LXIV.—*The Ageing of Alloys of Silver and Tin.*

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THIS communication deals with the ageing of filings* of alloys of silver and tin, and with the densities of unaged and aged filings of the alloy Ag_3Sn .

One of the first suggestions with regard to ageing was that it was due to superficial oxidation, and it must be admitted that this hypothesis is simple and attractive. Further than this, it is a

* In the experiments to be described all filings were obtained by means of files of the same degree of coarseness, and were freed from iron by means of a magnet. The bars of alloy were always filed slowly and were cooled in running water every ten seconds. All amalgams were prepared, and the excess of mercury was squeezed out exactly as described in a previous communication (T., 1911, 99, 198), and the ratio Hg :alloy should be taken to indicate

$$\frac{\text{Weight of mercury retained by the filings}}{\text{Weight of filings of alloy taken}}.$$

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matter of extreme difficulty—if indeed it is not impossible—to prove directly that superficial oxidation does not take place during the ageing of these alloys, and the hypothesis had not been abandoned here until investigations in this laboratory seemed to render it untenable (R. A. Joyner, T., 1911, **99**, 198; Knight and Joyner, T., 1913, **103**, 2247).

A. Further Experiments on the Ageing of Filings of Alloys of Silver and Tin.

(1) Is the ageing of filings of an alloy accompanied by a change in weight?

The alloy chosen was Ag_3Sn , as with this the effect of ageing is most pronounced, and the ageing was carried out by heating the filings to 100° in a current of coal-gas. In the two experiments carried out it was found that no change of weight greater than 0.0001 gram took place even after heating for one hour, and it was shown that replacing the current of coal-gas by a current of air was also without effect. The possible change of weight in these experiments was not greater than 0.002 per cent. of the weight of alloy taken.*

(2) Attempts to oxidise filings of the alloy Ag_3Sn at room temperature.

Three experiments were carried out for the purpose of determining whether ozone, dry or moist, had any effect on these filings. It was found that the value of the ratio Hg:alloy was not affected by this treatment, the actual values of this ratio in the three cases being:

$$(1) \text{Hg:alloy} = 7.178:3.525 = 2.04:1.$$

$$(2) \text{Hg:alloy} = 5.263:2.523 = 2.08:1.$$

$$(3) \text{Hg:alloy} = 6.157:3.062 = 2.01:1.$$

Hence the filings were unaged by ozone, and, in addition, no change in weight was detected.

Further, no change in the colour of the filings could be noticed, although it was found that moist ozone, under these same conditions, blackened silver almost instantaneously.

A concentrated solution of hydrogen peroxide to which a few

* From the point of view of the kinetic theory, 0.0001 gram of oxygen would actually have covered all the filings about 1 molecule deep, since their diameter was from 0.02 to 0.03 mm. In the form of oxide, on the other hand, only about one-third of the surface would have been covered, and it has been shown that characteristic physical properties are not exhibited until such a layer is many molecules thick (see, for instance, Oberbeck, *Ann. Phys. Chem.*, 1887, [iii], **31**, 336).

drops of sulphuric acid had been added had no effect on the ageing of these filings, as it was afterwards found that:

$$\text{Hg: alloy} = 4.788 : 2.289 = 2.09 : 1.$$

If filings of the alloy Ag_3Sn at room temperature are so resistant to the action of energetic oxidising agents like ozone and hydrogen peroxide, it is difficult to believe that they should become oxidised in coal-gas, in hydrogen, or in an exhausted vessel at 100° .

Further, if the ageing of these alloys is due to superficial oxidation, it is reasonable to suppose that the effect would be most pronounced in the case of the metal which oxidises most readily. Yet pure tin does not age (T., 1911, 99, 201).

