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Battery additives: any influence on separator behavior?

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Abstract

Additives to lead–acid battery active materials and components are categorized as physical and chemical attribute additives. Separators are equally divided into two classes, those that have inner skeletal structures, commonly made of mixtures of polymers and precipitated silica, and those that are made of loose fibers. Separator additives are also briefly discussed.

Both physical and chemical impacts of active material additives on separators are considered. With the noted exception of negative plate expanders, very little interaction has been reported thus far between active material additives and separators. This question should be further investigated in the light of the growing importance of additives in improving the performance of the lead–acid battery. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Battery additive; Skeletal structure separator; Fiber structure separator; Dendrite preventive additive (DPA); Physical attribute additive; Chemical attribute additive

1. Introduction

Some of the first types of separators used in lead–acid batteries were wood separators. Over many years of use, battery experts began to understand the beneficial influence of some of the components of these wood separators. Thus the first additive to battery active materials was pulverized wood added to the negative paste mixes. The earliest patent in this domain was given in 1919 [1].

This first active material additive was intended to preserve the spongy lead structure of negative plates. Besides pulverized wood, other materials as diverse as lamp black, barium sulfate, powdered charcoal, wood flour and other assorted wood extracts were used as additives. Additives to the negative active material became a major topic once lead–acid batteries stopped using wood separators that were the norm in the first half of the 20th century. Thus, it was the wood separator that inspired the need to use additives in the negative active material.

These early empirical additives were the forerunners of a complex array of materials that are currently employed throughout the lead–acid battery industry and are known collectively as ‘additives’. In the realm of the lead–acid battery an additive can be classified as any ingredient present in the active materials or components of the lead–acid battery that is not critical to the functioning of that active

material or component. However, an additive though not essential can achieve a desired modification to the functioning of the active material or component of which it is an ingredient.

Additives are normally considered to be ingredients present in small quantities. But this is not always necessarily, some additives may be present in rather substantial quantities sometimes in the range of a few percentage points of the total material weight.

Electrochemical active materials of the lead–acid battery are the positive active material (PAM), the negative active material (NAM), and the sulfuric acid electrolyte. Components that have an active role in the functioning of the battery are the separators, the metallic lead parts such as grids, posts and top lead connections, the containers and vent caps.

In the case of valve regulated lead acid (VRLA) batteries, separators and vent caps assume a special role. The former are in most cases the means of immobilizing the electrolyte and the latter are supplied with one way pressure sensitive gas valves that allow the build up of the necessary positive gas pressure inside the battery.

Both battery active materials and components have complex compositions and some of their constituent parts are available in small quantities. These constituent parts or ingredients only become additives if somehow they are introduced to achieve a specific effect. We can divide battery additives into two broad categories:

- Physical attribute additives.
- Chemical attribute additives.

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Additives in the first category are used with the purpose of modifying the physical characteristics of the active materials or components. The second class include all those additives that act on the chemical/electrochemical characteristics of the active materials or components. Because the field of additives in lead–acid batteries is so large, we shall only attempt to review the possible impact of some of them on separator behavior.

2. Active material additives

The key battery performance characteristics one attempts to influence by using additives are

- Higher energy density by increasing the active material utilization.
- Longer service life by reducing or eliminating the constraints of optimal cycling.

With these objectives in mind additives have been added to the active materials almost from the very start of the existence of lead–acid batteries. Here, we consider only the better known of these additives and look at their impact.

2.1. Physical attribute additives

Additives in this category are meant to modify the physical characteristics of the active materials by imparting mechanical strength, homogeneity, reduce shedding, increase porosity and conductivity of the active materials.

Given the very harsh environment that exists with the lead–acid battery, only a select group of materials are able to survive it and perform their function effectively. The situation around the positive plates is particularly difficult given that the positive plates are at very high potentials and the

PAM is a very strong oxidizer. Thus, most organic materials tend to do poorly in the proximity of the positive plates of the lead–acid battery.

