STORAGE BATTERY SYSTEMS, INC.

Stationary Lead-Acid Batteries With Selenium Alloys

Summary

Lead alloys characterized by the addition of selenium exhibit a fine grain structure even at very low antimony contents (less than 2%). This structure yields acceptable castability and quality of the castings. The hardness which is necessary for handling the battery plates is achieved by age hardening due to finely dispersed antimony.

Corrosion stability at constant potential or constant current proves to be slightly superior, but in the same order of magnitude compared to conventional antimony alloys (≥ 4%).

However, at constant cell voltage the amount of antimony released from the positive acid grid is too small to affect the potential of the negative electrode markedly. Therefore, the very low initial gassing rate, which is of the same order as experienced with antimony free batteries, remains almost constant.

Of special importance, is that the well known stabilizing effect of antimony in respect to the positive active material is virtually maintained with these selenium alloys. This results in capacity stability as well as rather good cycling performance.

Introduction

Until ten years ago the grids of lead-acid batteries were 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 from the grid, which proves to be both unfavorable as well as unfavorable with respect to battery performance. On the one hand, antimony stabilizes the active material of the positive electrode, the cycle life of the battery is improved and passivation effects disturbing mainly the discharge mechanism 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 over voltage. This leads to lower charge voltage increased self-discharge and therefore increased water loss of the battery.

As a consequence most battery manufacturers tried to minimize or even eliminate the antimony addition especially in batteries for stationary applications where smaller demands are made in respect to cycle service.

The present report deals with the development and test experience of a special group of alloys characterized by selenium as an alloying addictive. Using selenium, the antimony content can be reduced to the point that the drawbacks of antimony are almost eliminated, however the positive effects pf antimony are largely retained.

Extensive practical experience has confirmed the advantages of these alloys.

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 for industrial battery grids

Brinell hardness, HB (15.625/2.5-30)	12	-	14	kg/mm^2
Tensible strength, σ_B	4.5	-	6.5	kg/mm^2
Elongation, δ_B		>	3 %	

a) **Hardening by alloying (natural hardness**

Fig. 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 converted into a 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 produces 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 4% antimony.

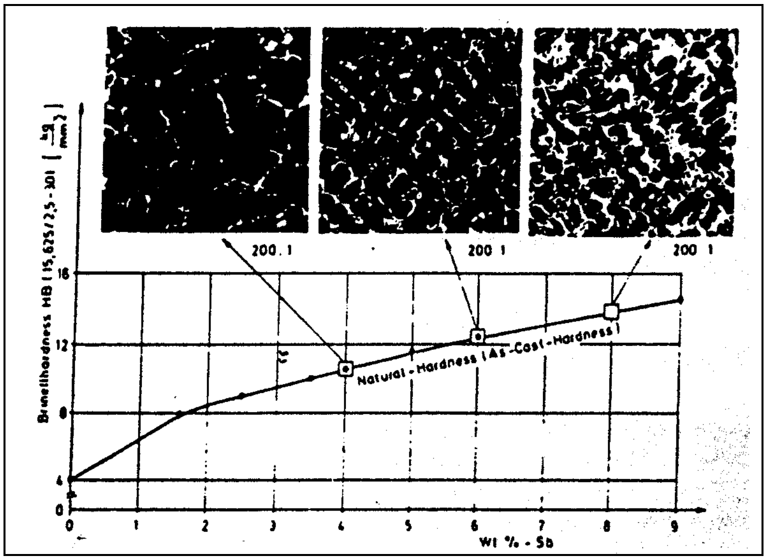


Fig 1: Natural hardness of lead-antimony alloys

b) Age-hardening

The above mentioned solid solution of antimony in lead causes supersaturation, when the usual technique of grid casting is applied, because 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 ever present age-hardening (Fig. 2).

