

LEAD-ACID BATTERIES WITH LOW ANTIMONY ALLOYS*

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Summary

A report is given on lead alloys which contain between 1 and 4% antimony and which are characterized by the addition of selenium. Using the selenium additive a very fine grain structure is achieved which improves castability and grid-quality to a great extent. The tendency to coarse dendritic solidification which gives rise to hot cracks and brittleness of the castings and usually occurs when alloys with low antimony content are used is not observed with these alloys. With the help of further additives and the application of fast cooling methods the necessary mechanical strength for further handling of the grids can be achieved.

The better grid quality combined with the low antimony content improves the corrosion resistance especially when long time overcharge is applied, and as a result the antimony poisoning of the negative electrode is decreased. Therefore such fine grain alloys are specially suited for maintenance-free batteries.

Some test results for both automotive and industrial batteries are shown, which confirm that by using these alloys water consumption can be reduced to a satisfactory degree without losing the advantages of antimony alloys in respect to the electrochemical behaviour of the cell.

Introduction

The grids of lead-acid batteries are usually made of lead-antimony alloys containing 5 - 11 wt.% antimony. The necessary mechanical strength and castability are easily achieved with this content of antimony. However, the unavoidable corrosion of the positive grid liberates antimony out of the grid which acts in two different ways in the battery: on the one hand, antimony stabilizes the active material of the positive electrode.

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The cycle life of the battery is increased and passivation effects are not observed when alloys with a high antimony content are used for positive grids. On the other hand, antimony migrates to the negative plate where it is precipitated and reduces the hydrogen overvoltage. This leads to lower charge voltage, increased self-discharge and therefore increased water loss of the battery.

The present report deals with the development of low antimony alloys, which reduce the said drawbacks of antimony almost completely without losing most of its advantages. Besides mechanical strength and castability the electrochemical behaviour of such alloys will also be discussed.

Mechanical strength

According to our experience, the mechanical properties required for battery-grids are given in Table 1. The necessary mechanical strength of cast lead-antimony grids can be achieved by means of (a) homogeneous or heterogeneous alloying (natural hardness), or (b) age-hardening.

TABLE 1
Required mechanical properties

Automotive grid	Brinell hardness, HB (15.625/2.5 - 30)	15 - 17	kg/mm ²
	Tensile strength, σ_B	5 - 7	kg/mm ²
	Elongation, δ_B	≥ 3	%
Industrial grid	Brinell hardness, HB (15.625/2.5 - 30)	12 - 14	kg/mm ²
	Tensile strength, σ_B	4.5 - 6.5	kg/mm ²
	Elongation, δ_B	≥ 3	%

Hardening by alloying (natural hardness)

Figure 1 illustrates the increase of hardness by using antimony as an alloying element. The curve shows the hardness of as-cast grids *versus* antimony content of the alloys. In the case of low antimony contents (<3% antimony), the antimony forms a solid solution with lead. An alloying element that goes into solid solution always hardens the solvent metal. When the antimony content is increased further, the solubility of antimony in lead is exceeded and two solid phases appear forming an intimate mixture, the so-called eutectic mixture. As shown in Fig. 1 the percentage of the eutectic mixture increases with rising antimony content above 4% and gives rise to a frame structure of the alloy (photographs in Fig. 1). This hard eutectic frame structure brings about the high natural hardness of lead-antimony alloys containing more than 5% antimony.

Age-hardening

The above mentioned solid solution of antimony in lead causes supersaturation, when the usual technique of grid casting is applied, because

