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Challenges for automotive battery separator development

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Abstract

Increased energy content, higher cold-cranking performance and improved quality level have driven the transition of automotive battery construction to the pocketing technology. Emphasis of future automotive battery development will be the adaptation to elevated ambient temperatures and continuously more demanding productivity requirements. Translated into a profile of separator requirements, this means improved oxidation resistance (especially at higher temperature), further increased puncture strength for unproblematical use in combination with expanded metal grids, combined with a backweb thickness as low as possible for reasons of cost efficiency. Improved oxidation resistance at higher temperatures can be achieved by the use of even better qualities of polyethylene and increased oil content (in general, or only at especially exposed locations), as well as by special gentle production processes. Results of development work aimed at the improvement of oxidation stability are presented and discussed. Ultra-high molecular polyethylene grades with further increased molecular weight approach manufacturing limitations; in general, increased oil content detrimentally affects important separator properties, whereas locally increased oil content in especially stressed areas, such as the creased edge of the separator, opens interesting possibilities for improving the oxidation stability at higher temperatures. Through modifications of the manufacturing process of polyethylene separators, the oxidation stability can also be enhanced significantly with even a simultaneous improvement in puncture strength. The latter facilitates a less problematic use in combination with expanded metal grids and leads, in turn, to productivity advantages. Furthermore, such improvement in separator properties opens the possibility of using lower backweb thickness and, thus, lower separator cost. The evaluation of important characteristics and the performance of recently developed products in batteries are presented. These will form the basis for an optimized separator design. © 1997 Elsevier Science S.A.

Keywords: Automotive batteries; Polyethylene separators; Thin backweb; Oxidation resistance; Puncture strength

1. Introduction

The microporous polyethylene pocket separator has achieved an enormous success around the world. Within the last two decades, more than 70% of all automotive batteries worldwide have been converted to this technology [1]. Improved energy content, higher cold-cranking performance and increased productivity have accelerated this transition from conventional leaf separation to the microporous polyethylene pocket. Under normal conditions of automotive battery use, this separation technology meets all requirements.

What are the development trends for the microporous polyethylene pocket foreseeable for the future?

The requirements placed on the separator result from the future demands placed on the automotive battery. From the experience of recent years, the continuing trend has been towards higher ambient temperatures, increased cycling loads and, especially, additional productivity. Translated into a requirement profile for the separator, this means: increased oxidation stability (especially at elevated temperatures), further improved puncture resistance for problem-free use in combination with expanded metal grids, and all of this with a minimum backweb thickness in order to be even more cost-competitive.

The goal of lower backweb thickness is a particular challenge, because this again increases the demands on oxidation stability and puncture strength. This cycle of problems, i.e., the effect of lower backweb thickness on the properties of the microporous polyethylene pocket separation, is the main topic of this paper.

2. Physical properties of separators with lower backweb thicknesses

2.1. Separator volume

The starting point for the request for lower backweb thicknesses is generally the cost pressure. Less volume, i.e. less material, will show its effect here.

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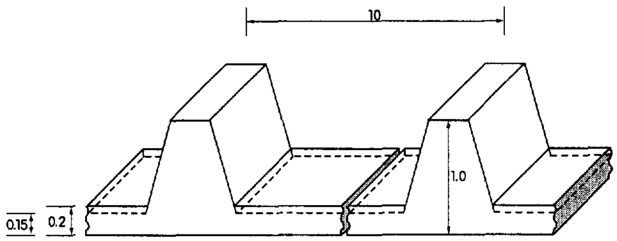

Fig. 1. Polyethylene separator: typical profile design (mm).

