Technical Bulletin

Topic: Oil in Polyethylene Separators

It is well known in the battery industry that polyethylene separators do contain a certain amount of mineral oil. There are, however, several features around this simple fact which are certainly not all self-explanatory. The following paragraphs shall concentrate on some aspects around the oil useful to the battery manufacturer.

1. Separator Manufacturing

A standard polyethylene separator should better be named “silica separator“ as it contains more than 50 wt.% silica and only 20 wt.% polyethylene. Recalling now that the separator material has to be extruded, it becomes obvious that a mixture like that would rapidly attack the extruder’s screw and die by its abrasive force.

Therefore the mixture has to contain a lubricant, e. g. a mineral oil. But there is another important reason which requires a considerable amount of oil in the blend: to act as a poreformer – the finished product has to be porous! During extrusion; the pores “added“ to the blend in the form of microporous silica should not be filled and irreversibly clogged with molten polyethylene. Again, this is avoided by the addition of oil. After extrusion the oil is extracted by a solvent, down to the desired remaining oil content.

The question immediately arising, “why not totally remove the oil“, concerns the needs of the battery and will be answered in the next paragraphs of this bulletin:

2. Oil in the Separator

2.1 Oxidation Stability

Rendering oxidation stability to the separator is the main purpose of the oil to the benefit of the battery. In fact, the oxidative force of lead dioxide and nascent oxygen, enhanced by the aggressive environment of sulfuric acid at elevated temperature, would soon degrade the polyethylene of the separator. The presence of oil however protects the polyethylene. The oil is somehow sacrificed by being oxidized first. The following diagram proves that [1].

Oxidation Stability vs. Backweb Oil Content

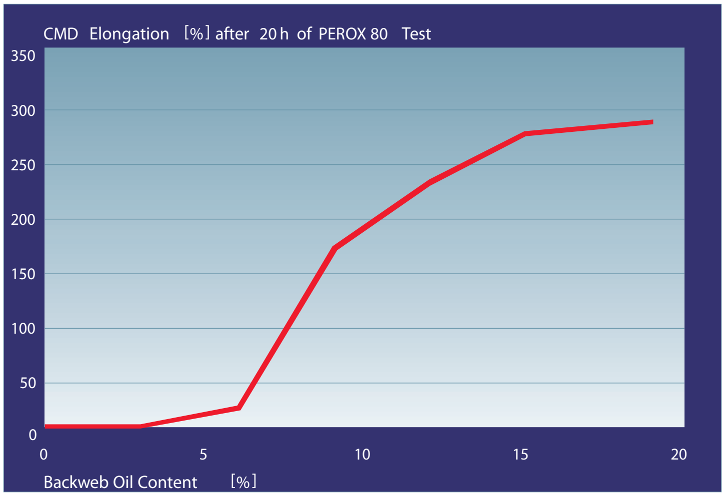

Fig. 1 Going below certain limits with the backweb oil content leads to severe separator damages in a relatively short time. Leaving too much oil in the separator would have a negative e ect on the electrical resistance.

2.2 Porosity

The oil of the separator has an impact on porosity: the higher the oil content, the lower the remaining porosity. This effect should not be overestimated and lead to the temptation to reduce the oil content of an automotive separator backweb on account of oxidation stability. An oil content of 6 % (weight percent) instead of typical 12 % results in only 4 % more porosity, concerning oxidation stability this is already in the dangerous range as Fig. 1 points out.

2.3 Electrical Resistance

The impact of the oil content on the electrical resistance is also not too strong. A similar argumentation as above shows that it would not be reasonable to improve the electrical resistance by lowering the oil content and at the same time reduce the protective force to the separator. Moreover, as the separator represents only roughly 5 % of the internal resistance of a starter battery, an improvement of that order would have only a marginal effect on battery performance.

3. Oil in the Battery

It cannot be neglected that part of the oil migrates out of the separator during the service life of the battery.

Particularly in traction cells where higher temperatures are prevailing, portions of the oil can be leached out by the acid and are released into the electrolyte. What they can do there can be summarized by two phenomena: generate black residues (a negative effect) and reduce the negative impact of antimony poisoning (certainly a positive effect).

3.1 Black Residues

The picture below illustrates the formation of black residues:

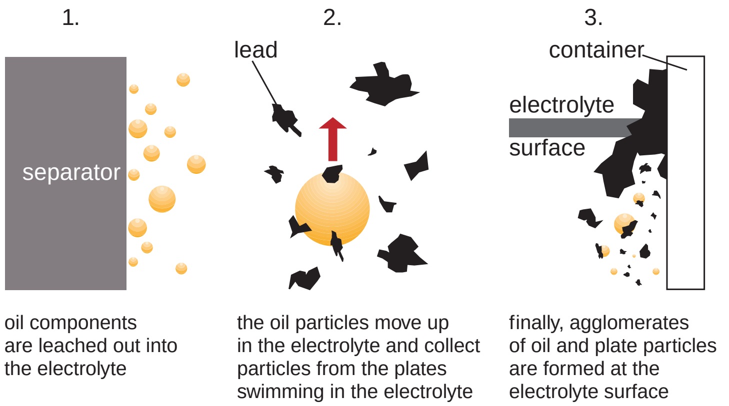

Fig. 2 Generation of Black Residues

Let us now have a closer look on the product of these reactions, the black residue itself. A rough analysis for batteries with lead antimony grids unveils it to be half organic and half inorganic in nature. The organic part comes from the oil, the inorganic part comprises lead and its oxides as well as antimony. The inorganic parts come from the plates. Taking into consideration that the distribution between organic and inorganic portions is more or less equal, it does not surprise that the amount of black residue strongly depends on the plates.

