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Connector corrosion under the microscope



UK Powertech & *BESTmag* evaluate solutions to formation energy losses in lead batteries

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Connector corrosion under the microscope

UK Powertech and *BESTmag* get down and dirty with connector corrosion chemistry to find solutions to formation energy losses in lead batteries.



In the Winter 2018 edition of *BESTmag*, we looked at the financial and quality consequences of using old and corroded connectors. That article showed that continued use of corroded and damaged connectors can result in huge financial penalties caused by high resistance energy losses at the connector/battery terminal interface.

The high resistance interface is the result of a non-conducting layer formed from the corrosion products of the lead connector head and sulfuric acid or moisture on the terminal surface. Modern fast formation methods with recirculating electrolyte and more efficient cooling have enabled reduced formation times. However, the same ampere-hour input of 5-7 times the battery capacity is still required to ensure full conversion of active materials and to guarantee battery performance and quality. This means higher currents are needed to compensate for the reduced formation time. However, as a result of the higher currents, problems created by a high resistance layer, which can result in higher formation temperatures,

resistance losses, battery damage and even fires, have greatly increased.

We return to the topic in this issue because Mark Rigby of UK Powertech and BESTmag have uniquely identified and begun quantifying this growing problem.

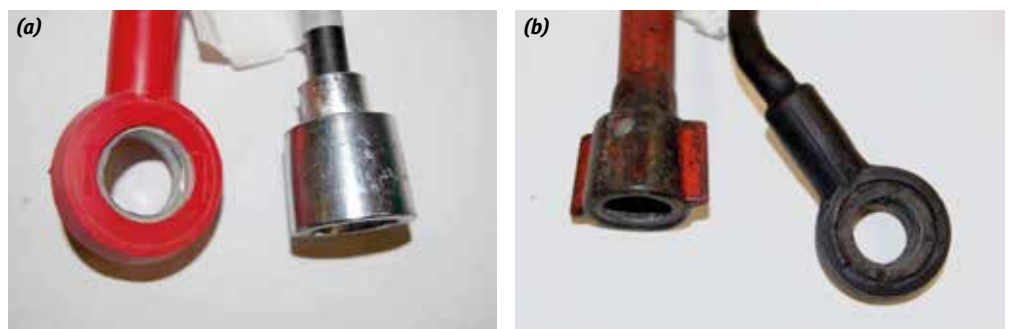
For this article, the nature of the corrosion layer on the connector surfaces, and its causes, are literally put under the microscope. A variety of analytical tools are used, including: scanning electron microscopy to see the depth and nature of the corrosion into the lead terminal; energy dispersive X-ray (EDX) analysis to ascertain the chemical species and their relative concentrations; and FTIR (fourier transform infrared spectroscopy) analysis to specify the molecular structure of the layer's components. Additional consideration is given to the connector cable and connector

head interface joint where corrosion has occurred in some samples.

In the first part (electrical test results) of this report, we compare the efficiency of new lead-acid battery formation connectors with those that have become corroded after a short time in service (**Fig 1**). A new, more user-friendly connector lead terminal design is also examined and compared with the existing design. The second part of the report examines the chemical nature of the corrosion layer and proposes reasons for its formation. The implications for the connector design, formation process modifications and potential damage to battery quality are discussed at the end of the report.

UK Powertech manufacture formation connectors and take-

Fig 1: Camera pictures of the reference (a) and used (b) connectors, both ring and cone terminals.



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off leads for lead-acid battery companies. In recent years they have noticed that connector life and battery damage due to fires has increased. This coincides with faster formation times, particularly with recirculating electrolyte cooling systems. Faster formation requires higher currents. This means that any problems related to resistance factors, such as corroded or badly fitting connectors, would be exaggerated. Apart from heating damage, UK Powertech and BESTmag have identified the cost of energy losses during

formation processes due to the higher resistance.

