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Short communication

A new polyethylene separator for heavy-duty traction batteries

Jörg Deiters *, Werner Böhnstedt, Jürgen Boesler, Klaus Ihmels

DARAMIC LLC., Erlengang 31, D-22844 Norderstedt, Germany

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Abstract

Nowadays, polyethylene separators are the predominantly used separators in industrial lead-acid traction batteries. A new polyethylene separator called DARAMIC heavy duty, that comprises an additive, was developed as an option for heavy-duty traction applications. This new separator combines the favorable polyethylene separator characteristics with an end-of-charge voltage behavior very similar to rubber separators. In this paper, physico-chemical separator properties and battery test results are presented showing the positive effect of this new separator in terms of antimony poisoning retardation.

Keywords: Lead-acid batteries; Polyethylene separator; Antimony poisoning; End-of-charge voltage

1. Introduction

The lead-acid battery industry provides different kinds of lead-acid batteries. Dependent on their application they can be simply classified into SLI, stationary and traction batteries [1]. Each battery type has been designed for special requirements. Beside battery construction, it became generally accepted, that the separator contributes and/or even makes a difference to the performance and life of these batteries.

One particular battery type is a lead-acid traction battery for heavy-duty application. Heavy-duty batteries are defined as batteries that are discharged by about 80% of their nominal capacity day after day and this especially at elevated ambient cell temperatures. Furthermore, heavy-duty cells are used in multi-shift operation. Due to this operating pattern, heavy-duty cells might create special problems. These will be discussed in some more detail later in this paper. Nowadays, polyethylene separators are the predominantly used separators in lead-acid traction batteries. The success of the polyethylene separator is determined by its favorable characteristics, for instance it offers micro-porosity, excellent mechanical properties, excellent oxidation resistance, minimized electrical resistance and excellent processability. While for most traction batteries the polyethylene separator is an excellent choice and does not impose any restrictions on the cell, under severe heavy-duty condition a tailor made separator may be desirable.

2. Antimony poisoning

An effect that is characteristic for heavy-duty traction cells is the deterioration of the end-of-charge voltage during cycle life. Ideal would be, if the end-of-charge voltage behavior is constant during the battery service life, i.e. independent of the number of cycles. Without any detrimental substances present in the battery this might hold true for an ideal case. A typical end-of-charge voltage behavior is shown in Fig. 1 for a polyethylene separator in heavy-duty application.

Especially under heavy-duty conditions, a decline of the end-of-charge voltage is monitored with advanced cycling under certain charging conditions. The reason for the end-of-charge voltage decrease can be explained by the potential decrease of the negative electrode due to antimony poisoning.

To provide battery grids of traction cells with sufficient strength and hardness, as well as with longer cycle life by improved electrical conductivity between the grid and the positive active mass (PAM), a lead-antimony alloy with up to 8% antimony is used in the positive grid. Antimony does not completely remain inside the positive plate during the whole service life of the battery. Quite the contrary, due to corrosion antimony is released from the positive grid into the electrolyte and migrates towards the negative plate and finally the antimony ions are reduced and deposited on the negative plate as metallic antimony [2]. With an increasing antimony concentration, the

* Corresponding author. Tel.: +49 40 53596 127; fax: +49 40 53596 440.
E-mail address: jdeiters@daramic.com (J. Deiters).

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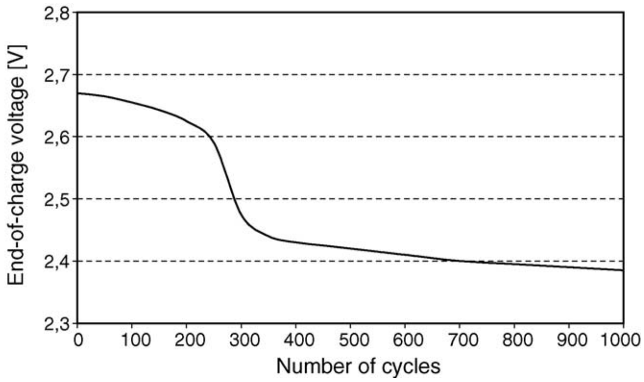

Fig. 1. Typical end-of-charge voltage trend for traction cells with polyethylene separators as a function of cycles at 55 °C at heavy-duty condition.

