Technical Note

Aspects of lead/acid battery technology
7. Separators

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Abstract

The separator is one of the most critical components of the lead/acid battery. Too often, its role in determining performance and life is ignored. Although its primary function is to prevent electrical contact between plates of opposite polarity, it must also give free movement to sulfate ions through the electrolyte space, but restrict the migration of antimony ions from the positive grid to the negative material when lead–antimony alloys are used. The main types of separator are described, from wood through to microporous synthetic material, together with the effect of their physical and electrical characteristics on battery performance and life.

Introduction

The separator is one of the most critical components of the lead/acid battery. Too often, however, its role in determining the performance and life of the battery is ignored. Although the primary function of the separator is to prevent electrical contact between plates of opposite polarity, there must be no restriction of the free movement of the sulfate ion through the electrolyte space. On the other hand, there must be restriction of the movement of the antimony ions from the positive grid metal to the negative active material in batteries where antimony–lead alloy grids are used and where the duty involves regular deep cycling.

In the early days of lead/acid battery development, the migration of antimony was not recognized and simple perforated insulators were used to separate plates. Short cycle lives were common with deep-cycling regimes. Later, the advent of the wood separator (sliced from straight, parallel-grained woods, such as Port Orford Cedar and Douglas Fir) changed significantly the overall performance and life of batteries on such regimes. The major advantage of these woods was the ease with which they could, after steaming, be sliced and grooved to accurate dimensions.

Wood separators

Wood is a composite of lignous and cellulosic material that is derived from both the changing conditions over a growing year and the year-by-year enlargement of the

trunk. Within the natural growth structure are other materials such as acetic acid, resinous compounds and minerals. Acetic acid in the separator reacts with the lead components of the positive plates to produce lead acetate and, in time, a sufficient corrosion reaction can take place to cause the positive pillars to 'neck' and come apart. The discontinuity in the pillar has been the cause of ignition of the cell interior gases and explosions. The resinous compounds tend to restrict the porosity of the separator and this results in poor ionic movement and a high electrical resistance between the positive and negative plates. Minerals can stimulate parasitic reactions and increase a loss in capacity whilst standing on open circuit.

After slicing and grooving the wood shims, they are soaked in hot 3% caustic soda solution for varying periods that depend upon the closeness of the grain, the ratio of lignous to cellulosic material and the thickness of the separator. It is unrealistic to specify a universal treatment time or to attempt to vary precisely that time from batch to batch of a particular size of separator. Compromise soaking times have to be fixed and this can result, from time to time, in some separators being undertreated and some overtreated. Undertreated separators tend to give higher electrical resistances and this reduces the voltage performances at engine-starting rates; overtreated separators tend to have lower electrical resistances and give higher voltage performances during engine starting. The latter separators are weaker than normal and are more easily crushed under the pressures of the expanding active materials so that the separator perforates and short circuits develop.

Table 1 summarizes the effect of temperature and electrolyte concentration on Port Orford Cedar separators of back-web thickness 0.75 mm and overall thickness 1.8 mm. These separators were troublesome in tropical climates and life suffered appreciably. This, as well as the overlogging of the timber, resulted in the replacement of the wood separator by synthetic material separators.

The engine-starting performances of automotive and aircraft batteries were closely related to the thickness of the back web of the separator used. The sensitivity of the voltage at high rates of discharge to the separator thickness is illustrated in Fig. 1. In this study, the plate groups were from the same production batch of plates. The only variable was the separator: in one the back web was 0.5 mm thick, in the other 0.75 mm thick. The difference in the voltage levels is considerable and could make all the difference between easy and difficult starting, particularly at low temperatures.

The accurate control of back-web thickness was not easy to achieve with steamed wood given the natural variables of growth rate, (dependent on the terrain where the tree grew), the position of the sliced shim with respect to the core wood, and the location along the length of the trunk that the cant of wood was cut. It was not surprising that the voltage performance variations between batches of batteries with wood separation was large. Clearly, the increasing power requirements for aircraft emergency engine starting and the regular automotive battery would have strained the continued credibility of wood separators, even if the problems of diminished forest reserves had not occurred.

At the same time as these performance problems developed, there was also a growing demand for dry-charged batteries where all components had to be fully dried and remain in this condition for long storage periods. Wood separators were not normally dried but were assembled into cell elements in the wet state. After the caustic soda treatment, the separators were thoroughly washed and sealed in metal foil until required for cell assembly. This effectively prevented the separators from drying out. With uncontrolled drying, the separators curled and split and were thus rendered unfit for use. With slow and controlled drying, it was possible to dry the

TABLE 1

Effect of temperature and electrolyte concentration on the oxidation of wood separators

| Electrolyte sp. gr.	Temperature of electrolyte (°C)			
	20	40	70	100
1.150	Separator unaffected after 250 h	Unaffected after 100 h	Slightly darkened after 60 h Slightly charred after 90 h	Charred after 8 h
1.200	Separator unaffected after 250 h	Unaffected after 100 h	Slightly darkened after 60 h Slightly charred after 90 h	Charred after 8 h
1.250	Separator unaffected after 250 h	Unaffected after 100 h	Darkened after 24 h Charred after 60 h	Charred after 4 h
1.300	Separator unaffected after 250 h	Unaffected after 100 h	Darkened after 24 h Charred after 60 h	Charred after 2.5 h
1.350	Separator unaffected after 250 h	Slightly darkened after 100 h	Darkened after 15 h Charred after 60 h	Charred after 1.5 h
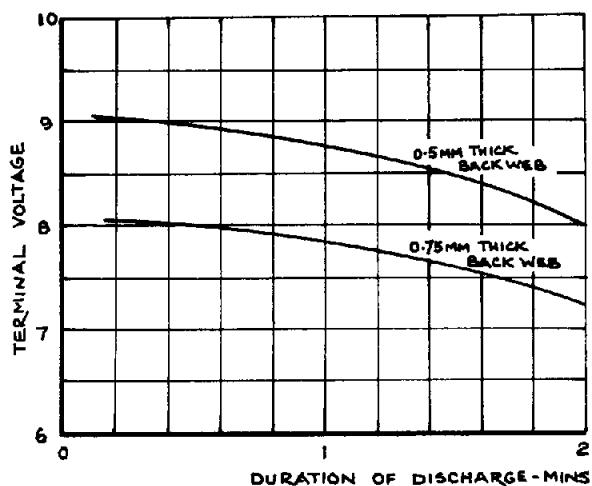
Fig. 1. Effect of thickness of separator back web on the voltage performance of 12 V/40 Ah aircraft batteries discharging at 300 A at 15 °C.

wood separators but scrap was high and, below 0.5 mm back-web thickness, was prohibitive in cost. All these factors stimulated the development of separators from synthetic materials that would not be subject to the manufacturing headaches with wood or to the uncertainty of continued supply.

Diatomaceous earth and microporous, hard-rubber separators were the earliest developments, although some temporary substitutes made from wood fibres and ground barks were used with little success. Later came microporous polyvinyl chloride (PVC) and resin-impregnated paper. These were followed by sintered plastics and resin-impregnated nonwoven plastic sheets.