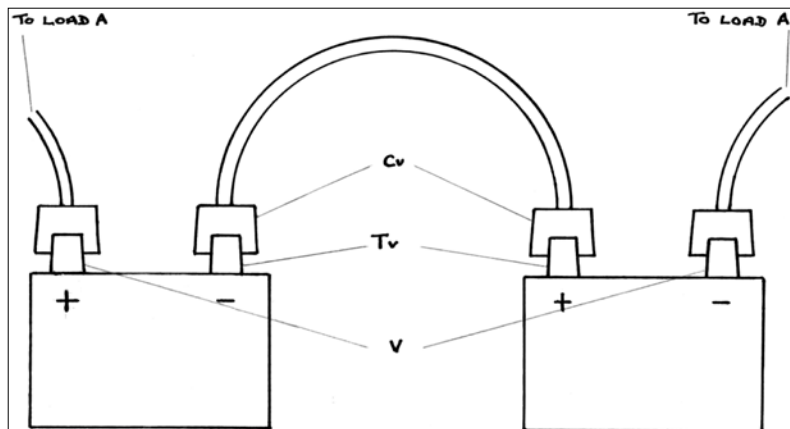
The energy losses resulting from this situation have previously been identified. The losses calculated were based on voltage differences between the connectors and battery terminals with and without corrosion when the same current was applied. The higher voltages from the corroded connectors resulted from the increased resistance of the surface corrosion layer between the connector terminals and the battery post ($V=I \times R$). The difference in energy loss

between good and corroded connectors was found to be an average of 7%. **Fig 2** shows the circuit arrangement for the initial single connector tests. The voltage across the positive and negative poles of two separate batteries in a series connection was measured with a 9A constant current. The voltage across the connectors was then measured at the same current. The voltage difference is created by the resistance drop across the connector terminal and battery post interface with a constant current flow. The higher the voltage the greater the resistance at the interface (Ohms law). The higher the resistance, the higher the voltage and therefore the higher the energy consumed in supplying the current ($V \times A \times t$).

Table 1 is a summary of some of the tests carried out using a low 9A current. This clearly shows that used connectors create a significantly higher resistance at the battery post/connector take off interface. The power loss and possible energy losses per one million batteries produced is also calculated.

The cost of the energy losses to a lead-acid battery

Fig 2: Method of measuring the connector/battery terminal interface resistance.



Tv = voltage measurement from battery terminal to terminal under load A amps
 Cv = voltage measurement from one connector end to other connector end under load A amps
 Tv-Cv = the voltage between the terminals and the connector ends under load A amps
 A = current flowing in the circuit.
 (Tv-Cv)/A = Connection resistance between battery terminals and connector ends

Table 1: Summary of findings from the test rig.

Connector	Total V (V)	Terminal V (Tv)	Connector V (Cv)	Amps (A)	Resistance R (mΩ) (Tv-Cv)*1000/A	Energy loss per million 100 ah batteries (kWh) 10 ³ xWx24h*
Old lead terminal	24.81	0.45 (Tva)	0.37 (Cva)	8.83	500**	7,500,000
New gravity cast lead terminal	26.82	0.0062 (Tvb)	0.0053 (Cvb)	9.39	0.09	1,350
New injection moulded terminal	25.149	0.0058 (Tvc)	0.005 (Cvc)	8.81	0.09	1,350

*Average formation power = (I² x R) x average formation time. Total ah input = 6xC₂₀ Formation current = 25A

