Battery separator design requirements and technology improvements for the modern lead/acid battery

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Abstract

The worldwide trends in battery-separator technology and usage are briefly reviewed and updated. A review is given of the separator design requirements of importance to the battery engineer. Finally, preliminary data are presented from the Entek/Cookson Entek research and development programme to characterize and improve the raw materials used in the manufacture of polyethylene separators, and to characterize the properties of the finished product.

1. Introduction

In 1992, the worldwide trends in battery-separator technology and usage were reviewed [1]. By way of introduction to this paper, the market trends in the previous paper [1] have been updated and included as Figs. 1–7. The following are brief comments on these graphs.

● The automotive battery market in the USA is now almost 100% converted to polyethylene.

● Although the Western European market for automotive batteries is in recession, there is still strong
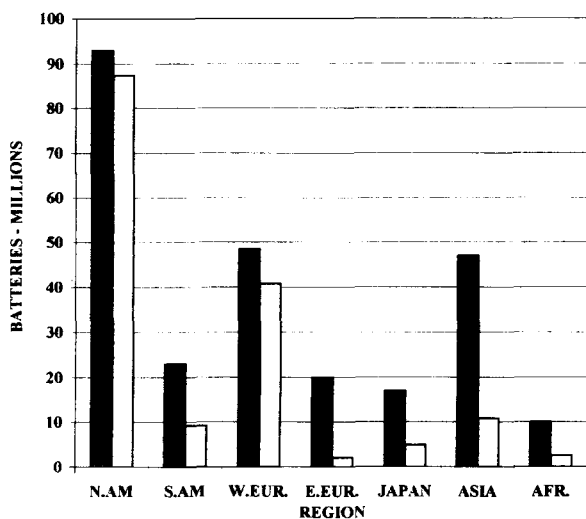

Fig. 1. Worldwide envelope separator usage: 1994. Total batteries (■) vs. envelope batteries (□) by region.
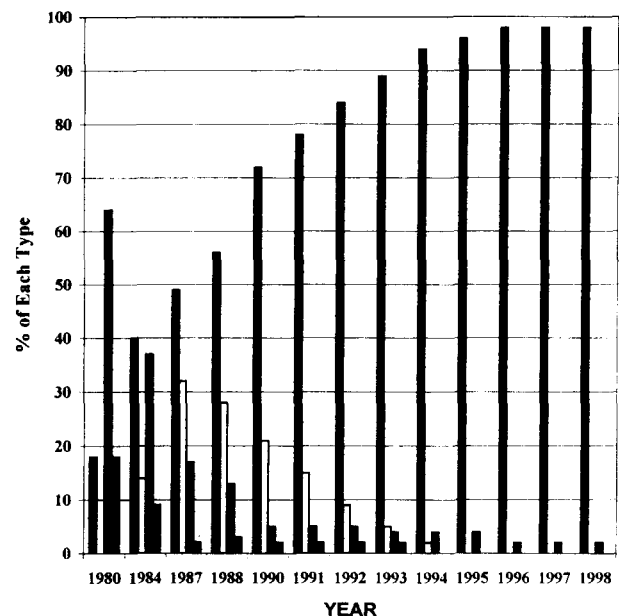

Fig. 2. Separator trends in automotive batteries in North America: ■, polymeric; □, glass; ☒, cellulosic; ▨, other.

growth in the use of polyethylene separators. It is anticipated to rise to 84% conversion in 1994.

● Other markets are growing strongly, and since they have started from a much lower base, there is considerable potential for further expansion.

● The recent decision by Evanite to cease manufacture of the '10-G' glass separator will fuel further growth in the market for polyethylene separators.
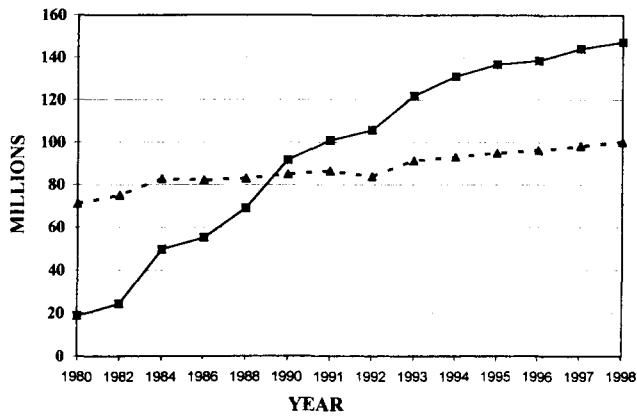
Fig. 3. Polyethylene separator usage in N. America. Total batteries (▲) and polyethylene usage in m² (■). Factor: 1.5 m² per battery.
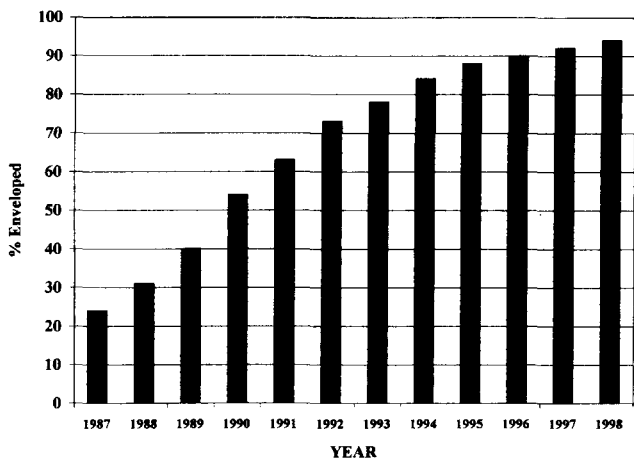

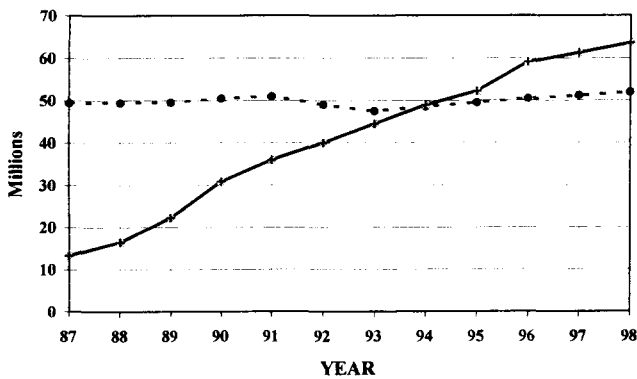Fig. 4. Separator trends in W. Europe. Percentage of automotive batteries enveloped.

