Separators and organics for lead–acid batteries

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Abstract

This review discusses various interactions between organic compounds, brought into the lead–acid battery via the separator, and their subsequent effect on battery performance. Historically, the interrelationship started with certain 'expander' actions on the lead morphology due to lignins, which leached out of the wooden separators of that time. Synthetic separator materials did not show this effect, but gained acceptance as they were far more stable in the hostile battery environment. The partially hydrophobic character of synthetic separators has been overcome by organic surfactants. Other organic compounds have been found to improve further the stability of separators against oxidation. Special organic molecules, namely aldehydes and ketones, have been identified to retard, or even suppress, the adverse effects of metals such as antimony, and thus prolong the cycle-life of traction batteries in heavy-duty applications or reduce water loss from automotive batteries. Knowledge about these interactions has opened ways to improve separators.
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1. Introduction

The separator is the distance-keeping component between the positive and the negative electrode of a galvanic cell. It does not participate directly in the electrochemical processes of electricity storage. Rather, its significance lies in the technical challenge to build batteries that are ever more compact and long-lasting [1]. Deriving from this definition, a separator has to serve over a long period of time as a physical separation of the electrodes without too much hindrance to the ionic current flow.

In the hostile environment of a lead–acid battery, i.e., sulfuric acid and very strong oxidizing species such as lead dioxide or nascent oxygen, only a few substances are stable over a long time. These substances include primarily silica, glass fibres, a few salts, and a few synthetics. All organics will – earlier or later – be decomposed and, via several intermediate steps, will be oxidized to carbon dioxide. This decomposition of organic molecules is of course dependent on their sensitivity to oxidation, on their solubility, on the temperature, and on the amount of electric charge (in particular overcharge). The size of the molecule is also very important; it takes longer for macro-

molecules to be degraded and, in some cases, even longer than a typical battery life.

2. Organics and lead morphology

In the early days of lead–acid batteries, wood veneers were widely used as separator material. At that time, no acid-stable synthetics were commercially available, or even invented. During the first trials with synthetic separators around 1940, it was observed that some of the desired battery characteristics were detrimentally affected. For example, cold-crank performance decreased very soon with cycling and there was a tendency towards increased sulfation and thus shorter battery life. In an extensive series of tests, these effects could be traced back to the complete lack of wooden lignin, which previously had leached from the veneer into the battery acid and thereby had interacted with the crystallization process at the negative electrode. By a dedicated addition of lignosulfonates – so-called organic 'expanders' – to the negative mass, not only were these disadvantages eliminated but also an improvement in battery performance was achieved. Consequently, this stimulated an intensive programme of research on expanders [2].

More than 300 organic compounds suspected to have the desired properties have been reported in the literature. Organic

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macromolecules (e.g., lignosulfonates) when adsorbed at the negative electrode surface, prevent a too dense an accumulation of lead sulfate, which otherwise would inhibit discharge of the deeper regions of the electrode. Together with the seed effect of barium sulfate as well as the influence of graphite or carbon black, the adsorbed lignosulfonate macromolecules maintain the porous structure of the negative lead electrode. This allows high current densities, i.e., good cold-cranking power, and efficient use of the active material. Expanders are not any longer brought into the battery via the separator. Rather, a specialized industry has developed to serve the needs of lead–acid battery manufacturers.

3. Organics and wettability

Modern synthetic lead–acid battery separators, e.g., polyethylene containing silica agglomerates, are reinforced by a network of extremely long macromolecules, shown as strings in Fig. 1.

In general, the inner surface of the separator has areas which are hydrophilic, i.e., prone to be wetted with aqueous liquids, and other areas which are hydrophobic, i.e., repellent to sulfuric acid. Thus, the acid will not wet all the pores, especially not the very small ones, so that the battery will not benefit fully from the high porosity of the separator.