**Calculated as (Tva-Tvb)/A to calculate energy loss c.f. a new connector

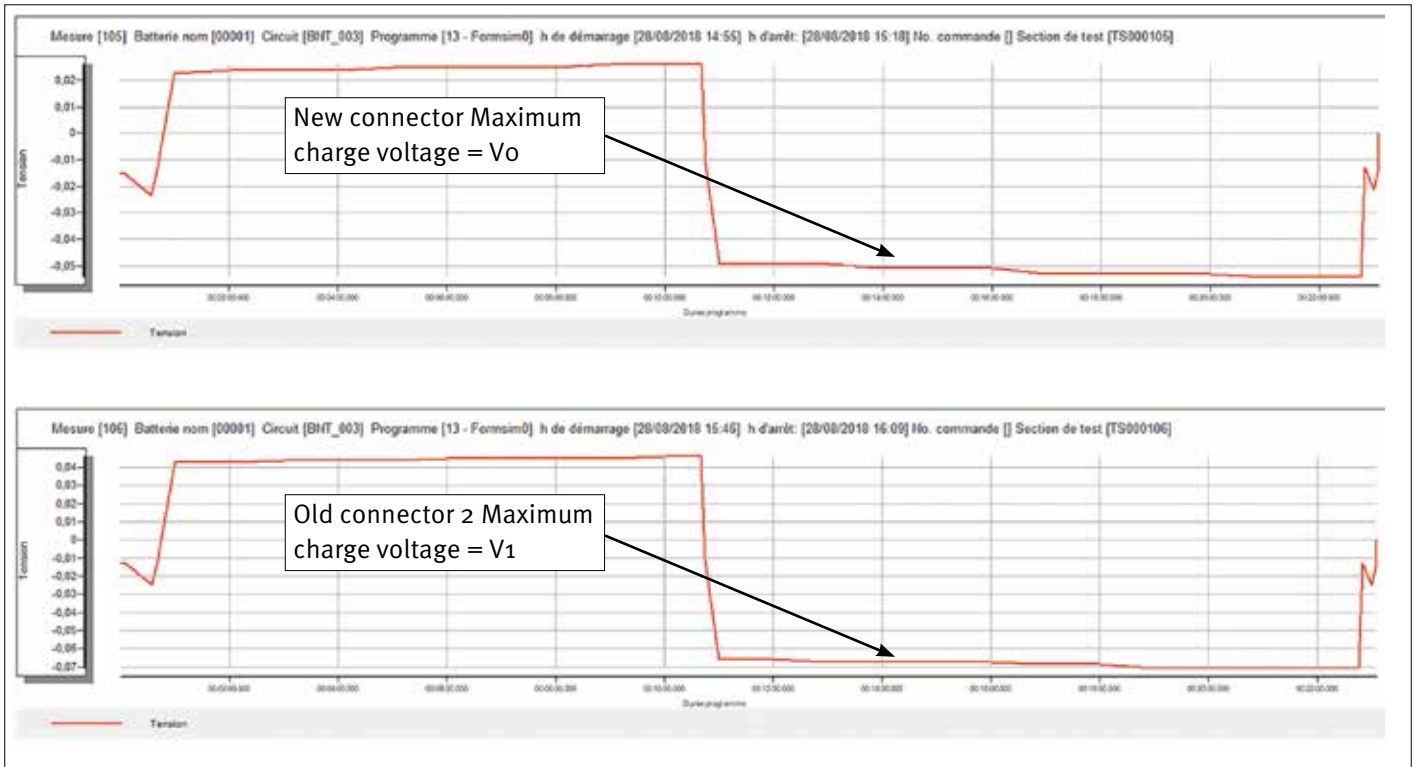


Fig 3: Typical results from the Digatron connector tests.

manufacturer from inefficient formation connectors was calculated as being between 3% and 12% based on the data from the connector resistance tests. For one million batteries per year, the cost of this energy loss, depending on the kWh price, could amount to €130,000 (US\$146,000).

For verification of these results, further tests were carried out on the Digatron test unit. In these tests, batteries were put on charge with new and old connectors. The charge current was kept constant and the resulting voltage responses were measured for the different connectors. **Fig 3** shows the voltage responses at 25A for the old and new connectors. This is in line with the manual measurements taken from the test rig which provides verification for the results.

Fig 4: Used connector showing corroded and pitted internal contact surface.

The main purpose of this study was to ascertain the cause of the higher interface resistance when using the old connectors. **Fig 4** shows the internal condition of a used lead terminal connector. There is evidence of corrosion and pitting, which would be the obvious cause of the higher resistance, provided that the corrosion product was non, or partially conducting. It is necessary to ascertain the nature of the corrosion layer



and the extent or depth of the corrosion in order to understand the mechanism and speed of its formation. It is hoped that this approach will also lead to setting guidelines for connector maintenance and replacement, based on correlations between depth of corrosion and time in service. Further work is also under way to provide the basis of the principles needed for a new connector design.