A representative section of the separator profile used in typical automotive batteries is shown in Fig. 1. In order to reduce the backweb thickness, the ribs have essentially to remain unchanged since they determine the distance of about 1 mm between positive and negative electrodes and, thus, the supply of sulfuric acid which participates in the electrochemical reactions. To reduce the amount of material, only the sheet between the two ribs can be modified. In modern types of battery, this sheet is typically 0.20 mm thick; a reduction to 0.15 mm brings a decrease in material of about 15%. Considering only the raw materials i.e. labour cost, energy, investment, etc., remain essentially unchanged, there is a cost advantage of about 5% for a 0.05 mm thinner backweb.

2.2. Acid displacement

An advantage immediately evident in such a diminution of material is a reduction of acid displacement. From a typical 95 ml m^{-2} for a 0.20 mm backweb separator, this decreases to about 80 ml m^{-2} for a 0.15 mm backweb. This is an advantage which with high-performance automotive batteries (i.e., with very narrow plate spacing and thus low acid supply) can help to avoid deep-discharges and the possibility of penetration shorts developing from the solution phase.

2.3. Electrical resistance

It is obvious that any reduction in backweb thickness entails a lowering of the electrical resistance of a separator.

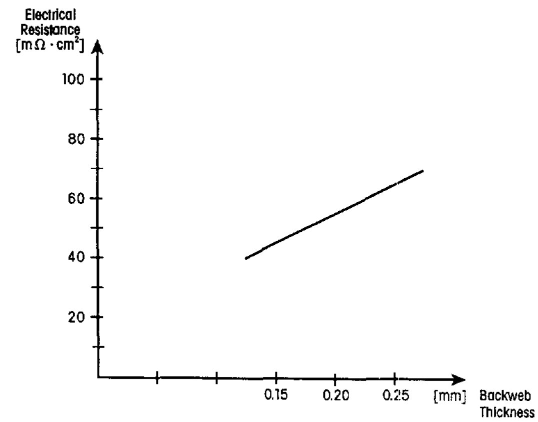

Fig. 3. Electrical resistance of battery separators (typical values).

The effect of the ribs is, however, not to be neglected in this respect.

Fig. 2 gives the theoretical correlation of the electrical resistance of the separator components with backweb thickness; measured values are presented in Fig. 3. The data show the expected trend, i.e. in addition to the cost advantage with a lower backweb, a 15% lower electrical resistance of the separator can be assumed by going from a 0.20 to 0.15 mm backweb.

3. Processing properties of separators with lower backweb thickness

3.1. Stiffness

From physical formulae of material science, it is generally known that the bending stiffness of a body increases or decreases with the cube of its thickness [2]. Applied to separators of reduced backweb thickness, this means a reduction of their stiffness both in the direction of their ribs and, especially, in the cross direction.

Consider first the machine direction, i.e. generally the direction of the ribs. Separators derive their stiffness in this direction essentially from the stiffness of the ribs; a de-

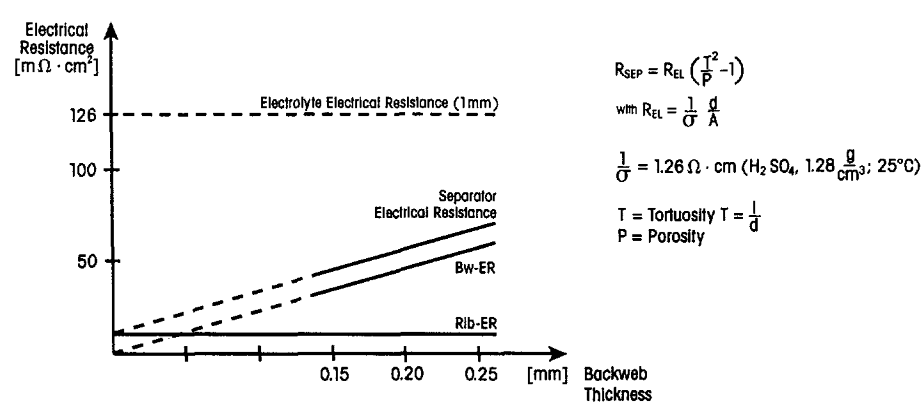

Fig. 2. Electrical resistance of battery separators (theoretical considerations).