Fig. 5. Polyethylene separator usage in W. Europe. Total batteries (●) and polyethylene usage in m² (+). Factor (m²/battery): 1.12 '87–92; 1.2 '93–95; 1.3 '95–98.

To support this market growth in the use of polyethylene separators, the research and development programme of the author's company is focused on further improvements to the existing product. This will come about through a better understanding of the properties of the raw materials used, and the effect of the raw materials and manufacturing process on the properties
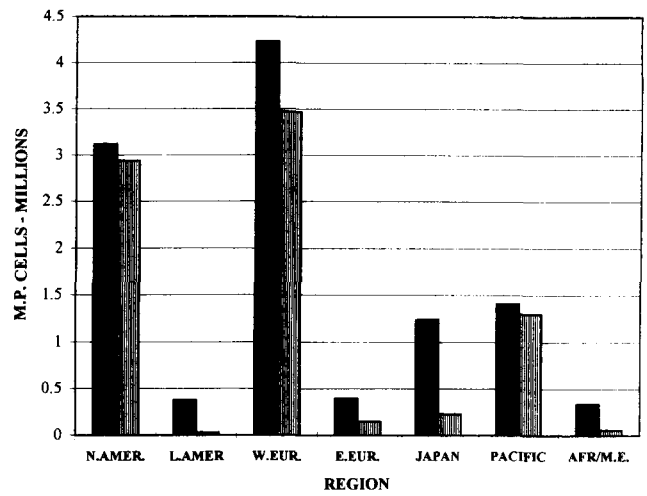

Fig. 6. World motive power market: 1994. Total cells (■) vs. cells with polyethylene separators (▒).
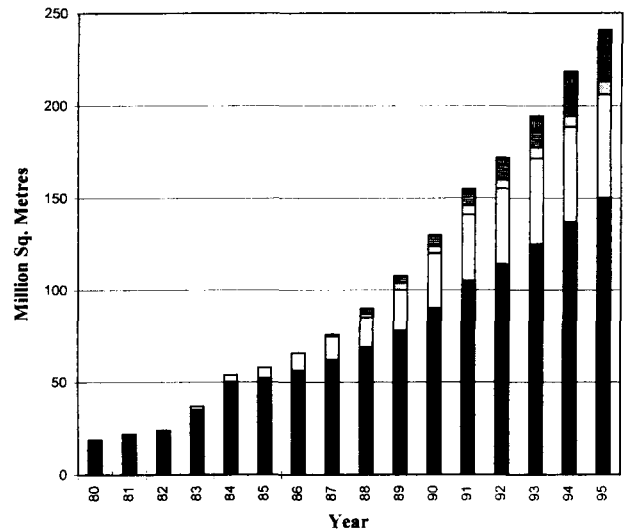

Fig. 7. World separator usage. Automotive polyethylene separators by region: 1980–1995. ■, N. America; □, Europe; ▒, Japan; ▓, Asia; ▥, S. America; ▨, Africa.

of the finished product. Thus, Entek and Cookson Entek are engaged in an ongoing programme to make further process and product improvements to the polyethylene separator. This work is also backed by the resources of the Cookson Technology Centre (CTC).

This paper reviews the separator design requirements of importance to the battery engineer, and reports preliminary data that have the aim of characterizing and improving the raw materials used in the manufacturing process for the polyethylene separator, with resultant improvements in the properties of the finished product. Scanning electron microscopic (SEM) characterization and pore-size distribution data by two techniques (Hg porosimetry and nitrogen adsorption/desorption) are presented and discussed. It should be noted that this work only deals with separators for flooded-cell systems.

2. Automotive batteries

2.1. Cold cranking — electrical resistance

The battery design parameters that influence the cold-cranking performance of an automotive battery include grid alloys, plate thickness, paste density, plate spacing, negative expander ingredients, and separator dimensions and properties. The key separator properties include the total volume porosity of the separator, the pore structure, and the tortuosity of the pores. These properties will influence the electrical resistance of the separator.

The separator design will also affect its electrical resistance, e.g., backweb thickness, number of ribs, overall thickness, plain back or mini backribs. Mini ribs on the back of the separator increase the electrical resistance, but provide increased acid around the negative plates and inhibit gas pocketing, especially in industrial battery designs.

Cookson Entek is pursuing a programme of joint research and development with its raw materials' suppliers to improve the polyethylene separator. This has already borne fruit in the development of an improved silica. The latter has enabled the electrical resistance of the separator to be reduced significantly, especially for material with backwebs > 0.4 mm. This work has demonstrated the critical dependence of the separator properties on the specifications and properties of the raw materials. Further developments are likely to come from continuing cooperation with the raw materials' suppliers.

2.2. High-temperature applications

In recent years, concern has been expressed about the effect of high under-bonnet temperatures on battery life. The obvious solution of moving the battery out of the engine compartment does not seem to be favoured by the vehicle manufacturers, and the battery manufacturers are, therefore, under pressure to develop improved batteries that are more resistant to high temperature. The polyethylene separator would not have been expected to be a limiting factor with traditional battery designs, as other life-limiting factors (e.g., grid corrosion) would cause battery failure before the separator failed. Some battery manufacturers, however, are now considering the use of alloys containing silver as this metal significantly improves the corrosion-resistance of the grids. The result is that separator degradation is more likely to be the life-limiting factor.