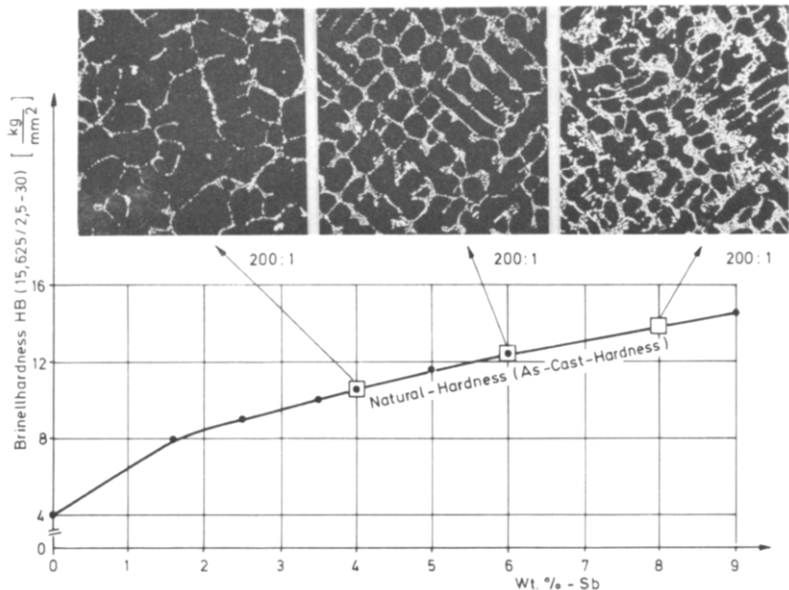


Fig. 1. Natural hardness of lead-antimony alloys.

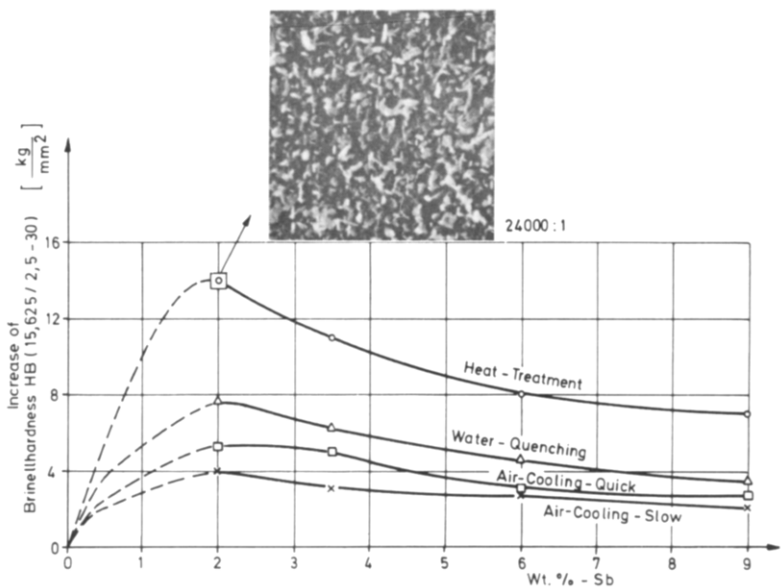


Fig. 2. Age-hardening of lead-antimony alloys.

at room temperature the solubility of antimony in lead is extremely low compared to the 3.5% solubility at 252 °C. The reduction of supersaturation by precipitation of finely dispersed antimony within the lead-antimony solid solution grains causes the always observed age-hardening (Fig. 2).

The supersaturation, and therewith the age-hardening of the grid, can be increased by fast cooling immediately after casting or by applying additional heat treatment (solution treatment and sudden quenching from about 250 °C). Figure 2 shows the effect of different treatments on age-hardening. As shown in the photograph the precipitation of very fine plates (about $10^5 - 10^{10}$ plates/cm²) of antimony, which are arranged parallel to the {111} planes of lead [1] and consist of almost pure antimony [2], causes the age-hardening. (Please note the high magnification obtained by using scanning electron microscopy.)

Figure 2 also shows that the age-hardening effect decreases with increasing antimony content [3]. This is reasonable, because the uniform finely dispersed precipitation of antimony within the lead matrix is replaced more and more by antimony precipitation at the eutectic mixture. Therefore with increasing antimony content increasing amounts of the originally supersaturated antimony which causes age-hardening by fine dispersion are lost due to precipitation of antimony within the eutectic mixture.

Total hardness

The total hardness finally achieved is the sum of natural hardness and hardness due to age-hardening (depending upon age-hardening conditions). Figure 3 shows the total hardness attained after 3 weeks. As can be seen a definite pretreatment can raise the hardness of grids made from 2% antimony alloys to values which are known for alloys with higher antimony contents. However, it must be mentioned, that the amount of hardness due to age-hardening decreases again when the grids are exposed to higher temperature (>50 <200 °C). This is caused by the dissolving or coarsening