Diatomaceous earth separators

There is a plentiful supply of the fossilized skeletons of microscopic unicellular algae in the world. These have been deposited over long periods of time and, when ground, form a highly-porous, low-density, inert powder in which each particle is also porous. When these ground particles are reconstructed by the addition of a latex and, usually, fine glass filaments, the separator so formed can be profiled to suit the cell assembly. Furthermore, the separator is virtually untouched or degraded throughout the battery life by either the electrolyte or the lead dioxide of the positive plate.

The general manufacturing method is to produce a diatomaceous earth/latex mix and to calendar roll the mix on to a glass-fibre mat to the required profile. After calendaring, the water content of the latex is driven off by heat. Although it is possible to calendar roll ribs, these ribs have little strength and are easily damaged. Because of this, diatomaceous earth separators are more commonly produced as flat shims. Flat separators tend to deny the positive active material of that excess of electrolyte, normally in the space between the ribs, which allows the positive material to be exploited. When the flat shim separator is used with conventional wet-paste densities, performance is often reduced. Nevertheless, as the flat surface of the separator is supporting the positive material, the density of that material can be reduced without the risk of material shedding prematurely and shortening the battery life. A reduction in the active material density increases the material porosity and, consequently, the amount of electrolyte that is held absorbed within the active material. Excellent performances and lives have been obtained using flat types of separator by applying this method of design as the pressure of the separator on both positive and negative materials prevents the plates from suffering uncontrolled expansion. The separator has been condemned unjustifiably through not recognising the above factors, as well as the very good control that it can exert, by virtue of the microporosity, on the rate of migration of the antimony ion from the positive grid to the negative active material.

Porous rubber separators

Microporous, hard-rubber separators were made by inverting a latex containing vulcanising agents and spreading the creamy mix on to a moving belt. The mix was combed to the required cross-section by using a doctor knife to form the rib profile. The strips were then vulcanized in an autoclave to remove the aqueous phase of the latex. The removal of the water through the thickness of the strip as minute droplets

creates a network of micropores. The sides of the strips were then trimmed to width and guillotined to the required separator lengths. These separators tended to be brittle so that, without some degree of softening, they could not be handled without creating high scrap. In an endeavor to reduce the brittleness, alternative manufacturing methods were employed such as incorporating glass fibres and/or silica gel in the mix, rolling the mix on to glass-fibre mats, or using natural rubber instead of the latex. Irrespective of the method employed, these separators were expensive. On the other hand, the behaviour of the separators in batteries was exemplary as they contributed little in the way of contaminants and the migration of antimony was less than most other quality separators. As a result, they conferred high-performance stability, reliability and long life to the product.

Microporous polyvinyl chloride separators

The high cost of microporous hard-rubber separators led to the development of the microporous PVC separator. The raw materials for PVC types were cheaper and the resulting separators were flexible so that scrap due to breakage in handling was much reduced.

Initially, microporous PVC separators were made by incorporating very finely powdered starch within a PVC/solvent mix. The mix was extruded as a thin sheet and passed immediately through calendaring rolls to develop the ribs and size the thickness of the back web. The solvent was then removed and recovered for further use. The solvent-free strip was immersed in boiling water and this caused the starch grains to swell and rupture the intervening PVC membrane. This brought the grains of starch in contact with each other. They were then removed by conversion into a sugar, through reaction with boiling sulfuric acid solution, and subsequent dissolution. This left an interconnecting network of micropores in a PVC matrix.

The strip still retained a proportion of the stresses induced by the mechanical work of the extrusion and rolling processes. These stresses were relieved by subjecting the material to jets of live steam that converted the strips into a material with flexibility, water repellency, and little wicking action. To overcome the latter two characteristics, the strips were treated with a wetting agent after which they were dried and cut into the required lengths.

Later developments were the incorporation of some wood flour into the mix. This had the effect of reducing the effective pore size and of providing a source of lignin to supplement the benefits that arise from the use of organic expanders in the negative active material. The restriction that the added wood flour gave to the migration of antimony gave rise to an increased life in service.

Over the forty or more years since microporous, hard-rubber and PVC separators were introduced, the methods whereby the microporosity was obtained have been modified and later separators have not had to resort to treatment with agents to obtain good wetting and wicking properties.

Other thermoplastic materials to PVC have been evaluated but only polyethylene has been found acceptable for commercial exploitation. Polyethylene compares well with PVC in terms of pore size, porosity and toughness.

There has been criticism of the PVC separator on the grounds that chlorine is released into the cell electrolyte and causes loss of life compared with other separators, such as hard rubber and equivalents.

Sintered thermoplastic separators

Powdered PVC and polyethylene readily sinter under radiant heat and, in the process, form a porous structure with good permeability and low electrical resistance. The usual manufacturing method has been to feed the thermoplastic powder by either vibration or direct pick-up from an open-bottomed silo, and to comb the powder to an approximation of the required thickness profile. The combed powder is then passed through calendar rolls to consolidate the ribs and to size the back-web thickness. The shaped powder is then passed through radiant heaters that are sufficiently hot to soften and coalesce the particles at the contact points, but not hot enough to melt the grains. The effect of this process is to produce a continuous porous structure or rigid thermoplastic sponge. The average pore size is related to the initial particle size. The grains of the thermoplastic powder are crudely spherical and this limits the maximum porosity to about 50%. By comparison, microporous PVC and polyethylene separators can achieve porosities of 60 to 70% without losing strength to such an extent that the separators become deformed under the expansion forces that are exerted by the active materials.

Both PVC and polyethylene powders have minimum angles of repose that limit the profile of the rolled ribs to a relatively broad-based truncated triangular form, instead of a rectangular geometry. Closely pitched ribs are likely to show collapsed areas and the production of deep, fine ribs is particularly difficult. As a result, sintered thermoplastic separators are generally characterized by widely spaced ribs and a smooth reversed side. The latter has the effect, when placed against the negative plate surface, of denying that plate the small reserve of electrolyte in excess of the absorbed volume that is beneficial in maintaining relatively high voltage levels when batteries are discharged at engine-starting rates at low-ambient temperatures.

The difference in powder costs and the greater water repellency of polyethylene compared with PVC has not favoured its use. Polyethylene separators are also prone to 'leading through' i.e., to lead forming within the thickness of the separator and causing short circuits.

Sintered plastic materials require treatment with a wetting agent before they are suitable as separators. Their greatest advantage is the precise control that is possible over the back-web thickness and the thinness of the back web that can consistently be maintained. A back-web thickness of 0.25 mm is practicable in bulk production. This is of great help in reducing the voltage loss under engine-starting currents, particularly at low temperatures.

Resin-impregnated paper separators

During the latter years of World War II, it was recognized that the requirements for separators for automotive batteries were different to those for motive-power batteries. In the latter, which are subject to regular deep discharging and subsequent recharging, the following two situations can arise:

(i) Antimony, passing into solution from the positive grid alloy, migrates to the negative where it is deposited on the plate material. The rate of deposition is reduced by interposing a finely microporous separator between the positive and negative plates. Such separators tend to be costly.

(ii) Lead sulfate, a direct product of discharge, has a small but finite solubility in low-concentration electrolyte. The maximum solubility of about 6.7 mg l^{-1} occurs at a sp.gr. of 1.060. Over a period of deep cycling, some lead sulfate goes into solution

and collects at the bottom of the element. As the electrolyte density increases with recharge the solubility of lead sulfate decreases and crystals of lead sulfate form. These crystals accumulate in the free electrolyte both at the bottom of the container and in the lower portions of the active materials and the separators. As the recharge proceeds further some of these crystals are converted into metallic lead that permeates the lower portions of the separators and renders them electrically conducting. This causes short circuits and internal discharge. In time, the battery fails prematurely.

