**TECHNIQUES TO PROMOTE OXIDATION RESISTANCE IN POLYETHYLENE BATTERY SEPARATORS**

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**Scope:**

Lead acid based energy storage systems offer an operating environment that is inherently conducive to the rise of free radical oxidation processes. The various material components of these batteries exhibit varying degrees of resistance to oxidation. It is certain however that oxidation is a destructive process. As technical requirements increase in complexity, driven by demands for consistently high levels of performance, component materials within the battery must evolve to meet the challenge of destructive oxidation. Components such as battery case containment are not directly involved in the chemical reactions that dictate electrical performance. These components (often comprised of polypropylene), are relatively inert and as such have required little to no development over the course of battery development. However, critical components such as electrode metallurgy and active material composition continue to undergo continuous improvement, focusing on extended cycle life by addressing grid corrosion root causes and various other critical performance considerations. Separator technology falls into this critical focus as well. The separator must perform at a consistent level over the life of the battery, it must maintain microporous structural integrity to insure a low contribution to battery internal resistance. The separator must provide an optimal degree of acid availability to the plates. In many cases the separator is now a “delivery vehicle” as well, diffusing agents to lower water loss and/or to enhance charge acceptance. The physical dimensions of the separator must remain relatively constant and unaffected by oxidative attack on backweb and ribs. This short communication will focus on the various methods employed to generate oxidation resistance within porous polymeric separators.

**Historical Methods Employed to Enhance Separator Oxidation Resistance:**

PE separators entered the industry over 30 years ago and rapidly became the dominant player in both Industrial and Automotive applications. In the early years of PE utilization, the most common means to retard the effects of oxidation was to simply add more polymer mass. This was achieved by adjusting the backweb thickness upwards, rib height was adjusted accordingly to attain existing plate spacing requirements, and (in some cases the spacing requirements were changed). This approach of simply “adding more mass to be consumed” does indeed yield extended separator life. Of course this rather crude approach compromises electrical resistance (ER); some energy storage applications indeed have more tolerance to increased ER. This approach was a “one size fits all” endeavor and as applications evolved, especially in the automotive sector, this approach proved to lack flexibility.

Separator manufacturers initiated a focus on the residual processing oil content of the product. Studies were undertaken to gain a more complete understanding of the oxidation resistance imparted over the cycle life of the battery from various processing oil fractional compositions. It was determined that adjusting the chemical composition of the processing oil (pore former) yielded significant benefit in terms of resisting the degradation brought about by oxidation. In brief, the paraffinic content of the pore forming oil was found to be “too resistant” to oxidation, the result was that the oxidative reaction attacked the polymer separator in deference to the oil. Blending a precise quantity of pore forming oil bearing Naphthenic composition allowed the oil to slowly oxidize in preference to the separator structure. Therefore, the separator industry adopted guidelines to dictate the optimal chemical composition of the process oil and further to instill an optimal quantity of said oil in the separator as residual. The result was less adjustment to separator dimensions (Backweb) and tighter specification on the quantity of residual oil employed. This no doubt was a beneficial development although the ER was still at risk for increase as the residual oil (as a liquid component) functions in a manner to occupy volume within the porous matrix.

In parallel to the optimization of pore forming oil composition and residual deployment, some separator manufacturers combined the “more mass” concept with the “enhanced residual oil” concept. That is, the separator formulation itself was adjusted to decrease the ratio of silica to polymer. Simply stated, the amount of silica, which acts as a vehicle to carry pore forming oil, was dramatically decreased. The result was a separator that was simply richer in PE. In this scenario the separator dimensions are unchanged as the actual composition of the separator contained more polymer and less pore volume. The decrease in separator porosity is combined with the higher mass of “sacrificial” polymer. Electrical resistance typical increases with increasing polymer content as porosity decreases.

In more recent times, the polymer industry became more proficient in producing ultra-high molecular weight PE (UHMWPE) at significantly higher molecular weights. Oxidation is a free radical chain reaction and it operates at a relatively well-known rate. Simply put, oxidation “chews” on bonds and degrades the structural integrity in doing so. It stands to reason that a denser, more complex, polymer will offer a longer structural life challenging the steady state degradation Vis a vis oxidative reaction. The ‘jury is out’ on the actual effectiveness of this paradigm. The principle depends upon the absolute consistency of polymer chain structure and molecular weight distribution. Processing typical 5 million UHMWPE polymer vs a 9 million MW UHMWPE polymer offers some production complexity.

