Effect of a special additive on the performance of standby valve-regulated lead acid batteries

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Abstract

This paper is devoted to the effect of FORAFAC 1033D (polyfluoroalkyl sulfonic acid) as electrolyte additive on the performance of standby VRLA AGM batteries. This additive has a surfactant character and its stability is increased by substitution of some hydrogen atoms by fluoride atoms in the molecule. With the use of FORAFAC, the objective is to improve the life of VRLA lead acid batteries for standby applications. Comparative accelerated floating tests with and without FORAFAC have been carried out on standard AGM batteries. Batteries containing FORAFAC in acid at low concentration (0.1%) show a remarkable electrical behaviour during the test. A good influence of FORAFAC on water consumption and on self-discharge is also observed. Results indicate that the life duration of standby VRLA lead acid batteries could be improved by a factor 1.5 to 2 with the use of FORAFAC. The mechanism of the FORAFAC action has been investigated and is discussed in this paper. The use of the FORAFAC method appears to be a very promising solution in order to improve the behaviour of batteries for standby applications. For example, it could be useful for applications at higher temperatures or to increase the specific energy of batteries by the utilisation of thinner grid collectors and plates. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Valve-regulated lead acid batteries; Anionic tensio active; Polyfluoroalkyl sulfonic acid

1. Introduction

The continuous growth of Uninterruptible Power Supply (UPS) and Telecom markets implies an increased demand for standby Valve-Regulated Lead Acid batteries (VRLA) which constitute the best solution in terms of performance and cost for these applications.

Users are very sensitive to the quality of such batteries, especially reliability and service life which are two critical parameters in the aim to reach lower maintenance cost on installations and to predict battery pack replacement. Typically in the field, the service life of standby VRLA batteries can be very likely estimated at 10 years [1] although predictions based on accelerated tests at high temperature can give more than 15 years.

Under float application, the main failure modes for VRLA batteries are grid corrosion and drying out of electrolyte [2]. The corrosion can be penetrating corrosion giving rupture of grids or/and general corrosion which causes grid elongation leading to deterioration of contact with active mass or rupture of current collectors.

For many years, progress has been made in these areas by a variety of approaches.

The first approach is to reduce corrosion rates of positive groups by a better control of the homogeneity of positive alloys. The drying out is also optimised by a better control of the permeability of the plastic box and valves.

The second approach, often made in parallel with the first, is the reduction of the parasite electrochemical activity at both electrodes during floating by the use of purer active materials and by the increase of oxygen transport through the AGM separator for better recombination. Consequences are beneficial reduction of corrosion and drying out rates. However, this approach is limited and, for example, the efforts to produce and to keep ever purer materials (active mass and grids) during battery manufacturing involves a significant overcost for the final user and this approach cannot be a realistic solution for the future.

In this paper, we propose another approach using tensio active additives in order to complete the reduction of the electrochemical activities at the electrodes during float duty. Of course, in the past, numerous studies have been

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Table 1
First discharge measurement with and without FORAFAC

	C20 (Ah)	C3 (Ah)	2C (Ah)
12 V/38 Ah Reference	39.2 ± 0.9	–	20.35 ± 1
12 V/38 Ah with FORAFAC 0.1%	38 ± 2	–	19.6 ± 0.6
6 V/10 Ah Reference	–	9.65 ± 0.1	5.98 ± 0.05
6 V/10 Ah with FORAFAC 0.1%	–	9.32 ± 0.08	5.98 ± 0.05

carried out with the idea to use organic surfactant materials for this purpose [3], but with limited success for VRLA batteries. The main difficulties are that additives playing a role at the negative electrodes are poorly efficient because their influence are masked by the low hydrogen evolution in such batteries due to oxygen reduction reaction (recombination). On the other hand, additives playing a role at the positive are often destroyed at the high potentials in concentrated sulphuric medium.