The absence of regular deep discharging and the accompanying low-concentration electrolyte in automotive batteries reduces the circumstances that favour the incidence of 'leading through'. Thus, liberties can be taken in the size of the pores of a separator without the introduction of sufficient freedom for antimony migration or 'leading through' to reduce significantly battery life and performance.

Paper is made by the random laying of cellulosic fibres. The only control that can be exercised over the pore structure is by varying the substance of the paper, i.e., the weight of cellulosic fibres per unit area of finished paper. The random lay permits marked differences to exist between the largest and the smallest spaces between the fibres. In practice, spaces that have an equivalent of pores greater than 50 μm in diameter form the greatest part of such papers. These could not be described as micropores.

The presence of such large spaces does not introduce serious risks of premature failures on life in automotive batteries, provided there are no pinholes present through which active material can pass. The fibres will accept acid-resistant coatings to protect them from oxidation in the presence of dilute sulfuric acid and lead dioxide.

The environment in which the separator has to operate without serious degradation is about 35% H_2SO_4 at temperatures up to 70 °C. Phenol formaldehyde polymers are compatible with cellulose fibres and types are available that will truly impregnate the fibres. Others do not fully wet the fibres but run back along the fibres to form a globule of resin at the fibre crossovers. These globules harden with cutting and give to the treated separator the appearance of strength and protection, but do not impart the oxidation resistance that is needed. Such separators soften rapidly during service in the battery and do not stand up to the physical pressures from either the expanding active materials or the frictional abrasion due to vibration.

In the early development period of paper-based separators, mixed fibres with a high content of cotton linters were used. The addition of cotton linters produced a paper of high quality that could be controlled relatively easily for substance and thickness. Cotton-linter fibres have a high α-cellulose content, are highly crystalline, and have a low value for specific surface. All these characteristics produce a good base material. In addition, α-cellulose is a highly purified cellulose and is therefore more resistant to oxidation in the presence of sulfuric acid than other, less pure, celluloses.

The greater the crystallinity of the cellulose, the lower is the rate of attack. This is because the crystallites are not so readily penetrated by the electrolyte as the amorphous areas. In general, the rate of chemical attack is approximately proportional to the specific surface.

Cotton linters tend to be more expensive than other cellulosic fibres. Developments concentrated on matching cheaper fibres with compatible impregnating resins in order to survive in a highly competitive market. Some matches were more successful than others, although the main difference between brands lay not so much in the direct differences in electrical resistance or comparative life, as in the reproducibility of those characteristics in bulk-production quantities over extended periods of time. As a

consequence, in assessing the acceptability (or otherwise) of differing makes of paper-based separators, the task became one of extended trials since the results of a single trial were unreliable. Where testing time was restricted, it was prudent to secure separators from suppliers with proven global sales, rather than to accept the lowest price commodity.

Whilst the compatibility of the impregnating resin and the paper base was of first importance, there were other factors that caused early failures in service. Those portions of separators (i.e. the ribs) directly in contact with the lead dioxide of the positive material, a powerful oxidizing agent, degraded faster than the remaining areas. The degraded material readily broke down and became perforated with vibration. Rib damage was reduced greatly either by kiss-coating the surface of the ribs with a viscous, hard thermosetting resin that was resistant to abrasion and oxidation, or by forming the ribs from extruded PVC filaments that were cemented to the surface of the separator which would be a flat impregnated sheet.

Surface oxidation of the back web was reduced by spraying it with a viscous PVC plastisol, or by brushing into the surface a fine PVC powder and then sintering this powder.

Resin-impregnated, paper-based separators are made either by corrugating the impregnated paper stock by passing it through profiled squeeze rollers and heat curing the resin, or by pleating the paper stock after impregnation and curing. The former is corrugated longitudinally, whilst the latter is pleated transversely. The pleated method produces a separator that is more pleasing visually, but the corrugating technique forms separators with an electrolyte reservoir in the corrugations that provides extra electrolyte to the negative material to improve the cold-starting performance.

The paper-based separator is associated with shallow discharge batteries where the problem of antimony migration is not serious. Where batteries with paper-based separators are sold for regular deep-discharge purposes, such as radio-controlled taxis, motive power supply, etc., the life expectancy is reduced. In such applications, it is usually economic to specify a more expensive, but truly microporous separator.

The problem arises where it is not economic to use the expensive separators and a compromise has to be adopted. One such compromise used for all but really heavy discharge applications has been a composite of sintered PVC and resin-impregnated paper. The combination of a sintered membrane and an impregnated cellulosic carrier greatly reduces the effective pore size through the mismatch of the two components' pore structures. The result is an improvement over the pore structures of either the sintered PVC or the impregnated paper. It is possible to incorporate wood flour into the powdered PVC before sintering. This will allow a further reduction in effective pore size, and will provide a small extra source of lignin to assist cold-start performance.

It is possible with the composite separate to manoeuvre the manufacturing cost by varying the propositions of sintered PVC to paper and, within limits, to exploit price differentials between the two. A typical automotive composite separator made on this laminate principle could have the following material contents for a rib thickness of 2 mm: paper base (1.65 g), phenolic resin, as solids (0.60 g), and PVC powder (6.75 g).

Separator characteristics that determine battery performance and life

Separator characteristics can be broadly categorized as those that will: (i) assist cell assembly; (ii) assist battery commissioning; (iii) control capacity and performance, and (iv) control life.

Cell assembly

Cell and element assembly methods vary according both to the size of the production batch quantities and to the type of cell concerned. In many automotive battery factories, it is common practice to break the production programme into cell types that are enjoying long production runs, those types that command, medium length runs, and those unpopular types for which only short runs can be contemplated.

The long-run types of cells can be highly mechanized and can use production aids such as element-stacking machines to reduce the labour content. Medium runs often cannot carry the high investment costs for mechanized machines to the same extent as the long-run types. The short-run types become uneconomic on highly mechanized lines due to the frequency with which those lines would have to be changed to accept batteries of a different size or design.

The insertion of separators into cell elements via the use of stacking machines is common on high-production output lines. These machines are difficult to maintain in continuous operation unless the separators are flat, rigid and without excessive brittleness. A degree of brittleness can be accepted, however, provided that the separators are flat. Stacking machines using suction pads to lift the separators from the stack and then to deposit them on the element pack will accept a degree of bowing across the width of the separator. By contrast, machines that employ pusher fingers inevitably produce a lot of scrap wherever separators cease to be truly flat. The most satisfactory separators for the pusher-type of machines are those made from a flat paper stock on which the ribs are formed by the cementing on of rigid thermoplastic filaments.

Pack building by hand is the most tolerant of element building methods and will accept both rigid and flexible separators, flat or bowed. Very brittle separators tend to develop splits not so much in the pack building, but later when the packs are inserted into containers, particularly if there is bowing.

Hand insertion of separators into interleaved plate groups calls for a degree of rigidity without brittleness. Very flexible separators, such as microporous PVC, tend to bend over and be pinched or creased during insertion and, therefore, cannot be settled evenly to overlap the edges of the plates unless they are close to that position when first they enter the groups. Under the cell pressures, pinches or creases become danger points that lead to the development of premature faults, often with adverse effect on life.