Straightforward mechanical degradation of the polyethylene separator at high under-bonnet temperatures is unlikely; the polyethylene melts at 140 °C and does not soften much below that point. Therefore, at temperatures up to 100 °C, the polyethylene separator will not deteriorate mechanically. The major potential problem is oxidative degradation.

The generic polyethylene separator has a number of benefits in relation to high-temperature operation. It has a low acid-displacement and a thin backweb compared with the overall thickness. Also, with the envelope separator, the 'mud space' at the bottom of the cell can be eliminated or reduced. This permits more acid space at the top of the cell and thus provides a good electrolyte reservoir for the electrochemical reaction and heat transfer.

An additional benefit of the generic polyethylene separator is that it can be supplied with a profile that has a thicker backweb in the shoulder area. This profile was developed 3–4 years ago by the author's company in cooperation with a European battery manufacturer to inhibit puncturing of the separator when expanded metal grids are used. By increasing the backweb to 0.32 mm in the shoulder area (for a separator with a nominal backweb thickness of 0.25 mm), the puncture resistance can be increased by up to 50%.

More recently, this thick-shouldered design of polyethylene separator has been used by at least one US battery manufacturer to improve the life of automotive batteries that are subjected to high under-bonnet temperatures. For batteries that experience more cycling and higher ambient temperatures than standard types, there is a tendency for positive-grid growth to occur. This causes extra stresses on the separator material. The use of thick-shouldered separator material helps to reduce battery failures that arise from this cause, particularly if the positive plates are enveloped.

Many battery manufacturers still envelope the positive plates. This decision is partly related to costs; for conventional batteries with an uneven number of plates in the cell group, there is normally one more negative plate than positive plate. Thus, to envelope the positive plates uses one less envelope per cell than to envelope the negative plates. Nevertheless, some battery designs now have an even number of plates per cell, and a few even have one more positive plate than negative plate. For these designs, it may be more appropriate to envelope the negative plates. This also has benefits for high-temperature operation. If the positive plate is enveloped, then under extreme conditions (e.g., high under-bonnet temperatures) growth of the positive plate causes stresses on the envelope that may rupture the envelope and permit a short circuit to develop. If the negative plate is enveloped, the envelope will not experience these stresses as the negative plate does not grow even under severe conditions. The use of a negative envelope instead of a positive envelope will also tend to improve the acid circulation around the positive plate.

2.3. Cyclic duty

An automotive battery fitted to an automobile does not normally experience deep cycling. The critical design parameters are cold-cranking performance and reserve capacity. The reserve capacity is only important if a failure of the vehicle electrical system (e.g., the alternator) results in the battery taking on the whole of the electrical load in an emergency. Even with conventional automobile applications, however, the 'key-off' loads are now quite significant (alarm systems, etc.), and thus the automotive battery may be subjected to more of a cyclic application than in the past.

Automotive batteries may also be fitted in heavier duty applications (e.g., commercial vehicles) and non-automotive applications (e.g., leisure/marine, etc.). In these applications, the battery may experience a more regular deep-discharge and/or abusive conditions of overcharge or overdischarge. With such types of duty cycle, the battery is liable to fail prematurely due to active-material shedding or grid growth/corrosion. Traditionally, for heavy-duty applications, leaf type separators with attached glass mat have been used. More recently, with the growth in polyethylene separator usage for standard automotive applications, the battery manufacturers are now also taking advantage of the benefits of polyethylene for heavy-duty applications. In these cases, a polyethylene envelope separator with a glass retainer mat is recommended. The mat may be fed in at the enveloper as a separate reel, as is possible with some types of enveloping machine. Alternatively, the glass retainer mat can be laminated to the polyethylene separator. This is normally achieved by applying glue to the ribs of the separator and then attaching the glass retainer mat to the glued ribs. In the battery, the compression of the glass mat against the positive plate provides improved resistance to vibration, and gives greater protection to the plates. Combined with the envelope construction, this significantly reduces the risk of separator failures in heavy-duty applications.

2.4. Separator oil content (polyethylene)

In the manufacturing process for polyethylene separators, a mineral oil is used to aid the extrusion and calendering of the sheet [2]. While most of this oil is removed in the solvent extraction process (thereby creating porosity in the sheet), some of it is left in the finished separator material. This also provides resistance to oxidation when the separator is in the battery.

Historically, a standard specification of 12±3% oil for automotive battery separators and 15±3% for motive-power battery separators has been used [2]. With the Entek manufacturing process, however, the oil can be removed to any desired level (e.g., 6%). Some work carried out on the oxidation resistance of motive-power

separators indicates that reducing the oil content from 15 to 7% has only a marginally adverse effect on the oxidation resistance. This has an added benefit in that porosity is also increased with the lower oil content, although there is some evidence that this does not necessarily apply if the oil content is reduced to below 5%.

2.5. Elimination of short circuits/separator failures

The microporous polyethylene separator with an average pore size of less than 1 μm will inhibit short circuits through the separator. The short circuits arise from particles of lead settling in the pores and eventually filling the pores. This type of separator failure is almost unknown with the polyethylene separator, whereas it used to be fairly common with the cellulose or polyvinylchloride type of separator (where because of the 'fragile' nature of the separator, a crack or break in the separator could also easily occur). Nevertheless, if dissolution and re-crystallization of lead occurs under conditions of full discharge/low acid sp. gr., then a short circuit may result, regardless of pore size, even with a microporous separator. This problem is aggravated by a tight plate pitch and an acid/Ah ratio of less than 9 ml/Ah, but can be reduced if an additive such as sodium sulfate is added to the electrolyte.