2.1.1. Mechanical strength enhancement

In order to reinforce mechanically the cohesion of the pasted plates, plastic synthetic fibers are used blended in both positive and negative active materials. Even though they are not mentioned in Vinal [1], organic fibers have been used for a long time as additives to both positive and negative paste preparations. These additions, range from 0.1 to 0.2% of oxide weight are added during the paste production process as stated above, the synthetic fibers are meant to prevent the plate pallets from shedding and to reduce mud formation at the bottom of the elements [2].

These organic fibers range in length from 1.6 to 3 mm and have diameters typically from 20 to 30 μm in diameter. It appears that the large size of these fibers contributes to the structural reinforcement of the active materials. Fig. 1 above illustrates this reinforcement action quite nicely.

2.1.2. Porosity enhancement

Porosity enhancement agents act by increasing the acid/active-material ratio in the plate. By facilitating the access of electrolyte to lead dioxide and to sponge lead, porosity enhancement agents contribute to an increase in the materials utilization [3].

Additives designed to enhance porosity can be both organic and inorganic and are available for both the positive or negative plates. There has been a considerable amount of activity in this area. Some of the very early advances in battery technology related to the porosity enhancement of the negative plate as noted earlier.

The negative plate can accept organic porosity formers. That is generally not the case at the positive, where inorganic

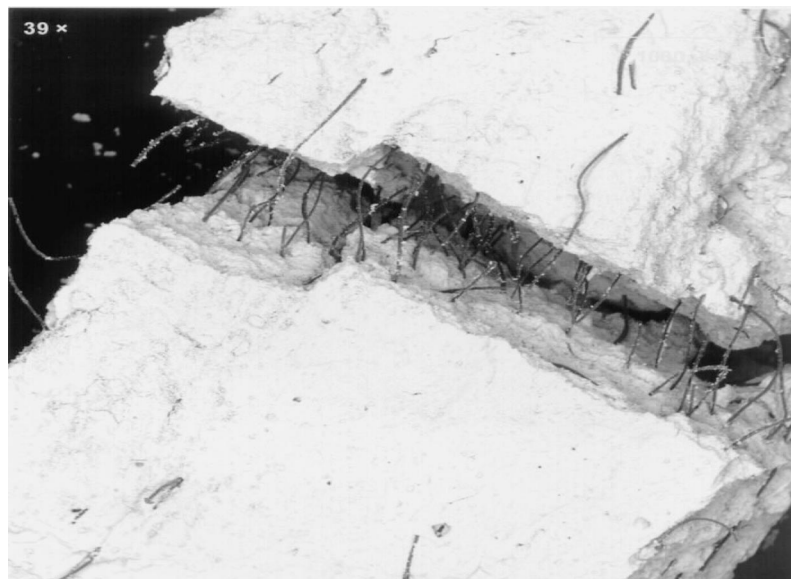


Fig. 1. View of active material with synthetic fibers.

materials are favored. Anisotropic graphite particles as studied by Tokunaga et al. [4,5] have been used successfully to enhance the porosity of positive active materials. Also Edwards [6] studied the impact of adding hollow, light glass micro-spheres. In this study, it was seen that the impact of adding 4.4% of these glass micro-spheres was to increase the material utilization significantly, particularly at high discharge rates.

One of the recent ALABC projects, ALABC Project No. B-005.1 [7] had as one of its main aims the study of the effectiveness of porosity enhancement agents. It was found in that study that the porosity additives used caused an increase of the 1 h rate output of 22–29% in the AGM cells and 22–40% in the gel cells tested. In addition, no decrease in cycle life was noticed with the use of these porosity enhancement agents. The authors of the ALABC study concluded that the output of the lead–acid could be improved from the present level of 35 W h/kg to over 40 W h/kg by the use of porosity enhancement agents using current designs. With design improvements, it is hoped that the performance could exceed 50 W h/kg.

The action of currently used additives to the negative active material goes beyond simple opening up of the active material pores. Negative plate additives are added in amounts of less than 1% of active materials and are usually composed of three groups of materials collectively known as expanders:

1. Inorganic additives, mainly barium sulfate.
2. Organic additives, such as lignin and its derivatives.
3. Lampblack (soot).