As the electrical resistance of a separator is reciprocally dependent on the porosity [1], to achieve the lowest possible electrical resistance of the separator, i.e., the best cold-cranking power, and to absorb as much sulfuric acid as possible, i.e., to achieve optimum battery capacity, all inner surface areas of the separator should be readily wetted. Depending on the proportion of hydrophobic to hydrophilic areas, incomplete wetting can result in lower 'effective' porosities. That is, the very small pores remain dry. In order to overcome this situation, the use of wetting agents is very helpful. These are surfactants, e.g., laurylsulfate, that act similar to a soap, i.e., these organic molecules have on one end a hydrophilic group and at the other a hydrophobic group. The agent will be adsorbed (ideally, as a monomolecular layer) on the separator surface, especially on the hydrophobic sites. According, the surfactant molecules will orientate themselves with their hydrophobic end towards the solid separator surface and present their hydrophilic end to the open pore, i.e., towards the acid, and thus converting a hydrophobic area into a hydrophilic one. When the separator is now soaked with electrolyte, all the pores will be filled with acid and thus offer optimum electrolyte absorption and lowest electrical resistance.

Normally, surfactant molecules are soluble in acid. After a relatively short time they are oxidized and will leave the battery as carbon dioxide (CO_2). Nevertheless, they have fulfilled their task, namely, wetting the inner surface of the separator. A significant gas pressure would be required to expel the electrolyte from the pores. This does not happen, however, when the average pores are sufficiently small, as found in microporous separators.

4. Organics and separator oxidation

All organics are decomposed with time in the hostile environment of a lead–acid cell. The separator should be as stable as possible, at least as long as the expected battery life, which can be up to 30 years in stationary batteries. Whereas silica is absolutely stable, this is not the case with the organics, even when they are macromolecules. Some organics, like polyolefines, are resistant against sulfuric acid, but are not completely inert to oxidative attack by lead dioxide or nascent oxygen.

Under oxidative attack, macromolecules are decomposed by chain rupture. The degree of oxidation can be determined by means of the PEROX 80 test [3], in which the reduction in elongation until breakage is determined as a function of exposure time to the oxidative electrolyte solution.

In order to improve the oxidation resistance of separators, a higher polymer content would result in a denser polymeric network for the filler agglomerates and a better oxidative stability. This benefit would be achieved, however, at the expense of a higher electrical resistance and an added cost. In fact, the impact of a higher polymer content on oxidation resistance has found to be only marginal [4]. Another approach would be to use even longer polyethylene macromolecules. A higher average molecular weight for the polyethylene does indeed result in some improvement in oxidation stability, but not to the extent that is expected theoretically [4]. This tendency is equally true for the effect of polyethylene molecular weight on puncture resistance (Fig. 2).

The main reason for these disappointing results is that during extrusion some of the extremely long molecules are already destroyed due to shear forces and temperature. In order to
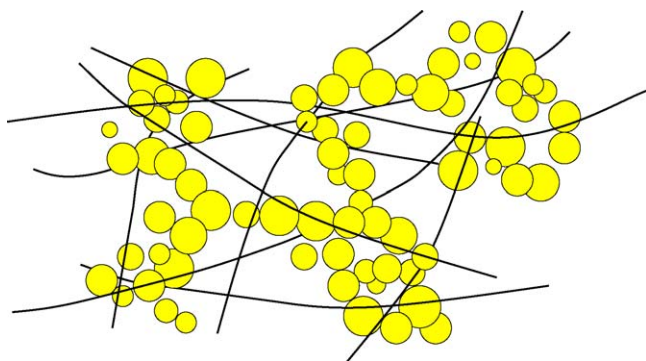