2.6. Rhinohide

'Rhinohide' is the latest development in polyethylene separator technology for automotive applications. This product was developed by Entek with the aim of manufacturing a thin backweb material (0.125 mm/0.005 in.) that has a strength and puncture resistance equivalent to the standard automotive product with a backweb of 0.2 mm (0.008 in.). The Rhinohide product increases the range of available options for the battery engineer. The electrical resistance will be higher per mm/mil of separator material. On balance, however, the separator will still have a lower electrical resistance and lower acid displacement, and, therefore, a higher battery performance. There will also be a cost benefit as material costs will be lower for the Rhinohide separator with a thinner backweb.

3. Motive-power batteries

3.1. 'Oily scum' phenomenon

In general, user experience with polyethylene separators has been very favourable, both for automotive and for industrial applications. One widely reported problem with polyethylene separators, however, is the tendency for certain component(s) to leach out into

the electrolyte. This causes the problem known as 'oily scum', or 'black scum', or 'black deposits', or 'black sludge' [2]. The term 'oily scum' may not be entirely correct, as evidence is emerging that this problem is not just related to leaching of the oil in the separator. The oil from the separator may be one of the components of the 'scum', but may also act as a 'carrier' for other components of the separator (such as the lubricant), and for carbon black from the expander ingredients in the negative plates. In the automotive application, it has been found that if there is no expander at all in the negative plates, no oily scum is produced during formation. With automotive batteries, the 'black scum' arises mainly during the initial formation process and can be minimized by holding formation temperatures below 60 °C. The 'black scum' does not cause any problems in relation to the performance or operation of the battery, but is cosmetically undesirable, particularly if translucent containers are used.

For motive-power batteries, the cosmetic problem is not significant because black containers are normally used. With certain automatic watering systems (i.e., the type widely used in Europe), however, the black scum can block the valves and cause failure of the system. Improved valves have now been developed that are less prone to blocking, but the battery manufacturer would still prefer to see this problem eliminated at source.

Work is in hand to identify the components of the oily scum and gain improvements to the polyethylene separator to eliminate the problem. Using a three-plate test cell at CTC, different separator materials are being tested under conditions where black scum is formed, and the components of the black scum are being analyzed. To data, this work has found that even with the cellulosic separator, a 'scum' is formed although it is less in quantity and arises more slowly than with the polyethylene separator.

3.2. Porosity/acid displacement

Total volume porosity is important because of its direct relationship to the acid displacement caused by the presence of the separator. Acid displacement is also influenced by separator design and backweb. With polyethylene separator materials there is also the option of reducing the separator backweb to reduce acid displacement (e.g., for motive-power applications) while retaining acceptable strength, puncture resistance, etc. There is also the option of reducing oil content, with a possible penalty of inferior oxidation resistance. For example, reducing the oil content of the polyethylene separator from 12 to 0% increases the porosity by 4%.

Work on raw materials and separator structure will lead to improvements in the porosity of the polyethylene

separator. Some of the separator characterization work is reported below.

3.3. Profile design

The separator profile is particularly important for industrial cells. A separator with a widely spaced vertical rib is suitable for both automotive and flat-plate motive-power applications. On the other hand, it is generally regarded as unsuitable for motive-power cells with tubular plates because the positive rib may become 'trapped' between the tubes, and thus cause acid starvation and gas pocketing. One alternative is to use a profile with a closely spaced vertical rib, but this will cause a significant increase in electrical resistance, particularly for separators with a high overall thickness.

For motive-power cells with tubular positive plates, a profile with diagonal ribs is widely used, permitting a wider spacing between the ribs. Nevertheless, some battery manufacturers report problems with gas pocketing with this design.

Another popular alternative for motive-power cells is the S-rib design. This is suitable for all plate types. It is claimed that with the S-rib design, shedding from the plates and the build-up of shed material at the bottom of the cell is more uniform. This design is also acceptable for minimizing gas pocketing. There will be problems, however, if the battery manufacturer wants to sleeve or envelope the plate, unless the S-rib profile has a land area for the welding process.

4. Separator characterization

4.1. Pore size/pore-size distribution

The pore size, pore-size distribution, tortuosity and total volume porosity of the separator have a direct influence on the electrical properties of the separator in the battery. All pores that are accessible from the surface of the separator will become filled with acid and contribute to the effective total volume porosity (acid displacement). 'Closed' pores are not beneficial, they will displace acid and do not contribute to the total volume porosity. Through pores are also needed for ionic transfer. These should be as small as possible to inhibit the growth of lead dendrites.

A previous study [2] gave some data on pore-size distribution analysis using mercury porosimetry. For the work reported here, additional information has been obtained. This has been analyzed in more detail. It has been supported by pore-size distribution data obtained using nitrogen porosimetry.

The mercury porosimetry work was carried out by PPG Industries using a Quantachrome Autoscan mercury porosimeter. This determined pore-size distribution

in the range 0.0065–10 μm. For the nitrogen porosimetry technique, a Micromeritics ASAP 2400 machine was used. This measured pore-size distribution in the range 0.001–0.1 μm. It should be noted that both techniques are only suitable for microporous separator materials. Because the maximum pore size measured by mercury porosimetry is typically 10 μm, it is possible that this technique may underestimate the total volume porosity of the separator material. The total volume porosity should also be determined using a conventional technique. The nitrogen porosimetry technique supplements the mercury porosimetry, but only provides a 'snapshot' of the very small pores in the range 0.001–0.1 μm.

