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New separators for industrial and specialty lead acid batteries

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Abstract

Standard Amersil calendered ribbed separators based on the cold extrusion of PVC and silica have successfully been used in industrial lead acid batteries for over 30 years.

The requirements of the battery industry for even more efficient separator systems have led Amersil to develop a new generation of highly porous polymeric material, well suited for traction as well as for stationary applications, both in flooded and gel VRLA technologies. The new polymeric separators are based on the unique Amersil production process and use the same raw materials of high chemical purity as the standard product, but the design has been optimised in order to improve the physical properties required to reach higher battery efficiency. Especially, the pore volume has been increased, the electrical resistance and acid displacement reduced to such an extent that the electrical output of batteries has been improved both in terms of higher capacity and longer cycle life.

This paper shows the beneficial impact of the new Amersil separators on various types of industrial lead acid batteries.

Keywords: Industrial lead acid batteries; Battery separator; Corrugated; Porosity

1. Introduction

Following the ongoing progress achieved in many technical areas, the need for even more powerful and reliable power supply has led battery manufacturers to develop improved production processes as well as optimised components, as each additional percent capacity or cycle life has become an economical challenge. Industrial lead acid batteries especially have been greatly improved thanks to the use of new expanders for the negative plate [1], new alloys for the positive grid [2,3], more accurate cell design and charging algorithms [4], as well as computer-based battery management systems to improve efficiency [5]. The separator also has become an important issue as its function is no longer simply reduced to electrically insulate the opposite electrodes, while allowing ion migration. It is nowadays considered a highly technical component, which can be instrumental in improving the cell electrical performance. Traditionally, rigid micro-porous separators have been used in all types of industrial lead acid batteries. They are made out of a polymer fused by heat or by the chemical action of a solvent and mixed with a mineral filler, mainly precipitated silica. These separators are available with ribs and aimed at creating an inter-plate spacing for electrolyte, while minimising the overall separator material.

For the last 20 years, Amersil standard polymer/silica calendered ribbed separators have been successfully used in many types of industrial flooded and gelled-electrolyte batteries. The newer corrugated separators both “S” and “T” profiles have been developed especially to further increase the electrical output of lead acid batteries, both in terms of higher capacity and longer cycle life. The results presented in this paper demonstrate the efficiency of this optimised separator in various applications like traction flooded, traction gel and heavy duty applications.

2. The new Amersil “S” and “T” corrugated separator design and properties

2.1. Composition and design

The new corrugated separators are made with the same raw material and extrusion process as the standard Amersil ribbed product. Their composition is limited to two basic materials, precipitated silica and pure polymer. There is no additive, mineral oil nor resin, therefore, the final product has very high chemical purity. The chemical resistance of the separator is also improved by the fact that the mixture of silica and polymer is not extruded by heat, but at ambient

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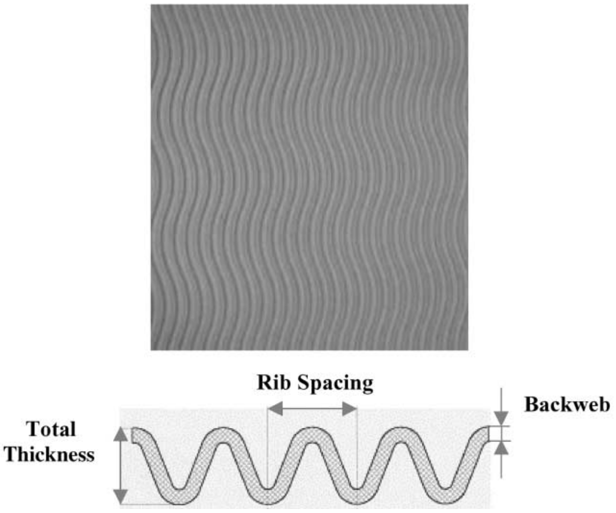

Fig. 1. Amersil "S" corrugated separator design.

