# Worldwide trends in battery separator technology and usage

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## Abstract

This paper reviews trends in battery separator usage for starting-lighting-and-ignition (SLI), motive power, and sealed valve-regulated lead/acid batteries.

For SLI batteries, the dominant trend in the USA and Western Europe has been a dramatic increase in polyethylene envelope separator usage, with other countries now following this trend. This is at the expense of traditional leaf-type separators such as cellulose or sintered polyvinyl chloride (PVC).

For motive power applications, several different types of separator materials are currently favoured, including polyethylene, microporous rubber, microporous PVC and resin-impregnated polyester fibres. Worldwide trends in the motive power battery and separator market are shown.

For sealed valve-regulated lead/acid batteries, the favoured construction uses a recombinant battery separator mat, normally of 100% borosilicate glass (binder free). Alternative mats containing a proportion of polymeric fibres are now being investigated. Market trends and factors affecting growth in the use of recombinant battery separator mats (RBSM) are reviewed.

Results of mercury-intrusion porosimetry data for different separator materials are shown and reviewed. This technique provides an interesting way of differentiating between different separator materials based on their pore size distributions.

## Introduction

In this paper we have sought to review trends in battery separator usage for starting-lighting-and-ignition (SLI), motive power, and sealed valve-regulated lead/acid batteries.

For SLI batteries, the dominant trend in the USA and Western Europe has been a dramatic increase in polyethylene separator usage, and other countries are now expected to follow this trend. It was this trend which prompted the formation of Cookson Entek Limited in August 1988, which is a joint venture agreement between Cookson Group plc and Entek Manufacturing Inc. In August 1989, Cookson Group plc signed a further agreement with Entek, giving Cookson the worldwide rights to the Entek technology, exclusive only of the USA, Canada and Mexico. Since that time, Cookson Entek have installed four manufacturing lines at their purpose-built plant at Killingworth, Newcastle upon Tyne, in order to meet the growing worldwide market for polyethylene battery separators. One of these lines has been specially designed to cater for the manufacture of industrial battery separators. A laminating machine has also been installed to enable a glass tissue to be laminated to the polyethylene separator material for heavy-duty SLI batteries.

A manufacturing plant in South Africa ('Zimtek') to service the growing South African market for polyethylene separators has been operational since March 1990.

For motive power applications, several different types of separator materials are currently favoured, including polyethylene, microporous rubber, microporous PVC and resin-impregnated polyester fibres. Worldwide trends in the motive power battery and separator market are also discussed.

For sealed lead/acid (SLA) valve-regulated batteries, the favoured construction uses a recombinant battery separator mat, normally of 100% borosilicate glass (binder free). Alternative mats containing a proportion of polymeric fibres are now being investigated. Market trends and factors affecting growth in the use of recombinant battery separator mats (RBSM) for valve-regulated batteries (VRBs) are worthy of review.

#### Market trends - SLI

## Worldwide envelope separator usage (SLI)

Figure 1 shows our estimate for worldwide envelope separator usage in SLI batteries for 1992. In North America and Western Europe envelope separator usage predominates and is still growing.

In the Pacific Basin (including Japan, South Korea, Taiwan, Singapore, India/ Pakistan, Thailand), the traditional separator is of the phenolic cellulose or sintered PVC leaf type. There are considerable variations, though, from country to country. In India, for example, the use of sintered PVC predominates. These separators are manufactured locally and some of the larger battery manufacturers have their own in-house PVC separator plants. With a large number of 'unregulated' battery manufacturers coupled with the ready local availability of PVC separators, progress towards envelope technology is likely to be slow.



Fig. 1. Worldwide envelope separator usage, 1992; total batteries vs. envelope batteries by region.

In countries such as South Korea where there is the influence of Western technology, and many of the batteries are exported, there is a progressive switch from conventional leaf-type separators to polyethylene envelope separators.

In Australia and New Zealand sintered PVC and glass fibre leaf separators were favoured but there is now a strong move towards the use of polyethylene. About 90% of the batteries manufactured in Australia now use polyethylene envelope separators.