These techniques generated a large amount of information that is still being analyzed. Only initial conclusions are given here. Curves of the log differential intrusion volume ($dV/d \log D$ or $dV/d \log R$) have been used to show the pore-size distributions, their location and volume. The curves for mercury porosimetry for a range of different separator samples are given in Figs. 8, 10, 12, 14, 16, 18 while the corresponding curves for nitrogen desorption are presented in Figs. 9, 11,
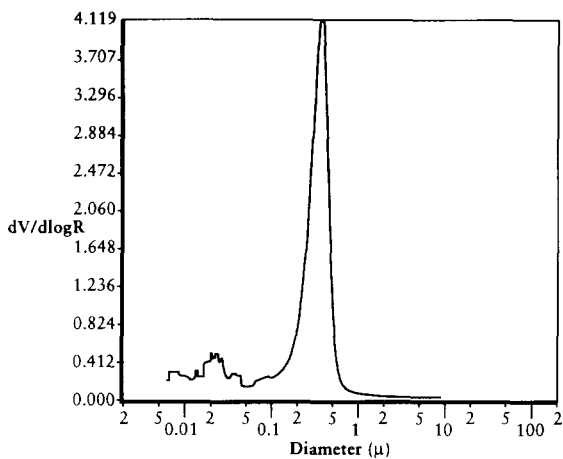
Fig. 8. Pore-size distribution data. Ref.: 0285 separator type: phenolic/polyester. Hg porosimetry.
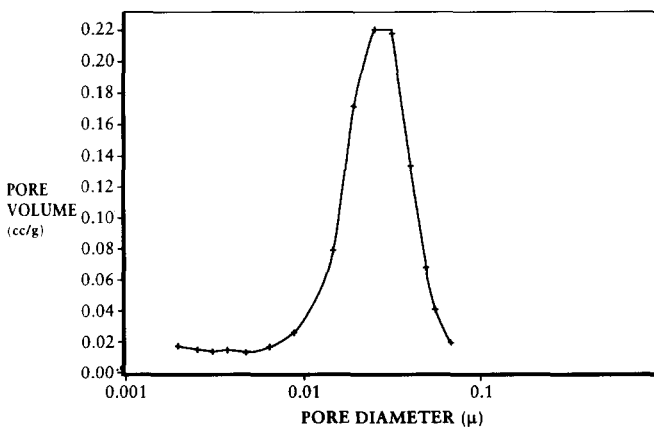
Fig. 9. dV/d log(D) desorption pore volume plot. Ref.: 0285 separator type: phenolic/polyester. N porosimetry.
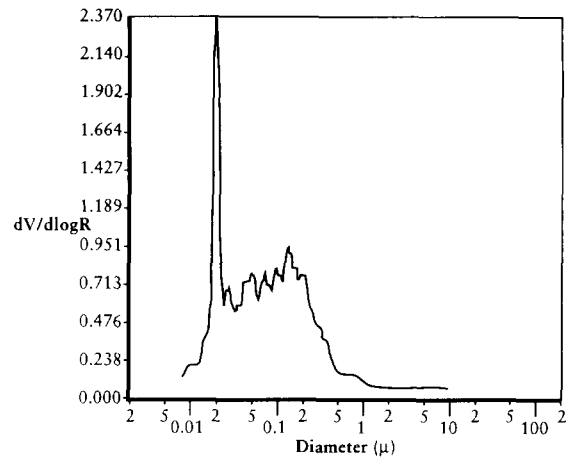

Fig. 10. Pore-size distribution data. Ref.: 0287 separator type: polyethylene. Hg porosimetry.
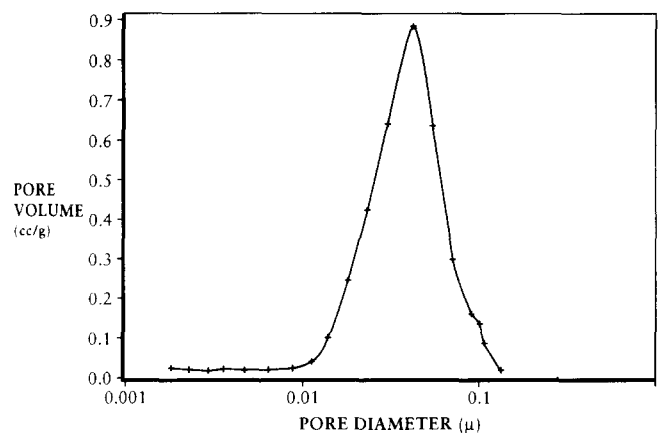

Fig. 11. dV/d log (D) desorption pore volume plot. Ref.: 0287 separator type: polyethylene. N porosimetry.
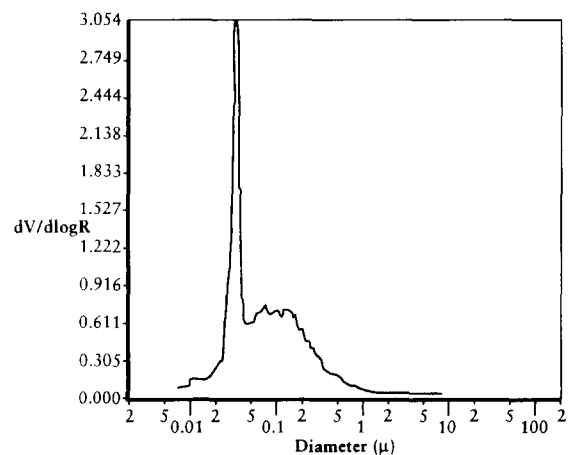

Fig. 12. Pore-size distribution data. Ref.: 0288 separator type: polyethylene. Hg porosimetry.

