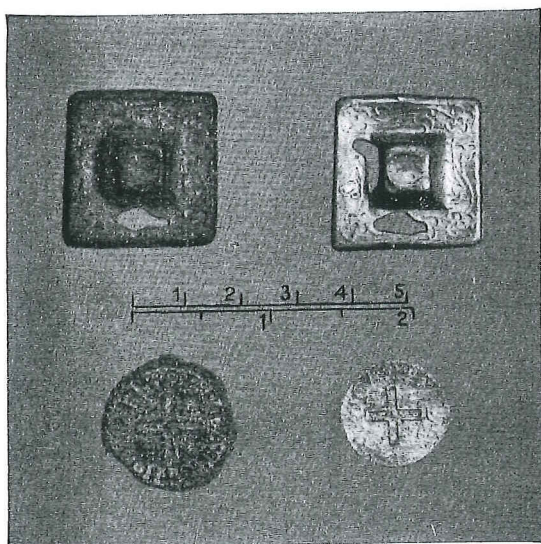


Fig. 6. Treatment by reduction
Left: A tin-hat and a Portuguese coin of John III, as
received. Right: Similar coins treated by reduction.
(Selangor Museum, Kuala Lumpur, Malaya)

good results and a rather better colour were achieved in the case of the round coin by using magnesium in place of zinc. The reduction of spotty metal can be achieved in the same way, though naturally depressions are likely to remain in the place of the spots, as there is always some loss from causes that are of mechanical as well as of chemical origin.

A very interesting tin plate known as the Hartogs plate was submitted by Dr A. van Schendel, who provides the following historical note:

It was left on a pole on the West coast of Australia by skipper Dirck Hartogs in 1616 as a token of his discovery. The inscription reads in Dutch:

1616—DEN 25 OCTOBER IS HIER AENGECOMEN HET SCHIP DEENDRACHT VAN AMSTERDAM DE OPPERKOPMAN GILLIS MIEBAIS VAN LVICK SCHIPPER DIRCK HATICH VAN AMSTERDAM DE 27^o DITO TE SEIL GEGHN NA BANTVM DE ONDERKOIPMAN JAN STINS DE OPPERSTVIERMAN PIETER DOOKE (?) VAN BIL.

[1616—On the 25th of October arrived here the ship *De Eendracht* from Amsterdam, chief trader being Gillis Miebaïs of Liège, master Dirck Hartogs from Amsterdam. On the 27th of the same month she left again for Bantam. Assistant trader was Jan Stins, mate Pieter Dooke van Bil.]

In 1697 the plate was found on the spot by another navigator, Willem de Vlaming, who removed it and replaced it by another tin plate recording the first landing as well as his own. De Vlaming took Hartogs's plate to Batavia, whence it was sent to the Governors of the East India Company in Holland. In 1820 it was given to the Koninklijk Kabinet van Zeldzaamheden in The Hague, which became a part of the Rijksmuseum collections in 1883. It bears the inventory number N.M. 825.

I find no record of earlier treatments, but it is clear that it has been coated, probably in the twentieth century, with some resinous matter.

Very little has been published about this object, but something is said about it in J. E. Heeres, *Het aandeel der Nederlanders in de ontdekking van Australië, 1606-1675*, Leiden 1899, p. 84.

The condition of the plate (Fig. 7) was obviously one of great frailty, and it had been supposed to be a victim of the tin pest. It proved, in fact, to be nothing of the kind, but merely another example of the metallic



Fig. 7. Hartogs's plate
(Rijksmuseum, Amsterdam)

corrosion of tin alloyed with some copper and lead. Such intercrystalline oxidation can be clearly seen in Fig. 8, where the crystal boundaries are outlined in places by white spots, and the black areas contain dirt and oxide. The photograph of the plate indicates that degradation of the surface to oxide has proceeded to a point where the strain is being released by the oxide layers splitting away from the core. The inscription is largely in the oxide layers which must accordingly be preserved and given mechanical strength. This might be achieved by encasing in plastic—see the coin fragments (Fig. 9)—or by impregnating with a neutral synthetic resin and framing in unplasticised 'perspex.'