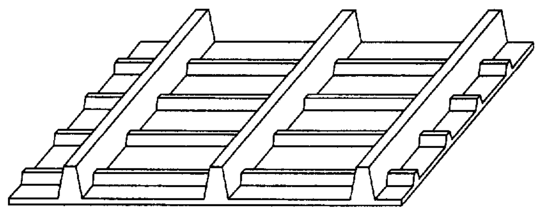

Fig. 4. Stiffness of separator: CMD rib design.

crease in backweb thickness from 0.20 to 0.15 mm has an effect of only about 2%.

Significantly more serious is the effect of reduced backweb thickness on the stiffness in the cross-machine direction (CMD), i.e. across the rib direction, since the ribs hardly contribute to this at all. Thus, a reduction of backweb thickness from 0.20 mm down to 0.15 mm results in a decrease of the stiffness in that direction by about 60%! This CMD stiffness is of considerable importance for the processability of separator material in roll form: higher stiffness avoids or lessens undulation of the sheet and thus ensures an exact width cutting. By increasing the CMD stiffness, better results are also achieved in the production of separator pockets due to better lateral guidance in the pocketing machine — not only in terms of quality, but also in quantity.

In order to utilize the advantages, which thinner backwebs undoubtedly offer, without simultaneously acquiring processing problems due to low CMD stiffness, separator profiles have been developed with additional cross ribs, which — of course — have to be significantly lower than the main ribs in order not to hinder the gas release from between the electrodes. Fig. 4 shows such a profile [3]; these cross ribs can more than compensate for the above loss of CMD bending stiffness without significantly affecting any other advantage.

3.2. Puncture strength

The microporous polyethylene separator normally withstands all demands placed on it during the production process of automotive batteries. Of course these demands

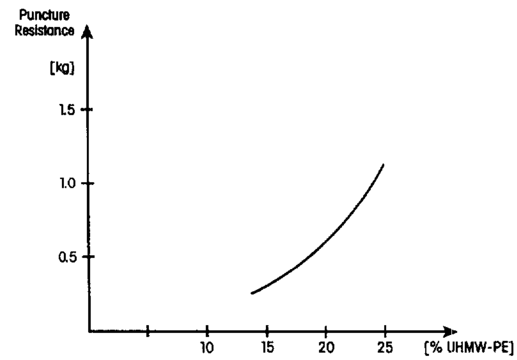

Fig. 6. Puncture resistance *f* (polymer content).

increase when, for instance, expanded metal grids are used instead of cast grids, possibly with sharp points or edges. This trend will gain even further acceptance in many parts of the world because the use of expanded metal technology can significantly lower the consumption of lead for a battery of given capacity — a fact certainly to be considered in periods of high lead prices!

The microporous polyethylene separator is the only separation system that has proven to be suitable as a pocket for expanded metal technology, but does this hold true even for reduced backweb thicknesses? The correlation between puncture resistance and backweb thickness is shown in Fig. 5. As expected, this resistance decreases with lower backwebs. Therefore, precautions have to be taken against possible processing difficulties.

One approach to a solution is to use an increased proportion of polymer versus filler. The data given in Fig. 6 proves the effectiveness of this approach. This advantage is paid for, however, with a lower porosity and, thus, a higher electrical resistance — mainly, however, with a higher raw material cost.

Another way to solve this problem is the use of polyethylenes of even higher average molecular weight. Fig. 7 shows that there is a limit to this approach; the processing of extremely high molecular weights causes considerable difficulties. The change in puncture resistance as a function of molecular weight points to a deterioration of the chain molecules, probably already during the extrusion

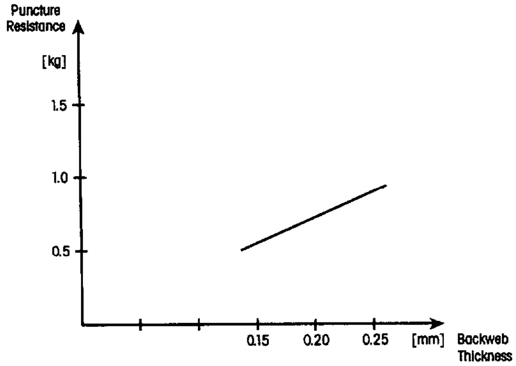

Fig. 5. Puncture resistance *f* (backweb thickness).