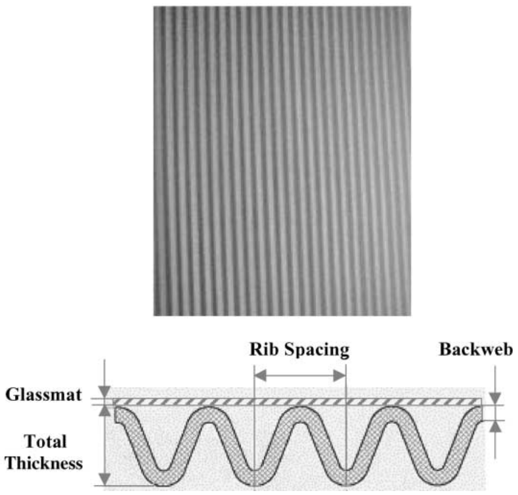

Fig. 2. Amersil "T" corrugated separator design (with glassmat).

temperature thanks to the chemical action of an appropriate solvent (which is extracted afterwards to create additional porosity).

After extrusion, a flat sheet is recovered from the calender and passed through a set of corrugating rolls to reach its final pattern, and thus, the overall thickness is achieved without the need of ribs. The corrugated separators are available in two different wave designs: type "S" is sinusoidal (Fig. 1), whereas type "T" is straight and vertical (Fig. 2). The overall thickness achieved by the flat sheet rolling process can range from 0.9 to 5.0 mm. The thickness of the preliminary flat sheet is proportional to the required overall thickness of the corrugated product. Therefore, the backweb of the corrugated separator increases slightly with the overall product thickness as illustrated in Table 1 (0.48 mm backweb for a 1.20 mm "S" separator compared to 0.70 mm backweb for a 4.0 mm "T" separator). Note that for certain applications, a glassmat can be laminated to one side of the corrugated product, as for standard ribbed separators.

The separator profile has been recognised to be particularly important in industrial cells. While widely spaced vertical ribs are well adapted to flat plates, they become unsuitable for tubular plates because the ribs can enter into the tubes inter space and lead to acid starvation. On the other hand, diagonal ribs are better suited for tubular plates. The advantage of the "S" or "T" corrugated separator is that its design is compatible with both plate types, allowing an equal repartition of acid in both positive and negative compartments, as the stochiometry of the reactions indicates that both electrodes need the same amount of electrolyte.

2.2. Properties

The composition and design of the material resulting from this unique manufacturing process have a great influence on the physical properties of the separator, and especially porosity, electrical resistance and acid displacement (Table 1).

Generally speaking, separator porosity refers to all the void spaces existing within the structure of the material. In the case of silica containing polymeric membranes, two sources of voids contribute to the overall pore volume: (i) the silica agglomerate void volume which is the empty space existing within each silica aggregate (intra-granular porosity) as well as the space in between different aggregates (inter-granular porosity), and (ii) the extraction void volume which results from the extraction of the solvent needed for the polymer extrusion.

Consequently, the pore size distribution in the material is bimodal. Pore size analysis performed by the mercury

Table 1
Physical properties of corrugated separators compared to Amersil and competition standard ribbed separators (typical values)

Pattern	Amersil ribbed			Amersil corrugated			Alternative
Thickness (mm)	1.20	2.0	4.0	1.20	2.0	4.0	2.0
Backweb (mm)	0.53	0.50	0.77	0.48	0.57	0.70	0.54
Pore volume (%)	67.4	67.0	67.4	68.4	73.9	78.5	69.7
Mean pore size (μm)	0.13	0.15	0.14	0.18	0.77	1.72	0.41
Min (μm)	0.04	0.04	0.04	0.04	0.04	0.04	0.03
Max (μm)	1.3	1.7	1.5	2.0	3.0	5.0	0.43
Electrical resistance (mΩ·cm^2)	162	160	221	75	80	120	145
Acid displacement (ml/m^2)	200	300	440	150	180	260	254

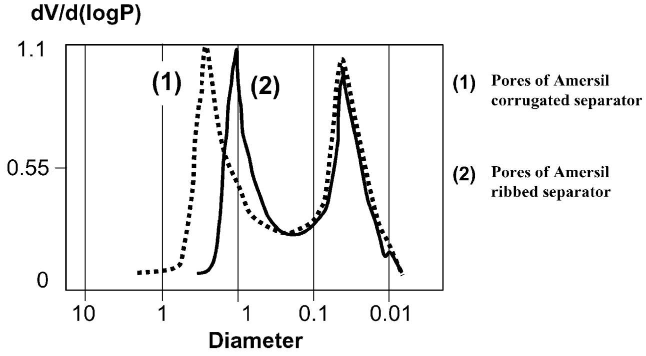

Fig. 3. Schematic representation of pore size distribution for Amersil standard ribbed and corrugated separators using mercury porosimetry.

intrusion porosimetry shows that the pores coming from the silica aggregates are around 0.04 μm, whereas the extraction pores have an average diameter of 1–2 μm for standard ribbed products (Fig. 3). The "S" and "T" separators however, have larger extraction pores (Fig. 3), resulting in higher mean pore size as well as higher overall pore volume as shown in Table 1.