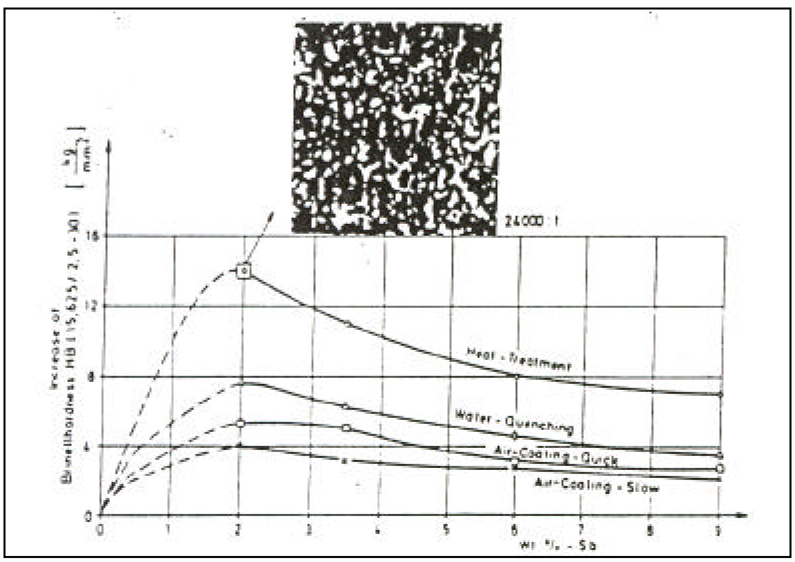


Fig.2. Age-hardening of lead-antimony alloys

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). Fig. 2 shows the effect of different treatments on age hardening. As shown in the photograph the precipitation of very fine planes (about 10^5-10^{10} planes/cm^2) of almost pure antimony (4), which are arranged parallel to the (111) planes of lead (3) causes the age-hardening. (The high magnification was obtained by using scanning electron microscopy.)

Fig 2 also shows that the age-hardening effect decreases with increasing antimony content (5). This is reasonable, because the hardness of the casted alloy is determined more and more by the frame work of the eutectic mixture which also reduces nucleation difficulties for antimony. Therefore with increasing antimony content increasing amounts of the originally supersatured antimony (which produces age-hardening by fine dispersion) are lost due to precipitation of antimony within the eutectic mixture.

c) **Total Hardness**

The total hardness finally achieved is the sum of natural hardness and hardness due to age-hardening (depending upon age-hardening conditions). Fig. 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 value 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 of finely dispersed antimony at higher temperature, so that the effectiveness of the antimony dispersion in producing age-hardening is decreased then.

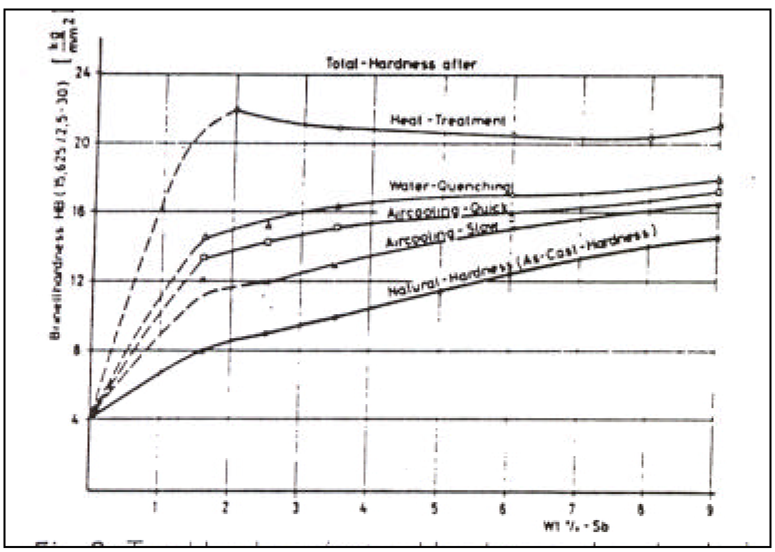


Fig. 3: Total hardness (natural hardness and age-hardening).

d) **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 (e.g. for grids which did not have a special heat treatment). Fig. 4 shows this effect; arsenic does not only increase, but also accelerates the age-hardening process.