In Japan, traditional battery design favoured a heavy glass retainer mat laminated to a flat separator of cellulosic fibre paper. A flat veneer separator is still used but with the veneer now also of filled resinous or synthetic fibre compositions. Silica may be included as a filler but still using a conventional wet-laid or paper-making process. The move to polyethylene is slow, but probably inevitable as the Japanese battery manufacturers become convinced of the benefits. An intermediate step is to continue to use a veneer with a glass retainer mat, but with the veneer of polyethylene rather than the traditional materials.

In Latin America, Africa/Middle East, Eastern Europe, growth in envelope separator usage has been inhibited by the capital cost of the associated enveloping and assembly equipment required. Normally, the purchase of enveloping equipment is linked with automated assembly techniques involving other capital equipment costs, e.g., for caston-strap machines. Many of the battery manufacturers in these countries are relatively small, making it more difficult to justify the capital equipment cost.

We have seen dramatic changes in Eastern Europe in recent months. Many of the battery manufacturers in Eastern Europe are now desperate to modernize their factories as they become exposed to Western technology. As this factory modernization takes place, they will want to use the latest equipment and technology, which will undoubtedly include envelope separation. In Fig. 1, Eastern Europe includes Russia, which we believe contributes about 10 million units to the total of 20 million units. However, we have very little detailed information concerning separator usage or future trends for the Russian Federation. For the former Eastern Block countries of Czechoslovakia, Poland, Hungary, Bulgaria, Yugoslavia and Romania, total SLI battery production is about 9 million units, of which only about 1.5% contain envelope separators. Generally, PVC separators are used, which are manufactured locally in each country. By 1994, envelope separator usage will have increased to about 28% of the total, but battery production may decline to about 7.5 million units.

As can be seen from Fig. 1 and the comments above, the potential for further worldwide growth in envelope separation is very significant.

#### North America separator trends

Figure 2 shows separator trends in North America from 1980 to 1996. An interesting feature of this graph is the increasing popularity of glass separators from 1980 to 1986. These became favoured because of their significantly lower electrical resistance compared with cellulose. However, from 1986 on the glass separator declined in usage as polyethylene gained in popularity. The increasing popularity of polyethylene also had a major effect on cellulose separator usage. The PVC separator was never particularly popular in North America.

The latest forecasts indicate that in 1992 80% of all the batteries manufactured in North America will be enveloped, and this will rise still further to 94% by 1996. Figure 3 translates this into separator usage in millions of square metres. This shows that the anticipated growth in polyethylene separator usage will result in a requirement for an additional 35 million square metres of polyethylene separator materials between 1991 and 1996.



Fig. 2. Separator trends in North America; separator type: SLI batteries.



Fig. 3. Polyethylene separator usage in North America; requirement of square metres of polyethylene separator materials, factor 1.5.

#### Western Europe separator trends

In Europe the favoured traditional leaf-type separator materials are cellulose and sintered PVC. The glass separator never became as popular as in North America because of its higher cost.

The move to enveloping initially took place more slowly in Western Europe than in North America. One reason for this was the slower move to lead-calcium batteries in Europe. However, the market for polyethylene envelope separators in Western Europe is now growing rapidly, due as much to the other benefits of polyethylene as the move to lead-calcium or hybrid batteries. The trend is shown in Fig. 4. In 1992 we estimate that over 70% of batteries will be enveloped, rising to 90% by 1996. This equates to a usage of approximately 41 million square metres in 1992 (compared with 22 million square metres in 1989), rising to 52 million in 1996 (Fig. 5).



Fig. 4. Separator trends in Western Europe; percentage of SLI batteries enveloped.



Fig. 5. Polyethylene separator usage in Western Europe; requirement of square metres of polyethylene separator materials, factor 1.12.

In comparing figures between North America and Western Europe it should be noted that the average North American battery uses significantly more separator material than the average European battery because of differences in the average number of plates per battery. A factor of 1.5 square metres per battery has been used for North America and 1.12 square metres per battery for Europe.

# Battery separator types

Traditionally, a wide variety of separator materials have been used, and these include:

- wood, e.g., Port Orford Cedar
- cellulose
- resin-impregnated non woven polyester fibres
- Kieselguhr
- sintered PVC
- microporous PVC
- microporous rubber
- glass
- microporous polyethylene

The natural products such as Port Orford Cedar are inherently porous. In the fibrous products, the random orientation of the fibres gives the required porosity. For the polymeric materials a pore-forming agent is required, e.g., silica in polyethylene separators. The silica has a highly-skeletal structure, prevents the pores from collapsing, is highly absorptive and hydrophilic. In the sintered PVC separator, the light fusion of the spherical particles of PVC provides the required porosity.