In traction cells, where the element height is large compared with the width, hand insertion is virtually impossible. Flexible separators jam, crease and double up; brittle separators tend to crack. It is necessary to build up plates and separators in sequence in a fixture. This allows the separators to be placed in position with no restriction, and the cell element to be eased to the correct thickness by pressure on the element over the whole area of the plates. Burning combs fix the correct pitch of the plates.

There are still some handling problems as some flexible separators are readily torn by sharp, pointed fingernails. This is especially so when using female labour. It can be quite a serious problem and some battery makers, wishing to avail themselves of the good life characteristics of microporous PVC separators, have found it expedient to armour the material with the addition of a separate thin, tough sintered PVC film. This adds to the cost of the separation and can give trouble with stagnant areas between the two membranes.

A comparison of the strengths of various separators can be obtained using a Mullen burst strength tester, a common tester in the papermaking industry. This

equipment applies a continuously increasing load over a fixed area of the back web of a separator until puncturing occurs. The pressure at burst of each particular separator type is a measure of the ability of the separator to withstand surface damage in initial handling. An empirical alternative to the Mullen tester is a procedure where steel balls are dropped from varying heights on to a clamped disc cut from a separator that is fixed with the ribs on the opposite side to the point of impact. The unit of comparison is the potential energy required to crack or penetrate the sample, whichever occurs first. If cracking precedes penetration, the separator is likely to split, crack or break in handling. If penetration precedes cracking, the separator is likely to give little trouble in assembly. If the separator is noticeably deformed before either penetration or cracking occurs, it is likely to give low scrap levels in stacking machines and hand pack assembly, but could give trouble where hand insertion into interleaved groups is used.

Based on a figure-of-merit of 1 for Port Orford Cedar or Douglas Fir separators, typical values of burst strength for various synthetic types of separators are given in Table 2. Sundberg [1] indicates that the method of manufacture of a microporous PVC separator can exert a considerable effect on the burst strength. He enumerated comparative data that related to a proprietary PVC separator that was sold under the trade name Amer–Sil, see Table 3.

The interpretation of either of these test data in terms of production economics and technical excellence is not straightforward. The data derived from the burst strength comparison that is based on the dropping-ball method gives a qualitative assessment of how well the separators can be handled during the battery assembly stages. On the other hand, the Mullen data give guidance of the ease, or otherwise, to which

TABLE 2

Strength of separator materials – typical values

Separator type	Relative burst strength
Port Orford Cedar (damp)	1
Resin-impregnated paper	0.2–0.3
Microporous rubber	0.15–0.3
Microporous PVC	1.5–2.5
Sintered PVC	0.3–0.5

TABLE 3

Measured values of separator burst pressure [1]

Separator type	Burst pressure (psi)
Resin-bonded paper	4–20
Sintered PVC	20
Microporous PVC	25
Microporous rubber	30
Amer–Sil	40
Microporous polyethylene	greater than the limit of the apparatus

the separators, when assembled in a battery, will withstand the physical pressures that occur during service.

Battery commissioning

When a battery is commissioned, other than as a wet formed unit, it is important that the electrolyte poured into each cell is rapidly absorbed by both the active materials and the separators. After the initial wetting, the electrolyte must be able to diffuse readily through the porous mass of the separator and not hinder the further diffusion of the electrolyte in the free space between the plates into the mass of the active materials. Unless this further diffusion occurs, the electrolyte that is rapidly consumed within the active materials at high discharge rates cannot be restored sufficiently fast to maintain the cell voltage.

Both the time for the separator to become saturated with electrolyte and the permeability of the separator material to standard concentrations of electrolyte are important characteristics. Only a few separator types wet satisfactorily without recourse to a previous impregnation with a wetting agent. There are dangers with the introduction of wetting agents; too much can reduce the efficiency of formation of the negative active material so that the material is not fully converted and the subsequent performance of the cell is adversely affected. Thick separators are more likely to be affected than thin ones as, with a standard concentration of wetting agent, the amount of the agent will be higher where the separator mass is greater. Where thick separators are required, it is preferable to use separators that have not been treated with a wetting agent, if cost allows this choice.

Insufficient impregnation by the wetting agent is only a problem in dry-charged batteries, where the units are required to start an engine soon after addition of the electrolyte. The illusion of a faulty battery is sometimes created in those circumstances unless the soaking time after filling is increased. This allows further time for the separators to become fully saturated. The danger is that this trouble will not be noticed until failure to start an engine after the allotted soaking time is experienced. Where automotive batteries are supplied as dry-charged stock, the purchaser should be informed of the minimum safe soaking-time in order to ensure that the full designed output at engine-starting rates is realized. Attention to this adds to customer satisfaction and minimizes complaints.

Whilst it is helpful to test incoming batches of proprietary separators for speed of wetting, the results can be misleading unless equated to the speed of wetting of the active materials. This is because the latter is sometimes the slower stage, and what may appear to be a poor separator batch in this respect may, in fact, be completely acceptable when compared with the active materials used. It is the gross cases that usually cause problems and these do occur from time to time. An electrical resistance test will often show up such inadequacies.

Accidents do happen in normal production and batteries are repaired to reduce scrap costs. The separators in wet-charged stock should not be allowed to dry out during the repair operation. If this does occur with separators, and depending on the use of wetting agents, the subsequent wetting can be slow and the designed starting performance may never be attained.

A water gauge is sometimes specified to test routinely the permeability of the separator to water under a moderate pressure, e.g., 50 cm. Care should be taken in interpreting the results since there are conflicting requirements to be balanced. A high permeability is needed at high discharge rates to assist the diffusion of electrolyte into the active materials and to maintain good voltage levels. Where a battery is to

be regularly deep cycled, and the migration of antimony has to be limited, the permeability should be low. High-permeability separators are preferable for automotive batteries, and lower permeability ones for traction applications.

Robinson and Walker [2] quote the permeability data given in Table 4.

Battery capacity

Invariably, the capacity of a battery at low discharge rates is determined by the volume of electrolyte that is available for the reaction. The displacement volume of the separators can be a critical factor in cases where capacities are difficult to obtain. Where the capacity is of prime importance, the choice of separator should be influenced by the weight of the dry separator and the volume porosity.

Volume porosity is usually determined by measuring either the amount of water that is soaked up by a number of samples or the amount of a mobile liquid like n-propanol. Volume porosities vary from about 50% for sintered plastic separators (where the original particles are crudely spherical) to 60 to 70% with resin-impregnated paper separators and microporous rubber separators, and as high as 80% for some microporous PVC separators. The Port Orford Cedar separators fall into the 80% volume–porosity class.

Port Orford Cedar separators consist of a parallel framework of ligneous material that encloses the cellulosic material. The material is naturally resistant to permanent compression by the active materials. High-porosity microporous PVC separators have not the same resistant structure and readily compress as the active materials expand during discharge. As a consequence, PVC separators can be reduced in thickness to less than half their original thickness in extreme cases of element tightness, high temperatures and hard working. The effect of this is a reduction in the volume porosity and an increase in the separator resistance. Some sacrifice in the volume porosity usually leads to a greater dimensional stability in the separators and a more predictable battery life.

