

Microporous polyethylene separators — today and tomorrow Separator development trends for modern automotive batteries

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Abstract

During the past decade, the design of modern automotive batteries has undergone a fundamental change. The introduction of microporous polyethylene pocket separators has resulted in an approximately 8% better volume utilization. Besides increasing the energy density, the polyethylene envelope has enabled an improvement in cold-cranking performance and has raised the production efficiency. A first failure-mode analysis of pocket-separated automotive batteries in Europe with respect to leaf separation is presented. For comparable service life, a shift in failure mode has been found. Although corrosion of the positive electrode still dominates, a significant increase in positive active-material shedding is noted. This is certainly a consequence of the general trend towards lower antimony contents. Shorting through the separator is only found in cases of severe battery mistreatment. This positive, intermediary result is supplemented by an outlook on emerging development trends. Future automotive batteries will experience elevated operating temperatures, higher cycling loads, and maintenance freedom. Battery tests at temperatures up to 75 °C with various alloy combinations show that the hybrid design is best suited to meet the expected requirements. Microporous polyethylene pocket separation is not expected to be a limiting factor; the trend to lower antimony alloy content and increased cycling load will demonstrate the advantage of this separation even more clearly than in the past. Optimization of the already achieved, balanced separator characteristics profile with the reference parameters of electrical performance, water loss, durability and machinability will stimulate further development work.

Zusammenfassung

Im letzten Jahrzehnt hat sich in Europa die Bauweise moderner Starterbatterien grundlegend verändert. Durch die Einführung von mikroporösen Polyethylentaschenseparatoren im Vergleich zur früheren Blattseparation ist eine um etwa 8% verbesserte Nutzung des zur Verfügung stehenden Raumes erreicht worden. Neben dieser Erhöhung der Energiedichte sind ein besseres Kaltstartverhalten und zusätzlich eine erhöhte Produktivität in der Fertigung ermöglicht worden. Eine erste Ausfallursachenanalyse für taschenseparierte Starterbatterien in Europa im Vergleich zur Blattseparation wird vorgestellt. Bei vergleichbarer Lebensdauer wird eine Verschiebung der Ausfallursachen festgestellt: Neben der weiterhin dominierenden Korrosion der positiven Elektroden wird weitaus häufiger ein Abschlammen derselben registriert, was sicherlich als Folge des parallel verlaufenden Trends zu niedrigen Antimongehalten begründet ist. Kurzschlüsse durch den Separator können nur als Folge gravierender Fehlbehandlung gefunden werden. Diese positive Zwischenbilanz wird ergänzt durch einen Ausblick auf die sich abzeichnenden Entwicklungstendenzen. Deutlich vor-

hersehbar sind für zukünftige Starterbatterien höhere Umgebungstemperaturen, verstärkte Zyklenbelastung und Wartungsfreiheit. Durch Batterieprüfungen bei erhöhten Temperaturen bis zu 75 °C mit verschiedenen Legierungskombinationen konnte gezeigt werden, daß die Hybridbauweise den zu erwartenden Anforderungen am besten gerecht werden dürfte. Die mikroporöse Polyethylentaschenseparation stellt vorhersehbar keine Begrenzung dar; der Trend zu geringeren Antimongehalten der Legierungen und die höhere Zyklenbeanspruchung wird ihre Vorteile noch deutlicher als bisher aufzeigen. Eine weitere Optimierung des bisher schon erreichten, ausgewogenen Eigenschaftsprofils mit den Eckpunkten elektrische Eigenschaften, Wasserverbrauch, Haltbarkeit und Verarbeitbarkeit wird die zukünftige Entwicklungsarbeit kennzeichnen.

Introduction

In recent years, the design of automotive batteries in Europe has undergone an enormous change. Whereas, in 1980, almost all batteries were still being built with mud spaces and leaf separation, nowadays more than half of all automotive batteries are being produced without mud spaces and with microporous polyethylene separator pockets. The advantages of this construction are well known, namely, increased energy density, improved cold-cranking performance, and increased productivity in assembly.

Status

After several years of experience with pocket batteries, now appears to be the time to evaluate how well such batteries have proven themselves in the field. One point has to be stated from the outset: no problems with regard to electric performance have been noted, nor has an increase in premature failures been reported. To verify this statement, a larger number of failed, pocketed batteries has been investigated in our laboratory during the past year and the results have been compared with previous studies of failure modes [1, 2].