The pore size, pore size distribution and total volume porosity of the separator have a direct influence on the electrical properties of the separator in the battery [6,7]. All pores which are accessible from the surface of the separator, will become filled with acid and will contribute to lower the acid displacement as well as decreasing the electrical resistance by promoting the ionic transfer. The advantage of the Amersil separator is that the silica aggregates are not embedded in a melted polymer matrix, but only distributed among polymer grains, which renders the membrane pores perfectly hydrophilic and allows the electrolyte diffusion through the whole separator structure. Because the extraction pores of the corrugated product are tortuous, the risk of dendrite growth remains limited, even if their size is larger than in the standard ribbed separator, resulting in a much lower electrical resistance.

3. Testing results

The beneficial effect of the corrugated separators with optimised properties has been tested, or is still on test in various types of industrial batteries. The testing procedures as well as final or intermediate results are described below.

3.1. Traction flooded batteries

Traction batteries, also known as Motive Power batteries, are commonly used as power sources for fork lifts or other light transportation vehicles operating with an electric motor in a closed area where exhaust can not be tolerated.

These batteries are designed for deep cycling and are expected to be fully discharged on each cycle. Generally, plates are relatively thick and large (flat in North America and tubular in the rest of the world) and the battery is expected to achieve a long cycle life.

The Amersil "S" corrugated separator has been tested in two different types of traction flooded batteries. In the first accelerated life cycle test performed at 47 °C, three 120 Ah traction cells with tubular positive plates have been assembled with corrugated S separator of 2 mm thickness (Table 1) and compared to three identical cells assembled with standard Amersil ribbed separator of the same thickness (Table 1). The discharge has been achieved during 1.8 h

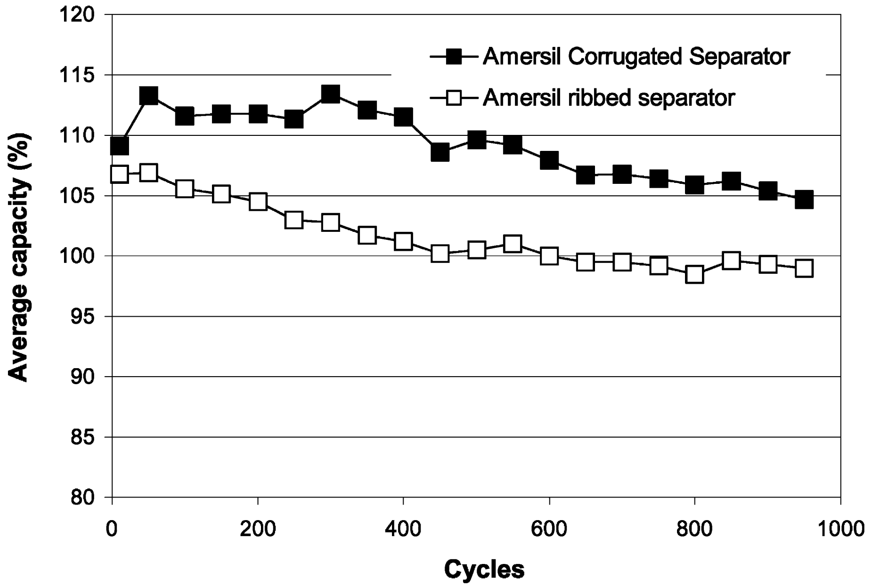

Fig. 4. Cycle life testing of three 120 Ah traction cells assembled with corrugated SL200 separator compared to three identical cells assembled with standard Amersil DC200 separator. Discharge: 1.8 h at 1.66 I_5 (39.8 A), i.e. 60% DOD. Charge: CC 1.25 I_5 (30 A) until 2.40 Vpc, then 0.25 I_5 (6 A) until charge factor of 1.20.