13, 15, 17, 19. Table 1 summarizes the most relevant data from the mercury intrusion porosimetry. In addition, the 'raw' data from the mercury intrusion porosimetry have been used to generate 'smooth' curves of % intruded volume versus pore diameter (see Figs.
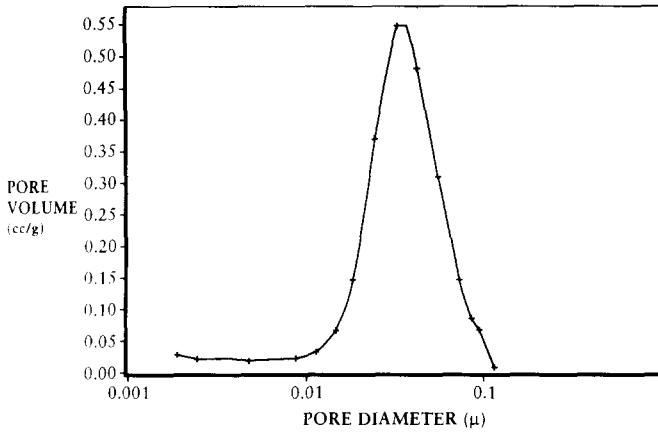
Fig. 13. dV/d log(D) desorption pore volume plot. Ref.: 0288 separator type: polyethylene. N porosimetry.
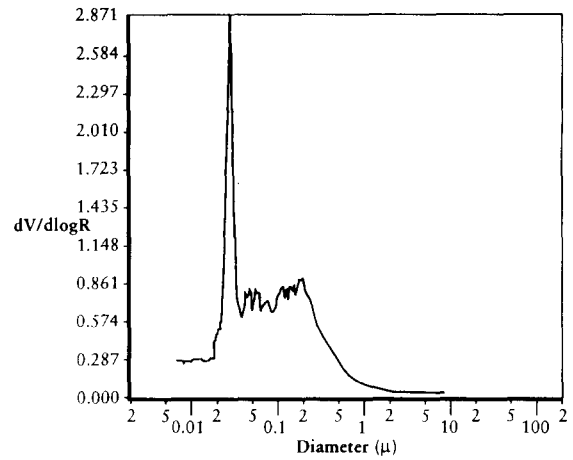

Fig. 16. Pore-size distribution data. Ref.: 0294 separator type: polyethylene. Hg porosimetry.
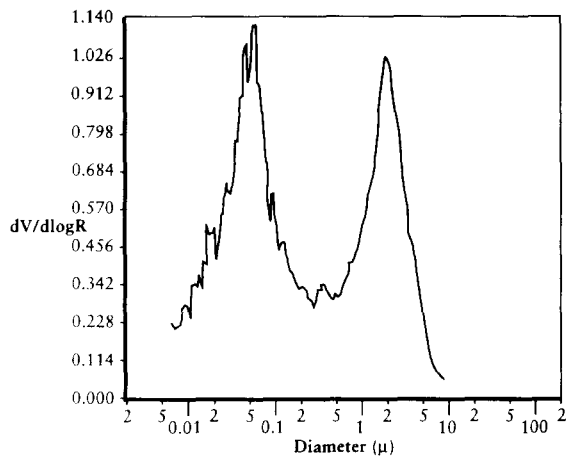

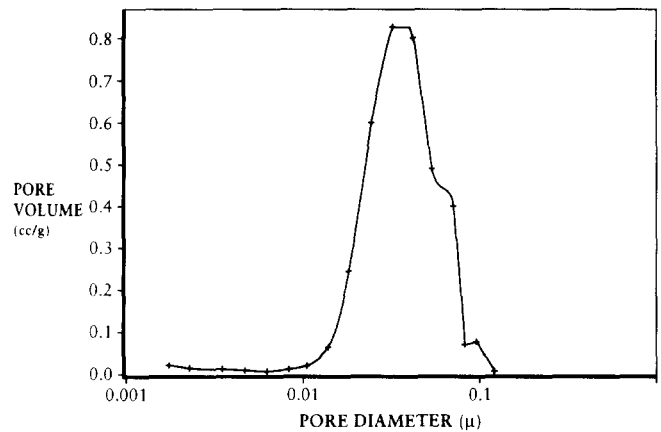Fig. 14. Pore-size distribution data. Ref.: 0290 separator type: microporous PVC. Hg porosimetry.

Fig. 17. dV/d log(D) desorption pore volume plot. Ref.: 0294 separator type: polyethylene. N porosimetry.
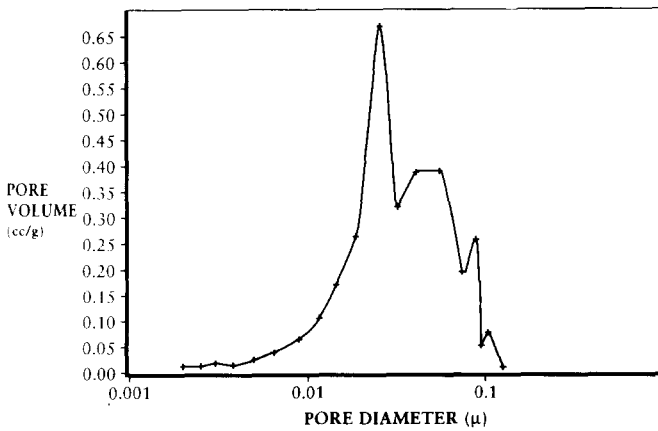

Fig. 15. dV/d log(D) desorption pore volume plot. Ref.: 0290 separator type: microporous PVC. N porosimetry.
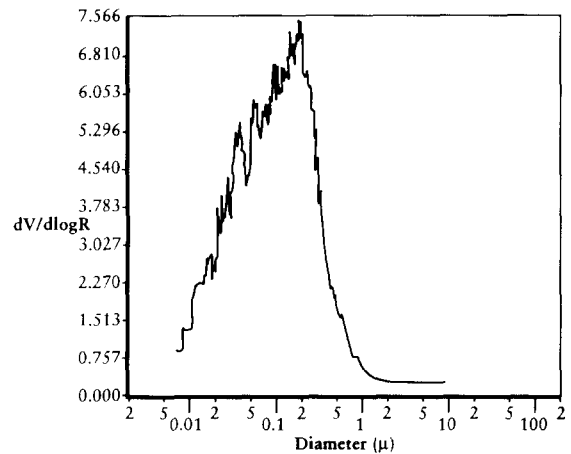

Fig. 18. Pore-size distribution data. Ref.: 0296 separator type: polyethylene. Hg porosimetry.

