

## MICROGRAVIMETRIC INVESTIGATION OF THE PREPARATION OF TETRAETHYL LEAD FROM LEAD–SODIUM ALLOY AND ETHYL CHLORIDE \*

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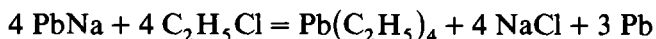
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### ABSTRACT

The apparatus used includes a vacuum microbalance according to Gast and a means to place the oxygen-sensitive sample into the vacuum apparatus. The sorption of ethyl chloride vapor on lead–sodium alloy as a function of pressure was measured. After an induction period due to corrosive surface layers, an autocatalytic process with increasing reaction rate takes place.

### INTRODUCTION

Tetraethyl lead is prepared from lead–sodium alloy and ethyl chloride according to the equation



The reaction rate depends upon the conditions under which the PbNa alloy has been prepared. Model investigations reported in the literature [1,2] showed contradictory results with respect to the reaction rate and the shape of the reaction curve for samples of different origin or differently pretreated samples. Thus, knowledge of the reaction mechanism of the technical process is still insufficient.

### MATERIALS

Various samples of NaPb (Ellesmere-Port and Northwich Alloy) of “Flake” and “Cast” type were supplied by the Associated Octel Company in the form of 0.5 mm particles or bars. These materials were investigated either

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as delivered or pretreated as described later to obtain a freshly prepared, corrosion-free surface.

As PbNa alloys react rapidly with oxygen [8–10] and water [5], the samples under investigation had to be protected by storing them under vacuum or under a protecting gas. A vacuum better than  $10^{-5}$  Pa was produced by means of diffusion pumps with nitrogen-cooled traps. Research-grade nitrogen was predried with Na zeolite and traces of oxygen were removed using BTS copper catalyst (BASF, Ludwigshafen) to achieve a concentration below 1 p.p.m. Subsequently, a cold trap supplied with liquid oxygen and columns filled with KNa were arranged for final gas cleaning.

Ethyl chloride, which had previously been dried with Na zeolite, was distilled at a column temperature of 287 K, the distillate being frozen with dry ice and degassed in vacuum by repeated heating and cooling. A cryostat permitted the ethyl chloride to be thermostatted at temperatures between 193 and 263 K, corresponding to vapor pressures between 660 and  $10^5$  Pa.

## EXPERIMENTAL PROCEDURE AND RESULTS

### *X-Ray diffraction*

For X-ray examination, each sample was ground within the nitrogen-filled preparation box in an agate mortar under dehydrated paraffin oil. The mixture was transfused into a small pyrex tube and investigated by means of a Debye–Scherrer camera with Ni-filtered  $\text{Cu}K_{\alpha}$  radiation.

Thorough investigations showed a fine-crystalline structure of crystals having diameters larger than  $0.1 \mu\text{m}$ . Within the margin of error, the lattice constants of the various samples, cast and flake, were identical. In some cases line broadening was observed, which we attributed to corrosion layers. In all samples small amounts of the  $\beta$ -phase of  $\text{Na}_2\text{Pb}_5$  were observed.

### *Light microscopy*

Because of the high sensitivity of PbNa to the atmosphere, a special metallographic technique had to be developed [5]. In a high-vacuum apparatus, the sample was embedded in polystyrene, and the PbNa surface to be investigated was covered with wax. Then the wax and thicker corrosion layers were removed using a file. Subsequently, the surface was polished under vacuum using various polishing agents and powders. Micrographs were made with a Leitz metallurgical stereomicroscope mounted outside the glass vacuum vessel. The apparatus is shown in Fig. 1.

Typical micrographs are shown in Fig. 2. The surface exhibits numerous spots interconnected by straight lines. These connecting lines constitute grain boundaries with spaces below  $100 \mu\text{m}$ .

