From leaf-type to pockets: development trends in Western Europe for automotive battery separators

Werner Böhnstedt* and Anton Weiss
Grace GmbH, Battery Separator Technical Center, Erlengang 31, P.O. Box 1480, D-2000 Norderstedt (FRG)

Abstract

During recent years, an enormous change has been taking place in Europe with respect to the construction of automotive lead/acid batteries. Whereas in 1980 almost all such batteries still used leaf separators and containers with mud spaces, nowadays already more than half of the batteries are produced with microporous polyethylene separator pockets and no mud space. Improved energy content, increased cold-cranking performance and higher productivity have all served to accelerate the introduction of new technology. Performance data for the various separation systems are compared and are based on battery test results. The superiority of pocket separation is demonstrated by excellent cold-cranking voltages as well as by significantly extended battery life under severe duty, i.e., more cycles at higher temperature. Analysis of likely development trends in the near future shows that cycling stability at elevated temperatures may attain prime importance.

Zusammenfassung

In Europa vollzieht sich in den letzten Jahren ein enormer Wandel hinsichtlich der Bauform der Blei-Säure-Starterbatterien: Während 1980 nahezu alle Starterbatterien noch mit Blattseparatoren und Gehäusen mit Schlammraum versehen waren, werden heute bereits mehr als 50% aller modernen Batterien mit mikroporösen Polyethylen-Separatorentaschen in vollausgebauten Gehäusen gefertigt. Verbesserter Energieinhalt, höhere Kaltstartleistung und gesteigerte Produktivität haben die Einführung dieser neuen Herstellungstechnologie begünstigt. Ein Vergleich der Leistungsdaten der verschiedenen Separationssysteme erfolgt anhand von Batterieprüfergebnissen: Die Überlegenheit der Taschenseparation zeigt sich in sehr guten Kaltstartspannungswerten sowie in signifikant verbesserter Lebensdauer bei stärkerer Beanspruchung, d.h. mehr Zyklen bei erhöhter Temperatur. Ein Ausblick auf die für die nähere Zukunft vorhersehbaren Entwicklungstrends bei Starterbatterien zeigt, dass insbesondere diese Zyklenfestigkeit bei erhöhter Temperatur entscheidende Bedeutung erlangen kann.

Introduction

Separators for automotive lead/acid batteries are an essential component of modern battery technology. Besides seeking a continuous improvement in the basic requirements for separators (i.e., electronic separation of electrodes of different polarity and as low

*Author to whom correspondence should be addressed.

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as possible increase in ionic resistance) increasing attention is being paid to the influence of the separators themselves upon battery manufacturing technology. During recent years, a new generation of separators for automotive batteries has been introduced, namely, the microporous polyethylene pocket. Whereas about 10 years ago, almost all automotive batteries used leaf separators and boxes with mud spaces, nowadays already more than half of all batteries are being produced with pocket separation and in containers without mud spaces. Improved energy density, higher cold-cranking performance and increased productivity have brought about this enormous change. These developments are discussed in detail in this paper.

The European battery market

An estimate of the market share of different battery types in Western Europe is presented in Fig. 1 [1, 2]. The sales value for each producer has been used as a basis for the percentages given. Thus, the total sales volume of battery systems for 1990 in Western Europe amounted to about 9000 million DM, of which lead/acid batteries alone represented about two-thirds. Other systems, which generally attract considerable interest by both research laboratories and the public, share the remainder of the sales. The latter include the well-known primary cells, nickel/cadmium batteries, numerous lithium systems, silver/zinc, mercury/zinc, and a series of other systems with minor market shares.

Within the lead/acid battery market, a differentiation can be made between automotive batteries, industrial batteries and consumer batteries. This is because, for each category, completely different types of construction and different markets have