The analysis used was a top-down investigation using scanning electron microscopy (SEM) with EDX analysis. Cross-sections of the lead connector terminals were prepared in order to identify the corrosion products, their penetration depth and the nature of the corrosion of the connector head. This also shed some light on the causes of the corrosion and on the electrochemical conditions

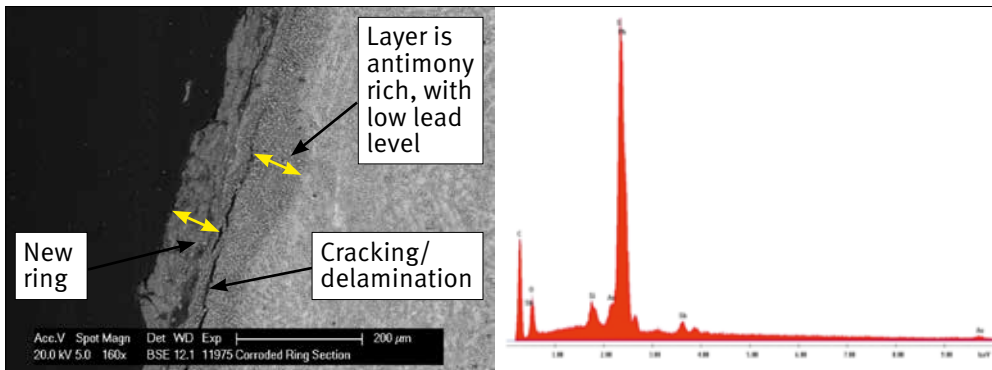


Fig 5: Cross section of the surface corrosion inside the connector terminal with an EDX reading of the elements in the corrosion layer.

which were responsible for this to be identified. Using these results, it may be possible to prescribe preventative measures which would reduce the severity of the corrosive deterioration and extend the connector's working life.

Cross sections of the connector leads were prepared by cutting samples from the terminals and mounting them in resin. This enabled the grinding, polishing and etching of the terminal sections to provide a suitable flat surface for the SEM and EDX investigations. Looking first at the visual results of the cross-section samples going from the outer surface into the bulk metal of the lead alloy terminal, we can see the corrosion layer at high magnifications.

Fig 5 shows extensive corrosion layers on the inside of the terminal ring, which are typically up to 160µm deep. The etchant used has delineated the bulk material from the outer delaminating corrosion deposit. It also indicates that the remaining bulk surface layer is richer in antimony and lower in lead than the bulk material.

The corrosion product is flaky and not well attached. The layer between the flaky part and

the substrate is antimony rich. This could form the basis of a conducting layer between the surface corrosion product and the lead substrate and would have a lower conductivity than the lead substrate due to the corrosion of lead. From the cross-sections, it appears that the depth of the corrosion level

is around 160µm. The surface can be heavily pitted with corrosion. This would manifest itself as localised pitting as shown in Fig 6. In other words, the connector will still function but at a reduced efficiency with increasing pitting corrosion and pit depth. The cone surface also showed that there was localised melting of the terminal/cone, perhaps through localised arcing or high current density. This resulted in metal splatter being seen at the base of the cone in the form of spherical balls (Fig 7). This was also found within some of the corroded zone of the cone inner surface.

The EDX spectra showed that the composition could vary from one place to another on the samples, as shown in Table 2.

