

# **The Influence of Rubber Separators On Electrochemical Behavior of Lead-Acid Batteries**

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## **Abstract**

This paper represents manufacturing processes; physical, chemical and electrochemical properties; performance in batteries; and their application of currently available three types of battery separators. Many aspects of lead-acid battery performance characteristics which are unique electrochemical properties of rubber are given.

## **Introduction**

During the early period of lead-acid batteries and their separator development, introduction of microporous hard rubber separators greatly improved performances of lead-acid batteries over wood separators extending battery life and improving cold cranking capabilities. Even after the coming of age of microporous plastic separators, rubber separators have maintained a unique position in the battery industry due to certain performance characteristics which could only be found in microporous rubber separators.

Presently, there are several types of separators which differ by their material composition, namely separators made of plastic (polyethylene, polyvinyl chloride, phenolic resorcinol), fiber glass, resin impregnated cellulosic paper and rubber.

The performance success of microporous hard rubber separators over the years lead to the introduction of two new variations of rubber products. These are electron beam radiation crosslinked microporous flexible rubber separators and coated fiber glass mat separators containing rubber.

In addition to providing physical, mechanical and chemical requirements necessary for designing good lead-acid batteries, rubber separators impart electrochemical performance characteristics which enhance overall performance of battery.

## **Requirements for Battery Separators**

The separator placed between positive plate and negative plate provides electrical insulation and physical space for electrolyte but permits ionic conduction through the pores of the separator.

There are two functional aspects of battery separators required for batteries one is physical and the other is electrochemical.

### **Physical requirements:**

- High porosity
- Small mean pore diameter
- Oxidation resistance
- Puncture resistance
- Thermal dimensional stability
- Freedom from harmful chemical contaminants

### **Electrochemical requirements:**

- Favorable voltage characteristics
- Retardation of antimony transfer
- Good Tafel behavior
- Electrochemical compatibility
- Prevention of dendrite growth

### **Types of Separators**

Battery separators can be classified by the materials of construction, microporosity or forms of separator such as leaf or envelop.

#### **Microporous Separators:**

- Polyethylene/silica
- Phenolic resin/silica
- PVS/Silica
- Polymeric membrane/Organic fiber
- Rubber/silica

#### **Macroporous Separators**

- Glass fiber mat
- Sintered PVC
- Resin-impregnated cellulosic paper

Of all the types of separators listed above, polyethylene separators can be enveloped while all others are in general can be made into leaf separators.

### **Pore Size Comparison of Various Separators**

Table I below shows total porosity and mean pore diameters of various types of separators tested lately using mercury intrusion porosimeter at Amerace laboratory. The test results reported are based on the individual samples rather than average or ranges of test values.

**Table 1 Mean Pore Diameters and Total Porosities of Various Separators**

Separator Type (Brand Name)	Mean Pore Diameter $\mu\text{m}$	Total Porosity, $\text{cm}^3/\text{g}$
Polyethylene (Daramic)	0.07	0.84
Phenolic/silica (Darak 5000)	0.34	1.44
PVC/silica (Amer-Sil)	0.15	1.21
Organic membrane (Yumicron)	0.13	0.37
Rubber (Ace-Sil)	0.15	0.83
Rubber (Flex-Sil)	0.06	0.47
Rubber (Micropor-Sil)	0.13	1.22
Glass fiber mat (Hyalite)	35.0	2.20
Sintered PVC (Jungfer)	10.0	0.37
Paper (Armorib)	26.0	1.61

### Rubber Separators

Microporous hard rubber separators (e.g. ACE-SIL®, Mipor B) have been used in industrial batteries as well as automotive batteries for the last 5 years. Even though most SLI (starting, lighting, ignition) applications were switched to polyethylene separators, the value of hard rubber separators stemming from their superior electrochemical performance in the batteries is widely recognized and their use in industrial batteries is expanding throughout the world.

Amerace, Microporous Products, L.P. developed a new electron beam crosslinked flexible microporous rubber separator called FLEX-SIL® 15 years ago. The product design concept behind this separator was to make the separator flexible, reduce mean pore diameter and make manufacturing process more efficient and cost effective while retaining the good electrochemical properties of hard rubber separators.

Recently Amerace Microporous Products, L.P. developed another generation of rubber separator called MICROPOR-SIL®. The main distinction from the other two rubber separators is thin backweb and low electrical resistance.

Each of these three microporous rubber separators has its own unique physical properties for specific application while retaining common electrochemical performance characteristics of rubber separators.

### Composition and Manufacturing Processes of Rubber Separators

Microporous hard rubber ACE-SIL separators are made by mixing natural rubber, rehydrated precipitated silica and sulfur together in internal mixer. The mixed rubber stock is then extruded and calendered to particular rib pattern. The calendered sheet is vulcanized in a large autoclave under water, dried and cut to dimensions to customer specifications.

The compound mixing, calendering procedures and composition of microporous FLEX-SIL separators are very similar to those of ACE-SIL separators except that it does not require sulfur to cure the rubber product. The calendered sheet is continuously fed into

an electron beam processor where it is irradiated with ionizing electron beam. The crosslinked rubber sheet is subsequently dried and cut to final separator sizes.