Battery performance

Battery performance at high rates depends initially on: (i) the wetted area that is developed within the active material, and (ii) how the voltage at the cell terminals is modified by the resistance losses in the electrolyte and the separation. Ideally, the separators should have negligible resistance; this is not possible, but the lower the electrical resistance the greater is the power developed at the battery terminals.

TABLE 4

Permeability of various separator materials [2]

Separator type	Permeability to water ml cm^{-2} min^{-1} at 50 cm water gauge and 15 °C
Microporous PVC	1.6
Sintered PVC	92
Sintered polyethylene	240
Microporous rubber	1.8
Resin-bonded paper	129
Latex/kieselguhr/glass-fibre	37
Polyethylene/cellulose	52
Port Orford Cedar	0.0007

The electrical resistance of the separators is more important in automotive batteries than in traction batteries. In the latter, the highest discharge rates are rarely greater than the 15-min rate.

Opinions differ over which method of measuring the electrical resistance is the more meaningful, i.e., d.c. or a.c. technique. One d.c. method of deriving electrical resistance depends on measuring the difference in voltage across a test cell with and without a separator in the circuit. A suitable test cell is shown schematically in Fig. 2. It comprises two positive plates with a single negative plate in between. The plates are fixed apart and the separator under test is interposed between one positive plate and the negative plate with a known area exposed to the current flow. The test and balancing cell arrangement is connected into the circuit shown in Fig. 3. The method of operation is to adjust the current in the test cell, without the separator in position, to a fixed value of the order of 0.1 A per cm^2 of separator exposed. The current in the balancing cell is then adjusted to give zero voltage difference as indicated on the voltmeter, V, and the millivoltmeter, MV. The use of both a voltmeter and a millivoltmeter is to protect the millivoltmeter during the initial setting-up as there may be a considerable out-of-balance current until the adjustments approach a balance. When the voltmeter indicates zero voltage difference, it is then safe to switch over to the millivoltmeter and obtain a final balance.

The separator, which is soaked previously in electrolyte for at least 24 h, is then inserted into the test cell; this creates an out-of-balance. The millivoltmeter reading indicates the voltage loss due to the separator. The electrolytic resistance of the separator is then calculated by dividing the voltage indicated by the current density.

Values for the electrolytic resistance of different types of separators, as determined by the above method, are given in Table 5.

The design of the rib profile and the thickness of the back web have a major bearing on the value of the electrolytic resistance. Where improvements in engine-starting performance are being sought, some success is usually forthcoming by using separators with narrow ribs and a back web of reduced thickness. These, coupled with some bowing of the back web or hollowing behind the rib profile, can cause an increase in the terminal voltage of a 12-V battery of as much as 0.5 V at currents of the order of $5C_{20}$ A.

The effect of reducing the back-web thickness of porous polyethylene separators on the electrolytic resistance is shown in Fig. 4.
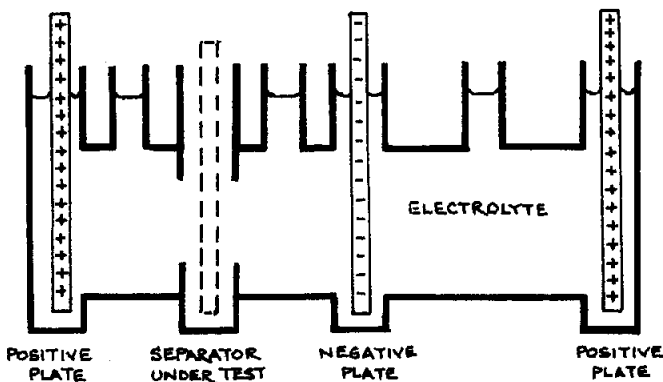

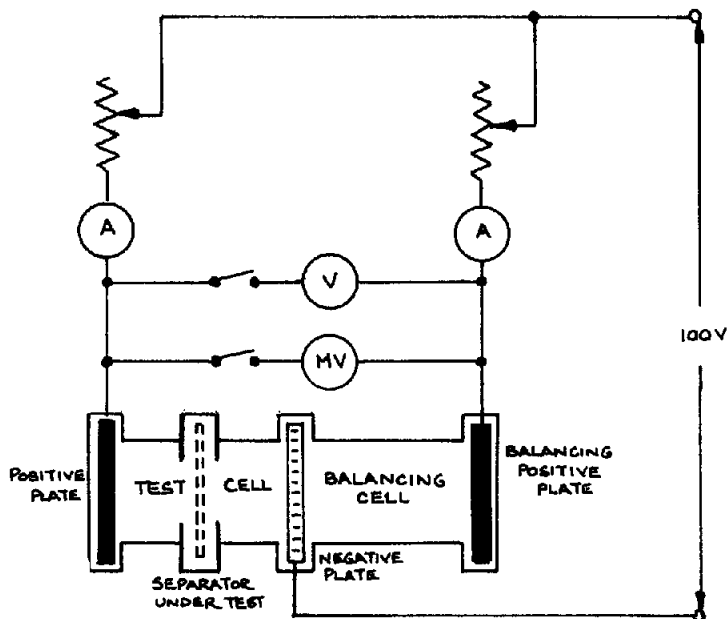Fig. 2. Combined separator-resistance test and balancing cells.

Fig. 3. D.c. test circuit for measuring separator resistance.

TABLE 5

Electrolyte resistance of battery separators

Separator type	Resistance (Ω cm^{-2})
Port Orford Cedar	0.2–0.3
Resin-impregnated paper	0.15–0.25
Sintered PVC	0.15–0.25
Microporous rubber	0.3–0.4
Microporous PVC	0.2–0.3

The use of a.c. for the voltage supply is claimed by some operators to give more reproducible and representative results for the impedance offered by separators. Vinal [3] gives details of one circuit that employs an a.c. supply. This circuit is shown in Fig. 5. It differs from the d.c. method described above in having two potential electrodes separated from the current circuit and fed with current from one section of a split secondary winding of the input transformer. The other section of the secondary winding feeds the main current path. The separator is soaked in electrolyte for at least 24 h and is then placed in position in the test cell. The orifice in the separator compartment determines the separator area for the test. The current in the main circuit is set at a predetermined value, usually of the same order as for the d.c. test. The slide-wire in the calibrating circuit is adjusted until there is a balance as indicated by the a.c. galvanometer in phase with the a.c. supply. The calibrating circuit forms a potentiometer circuit and an accuracy of ~1% is claimed.
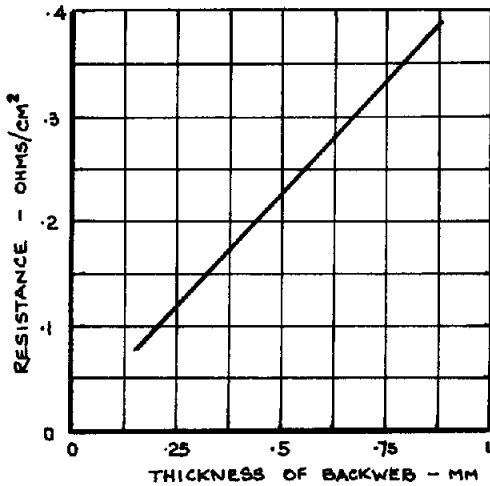
Fig. 4. Effect of back-web thickness on the resistance of porous polyethylene separators.
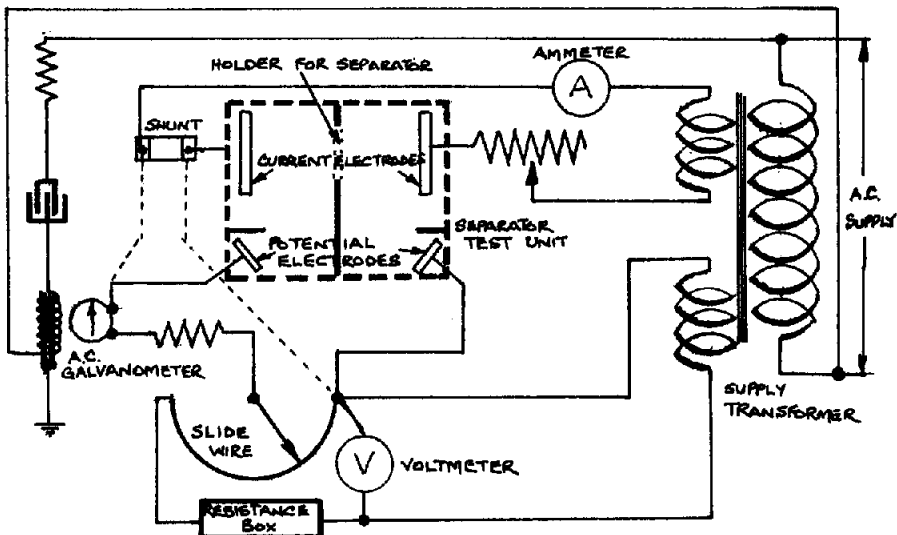