In an attempt to decrease the electrochemical activity at the electrodes and to limit corrosion and drying out without reducing the battery performances, we suggest the use of an anionic surfactant additive with excellent water solubility called FORAFAC 1033D (polyfluoroalkyl sulfonic acid) which has a high stability in sulphuric acid even at high potentials. The stability of FORAFAC is increased by substitution of some hydrogen atoms by fluoride atoms in the molecule giving the following formulation: $CF_3-(CF_2)_5-(CH_2)_2-SO_3H$. A special method has been developed by CEAC for the use of FORAFAC 1033D in VRLA AGM batteries for float application. This paper reports the results obtained with the FORAFAC

method under accelerated float tests (45°C). The action of FORAFAC will also be discussed.

2. Experimental

Firstly, two different types of standard VRLA AGM batteries (12 V/38 Ah and 6 V/10 Ah) were tested, with and without FORAFAC 1033D, with an accelerated float duty test. For each case, six reference batteries without FORAFAC 1033D and six batteries with 0.1% FORAFAC in electrolyte were submitted to a standard first service procedure (C/20 or C3 and 2C discharge capacities measurement).

After the initial performance tests, batteries were submitted to an accelerated float duty procedure at a fixed voltage of 2.275 V per cell and at 45°C. This test is carried out at 45°C in order to accelerate the battery ageing. The 45°C is a relatively low temperature in order not to favour too much general corrosion against penetrating corrosion.

To conserve the water drying out failure mode, batteries were placed in an air-ventilated chamber.

Measurements of 2C capacities were made at 25°C, discharging until 1.6 V/cell, at regular intervals during the batteries' service life. The battery was considered to be at end of life when the 2C capacity reached 50% of its original 2C capacity.

In order to better understand the role of FORAFAC, float duty test results of the 6 V/10 Ah batteries have been examined in detail (float current evolution and weight losses during float test) and the 12 V/38 Ah batteries have been investigated in terms of self-discharge behaviour at
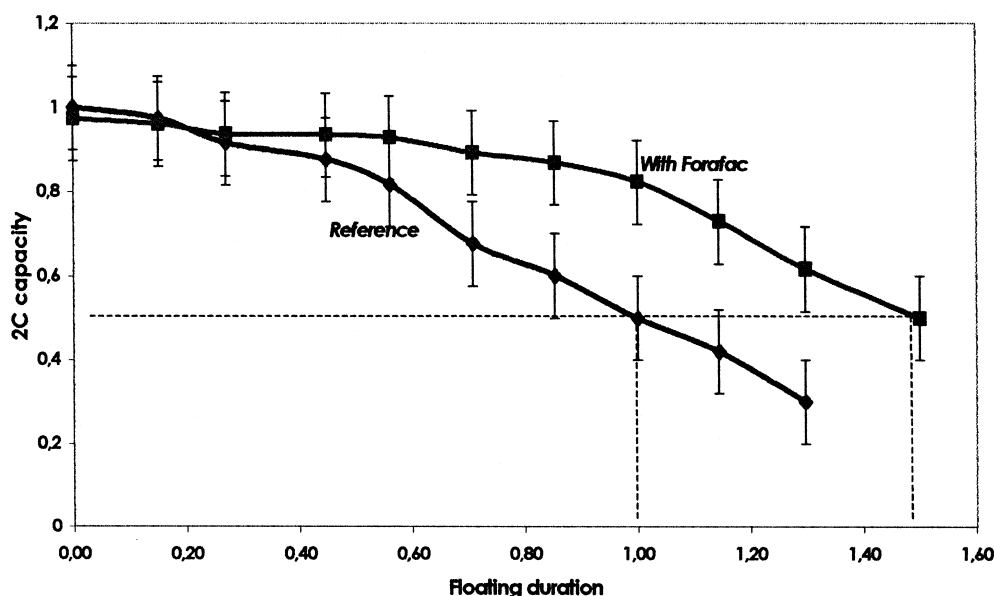