It is generally agreed that barium sulfate is needed as a crystallization seed for the formation of lead sulfate during the discharging of the battery. This is possible because barium sulfate and lead sulfate are isomorphous. The use of lampblack is believed to enhance the cold starting and decrease the end-of-charge voltage. The organic components are the actual expanders. These act by decreasing the surface energy of the negative active material and prevent the formation of large crystals. These organic compounds

also prevent the formation of dense insulating sulfate layers [2].

2.1.3. Conductivity and homogeneity enhancement

Both positive active materials of the lead–acid battery are good conductors and collect current and transfer it to the nearest current collector that is a grid wire or the spine in a tubular plate during discharge. As discharge proceeds, lead sulfate is being formed and conductivity is reduced with an accompanying increase in plate resistance as illustrated in Fig. 2 below [8]. This mechanism accounts for the severe limitation to discharge time that one encounters in lead–acid batteries and the limitation of active materials to 35–40% [3].

Past efforts at increasing conductivity have involved the addition of tin oxide coated chopped glass fibers added to the PAM [9] and the inclusion of graphite [4,5]. More recent efforts have been the inclusion of titanium dioxides with the general formula Ti_nO_{2n-1} . These are available under the trade name Ebonex, their use as conductivity enhancement agents has been studied and found to give encouraging results [3,10].

Conductivity enhancement additives gave promising results in the previously mentioned ALABC study that also looked into this kind of additive. These results pointed to an increase in energy output of the cells with the additive. Also, as an added bonus extra cycles to failure were obtained [7]. Conductivity enhancement agents are believed to lead to a more homogeneous utilization of the active materials. Current collection within each plate pallet is apparently made easier when these additives are present.

2.2. Chemical attribute additives

This category of additives act at a more intimate level in the functioning of the lead–acid battery since they actually participate and influence the electrochemical reaction mechanisms that go on inside the battery. It could be argued that the organic components of negative expanders fall in this category, but given their overwhelming activity as

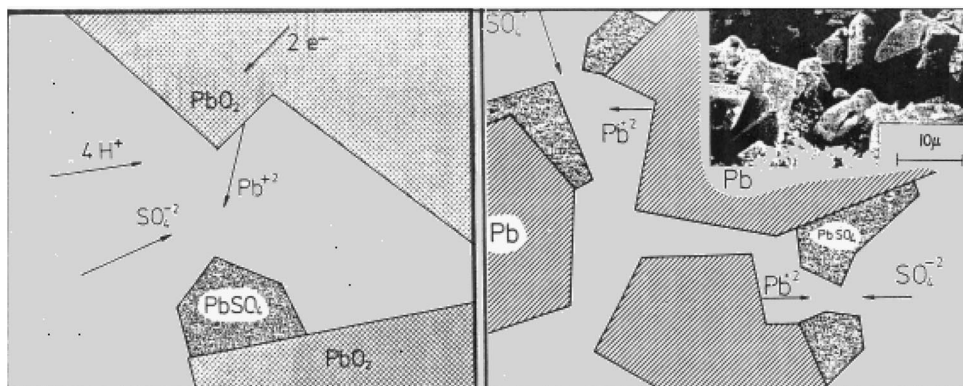


Fig. 2. Precipitation/dissolution mechanism of lead sulfate in active material pores.

porosity enhancement agents, they were left under physical attribute additives and will not be considered here.

2.2.1. Doping of the active materials

Manganese and chromium have been used in the past to dope positive plates and claims were made that such additions increased battery cycle life, increased plate hardness and reduced positive plate shedding. The levels of addition were low set at 0.1–0.3% of PAM weight [12].

The addition of trace elements to the oxides used in the manufacture of the plates has been investigated at various occasions. Antimony in the positive active material has been reported to eliminate the premature capacity loss in the test batteries and extend thus extend battery cycle life. The levels of antimony used were 1% for the flooded test batteries and 0.01% for the VRLA type.

The action of antimony in extending the cycle life of the lead–acid battery is explained in terms of the effect of antimony in the formation of lead sulfate upon discharge and also in the increase in difficulty of discharging antimony-containing corrosion layers. Because of this, the active material discharges more readily than the corrosion layer and a passivation layer is not created at the grid-active material interface [13].