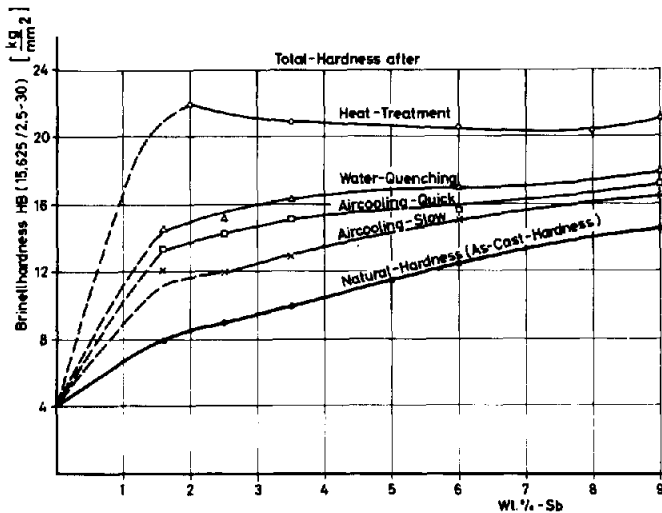


Fig. 3. Total hardness (natural hardness and age-hardening).

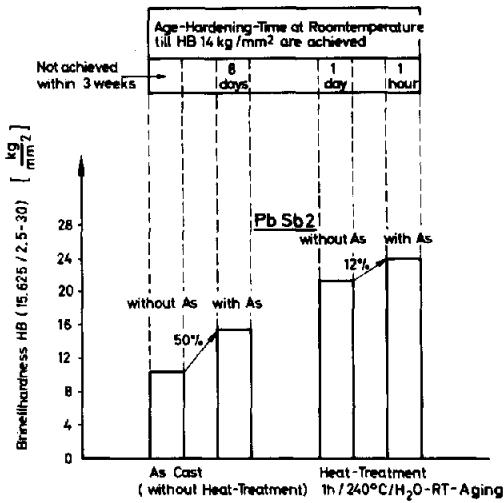


Fig. 4. Influence of arsenic on the age-hardening of lead/2% antimony alloy.

of finely dispersed antimony at higher temperature, so that the effectiveness of antimony dispersion in producing age-hardening is decreased.

Increase of age-hardening by further additives (e.g. arsenic)

The age-hardening, which is based on finely dispersed precipitation of antimony, is not only increased by supersaturation (special pretreatment of grids), but also by further additives, e.g. arsenic. The influence of arsenic is more effective, when the supersaturation of antimony in lead is relatively low (for example for grids, which did not have a special heat treatment). Figure 4 shows this effect; arsenic does not only increase, but also accelerates the age-hardening process.

Castability

In addition to the mechanical strength required for further treatment of the grids, the castability is another important factor for producing sound grids at tolerable cost.

For comparative measurements of castability and casting-quality, the mould shown in Fig. 5 was used [4]. The construction of this mould resembles the production moulds. By decreasing thickness of the vertical straps from 4 mm to 0.8 mm the flow of the melt was made more difficult with progressing length of the straps.

By counting the filled grid passages, the castability of different alloys was determined as shown in Fig. 6. This is, of course, a comparative test only, and Fig. 6 is valid only for the chosen conditions. Several authors [5 - 7] observed a new increase in castability for alloys containing less than 3.5% antimony, which was not observed in our case with gravity