Even though these analyses are not yet fully completed, some conclusions can be drawn (Table 1). A statistically-significant difference in battery life could not be detected; the average life expectancy for both pocketed and leaf-separated batteries is 4 to 5 years.

For the sake of failure mode comparison, the results of column 1 in Table 1 have been adjusted for the asymmetric total envelope batteries population in column 2. Column 3 shows the results of an earlier failure-mode analysis on leaf-type separator batteries. Ignoring all batteries that failed due to construction or assembly errors, to mechanical destruction (i.e., such as accidents) or to incorrect charging, it can be stated that among the remaining failure modes, positive grid corrosion dominated. This finding is in agreement with previous analyses.

By contrast, a greater incidence of failure due to shedding of positive active material has been observed. This is probably not associated with the introduction of polyethylene pocket separation, but rather to the concomitant shift to lower antimony contents in the grid alloys.

Microshorts grow through the microporous separator only after deep discharges, when lead sulfate is increasingly dissolved and reprecipitated during subsequent charging from the dissolved state; these sulfate films are then reduced to microscopically fine metallic bridges. This failure mode cannot be avoided even with further reduced

TABLE 1
Failure-mode analysis of automotive batteries (post-mortem analysis)

Failure mode	Envelope batteries – 1992		Leaf-type batteries – 1986 (%)
	(%)	(%) ^a	
Corrosion	24	37	60
Worn-out positive plates	14	20	7
Shorts through separator			
due to deep discharge	11	6	2
due to lead particles	0	0	4
Other shorts (bottom, sides, top)	0	0	10
Discharged batteries	15	11	3
Other reasons	36	26	14
Total	100	100	100

^aAdjusted for the still asymmetric total envelope batteries population.

separator pore size and is favoured by the very narrow spacing between the plates of opposite polarity that is common in today's high-power batteries.

Shorts due to lead particles were not detected. Needless to say, the pocketed batteries did not show any bottom or side shorts. Furthermore, no shorts arising from the top plate edge through the open side of the pocket by bridging to the opposite plates (so-called 'top-mossing') were found, a not infrequently occurring fault during laboratory battery tests!

What conclusions can be drawn from these results? First, the microporous polyethylene pocket has brought about a distinct improvement in the electrical performance data of modern automotive batteries [3] without decreasing the battery life. Moreover, such separation has contributed to a significant increase in the productivity of battery manufacturing. The microporous polyethylene pocket is an optimum separation for the automotive battery of today! and tomorrow?

Profile of future requirements

The following is an attempt to predict the requirements for automotive batteries in Europe to the year 2000, in order to derive the necessary demands that will be made on the separators.

What, anyway, is 'foreseeable' for these remaining seven years? This may only be an extrapolation of existing trends, or plainly visible development directions, with the tacit assumption of no 'revolutionary' developments (Table 2).

It is safely concluded from the assumption that during the next few years only the lead/acid battery will be able to meet the tasks of an automotive starter battery in both technical and economic terms. The nominal voltage will probably remain at 12 V, even though good reasons may exist for a conversion to 24 V. Increasing demands will be made on capacity and cold-cranking performance, but these will be restrained by volume and weight limitations in the car. The temperatures under the aerodynamically-designed, lower engine hoods will rise significantly. Levels of up to 80 °C are being discussed, but 65 °C may be more realistic.

TABLE 2

Development trends for automotive batteries to the year 2000 [3]

System	Pb/H ₂ SO ₄ /PbO ₂ ; 12 V
Capacity	+ 10%
Cold-cranking power	+ 10%
	} at equal weight and volume
Temperature	up to 65 °C
Cycle life	up to +50%
Charge acceptance	improved
Life expectancy	5 years
Maintenance freedom	all batteries

Common to almost all forecasts is a drastic increase in the power consumption of future vehicles. First, there is the trend to more luxurious options, such as electrically-operated window and seat adjustments, etc. Second, increased safety features demand extra electric power for heated wind-shields or the increasing use of electronically-controlled functions. Third, there are environmental requirements: the electrically-heated exhaust catalyst requires amounts of energy that are probably not additionally available from conventional batteries. The increase in electric demand for a battery of constant size will result in increased cycling. In this context, the charge acceptance — especially at low temperatures — as well as the battery life will have to receive special consideration.

