

Techniques to reduce failure in lead–calcium batteries using expanded type grids

K. Takahashi, H. Yasuda, K. Yonezu and H. Okamoto

Storage Battery Division, Matsushita Battery Industrial Corporation Ltd., 555 Sakaijyuku Kosai Shizuoka 431-04 (Japan)

Abstract

Recent developments have improved the following characteristics of lead/acid batteries that employ expanded lead–calcium grids: (i) recovery after overdischarging and long standing; (ii) battery life at high temperature; (iii) battery life under deep-cycling conditions. It is widely known that the addition of tin to Pb–Ca–Sn alloys is effective in assisting recovery after overdischarging and long standing. It has also been found that the surface-treatment technology developed to make a Pb–Sn alloy thin layer on the expanded Pb–Ca–Sn wrought alloy grid has improved these characteristics. Since the temperature of engine compartments in Japanese automobiles has risen in recent times, the life of batteries subjected to these temperatures has become increasingly important. Through combination of surface treatment with a thin Pb–Sb–Sn alloy layer, and increases in the corrosion resistance and mechanical strength of Pb–Ca–Sn wrought alloys, the life of automotive batteries at high temperatures has been extended remarkably. Such an approach has also improved the life of batteries used in deep-cycling conditions.

Introduction

Recently, lead/acid batteries that use lead–calcium grids have been widely introduced in the automotive market. The expanded production method for the grids is important not only for practical reasons because of the higher productivity, but also because it is useful as a key technology for improving the characteristics of calcium-type batteries. Despite the fact that these batteries exhibit superior maintenance-free performance compared with batteries using antimony-based grids, the following problems still persist:

- poor recovery after overdischarge and long standing
- inferior cycle life at high temperatures
- inferior cycle life under deep-discharge service

Many studies of these problems have been reported from the beginning of the development of the calcium-type battery [1–3]. In particular, significant advances have been made during the past decade on the problem of poor recovery [4–6].

The first problem to be witnessed was the decrease in rechargeability after lead–calcium batteries had been overdischarged or subjected to long stand periods. This phenomenon has sometimes been called the ‘airport effect’ in Europe and USA. Similar behaviour has also been experienced in Japan, particularly in exported cars that suffer leakage of current during long trips through, for example, the door being left half-open. This problem was attributed [7] to passivation processes in a thin

interface layer between the active material and the calcium-alloy grid in the positive plates under the combined effects of high potential by the remaining PbO_2 and high pH after overdischarge.

Although it was found that inclusion of a high content of tin in the grid alloy was effective in alleviating this problem, such an approach was difficult because of the high cost of tin, lower grid productivity, etc. A new surface-treatment technique was developed [8] in order to solve these difficulties. This involved application of a very thin, tin-rich layer on either one or both sides of the calcium-alloy sheet that is usually employed in the fabrication of expanded grids. The process is known as the 'clad method' and integrates two kinds of alloys during the wrought processing of the base alloy slab. Despite the fact that the resulting grid surface protected only part of the expanded grid network, an effective improvement in passivation was realized.

Figure 1 presents a schematic of the clad method and Fig. 2 shows a cross section of a wrought sheet with a coated surface. An example of the beneficial effect of surface treatment on improving recovery is given in Fig. 3.

The problems of poor cycle life at high temperatures or under deep discharge have not been solved completely. Furthermore, these problems have become increasingly important because the temperature in engine compartments has tended to increase as a result of aerodynamic vehicle design, an increase in the many optional items of electric equipment, and a change in city traffic conditions especially in Japan [9]. Therefore, the reliability of batteries subjected to these high temperatures and deep charge/discharge cycling has become an important issue in addition to the requirement for decreasing water consumption.

The main failure modes of calcium-type batteries at high temperatures are positive grid corrosion and growth, loss of contact between the grid and the positive active material and shedding of active material. In this paper, a discussion is presented of improvements to increase cycle life at high temperatures by means of a combination of surface treatment of the grid with a thin Pb-Sb-Sn alloy layer, and improvements to the mechanical strength and corrosion resistance of the Pb-Ca-Sn alloy wrought grid.