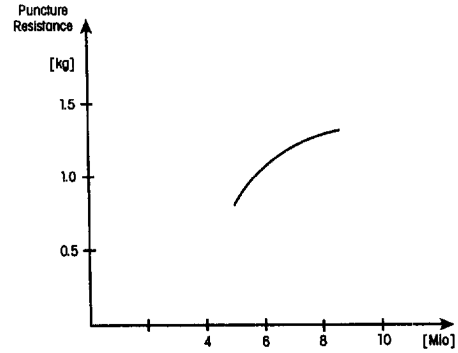

Fig. 7. Puncture resistance *f* (average molecular weight of polymer).

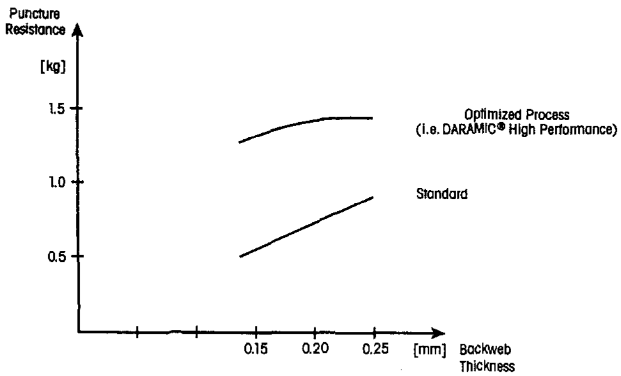

Fig. 8. Puncture resistance *f* (processing).

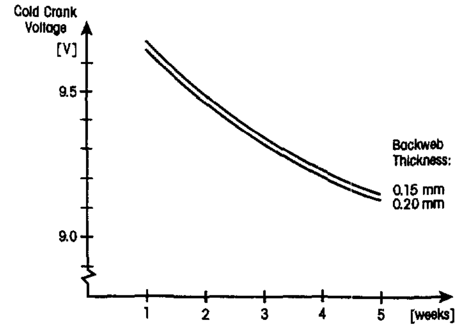

Fig. 9. Cold-cranking voltages of thinner backweb separators (*DIN 43 539-02 E*).

process. The result is a lack of increase in puncture strength with increase in molecular weight.

From the above, it can be seen that a gentle production process is extremely important for microporous polyethylene separators: a decisive break-through has been achieved in this area recently, the procedural details of which must be treated confidentially for obvious reasons. Fig. 8 presents a comparison between conventional polyethylene separator material and this novel product. Even at 0.15 mm backweb thickness, the puncture strength is significantly above that of conventional polyethylene separators with a 0.25 mm backweb. The puncture strength thus achieved should therefore be completely sufficient to satisfy all demands in the foreseeable future with increased use of expanded metal grids, and should contribute to lowering the production cost of automotive batteries.

4. Battery properties of separators with lower backweb thickness

4.1. Cold-cranking performance

In connection with the physical properties of microporous polyethylene separators with reduced backweb thicknesses, 15% more favourable electrical resistance data can be shown for the transition from 0.20 to 0.15 mm. It is common knowledge that the electrical resistance of the separator in modern automotive batteries contributes only about 5 to 6% to the total resistance during the cold-cranking test or — expressed differently — a decrease in separator backweb by 0.05 mm results in a reduction of the total internal battery resistance by about 1%, corresponding to an improvement in cold-cranking performance of about 0.4%. This may appear to be low, in the current competitive situation, however, it represents a not to be neglected advance. Fig. 9 shows the cold-cranking voltages according to *DIN 43 539-02 E* during the cycle-life test; the advantage in cold-cranking voltage due to the 0.05 mm lower backweb thickness of about 35 mV meets the expectation.