Equally promising results in enhancing capacity and cycle life of lead–acid batteries particularly of the VRLA design, have been obtained by introducing bismuth to the oxide used to manufacture the plates for these batteries. The great advantage of using bismuth over antimony is that one side steps the very negative impact of antimony in lowering the negative plate over-voltage and increasing the water loss of the lead–acid battery. The levels of bismuth addition are reported to be about 0.05% by weight [14].

2.2.2. Antimony transfer control

Antimony entrapping additives were included in the ALABC Project B-005.1 on additives previously mentioned. These additives were included in the negative active material of the test batteries. Unfortunately, they appeared to lose their effectiveness and the hoped for life improvements expected from the presence of antimony on the positive plates did not materialize. It was noted, however, that some of these additives did contribute to cell performance by causing a higher amount of energy delivered by the battery during its cycle life. This effect is probably similar to the impact of the porosity enhancement additives discussed earlier [7].

2.2.3. Electrolyte additives

Besides the above elements added to the plate active materials. One has to consider a whole category of additives to the electrolyte. One such electrolyte additive, whose use dates back to the 1920s is phosphoric acid. Its addition was motivated by its impact in reducing sulfation in the deep discharge state and extension of cycle life by reduced shedding of the positive plates. Some reduction in capacity

was the price to be paid for these benefits. In latter studies, phosphoric acid additions to the electrolyte were found to benefit the recharging characteristics of gelled electrolyte batteries [15].

In the AGM type of VRLA battery, a commonly used electrolyte additive is sodium sulfate. This additive is added in powder form to the electrolyte in amounts of about 1% of its weight. The *common ion effect* explains why sodium sulfate helps to prevent the harmful depletion of sulfate ion that is always a present danger in the discharge of acid starved batteries.

Another interesting electrolyte chemical additive is poly-fluoroalkyl sulfonic acid added in levels of 0.1% to the electrolyte immobilized in AGM in VRLA batteries. This additive is reported to increase the life of VRLA batteries on float service by a factor of 1.5–2, while also reducing the water consumption and self-discharge [16].

Unfortunately, not all electrolyte additives have been as beneficial as the ones described above. Even going back to 1915, hundreds of various additives have been offered to the gullible public in an attempt to ‘cure’ and resuscitate sulfated, worn out ‘dead’ batteries. Some of these additives were in some instances nothing but expensive colored water [1]!

2.2.4. Special chemical attribute additives

One very common failure mode in lead–acid batteries is the creation of very tiny short-circuits that develop between the negative and positive plates. One possible mechanism for the development of these tiny bridges is the build up in plate areas of high current density of growths that are caused by the deposition of colloidal lead particles.

It is also possible that these lead accumulations have their origin in dissolved lead.

The solubility of lead sulfate undergoes a dramatic shift depending on the concentration of the sulfuric acid electrolyte. This solubility increases more than four-fold as the sulfuric acid density decreases from 1.300 to 1.100 kg/l (see Figs. 3 and 4). Thus, it is possible that under certain over discharge conditions the amount of dissolved lead sulfate is such that upon recharging the reduced lead will be forming metallic bridges between the plates.

A strategy to avoid the danger posed by the high lead sulfate solubility that occurs during deep discharging to add sodium sulfate to the electrolyte as previously mentioned. An alternate approach to overcome this danger is to add to the electrolyte additives that actively seek out and deactivate the dangerous growths of lead particulate. This class of additives is known as dendrite prevention additives, DPA for short.

The additives of this type are polar organic compounds that are believed to deactivate a growing lead growth by coating its tip with a layer of oriented molecules. Once the lead growth deactivated, these molecules are available to move on to the next site. A visualization of this mechanism is sketched below.

