

## INFLUENCE OF COBALT IONS ON THE BEHAVIOUR OF MAINTENANCE-FREE LEAD/ACID BATTERIES WITH ANTIMONY ALLOYS

K.-H. CHRISTIAN\* and R. ACKERMANN

*VEB Grubenlampen- und Akkumulatorenwerke Zwickau, PSF 823, Zwickau 9502 (G.D.R.)*

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### Introduction

The best way to avoid poisoning of the negative plates of maintenance-free lead/acid batteries with regard to hydrogen overvoltage is to use antimony-free alloys. Unfortunately, antimony-free alloys (*e.g.*, lead-calcium alloys) do not perform well under cycling conditions; this behaviour is commonly described as the 'antimony-free effect'. For this reason, it is general practice to include a small amount of antimony in the positive grids.

The possible use of cobalt ions as a beneficial additive for lead/acid batteries has been discussed for many years (see, for example, ref. 1). The present view of the battery industry, however, is to avoid cobalt-containing additives [2]. The action of cobalt is to decrease the oxygen overvoltage on the  $\text{PbO}_2$  electrode and thereby increase the rate of oxygen evolution during voltage-controlled charging, as well as on open circuit. Cobalt is also well known to act as an inhibitor of grid corrosion, not only because it causes a decrease in the positive potential, but also because cobalt changes the properties of the corrosion layer on the grid surface. This suggests that small additions of cobalt may reduce the loss of antimony from positive grids and, in turn, lessen the poisoning of the negative electrodes by antimony. This possibility is investigated here by examining the effect on battery behaviour of small quantities of cobalt added to the positive plate paste-mix.

### Results and discussion

Small model cells comprising pasted positive and negative plates were constructed. The antimony content of the grids of the positive plates was 0, 1.2 or 2.5 wt.%. For each grid alloy, the active mass was prepared either without cobalt ions or with a content of 30 ppm cobalt in the form of sulphate. Pure lead grids were used for the negative plates. Table 1 gives the overcharge currents after 100 h of constant-voltage overcharge at 2.40 V and 40 °C. It can be seen that for antimony alloys cobalt decreases the

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\*Author to whom correspondence should be addressed.

TABLE 1

Overcharge currents of model cells at 2.40 V and 40 °C

Positive grid alloy	Co <sup>2+</sup> content (ppm)	Overcharge current (mA (A h) <sup>-1</sup> positive plate capacity)
Pure lead	0	2.3
	30	3.3
Pb-1.2wt.%Sb	0	5.0
	30	3.3
Pb-2.5wt.%Sb	0	6.0
	30	5.3

overcharge current, whereas for pure lead, cobalt increases the current. The latter result may be due to contamination of the negative grid with cobalt resulting in lowering the hydrogen overvoltage.

In a second series of experiments, the water loss of standard batteries with Pb-2.5wt.%Sb grids, both in the positive and negative plates, was examined. The batteries were of 12 V/42 A h size and contained 0, 8 or 30 ppm of cobalt ions in the positive active material. Both weight loss and electrical charge during 500 h of charging at a constant voltage of 2.35 V/cell and at 50 °C were recorded. The results are given in Table 2 and show that increasing amounts of cobalt yield a significant decrease in the weight loss. Surprisingly, the decrease in the electrical charge was less pronounced. It is possible that the difference between the changes in the water loss and the electrical input are associated with a Co<sup>3+</sup>/Co<sup>2+</sup> shuttle that gives rise to a non-faradaic current. For this reason, the influence of cobalt on the self-discharge of batteries was examined.

Table 3 shows the results of investigations of the self-discharge of 12 V/135 A h batteries without/with cobalt additive by measuring the cold cranking performance after a rest period of 49 days at 40 °C. The results show that there is no evidence for a shuttle-induced self-discharge at open circuit. Indeed, cobalt improved the cold-cranking performance after the rest period.

TABLE 2

Weight loss and accepted electrical charge of 12 V/42 A h batteries during 500 h at 2.35 V/cell overcharge at 50 °C

Co <sup>2+</sup> content (ppm)	Weight loss <sup>a</sup> (g (A h × cell) <sup>-1</sup> )	Electrical charge (A h)
0	1.33	130
8	1.08	122
30	0.97	117

<sup>a</sup> The relative high amount is due to the elevated temperature (50 °C).

TABLE 3

Cold-cranking performance of 12 V/135 A h batteries at  $-18^{\circ}\text{C}$  after 49 days rest period at  $40^{\circ}\text{C}$   
 Discharge current = 405 A.

Co <sup>2+</sup> content (ppm)	30 s voltage (V)	Time to 6.0 V (s)
0	7.90 - 8.05	86 - 101
30	8.00 - 8.30	116 - 126

In summary, it would appear that the addition of small quantities of cobalt ions to the positive plates of low-antimony batteries improves the maintenance-free behaviour. Further investigations are necessary in order to establish the exact mechanism of the action of cobalt in these batteries.

### References

- 1 J. A. Hamilton, J. F. Moresby and D. A. J. Rand, in K. R. Bullock and D. Pavlov (eds.), *Advances in Lead/Acid Batteries, Proc. Vol. 84-14*, The Electrochem. Soc., Pennington, NJ, U.S.A., 1984, pp. 378 - 405.
- 2 J. R. Pierson, C. E. Weinlein and C. E. Wright, *J. Power Sources*, 5 (1974) 97.