4.2. Service life of an automotive battery with separators of lower backweb thickness

The service life of automotive batteries and their failure modes have been the subject of many comprehensive investigations [4,5]. Modern microporous polyethylene pockets normally do not contribute to the failure of automotive batteries. Even at high ambient temperatures, as experienced in the south of the USA, corrosion and concomitant shedding of the positive electrode is the predominant cause of failure. In these cases, the separator also approaches the limits of its durability. A similar situation occurs in battery tests according to DIN or SAE at elevated temperatures, which confirms their efficacy in accurately representing actual field conditions, but within a shorter period of time.

What effect will separators with reduced backweb thickness have on the durability of automotive batteries — especially at elevated temperatures? To date, there has been a lack of field experience to provide an answer to this question. Therefore, it is necessary to rely on laboratory studies. As a starting point for the demands to be met, it is possible to use the fact that conventional microporous polyethylene separators of 0.25 mm backweb thickness do not cause any problems in practice.

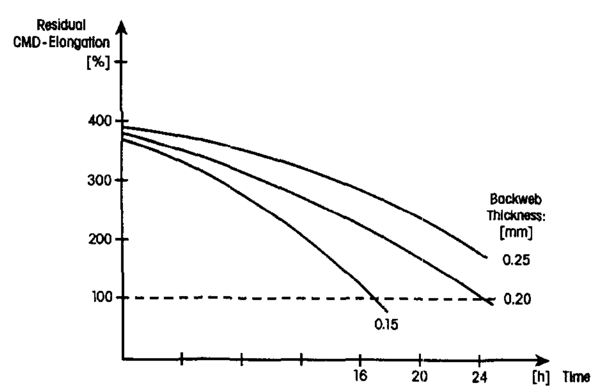

Fig. 10. PEROX-80 oxidation resistance *f* (backweb thickness).

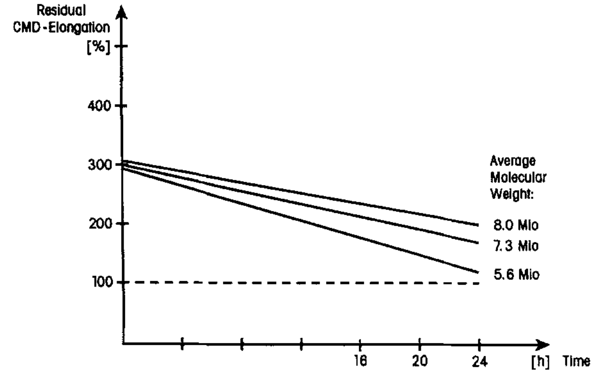

Fig. 11. PEROX-80 oxidation resistance *f* (average molecular weight of polymer).

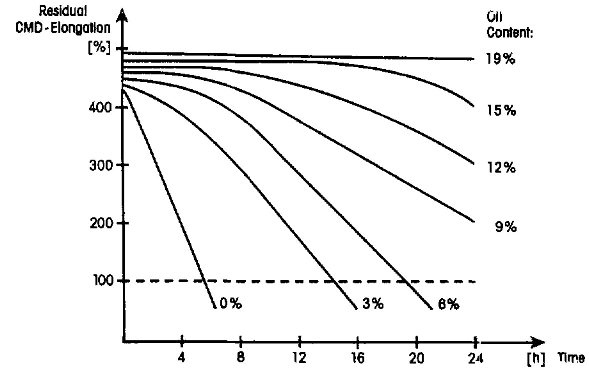

Fig. 13. PEROX-80 oxidation resistance *f* (oil content).