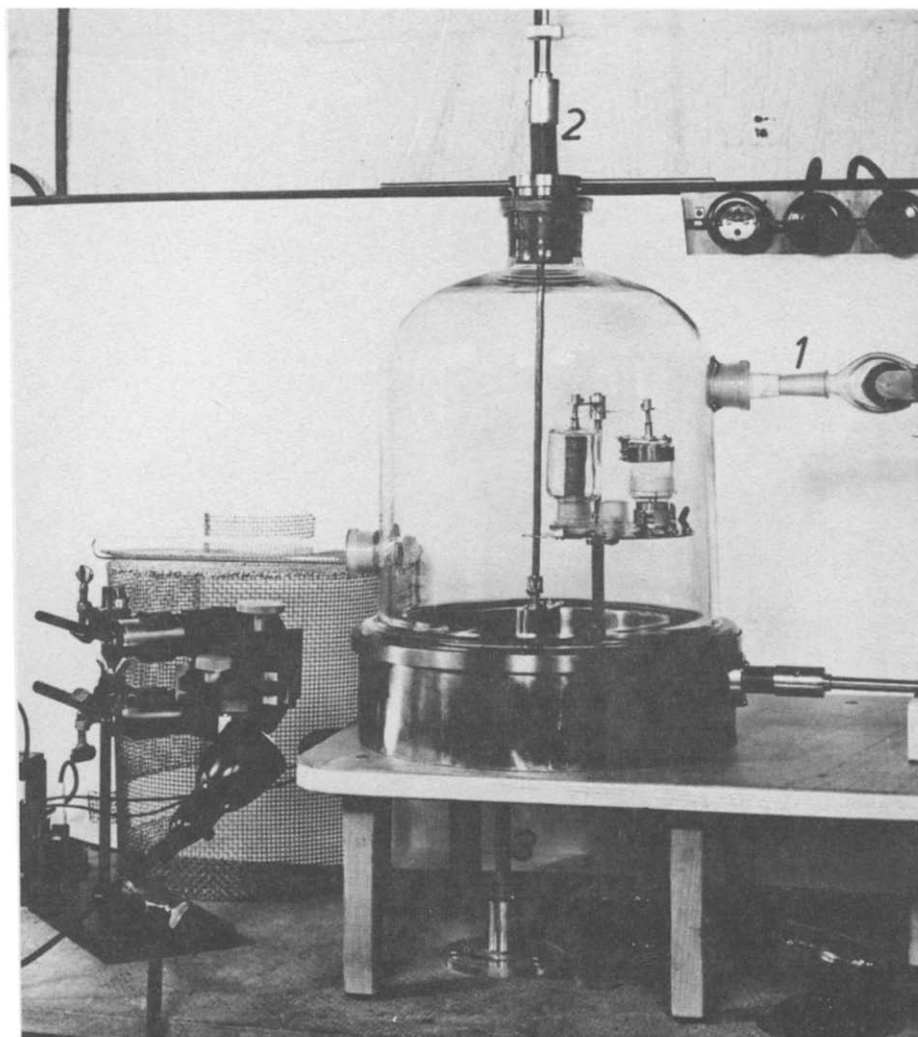


Fig. 1. Vacuum apparatus for polishing and light-microscopic investigation of PbNa samples. 1, Ionization vacuum gauge; 2, manipulator; 3, motor drive for the polishing plate; 4, vacuum line; 5, stereomicroscope.

### *Electron microscopy*

For electron microscopy we used a Siemens transmission microscope. The samples were prepared as described. A  $\sim 1$  mm thick film of polystyrene which had been degassed in a vacuum was brought to swell in the nitrogen box with water-free chloroform. Thereupon, pieces of PbNa were at once pressed into the film. After hardening, the film with the adhering PbNa was removed from the box and the alloy was washed off with diluted HCl. Then, in a high vacuum, the washed film was shadowed with tungsten oxide and,