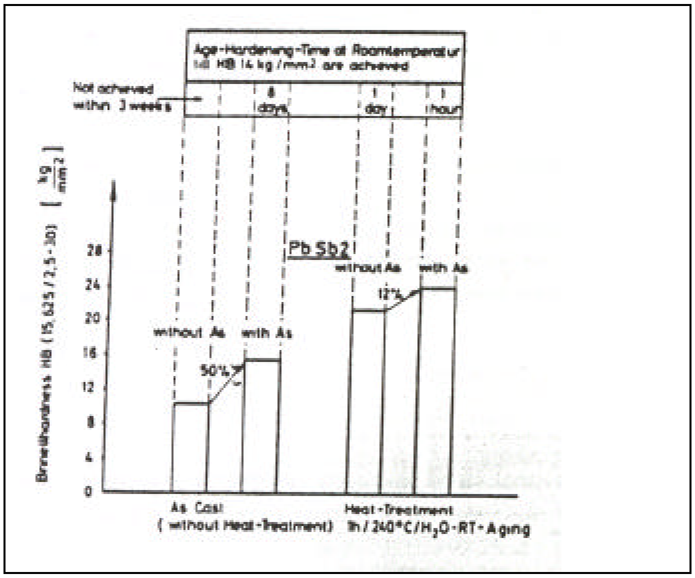


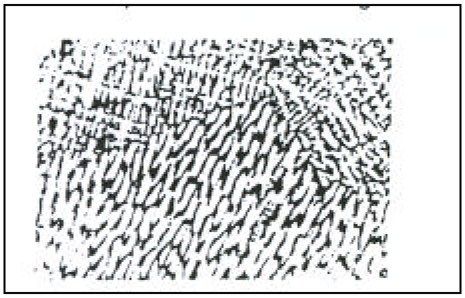
Fig 4: Influence of arsenic on the age-hardening of lead / 2% antimony alloy.

Castibility

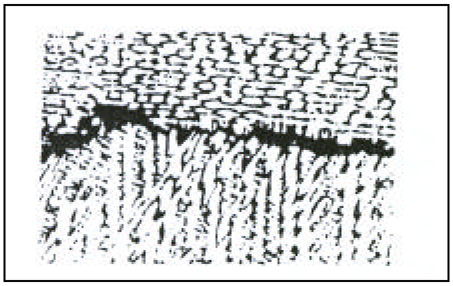
In addition to the mechanical strength required for further treatment of the grids, the castability is another important factor for producing sound grids at tolerable cost.

The main difficulty with casting low antimony alloys is that the decrease of antimony content ia accompanied by the appearance of hot cracks (6-8), if no special precautions are taken.

For example: Fig. 5 shows the cast structure of grids containing 2% antimony. The solidification takes place in a coarse dendritic structure containing cracks along grain boundaries. Inadequate formerly not used on a large scale in the battery industry.



5 a)

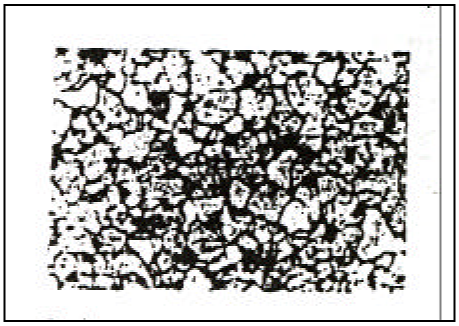


5 b)

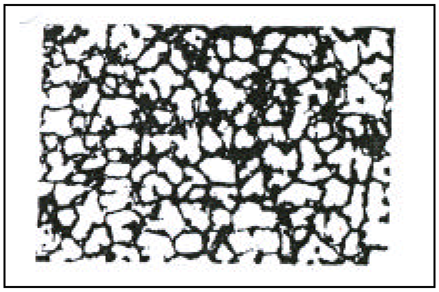
Figure 5: Coarse dendritic cast structure with cracks (lead/2% antimony alloy). (a), (b) Industrial grid (x 100).

The poor grid-quality of low antimony alloys can be overcome by the addition of selenium (9,10). This addition forms a fine globulitic solidification, which results in fewer casting faults (Fig. 6). The grain size of an alloy containing 2% antimony decreases from about 100µm to about 60µm, when 0.02% selenium is added. With respect to grain refinement, selenium proved to be superior to all other additives (11). 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 (9).

Using the combination of alloying elements: antimony (1.5-3.5%), arsenic, selenium (and tin to increase the castability, (11-13) with lead it is feasible to manufacture battery grids with very low antimony contents which achieve the necessary mechanical strength within suitable ageing times, and show the necessary grid-quality.