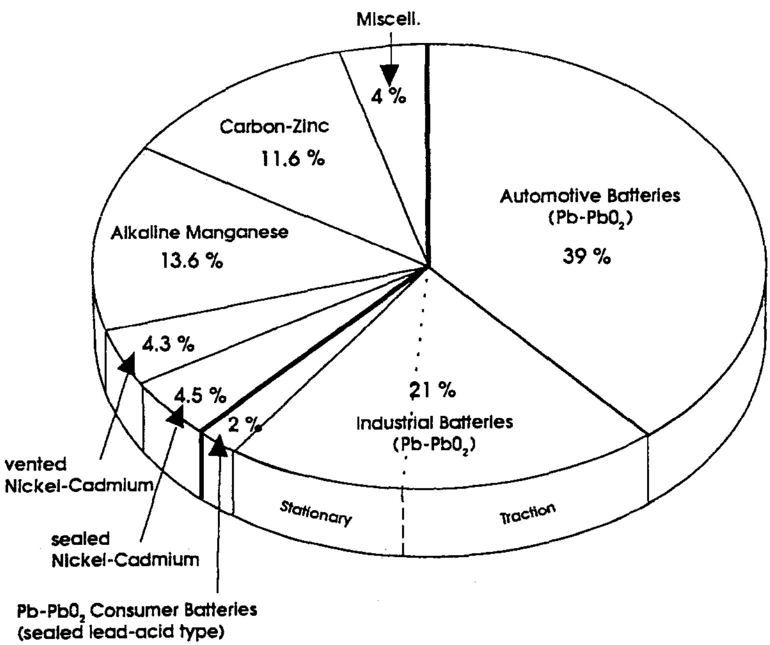

Fig. 1. Battery production in Western Europe (1990: est. 9000 million DM/5500 million US$).

developed. Of these, that for automotive batteries dominates by value; it comprises about 40% of total battery sales.

Types of automotive battery construction

The competing types of automotive battery construction are shown in Table 1. Conventional designs use plates with grids cast from lead–antimony alloys containing ~2.5 wt.% Sb and a container with a mud space. A leaf separator is employed, and can be made from a variety of suitable materials.

Construction without a mud space (in German called 'full use of box volume') allows a more intensive utilization of the available volume. In addition, about 8% more capacity and cold-cranking performance can be achieved with the same box size. Such batteries use plates with grids made either from expanded-metal lead–calcium alloys or cast lead–calcium or low-antimony alloys (i.e., Pb–1.6wt.%Sb).

For the separation system, a microporous pocket is required in order to prevent the formation of bottom shorts due to the missing mud space. To date, the only material that can reliably achieve this function is the microporous polyethylene separator. This has a structure of ultra-high molecular weight polyethylene that has been filled with silica as a pore former.

The above two types of construction presently share the automotive battery market almost equally. A third system — the starved electrolyte system — has not yet progressed beyond the development stage. In this latter design, the use of lead–calcium alloys is obligatory in order to minimize hydrogen evolution. Two possible approaches compete for facilitating the oxygen transport from the positive to the negative electrode, namely, microfibre glass fleece and gelled electrolyte. Both technologies — mainly for cost reasons — have not yet secured market shares in the automotive battery business. Nevertheless, such batteries are attracting considerable attention in development laboratories.

Separator market shares

The various battery construction types are reflected in the market shares for the different separator systems. Figure 2 clearly illustrates the rapid conversion of battery separation to microporous polyethylene pockets. In less than one decade — between 1980 and 1990 — pocket-designs have taken over more than half of the market in Western Europe, despite the need to introduce new manufacturing technologies. Suitable machines have been developed and introduced for enveloping the plates. Figure 3 shows a schematic of the construction of a pocketing machine. Besides an increased reliability in the production process, experience has shown that the scrap rate can be lowered considerably due to the pocket-type construction. The overall increase in productivity has also been combined with a significant improvement in electrical performance.

Performance comparison

The characteristics of leaf and microporous pocket separators for automotive batteries are compared in Table 2. The separator properties (rows 1 to 4) have to

TABLE 1

Competing separator systems for automotive batteries

Conventional construction	Cast grid electrodes, i.e., Pb–2.5wt.%Sb Leaf-type separator	Sinter-PVC separator α-Cellulose-phenolic resin separator (i.e., ARMORIB-A) Linters-cell.-phenolic resin separator (i.e., ARMORIB-L) L.-cell./glassfibre-phenolic resin separator (i.e., DARAK 101) Glass separator (i.e. HYALITE) Phenolic resin resorcinol separator (i.e., DARAK 2000)
Construction without mud space	Pb–1.6wt.%Sb or Pb–Ca (cast) or Pb-Ca (expanded) metal electrodes Microporous pocket separator	Microporous polyethylene pocket separator (i.e., DARAMIC 250)
Starved electrolyte system	Pb–Ca (cast or expanded metal electrodes) Absorbed or gelled electrolyte	Microfibre glassfleece (i.e., SEALYTE) Gelled electrolyte with microporous separator (i.e., DARAK 2000 GM)