The manufacturing process of microporous MICROPOR-SIL is somewhat different from the other two rubber separators. Battery grade glass mat is used as a substrate which is coated with a mixture of polymeric emulsion, precipitated silica and rubber compound. Extruded ribs are attached to the coated sheet, cured and dried.

### **Physical Properties of Rubber Separators**

All three types of rubber separators have similar electrochemical properties associated with rubber composition and ultra fine pore structure. They do not contain harmful chemical impurities, leachable oil, wetting agent or voltage control additive (VCA). But each has specific individual physical features which can be utilized in applying to certain types of battery.

Microporous ACE-SIL rubber separators have physical rigidity, resistance against oxidation, good wettability and dimensional stability. They are versatile in separator design capable of providing high ribs for very thick products enabling elimination of perforated corrugated plastic spacer, interrupted diagonal ribs or narrowly spaced ribs for tubular positive plates, glass mat attachment and mini-ribs (cannelure ribs) to be faced against negative plate.

The main differences of microporous FLEX-SIL rubber separator from ACE-SIL separator are flexibility and finer pore structure having mean pore diameter of only 0.05  $\mu$ m. They also have separator design capabilities such as mini-ribs on negative side or attachment of glass retainer mat.

Microporous MICROPOR-SIL rubber separators have comparatively thin backweb with low electrical resistance, excellent dimensional thermal stability and good wetting properties.

### **Influence of Rubber Separators on Electrochemical Behavior Lead-Acid Batteries**

Through the experience of serving the lead-acid battery industry for a long period of time and through conducting laboratory experiments, it has been well proven that rubber separators exhibit certain electrochemical properties no other types of separator have. These properties include on-charge voltage characteristics, ability to retard antimony transfer, electrochemical compatibility, Tafel behavior and ability to prevent dendrite growth in the cell. Some of these properties are interrelated, but for the purpose of analyzing and evaluating different aspects of battery performance, these will be discussed individually.

### **On-charge Voltage of Cells**

Since almost all battery chargers today are based on voltage regulation, it becomes critical to understand voltage characteristics of a battery. A fully charged battery with the low end-of-charge voltage will not only charge the battery at higher currents near the end

of charging but also continue to accept excessive currents. This will use more electricity wastefully only to generate gas and increase cell temperature. The gassing in turn will cause loss of water and the high cell temperature will cause grid corrosion and shedding of active material leading to eventual failure of the battery.

There are many factors which affect voltage of batteries during charging. The on-charge voltage can be affected by the internal resistance of battery components, but certain organic or inorganic contaminants in the cell, in larger degree, will determine the on-charge voltage by altering hydrogen overvoltage and oxygen overvoltage at negative plates and positive plates. Rubber separators impart higher on-charge voltage in lead-acid batteries than those with plastic, glass or paper separators, preventing batteries from being over charged when they reach fully charged state. Recognizing the fact that rubber separators give higher end-of-charge voltage, a company invented voltage control additive (VCA), made of a surface active organic compound, which simulated voltage characteristics of rubber separators. However, this VCA has proven to adversely affect overall battery performance and life, even though it has achieved temporary adjustment of cell voltage.

### **Antimony Transfer**

Grids of many industrial batteries and some automotive batteries use lead-antimony alloys because it is easier to cast, produces stronger grids, improves corrosion resistance and increases the ability of the battery to recover from deep discharge. However, some antimony transported from positive grid, in the form of an ion, to the negative plate and subsequently deposited on the surface of the plate, can cause lowering of hydrogen overvoltage and liberation of hydrogen (1). Many laboratory studies have shown that the batteries insulated with rubber separators retarded transportation of antimony from the positive grid to negative plate. The advantage of the rubber separators in deep cycling gold car batteries is well demonstrated by the excellent record of battery life in the field.

As in the case of addition of VCA to plastic separators to artificially simulate improved voltage characteristics of rubber, some separator developers have attempted to adopt incorporation of rubber to plastic separators, in an attempt to impart properties of rubber separators which showed favorable end-of-charge voltage characteristics and reduction of antimony poisoning effect for deep cycling batteries.

Much studies have been conducted on the subject of premature capacity loss (PCL) also known as antimony free effect. PCL phenomenon in lead-acid batteries is characterized by rapid loss of positive plate capacity without indicating usual battery failure mode of grid growth or active material shedding. It may be suggested that battery designer may keep beneficial effect of antimony in the battery but reduce deleterious effect of antimony by adopting rubber separators.

### **Electrochemical Compatibility and Tafel Behavior**

It has been shown that a small amount of electroactive organic substances in the cell electrolyte leached out from the battery separator can change the Tafel line of the electrode upsetting the electrochemical behavior of the cell. This will acutely affect

stationary batteries which are floated to maintain the cell are fully charged state (2). Since the batteries are kept at full charge by overcharging the cell at fixed voltage at slightly about the thermodynamic reversible potential, shifting of the negative polarization curve, for example, may deprive the excess potential needed at positive electrode, causing grid corrosion in the positive plate.