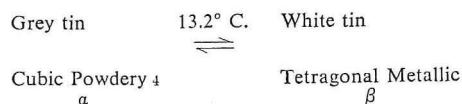
TIN PEST

The cause of tin pest lies in the fact that near a room-temperature of 20° C: tin can exist in either one of two allotropic modifications: either as powdery grey tin of density equal to 5.8466 at 18° C.,² or as tetragonal white tin of density equal to 7.28 at 25° C.³: equilibrium exists at 13.2° C., according to E. Cohen³ who measured the e.m.f. between half-cells of grey tin and white tin, in aqueous solutions

² E. Cohen and J. Olie in *Zeitschrift für physikalische Chemie*, LXXI (1910), p. 385.

³ E. Cohen in the *Transactions of the Faraday Society*, VII (1911), p. 126.

of 'pink salt,' $(\text{NH}_4)_2\text{SnCl}_6$ of the same concentration.



Other workers by other methods have found different values for the equilibrium temperature: thus Cohen and Dekker⁵ by a dilatometric method found a value between 12° and 14.3° C. (probably very nearly 13° C.), and a value of 20° C. has also been given by a much earlier e.m.f. determination.⁶ The currently accepted value due to Cohen is 13.2° C., and there may be many occasions in an unheated museum when a white tin object is below this temperature, so that the shift of equilibrium is towards the grey state, the effect increasing the lower the temperature.

I. Factors affecting the Transformation

The factors affecting the initiation of the change at a temperature below equilibrium are many: most investigators have found it necessary to cool white tin strongly; inoculation with grey tin in the presence of an electrolyte such as aqueous solution of pink-salt hastens initiation. Thus Murphy⁷ cooled his specimens to -78° C. in the absence of both electrolyte and the grey form, and found initiation required 10-11 days in cast unworked tin; Tamman and Dreyer⁸ cooled their specimens to between 0° C. and -20° C. in the presence of both electrolyte and tin. The initiation required 10 days. Cohen and

De Meester⁹ worked their specimens at -80° C. and kept them at -50° C., photographing them hourly, until the α form appeared, but it is not clear from their paper how many hours initiation required. The constitution of the tin is also of importance, most workers having used 'Chempur' or tin of similar (99.98%) purity, but, for example, Murphy⁷ found that 0.2% silver prevented initiation, even after cold working and in the presence of grey tin, for at least 6 weeks at -78° C.

The most important single factor in initiating the change is probably inoculation with α -nuclei; indeed it is suggested that the difficulty found by one laboratory in repeating the later work on α -tin by another laboratory is due to the latter having been 'infected' with particles of grey tin. These may take so long to transform back to white tin at a room-temperature so little above 13.2° C. that they may vitiate subsequent experiments.

The clearest work on the rate of transformation of β to α after initiation has been done by Tamman and Dreyer⁸ who used plates of Kahlbaum-tin and of Banka-tin, 0.6 mm. thick. 'Warts' of grey tin (due to the 25% greater volume of α -tin compared with β -tin) were produced by inoculation under the above-mentioned conditions, and the diameters of six selected 'warts' were measured in a given direction every 20 hours at a temperature of -10° C. \pm 2°. They ascertained that the surface velocity of growth was independent of the thickness of the plate. This velocity was greater than the rate of penetration, which was of the order of 0.2 mm.

⁴ A. J. Bijl and N. H. Kolkmeijer quoted by Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, VII (1927), p. 301. The edge of the unit cube is equal to 6.46 Å.

⁵ E. Cohen and K. D. Dekker in *Zeitschrift für physikalische Chemie*, CXXVII (1927), pp. 178-82. Abstracted in the *Journal of the Institute of Metals*, XXXVIII (1927), p. 383.