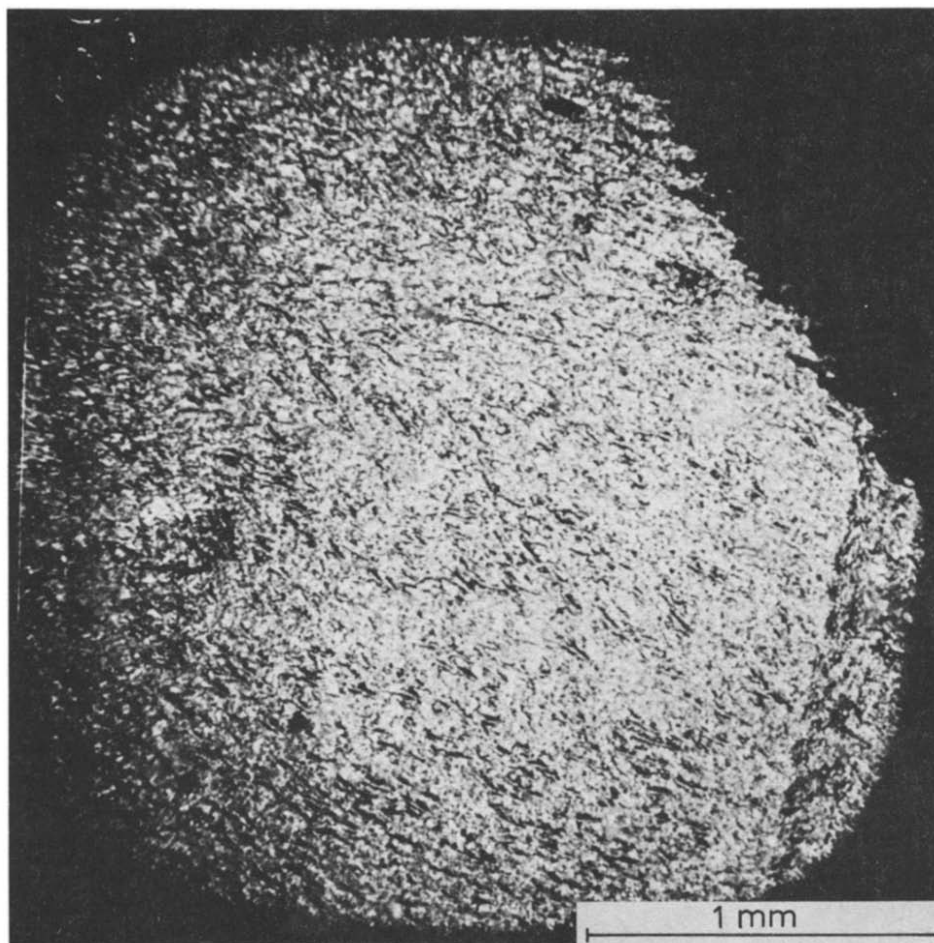


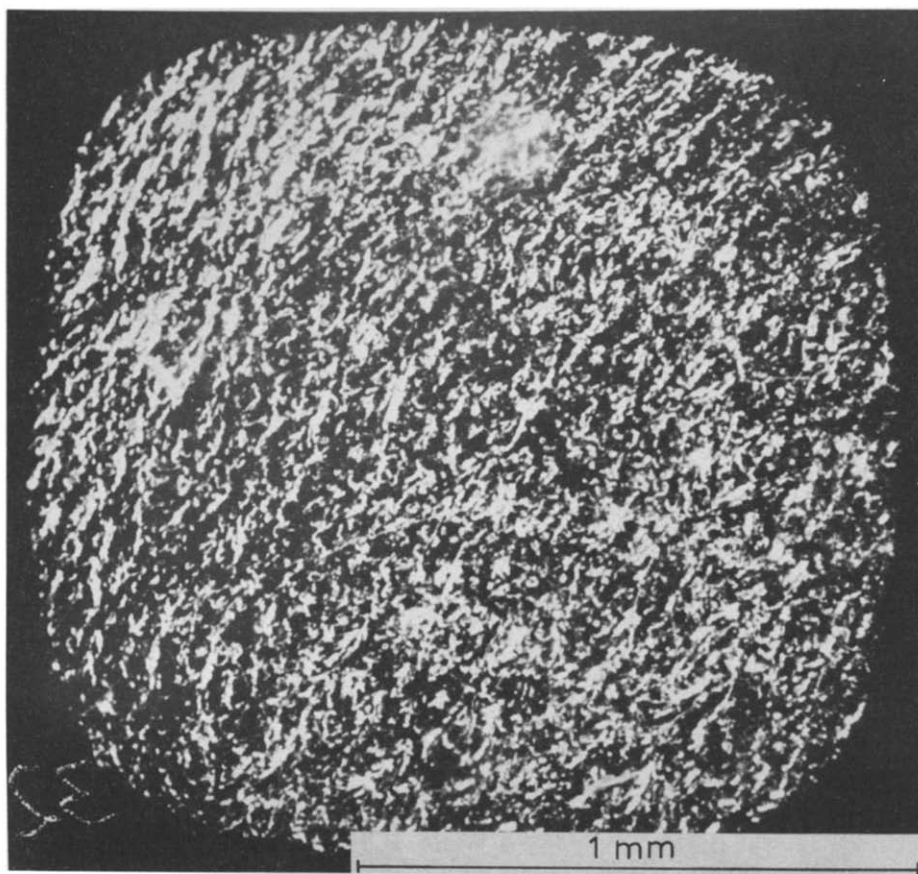
Fig. 2. Polished surface of PbNa samples.