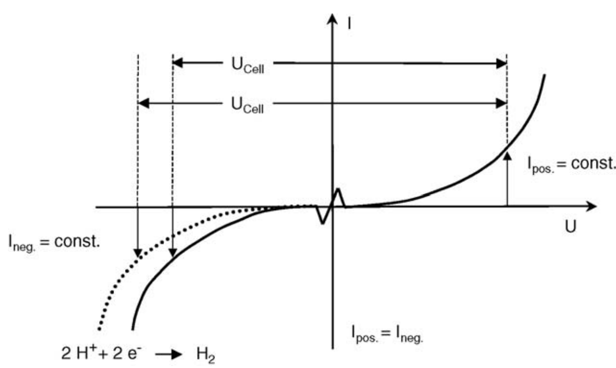

Fig. 2. In presence of the more noble antimony, the potential of the hydrogen evolution is shifted to more positive potentials causing a reduction of the hydrogen overvoltage.

current–voltage characteristic of the negative electrode is shifted to more positive potentials (Fig. 2).

Now, by charging the battery, the current can flow via the antimony, which has a significantly lower hydrogen over-voltage with regard to the decomposition of water compared to pure lead. This process, well-known as antimony poisoning, causes an increasing water consumption, because part of the charging current is consumed for hydrogen evolution instead of cell charging. Moreover, under certain charging conditions, additional heat is generated, which raises the cell temperature. Finally an incomplete charging of the battery or in worst case an early battery failure can occur.

3. Concept of a tailor-made polyethylene separator

The logical step to reduce antimony poisoning and to improve the end-of-charge voltage characteristic is therefore, either to reduce the amount of antimony in the positive grid alloy, or to modify the battery service conditions and/or to use a separator, which is able to release substances that are designed to remedy the effect of antimony deposition on the negative plate. As lead–antimony alloys in positive grids offer substantial advantages, a separator counteracting the undesirable effect of antimony poisoning would be helpful. To optimize the polyethylene separator in terms of antimony poisoning, a substance that remedies the deficiency of the antimony poisoning without deterioration of other favorable separator characteristics has to be added. Traditional rubber separators are known to significantly delay the process of antimony poisoning, but show disadvantages with respect to acid displacement, electrical resistance and processability. They are quite brittle.

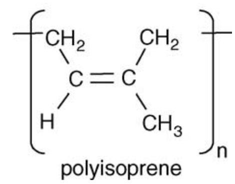

Fig. 3. Molecular chemical structure of natural rubber, i.e. *cis*-1,4-polyisoprene.

The objective of the new tailor-made polyethylene separator was to add an uncrosslinked natural rubber grade, in the optimum concentration, to the well established polyethylene separator. The molecular chemical structure of natural rubber is given in Fig. 3. Natural rubber is a *cis*-1,4-polyisoprene.

As natural rubber is available in many types, forms and grades, initial development work was conducted in laboratory scale on the pilot extruder in order to define in an efficient way at maximum benefit the best separator version. Samples were produced in the typical backweb thickness of 0.50 mm with the variation of the natural rubber grade and their concentration in the polyethylene separator. After the determination of the physico-chemical separator characteristics, the assumed optimum version has been checked on the end-of-charge voltage behavior in a battery test. The test method used to determine the end-of-charge behavior is an accelerated life cycle test performed at 55 °C. This test procedure provides a test that is intended to simulate the effect of the separator on the end-of-charge voltage at an accelerated rate.

The cells are cycled (75% discharged–IU recharged) twice a day and every 50 cycles the cells are fully recharged. Fig. 4 shows a schematic discharge–charge curve for a traction cell having a capacity of 240 Ah.

When discharging the cell for 3 h with 60 A ($1.25 \times I_5$), the cell voltage is reduced. During stage 1 of the charging step, the maximum current of 50.4 A ($I_{max} = 1.05 \times I_5$) is consumed, until the cell voltage raises to 2.4 V. During the further charge with

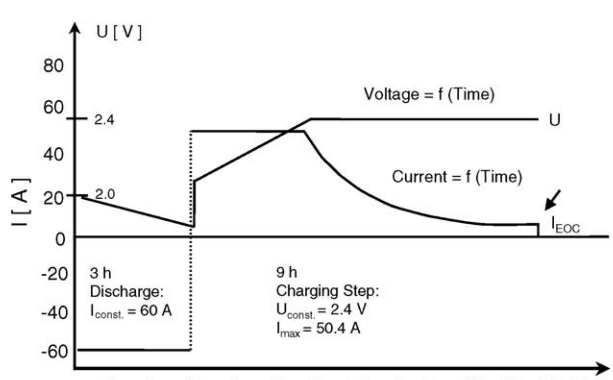

Fig. 4. Schematic discharge—charge cycle for the accelerated life cycle test performed at 55 °C with a 240 Ah traction cell (IU-characteristic); EOC = end-of-charge current.