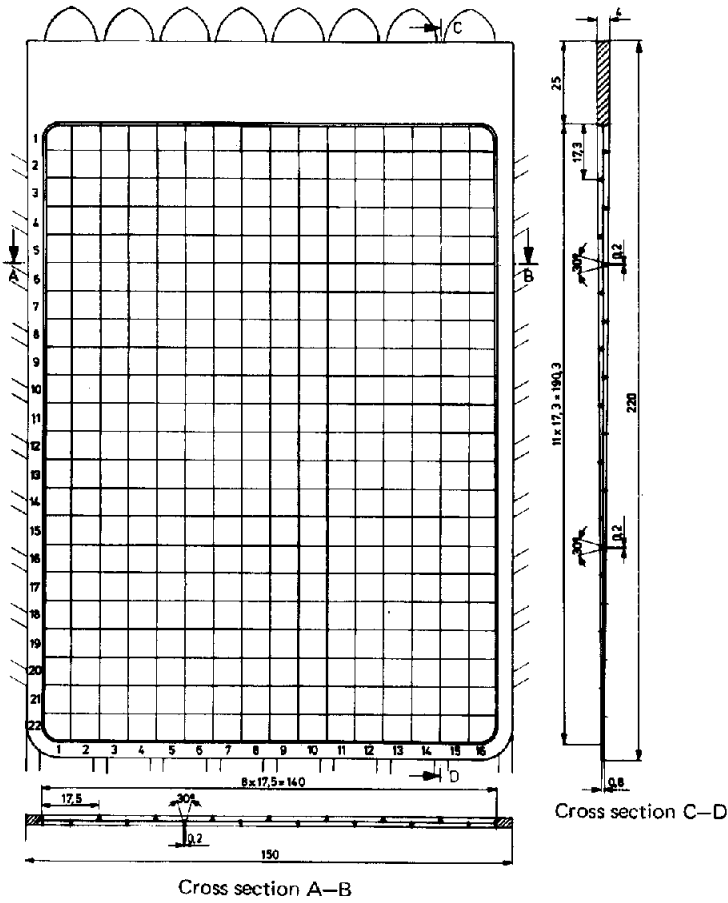


Fig. 5. Mould design for testing castability and grid quality.

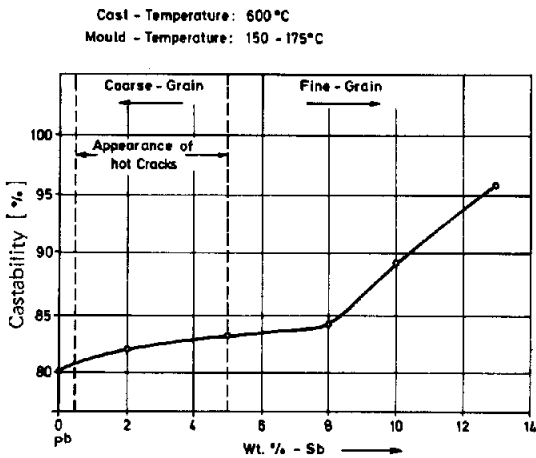
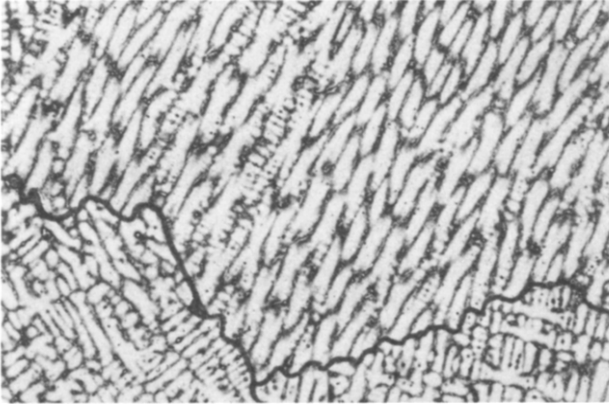


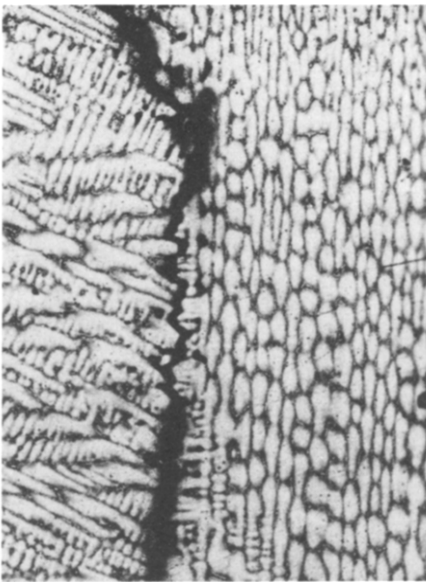
Fig. 6. Castability of lead-antimony alloys.

casting. In production by pressure casting, the increase of castability with decreasing antimony content ($<3.5\%$) was also observed by us.