It is well known that hybrid-type batteries with antimony alloy positive grids are preferred under conditions of deep discharge in comparison with calcium-type batteries. In this case, the failure modes of calcium-type batteries are softening of the positive active material and a decrease in the contact strength between the active material

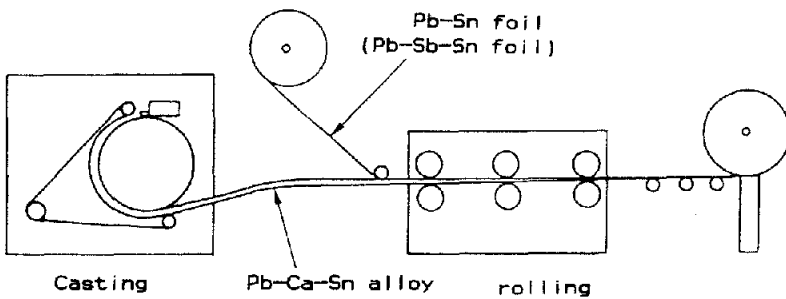


Fig. 1. Schematic representation of the process for producing wrought sheet with a surface treatment.

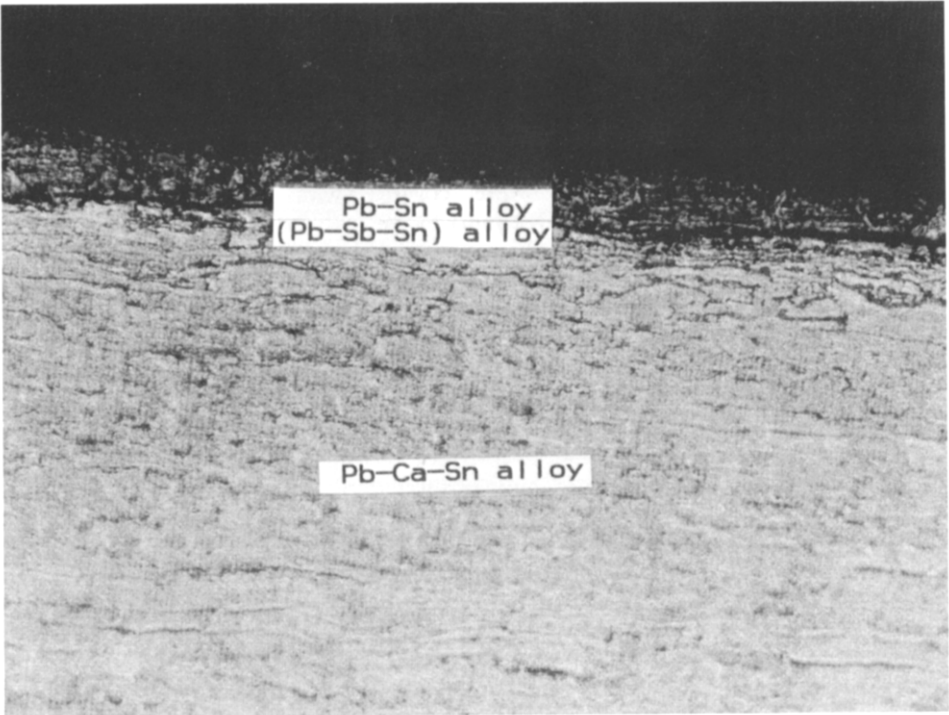


Fig. 2. Cross section of wrought sheet.

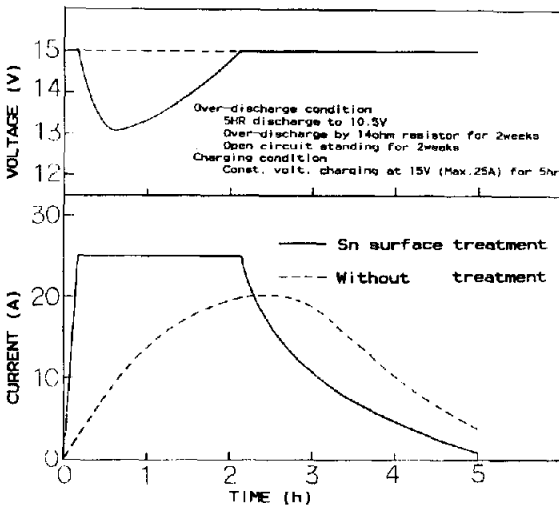


Fig. 3. Charge-acceptance characteristics after overdischarging.

and the grid. Such failure modes are enhanced at high temperatures. Therefore, the performance of antimony-rich and tin-rich thin alloy layers was re-examined. The methods employed and the results obtained are discussed below.