In the future, it is obvious that all batteries will have to be 'maintenance-free'. A discussion has started, however, on whether the batteries have to be 'theoretically' maintenance free (i.e., via an internal oxygen cycle) or if the current 'practically' maintenance-free batteries will suffice.

Battery testing at increased temperatures

This section discusses the list of requirements and examines the extent to which the separator may contribute to meet these demands.

The capacity of an automotive battery is, to a small degree, affected by the separator. Low acid displacement and low electrical resistance are required. The introduction of polyethylene pocket separators has largely optimized these parameters. In a modern high-performance battery, the separator affects the capacity by only 2 to 3%, due to its acid displacement.

The cold-cranking performance of a modern automotive battery is, besides other important parameters, also essentially influenced by the electrical resistance of the separator. In this case, the polyethylene separator exhibits a substantial advantage compared with earlier separation systems (Fig. 1).

The electrical resistance of a separator is reflected by the cold-cranking performance of a battery. At present, the separator resistance represents only 5 to 6% of all the sources of loss. Nevertheless, for a high-current design, this minute share may be decisive! Higher porosity and a thinner backweb are essential development targets for separators, whatever the concomitant influences on the machinability of the separator and the service life of the battery may be.

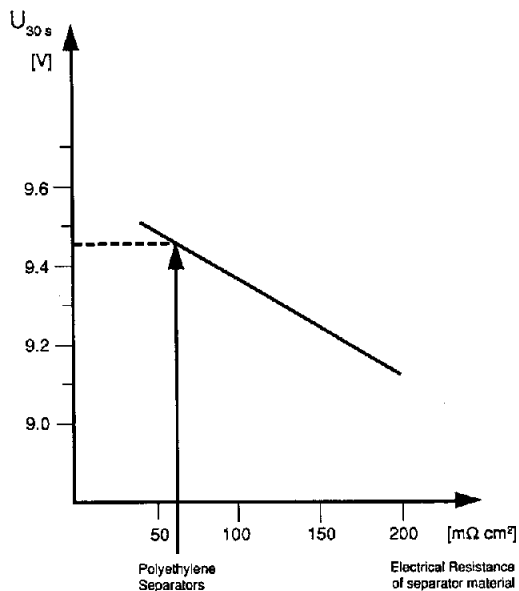


Fig. 1. Cold-cranking voltage, according to DIN 43 539-02, typical values.

The temperature stability in acid up to 80 °C creates, by itself, no difficulties for polyethylene separators.

With regard to the total battery system, the oxidation reactions, that proceed at a considerably increased rate at higher temperatures, have to be studied in more detail.

Figure 2 shows the cold-cranking voltage that was obtained after various battery types (lead-antimony, Pb-2.5wt.%Sb/Pb-2.5wt.%Sb; hybrid construction, Pb-2.5wt.%Sb/Pb-Ca; lead-calcium, Pb-Ca/Pb-Ca) have been subjected to one weekly cycle of the DIN 43 539-02 regime at different temperatures. The result is quite clear: all three systems suffer losses at elevated temperatures, with lead-calcium being the least, and lead-antimony the most, affected.

A similar, but more balanced, picture results by plotting the time in seconds to reach the 6 V cutoff level during the cold-cranking test (Fig. 3). Since all batteries start from approximately the same initial level, a notable deterioration of the expander system within only one cycle appears to be caused by the increased temperature. Clearly, the desire for batteries with a temperature stability of up to 80 °C requires significant improvement in the stability of the expander. In these studies, no influence of the separator was discernible.

Cycle-life testing at different temperatures

From the future demands on automotive batteries, a considerably increased cycling is to be expected. Of course, this has to be seen in conjunction with the background of increased temperatures.

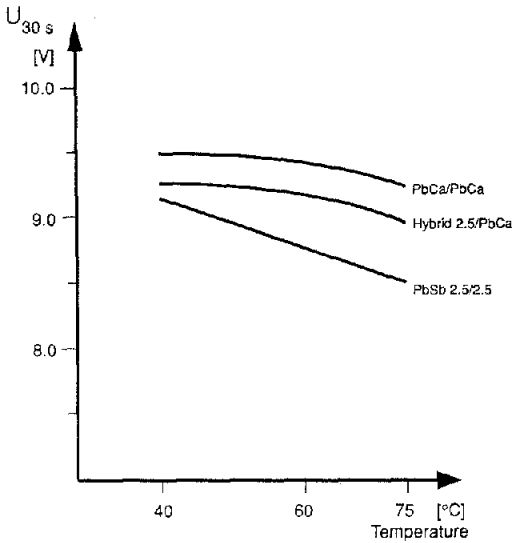


Fig. 2. Cold-cranking voltage, according to DIN 43 539-02, after 1 week cycling.