4.2.1. Oxidation tests

In the history of separators, a great number of different chemical oxidation tests has been proposed — and discarded again — for the accelerated evaluation of this property of the separator. In the majority of cases, the test results could not be correlated with the practical experience. Moreover, it was shown that substances 'foreign' to the battery, e.g. chromium or platinum ions, led to results of little significance due to catalytic effects.

Based on the current state of experience, polyethylene separators can be most realistically tested for their use in lead storage batteries by chemical means according to the PEROX method [6] in which an oxidation is performed for up to 24 h at 80 °C in a 5.45% H_2O_2 solution in sulfuric acid of 1.28 sp. gr.

Somewhat more elaborate — but also more realistic — is the so-called rapid-over-charge (ROC) test method [7], where automotive cells of, for instance, 36 Ah capacity are overcharged at 60 °C at a constant current of 3 A. After predetermined intervals, cells are removed from the test circuit, disassembled, and the separators analysed. An overcharge duration of 800 h is considered to be a target value.

Finally, a battery test according to *DIN 43 539-02 E* (1980) at 50 °C and over 10 weeks of cycling can yield valuable indications of the stability of separators.

After definition of the oxidation conditions most relevant to practice, the question remains how separator oxidation can be recognized. This certainly depends on the type of separator. For instance, the weight loss is a parameter which may lead to erroneous conclusions on microporous polyethylene, since it mainly comprises the stability of the oil and other additives. The degradation of a microporous polyethylene separator by oxidative attack becomes evident by a loss in elasticity, i.e. through disintegration of molecular polyethylene chains after strong oxidative attack, the separator begins to become brittle and fragile. In a battery, tears can occur (especially in exposed locations such as the lower pocket crease area) and these can lead to shorts.

For test purposes, the elongation to break at right angles to the machine direction, i.e. generally across the rib direction, is determined in order to obtain information on the oxidative attack that has taken place. A decrease in elongation signifies oxidative attack.

Since the residual elongation to break is subject to considerable statistical variation, the requirement has proven a useful criterion, namely, not to fall below an average of 100% elongation after an oxidative attack, which is relevant to practice. This criterion will also be used below as a measure of oxidative stability.

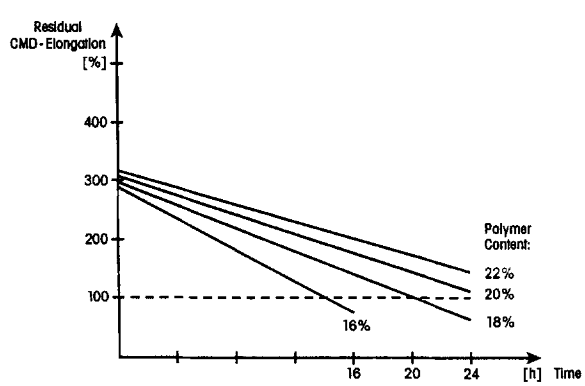

Fig. 12. PEROX-80 oxidation resistance *f* (polymer content).

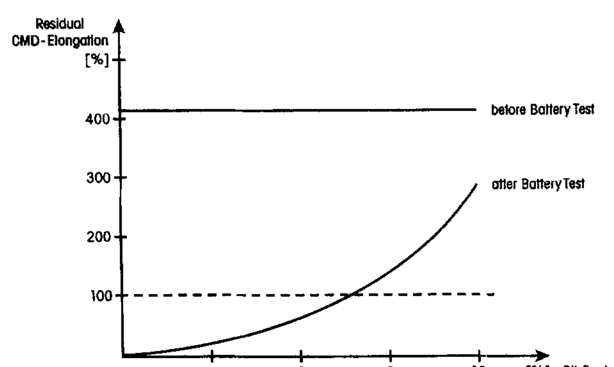

Fig. 14. Battery test-oxidation resistance *f* (oil content).