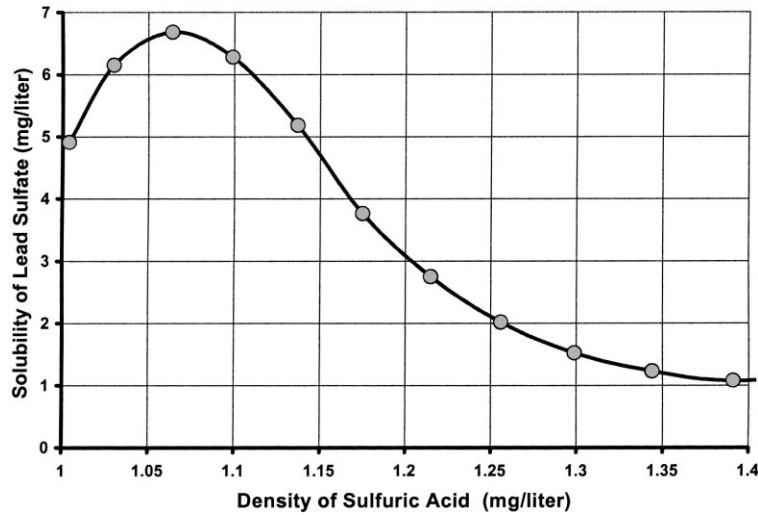


Fig. 3. Solubility of lead sulfate in sulfuric acid at 25°C.

3. The separator and additives

Now the interaction between additives and the function of the separator in the lead–acid battery is examined.

3.1. Separator types

First a classification of the different separators is in order. There are two broad categories of lead–acid battery separators:

- Skeletal structure separators.
- Fiber structure separators.

As their names imply, skeletal separators are made of materials that have a rigid inner structure, usually a polymer

that has been fused by heat or chemical action and is mixed with a filler, typically precipitated silica. These separators are usually available with ribs. Ribs enable the separator to create an inter-plate spacing while keeping overall separator mass to a minimum. An example of this kind of separator is the well known polyethylene type of material whose inner structure is shown on Fig. 5.

The second class encompasses all those separators that have fibers as their basic material. These fibers can be organic or inorganic. They can be bound together with a resin or be laid together loosely without a binder. Figs. 6 and 7 give a view of the fiber structure of this type of material. Both types of separators can be made available in sheets or in rolls depending on how flexible and mechanically strong they are.

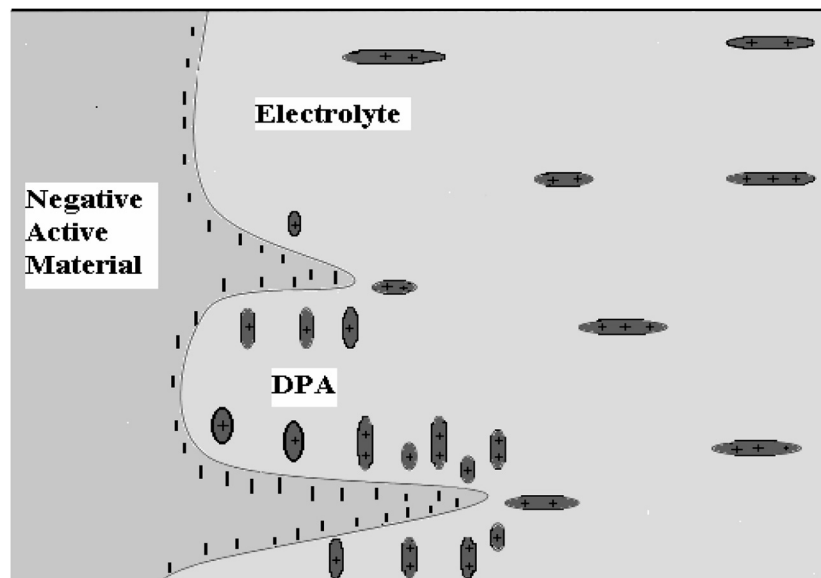


Fig. 4. Dendrite growth being deactivated by dendrite preventive additive.