⁶ E. Cohen quoted in paper by Tamman and Dreyer (8).

⁷ A. J. Murphy in the *Journal of the Institute of Metals*, XXXV (1926), p. 118.

⁸ G. Tamman and K. L. Dreyer in the *Zeitschrift für anorganische und Allgemeine Chemie*, CXC (1931), pp. 97-108.

⁹ E. Cohen and W. A. T. Cohen de Meester in *Verslag Koninklijke Nederlandsche Akademie von Wetenschappen*; Amsterdam, XC (1938), p. 9; *op. cit.* XCI (1938), p. 5; *op. cit.* XCI (1938), p. 8. (Work done in Van 't Hoff Laboratory, Utrecht.)

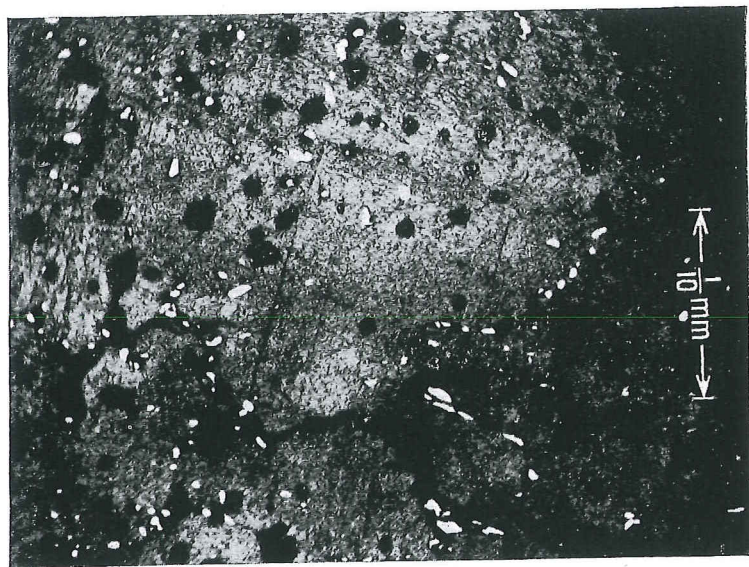


Fig. 8. Micro-section from Hartogs's plate (25 x)

