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Journal of Power Sources 59 (1996) 45–50

JOURNAL OF POWER SOURCES

Automotive lead/acid battery separators: a global overview

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Received 4 September 1995; accepted 13 November 1995

Abstract

This paper describes the present status and the future trends for separators for automotive lead/acid batteries. During the past decade, the design of modern automotive batteries has undergone a fundamental change. Whereas in 1980 almost all batteries used leaf separators, nowadays already two-thirds of the batteries produced worldwide have microporous polyethylene pocket separators. The extent of this conversion is quantified for the geographical regions. The impetus behind the change, as well as the future development trends, are outlined.

Keywords: Battery separators; Lead/acid batteries; Construction principles; Market shares; Development trends

1. Introduction

The technology of lead/acid battery separators is undergoing a radical change. Globally, it is in the middle of the conversion from conventional leaf to modern pocketing separation. Obviously, the transition is in different stages of progress in the various geographical regions, with consequential effects on the local battery industries. The separators and their basic properties are examined in this paper, as well as the different construction types of automotive batteries with their advantages and disadvantages, in order to illustrate the causes of, and the impetus behind, this change in separator technology. The extent of the change is quantified for combined geographical regions. Finally, lessons to be learned for the developments ahead are presented as a guideline for further advances in the immediate future.

2. Basic functions of the separator

In simple terms, the separator has to meet two requirements simultaneously which, at first glance, appear to be contradictory. On one hand, the separator has to prevent electronic current flow between electrodes of opposite polarity — and this feature must be provided reliably in a highly chemically-aggressive environment — and, on the other hand, the separators must allow an unhindered and free flow of ionic current between the electrodes in order to close the circuit inside the battery. This apparent contradiction can only be resolved by a compromise, namely, a porous non-conductor.

2.1. Electronic non-conductor

The demand for electronic insulation is, as indicated by its name, the original reason for the separator. Most simply, this can be achieved by enveloping the electrodes completely in material that is stable towards both acid and oxidation. Minimum possible hindrance to the ionic current flow through this insulating barrier has to be met simultaneously. The required structure is highly porous and creates large internal surfaces within the separation material, which inevitably results in increased vulnerability to chemical attack. The resistance against medium-strength sulfuric acid, nascent oxygen or other chemical oxidation agents formed in the storage battery (and this over a temperature range of −40 to +100 °C) can be assured by only a few substances for the necessary periods. These periods can easily be ten years or more!

An additional demand on the electronic insulator is the maintenance of the distance between the electrodes. This is necessary to counteract external vibratory influences during the battery service, and to assure a sufficient supply of acid to the electrodes. In the lead/acid cell — contrary to the nickel/cadmium cell, for instance — the electrolyte is part of the electrochemical reaction. Thus, a uniform supply of acid has to be maintained for optimum efficiency of the active material.

It is advantageous to achieve the electronic insulation by a thin film, made of highly porous, insulating material and fitted with ribs to maintain inter-electrode distance (Fig. 1). Moreover, this has the added benefit of securing a maximum distance between the origin of the oxidizing substances at the

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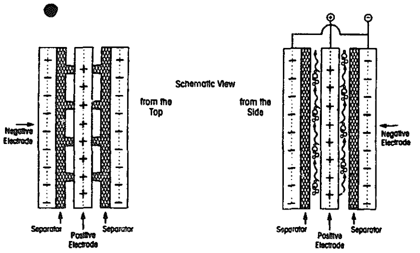

Fig. 1. Separator insertion in lead/acid batteries.

positive electrode and the sensitive, highly porous, high inner surface, separator.

The pores of the separator film should be of minimum size and of uniform distribution. A distinction can be made between macroporous and microporous separators; the latter have to show pore sizes below 1 μm. This is necessary in order to prevent lead particles (typically, 1 to 5 μm diameter) that are washed out of the electrodes from depositing inside the pores and initiating electronic shorts.