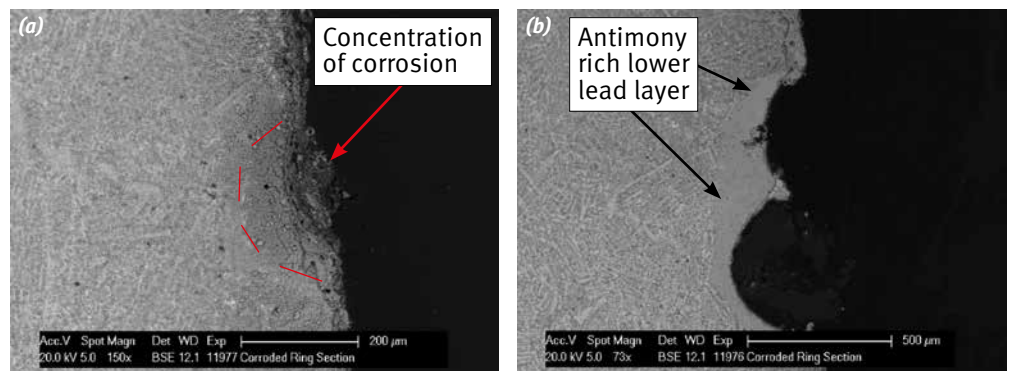


Fig 6: 6a is an SEM image of a corrosion pit. The corrosion is moving inward with a circular wave front. 6b is an image of a corrosion pit with the corrosion deposits crumbled away. The base is composed of an antimony rich and a lower lead layer.

Fig 7: SEM picture of spherical nodules. 7a Balls resulting from arcing which create a point contact. 7b Melted metal forming spherical balls, some of them re-melted into the surface.

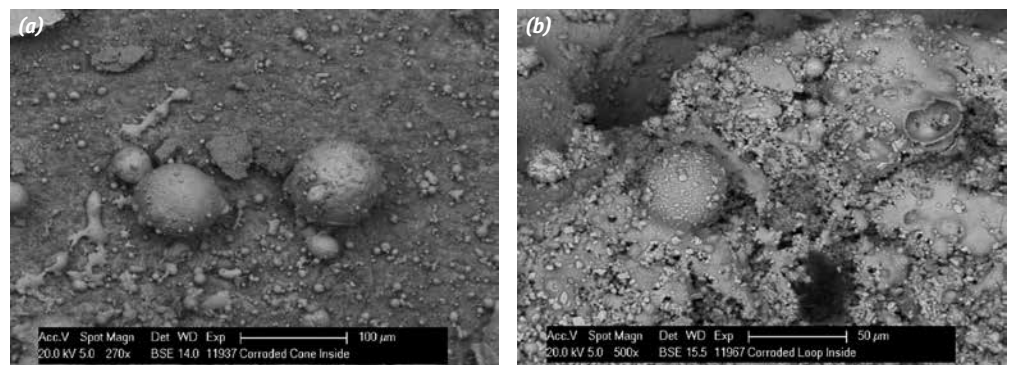


Table 2: Summary of EDX data expressed as atomic weight percent.

Element	Cone				Ring
	Reference*	Corroded Surface	Crumbly Surface	Nodular Background	Inside Average
Oxygen		63.1	60.9	57.6	58.4
Sodium			0.5		0.8
Arsenic			0.3		0.2
Sulfur		19.2	16.9	21.3	19.9
Lead	73.5	16.4	12.3	19.1	16.2
Antimony	26.6	1.4	8.8	2.0	3.0
Iron			0.3		0.9
Nickel					0.5

*To obtain the ratios of elements in the compounds a reference was used which was the lead alloy terminal of a new connector known to be a 10% antimony/lead alloy.

Table 3: The atomic % data expressed as ratios (relative to lead = 1), and as whole numbers

Element	Cone				Ring
	Reference	Corroded Surface	Crumbly Surface	Nodular Background	Inside Average
Oxygen		4	5	3	4
Sulfur		1	1	1	1
Lead	1	1	1	1	1
Antimony	0.4		1		

The main contributor to both areas was that of lead, sulfur and oxygen in the ratio range of 1:1:3-4. This suggests that the corrosion deposit is lead sulfate, but could be combinations of lead oxide, lead sulfide and lead sulfate. The surface of the spherical balls is mainly composed of lead, oxygen, antimony and sulfur. This represents molten alloy splatter, which likely has a film of lead sulfate on the surface