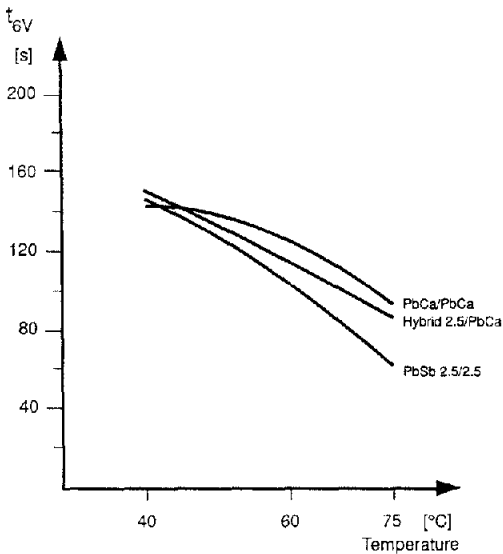


Fig. 3. Cold-cranking capacity, according to DIN 43 539-02, after 1 week cycling.

To study these correlations the above-mentioned battery types have been subjected to a cycle-life test according to DIN 43 539-02, but not only, as provided for in the standard at 40 °C, but also at 60 °C and even at 75 °C (Fig. 4).

During the test at 40 °C ambient temperature (Fig. 5), all three systems exhibit, as expected, a slight decrease in cold-cranking voltages from week to week. Nevertheless, the voltage always well exceeds the required 7.2 V. For the duration to 6 V, a significant advantage of the hybrid construction over both the lead-calcium and the lead-antimony

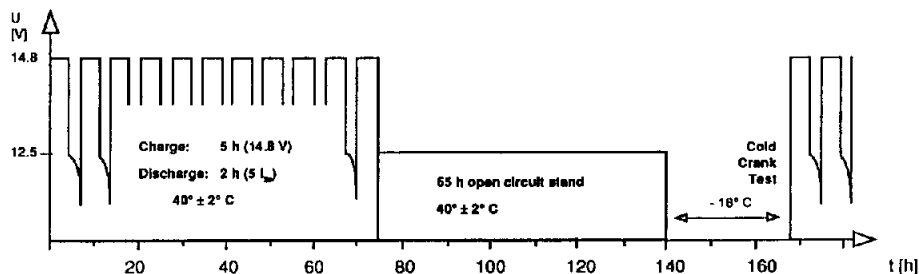


Fig. 4. Weekly cycle of DIN 43 539-02 cycle-life test.

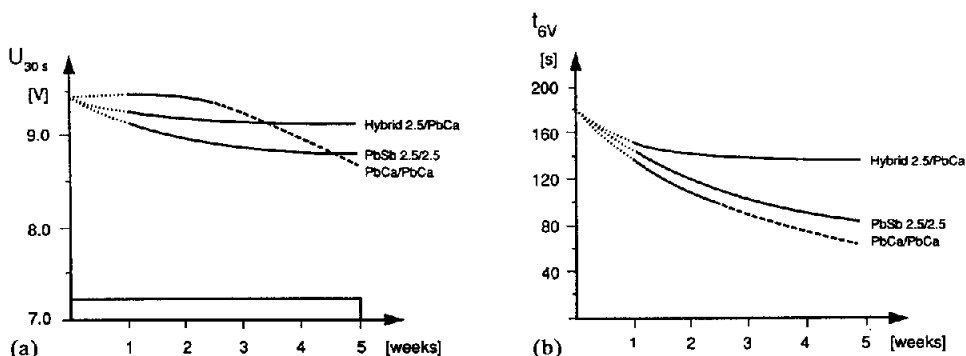


Fig. 5 (a, b). Cycle-life test at 40 °C, according to DIN 43 539-02.