Fig. 1. Evolution of 2C discharge capacity during float test at 2.275 V/cell and 45°C for VRLA 12 V/38 Ah batteries with and without FORAFAC 0.1%. (See text for an explanation of the units.)
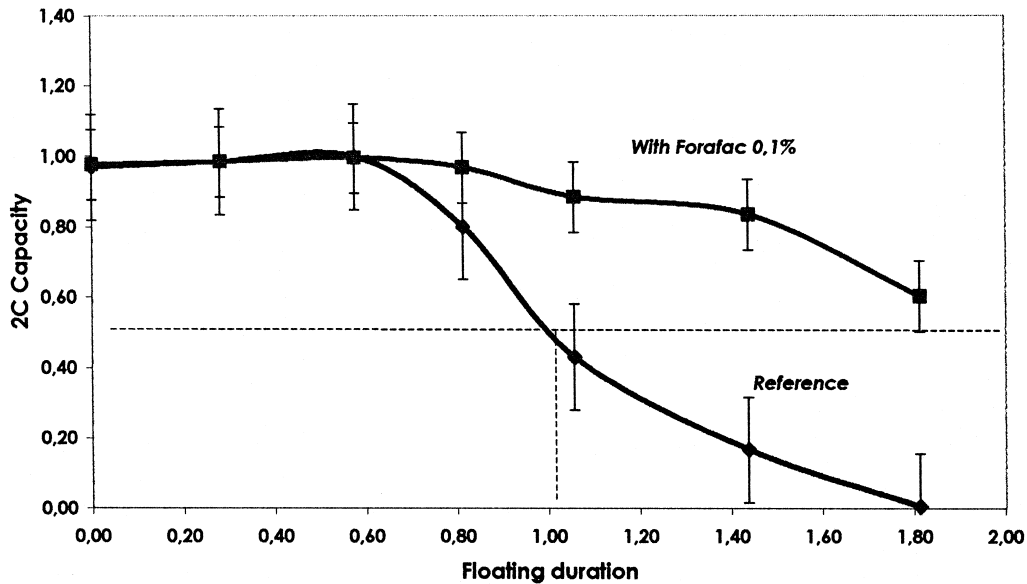
Fig. 2. Evolution of 2C discharge capacity during float test at 2.275 V/cell and 45°C for VRLA 6 V/10 Ah batteries with and without FORAFAC 0.1%. (See text for an explanation of the units.)

25°C. Furthermore, the failure mode after float duty for the 6 V/10 Ah batteries has been examined through post-mortem analysis. For this purpose, one reference battery and one battery with FORAFAC have been dismantled and examined at the same time (when the reference batteries reached 50% of its initial capacity).

Observation of corrosion was made by scanning electron microscope (JEOL33CF). A corrosion study was performed on grid sections from the centre of the plates after standard metallographic preparation. Corrosion observed at

the centre of the plate was not spectacular, but revealed the mode of corrosion before failure.

X-ray diffraction observations were carried out with INEL CPS120 diffractometer using PEAKS and WINEL software for phase quantification [4] and textural information [5]. Plates were treated with standard rinsing and drying procedures. Active material was removed from the grid and weakly crushed before analysis.

The electrochemical mechanism of FORAFAC was further investigated by cyclic voltammetry on pure lead elec-
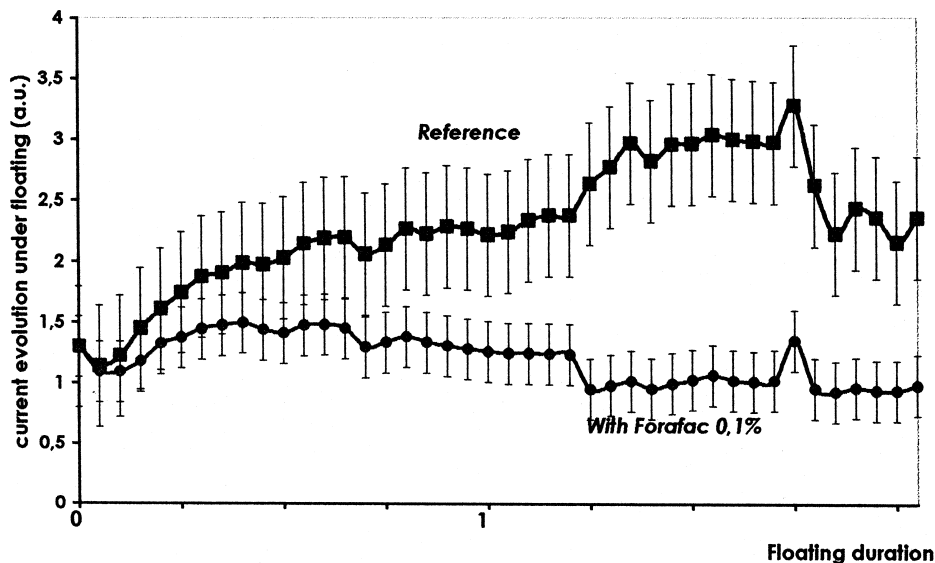