The EDX data obtained can be expressed as weight% or as atomic%. For elemental ratios used in formulas the atomic

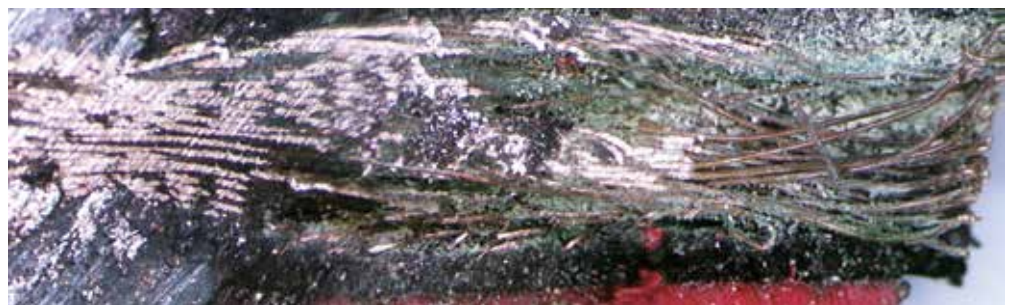
% is particularly useful. The reference data for a new, unused connector terminal is shown for comparison.

The same data was expressed as a ratio with respect to lead, and is shown in **Table 3**. The formula

for lead sulfate is $PbSO_4$, an atomic ratio of 1:1:4. The results indicate that the ratio is between 1:1:3 and 1:1:5, with sometimes being 1:1:4. This suggests that the main corrosion deposit observed was lead sulfate. The reference appears to have a high percentage of antimony compared to lead, and should be a ratio of (lead) 1 :0.1 (antimony) for a 10% antimony alloy with lead as the normalised unit.

From all the results above it is very likely that the corrosion layer formed on the inner surface of the connector terminals is a non-conducting sulfate and that there is also an intermediate layer between this sulfate and the bulk metal that is a partially-converted lead compound, probably a semiconductor. This would certainly explain most of the high resistance values given in **Table 1**, resulting from the interface contact between the connector terminals and the battery posts from previous tests. However, in addition to the connector surface being corroded and having a higher resistance, there was also corrosion product found on the cable insert into the head of the connector. **Fig 8** is a cross section through the length of a connector with the

Fig 8: Section through the ring connector and the wire (ring on left of image). Green corrosion seen through wire showing wire coating has become compromised.



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cable entry on the left of the photograph. In this, greenish and white compounds can be seen that appear to be affecting the individual copper strands of the cable bunch. Although not identified, the corrosion products may be cupric chloride, which is green, and lead chloride, which is white. These could be the result of a reaction between HCl released from the charred PVC coating and the lead and copper of the terminal and cable respectively.

This situation might occur when the higher resistance caused by the corrosion and pitting on the connector terminal surface would

create heat. Overheating of the wire insulation of the connector cable could assist in plasticiser migrating out of the PVC material leading to embrittlement. The insulation material would then crack and expose the copper and lead metals when subjected to the normal handling procedures of the formation process. This would conceivably allow sulfuric acid to penetrate the insulation material and corrode both the copper wires and lead where they are joined in the connector terminal. There would be a further increase in the resistance of the connector, adding to the already inefficient

electrical performance.

A further analytical method, FTIR, was used to provide further confirmation of the composition of the layers on the terminal surface. For those unfamiliar with this analytical method, it simply bombards a sample with a wide range of light frequencies and records how much light is absorbed, transmitted or passed through. The clever bit is the interpretation of the results based on Fourier's analytical technique to interpret the mass of data generated. It is mostly used for organics, but is also good for inorganic materials. It is known that connectors are often contaminated with oils or grease, so for this reason it was an appropriate technique to use for this investigation.