The requirements for the size and the homogeneous distribution of the pores become even more stringent with decreasing thickness of the separator film. The risk of faults (so-called 'pin holes') that can, for instance, be caused by bubble inclusion during the production process, will also increase as the separator backweb becomes thinner.

2.2. *Electric (ion flow) resistance*

The theoretically derived formula for the electrical resistance of a separator, R_{sep}, is as follows:

$$R_{\text{sep}}=R_{\text{el}}\left(\frac{T^2}{P}-1\right) \tag{1}$$

where R_{el} is the electrical resistance of the electrolyte (area, A, and thickness, d), $R_{\text{el}}=d/\sigma A$, T the tortuosity ($T=l/d$), P the porosity, and σ the electrolytic conductivity.

This formula demonstrates the need to minimize the thickness of the separator film, the so-called 'backweb' thickness, and to adjust the desired total thickness of the separator by the applied ribs. The thickness of the separator film contributes to the electrical resistance of the separator.

The tortuosity, T, is a measure of the detour that an ion is forced to take in comparison with the straight path from the positive to the negative electrode, or vice versa. According to experience gained with plastic bodies that consist essentially of spherical, cohering particles with voids in between, the tortuosity has a value of 1.3. Of course, the tortuosity approaches a value of 1 at high porosities. Because of the increasing danger of direct electronic microshorts developing through lead deposits, extreme porosities have to be approached carefully.

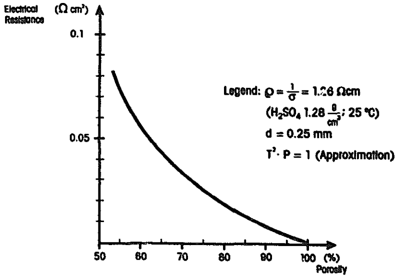

Fig. 2. Electrical resistance of a separator as a function of porosity.

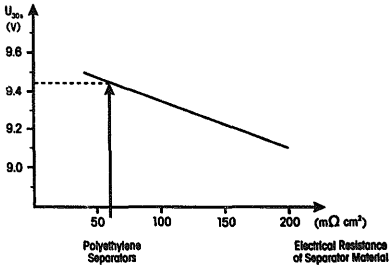

Fig. 3. Cold-cranking voltage according to DIN 43 539-02.

The porosity, the ratio of void volume to total geometric volume, should be as high as possible without sacrificing mechanical stability. Porosities are typically about 60%. The theoretical dependence of the electric resistance as function of porosity is shown in Fig. 2.

The electric resistance of the separator should not be overestimated. It contributes only a small (additive) share to the total resistance of an automotive battery, which consists of: (i) the electronic internal resistances of the conductive parts, such as posts, connectors, lugs, grids and active-mass particles; (ii) the transition resistance at the active-mass/electrolyte interface; (iii) the electric resistance of the electrolyte, and (iv) the electric resistance of the separator itself.

During the cold-cranking testing of automotive batteries, the separator contributes only about 5% of the total resistance. Even assuming the development of a totally resistance-free separator, the cold-cranking voltage for an otherwise identical construction would increase by only 0.2 V from 9.4 to 9.6 V, cf., Fig. 3.

2.3. *Handling properties*

The handling characteristic is an important property of a separator. This parameter is often underestimated, probably because it can only be poorly defined in physical terms without ambiguity. The above-mentioned desire for separation

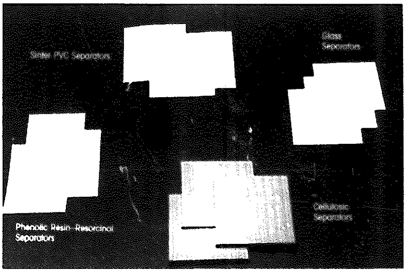

Fig. 4. Leaf-type separators.