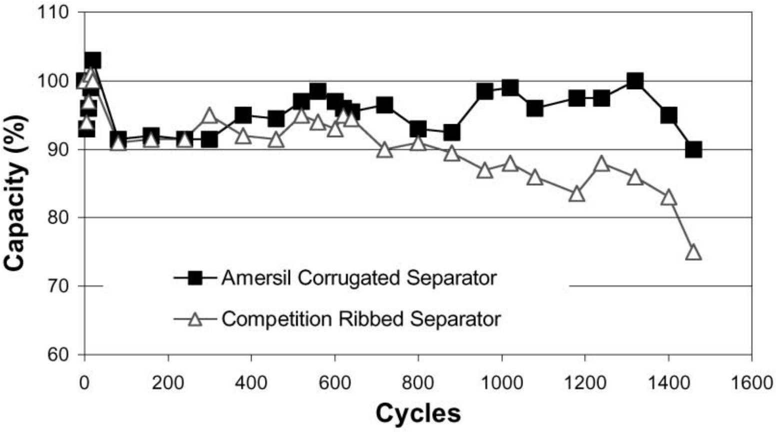

Fig. 5. Cycle life testing of traction flooded Type 3 PzS cells assembled with TK210 separator compared to standard ribbed separator. Beginning: DIN standard algorithm, then 3 cycles per day at 47 °C (discharge at 1.66 I_5 during 1.8 h, charge with 1.20 charge factor).

at 1.66 I_5 (39.8 A) and the charging procedure was with constant current of 1.25 I_5 (30 A) until voltage reached 2.40 Vpc, then 0.25 I_5 (6 A) with a charge factor of 1.20.

The results on Fig. 4 show that 7–10% additional capacity was available with the corrugated separator. The cells have reached 950 cycles and have still 105% of nominal capacity compared to 99% with ribbed DC200 separator.

In the second test, PzS 360 Ah cells have been assembled with corrugated TK210 separators and compared to standard ribbed competition. The testing procedure was a standard DIN for the beginning, then a cycling procedure as follows: 3 cycles per day at 47 °C, discharge at 1.66 I_5 during 1.8 h and charge factor of 1.20.

At the beginning, with the DIN algorithm, the cells using TK210 separators showed 2% additional capacity (Fig. 5). Then, during 600 cycles, the capacity of cells with TK 210 was alternately slightly higher or lower than standard cells. After 600 cycles, however, the capacity of cells with standard ribbed separators started to decline, whereas cells with TK separators recovered slightly between cycle 600 and 1300, where they only started to decline. The gain in capacity from cycle 600 to the end of test was around 10% with Amersil new corrugated separator. These good results are attributed to the lower electrical resistance as well as lower acid displacement and specific wave design (higher electrolyte available against each electrode) of the new Amersil corrugated separator.

3.2. Traction gel

This type of valve regulated lead acid battery represents the latest development for traction applications and requires the most performance from the separator. Contrary to flooded cells, the oxygen generated at the positive electrode after 80% charge, has to reach the negative plate through micro-cracks in the gel structure and through the separator's void space in order to be reduced and react with protons to form water again. Ideally, no separator should be added in this type of battery, as the electrical resistance of the gelled electrolyte is already quite high. However, a separator is

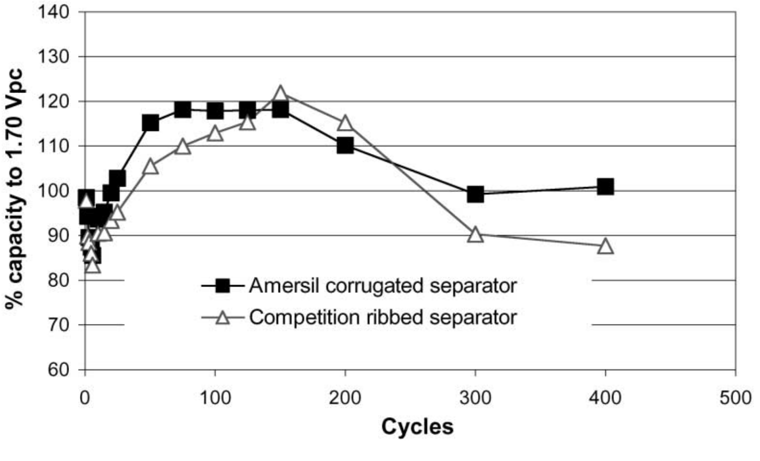

Fig. 6. Testing of industrial gel motive power cells assembled with Amersil corrugated TGL separator compared to ribbed competition. Discharge at 62.5 A (6 h rate) to 1.70 Vpc (100% DOD, charge at 75 A max at 2.33 Vpc until 1.08 charge factor).