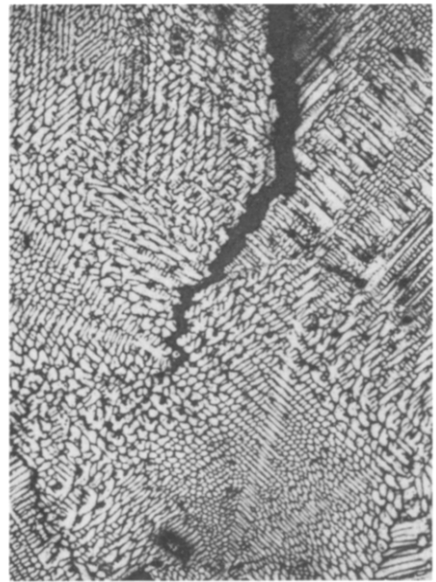
Figure 6 shows that with varying antimony content from 13 to 8% the castability decreases markedly. Below 8% antimony content there is only a small change in castability and the casting process can be adjusted as required by regulating the cast (melt) and mould temperatures. Below 5% antimony content, however, the tendency to hot cracks and brittleness of the grids increases. Figure 7 shows for example the cast structure of grids containing 2% antimony. The solidification takes place in a coarse dendritic structure containing cracks along grain boundaries. Insufficient



(a)

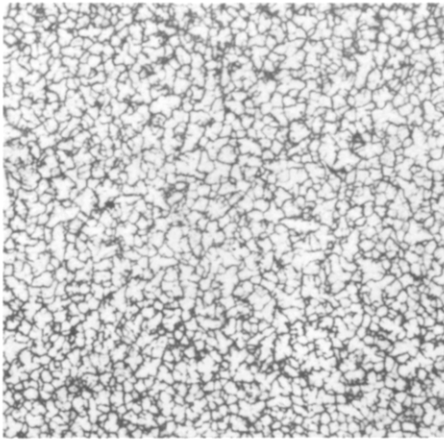


(b)

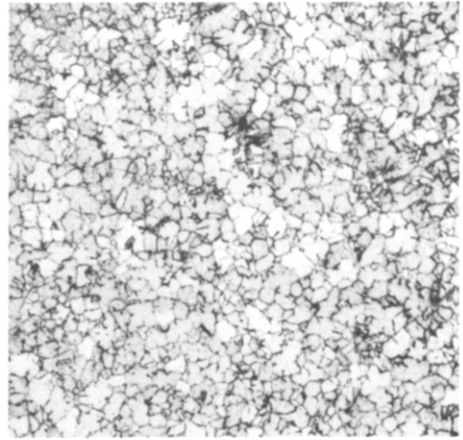


(c)

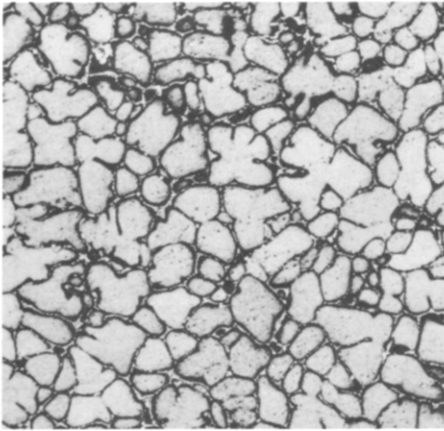
Fig. 7. Coarse dendritic cast structure with cracks (lead/2% antimony alloy). (a), (b) Industrial grid, ($\times 100$), (c) automotive grid ($\times 100$).



(a)



(b)



(c)

Fig. 8. Fine globulitic cast structure (lead/2% antimony/0.02% selenium alloy). (a) Automotive grid ($\times 50$), (b) automotive grid ($\times 100$), (c) industrial grid ($\times 200$).

grid-quality (caused by these cracks) was one of the main reasons why low antimony alloys were formerly not used on a large scale in the accumulator industry.

The originally poor grid-quality of low antimony alloys could be improved by the addition of selenium [8, 9]. This addition forms a fine globulitic solidification, which is free from casting faults (Fig. 8). The grain size of an alloy containing 2% antimony decreases from about $1000 \mu\text{m}$ to about $60 \mu\text{m}$, when 0.02% selenium is added. The formation of dendrites, which disturbs the feeding capacity of the mould during casting and leads to casting faults, is almost fully suppressed. With fine globulitic solidification uniform mechanical properties are achieved in all directions, and hence the ductility is increased [8].