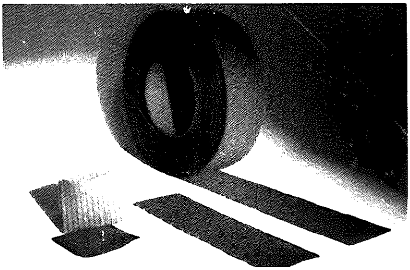

Fig. 5. Polyethylene pocket separators.

films with extremely small thicknesses finds its limitation here. Depending on the type of separator processing, either a certain separator stiffness or a certain flexibility are the alternatives. The conventional leaf-type separator requires a minimum stiffness in order to push a single cut-piece separator between two electrodes of opposite polarity and to align it there without corner breaking or folding. Since the cube of thickness (in this case, the backweb thickness) determines the stiffness of a body, a backweb thickness of at least 0.4 mm (typically, however, 0.5 to 0.6 mm) has been found necessary to withstand the rough handling during cell assembly (Fig. 4).

The modern pocketing technology for automotive batteries, however, calls for flexible and tear-resistant material (Fig. 5). In today's market, the best filled polyethylene separators have a backweb thickness of 0.2 to 0.25 mm, but there are significant development trends towards even lower values. These will be considered later.

3. Construction of automotive batteries

From the viewpoint of the separator producer, two types of automotive battery construction compete with each other: the conventional one with leaf separation and the modern one with pocket separation [1–3].

The conventional construction uses stiff separators, i.e., leaf separators made, for instance, from sintered poly(vinyl chloride) (PVC) or from phenolic resin impregnated cellulosic or glass papers, to which ribs of thermoplastic material are applied to achieve the desired total thickness. These stiff separators are placed by automatic stacking machines between two electrodes of opposite polarity, with the ribs directed towards the positive plate, and, finally, the group is aligned. This is a tough performance test for the separator edge!

The stacked electrode groups, still frequently with grid antimony contents of 1.6 to 2.5 wt.% in order to reach rapidly the hardness for further processing, are pushed into the battery containers. The groups rest on bottom spacers to leave room for sedimenting lead particles to collect and prevent premature bottom shorts (Fig. 6).

A unique version of leaf separation merits a special mention, namely, the Japanese version with separators of paper from organic fibres, without ribs, which are provided with a heavy glass mat that is sufficiently thick to reach the desired total thickness (Fig. 7). This expensive version of a leaf separator offers the advantage of improving the retention of positive active material inside the electrode grid, compared with systems without glass mat. Thus, such a porous positive active-material has been adopted in Japan that, without this

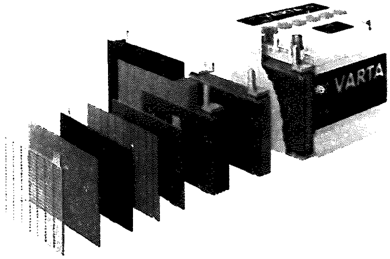

Fig. 6. Automotive batteries: conventional construction with leaf-type separators.

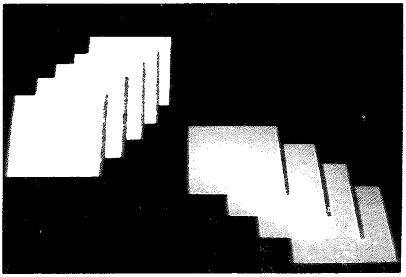

Fig. 7. Japanese separators.

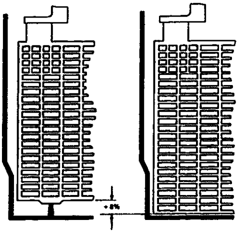

Fig. 8. Design detail: conventional vs. pocket battery. (Courtesy: VARTA Batterie AG.)

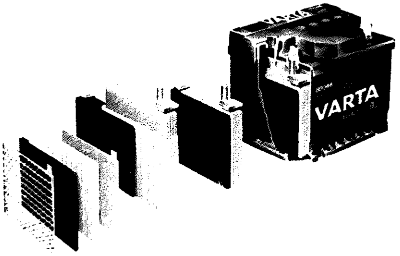

Fig. 9. Automotive battery: envelope construction with polyethylene pockets.

glass mat, would lead to premature loss of capacity and shorts. The expensive separation system has been balanced by cost advantages from using less positive active material.