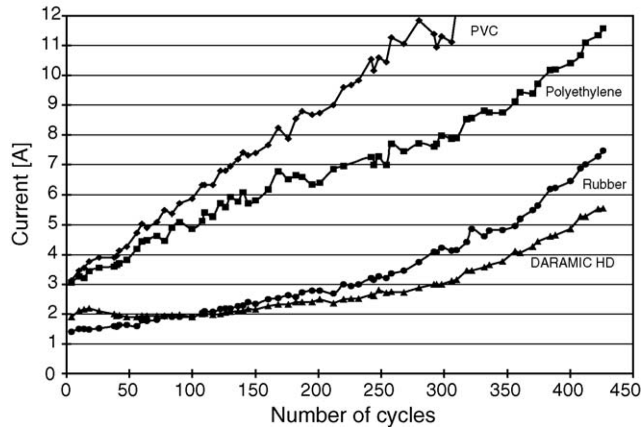

Fig. 5. End-of-charge current vs. number of cycles of DARAMIC Heavy-Duty in comparison to a number of other separators (accelerated life cycle test with DARAMIC HD pilot extruder version).

a constant voltage of 2.4 V, to prevent stibine cleaning effects, the charge current is gradually reduced. During cycling, the final charging current I_{EOC} is determined, which gives an indication of the degree of antimony poisoning of the negative electrode in the cell.

In this test the best pilot separator version has been examined in comparison to a number of other separators. A realistic comparison was possible, because only identical cells from one batch were used in the same test. Clearly, the polyethylene separator version with uncrosslinked natural rubber, now referred as PE "Heavy-Duty", is better than the polyethylene separator without additive and even comparable to the rubber separator in terms of end-of-charge current (Fig. 5). Its mechanism is based on uncrosslinked rubber components inhibiting the hydrogen evolution: While the rate of the hydrogen evolution reaction is increased by the presence of antimony on the negative plate, now the antimony sites are covered by selectively adsorbed organic molecules (released due to oxidative degradation of the uncrosslinked natural rubber) decreasing the hydrogen absorption rate and thus increasing the hydrogen overpotential [3,4]. The lead–lead sulfate reaction is not significantly affected.

With the positive results from the battery test using pilot samples, the scale-up of the PE "Heavy-Duty" product to plant production for commercial manufacturing of the subject product was performed. The key characteristics of the plant product in respect of their application as separator for traction batteries were determined. Key separator properties for the use in traction cells are chemical resistance against oxidation, adequate mechanical stability to withstand handling through assembly and the stresses met during battery life, a micro-porous structure and, last but not least, an antimony poisoning suppression effect.

The requirement for traction battery separators on oxidation stability is considerably high regarding the cell life of 1500 cycles. The oxidation stability of a polyethylene separator is most commonly tested by means of the Perox 80 test [5]. In this test, specimens are treated with hydrogen peroxide in sulfuric acid solution at 80 °C. The CMD elongation before and after specific test intervals is measured. The lower the loss of elongation as better is the oxidation stability of the separator. As shown in this test the PE "Heavy-Duty" separator matched the polyethylene separator performance, which is proven to be on a good level, because it is known to survive 1500 traction battery cycles without any issue (Fig. 6).

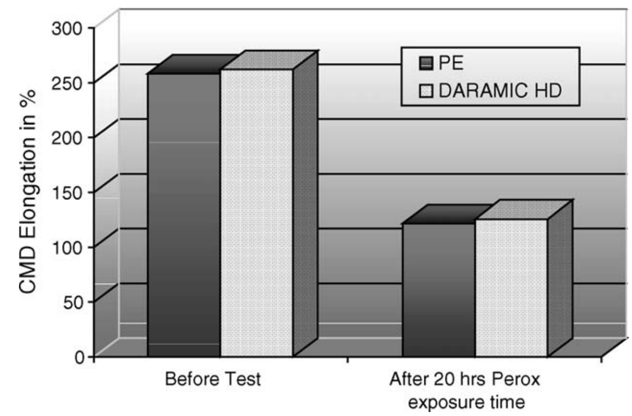

Fig. 6. Oxidation stability of DARAMIC HD determined by means of the Perox 80 test.