Fig 9 compares the FTIR spectra of scrapings taken from the new and corroded cones. In **Fig 10**, the open ring type connectors are analysed and this compares the FTIR spectra of scrapings taken from the new and corroded rings. Both show a large broad peak at about 3500cm^{-1} , which is normally indicative of hydrogen bonded hydroxyl (OH) groups. The main difference is the presence of a large broad peak centred at about 1060cm^{-1} that is related to the polyatomic sulfate (SO_4^{2-}) ion. The scrapings taken from the corroded cone also contain traces of aliphatic hydrocarbon species, suggesting that the PVC has lost some plasticiser materials. This bears out the previous conclusion relating to cable embrittlement and subsequent acid ingress to the

Figure 9. Overlay of FTIR spectra of scrapings from new and corroded cones

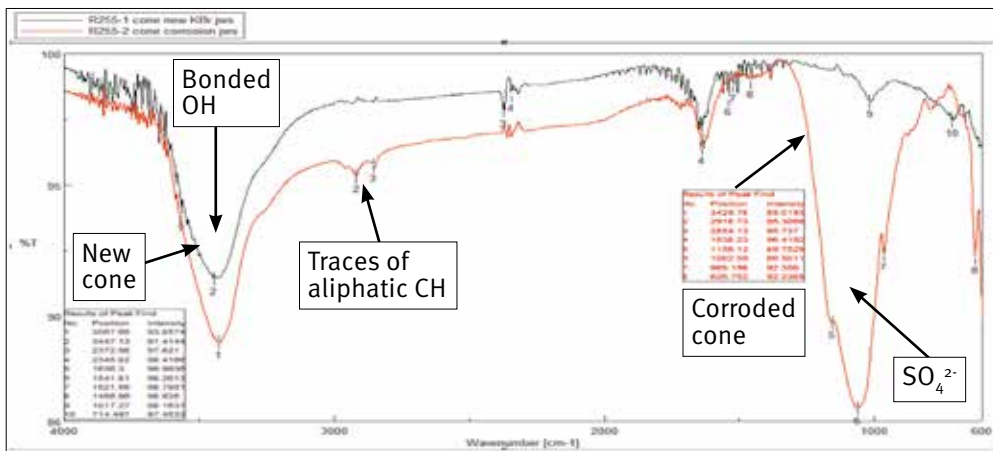
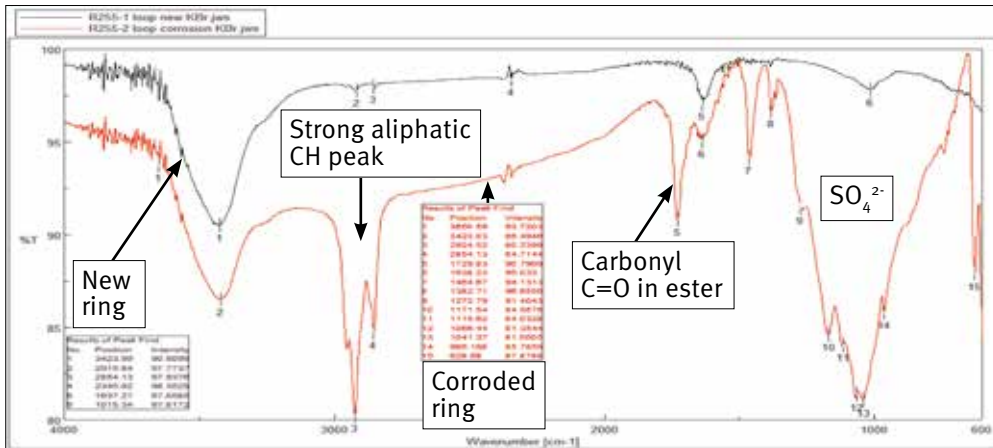


Figure 10. Overlay of FTIR spectra of scrapings from new and corroded rings



connector terminal/cable joint.

Both sets of connectors show major peaks for OH and SO_4^{2-} groups, which suggests that the lead terminals of the connectors have both lead hydroxide and lead sulfate on their surfaces. This is entirely consistent with the range of voltages and pH conditions which the connectors will be subjected to in normal use.