thereupon, covered with carbon by evaporation. After the polystyrene had been dissolved in an organic solvent, the shadowed carbon film was examined using the electron microscope [3].

We observed grains of about  $1\ \mu\text{m}$  in diameter. In the case of the cast alloy, boundary layers of approximately  $0.1\ \mu\text{m}$  thickness, constituting a metallic phase different from the bulk phase, were detected (Figs. 3 and 4).

#### *Adsorption measurements with nitrogen*

In order to determine the specific surface area according to Brunauer, Emmett and Teller (BET) [4,5], a microgravimetric apparatus as schematically represented in fig. 5 was used. It comprised an electromagnetic microbalance according to Gast [6] (manufacturer: Sartorius, Göttingen, FRG), a rotary vane pump, a pressure vessel and a diffusion pump with nitrogen cold trap [7].



For the test, approximately 1 g of the PbNa sample was placed under water-free xylene into the weighing glass. The weighing glass had been attached to the balance, the vessel was closed by a glass tube and the xylene evaporated in vacuum. Then the vessel was filled with pure nitrogen and opened at the counterweight side in order to adjust the balance. To avoid buoyancy, the counterweight was made of a mixture of gold and quartz of the same density as the sample. Then the balance was evacuated again, and sample and counterweight were cooled down by means of liquid nitrogen in Dewar vessels placed around the balance tubes. Subsequently, nitrogen gas, which had been purified by KNa alloy in wash bottles, was fed in, and the isotherm at stepwise increasing pressure was recorded.

In such adsorption measurements, an adsorbed amount of 10 micromole ( $= 280 \mu\text{g N}_2$ ) corresponds to a surface of  $1 \text{ m}^2$ . At a pressure (about  $1.2 \times 10^4 \text{ Pa}$ ) corresponding to the monomolecular cover, a weight increase of  $1.5 \mu\text{g}$  was recorded. If the  $1.5 \mu\text{g}$  could be attributed to adsorbed  $\text{N}_2$ , the



Fig. 3. PbNa flake alloy with grain boundary.

sample would have had an inner surface of  $50 \text{ cm}^2$ . However, if one considers the buoyancy caused by the thermal contraction of the PbNa, the result is that the specific inner surface of the sample will be less than  $30 \text{ cm}^2 \text{ g}^{-1}$ , probably equal to the size of the geometric projection area.



*Adsorption measurements with ethyl chloride*

For the measurement of the reaction rate with ethyl chloride, a modified balance was used, where the diamond pins and sapphire cups supporting the suspension parts were clamped to the suspension frames in order to avoid





Fig. 4. PbNa cast alloy with the grain boundary filled with a separate phase of NaPb-Na<sub>2</sub>Pb<sub>5</sub> eutectic.

gluing. Furthermore, the beam coil was made of wires coated and pasted on with polytetrafluoroethylene lacquer. As it was observed that small amounts (up to 10 μm) of ethyl chloride were dissolved by the lacquer, the results of