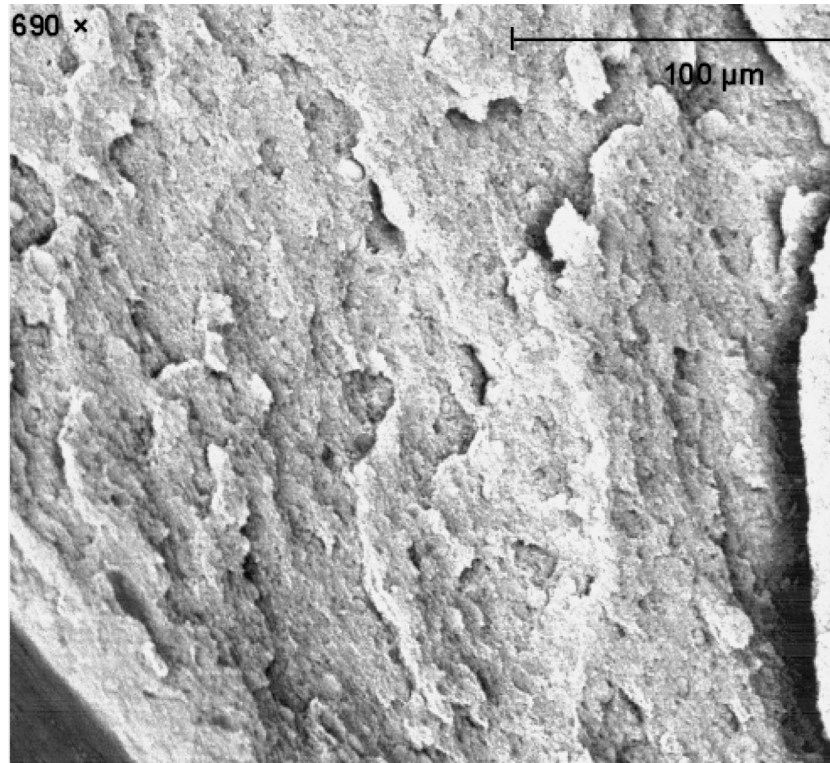


Fig. 5. Structure of skeletal separator.

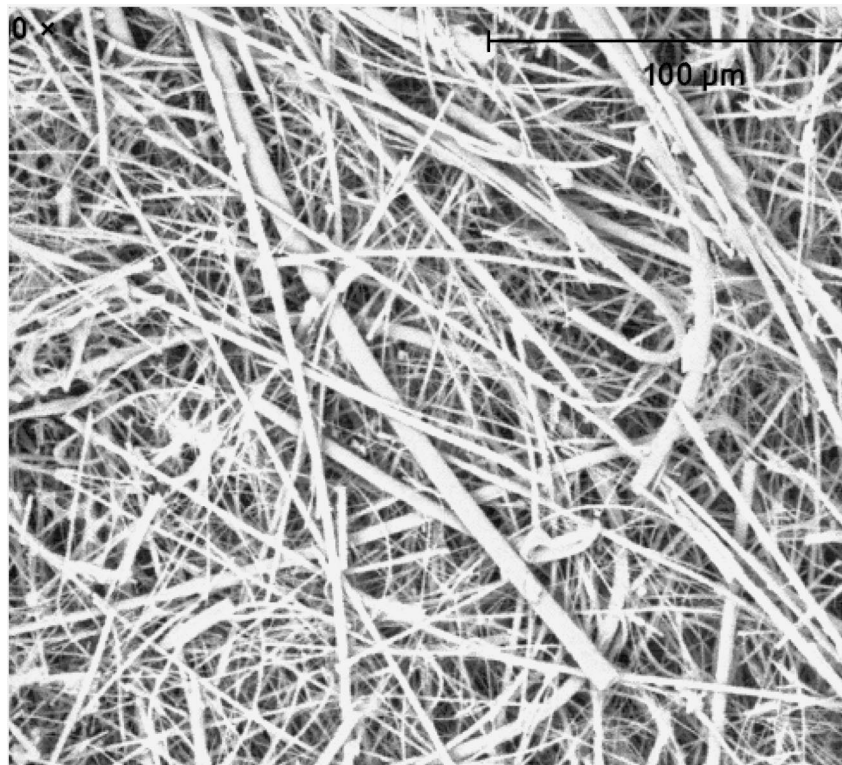


Fig. 6. Structure of fiber separator.