Table 1
Mechanical properties of DARAMIC HD

Item	Unit	PE	DARAMIC Heavy-Duty
MD elongation	%	189	194
CMD elongation	%	258	260
MD tensile strength	$N\,mm^{-2}$	8.1	7.1
CMD tensile strength	$N\,mm^{-2}$	6.4	5.4

The handling characteristic is a further important property of the polyethylene separator, e.g. for the processing with established separator manufacturing methods. This parameter is determined by the mechanical separator properties. The mechanical strength of the PE "Heavy-Duty" separator, characterized by the elongation and the tensile strength values, is fully satisfying to allow the usual handling procedure (Table 1). The PE "Heavy-Duty" should be able to withstand the rough handling during cell assembly. Furthermore, the flexibility of the PE "Heavy-Duty" allows as well the folding into sleeves.

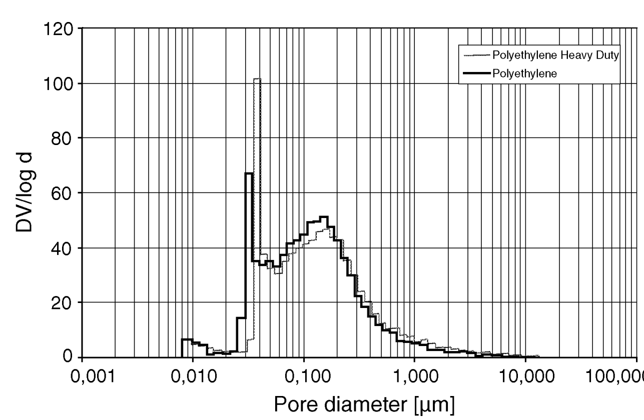

Fig. 7. Pore size distribution curve of DARAMIC HD (thin line) and industrial polyethylene (bold line) determined by means of mercury intrusion.

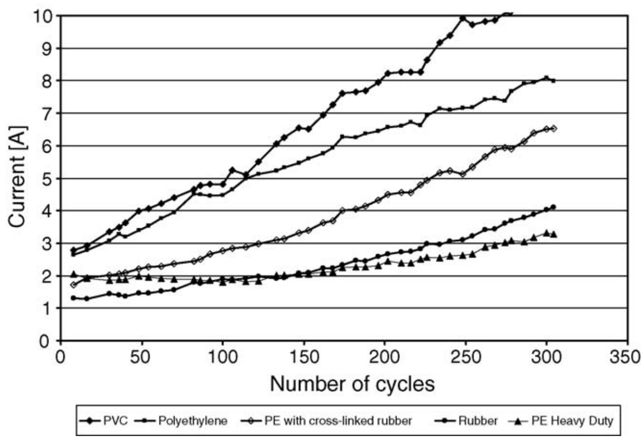

Fig. 8. End-of-charge current vs. number of cycles of DARAMIC Heavy-Duty in comparison to a number of other separators (accelerated life cycle test with DARAMIC HD plant produced version).

The micro-porous structure, with an excellent overall porosity, to allow free diffusion of electrolyte and migration of ions, has been maintained (Fig. 7). The micro-porosity is important in order not to allow shorts through the separator backweb during battery life.

Last but not least the effect of the plant produced PE "Heavy-Duty" separator on the end-of-charge voltage was also checked in the accelerated battery cycling test.

From Fig. 8, it is clearly visible, that there is a distinct ranking of the separators with respect to the antimony poisoning retardation. While the PVC separator is a non-active separator, the contribution of the separator on antimony poisoning retardation increases from polyethylene separators (without any additive) over polyethylene with cross-linked rubber additive to the rubber separator. The DARAMIC PE "Heavy-Duty" separator is again at least comparable to the rubber separator in respect to end-of-charge current.

4. Summary

The polyethylene separator with uncrosslinked rubber additive, i.e. DARAMIC PE "Heavy- Duty" is fully compatible with established separator manufacturing methods and offers a balanced spectrum of excellent mechanical and chemical stability as well as a significant reduction of antimony poisoning.

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