Not only the consistency of the plates with regard to their tendency to "participate" in the black residue forming mechanism, but also the nature of the oil in the separator can vary as well. Some separators do release more, some release less portions of their oil.

Industrial CL, our standard separator for industrial batteries has an unrivaled black residue behavior. By a sophisticated optimization of the mineral oil, DARAMIC, LLC. success in drastically reducing the black residues without reducing its oxidation stability [2]. Black residues are more than a cosmetic defect, they can affect e. g. automatic water replenishing systems. Although having proven the superiority of DARAMIC® Industrial CL it has to be stated clearly that even with a clean separator, certain plates can generate black residues. This can be proven by using "oil-free" separators like DARAK® from which no black residues are originating at all unless the plates itself generate black deposits, e.g. due to oil, which has been added for oxidation protection of the plates.

3.2 Antimony Poisoning

Particularly the positive plates of industrial traction cells may contain a relatively high percentage of antimony (Sb). The following complicated transition states implying SbV and SbIII, at the end it is deposited as metal at the negative plate. Being more noble than lead it lowers the hydrogen over voltage of the negative electrode.

Especially during charging, the negative plate then tends to generate more gas at a lower voltage and the top-of-charge voltage level is suffering. Instead of transforming lead suphate back into lead, the charging current is used for hydrogen evolution. The cell consumes more current without being fully charged. Surprisingly, ingredients of the separator can at least suppress, sometimes even remedy the harmful effects of antimony at the negative plate [3]. Certain parts of oil can do that as well.

4. The Optimum Oil

Various aspects linked with the oil in the PE separator have now been highlighted without focusing so far on the composition of the oil itself. A mineral oil consists of polar and non-polar substances. An in-depth evaluation of oils of different compositions with regard to oxidation stability of the separator, its tendency to participate in the generation of black residues and water consumption of the battery shows that mostly the polar part of the oil determines the behavior. Therefore, optimizing the oil means designing amount and chemical nature of the polar parts. The improvement of the chemical composition of an oil is rather tricky as they typically comprise around 500 substances. Unfortunately, the effects on battery performance do not all depend in the same direction from the amount of polar parts: more polar parts mean better oxidation stability but also more black residue, which can be attributed to the polar parts. The water consumption (or top-of-charge behavior) also is improved by polar parts. (Fig. 4)

5. DARAMIC® and DARAMIC® Industrial CL

The mineral oil used in DARAMIC® separators is the result of a consequent development process to achieve low water consumption and highest oxidation stability at an acceptable level of black residues.

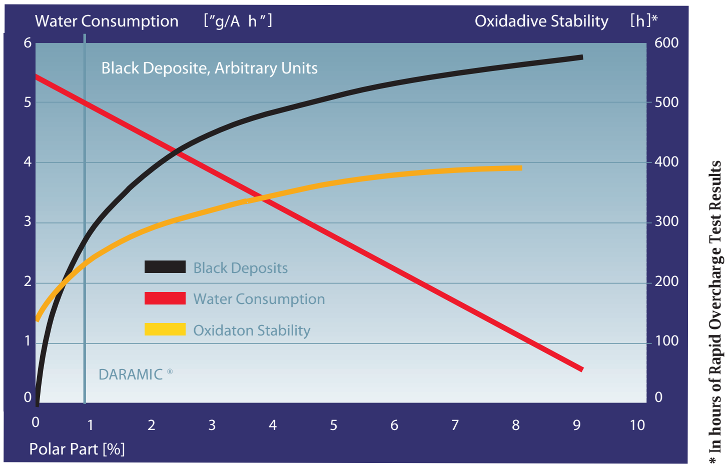

Fig. 4 The amount of polar part in the mineral oil of the PE separator determines its oxidation stability, its tendency to generate black residues and the water consumption of the battery Optimizing oxidation stability by increasing the polar parts would at the same time increase the separator's tendency to participate in black residue generation.

[1] W. Böhnstedt "Challenges for Automotive Battery Separator Development" J Power Sources 67/1-2, 299-305 (1997)

[2] K. Ihmels, H. Bunsch, F. Theubert, US Patent 6,403,264 (1999)

[3] W. Böhnstedt, F. Scholten and C. Radel "Antimony Poisoning in Lead Acid Batteries" J. Power Sources 19, 301-314, (1989)

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