6 a)



6 b)

Fig. 6: Fine globulitic cast structure (lead/2% antimony/0.02 % selenium-alloy). (a) Automotive grid (x 200), (b) industrial grid (x 200).

Electrochemical Behavior

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 behavior of the battery. New alloys have, therefore, to be tested very carefully in this respect also.

Corrosion Behavior

Due to the extremely high potential of the positive electrode only lead can be used as grid material. This lead unavoidably is subject to gradual erosion from corrosion. For battery applications this corrosion rate must be reasonably low, otherwise the battery life is limited by the corrosion rate of the positive grid.

Potentiostatic Corrosion Tests

The potential of the electrode as the most important parameter determines the electrochemical corrosion of lead. Therefore, Potentiostatic corrosion tests are very suited for comparing corrosion rates for different grid alloys. Fig.7 shows the results obtained for different lead-antimony alloys. The samples used in these experiments were metal rods prepared carefully to avoid any sources of error e.g. caused by poor casting quality. The applied corrosion potential corresponds to about 2.6 Volts cell voltage.

As can be seen in Fig.7, the Potentiostatic corrosion rate is of a comparable order of magnitude for all tested Sb/Pb-alloys. On the basis of these experiments the selenium alloys can be expected to perform slightly better concerning corrosion attack compared to conventional lead antimony alloys.

Lead – Corrosion at Constant Potential

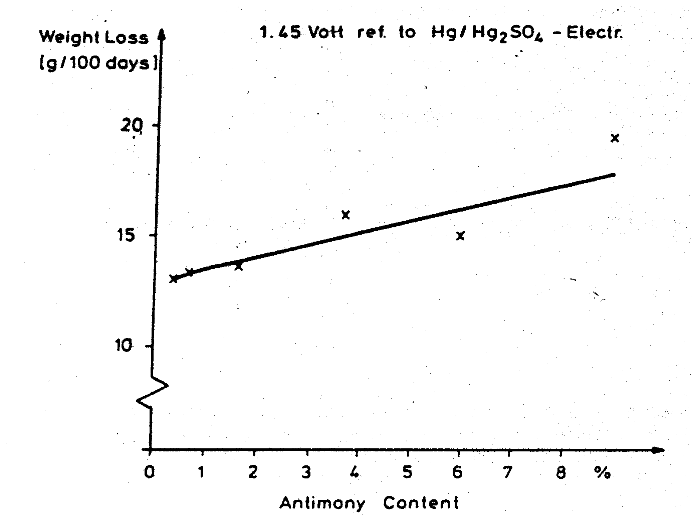


Fig. 7

Corrosion Experiments With Battery Grids

Corrosion tests on battery grids usually were carried out in cells using a negative battery plate as the counter electrode. Fig. 8 shows results for battery grids with reference to antimony content. As can be seen, the result is fundamentally different, depending on the testing procedures. When a cycling regime was applied, which means constant current was impressed on the electrode, the differences in corrosion attack are small. Actually the performance should be expected, to be very similar to the result shown in Fig.7, because constant current more or less means constant potential of the positive electrode.