The combination of alloying elements: antimony (1.5 - 3.5%), arsenic, selenium (and tin to increase the castability [10 - 12]) with lead

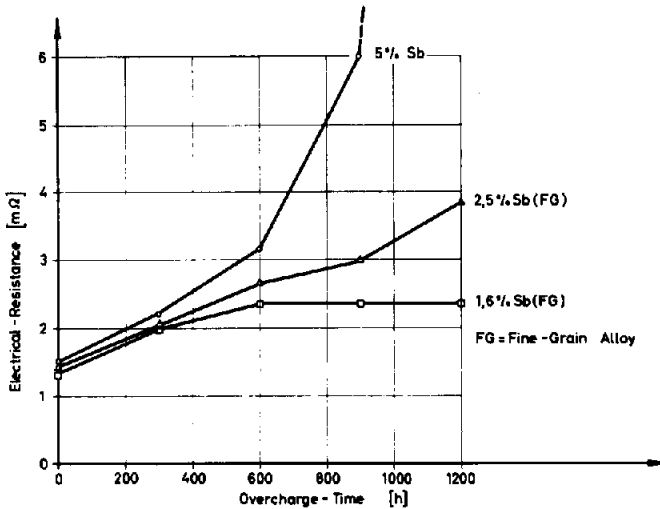


Fig. 9. Increase of resistance due to corrosion.

makes it possible to manufacture battery grids with low antimony alloys which achieve the necessary mechanical strength within suitable ageing-times, and show the necessary grid-quality [10].

Electrochemical behaviour

The so-far-mentioned metallurgical properties of alloys are of great importance with reference to the economical manufacturing and further treatment of grids. However, the battery-grid is not only a passive part in the battery, but owing to unavoidable corrosion reactions it affects the electrochemical behaviour of the battery. New alloys have, therefore, to be tested very carefully in this respect also.

Corrosion behaviour

Figure 9 shows comparable corrosion rates for small test grids, which were exposed to corrosion at 40 °C for different periods applying constant current. As a quantity for measuring the corrosion attack the electrical resistance of the grid network was used. After finishing the corrosion process, the frame of the grid was cut at two opposite corners, and the electrical resistance was measured between the remaining two opposite corners. By this way the electrical resistance of the grid-network only is measured and errors due to the relatively thick frame are avoided. The measurement has to be performed in such a way that the resistance between the probe and the power source does not have any influence on the result. As shown in Fig. 9 the rate of corrosion is reduced with decreasing antimony content. The above mentioned low antimony alloys show higher corrosion resistance than conventional higher antimony content

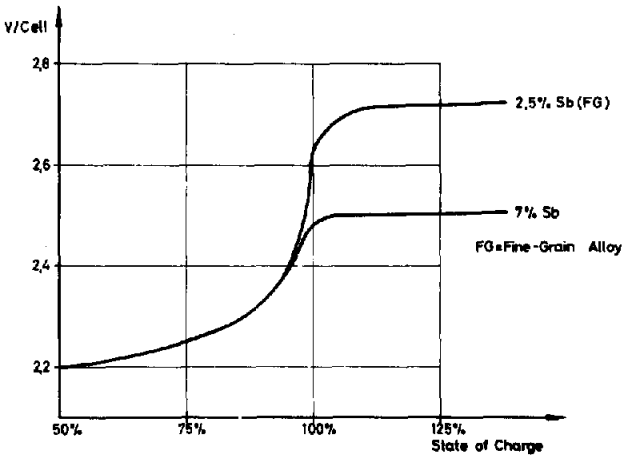


Fig. 10. Charge characteristic of automotive batteries containing different grid alloys.

alloys. Corresponding results were also observed when different corrosion conditions were applied (*i.e.* constant voltage).

The low corrosion rate of alloys is an important factor for using them in batteries, otherwise the battery life may be limited by the corrosion rate of positive grids. Besides this, according to the corrosion rate, antimony is released from the positive electrode and is deposited at the negative electrode where it reduces the over-voltage thus resulting in an inferior charge performance and increased water loss.

Test results

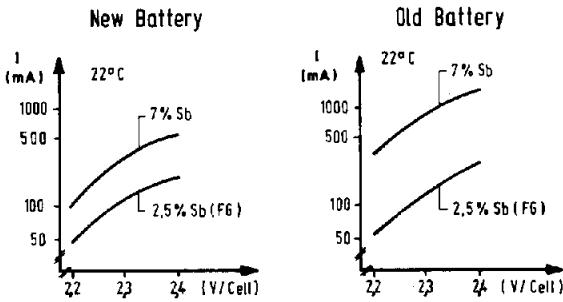
The influence of low antimony alloys on batteries is shown in the following examples.