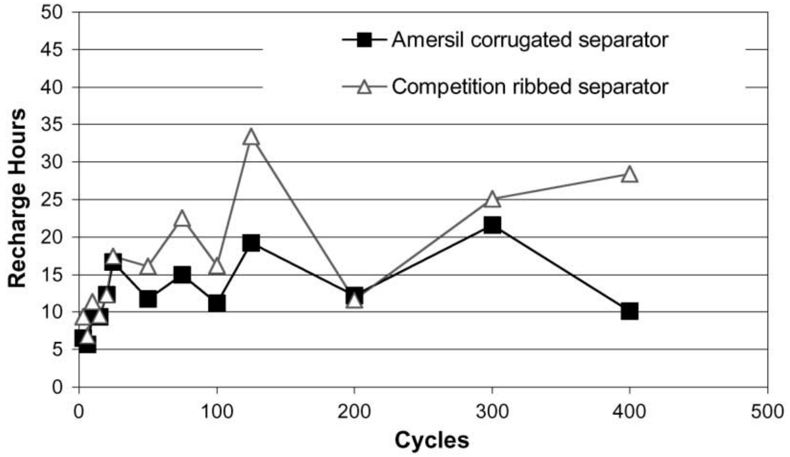

Fig. 7. Testing of industrial gel motive power cells assembled with Amersil corrugated TGL separator compared to ribbed competition. Discharge at 62.5 A (6 h rate) to 1.70 Vpc (100% DOD, charge at 75 A max at 2.33 Vpc until 1.08 charge factor).

needed to keep inter plate spacing and also to prevent any short circuit due to plate contact or dendrite growth. Therefore, the separator should have as low electrical resistance as possible and very high porosity, with a structure allowing oxygen transfer and an homogeneous internal oxygen cycle.

The Amersil corrugated TGL400 separator with 78.5% volume porosity has been tested in gel motive power cells and compared to a competitor's ribbed separator with 70% porosity. The discharge was performed with 62.5 A at 6 h rate to 1.70 Vpc (100% depth of discharge). The charge was performed at 75 A until 1.08 charge factor with a cut-off voltage of 2.33 Vpc.

Results of capacity and recharge times are shown on Figs. 6 and 7. From beginning to 200 cycles, the capacity of cells insulated with Amersil TGL is slightly higher or comparable to the competition separator. After 250 cycles, however, the capacity is 10% higher with the Amersil corrugated separator, due to higher porosity and lower electrical resistance (Fig. 6). A second test performed with a 12 h standard BCI cycle-life test confirms these results on capacity (Fig. 8).

Concerning recharge efficiency, Fig. 7 shows that, from 50 to 400 cycles, the time needed to fully recharge the cells is longer for the competition separator than for TGL400. More than the single effect of higher porosity and larger pore size, the tortuosity of the Amersil separator helps slowing the oxygen transfer in order to allow an easier recharge of the negative plate before current is used for oxygen reduction.

Moreover, even though no detailed study has been performed yet concerning compression in gelled-electrolyte batteries, one can assume that compression is also an issue, as gel VRLA may also suffer from poor contact between the immobilised electrolyte and the plates, when battery is ageing and gel is drying out due to water loss. In that case, the springiness of the Amersil separator might be highly beneficial to maintain plate–electrolyte contact. This important aspect has to be further evaluated.

3.3. Heavy duty

The first test performed was a high rate discharge test on train monoblocs assembled with Amersil corrugated SK120

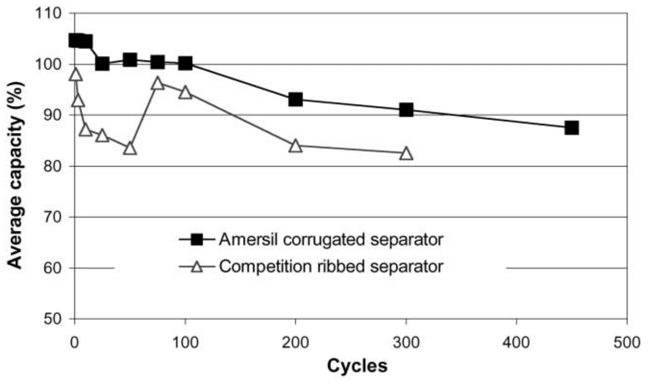

Fig. 8. Testing of industrial gel motive power cells assembled with Amersil corrugated TGL separator compared to ribbed competition. Twelve hour standard BCI cycle life testing.