Experimental

Preparation of sheet and grid

In order to investigate the corrosion resistance and mechanical strength of the base grid alloy in a standard form under high temperature use, several sheets were prepared and contained calcium from 0.07 to 0.12 wt.% and tin from 0.3 to 1.8 wt.%.

Both sides of other sheets were covered with a thin alloy layer of Pb-5wt.%Sb-5wt.%Sn (thickness 0.012 mm) by means of the clad method shown in Fig. 1. In order to study effect of this treatment, three types of sheet were prepared. The first was bare, the second had a coating on only one side, and the third had both sides covered. In this case, base sheet alloys of composition Pb-0.07wt.%Ca-0.3wt.%Sn and Pb-0.07wt.%Ca-1.3wt.%Sn were used. Figure 4 is a schematic representation of the grid design. The sheets were expanded, pasted, and then assembled for battery testing. The batteries were constructed for life tests at high temperature. The construction details are given in Table 1.

The test method for evaluating the corrosion resistance of the grids was as follows: overcharge test at high temperature, temperature: 75 °C, overcharge current: 5 A, and duration: 750 h.

Two different cycle-life tests were conducted at high temperature. One involved a shallow depth-of-discharge and the other a rather deep depth-of-discharge. The schedules were as follows.

(i) Cycle-life test under shallow discharge at high temperature (SAE life test at 75 °C):

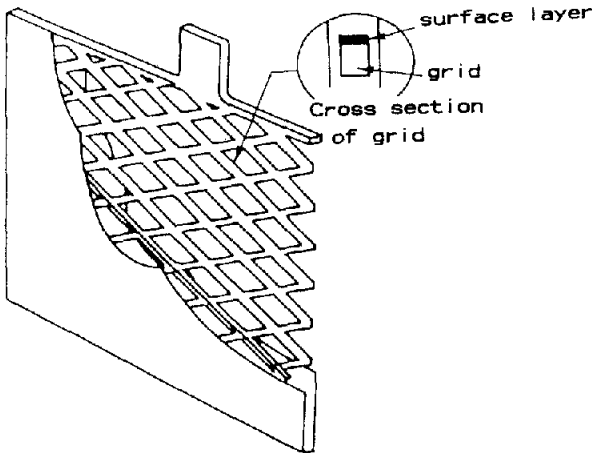


Fig. 4. Structure of grid with surface treatment.

TABLE 1

Test battery design

No. positive plates:	5
No. negative plates:	6
Separator:	polyethylene envelope
Capacity:	48 A h (C/5 rate)

- discharge: 25 A×4 min
- charge: maximum 25 A; 14.8 V/6 cells×10 min
- temperature: 75 °C in air oven
- measurement: 30 s voltage at 310 A discharge
- water consumption measured every 480 cycles
- (ii) Cycle-life test under deep discharge at high temperature
- discharge: 25 A×60 min
- charge: maximum 25 A; 14.8 V/6 cells×120 min
- temperature: 75 °C in air oven
- measurement: 30 s voltage at 310 A discharge (every 40 cycles)

Results and discussion

Investigation of alloy constitution

Figure 5 shows cross sections of grids after the overcharge test at high temperature (75 °C) with constant current. A metallic portion remained in the centre of each grid wire. A corroded layer of lead dioxide can be seen around each metallic portion. The ratio of remaining metallic area to the initial area was measured after each corrosion test and was taken as an estimate of the corrosion resistance level.

Figure 6 gives the tensile strength of the wrought sheet after ageing. The data of Figs. 5 and 6 demonstrate that addition of tin to the base alloy sheet increases both the tensile strength and the corrosion resistance of the alloy. Thus, tin is expected to reduce the shape change of the grid during high-temperature use.


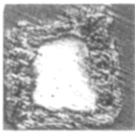

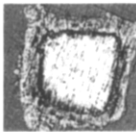


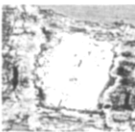


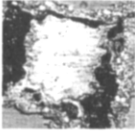
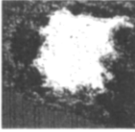
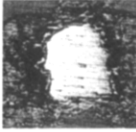
		Sn CONTENTS (%)			
		0. 30	0. 80	1. 30	1. 80
Ca CONTENTS (%)	0. 07				
		38%	52%	61%	64%
	0. 10				
		32%	44%	52%	54%
	0. 12				
		20%	37%	46%	49%

Fig. 5. Cross section of grids after constant-current overcharging at 75 °C.