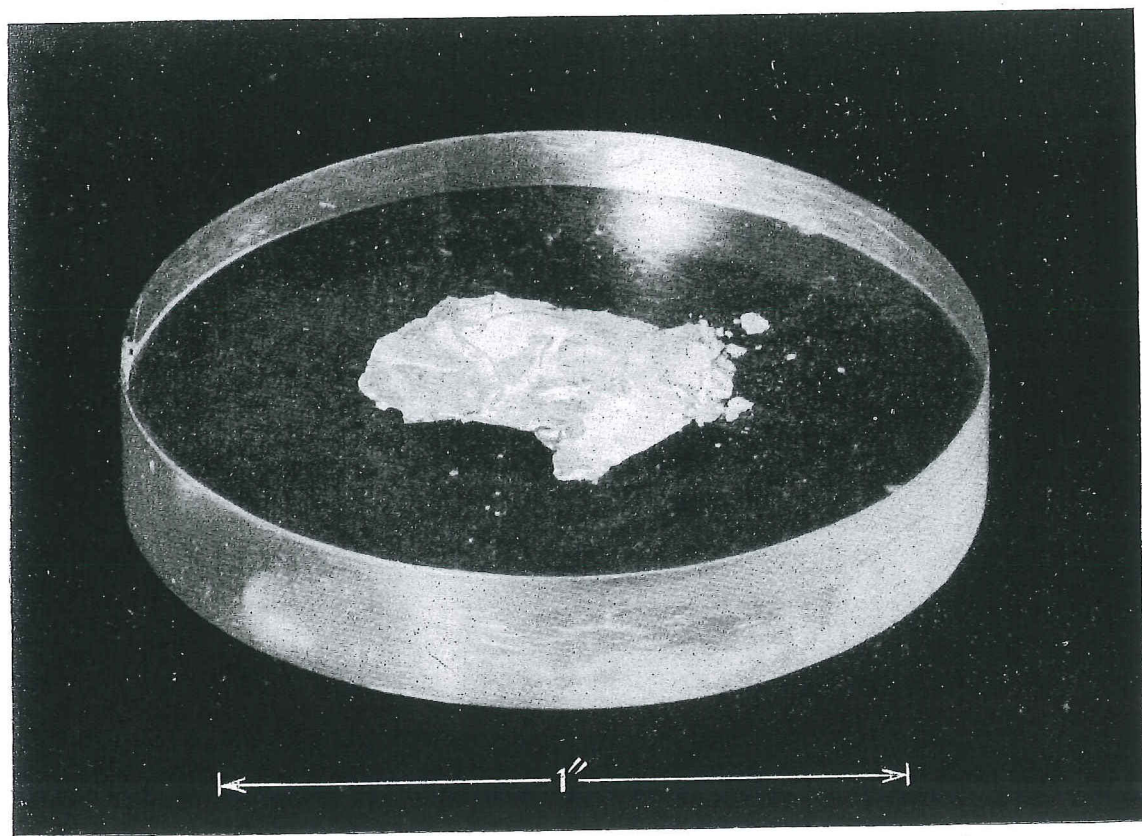


Fig. 9. Fragile pieces of corroded coin embedded, as an experiment, in plastic disc

TABLE II

Temperature	+ 10° ± 2°	+ 8° ± 2°	+ 5° ± 1°	0° ± 1°	- 5° ± 2°	- 10° ± 2°	- 20° ± 2°	- 30° ± 2°	- 40° ± 2°	- 50° ± 2°
Velocity (mm./10 hrs) (a) with pink-salt (b) without pink-salt	.0025	.003	.004	.009	.013	.0195 .013	.0325 .018	.0405	.025	.0015

in several days, and 1.0 mm. in several months.
Table II on page 70 summarises these results.

II. Variation of the Velocity of Transformation $\beta \rightarrow \alpha$ with Change of Temperature

A curve derived from the data contained in the accompanying Table II is shown on p. 71. This indicates a maximum rate of transformation at about -30°C .

III. Variation of the Velocity of Transformation $\beta \rightarrow \alpha$ with Grain Size of Metal

Tamman and Dreyer⁸ showed that the linear velocity of transformation was greatest on tin of small grain size. Hence specimens strongly cold-worked and not subsequently annealed will allow the pest to develop rapidly. Their results are summarised in Table III.

IV. Variation of the Velocity of Transformation $\beta \rightarrow \alpha$ with Composition of the Metal

The results of Tamman and Dreyer given in Table III for grain size show that the addition of cadmium or lead reduces the linear velocity

of transformation to a greater extent than can be explained by the consequential grain refinement. Their results at $-10^\circ \pm 2^\circ$ are summarised in Table IV.

Here bismuth and antimony are shown to be most effective in delaying the transformation. One of these observations is supported by Cohen and De Meester,⁹ who report in their first paper that the presence of small traces of bismuth greatly retards the transformation at -50°C . They also note that of two blocks of Banca-tin in their possession, one containing .004% bismuth had fallen to a grey powder, whereas the other, containing .01% bismuth, was after a longer time still in the metallic form. Mason and Forgeng¹⁰ note the influence of the distribution of alloyed bismuth: "The usual grades of "chemically pure tin" contain .0035% bismuth and exhibit, as cast, a cored structure resembling a eutectoid when etched in 5% nitric acid in absolute ethyl alcohol. Bismuth may be removed by electrolysis in a bath containing $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$

¹⁰ C. W. Mason and W. D. Forgeng in *Metals and Alloys*, vi (1935), pp. 87-90. Abstracted in *British Chemical Abstracts* 1935 B, p. 595.