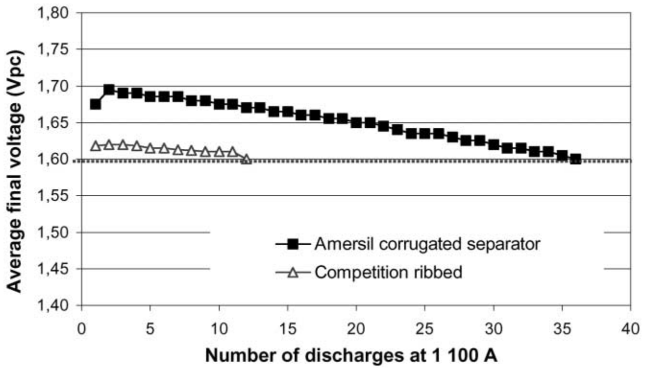

Fig. 9. High rate discharge test results on monoblocs for train batteries assembled with Amersil SK corrugated separator compared to ribbed competition. Average final voltage after discharge at 1100 A during 10 s (cut-off at 1.60 V).

Table 2
Capacity C/5, C/20 and cold cranking performance at −18 °C of Amersil "S" corrugated separator compared to standard ribbed AGC in two types of flooded heavy duty batteries

		Cold cranking		Capacity C/5 (Ah)			Capacity C/20 (Ah)			Charge acceptance (A)
		V_{30s} (V)	T_{6V} (s)	Min	Mean	Max	Min	Mean	Max	
Type 1	AGC	9.22	282	141.1	142.8	144.4	172.3	174.6	176.9	35.9
	"S"	9.38	288	155.5	155.9	156.3	175.8	177.3	178.7	34.9
Type 2	AGC	9.16	296	188.3	191.9	199.4	215.5	223.9	233.7	39.1
	"S"	9.41	335	185.8	198.7	205.6	198.4	233.2	244.6	49.0

separator compared to standard ribbed competitor. The test consisted in discharging the monoblocs at a rate of 1100 A for 10 s, the terminal voltage of each cell being measured before and during each discharge. After a rest period of 5 min, the monoblocs were discharged again. This sequence was repeated until the end voltage reached 1.60 V. The results are presented on Fig. 9.

The impact of the separator on the high rate discharge performance of the present type of battery is well pronounced. The data show that the Amersil SK120 separator allowed three times as many discharges than the standard competition separator before reaching the cut-off voltage of 1.6 V (36 discharges compared to 12). The efficiency of the corrugated separator led also to 5% higher terminal voltage compared to competition. To explain these results, one has to keep in mind that high rate discharge tests are the most sensitive to electrical resistance. As the Amersil corrugated material has the lowest possible electrical resistance for a given backweb thickness (only 75 $\mathrm{m\Omega \cdot cm^2}$), this results in a higher voltage profile under a high discharge load. Additionally, besides the low electrical resistance due to its high porosity and absence of rib, the SK separator has very low acid displacement. The extra electrolyte volume available compared to lower porosity, standard ribbed material, helps the cell perform well under load and better recover from discharge.

Two other types of batteries assembled with Amersil "S" separators with glassmat compared to standard ribbed with glass mat have been subjected to cold cranking test. The results are summarised in Table 2. It is directly noticeable that about 0.2 V higher voltage has been reached after 30 s at −18 °C with the corrugated separator compared to ribbed one. This, as well as the higher charge acceptance for battery type 2, indicate that the internal resistance of the battery is considerably lower, thanks to the better conductivity of the "S" separator. Moreover, both battery types show a significantly higher capacity at the C/5 rate, related to the higher porosity of the corrugated separator.

4. Conclusion

This study confirms the great impact of separator's design and properties on industrial lead acid batteries performances. The use of the new Amersil corrugated separator, "S" or "T" pattern, improves the capacity and cycle life of the cells in various type of applications (traction flooded, traction gel and heavy duty), thanks to its lower electrical resistance, higher porosity and pore size and lower acid displacement. Additionally, its springiness may be an advantage for gel VRLA batteries, where contact has to be maintained between the plate and the gelled electrolyte, while batteries are aging.

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