Fig. 5. A.c. test circuit for measuring separator resistance.

Battery life

Battery life is usually designed into a cell on the basis of the corrosion life of the positive grids. This corrosion is predictable under controlled grid production and can be assessed on the basis of corrosion tests that simulate average working conditions. Positive grid corrosion is controlled mainly by the magnitude of the charging current and the duration after the active materials have been substantially converted. The migration of antimony from antimony–lead alloy grids and its deposition on the negative active material cause the evolution of oxygen to occur at a lower voltage than if antimony deposits were not present. The top-of-charge voltage is reduced and this results in an increase in the charge current. The latter, added to the increase in the

oxygen present, leads to more rapid corrosion of the positive grid metal. Since the release of antimony occurs more readily under deep-discharge conditions, the problem of antimony migration is more relevant to traction than to automotive batteries.

The separator has the important role of hindering the migration of antimony. One factor that contributes to the excellence, or otherwise, of the control exercised by the separator is the smallness of the pores and the tortuous nature of the pore paths.

The outdated Port Orford Cedar and Douglas Fir wood separators were excellent in restricting the movement of antimony because of the natural growth pattern in which the cellulosic sections consisted of a series of discrete vacuoles. Each vacuole was, in effect, a rough cube in which the sides were osmotic membranes, see Fig. 6. The pore structure was exceedingly fine. Also, the nature of the wood surface was such that it clung tightly to the surface of the negative active material against which it was placed. This meant that soon after a battery had gone into service, there were little or no areas where the wood separator and the negative material were not in intimate contact. Any antimony released had to pass through the vacuole structure in order to reach the negative material. In comparison, the pore structure of synthetic separators is coarse. In the main, the structure consists of a mixture of solid particles and air passages. Moreover, the intimate contact between separator and the negative material is missing. Many types of synthetic separator have fine ribs on the side that is adjacent to the negative active material in order to overcome the lack of intimate contact and to control the free release of gases.

Figure 7 gives data for the pore-size distributions in various types of synthetic separators. Over many years, it has been confirmed that, under regular deep-discharge regimes, resin-impregnated paper and sintered PVC or polyethylene separators do not restrict the movement of antimony to any extent. By contrast, the other types of separator have amply demonstrated their ability to restrict antimony migration to within the limits of market acceptance. On the basis of this, it is reasonable to accept that, for satisfactory traction cell life, the dominant pore diameter should not exceed 3 μm, with not more than 10% of pores exceeding a diameter of 5 μm. Separators that combine in a lower dominant pore diameter than this, and have a volume porosity of 70% or more, should produce cells with long positive-grid corrosion lives, when there are no grid-casting blemishes that provide preferential sites for corrosion.

Where the dominant pore diameter exceeds 10 μm, there is a danger, on deep discharge, for lead sulfate crystals to lodge within the large pores and to be converted
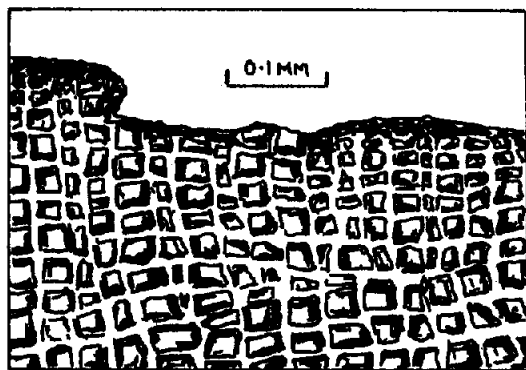

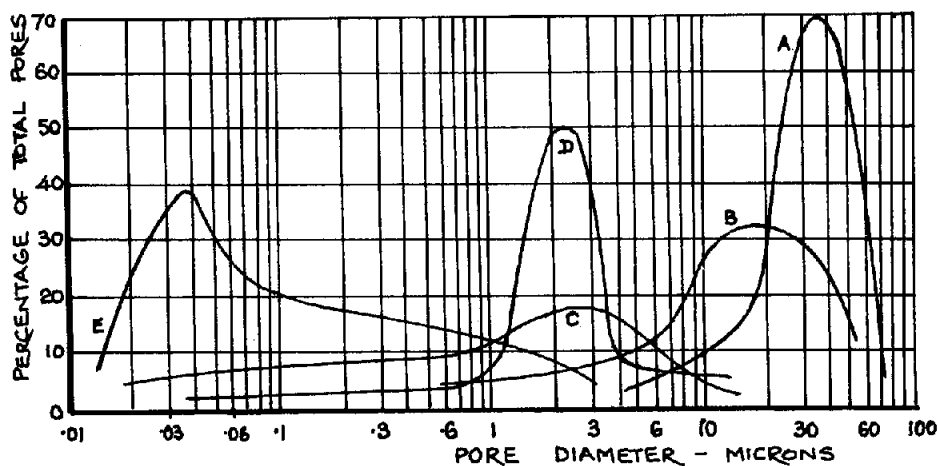Fig. 6. Section through a treated wood separator showing the vacuole network.

Fig. 7. Typical pore diameter distributions: (A) resin-impregnated paper separators; (B) sintered PVC separators; (C) microporous rubber separators; (D) and (E) microporous PVC separators of different makes.

into conducting lead on charge. The result is a conducting separator and internal short circuits.

The incidence of pinholes in separators is equivalent to the presence in the pore-diameter distribution of an extension beyond the 100 μm range. If there are many pinholes, the risk of lead forming within the pores is increased. This is because, depending on the equivalent diameter of the pinholes, active material can penetrate in addition to the lead sulfate crystal.