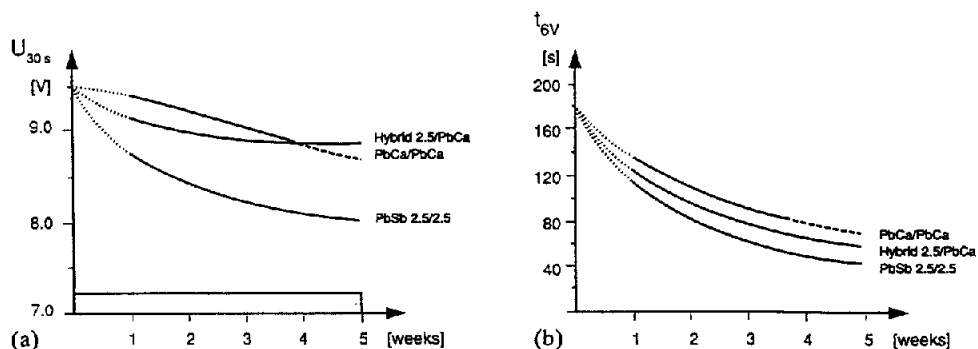


Fig. 6 (a, b). Cycle-life test at 60 °C, according to DIN 43 539-02.

systems is observed. For lead–calcium, this is attributed to the reduction of positive active material and for lead–antimony to increased self-discharge. In neither case does the separator exert a detrimental effect.

At 60 °C, the cold-cranking voltage deteriorates severely during the cycle-life testing of lead–antimony batteries, whereas hybrid and lead–calcium exhibit similar behaviour (Fig. 6). The duration to 6 V suffers a severe decline; this is presumably due to expander damage at 60 °C together with superimposed self-discharge.

These trends are even more pronounced at 75 °C (Fig. 7). In terms of cold-cranking voltage, lead–calcium has a distinct advantage over antimonial systems;

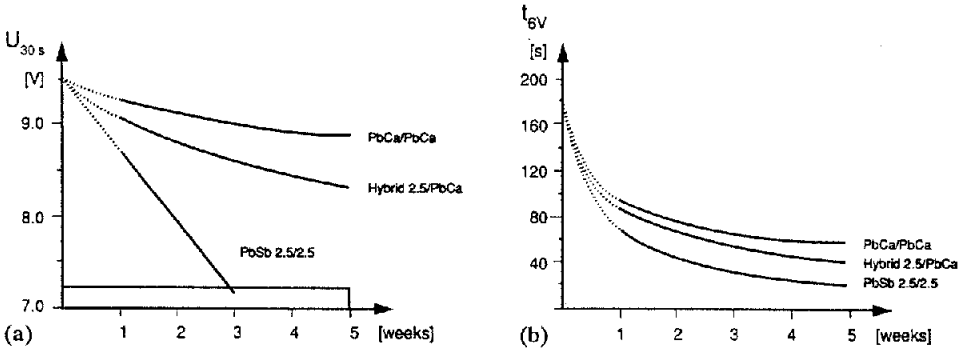


Fig. 7 (a, b). Cycle-life test at 75 °C, according to DIN 43 539-02.

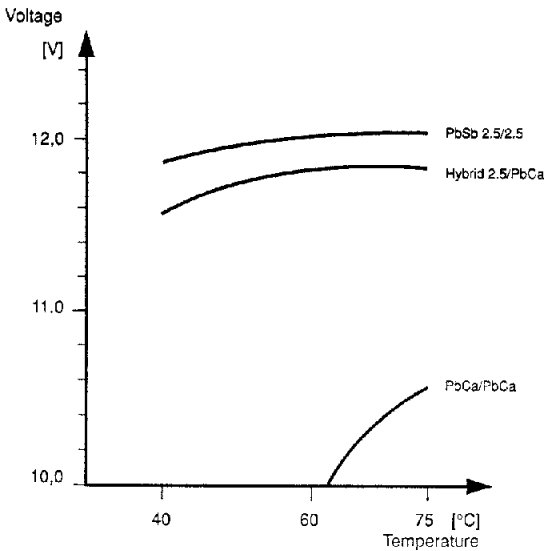


Fig. 8. Final discharge voltage, according to DIN 43 539-02.

lead-antimony fails to meet the required 7.2 V after only the third weekly cycle. The duration to 6 V shows an increased deterioration compared with that recorded for 60 °C. The separator meets all requirements up to 75 °C. The electrical data provide no indications of any detrimental effects.

The standard DIN 43 539-02 specifies (besides the cold-cranking test requirements) that during the weekly cycling the discharge voltage should not fall below 10 V. The tests discussed here have shown that lead-calcium batteries fail to meet this requirement at 40 °C during the third weekly cycle, and at 60 °C during the fourth weekly cycle.