**Extending Oxidation Resistance to Present Day Applications:**

In present day, separator performance requirements are rapidly evolving with the advent of the Enhanced Flood Battery (EFB). These batteries support Idle-Stop-Start (ISS) operation and operate under a partial state of charge (pSOC). The typical battery typically maintains a pSOC of 70%-80% in routine service conditions. Under these conditions, it is especially critical that the separator minimizes contribution to battery internal resistance and this indirectly supports enhanced charge acceptance. Separator porosity may be adjusted upward to produce a pore matrix best suited to provide optimal ionic flux. There are many considerations when manipulating the separator pore matrix, pore geometry and tortuosity of the matrix are only a few. This topic falls outside the scope of this review abstract, there is always a balance that must be considered when striving for ultra-low ER; surface area arising from porosity vs acceleration of free radical oxidation mechanism over the increased internal surfaces. Most separator manufacturers utilize a BCI test method to measure the separator’s resistance to oxidation. This method combines 35% Hydrogen Peroxide with 1.30 specific gravity H2SO4 at a temperature of 80 degrees C. The separator specimen is immersed in this mixture for 40 hours. Upon completion of the exposure, the Cross Machine Direction (CMD) Elongation is obtained and compared to that for the separator prior to exposure. This test method is useful to simulate extended cycle life under battery conditions. The output data from this BCI test may be interpreted as a %loss in structural integrity (CMD Elong). It is also useful to examine the actual CMD Elong value. Many battery manufacturers have established minimum elongation guidelines based on this methodology.

**A Novel Approach to Oxidation Resistance**

Microporous LLC has introduced a new separator product (Cellforce® ULR™) designed to meet the requirements of the automotive EFB application. This product has been engineered to achieve minimum contribution to battery internal resistance. Through a combination of an innovative manufacturing process and specialized raw materials, the pore matrix consistently supports low ER. As discussed earlier within this abstract, porosity can often introduce a vulnerability to oxidative attack. In the case of Cellforce® ULR™, Microporous leveraged experience unique in the industry to mitigate deleterious oxidation while preserving the low ER benefit from optimized porosity. Microporous is the sole manufacturer of rubber-based separators for deep cycle and motive power applications. The experience gained over many years of natural rubber separator development has led to hybrid separators such as the Cellforce® Rubber-PE separator family as well as Deep Cycle separators in the Flex-Sil® and Ace-Sil® product lines. These rubber and hybrid rubber products are focused on the suppression of Antimony migration (Antimony Poisoning). However, it was determined through research efforts that several of these crosslinked natural rubber formula components demonstrated potent resistance to oxidative attack. A balance of crosslinked rubber and conventional raw materials was achieved that best supported ultra-low ER coupled with excellent resistance to the oxidative environment within the EFB battery application. Therefore, with the silica and polymer content optimized along with a process insuring consistent residual oil content, the cross-linked rubber component was employed to insure the most stable low ER separator for EFB application (also considered for Industrial “Opportunity Charging” scenarios.)

The optimal cross-linked rubber for these separator applications is added directly to the raw material batch formulation. Natural rubber in cross-linked form does not exhibit a defined melting point, instead this material reaches a “smear point” which occurs within the 210C to 240C temperature range within the extrusion process. Interestingly, the ER is relatively unchanged over a wide range of rubber loading formulation. The oxidative resistance vs rubber loading only slightly favors increased rubber in the formula content. Please refer to the SEM micrographs, SEM 1 and SEM 2. The rubber component appears as a “paste-like” component adhering along the surfaces of the polymer fibril structures, it may be observed within the polymer-silica interstitial voids occasional as well.

In sum, separator oxidation resistance will remain an area for continued innovation, as the demands for reduced battery internal resistance are driven by charge acceptance concerns. Pore matrix design will no doubt increase in complexity highlighting oxidation vulnerabilities.