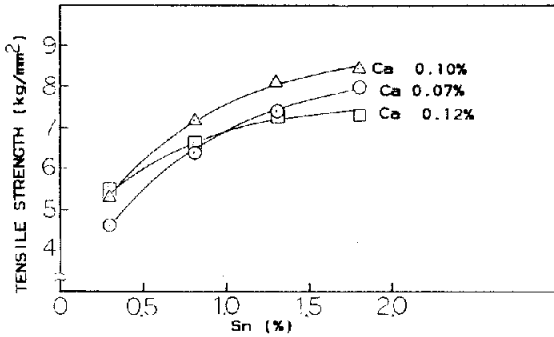


Fig. 6. Influence of tin and calcium on grid tensile strength.

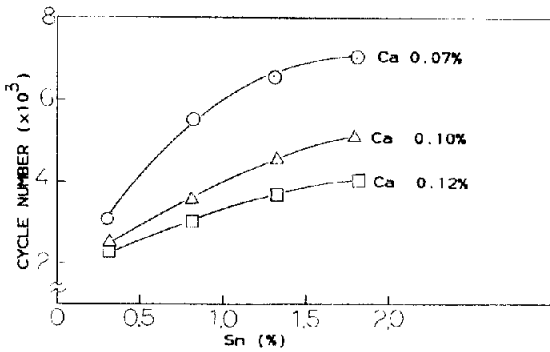


Fig. 7. Influence of tin and calcium on 75 °C SAE cycle-life performance.

With increase in the calcium content of the alloy, a corresponding decrease in corrosion resistance is observed at high temperature (Fig. 5). The cycle-life performance at 75 °C (SAE mode) with different base alloys is presented in Fig. 7. It can be seen that an increase in tin content extends life at high temperature. This is in agreement with the corrosion test results discussed above.

Effect of surface treatment with Pb-Sb-Sn alloy thin layer

The data presented in Fig. 8 demonstrate that cycle life is also prolonged by surface treatment with a thin layer of Pb-Sb-Sn alloy. The effect is particularly marked in the case of Pb-0.07wt.%Ca-1.3wt.%Sn base sheet compared with Pb-0.07%Ca-0.3wt.%Sn sheet. A microphotograph of the positive active material, is given in Fig. 9.

Shedding and aggregation of active-material particles is prevented by the antimony- and tin-rich surface layer. There was little change in grid growth with surface treatment. Figure 10 presents the change in charging potential of each plate during the SAE cycle-life test at high temperature. For hybrid and conventional batteries, the charging potential of the negative plate tended to increase due to the deposition of antimony. Calcium-type batteries with no surface-treatment layer exhibited a decrease in the potential of the negative plate because of a decrease in the specific surface area that was brought about by shrinkage at high-temperature use. As expected, the positive-

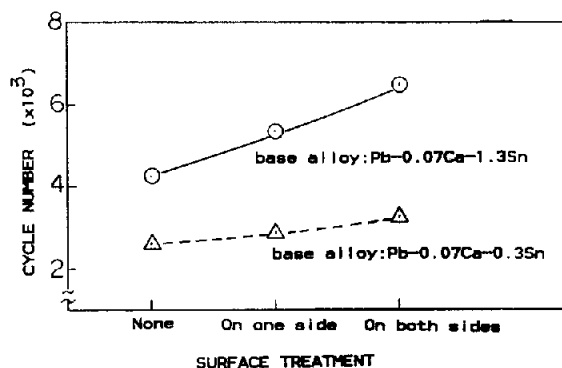


Fig. 8. Effect of surface treatment with a Pb-Sb-Sn alloy on SAE cycle-life test at 75 °C.