Fig. 1. Schematic of silica–polyethylene network in synthetic separators.
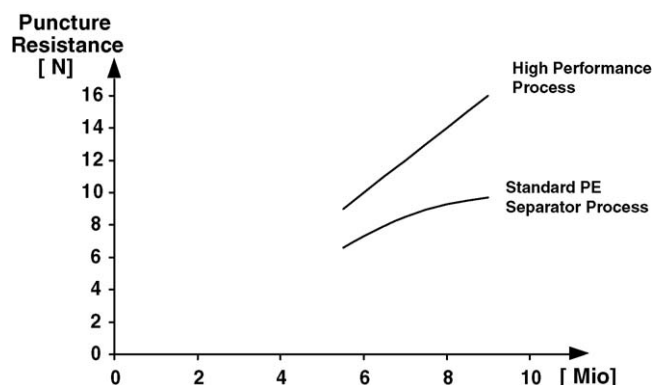

Fig. 2. Puncture resistance as a function of polyethylene molecular weight.

prevent any premature chain deterioration of the polyethylene macromolecules, a more gentle separator production process – the so-called 'high performance process' – is of significant advantage as it almost maintains the original length of the polymer chain and thus improves puncture strength [5] (Fig. 2).

Oil content is another aspect of separator oxidation stability. At a first glance, it is quite surprising that oil has any impact on the oxidation stability of the polyethylene separator. In fact, however, the higher the oil content, the greater is the stability of the polyethylene separator to oxidative attack. This result can be interpreted by assuming the oil covers the polymer to form a protective film that sacrifices itself for the polyethylene and thus reduces the oxidizing species and renders them harmless.

In general, oils with a higher polar content contribute more to the oxidative stability of separators than pure paraffinic oils, which do not show any such effect. Therefore, the protective mechanism of oils is based on the fact that the oxidizing substances, which come from the positive electrode, attack the relatively easily oxidizable polar components and become themselves reduced and thus innocuous. While the polar compounds sacrifice themselves, paraffines evidently are sufficiently stable to resist this oxidative attack [4].

5. Organics and antimony poisoning

Another highly interesting field of interaction between separator organics and lead–acid battery electrochemistry is the so-called antimony poisoning. During the cycling of conventional traction batteries and golf-cart batteries, which use lead alloys with antimony contents of about 4–8 wt.% Sb, a decline in voltage at the end of the recharge is recorded. This voltage decrease occurs mainly during the overcharge part of the recharge, i.e., when only the gassing reactions are involved. It has been shown that it is primarily the hydrogen evolution at the negative electrode that becomes facilitated; the reaction takes place at a lower potential. The reason for this behaviour is that antimony has plated out on the negative electrode and allows hydrogen evolution to proceed more easily than on pure lead [6]. Facilitated hydrogen evolution means a lower charging efficiency, which results in higher water consumption and increased battery temperature. Especially in so-called 'heavy duty' traction applications, i.e., frequent cycling at elevated ambient temperatures often linked with deep discharges, this can result in further increase in temperature, and thus a higher corrosion rate and sometimes, finally, an even shorter battery life.

It is well known that the effects of antimony poisoning can be retarded by the use of rubber separators. All effects then occur in a similar manner, but significantly later during battery cycling life. This is remarkable, as it differentiates rubber separators – independent of their origin – from all 'non-active' separators, be they polyvinyl chloride, phenolic resin, or polyethylene separators. This 'magic' effect of rubber separators has long been recognized and has encouraged much speculative explanations. For example, it has been related to the pore size distribution of the separator. This is not acceptable because, under controlled conditions, separators with different pore sizes exhibit a behaviour
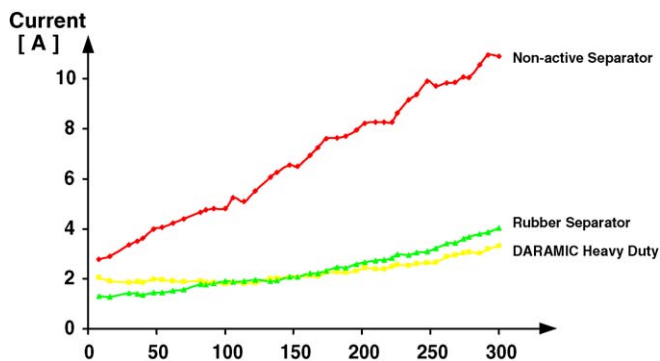

Fig. 3. Battery test results with industrial separators at 55 °C with current–voltage (2.4 V) charge regime.

exactly according to the laws of hydrodynamics or diffusion, respectively.