To sum up the evidence unfavourable to the explanation of ageing as being due to superficial oxidation: ageing is not accompanied by a change in weight, although (see below) it is accompanied by a change in density; it takes place alike on heating the filings in hydrogen, in coal-gas, or in a vacuum; it is not induced by ozone, moist ozone, hydrogen peroxide, or hydrogen sulphide (see below) at room temperature; it is not prevented by the presence of magnesium in the alloy; grinding in an agate mortar neither ages unaged filings nor renders aged filings unaged. It may be impossible directly to disprove such a hypothesis, but it is evidently untenable.

Since bars of these alloys definitely do not age, the hypothesis (d) (T., 1911, 99, 203) will receive further experimental examination.

(3) What is the effect of hydrogen sulphide on filings of the alloy Ag_3Sn ?

Dry hydrogen sulphide appeared to have no action on the filings, and the undried gas also seemed to be without effect, so a quantity of the filings of known weight was moistened with water and exposed to the action of the gas for thirty minutes. After drying the filings over phosphoric oxide at room temperature, the weight was re-determined. The results were as follows:

The weight before treatment was 2.7454 grams, and after treatment was 2.7455 grams. It seems possible that the slight increase in weight (if any) may be due to a small amount of sulphur introduced by decomposition of the hydrogen sulphide by the water present.

Further, it was found that

$$\text{Hg: alloy} = 5.331 : 2.730 = 1.95 : 1,$$

and, therefore, the filings had remained unaged.

At 100° it was found that a pronounced change of colour occurred on exposing filings of the alloy Ag_3Sn to the action of hydrogen sulphide. Filings aged in air or in coal-gas are grey, those

aged in hydrogen sulphide are brownish-black. This shows that the ordinary phenomenon of ageing is not due to any small amount of hydrogen sulphide present in the gas (air, hydrogen, coal-gas, or vacuum) in which the filings are aged.

(4) What is the effect on the ageing of dental alloys of the presence of solid solutions of silver in the alloy Ag_3Sn ?

Alloys containing less than 75 atoms per cent. of silver, if well annealed, contain only the compound Ag_3Sn and free tin (Petrenko, *Zeitsch. anorg. Chem.*, 1907, **53**, 200; and also Joyner, *loc. cit.*), and Joyner has shown that for these alloys the phenomenon of ageing is roughly proportional to the amount of Ag_3Sn present, and vanishes entirely for pure tin.

It seemed desirable, therefore, to determine the effect on the ageing of an alloy of the presence of solid solutions of silver in the compound Ag_3Sn .

For this purpose the value of the ratio Hg:alloy was determined for filings (unaged and aged) of an alloy containing 85 atoms per cent. of silver.

The following values were found:

<i>Unaged:</i>	Hg:alloy=1.99:1
<i>Aged:</i>	(1) Hg:alloy=1.57:1
	(2) Hg:alloy=1.68:1

Hence the effect of the presence of solid solutions of silver in the compound Ag_3Sn is to make the difference between the mercury retained by aged and unaged filings less pronounced, corresponding with the influence of the free tin in those alloys which contain less than 75 atoms per cent. of silver.

It was noticed that the amalgams resulting from the alloy containing 85 atoms per cent. of silver were quite soft and would nearly flow, although the excess of mercury had been squeezed out exactly as in previous experiments. After three and a-half hours the mass had become quite hard, although the edges could still be rubbed off with the fingers.

For pure silver it was found that $\text{Hg:Ag}=1.26:1$, but it was obvious that the filings retained, mechanically, a considerable quantity of mercury, which could not be squeezed out through chamois leather.

The resulting amalgams were so fluid that they would readily flow on the hand, yet when squeezed they seemed to become harder, and appeared to take up more of the adhering mercury. Their behaviour in this respect was exactly similar to that of moist sand. When left overnight these amalgams became quite hard and dry.

(5) Can ageing be due to catalytic action of the iron or products

of iron introduced during the filing (compare Knight and Joyner, *loc. cit.*, p. 2250)?