The fibrous (cellulosic) materials have a larger pore diameter, low electrical resistance and low cost. Both cellulosic and PVC separators suffer from the disadvantages that they are relatively brittle and can be damaged easily during the battery assembly process.

Polyethylene now has a cost similar to conventional leaf separators, and has a much smaller pore size, which inhibits dendrite growth. To date, microporous polyethylene has been the only separator material which has combined microporosity, low electrical resistance, high oxidation resistance, chemical purity, high elongation and high strength, with the ability to seal the material at the edges using, e.g., pressure, ultrasonic, or thermal welding to form the separator into an envelope which completely protects the plate against short circuits. The ability to envelope the plates also has other design advantages such as the elimination of the 'mudtrap' at the bottom of the container. This gives much greater design flexibility including the ability to use taller plates in the same size of container. For example, elimination of the mudtrap enables an 8% increase in capacity and cold-cranking performance on a typical SLI battery. This unique mix of benefits helps to explain the rapid growth in usage of polyethylene separators. The lower manufacturing costs arising from the Entek technology plus the additional competition arising from the entry of Entek and Cookson Entek into the marketplace have resulted in the current prices of polyethylene separators being comparable to their leaf separator equivalents.

## Battery separator design

Unlike most other battery systems, in the lead/acid battery the electrolyte (sulfuric acid) takes part in the electrochemical reaction between lead and lead dioxide at the opposing electrodes. Thus, the separator design is of critical importance as it will

influence the amount of acid available to the plates. Some of the design considerations include:

- low electrical resistance
- high overall porosity
- thin backweb in relation to overall thickness
- separator rib design to ensure correct spacing between the plates while taking up as little of the available acid space as possible
- good oxidation resistance
- small average pore size to prevent 'treeing' (dendrite growth) through the separator
- freedom from defects-splits, tears, large pinholes, etc.

In addition, modern assembly techniques require that the separator should be tough and resistant to damage during the assembly process.

The polyethylene separator performs well overall when judged against the above criteria. In addition, the ability to form the separator into a protective envelope around the plate which can be sealed at the edges is a major advantage.

The detailed design of the separator, e.g., in terms of rib pattern and dimensions, backweb, etc., is subject to considerable variation.

For batteries containing expanded-metal grids, it is essential to envelope the plates, and the separator must have a good puncture resistance. At the present time, the polyethylene separator is the only one which meets these requirements. Cookson Entek can also supply a slightly different design of separator for this application in which the backweb in the shoulder area of the separator is increased compared with the backweb in the rest of the separator. Our tests have shown that this can increase puncture resistance by up to 50%.

#### Glass retainer mat

Until recently, polyethylene separators have been used mainly for the fast-moving smaller SLI batteries, while for the large heavy-duty batteries conventional leaf separators have been used.

For some applications, e.g. heavy-duty truck batteries, leisure batteries, etc., a glass retainer mat is used to provide protection to the positive plates against vibration and to provide support to the positive plate in deep-cycling applications. With cellulosic or sintered PVC leaf separators, this glass retainer mat is normally glued to the ribs of the separator.

Users of polyethylene separators now want to convert as many of their batteries as possible — including the heavy-duty glass matted batteries — to envelope separation. They are keen to see the benefits of polyethylene separators and of plate enveloping across their whole range of batteries. To achieve this requires the separator supplier to provide a polyethylene separator to which a glass tissue has been laminated. The material needs to be supplied in roll form so that it can be processed through the enveloping machine in the normal way.

Entek has now developed a laminating machine which enables a glass tissue to be laminated to the polyethylene roll stock, and the laminated material can then be rolled up again or cut into pieces.

The machine applies a thin layer of glue to the major ribs only, ensuring that the effect on the electrical resistance is minimized. The glue used is of a type which has no adverse effect on the battery. For laminated material supplied in roll form, the glass tissue should normally be 14 mm narrower than the polyethylene roll stock, to allow enough space between the edge of the glass mat and the edge of the separator for welding.