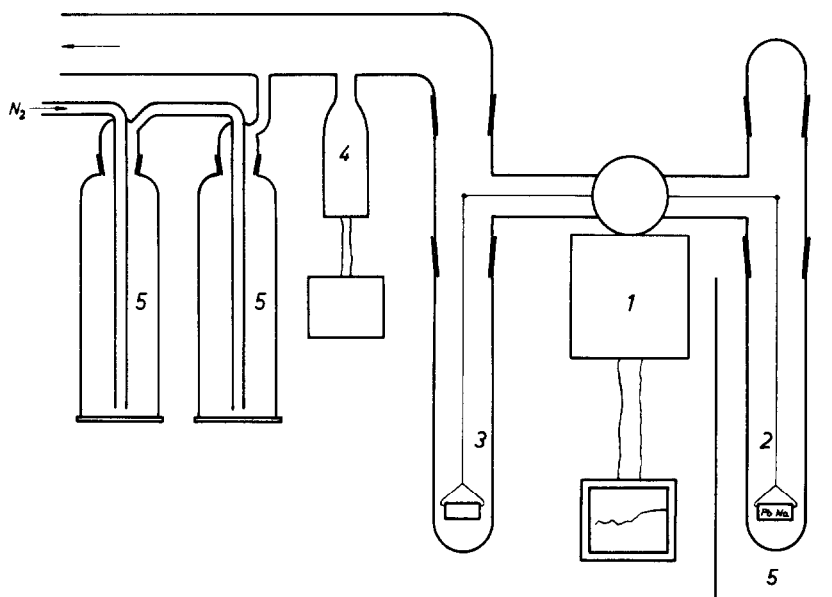


Fig. 5. Microgravimetric apparatus for recording nitrogen isotherms. 1, Electronic balance after Gast; 2, sample; 3, counterweight; 4, ionization gauge; 5, wash bottles filled with KNa.

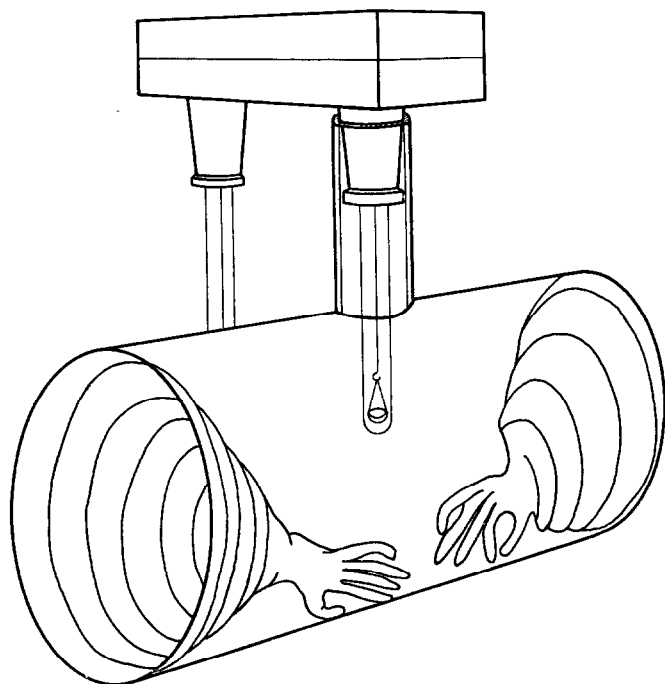


Fig. 6. Vacuum microbalance with glove box.