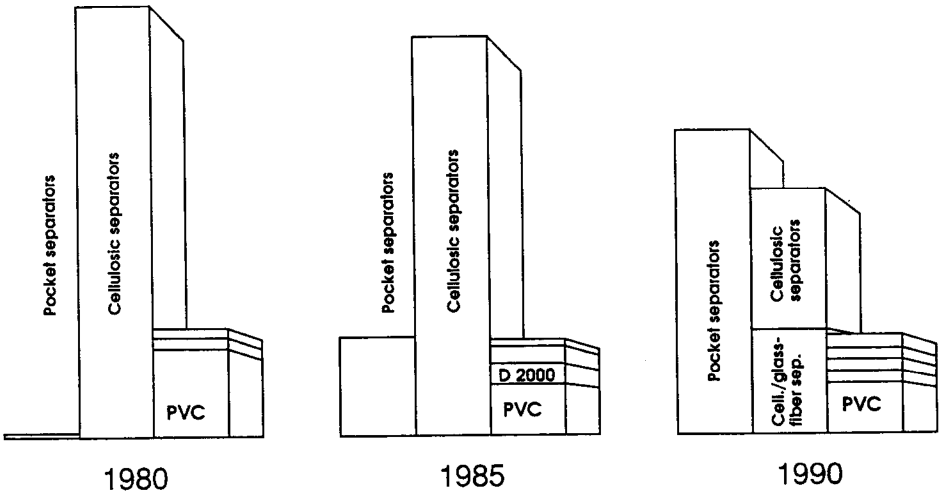

Fig. 2. Automotive battery separators: market shares.

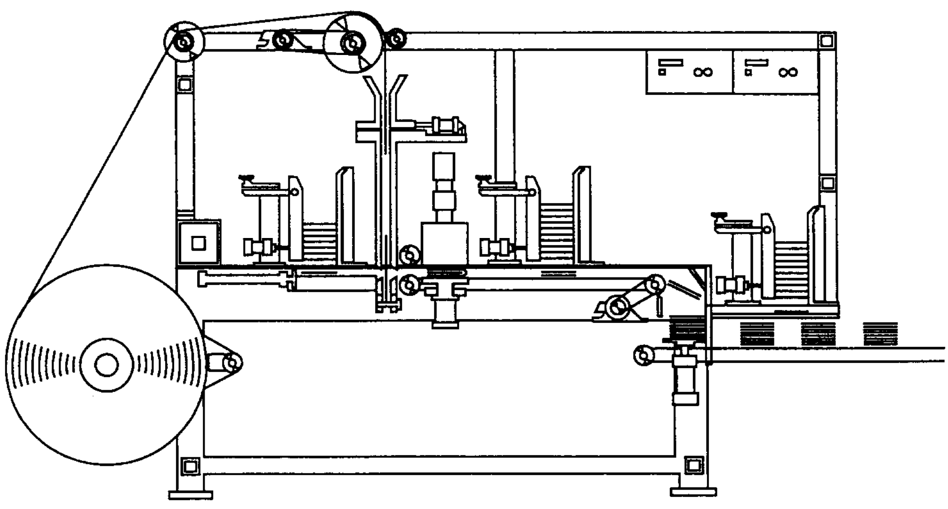

Fig. 3. Enveloping machine: basic principles.

be confirmed by electrical data obtained from battery tests (rows 5 to 8). The cold-cranking voltage is sufficient for all separation systems to meet the usual standards. Mixed cellulose/glass-fibre systems, all-glass separators, phenolic resin/resorcinol separators and polyethylene separators all present significant advantages. The latter often provide the only way to meet reliably the test criteria required for high-performance batteries.

The cycle life of an automotive battery (as defined according to DIN 43 539-02) is not, or only to a small degree, affected by the separator. Experience has shown that all batteries with modern standard separators not only achieve the required 5

TABLE 2

Properties of separators for automotive batteries

	Sinter-PVC separators	α-Cellulosic separators	Linters-cell./glassfibre separators	Glassfibre separators	Phenolic resin/resorcinol separators	Polyethylene/SiO_2-pocket separators
1 Backweb thickness (mm)	0.3	0.6	0.5	0.5	0.4	0.25
2 Pore size (average) (μm)	15	25	25	25	0.5	0.1
3 Acid displacement (1.3 mm) (ml/m^2)	230	180	150	100	150	130
4 Electrical resistance (Ω cm^2)	0.16	0.15–0.20	0.10	0.06	0.09	0.06
Test results (DIN 43 539-02) with PbSb 2.5 electrodes						
5 Voltage (−18 °C, 30 s) (V)	9.20	9.10–9.25	9.35	9.45	9.35	9.45
6 Cycle-life test (weeks)	> 10	> 10	> 10	> 10	> 10	> 10
7 Accelerated cycle-life test (DIN 43 539 E-1980) (weeks)	5	6	6	6	8	> 10
8 Water consumption (g/A h)	6	3–5	3	6	4	3–6

weeks of cycle life, but may also give 10 or more weeks. Battery failure is typically due to corrosion of the positive grids.