Figure 8 shows the end-of-discharge voltage after completion of the fifth weekly cycle. Whereas lead-calcium batteries, as mentioned above, were only able to meet this test requirement at 75 °C, it was not a serious problem for the antimonial or the hybrid systems. The low gassing of the lead-calcium system at a charging voltage of 14.8 V and at low temperatures may, due to the lack of 'stirring' under laboratory

TABLE 3

Water loss according to DIN 43 539-02; requirement ≤ 6 g/Ah

System	Water loss (g/Ah)
Pb-Ca/Pb-Ca	0.4
Pb-2.5wt.%Sb/Pb-Ca (hybrid)	2.4
Pb-2.5wt.%Sb/Pb-2.5wt.%Sb	6.0

conditions, lead to acid-stratification effects that finally prevent a complete charging of the battery.

By summarizing all results of the cycle-life testing, it can be stated that the separator passes all tests with flying colours. The microporous polyethylene pocket withstands all criteria of this test, even at 75 °C. The battery tests at increased temperatures have shown that the choice of both expander and alloy composition is to be given priority.

Water-loss test

The choice of alloy compositions leads directly to the question of 'maintenance freedom'. The latter should be understood as a sufficiently low water consumption. Whereas 'theoretically' maintenance-free systems with an internal oxygen cycle have no water loss at all, the systems studied here for their other advantages show a certain water loss during the overcharge phase. The type of construction provides for a sufficient acid supply which eliminates the need for any water replenishing under normal operating conditions throughout the service life of the battery.

The DIN standard provides for a water-loss test at 40 °C. The results are given in Table 3. Lead-calcium batteries exhibit a very low water loss, the hybrid construction offers an interesting compromise, whereas the lead-antimony alloy already begins to touch the limit set by the DIN standard.

How is the water loss affected by higher temperatures? During the cycle-life tests described in detail above, the water loss has been determined simultaneously, see Fig. 9. As expected, water loss increases with temperature moderately for lead-calcium, distinctly for hybrid, and sharply for lead-antimony batteries. This is because antimony-poisoning reactions are accelerated by increased temperatures. It is known that the water loss of antimonial batteries can be lowered by using separators especially developed for this purpose. The electrochemical processes involved in this case are very complex and discussion of these details would exceed the scope of this paper. In brief, the basic principle is that separators designed to reduce water loss continuously release special organic molecules, such as aromatic aldehydes, that have the capability of being selectively adsorbed on the antimony sites of the negative electrode and, thus, of inhibiting the catalytic effect of antimony on the hydrogen evolution [4-6].

Conclusions

In summarizing, it can be stated that the foreseeable future demands on modern starter batteries will lead primarily to increased cycling at elevated temperatures.

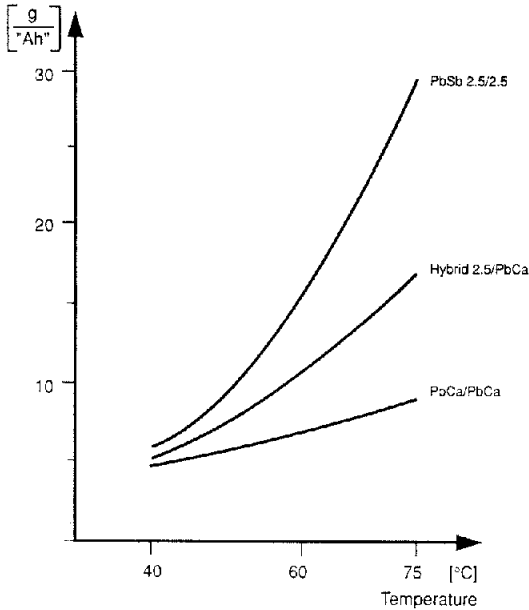


Fig. 9. Water consumption during cycle-life test, according to DIN 43 539-02.

Combined with the requirement for a minimized water loss, the hybrid construction appears to incorporate the most advantages.

The trend towards lower antimony content of the alloys and increased cycling load will push the advantages of microporous polyethylene pocket separation more prominently into the focus than this has been the case in the past.

Optimization of the achieved, balanced separator characteristics profile with the reference parameters of electrical performance, water loss, durability and machinability will stimulate further development work.

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