Another theory assumes a 'capturing effect', i.e., the antimony is trapped inside the rubber separator and is retained there so that it cannot poison the negative electrode. It has been demonstrated [7] by analyzing all parts of traction battery cells after cycling for their antimony content, that in rubber-separated cells the negative active-material contains significantly less deposited antimony compared with that in cells with other separators. Furthermore, the rubber-separated cells exhibit a significant antimony loss, which can be explained by a more intensive cleaning effect via stibine generation.

How can a rubber separator influence the antimony content of the negative electrodes? It is reasonable to assume that it is not due to a physical effect by the separator, for example a filtering off or a capturing of antimony ions, but to a chemical interaction. In the presence of extracts from rubber separators, as well as in the presence of aldehydes or ketones [8], antimony will be deposited on the negative electrode in a different modification, which is less poisonous, i.e., reduces the hydrogen evolution reaction. This results in more and longer intensive stibine generation and thus electrode cleaning from antimony and, finally, in less total antimony deposition [7].

These insights [9] have been used to develop a new industrial traction battery polyethylene separator, i.e., the Daramic 'Heavy Duty' product [10], which matches the antimony poisoning retardation of rubber separators, while maintaining all other superior performance properties of polyethylene separators (Fig. 3).

6. Organics and water-loss tests

This effect of separator organic chemical compounds on the performance of a lead–acid battery can also be assessed by means of a water-loss test. In this procedure, automotive batteries are fully charged before an overcharge at a constant voltage of 14.4 V is started for several weeks; the details depend on the standard specifications. The current is recorded, see Fig. 4. The higher current level at the start is due to residual lead conversion, e.g., as compensation for some prior self-discharge. The current increases slightly with time due to poisoning of the neg-
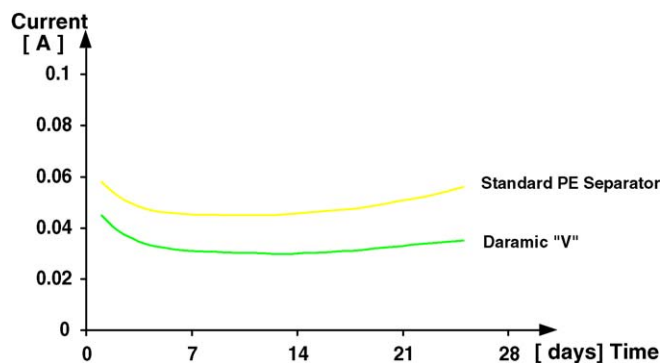
Fig. 4. Water loss test at 40 °C and 14.4 V (12 V/44 Ah battery; positive-plate alloy: Pb–1.6 wt.% Sb, negative-plate alloy: Pb–Ca).

ative plates by antimony or other elements that are more noble than lead. In the case of lead–calcium alloys, traces of nickel, selenium, tellurium or manganese and tin can cause an increase in current.

When using a separator that contains an organic additive with water loss reducing properties, e.g., Daramic V, the current flow is reduced significantly, i.e., by about 30–40% as demonstrated by the lower curve in Fig. 4. The weight loss that these batteries exhibit due to decomposition of water by electrolysis is proportional to the total overcharge, i.e., the integral of current over time, in accordance with Faraday's law.

7. Conclusion

Are there any disadvantages to be considered when using organic additives in batteries? The situation is akin to that found in the medical field; medicaments always have good and less good effects — a good medicament is one in which the advantageous effects outweigh the others by far. The same is true for batteries: additives can only be justified in a certain application when positive results dominate.

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