The only way to confirm the above is to carry out large-scale life tests with the separator material as the variable. There is a danger in taking life tests to ultimate failure as that failure may not be the same for all trial cells. By the time that the cells have deteriorated to such an extent that they cannot deliver their specified minimum capacity, it is difficult to determine the true cause of failure. In order to compare the effect of average separator pore diameter on cell life, a reasonable approximation can be obtained by measuring the change of negative potential during a sequence of charge/discharge cycles and then comparing the cycle life to an end-point defined as a negative-to-cadmium voltage of − 0.1 V. Up to this negative potential, the loss of potential can be attributed mainly to the effect of antimony transfer from positive grid metal to negative active material. Over a long period of monitoring traction batteries in service, it has been found that a laboratory life test, in which 80% of rated capacity is removed at each discharge and 17 to 20% excess capacity is replaced each recharge, will represent a service life of 4 to 5 years of relatively onerous working if a laboratory life of not less than 1000 cycles is realized to a negative to cadmium voltage of − 0.1 V. This is a useful guide and in Fig. 8 the distribution curves of cycle life are shown for: (i) microporous rubber separators with a dominant pore diameter of 2 to 3 μm, and (ii) a composite separator with a dominant pore diameter of 8 to 10 μm. Whilst the larger pore-diameter separator will, on average, meet a 4-year life under medium-to-heavy usage, there is a risk of an excessive proportion failing to meet that life under heavy operating conditions.
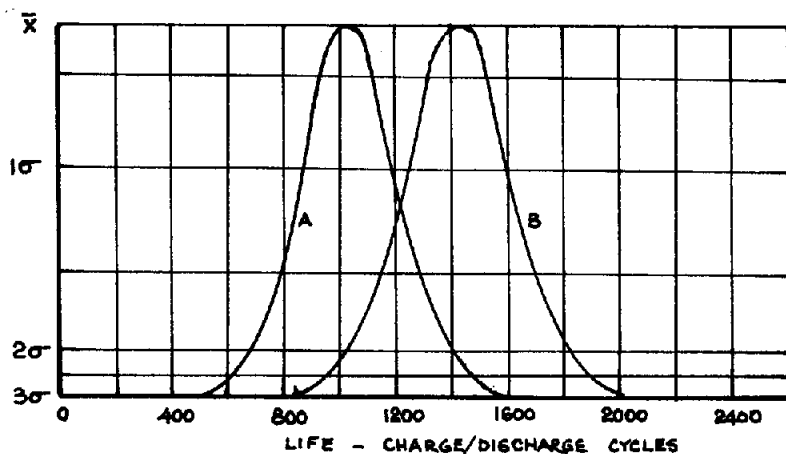
Fig. 8. Distribution curves of cycle life to −0.1 V negative-to-cadmium voltage for separators of varying dominant pore diameter: (A) dominant pore size 8–10 μm, and (B) dominant pore size 2–3 μm.

Influence of separator profile on negative material behaviour

It has often been said by those who have passed through the era of wood separators to that of the synthetic separator that, despite the incorporation of consistent organic expanders into the negative active material, the texture and activity of modern negative materials never matches up to those levels that were common during the days of wood separators. To some extent this is true. For example, after some months's use, the negative material of many manufacturers often fails to exhibit the clean, even silvery appearance that, one time, was associated with a good healthy negative. Most negative plates appear dull and often there are patches of unexpanded material surrounded by sound, healthy material.

One major advantage of the wood separator was its inherent tendency to cling to the surface of the negative material. Very soon after entering into service, the negative material would distort and mould itself to the profile of the back of the separator unless there were gross variations in the surface flatness of the material. The combination of this clinging and the vacuole structure of the wood caused the evolved gases from the negative material, as it neared full charge, to have to pass through the wood and not escape from between the separator and the plate. As a result the evolved gases issued evenly from over the whole surface of the separator as a cloud of minute bubbles. Studies of this gassing behaviour have shown that the electrolyte adjacent to the ribbed side of the separator, away from the negative surface, turns a milky colour due to the presence of very large numbers of these minute bubbles. The effect of this on the negative active material is to encourage a fine and evenly expanded structure over the full surface area of the plate.

The replacement of wood by synthetic separators demanded a source of ligneous material that would be uniformly distributed throughout the negative active material, since none was forthcoming from the separator. Also, some means was necessary to ensure the free escape of evolved gases evenly over the full area of the active material.

Very few, if any, synthetic separators will conform readily to the surface profile of the negative plate surfaces. This is particularly true with the machine-pasted plates

that do not have the trueness of surface possible with hand pasting, especially when pasted on a glass surface. As a result, the separator will be in intimate contact with the active materials only at the high spots of the plate. When gassing commences, the bubbles emerging from the pores of the active material tend to escape between the surface of the active material and the back of the separator in contact with the plate, instead of passing through the separator. The presence of contact points between the separator and the plate tends to cause the gases to concentrate in the noncontact areas and, then, to emerge from the top of the cell element as large bubbles. In some areas, however, the escape path is such that some of the large bubbles fail to move upwards and are trapped. By remaining static, these gas entrapments deny the plate surface of essential electrolyte for it to continue to take part in the subsequent charge/discharge reaction.

Rigid and semirigid separators tend to exaggerate this phenomenon wherever they present a flat back to the negative active material. The more flexible microporous PVC separators are less prone to this problem, but still show sufficient tendency for disquiet wherever they are supplied with a flat back.

Several expedients have been adopted to mitigate this undesirable phenomenon. One approach was to overpaste the negative grid and then corrugate the overpasted surface by pressing a contoured form into the wet paste. This required an additional operation and labour. Another, and more popular, approach was to calendar the back of the separator with a fine cannelure of a close-pitched shallow ribbing, see Fig. 9. The effect of the back ribbing was to avoid initially any sunken area of negative material being turned into a 'land-locked' area by the pressure of the separator on the high spots of the active material. The vertical fine ribs channel the gases to the surface of the electrolyte evenly over the whole surface of the material and eliminate the tendency to blank off portions of the plate surface. The material initially expands into the spaces between the cannelure or fine ribs and, in so doing, forms itself closely in contact with the back face of the separator. Thereafter, the gases pass through the separator in the manner of the wood separator.

The cannelure, or fine rib, configuration is particularly valuable in the case of traction batteries with tubular positive plates. In these designs, there is little or no
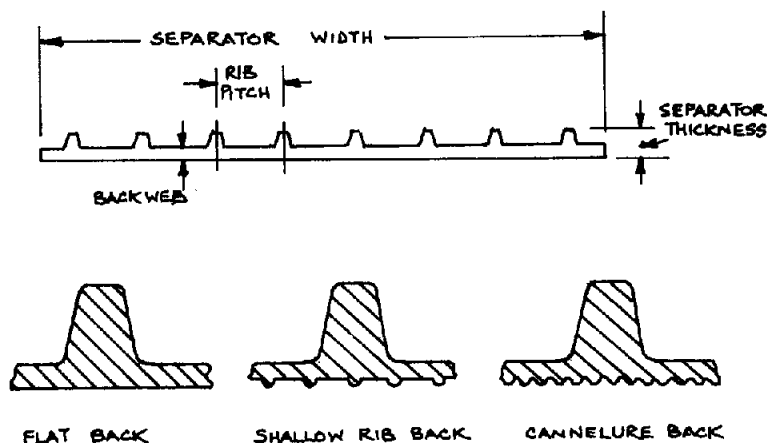

Fig. 9. Separator rib profiles.

space for any resilience in the element and, therefore, the interplay of normal dimensional tolerances can produce a variable degree of tightness of the element within the cell container. Whilst it is common practice to shim the element where it is slack in the container, these shims cannot give a uniform support over the whole of the plate surface due to the moulding taper or draught of the container. Inevitably, there will be tight spots and these are potential trouble areas for poor material expansion later on in battery service life. This problem can be lessened if the separation space is filled with a composite of a flat separator and a resilient spacer, such as perforated and corrugated plastic sheet. The hazard with this arrangement is the possibility that the resilient spacer will relax under the combination of heat and pressure and that undesirable contaminants will leach into the electrolyte.