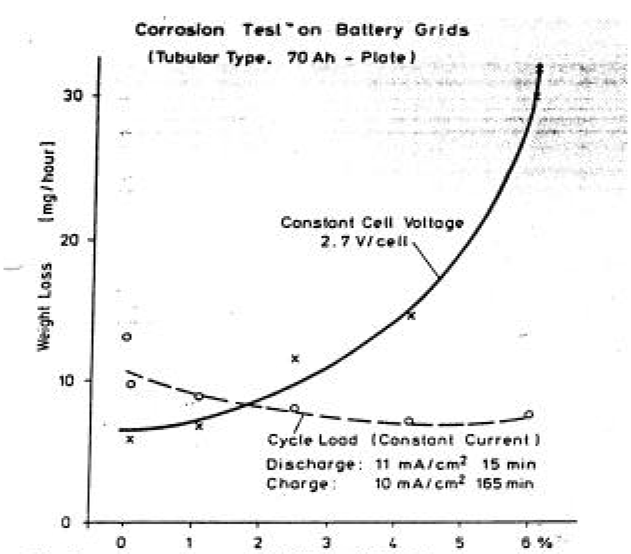


Fig. 8

However, when constant cell voltage is applied in the experiment, the antimony content of the corroding grid largely is determining the result as can be seen in Fig. 8. The reason is, that antimony, released at the corroding positive grid, is precipitated at the negative electrode which results in a reduced hydrogen over voltage. This means that the rate of hydrogen evolution is the same at a less negative electrode potential. Therefore, the negative electrode potential is shifted in a positive direction and consequently the positive electrode potential is raised, because the cell voltage is kept constant. The rise in positive electrode potential leads to an increase in corrosion which again produces antimony at a faster rate and therefore, gives rise to increased contamination of the negative electrode. In this way a self-accelerating process originates causing the strong effect of antimony content shown in Fig.8. The corrosion test at constant cell voltage therefore does not compare pure corrosion rates, but rather is a mixture of corrosion and potential shift by antimony contamination of the negative electrode. However, this test reflects the situation in many battery applications, because lead acid batteries to a large degree are charged at constant voltage, especially stationary batteries which are kept on a constant floating voltage.

Therefore, battery performance in the field to a large extent corresponds to the constant voltage corrosion test, which shows the strong antimony effect caused by the combination of positive grid corrosion and potential shift of the negative electrode due to antimony contamination. Compared to the bare grid the rate of antimony release only is somewhat reduced at a complete positive plate, because antimony is absorbed to a marked degree by Pb O_2 (14).

Battery Performance

Float Test

The above discussed antimony-effect on battery performance is stated by results of an accelerated floating test shown in Fig. 9. Industrial batteries of the same type were used with the only difference that the positive grids consisted of various alloys. The floating voltage 2.23 volts/cell

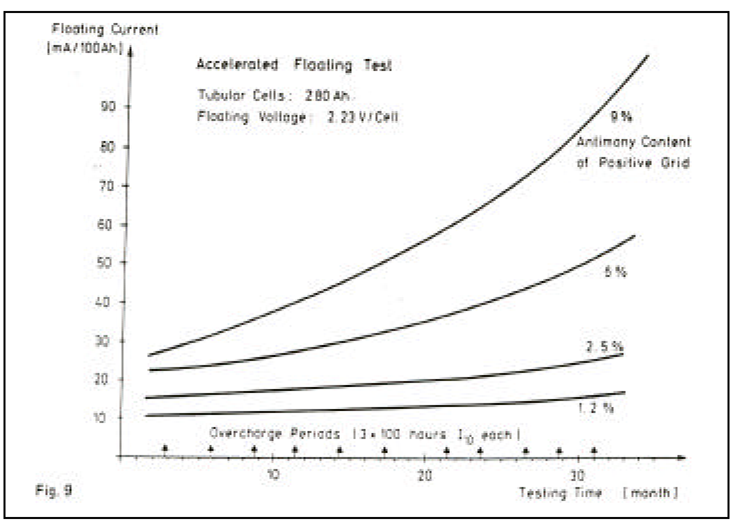


Fig.9

Was applied as usual for stationary batteries. The acceleration of the test was achieved by periods of heavy overcharge 3 times 100 hours at a three month time interval, which means “Artificial Ageing” to the cells.

Fig.9 completely states the situation of constant voltage floating described above, discussing Fig.8. At an antimony content of less than 2% in the positive grid, the amount of antimony reaching the negative electrodes is obviously too small to cause a marked effect on the electrode potential, and the floating current is therefore stabilized at the low initial level.

In Fig. 10 results of floating tests on stationary batteries with selenium alloys are compared to tests published by the Swiss Post Office in 1976. For his well founded experiments, GERBER used industrial batteries which were supplied by several manufacturers. The grid material of these batteries contained about 10% antimony. Some results on stationary batteries equipped with lead/calcium-alloys were entered in Fig. 10 too.

This comparison again shows the advantages of the extreme reduction of antimony content which is feasible in selenium alloys. The floating current at 2.23 volts/cell is even smaller than the floating current for “old batteries” at 2.20 volts/cell. Furthermore for the “selenium batteries” the increase of floating current is much smaller, which means that the described self-accelerating process of corrosion and potential shift nearly ceased, which will be beneficial concerning watering intervals with elapsed times as well as shelf life.