Starting around 1975, and originating in the USA, a new separation system gained acceptance. viz., the microporous pocket. The following three advantages have determined the success of this product:

1. The cell construction has no mud space and, thereby, allows more effective use of the space available; about 8% more capacity and cold-cranking performance can be packed into the same container size (Fig. 8).
2. The use of low-antimony or lead–calcium alloys, and the consequent increased shedding, requires a pocket separator. The latter not only protects the three sides against shorts, but also prevents a direct penetration by virtue of its microporosity. To date, only one material, the microporous polyethylene pocket separator, has been able to meet this requirement reliably (Fig. 9).
3. The experience in producing pocketed batteries has proven that this construction reduces significantly the number of early battery failures, e.g. due to broken or completely missing separators, and thus has allowed improvements not only in cost, but also in quality.

The above construction types comprise almost all of the automotive battery market. Nevertheless, one fundamentally different system should not be overlooked, namely, the sealed automotive battery with internal oxygen consumption. This is often, and slightly misleadingly, called a recombination battery. To date, this type of construction has not yet gained acceptance in the automotive battery market, less for technical reasons, but mainly for cost reasons. The sealed lead/acid battery uses lead–calcium alloys to minimize the development of hydrogen. The oxygen evolved during charging diffuses through the highly porous glass microfibre fleece in order to be reduced again at the negative electrode (Fig. 10). Viewed externally, the total overcharge current is thus converted into heat. No significant water loss occurs and this is certainly a desirable feature. Also, the complete absorption of the electrolyte by the glass microfibre fleece provides desired leak-proofness. Nevertheless, high production costs and performance problems under the arduous day-to-day service in cars (that involves widely varying operating conditions) have prevented this sealed construction from breaking through into the present market.

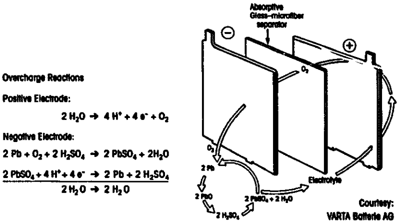

Fig. 10. Internal oxygen consumption.

4. Market shares of different separator systems

As stated earlier, since about 1975, starting in the USA, remarkable change has taken place in the separator technology used for automotive batteries. Whereas, up to then, nearly all batteries were equipped with leaf separation and containers with mud spaces, today already almost 70% of all automotive batteries worldwide are built with microporous polyethylene separator pockets in boxes without mud spaces. This is all the more noteworthy, since it has required the introduction of new manufacturing technologies, e.g., suitable pocketing machines have had to be developed and integrated into the manufacturing process (Table 1).

Improved energy content, increased cold-cranking performance and higher productivity have driven this conversion to the extent that conventional leaf separators are on the retreat everywhere. Sintered PVC separators, because of their good resistance against increased temperatures and vibration effects, are still popular in warm climates: often, their low price is a decisive fact. Cellulosic and glass separators, favoured because of their balanced property spectrum and ready processability, continue to be used in the replacement battery market, especially in regions with moderate climates.

Table 1
Automotive lead/acid batteries 1995: estimate millions of batteries [a]

	Polyethylene pocket separators	Sinter-PVC/rubber leaf separators	Cellulosic/glass leaf separators	Synthetic pulp-glass mat separators	Sealed lead/acid automotive batteries	Total
USA/Canada	91.9	1.8	1.2		0.1	95.0
Europe	44.0	19.0	8.2		0.1	71.3
Asia–Pacific	21.6	18.6	8.0	16.2	0.3	64.7
Latin America	15.7	2.0	8.0			25.7
Total	173.5	41.4	25.4	16.2	0.5	256.7
(%)	67.5	16.1	9.9	6.3	0.2	100.0

[a] Based on: BCI statistics, EUROBAT statistics, DARAMIC, Inc. estimates.