## Water loss – SLI batteries

In Western Europe the majority of SLI batteries use low-antimony grids (typically 1.8% antimony) or a 'hybrid' construction, i.e., low-antimony positives and lead-calcium negatives. The separator therefore plays a significant part in blocking transfer of antimony from the positive to the negative plates.

Water loss requirements are defined by a standard test such as the DIN water loss test. This requires that water loss should not exceed 6 g/A h after the battery has been on float charge for 500 h at 14.4 V. The new Eurobat test (currently in draft) reduces this to 4 g/A h, but some European battery manufacturers already specify 3 g/A h.

Some traditional cellulosic separators actually do quite well on this test, possibly because the organic resin used in these separators inhibits the transfer of antimony between the plates.

With polyethylene separators, it has been found that the silica used in the separator has a significant effect on water loss. Laboratory tests on two sources of silica – one of which gave a leachable iron content in the polyethylene separator of >120 ppm, the other of which gave a leachable iron content in the polyethylene separator of 50 ppm – showed that the water loss in accordance with the DIN test reduced from >4 g/A h to less than 2 g/A h.

At this time, it is not certain whether it is the leachable iron content of the silica or the intrinsic properties of the silica which result in this reduction in water loss. The leachable iron content may simply be an 'indicator' of silica purity in the same way as the bismuth content of lead and lead alloys can be an indicator of the purity of the lead.

## Market trends - motive power

## World motive power market

Figure 6 shows our estimate for the world motive power market in 1992. Western Europe is the biggest market, closely followed by North America. For North America, Western Europe and the Pacific Rim countries, polyethylene is the favoured separator material. However, this is still predominately supplied in leaf form, although some manufacturers are now forming the separator material into sleeves or envelopes around the plates.

In the Pacific Rim countries, polyethylene is also the favoured separator material, although the total market is much smaller than in Europe or America.

Figure 7 shows our forecast of the annual percentage growth in production of motive power cells in each region. We expect very strong growth in the Pacific Rim and Latin America, slower growth in Africa/Middle East and Japan, and very slow growth in Western Europe and North America.

Figures 8 and 9 show our forecasts for motive power cell production and polyethylene separator usage between 1991 and 1995 for the two biggest markets, North America and Western Europe. We expect the proportion of motive power cells containing polyethylene separators to increase in both these regions.

## Motive power separator types

In the traditional industrial battery design, the separator was a thin, flat microporous rubber or plastic veneer which acted as the antimony-transfer barrier, combined with an extruded or corrugated plastic sheet with relatively large holes used as a mechanical



Fig. 6. World motive power market, 1992; total cells vs. cells with polyethylene separators.



Fig. 7. Worldwide motive power cell market; annual percentage growth in production.

spacer. In modern designs, a separator such as microporous polyethylene or microporous PVC is used, ribbed to give the correct overall thickness.

The types of industrial separators commonly used include the following:

- microporous polyethylene
- microporous PVC
- resin-impregnated non woven polymeric fibres
- microporous rubber
- sintered PVC



Fig. 8. North America motive power market, 1991–1995; total cells vs. cells with polyethylene separators.



Fig. 9. Western Europe motive power market, 1991–1995; total cells vs. cells with polyethylene separators.

The industrial separator materials are characterized by higher backweb thicknesses and overall thicknesses than for SLI separator materials. They also have different profiles compared with automotive. With tall industrial plates acid stratification and gas trapping are potential problems which are influenced by the separator profile. For tubular-plate industrial battery designs, a diagonal rib design is favoured. Industrial batteries experience regular deep discharge and recharge and have a longer guaranteed life than an SLI battery. All this places extra demands on the separator material.

In the USA, polyethylene is the favoured material because of its special properties, e.g., toughness, low electrical resistance, stability, good oxidation resistance, etc. Polyethylene accounts for over 90% of all the industrial motive power separator usage in the USA.

In Western Europe, while polyethylene is popular, other separator materials are also favoured, e.g., microporous PVC and the resin-impregnated polyester mat separator. Microporous PVC is favoured because it is a 'clean' separator (no oily scum release) and has a higher porosity, typically 70% compared with 60% for polyethylene. However, it does not possess the flexibility and strength of the polyethylene separator, and in the future may become the victim of tighter legislation affecting emissions from battery recycling plants. The perceived disadvantages of polyethylene are: (i) oil release and (ii) lower porosity (acid displacement). Both these problems are now being addressed by the polyethylene separator manufacturers.