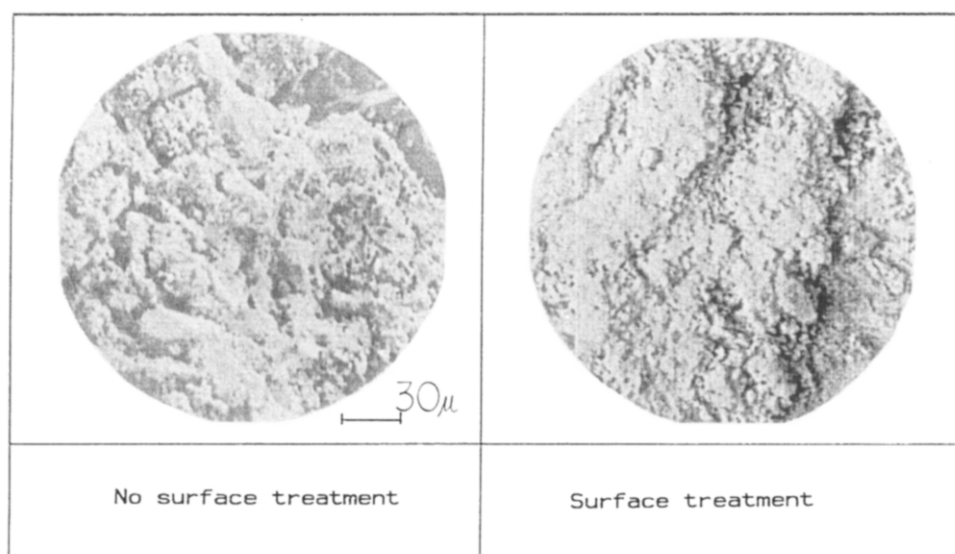


Fig. 9. Positive active material after SAE cycle-life test at 75 °C.

plate potential moved in correspondence with the negative-plate potential under constant-voltage charging.

The charge acceptance of normal calcium-type batteries tended to decrease and the maintenance-free performance of hybrid batteries tended to decrease. By contrast, calcium-type batteries with an antimony-rich surface layer did not exhibit any significant changes in potential, charge acceptance or maintenance-free characteristics. Consequently, the initial performance was maintained during high-temperature operation.

Cycle-life data obtained from the 75 °C SAE schedule are presented in Fig. 11. Water consumption by the calcium-type battery with an antimony-rich surface layer was virtually the same as that of its conventional counterpart.

As mentioned above, a very small quantity of antimony introduced into the thin surface layer may serve to connect the active materials with each other and may improve the contact with the grid. Further, the antimony may also act as potential

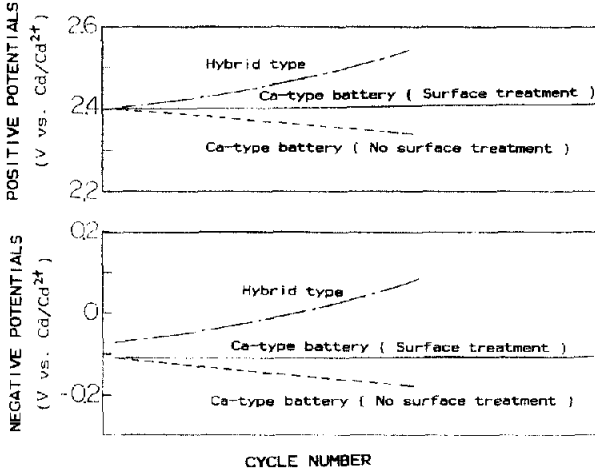


Fig. 10. Change in charging potentials during SAE cycle-life test at 75 °C.