TABLE III

Grain size (no./sq. mm.)	Pure (Kahlbaum) tin at $-12^\circ \pm 2^\circ$							Sn + 2% Cd $-10^\circ \pm 2^\circ$		Sn + 1% Pb $-10^\circ \pm 2^\circ$	
	50	50	30-50	15-20	5-10	$\frac{1}{2}$ -3	20	90	40	75	25
Temp. of recrystallisation after cold work	10°	50°	100°	150°	150°	200°	200°	10°	200°	10°	200°
Velocity (mm./10 hrs.) (a) not rubbed (b) rubbed with emery-paper	.022 .025	.025	.022 .024	.017 .024	.015	.011 .020	.006	.010	.005	.008	.004

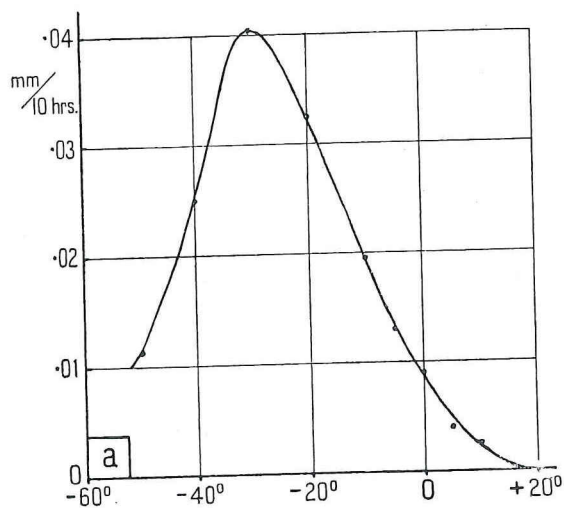
It is noteworthy that the transformation is very rapid in a surface layer of small crystals produced by rubbing. Hence the dusting of tin objects in museums should be of the gentlest if tin pest is considered a possible danger.

TABLE IV

Metal	Velocity (mm./10 hrs.)	
	Tin—Kahlbaum	.0205
Tin—Banka (containing traces Fe, Cu, Sb, Pb)	.0125	.013
Tin—Banka + 1% Pb	.0075	.008
Tin—Banka + 2% Cd	.0095	.010
Tin—Kahlbaum + 0.1% Bi	.002	.002
Tin—Kahlbaum + 0.1% Sb	.001	.0015

(250 gm.), nitric acid (d 1.42; 10 ml.) and water (990 ml.). The transformation into grey tin occurs readily in the purified tin and in cored metal but not in tin containing bismuth evenly distributed by annealing.

Cohen and De Meester also found that traces of aluminium (of the order of 0.25%



Curve derived from Table II.

melted with tin¹¹ *in vacuo*)⁹ accelerate the transformation which occurred in 24 hours at -50° C. In their second paper they showed that this 'does not occur when special precautions are taken to prevent access of traces of water (drying over phosphorous pentoxide). The acceleration observed under ordinary conditions is due to deformation of the tin lattice by reaction of the alloy with water.' In their third paper they state that 'extremely small amounts (.01%) of magnesium added to purest tin produce acute tin

plague, i.e. greatly accelerate the rate of transformation.' Murphy⁷ observed that solid solutions of antimony, cadmium and bismuth in tin show no transformation in the presence of α -tin and absence of electrolyte after 3-4 weeks at -78° C. J. W. Price¹² has noted the presence of traces of arsenic, antimony, lead and bismuth in refined tin and removal of these may render initiation of the transformation easier.¹³

To summarise the factors affecting the progression of the pest, they may be listed as: period and degree of temperature below equilibrium compared with these conditions above equilibrium temperature; presence of the grey form; presence of an electrolyte; previous history of cold-work and annealing; care in storage; and finally the purity of the metal.