20 and 21). Sample reference 0.288 is Cookson Entek polyethylene, while references 0287, 0294, 0296 are samples from other suppliers of polyethylene separators. Sample reference 0285 is a phenolic/polyester separator, and 0290 is a microporous poly vinylchloride separator.

Mercury intrusion porosimetry (MIP) is a valuable technique for microporous separator materials because the pore-size range measured corresponds well with the pore-size distribution of microporous separator materials. A potential criticism of the mercury poro-
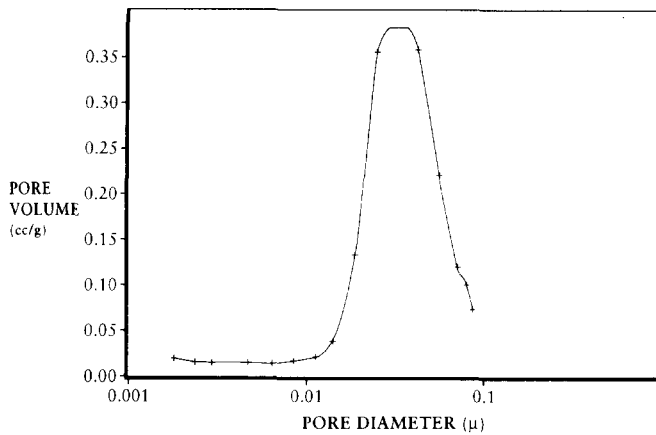
Fig. 19. dV/d log(D) desorption pore volume plot. Ref.: 0296 separator type: polyethylene. N porosimetry.

simetry technique, however, is that the high pressures used tend to 'crush' the pores — particularly the smaller pores — and, therefore, the pore-size spectra for pores of <0.1 μm may not be accurate. The nitrogen porosimetry technique cannot be used in isolation because of its restricted pore size range but, in this study, it has been used to obtain more information about the pore size spectra in the range 0.001–0.1 μm. The correlation between these two techniques is still being analyzed. For the polyethylene separator, the correlation appears to be good. By contrast, it appears to be not so good for the other separator materials. For example, for the Cookson Entek polyethylene separator (reference 0288) the intruded volume in the range 0.01–0.1 μm is approximately 0.62 cc/g from the mercury porosimetry data, 0.25 cc/g from the nitrogen desorption data (these values were derived from the 'raw' data

which it has not been possible to publish in full). The intruded pore volume 'peak' occurs at almost exactly the same pore diameter (0.035 μm) for both techniques, as seen from a comparison of Figs. 12 and 13. The MIP data also give a good agreement with the total volume porosity values, as determined independently. The total intruded volume (1 cc/g, Table 1) for sample 0288 (Cookson Entek polyethylene) is equivalent to a volume porosity of 60% (using known values for the sp. gr. of the solid matrix of the separator), which is the normal volume porosity for Cookson Entek polyethylene separator material. The total intruded volume for sample 0290 indicates a higher volume porosity, and for sample 0296 indicates a lower volume porosity than for sample 0288. This is in accordance with the results from conventional volume porosity measurements on these separator materials. It should be noted that for separator samples from other suppliers, it is not possible to obtain an accurate value for the volume porosity from the MIP data, because the sp. gr. of the solid matrix of the separator is unknown.

Fig. 20 shows the differences between three types of separator materials, namely, phenolic/polyester; Cookson Entek polyethylene; microporous poly vinylchloride. The last mentioned has the highest volume porosity of typically 70% compared with about 60% for Cookson Entek polyethylene (as determined by a conventional test method for total volume porosity). It also has two distinct peaks in the pore spectra, i.e., at <0.1 and ~2 μm. This suggests that the increased total volume porosity has been achieved because the microporous poly vinylchloride separator has a signif-

Table 1
Summary of mercury intrusion porosimetry data for different separators

	Total intruded volume (cc/g)	Total surface area (m²/g)	Pore diameter at mean volume [a] (μm)	Pore diameter at mode volume [b] (μm)	Pore diameter at median volume [c] (μm)
0285 Supplier 2 Phenolic/polyester	1.35	46.6	0.12	0.67	0.32
0287 Supplier 3 Polyethylene	1.06	96.9	0.044	0.018	0.074
0288 Cookson Entek Polyethylene	1	78	0.051	0.033	0.064
0290 Supplier 4 Microporous PVC	1.4	76.5	0.073	0.0065	0.21
0294 Supplier 1 Polyethylene	1.14	86.2	0.053	0.026	0.082
0296 Supplier 2 Polyethylene	0.78	50.2	0.062	0.011	0.11