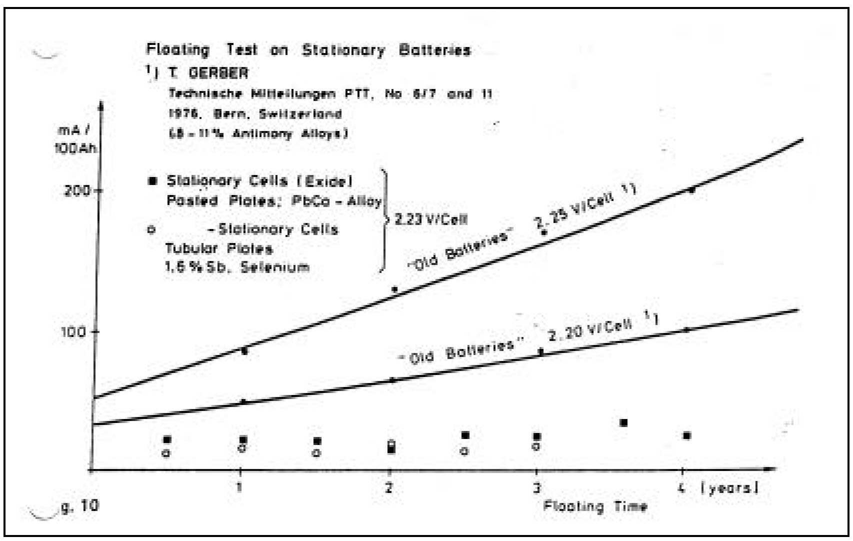


Fig. 10

Cycling Test

As already mentioned at the beginning, besides the disadvantages of antimony, which were discussed in the proceeding chapters, the antimony, content in the positive grid material contributes beneficial effects for the lead acid battery: antimony stabilizes the positive active material which results in good cycling performance and less sensitivity to deep discharges (14).

This beneficial effect of antimony is illustrated by Fig. 11, which shows the results of a cycling test, usually applied for motive power batteries. Each cycle in this test includes a discharge of 75% of nominal capacity, two cycles are performed per day. In intervals of about 50 cycles, the capacity is determined by complete discharge. For the single cell, the test is finished as soon as the capacity is less than 80% of nominal capacity. The cells used for the test shown in Fig.11 differed in antimony content of the positive grid.

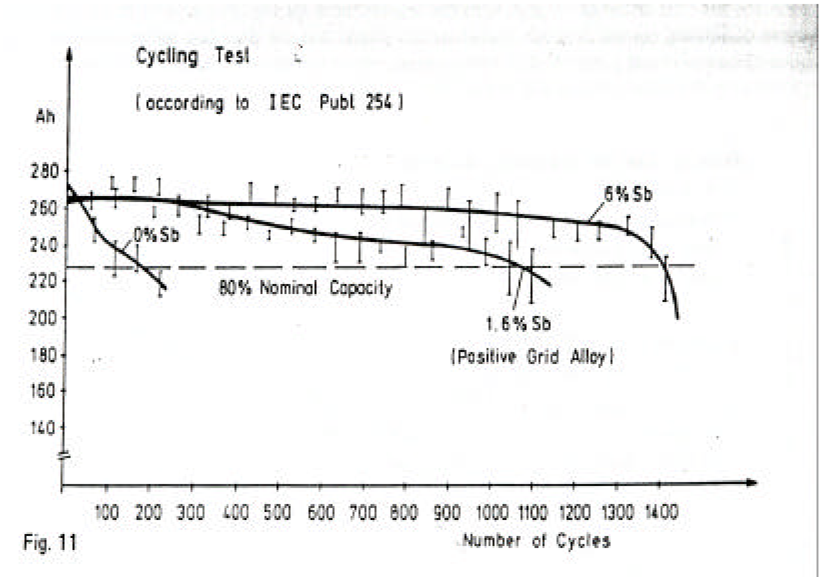


Fig. 11

The stabilizing effect of the antimony is obvious. While the cells without any antimony failed after about 200 cycles (6 cells of each version were tested), the cells equipped with selenium alloy containing only 1.6% antimony performed about 1,000 cycles. This stabilizing effect obviously is an important advantage of selenium alloys. Even for batteries which definitely are not cycled, this stabilizing effect means less sensitivity to deep discharges which may occur occasionally, apart from the fact that for many stationary battery applications a certain cycle service cannot be excluded.