A bar of the alloy Ag_3Sn was heated in an atmosphere of coal-gas to 418° for six hours, and then to 300° for a further thirty-six hours, in order to obtain a loose crystalline structure. The bar was then wrapped in chamois leather, and broken into several pieces. One of these pieces was placed between two silver plates, wrapped up in chamois leather, and was beaten up quite fine. The small particles thus obtained were ground up in an agate mortar, and the value of the ratio Hg:alloy was determined for unaged and aged particles.

The values found were:

Unaged: Hg:alloy = 1.90 : 1

Aged: (1) Hg:alloy = 0.63 : 1

(2) Hg:alloy = 0.61 : 1

These values show that particles obtained in this way, which had not been in contact with iron, age as do filings. Hence, the hypothesis that ageing is due to catalytic action of the iron introduced during the filing is untenable.

(6) Time required for the ageing of the alloy Ag_3Sn .

Separate lots of filings of the alloy were heated at 100° in coal-gas for five, ten, twenty minutes, and the corresponding values of the ratio Hg:alloy were determined. The values are given below:

Time of heating	0	5	10	20	40	80	320 min.
Ratio Hg: alloy	2.15	1.33	1.21	1.14	1.08	1.12	1.12

Hence, the alloy is completely aged in twenty minutes at 100° , the last three values above differing from the value after twenty minutes by less than the experimental error.

B. Density at 25° of Filings of the Alloy Ag_3Sn , and Contraction in Volume on Ageing.

The densities of unaged and of aged filings of this alloy were determined in the usual way by means of the specific gravity bottle. All the water used in the determinations was air-free distilled water, and efforts were made to free the filings from the air adhering to them before filling the specific gravity bottle with water for the final weighing. The values obtained were as follows:

Unaged Filings.

	Weight of filings taken. Grams.	D_{40}^{25} .
(1)	7.8029	9.78
(2)	10.3473	9.79
(3)	16.9216	9.85

The values (1) and (2) were obtained for filings of the same sample of alloy, whilst (3) was obtained from a different (much coarser) sample. Fenchel (*Dental Cosmos*, January, 1910) found that the specific volume of the alloy Ag_3Sn was 0.102 (temperature not stated), giving a density of 9.80.

Aged Filings.

	Weight of filings taken. Grams.	D_4^{25} .
(1)	7.8029	9.89
(2)	11.6688	9.88
(3)	27.5410	9.86
(4)	16.5507	9.93

In the first of these determinations for aged filings the ageing was carried out under water in the specific gravity bottle. In the other cases the ageing was carried out in coal-gas. The last value, 9.93, was obtained from filings of the same sample of alloy as was used in obtaining the last value, 9.85, for the density of unaged filings.

The above results show that the ageing of filings of the alloy Ag_3Sn is accompanied by an increase in density, and, as it has already been proved that there is no detectable increase in weight, it follows that there must be a contraction in volume.

Dilatometer measurements showed that this is the case, although the results did not agree well amongst themselves or with those indicated by the density determinations. The indicating liquid in the first of the dilatometer measurements was paraffin oil, in the other cases, xylene was used for this purpose. The ageing of the filings was carried out in the dilatometer, and in each case, after the alloy had been aged, the dilatometer was left for twenty-four hours at 25° in order to recover its original volume, a blank experiment having shown that eighteen hours was sufficient. The contraction in volume of the alloy was found by weighing the amount of mercury which could be contained between two marks on the capillary of the dilatometer—the upper mark showing the level of the indicating liquid at 25° before the alloy was aged, and the lower mark showing the corresponding level after the alloy had been aged. The results were as follows:

Weight of filings in the dilatometer. Grams.	Contraction (as a percentage of the original volume).
6.70	0.88
4.742	0.45
25.620	0.30
26.952	0.37

Summary.

1. The ageing of filings of alloys of silver and tin, whether in coal-gas or in air, is not accompanied by a change of weight, but there is a contraction in volume amounting to about 0·4 per cent.

2. The evidence now accumulated appears to render untenable any explanation of ageing as being due to superficial oxidation of the filings.

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