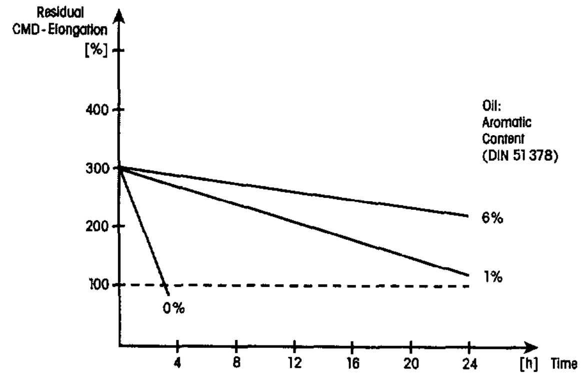

Fig. 15. PEROX-80 oxidation resistance f (oil: aromatic content).

4.2.2. Parameters for the oxidative stability of microporous polyethylene separators

4.2.2.1. Backweb thickness of separator. It is not particularly surprising that the oxidation stability decreases with a lower backweb thickness. Fig. 10 shows this decrease of elongation after chemical oxidative attack. According to the above criterion, i.e. a minimum of 100% residual elongation after 20 h of oxidation, a backweb thickness of 0.15 mm must be viewed as critical and cannot be used unhesitatingly without supportive measures in automotive batteries.

4.2.2.2. Mean molecular weight of polyethylene used. A higher average molecular weight of the polyethylene has advantageous effects on the oxidation stability; the effect is, however, not as pronounced as to justify tolerating the disadvantages already reported, see Fig. 11.

4.2.2.3. Increased polymer content in the separator. Higher polymer content results in a denser and more elastic network for the filler; thus, it is not surprising that this is also expressed in the oxidative stability, see Fig. 12.

Table 1
Rapid overcharge test-hole count

	Number of holes
Polyethylene separator: 9% oil	22
Polyethylene separator: 25% oil	3
Polyethylene separator: 9% oil + oil film on container bottom	5
Polyethylene separator: optimized process	5

4.2.2.4. Oil content. At the first glance, it is surprising that the oil content of a separator affects its oxidative stability. Nevertheless, the data after the chemical oxidation test (Fig. 13) and after 10 weeks of *DIN 43 539-02 E* battery test (Fig. 14) confirm the following relationship: the higher the oil content, the greater the stability of the polyethylene separator against oxidative attack. From the data presented follows a minimum oil content in the backweb of about 8%. The results can be interpreted by assuming that the oil covers the polymer in the form of a protective film, to sacrifice itself for the polyethylene and, thus, to reduce the oxidizing species.

4.2.2.5. Selective oil content. The results regarding the oil content suggest that it is desirable to use an oil content as high as possible. This is, however, in contrast to a low electrical resistance, high porosity and good wettability. An interesting compromise could be reached by adjusting to a higher oil content only at selective locations, such as at pocket crease edges [8]. This can be achieved, for example, by the prior placing of a thin oil film coating at the container bottom, which is absorbed by the folded separator edges on insertion of the pocketed plate group. Relevant battery tests have shown a significantly lower oxidative attack within this critical area, which also produces a significantly reduced incidence of holes. Table 1

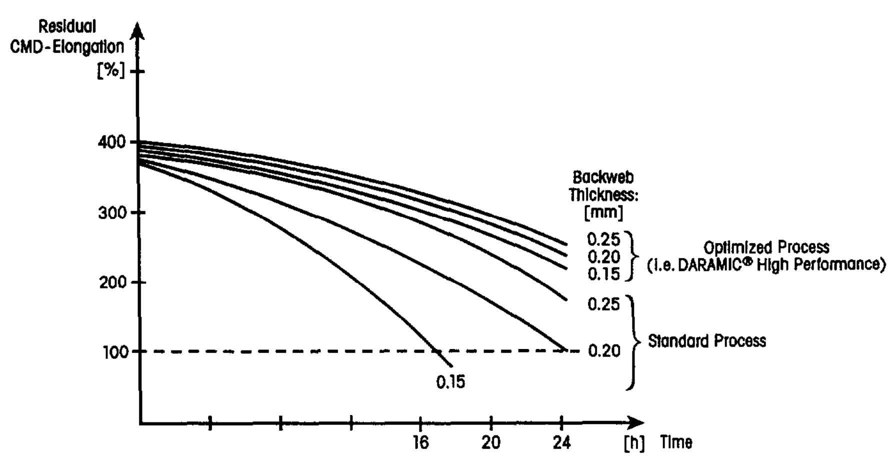

Fig. 16. PEROX-80 oxidation resistance f (processing).