[a] Mean pore diameter is the size of the 'average' pore.
[b] Mode pore diameter is the most common size.
[c] Median pore diameter is the size above or below which half the distribution lies.
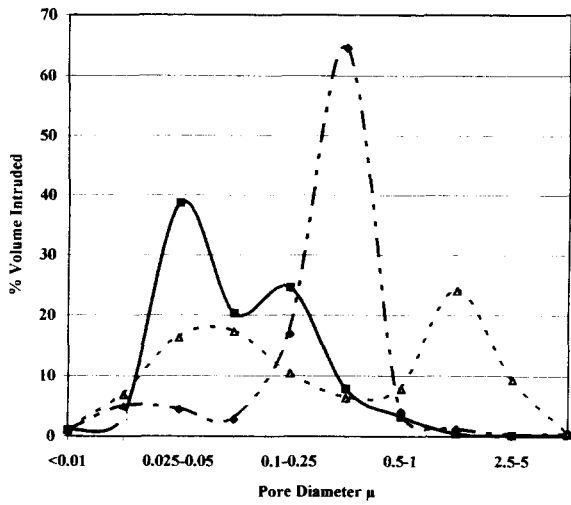
Fig. 20. Pore-size spectra. Cookson Entek polyethylene compared with other separator types. ◆, 654-0285 phenolic/polyester; ■, 654-0288 PE — Cookson Entek; △, 654-0290 microporous PVC.
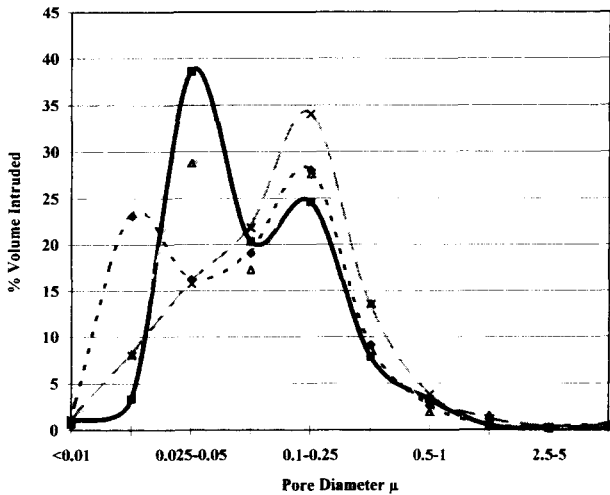

Fig. 21. Pore-size spectra. Cookson Entek polyethylene compared with other polyethylene separator suppliers. ■, 654-0288 PE — Cookson Entek; △, 654-0294 PE — Supplier 1; ×, 654-0296 PE — Supplier 2; ◆, 654-0287 PE — Supplier 3.

icant percentage of pores above 1 μm. It would presumably be much more difficult to achieve this high total volume porosity if the majority of the pores are below 1 μm.

Fig. 21 shows the pore-size spectra for four different polyethylene separator materials. The spectra are broadly similar, but show detailed differences, e.g., in the shape of the pore-size spectra curve for supplier 3 compared with the other samples.

The range covered by the three 'averages' (Table 1, mean/mode/median) is indicative of the uniformity of the separator structure. The values are much closer for the Cookson Entek separator than for the other separator types. This suggests a narrower distribution of pore sizes.
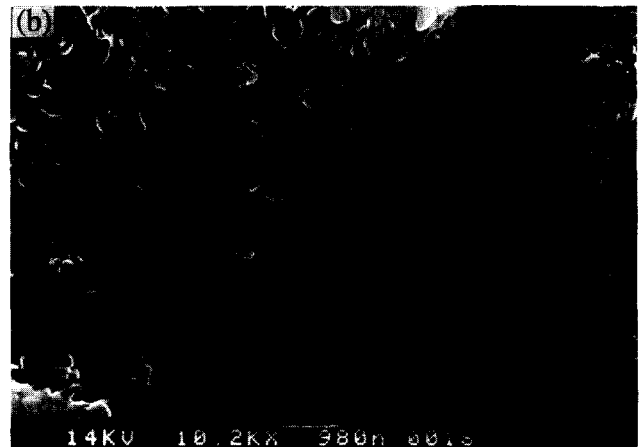

Fig. 22. Electron micrograph of Cookson Entek polyethylene separator: (a) 5.04 KX; (b) 10.2 KX; (c) 50.4 KX.

This study has shown that MIP is a very useful technique for determining the pore-size spectra of microporous separator materials, although the results need to be interpreted with care. It is intended to continue this work in order to obtain a more detailed understanding of the pore-size distribution of different separator materials, and the influence of this distribution on separator performance. This will involve testing separator materials with different values for electrical

resistance, total volume porosity, etc., and establishing whether these differences are shown up in differences in the pore-size spectra, intruded volume and surface area.

4.2. Surface structure

Scanning electron microscopy (SEM) has been used to study the structure of the raw materials (silica and polyethylene) used in the manufacture of the polyethylene separators, and the microstructure of the polyethylene separator. Typical electron micrographs of the Cookson Entek polyethylene separator are shown in Fig. 22. It is apparent that the silica aggregates form the basic building block of the separator structure. The polymer is smeared out over the silica particles to form a skin that produces the lobed appearance.

Low-magnification micrographs show an apparently solid surface with occasional openings and only a poorly defined texture. At high magnifications, the surface texture becomes clearer and is seen to consist of clusters of fine lobed structures (200–500 nm across). There is significant surface roughness (porosity) between the lobes and the clusters of lobes. The large lobes appear to have some internal structure, and there are lines of division between lobes and clusters of lobes, as if they are only partially joined together. The porosity is on all scales down to a few tens of nanometres; the pores that penetrate the full thickness of the separator, and are therefore able to conduct current, are probably just the connected parts of the network of porosity

that inter-penetrates the polymer/silica/oil lobed structure.

The micrographs confirm the MIP data reported above. The 'spike' in the MIP pore spectra at around 0.035 μm is real, as this is about the size of the smallest holes and cavities in the structure as seen in the micrographs.

Obviously, the detailed structure of the separator will relate directly to the separator properties such as porosity and electrical resistance. SEM has been shown to be a valuable technique that, if taken together with other techniques, will lead to greater understanding of the separator structure. This, in turn, will indicate ways in which that structure can be modified to improve the properties of the separator.

Acknowledgements

References

[1] M.J. Weighall, J. Power Sources, 40 (1992) 195–212.
[2] M.J. Weighall, J. Power Sources, 34 (1991) 257–268.