In order to learn more about the effects of separators on battery life, a battery test according to the previous DIN draft is recommended. Figure 4 provides a comparison of the two test regimes. The recommended test simulates a more severe cycling service at elevated temperature as this will probably be required in the future. Under such test conditions, significant differences appear between the different types of separation. For example, the macroporous separators (mean pore size about 15 to 25 μm), such as PVC, cellulosic or glass-fibre separators, are just able to meet the required minimum of life performance. By contrast, the phenolic resin/resorcinol system provides noticeably better results; the microporous pore structure prevents penetration through the separator leaf but bottom shorts and side or top mossing eventually terminate the cycle life. Without doubt, the polyethylene pocket is the best choice. This design prevents not only penetration through the separator but also bottom shorts and side mossing, and to such an extent that even during the more severe cycle-life test the separation is no longer the limiting factor.

Surprisingly, the water consumption of a lead/antimony automotive battery depends on the type of separator used. Some cellulosic types as well as purpose-designed polyethylene separators are able to bring about significant reductions in water consumption. The electrochemical processes of importance in this respect are very complex and a detailed discussion would exceed the limits of this overview. In brief, separator systems that reduce water loss continuously release special organic molecules, such as aromatic aldehydes, that can be selectively adsorbed at the antimony sites on the negative plates and thus can inhibit the catalytic effect of antimony on hydrogen evolution [3–5].

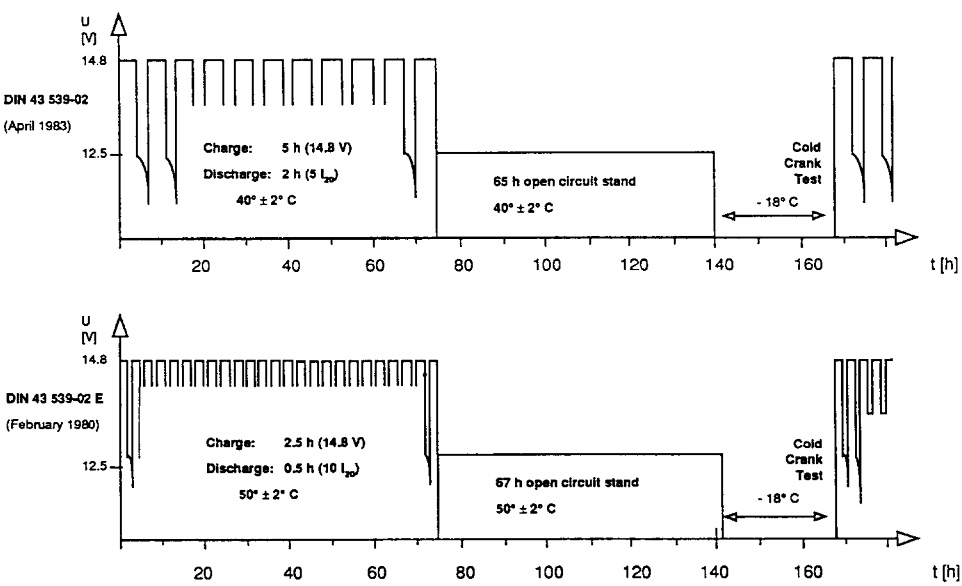

Fig. 4. Weekly cycle of DIN 43 539-02 and DIN 43 539-02E cycle-life tests.

TABLE 3

Development trends to 1995 for automotive batteries [2, 6]

System	$Pb/H_2SO_4/PbO_2$ – unchanged
Voltage	12 V – unchanged
Capacity	+10% } at the same weight and volume
Cold-cranking power	+10% } at the same weight and volume
Temperature	up to 65 °C
Cycle life	up to +50%
Charge acceptance	improved
2-Battery-concept	occasionally
Maintenance-free	all batteries
Life expectancy	5 years – unchanged

Outlook

Trends in the design of automotive batteries until 1995 are forecast in Table 3. Clearly, the lead/acid battery will continue to be the only suitable system to meet the electrical requirements of vehicles powered by internal combustion engines, both technically and economically. The nominal voltage is expected to remain at 12 V, but requirements for capacity and cold-cranking performance may increase by 10% for the same battery weight and volume.

As engine bonnets are continually lowered – to provide vehicle bodies with greater aerodynamical efficiency – battery temperatures will increase up to 65 °C. This will place additional demands on the corrosion resistance of the plates and on the temperature stability of the organic components i.e., negative-plate expanders, as well as of the separators.

The largest change is to be expected in considerably higher demands on the cycling stability of automotive batteries resulting from increased electrical loads for equal battery weight or volume. In this respect, charge-acceptance performance, especially at low temperatures, will grow in importance.

Finally, it is clear that all batteries have to be maintenance-free. A debate has started on the advantages and disadvantages of 'theoretically' maintenance-free batteries versus the present 'practically' maintenance-free units. It appears that the cost–benefit ratio will be the decisive factor.

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