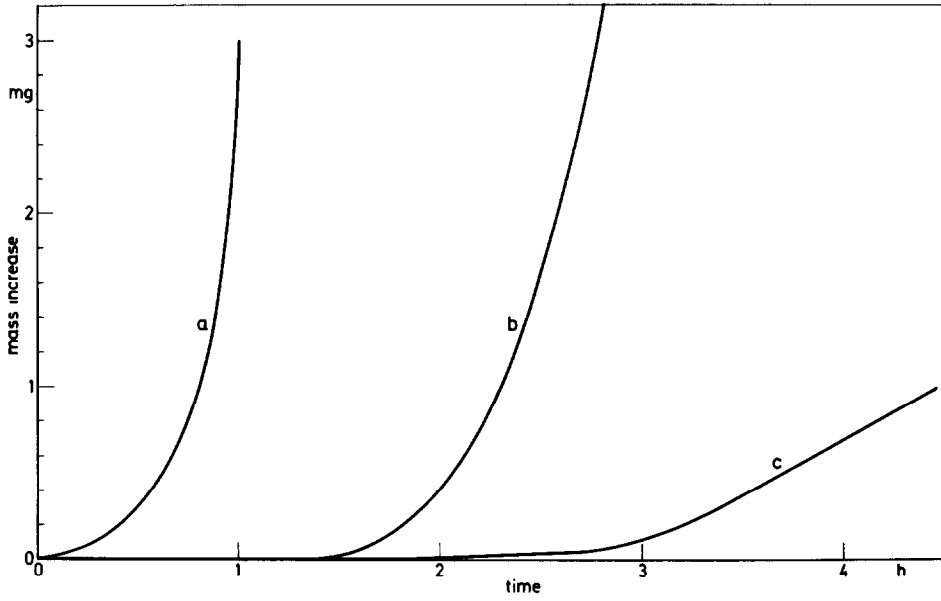


Fig. 7. Reaction of  $7 \times 10^4$  Pa ethyl chloride with PbNa alloy at 363 K. a, Flake alloy; b, cast alloy; c, highly corroded sample of cast alloy.

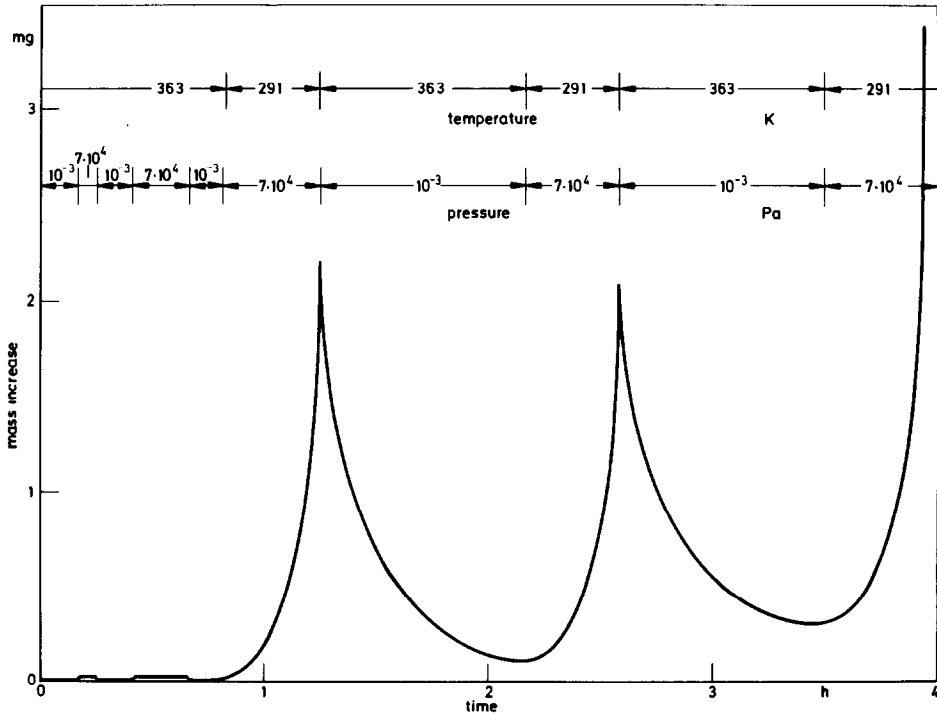


Fig. 8. Repeated adsorption and desorption of ethyl chloride by PbNa cast alloy.

the measurements were corrected accordingly. To be able to treat the surface of the sample immediately before the experiment, the balance was equipped with a glove box, i.e. a plexiglass tube of 400 mm length and 200 mm diameter which could be evacuated or filled with protecting gas via the balance (Fig. 6).

Using this apparatus, the samples could be placed into the weighing glasses under protecting gas. Subsequently, the balance was closed with a glass tube and, in case a thermostat had been arranged, the glove box was removed.