Figure 10 shows the favourable influence on the end-of-charge voltage. Owing to the low amount of antimony which is released from the positive grid, even in old batteries, the end of charge voltage remains high and excludes unnecessary gassing of the battery during charging.

The floating current *versus* floating voltage is compared for batteries with low antimony alloys and conventional alloys in Fig. 11. The right side of the Fig. shows the test results for old batteries. As can be seen, the floating current remains almost unchanged for batteries with low antimony alloys, the conventional batteries on the contrary consume much more current.

The influence of antimony-content on the performance of stationary cells is shown in Fig. 12. The Fig. shows floating currents at 2.26 V/cell and 35 °C. The floating current rises with increasing antimony-content of the positive electrode. The special test conditions, which were selected to reduce test time, are unusual for stationary battery application.

Table 2 is a survey of test results obtained for automotive batteries. For comparison, besides the results with low antimony alloys, some test results for a conventional alloy (6% antimony) as well as for a lead-calcium alloy are also included.



FG = Fine-Grain Alloy

Fig. 11. Floating current versus floating voltage (automotive batteries).

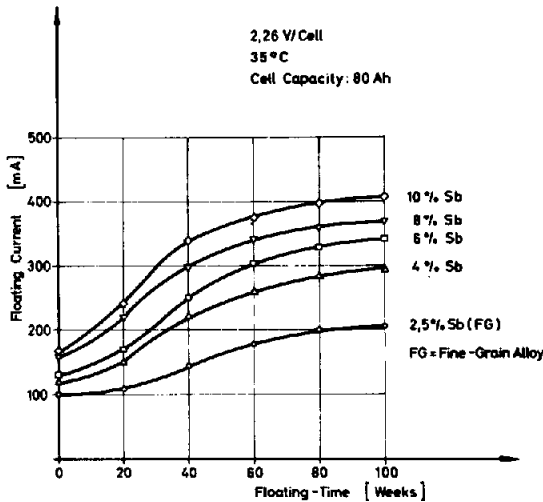


Fig. 12. Floating current versus floating voltage (industrial batteries).

The DIN overcharge life test has proved to be very useful with respect to the practical life of the batteries (6 DIN overcharge life cycles means about 3 years practical life). The increase of overcharge life cycles for low antimony alloys seems to have several reasons. The cast structure attained improves the grid quality to a great extent, the favourable corrosion behaviour prevents early grid destruction and the very low antimony release from the positive electrode stabilizes the voltage at the end of the charge and reduces overcharging. The poor performance of lead-calcium batteries in this test seems partly to be due to shedding of positive active material.

The DIN charge-discharge life test has lost its importance, because automotive batteries in practice are not usually discharged. Only special applications (buses, taxis) correspond to this test. The already mentioned fact, that antimony stabilizes the positive active material and hence raises the cycle-life is proved here. Batteries with lead-calcium grids are destroyed due to shedding of active material.

TABLE 2
Test results (automotive)

Alloy	DIN overcharge life test 100 h Charge with 0.1 c ₂₀ A at 40 °C 39 h Rest at 40 °C 4 h Charge with 0.1 c ₂₀ A at 40 °C Cold cranking test (-18 °C)	DIN charge-discharge cyclic life test 1 h Discharge with 0.4 c ₂₀ A 5 h Charge with 0.1 c ₂₀ A 1 cycle = 6 h; 4 cycles/day	Water loss (Practical test) Average service 15,000 km/year
6% Sb	Number of cycles 6 - 7	Number of cycles >250	
3.5% Sb FG	7 - 9	~250	
2.5% Sb FG	11 - 12	~250	3 g/cell, month >60 months (LT)
Pb-Ca	~3	~50	0.4 g/cell, month >37 years (LT)

FG = Fine-grain alloy; LT = projected lifetime due to water loss.

The last column in Table 2 shows the water loss in a practical test. As can be seen, the water loss of lead-calcium batteries proved to be extremely low; however, this does not influence the life-time of the battery, which in the case of low antimony alloys also is limited by different parameters.

Table 2 confirms the above mentioned facts, for the low antimony alloys discussed. The disadvantages connected with antimony are reduced to a great extent, therefore maintenance-free batteries can be produced without losing the advantages of antimony, *i.e.* the cycle performance of the battery.

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