Effect of temperature on separator resistance

Sundberg [1] gives data of the change in electrolytic resistance of three separator types over the temperature range −30 °C to +20 °C. The data are reproduced in Fig. 10. The change of resistance is broadly exponential and, irrespective of type, follows approximately the same curve. The only difference is the magnitude of the resistance value at each temperature level.

Whilst the changes in resistance with temperature allow calculations to be made of the increase in voltage losses at reduced temperatures, they are not sufficiently accurate to make estimates of low-temperature voltage performances, particularly in the case of resin-impregnated paper separators. These separators do not behave in exactly the same way as the truly microporous separators, such as the small pore-diameter microporous PVC, rubber or wood separators, where osmosis plays such an important part in determining the pattern of resistance behaviour. A much greater variability exists between different makes of resin-impregnated paper separators; this shows up more at low temperatures than at normal temperatures. The approximately hyperbolic characteristic curves for the resin-impregnated paper separators, although
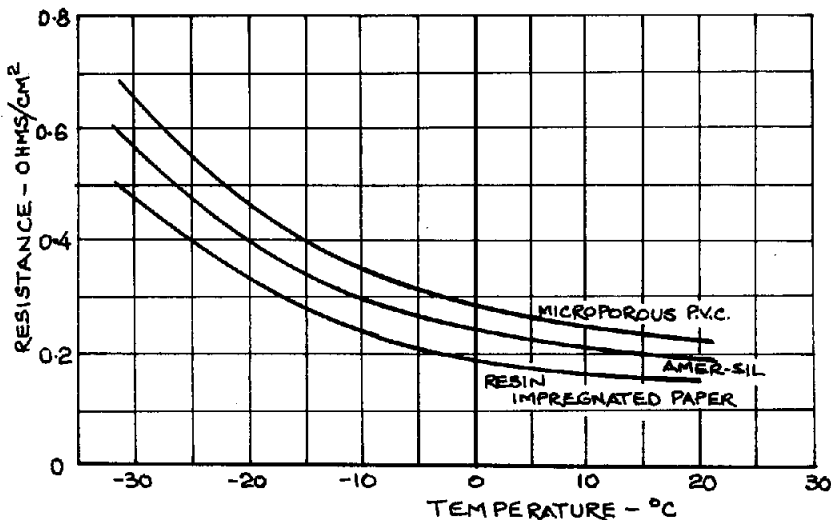

Fig. 10. Effect of temperature on separator resistance.

quite close together at normal temperatures, move apart as the temperature is reduced. This becomes an important factor in the case of automotive batteries. For example, a designer was tempted to reduce the active-material densities in order to improve the voltage levels on cold-start duties with some sacrifice in life only to find that a change in the make of paper separator, possibly to save money, lost more in voltage than the design had set out to gain. The converse can happen, i.e., the gain through the choice of separator can exceed the gain planned by the reduction in material density.

In a particular example of the same element (made from the same batch of plates) separated by two different makes of alleged similar separators, the voltage difference, at -18 °C, of 9-plate cells discharging at 50 A/positive was 0.125 V. The plates were rated at 10 Ah at the 20-h rate. This was equivalent to a difference of 0.75 V per 12-V battery, and, in some designs of battery, had the effect of lifting the cold-start voltage from an area of uncertainty to reliable starting.

This underlines the need to check thoroughly the low-temperature characteristics of the separators and to avoid changes for economy reasons before such checks have been made.

Effect of separator thickness on cycle-life expectancy

The operation of automotive batteries is mainly on shallow cycling with the emphasis on an ability to withstand considerable overcharging. Propulsion and traction batteries must, however, withstand regular deep cycling and, in the latter, continue to deliver close to the rated capacity for at least four years. It is the designer's aim to ensure
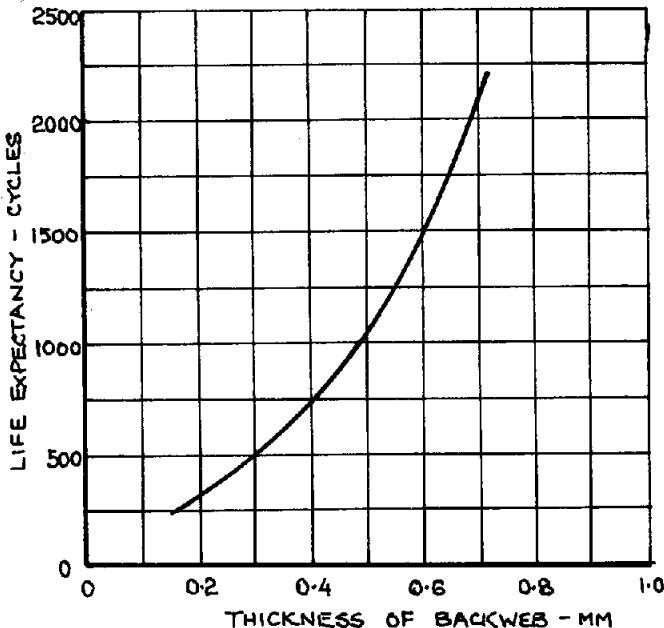

Fig. 11. Effect of separator back-web thickness on cycle-life expectancy with deep-discharge regimes (lead–antimony grids).

that the ultimate cause of failure is corrosion of the positive grid. A large factor in dictating the rate of such corrosion is the rate of antimony migration from the positive grid to be deposited on the negative material. The greatest restriction on the migration of antimony comes from the use of separators with the combination of small pore diameters and long, tortuous pore paths.

Earlier (Fig. 8), the difference in life expectancy with large and small pore diameter separators was recorded. On the basis of these and other data, the separators for traction cells were restricted to those with dominant pore diameters of 2 to 3 μm. This satisfies the requirement of small pore diameter. The tortuous pore path is a function of the back-web thickness.

Figure 11 gives data of the effect of varying the back-web thickness of 2 to 3 μm dominant pore-diameter separators on the cycle-life expectancy of traction cells with positive grids cast in 7 to 8 wt.% lead–antimony alloy. Discharging was conducted to 80% of rated capacity to a minimum capacity of 80% of rated capacity. Whilst the data are dependent on no other failure mechanism than that of positive grid failure and, as such, is limited, it does give an indication to design of the minimum thicknesses that should be considered. Unless the attainment of any high-rate performance of traction batteries is made difficult, it is prudent to err on the higher side of the indicated back-web thickness.

In the case of automotive plates used for regular, deep charge/discharge regimes, the above data cannot be used where resin-impregnated paper separators are employed. Antimony migration can be high with these separators and cycle-life performance may be low in practice.

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