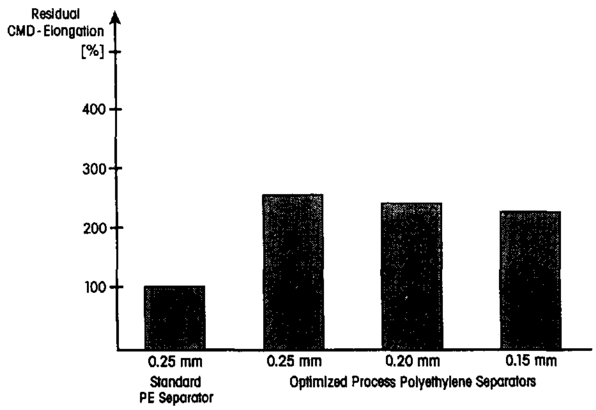

Fig. 17. Residual elongation after battery test (according to *DIN 43 539-02 E*, 16 weeks, 50 °C).

shows a comparison to a low standard oil content of 9% as well as to a separator of higher oil content, i.e. 25%.

4.2.2.6. Oil type. It is generally known that mineral oils consist of a mixture of up to 500 chemical substances. According to the predominant chemical composition, they are classified as paraffinic, aromatic or naphthenic.

The sacrifice hypothesis discussed above leads to the suspicion that the oil composition must exert some effect on the oxidative stability of the separator. There have been prior empirical findings that oils of high aromatic content offer good oxidative properties [9], but such oils are no longer of practical importance, due to black deposits accompanying their use.

Recent detailed investigations have enabled an optimization and have simultaneously shown that paraffinic oils of high purity are unable to exert any protective action [10]. Fig. 15 clearly shows this effect: paraffines cannot prevent the attack on the polyethylene.

4.2.2.7. Production process. As already shown in connection with the puncture strength, an especially gentle production process for polyethylene separators can significantly improve their property profile [11].

With identical separator formulation, an increased oxidation stability can be shown for all backweb thicknesses. The data in Fig. 16 clearly demonstrate this progress; it also shows a dependence of the optimized material upon backweb thickness, but at a significantly higher level. Even at the lowest thickness of 0.15 mm the optimized process material surpasses the value of conventional material at a backweb thickness of 0.25 mm.

A similar result is shown by the analysis after an excessive overcharge test (ROC test method [7]); in the most severely strained area, i.e. in the folded edge of the positive separator pocket, significantly fewer holes are found than for standard material, see Table 1.

Battery life-cycle tests generally show — even at elevated temperatures — no significant difference with regard to the separator. This is due to the fact, that the positive electrodes limit the life of automotive batteries. After completion of the electrical tests and subsequent disassembly, differences in the appearance of separators have been observed: a very low incidence of visible damage as well as a higher residual elongation are displayed by the process-optimized material, see Fig. 17. These results provide unequivocal evidence of the usefulness of low backweb thickness separators when using process-optimized material — even under extreme conditions.

5. Conclusions

For the foreseeable future, the lead/acid battery will remain the only technically and economically suitable system for starting cars.

The trends for the starter battery, such as higher ambient temperature, increased cycling load and further productivity advance, also place higher demands on the separator. The parameters analysed show a variety of approaches to solving the required demands. Therefore, optimism in the continued development of the microporous polyethylene pocket-type of separator is justified.

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