Where automatic topping-up systems are used, it has been found that the 'oily scum' which may be released from polyethylene separators can block up the valves in the automatic topping-up system. This is not a problem with the type of toppingup system generally used in the UK, but it inhibits the use of polyethylene separators in other European countries, e.g., France and Germany.

This problem is now being resolved in two ways: (i) redesign of the valves used in the automatic watering systems and (ii) polyethylene separator manufacturers are now developing improved separators in which the oily-scum problem is reduced or eliminated.

Polyethylene separator manufacturers are also looking at ways of developing an industrial battery separator with a higher porosity. A high porosity for an industrial battery separator is important because industrial batteries need a good low-rate performance. The industrial battery design tends to be acid limited at low discharge rate and therefore the more acid available to the plates, the longer the discharge.

#### Polyethylene separator electrical resistance

The electrical resistance of the separator has already been mentioned as an important factor in the choice of separator material. Figure 10 shows a plot of separator backweb versus electrical resistance for the Cookson Entek polyethylene separator. The Entek manufacturing process permits the manufacture of separator material with a backweb as low as 0.125 mm, resulting in a significantly lower electrical resistance.

The use of a separator with mini-backribs is favoured by some battery manufacturers, either for specific battery types or for their whole range of batteries. The use of minibackrib material results in a higher electrical resistance separator, as can be seen from Fig. 10. The main benefit is increased acid availability to the negative plates, which in certain applications/battery designs may result in improved performance at high discharge rates. The separator manufacturer may charge a premium for the minibackrib material to cover his higher manufacturing costs.

## Pore-size distribution

We have subjected our own polyethylene separator material and samples of competitors' separator materials to pore-size distribution analysis using the technique known as mercury-intrusion porosimetry. Some interesting results have been obtained (Figs. 11-19).



Fig. 10. Backweb vs. electrical resistance; Cookson Entek polyethylene separator.



Fig. 11. Pore-size distribution data; Cookson Entek polyethylene, SLI.

The Cookson Entek polyethylene separator is characterized by a small average pore size (0.013  $\mu$ m radius) and narrow pore-size distribution. Determination of pore-size distribution of competitors' separators suggests that each separator type – even if it is also polyethylene – has its own characteristic pore-size distribution 'footprint'.

For our own separator material, we have also shown that changes in raw materials – the silica, polyethylene, or oil used – have very little effect on pore-size distribution.



Fig. 12. Pore-size distribution data; Cookson Entek polyethylene, industrial.



Fig. 13. Pore-size distribution data; competitor 1, industrial.

The 'footprint' of each material appears to be determined by the processing conditions used, which are different for each competitive material. The solvent extraction process may be one of the critical factors influencing the separator footprint. For example, the Entek patented extraction process differs significantly from that used by our competitors. It is also worth noting that for the Cookson Entek polyethylene separator the pore-size distributions for both the SLI and the industrial separator material are substantially the same.



Fig. 14. Pore-size distribution data; competitor 2, SLI.



Fig. 15. Pore-size distribution data; competitor 2, industrial.

A certain amount of caution should be used when interpreting MIP results. For example, the pore-size distribution which is obtained may be influenced by the pretreatment which the sample receives (e.g., sample drying), and this should remain constant from batch to batch. Also, the technique may underestimate the total volume of the separator. For this reason, we prefer to measure total pore volume by a simple test which measures the total volume of liquid absorbed by the separator.

Table 1 summarizes the average pore size and total volume porosity for each of the separator samples tested.



Fig. 16. Pore-size distribution data; competitor 3, SLI.



Fig. 17. Pore-size distribution data; competitor 3, industrial.

## Recombinant battery separator mats

The strongest growing market sector is for batteries of the sealed valve-regulated design, using recombinant battery separator mats (RBMS). These are used in applications such as telecoms, standby power, uninterruptable power system (UPS), etc. To date, SLA valve-regulated batteries (VRB) are in very limited use in SLI or motive power applications, but this is expected to change in the future.