Typical results are shown in Figs. 7 and 8. Whereas in the case of the flake-type alloy the reaction started immediately, with the rate increasing exponentially, the reaction was inhibited in the case of the cast alloy. When the ethyl chloride was pumped off after the reaction had started and reintroduced, this inhibition effect disappeared (Fig. 8). Some samples covered with a thick corrosion layer due to contact with air showed a linear increase in mass after strong initial inhibition (Fig. 7).

## CONCLUSIONS

In the literature [1,2] different reaction rates are reported. Typical rate curves are compiled in Fig. 9 [5]. Our observations correspond to shape e

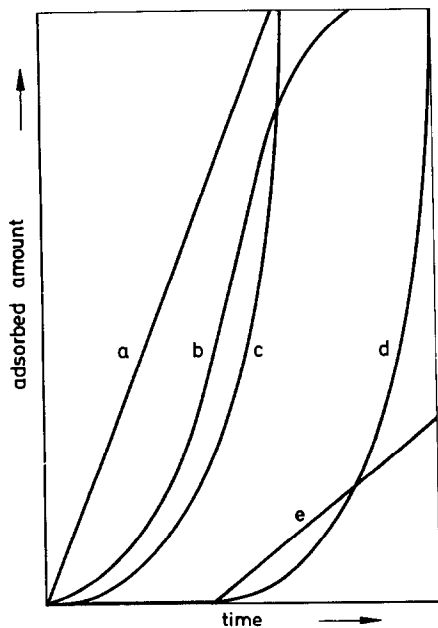


Fig. 9. Reaction curves for PbNa with ethyl chloride [5]. a, Reaction with corroded surface; b, reaction with sample of limited area; c, autocatalytic reaction; d, inhibited autocatalytic reaction; e, inhibited reaction with corroded surface.

with strong inhibition in the case of the highly corroded alloy. Therefore, in practice, corrosion has to be avoided in the preparation of tetraethyl lead. For the flake alloy we observed curve c, and for the cast alloy curve d, i.e. with a delayed start of the reaction.

Since the X-ray investigations did not reveal any differences in the crystal structure of cast and flake alloys, the inhibition effect must have other causes. Another possible cause, a porous structure of the material, can also be excluded, as adsorption measurements gave no indication of an internal surface. The differences in behavior are very probably due to the metallic phase of  $\text{Na}_2\text{Pb}_5$  in the grain boundaries as detected by electron microscopy.

Only the alloy NaPb reacts with ethyl chloride. From the results of the X-ray investigations it may be concluded that the boundary layer consists of the eutectic NaPb– $\text{Na}_2\text{Pb}_5$  with an  $\text{Na}_2\text{Pb}_5$  content of 93%. Such a grain boundary layer will at least strongly inhibit the reaction.

#### ACKNOWLEDGEMENT

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#### REFERENCES

- 1 F. Spausta, *Treibstoffe für Verbrennungsmotoren*, Vol. 2, Springer, Vienna, 2nd edn., 1953.
- 2 V.A. Susunov, *Zh. Fiz. Khim.*, 27 (1953) 830.
- 3 G. Schimmel, *Elektronenmikroskopische Methodik*, Springer, Berlin, 1969.
- 4 S. Brunauer, P.H. Emmett and E. Teller, *J. Am. Chem. Soc.*, 60 (1938) 309.
- 5 R.S. Mikhail and E. Robens, *Microstructure of Solid Surfaces*, Wiley, Chichester, 1983.
- 6 T. Gast, *Vak. Tech.*, 14 (1965) 41.
- 7 E. Robens, in A.W. Czanderna and S.P. Wolsky (Eds.), *Microweighing in Vacuum and Controlled Environments*, Elsevier, Amsterdam, 1980.
- 8 G.P. Smith, M.E. Steidlitz and L.L. Hall, *J. Am. Chem. Soc.*, 77 (1955) 4533.
- 9 Z. Maslanka-Ormanova, *Pr. Inst. Hutn.*, 6 (1954) 305.
- 10 H. Bitterer (Ed.), *Gmelins Handbuch der Anorganischen Chemie, Blei, Part C3*, Verlag Chemie, Weinheim, 8th edn., 1970.