Phenomena other than chemical attack which might possibly be confused with tin pest have been observed. Thiel¹⁴ records that tin falls into a powder composed of small crystals if left standing in a solution of stannous chloride partially oxidised to stannic acid. This is probably due to intercrystalline attack. Von Hasslinger¹⁵ mentions that bright tin foil assumes a dull appearance in contact with dull tin at ordinary temperatures (and more rapidly at higher temperatures). He states that this is because the tin foil is polished by cold-work, resulting in crystalline deformation (Beilby

¹¹ Both metals were of Hilges and Watt H.S. quality.

¹² J. W. Price in *Nature*, CLXIX (1952), p. 792.

¹³ E. S. Hedges and J. Y. Higgs in *Nature*, CLXIX (1952), p. 621.

¹⁴ A. Thiel in *Berichte der deutschen chemischen Gesellschaft*, LIV (1921), p. B2755.

layer); contact with normally crystalline (dull) tin initiates the recrystallisation of this layer, a process proceeding faster at higher temperatures. The recrystallised layer lacks polish. Yet another plausible explanation would be that the thin oxide layer which is normally present would develop rapidly on the bright tin by electro-chemical action in the presence of moisture.

The possibility of restoring an infected object depends upon what stage the process has reached. The damage is due to each 'wart' taking on a pyramidal shape owing to the 25% increase in volume on transformation. It is possible that the original volume can be re-established by heating for a sufficient time to a temperature above the transition point, provided that serious oxidation has not already occurred. Tamman and Dreyer have observed that the grey warts become white in boiling water, but the white tin will probably remain in powder form owing to the oxide coating upon each particle. Unless this oxide coating can be reduced and the particles

somehow be sintered together into their original position, the possibility of the restoration of a truly infected tin object seems slight.

At the same time it should be emphasised that the occurrence of true tin pest is a rarity both in Europe and U.S.A.: the literature indicates how difficult it has been found to initiate the transformation, and of the many cases of so-called tin pest reported to the Tin Research Institute, the overwhelming majority have been clearly cases of ordinary corrosion. It has not, in fact, been found possible to obtain a single illustration known with certainty to represent authentic tin pest of natural occurrence.

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.

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LE PROCESSUS DE DESTRUCTION ET LES MÉTHODES DE CONSERVATION DES ÉTAINS DE MUSÉES

Sommaire

On fait une distinction entre la désintégration des objets en étain due à une action chimique et celle due à la transformation allotropique connue sur le nom d'étain gris ou peste de l'étain. On se rapporte à l'assiette d'Hartog et aux pièces de monnaie malaise en forme de casque. Sur les titres « cause » et « facteurs influant la transformation » on rend compte de ce qui a été écrit sur l'étain gris. On con-

clut enfin que dans un laboratoire de musée il est possible de réduire tous les cas de corrosion d'étain par la méthode électro-chimique usuelle. Ceci est confirmé par le fait qu'il est impossible d'obtenir une seule photographie de la véritable peste de l'étain de l'événement naturel.

H. J. P.
R. M. O.

¹⁵ R. von Hasslinger in *Sitzungsberichte der kaiserlichen Akademie der Wissenschaft in Wien*, cxvii (1908), p. 501.

Note: M. Tschertok. *Technical Physics U.S.S.R.*, II (1935), pp. 591-7. Abstracted by *British Chemical Abstracts* 1938 B, p. 1432 as follows: Temp. (-10° C. -76° C.), grain size and plastic deformation affect the transition in mono- and poly-crystalline plates. The linear speed of transition is a maxm. at -30° C.; it increases with decreasing grain dia. < 1 mm. The nature and accelerated growth of α nuclei caused by plastic

deformation are described, with photomicrographs, and these confirm theory.

A. Komar and B. G. Lasarev, *Journal of Physical Chemistry U.S.S.R.*, VII (1935), pp. 468-73. Abstracted by *British Chemical Abstracts* 1935 B as follows: Method is given for the electrolytic infection of white tin by grey tin. The linear velocities of transformation have been investigated from 18° to -80° and are 200 times recorded values. The dependence of the velocity on supercooling and pressure are discussed.