Technical problems encountered with early VRB SLI batteries (particularly in the USA) delayed further developments and inhibited other battery manufacturers



Fig. 18. Pore-size distribution data; competitor 4, industrial.



Fig. 19. Pore-size distribution data; competitor 5, SLI.

from developing this market. This was unfortunate, as better applied manufacturing technology could have avoided some of these early problems.

Currently, the major separator-related problems inhibiting the use of RBSMs in SLI batteries are: (i) the relatively high cost of the glass separator; (ii) the low tensile strength of the RBSM which makes it more difficult to use in automated assembly systems, and (iii) aspects of separator performance which need to be improved, particularly for cycling applications.

#### TABLE 1

Separator	Туре	Average pore radius (µm)	Total volume porosity (%)
Cookson Entek, SLI	Polyethylene	0.013	59.8
Cookson Entek, industrial	Polyethylene	0.013	57.9
Competitor 1, industrial	Microporous PVC	1.98	70.7
Competitor 2, SLI	Polyethylene	0.1	53.3
Competitor 2, industrial	Polyethylene	0.1	51.0
Competitor 3, SLI	Polyethylene	0.05	58.3
Competitor 3, industrial	Polyethylene	0.063	53.4
Competitor 4, industrial	Microporous rubber	0.016	N/A
Competitor 5, SLI	Sintered PVC	6.92	N/A

The average pore size and total volume porosity of several separators

To reduce the cost of the RBSM, the use of a lower surface-area (higher poresize) separator can be considered, however this may also decrease tensile strength.

The use of binders may improve the tensile strength and robustness of the sheet. Equipment manufacturers are also developing automated assembly equipment which is capable of handling the more fragile microfine glass separator mats.

Improvements in the separator performance may be achieved by incorporating polymeric fibres, binders or other additives into the sheet. However, such developments may also incur a cost penalty. One separator manufacturer has recently launched a RBSM which includes a proportion of polymeric fibres, imparting a higher tensile strength to the sheet. It is also claimed that the separator material is heat-sealable.

We anticipate that in the next five years the majority of SLI batteries will continue to use conventional 'flooded' construction and separators, with these separators being predominantly of the microporous polyethylene type. However, a small proportion of SLI batteries will use the valve-regulated starved-electrolyte system with a RBSM. This proportion will slowly increase as the remaining technical problems are solved. In fact, even if only 5 to 10% of SLI batteries were to be sold as the sealed valveregulated type, this would make a dramatic difference to the total market for recombinant battery separator mats. For example, if 5 million SLI battery units were converted to VRB technology using RBSMs, this would require an additional 1000 metric tonnes of RBSM per annum, which can be compared with a total worldwide market in 1991 of 2500 metric tonnes.

There will continue to be significant growth in the market for SLA batteries for telecoms, UPS, standby power, consumer applications etc., which is currently growing at 10% per annum. Figure 20 shows our estimate for the growth in the RBSM market through to 1995. This uses a conservative growth figure of approximately 10% per annum. However, a number of factors could significantly affect these figures.

The factors affecting growth in the market for SLA VBRs include:

- expiry of the Gates patent
- increase in electrical power in automobiles, resulting in a requirement for two batteries per vehicle, one of which would be of a sealed valve-regulated construction
- growth in the market for electric vehicles fuelled by legislation such as that enacted in California



Fig. 20. Market projections for recombinant battery separator mats (RBSM), 1990-1995.

- the present electric vehicle development programmes and the forward policy on battery energy management schemes (load levelling, etc.) are based on the successful use of valve-regulated batteries
- the requirement for a low/zero-maintenance battery in a wide variety of applications
- possible moves by car manufacturers to a requirement for a 'fit and forget' battery which can be safely installed and located away from the engine compartment
- the desire by battery manufacturers to escape the fiercely competitive end of the SLI battery market and develop a 'premium' sealed VRB for SLI applications, which commands a 'premium' price
- resolution of various technical problems (e.g., deep-cycle capability) which to date have inhibited wider use of VRBs, e.g., in motive power applications

These factors suggest that our anticipated growth of 10% per annum in the VRB market represents a 'minimum' growth figure, and that by 1994–1995, growth in this market could easily exceed 20% per annum.