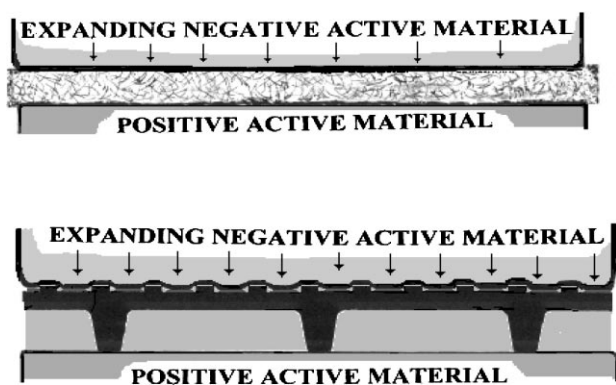


Fig. 7. Expanding negative active material exerting pressure on separator. Fiber structure (top) and skeletal structure separator (bottom).

3.2. Separator additives

As a key component of the battery, the separator is also a target for quite a few special additives. These additives can have a significant impact on their behavior.

3.2.1. Skeletal separator additives

Additives are important to the manufacture and functioning of skeletal separators. The manufacture of polymer/silica separators such as the well known polyethylene separator, necessitate the use of additives that both facilitate the critical extrusion step and also protect the separator from oxidation attack in the battery.

The major lubricant additive in this process is mineral oil, most of it is removed during the subsequent extraction process, but a substantial amount remains in the finished separator. In some battery applications, the slow leaching out of this remaining mineral oil created problems for the proper functioning of the battery.

Separator additives can directly influence the functioning of skeletal separators by rendering inherently rigid polymers more flexible. This is the case of polyvinyl chloride (PVC) separators, where plasticizers can be added to make the separator more flexible. Additives can also be used in this type of separator to stabilize it against undesirable chloride degradation. The presence of chlorides in a battery can lead to battery failure because of the attack of chloride on both the positive and negative plates and the catastrophic corrosion that it promotes [1].

An additive can be also deliberately added to a separator in order to modify its electrochemical properties. This is the case of the voltage control additive that is sometimes added to industrial grades of polyethylene separators that are to be used in flooded traction batteries [17].

3.2.2. Fiber separator additives

Generally, fiber separators are free of additives, but in some instances efforts have been made to include additions of substances designed to modify the performance of this type of separator. Precipitated silica particles added in

amounts of 2–8% of separator weight are reported to have had an impact the key separator properties and to have had a beneficial impact on test battery cycle life [18].

Additives as binders to fiber separators have been applied with various degrees of success. In one instance, aqueous mixtures of colloidal silica particles and a magnesium sulfate salt [19]. Thus treated, the fiber separator acquires different characteristics, becoming rigid and compressed. The argument for additive free fiber structure separators though is quite strong. The purity of this key battery component is of paramount importance for proper battery functioning.

3.3. Impact of additives on separators

Now the possible impacts of active material additives are addressed for both physical and chemical attribute additives.

3.3.1. Impact of physical attribute additives

As the name implies, the ‘expander’ in the negative active material will cause it to expand. The increase in the negative material void volume results in an increase in the apparent volume of the plate. The expanding negative plate will naturally come up against the separator that is in its way. The way that the separator reacts to the pressure exerted by this material expansion will depend on its material composition as sketched below [2].

Let us consider the situation of the ‘flooded’ battery where electrolyte is present in excess and in VRLA designs, where the electrolyte amount is severely restricted and is immobilized within a fiber structure.

In the first case, the skeletal structure separators are used. These separators are meant to withstand the pressures exerted by the expanding negative active material. In some cases, they fail to do so, especially if there are weak areas in the backwebs that may fracture and lead to short circuits. It is a common feature of all these polymeric separators that they have small ribs facing the negative plates. These closely spaced ribs are designed to facilitate the escape of the hydrogen gas that is always associated with the battery recharging. When flat polymeric surfaces are used against the negative plate, there is always the danger of hydrogen gas entrapment leading to loss of negative plate capacity and eventually premature life cycling failure. This phenomenon has been observed in flooded lead–acid batteries and it may also occur in VRLA batteries.