The organic molecules identified, ie. aliphatic CH and carbonyl C=O in ester groups, are present in both the used cone and ring connector samples. Again, as with the cone design of connector, the used ring scrapings show the presence of a large broad peak centred at about 1060cm^{-1} , that is related to the polyatomic sulfate ion (SO_4^{2-}), a strong aliphatic CH peak at about 2900cm^{-1} , together with a carbonyl (C=O) peak at about 1730cm^{-1} both of which point to release of plasticiser. The scrapings taken from the corroded ring also appear to show significant levels of an esterified aliphatic hydrocarbon species, suggesting that the used ring may have been exposed to high temperatures, resulting in the PVC losing significant plasticiser material.

Whilst there are some similarities in the positions of the peaks, there is a big difference in the peak amplitudes. These are most significant for the aliphatic CH and the carbonyl C=O in ester. The main conclusion to draw here is that the insulation breakdown of the connector cable is more severe in the ring

“Electrical tests have shown unequivocally that use of old and used connectors can substantially increase the energy use and cost of the lead-acid battery formation process.”

type connector than the cone. That is, however, a coincidence of sampling rather than a general consequence of the connector design.

This study was part of an ongoing development programme by UK Powertech and *BESTmag* to provide a formation energy reduction methodology and an improved connector design for the lead-acid battery industry. Electrical tests have shown unequivocally that use of old and used connectors can substantially increase the energy use and cost of the lead-acid battery formation process. This study on behalf of UK Powertech has shown conclusively that there is a high resistance barrier layer formed on the surface of the lead alloy terminal. It consists mostly of lead sulfate with an intermediate layer depleted in lead, leaving the antimony rich phase as a metal. This is entirely consistent with the electrochemical corrosion of lead-acid battery grids from normal charge and discharge cycling and is the result of surface sulfuric acid from either liquid or vapour/spray sources during the formation process.

In previous tests, this high resistance barrier layer combined with arc-pitting has already been shown to increase the energy required to form batteries by around 7% on average. Knowledge of the chemical composition and the mechanism of formation gained from this study has pointed to possible methods of reducing the extent of the corrosion and also methods of removing it. The crumbly but soft nature of the insulating outer layer means that mechanical removal would be best served by vibration rather than attrition methods. The samples used in these tests had an outer layer approximately 160 microns deep. However, removing this layer would not increase the internal diameter of the connectors by 320 microns (0.32 mm). The volume of the lead sulfate product is 164% greater than metallic lead, so the layer thickness removed would most likely result in an internal diameter increase of around 0.13mm. Considering the variables in most production environments, this should not cause any significant problems. Of more concern is the possibility of localised electrochemical action—causing the pitting seen in **Fig 6**— which could lead to some serious damage from arcing.

The underlying partially transformed corrosion layer is not removable, or easily converted back to lead. Even cleaning connectors would not restore full conductivity and there would still be an inefficiency in the formation process. When this is combined

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with the difficulty that operators have in properly and securely fitting connectors under extremely difficult conditions, it is no surprise that the industry is experiencing high levels of damaged battery rework as well as higher energy costs. For this reason, UK Powertech and *BESTmag* are working together to find solutions, possibly with the formation programme and process methods, to reduce the rate of corrosion in conventional connectors.

In parallel with this, new connector designs which prevent acid and water ingress to the connector terminal— and which also provide better

and more consistent contact with battery posts, even those with defects— are now being tested. It is planned that the next round of tests will include new connector designs and data from field trials taken in battery manufacturers' formation departments. These new and existing designs will also be subjected to simulated formation schedules using the Digatron test equipment. From these simulation tests, we will be able to accurately predict the energy, warranty and damage savings that are possible by replacing connectors at clearly identifiable stages. It is also the intention to produce

clear guidelines using visible markers to prescribe when these stages occur. With this information it will be possible to predict when the losses due to the continued use of a connector will outweigh the cost of its replacement.

As usual it will be the subscribers to *BESTmag* who will benefit by getting this information first hand. And remember, this testing facility, both chemical and electrical is available to all subscribers. It is bespoke, and because it includes free access to more than 40 years of battery design and manufacturing expertise, it is entirely unique. +