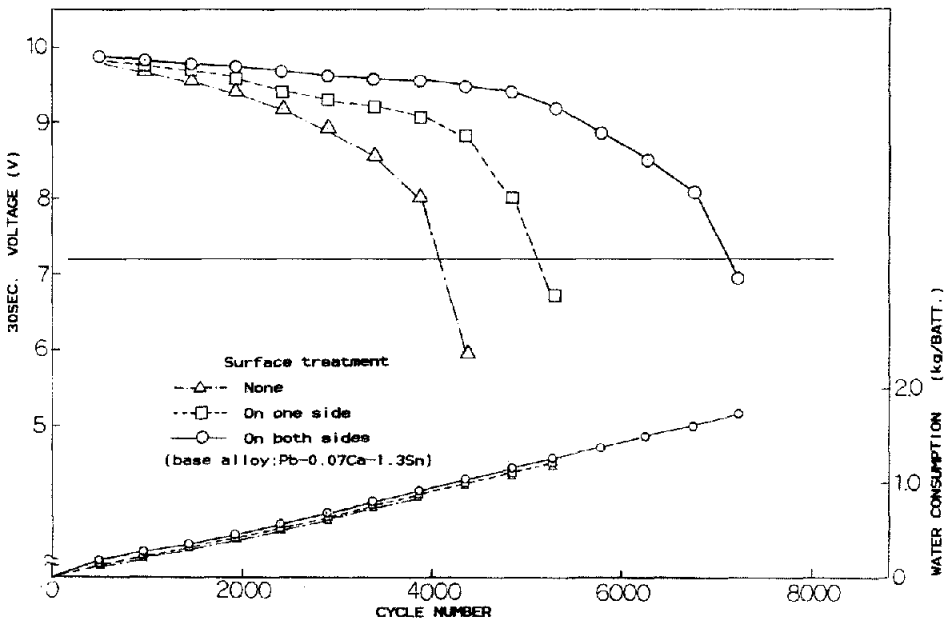


Fig. 11. Cycle life under shallow-discharge at high temperature (75 °C, SAE J240 test).

to adjust the negative plate. By contrast, tin in the base sheet alloy increases mainly the corrosion resistance and the strength of the grid. Consequently, tin prevents both elongation of the grid and the development of cracks between the grid and the active material.

Results from the deep-discharge cycle-life test at high temperature are given in Fig. 12. Clearly, performance is improved by application of the clad method.

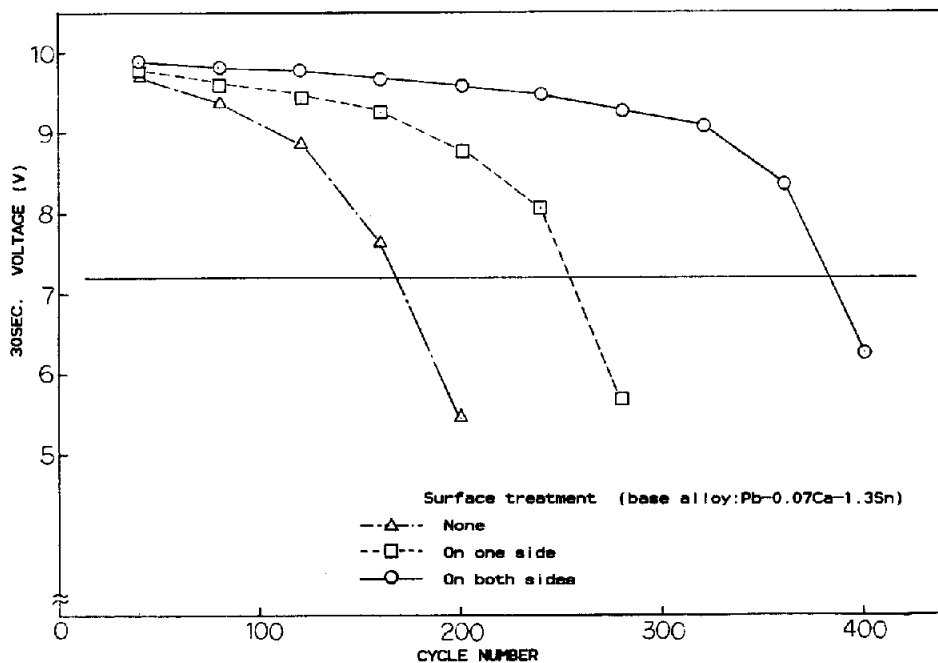


Fig. 12. Cycle life under deep discharge at high temperature.

Conclusions

Two grid technologies have been combined to improve the life characteristics of calcium-type batteries under conditions of deep discharge and/or high temperature. One approach involved application of the clad technique with an antimony-rich layer, the other involved increasing the tin content.

Antimony probably acts not only as a binder of the active-material particles but also as a potential adjuster to prevent decrease in the charge acceptance.

Addition of tin to the base sheet alloy results in good corrosion resistance and higher tensile strength of the grid. As a result, grid growth is prevented. Through a combination of these effects, the problems of deep discharge and high temperature are reduced for calcium-type batteries and the life characteristics are markedly increased.

Finally, addition of tin by either technology does not disturb the maintenance-free performance of conventional calcium-type batteries.

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