An interesting illustration of this possibility is given in US Patent 5,376,477 authored by Aidman et al. [20]. Here, two VRLA configurations were tried out, one had a microporous membrane inserted between two sheets of fiber separator and in the other configuration, the microporous membrane contacted the negative plates directly. The life cycle performance of the second configuration was only 20% of the first one! These results are illustrated in Fig. 8. The poor showing of the membrane/negative plate configuration cells, also support the requirement that in

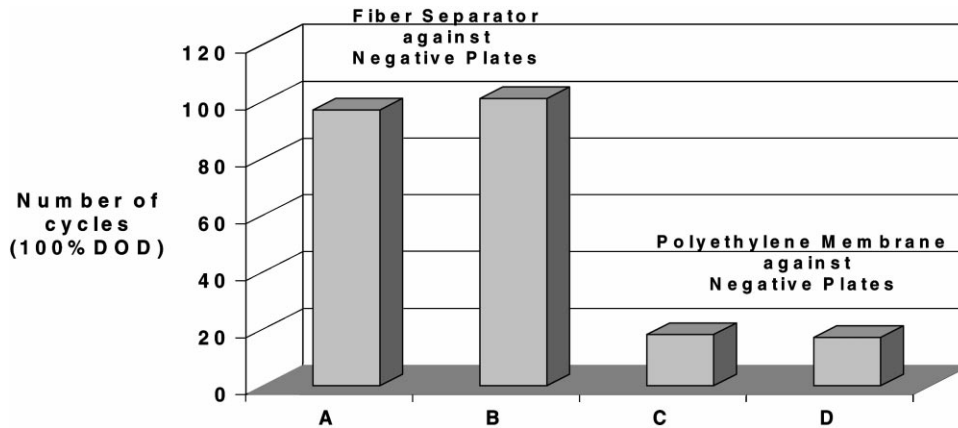


Fig. 8. Effect on cycle life of different separators against negative plates of VRLA cells.

VRLA batteries intimate plate to separator contact is a must. Loss of contact leads to poor ionic flow and hence poor performance.

When an expanding negative active material confronts a fiber structure separator, there is an overall slight deformation of the separator to accommodate the slight change of active material volume. However, given the nature of this kind of material, gas entrapment does not occur since gas can be transported across partly saturated fiber structure separators.

Other physical additives do not seem to create any additional pressures or restraints on the separator. At the end of the recently completed ALABC study on additives, post mortem of the test cells did not reveal that the separators had been unduly affected by any of the porosity or conductivity/homogeneity enhancing additives [11].

3.3.2. Impact of chemical attribute additives

When considering the impact of the additives on the separator, their chemical compatibility is the key factor. Generally speaking, all glass separators made of borosilicate glass will stand up to anything that can be added to a battery. These fiber separators are essentially chemically inert and can perform their important function of electrolyte management free of any chemical hindrance.

The same cannot be claimed for other separator materials, particularly organic based microporous separators. One class of additives, the manganese and chromium doping of positive plates [12] causes serious attack of organic components, although it is claimed that the use of those additives did not interfere with the functioning of microporous polyethylene and polyvinyl chloride separators.

Phosphoric acid addition to electrolyte does not lead to any serious deterioration of any of the known separator materials currently used in lead–acid batteries. None of the other chemical additive studies mentions any interference with proper separator function.

Special action additives such as the dendrite preventive additive (DPA) should have a generally positive influence on separator behavior, since the polar organic molecules

could in principle deactivate any lead growths that could develop at the surface of the separator and penetrate into its body.

4. Conclusions

An analysis of the various kinds of battery additives shows that these additives can be broadly divided into physical and chemical action additives. Separators used in lead–acid batteries have equally been classified according to their structure as skeletal and fiber separators. The first class is generally found in ‘flooded’ vented lead–acid batteries and also in VRLA batteries where the electrolyte is immobilized as a gel. The fiber structure separator is used extensively in VRLA batteries and it constitutes the means of immobilizing the electrolyte.

No major interaction has been reported between either type of battery separators and additives present in the active materials. The noted exception to this lack of interaction is the case of negative plate expanders. Negative plate expanders, by increasing the void volume of the negative active material tend to cause a deformation of this same material that will put a pressure on a flat surface separator placed next to it. This increased pressure can lead to deformation of the structural separator, but it is absorbed by the more flexible structure of fiber separators.

Chemical compatibility is an important criterion for the interaction of additive and separator. Modern separator materials are quite resistant to even the strongest chemical attack. This is particularly the case for fiber separators made of borosilicate microglass fibers, probably the most stable ever employed in lead–acid batteries.

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