In order to determine material compatibility of battery components, such as separators, in the battery, the Bell Laboratories established an accelerated test method. The electrochemical compatibility test procedure measures the hydrogen and oxygen over-potential shifts in the test solutions compared to a pure acid solution using rotating disk electrodes and Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrode (2). The test solution is prepared by extracting leachants of the test sample in sulfuric acid at elevated temperature. This test will enable a battery engineer to predict long term effect of chemical residues leached into electrolyte from separators.

Rubber separators show good electrochemical compatibility and favorable Tafel behavior for floated stationary batteries.

### **Dendrite Growth**

A dendritic growth or treeing from the negative to the positive plates, which causes short circuits by means of metallic conduction, will lead a battery to an eventual failure. The presence of certain material in the grids such as cadmium (1) or certain organic solutes leached from the separator or other battery components can cause the growth of dendrites (2).

It was found that rubber separators do not cause growth of dendrite but was believed to prevent it from taking place in the cell. A manufacturer of stationary batteries, in an attempt to prevent dendrite growth and impart favorable electrochemical attributes of rubber practiced battery construction by inserting one piece of rubber separator per cell which was otherwise insulated with plastic separators.

### **Application of Rubber Separators in Lead-Acid Batteries**

#### **Rubber Separators in Industrial Stationary Batteries**

##### **Telecommunication**

The standby battery system for telecommunications requires long life ranging from 10 years to 30 years. The batteries for reserve power supply are floated to maintain them at fully charged state. For this reason it is critical that the separators used in this application have good electrochemical compatibility. Microporous hard rubber separator Ace-Sil does not release harmful organic solutes to electrolyte during the service of battery which may change overpotentials of the cell and upset the float balance. Imbalance of Tafel line will cause detrimental effect on positive grid causing premature failure of the battery. Rubber separators provide good electrochemical compatibility to give long battery life.

### **Uninterruptible Power System (UPS)**

UPS or switch gear battery is served as standby battery, as the batteries for telecommunication, but requires higher rate of discharge for short duration of time. Therefore, it not only requires separators which can impart good electrochemical compatibility and thinner backweb for low electrical resistance can serve well in the batteries for float charging and high rate discharging purposes.

### **Load leveling and Energy Storage System for Utility**

Lead-acid batteries are used for the purpose of load leveling, spinning reserve and voltage regulation. The batteries are charged during off peak hours and discharged during peak usage, reducing costs of generating additional electricity during the period of peak demand. Chino 10MW Battery Energy Storage facility located at Southern California Edison's substation near Los Angeles, uses batteries insulated with Ace-Sil hard rubber separators. Chino battery is the largest battery facility in the world consisting of 8,256 battery cells which can store enough energy to supply 5,000 customers with electricity (3). The rubber separators meet the rigorous demand comprising electrochemical performance characteristics as well as oxidation resistance required by the special mode of battery use.

### **Rubber Separators in Industrial Motive Power (Traction) Batteries**

Motive power batteries such as forklift trucks, automated guided vehicles or mine vehicles operate in deep cycling mode of use. The separators for this type of battery must survive severe deep discharging as well as daily recharging cycles. Hard rubber separator, because of its ability to retard antimony transfer, give high end of charge voltage and prevent dendrite growth, is well suited for traction applications particularly batteries with positive tubular plate construction

### **Rubber Separators in Deep Cycle Batteries (Golf Car, Marine, Floor Sweeper Scrubber and Recreational Vehicle)**

Microporous flexible rubber separator Flex-Sil gives excellent performances for the deep cycling batteries which are normally constructed with high antimony grid alloy. Batteries insulated with Flex-Sil rubber separators, compared to PE separators, show much longer life due to its ability to retard antimony transfer thereby reducing its harmful effect on positive plate. The batteries showing low end of charge current will generate less gas and require less amount of water addition.

### **Rubber Separators in Automotive Batteries**

PE envelope separators are used for most of SLI batteries in North America. Conversion of lead to enveloped separator in Europe is taking place at a slower pace, but elsewhere in the world majority of SLI batteries are still made using conventional leaf separators. Since the SLI batteries with leaf separators contain plates with lead-antimony grid, microporous MICROPOR-SIL rubber separator can contribute to the performance improvement of conventional SLI batteries. This improvement can be made possible because of MICROPOR-SIL rubber separators have mean pore diameter of only 0.2  $\mu\text{m}$  compared to Sintered PVC, glass fiber or paper separators which have mean pore diameter on in the order of magnitude of 10 to 60  $\mu\text{m}$ .

### **Rubber Separators in Gel Batteries**

MICROPOR-SIL separators are especially well suited for all types of gel batteries because of low electrical resistance, good wettability and affinity of the separator surface to gel environment.

## **Conclusion**

Rubber separators, in addition to exhibiting the physical chemical features necessary to perform in a battery, have electrochemical properties that will enhance battery performances. Rubber separators in the lead-acid batteries impart electrochemical characteristics including high end-of-charge voltage, ability to retard antimony transfer, electrochemical compatibility, ability to prevent dendrite growth and favorable Tafel behavior.

Owing to these unique electrochemical characteristics, batteries built with rubber separators will improve overall cell performance and extend battery life.

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