Table 2
Polyethylene pocket-separated automotive batteries: 1995 vs. 2000 (millions of batteries)

	1995			2000		
	Total	PE pockets	(%)	Total	PE pockets	(%)
USA/Canada	95.0	91.9	96.7	110.1	107.9	98.0
Europe	71.3	44.0	61.7	82.6	62.0	75.0
Asia–Pacific	64.7	21.6	33.4	86.6	60.6	70.0
Latin America	25.7	15.7	61.1	31.3	23.5	75.0
Total	256.7	173.2	67.5	310.6	254.0	81.8

The peculiarities of the Japanese type of automotive battery construction, with its rather porous positive active-material and glass-mat reinforced separators of synthetic paper, have been noted above.

Despite its undisputed advantages, the sealed construction with its internal oxygen consumption, where the electrolyte is either absorbed in a glass microfibre fleece or is formed into a gel with highly dispersed fumed silica, has not yet gained wide acceptance. This is primarily because of the higher cost.

Considering the extent of conversion to microporous polyethylene pockets in the various geographical areas, the trend becomes obvious, despite the levelling effect of sampling whole continents: the conversion that started twenty years ago in the USA has been virtually completed there. Both in Europe (where the introduction of polyethylene pockets commenced in the early 1980s) and in Latin America, currently about 60% of all automotive batteries are built with pocket separators. In the Asia–Pacific region — in the individual countries however very different advanced — the process is still in the early stages; a development similar to that witnessed in the USA and in Europe is expected in the coming years.

A forecast that includes the market growth in the year 2000 is given in Table 2. The data predict an enormous growth rate for this market segment. This will be accommodated by manufacturers of micorporous polyethylene through expansions and new installations.

5. Technological trends in separators for automotive batteries

As discussed above, the microporous polyethylene pocket separator has reached the leading position worldwide. There is no alternative separation system visible on the horizon that might contest this standing within the next few years. Therefore, what are the foreseeable development trends for the microporous polyethylene pocket separator?

Future trends have to be seen in connection with future demands on automotive batteries. Here, it is generally assumed that higher ambient temperatures under the hood, increased cycling loads and greater manufacturing productivity will form the focus for development work also in the years to come [3]. Translated into a requirement profile for the separator, this means: (i) increased oxidation stability, especially at higher temperatures; (ii) further improved puncture strength for trouble-free use in combination with expanded metal grids, and (iii) the lowest possible backweb thickness in order to become even more cost-competitive. The leading separator manufacturers are working intensely in these areas and the first results have been presented to the market. In some cases, the products have been given the names of exotic animals or, more prosaically, they are termed 'high-performance' separators [4,5].

Common to these developments is the goal that oxidation stability and puncture strength are to be increased further by optimum formulation and gentle manufacturing processes, or at least maintained at the existing level, when reducing the separator backweb thickness. Going to thinner backwebs could be limited by difficulties in processing this material. Intelligent solutions continue to be explored: a new generation of pocketing machines could also be an option.

6. Outlook

There is no doubt that the lead/acid battery will also continue, to the year 2000 and beyond, to be the only suitable system, both technically and economically, to meet the electrical requirements of starting a combustion-engined automobiles.

For aerodynamic reasons, the temperature under the hood will continue to rise and this will place further demands on the batteries and, thus, also on the separators, with respect to temperature stability and, especially, to oxidation stability at these temperatures.

The ongoing and ever-increasing pressure to cut costs demands efficient processing of separators. This can only be achieved by a further harmonization of separator properties with the requirements of the pocketing machines, as well as increased puncture strength to utilize the cost advantages of expanded metal grids to the fullest.

Finally, it is obvious that the automotive battery has to be maintenance free. Whether this will be achieved 'theoretically' via internal oxygen consumption, or 'practically' via a sufficient supply of liquid (as is the case today), only the future will tell.

Whatever direction battery development will take, the separator manufacturers will continue to contribute to the progress of the total system.

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