Fig. 3. Evolution of float current during float test at 2.275 V/cell and 45°C for VRLA 6 V/10 Ah batteries with and without FORAFAC 0.1%. (See text for an explanation of the units.)
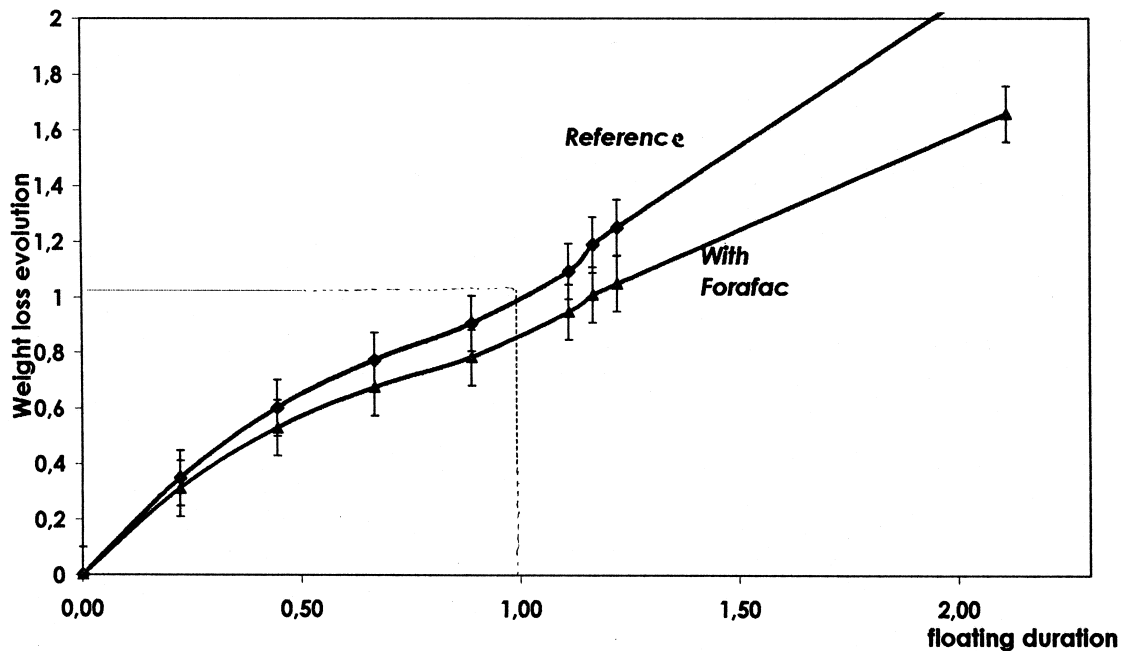
Fig. 4. Evolution of the weight loss during float test at 2.275 V/cell and 45°C for VRLA 6 V/10 Ah batteries with and without FORAFAC 0.1%. (See text for an explanation of the units.)

trodes at 25°C with and without FORAFAC at 0.1% in sulphuric acid ($d = 1.28$) and with Hg/Hg_2SO_4 reference electrode (ESS) saturated with H_2SO_4 ($d = 1.28$) ($E = +0.758$ V/SHE). First, a few cycles of cyclic voltammetry were performed without FORAFAC, then a small quantity of FORAFAC (giving 0.1%) was added to the

electrolyte and a new voltage scan was started. This method allowed the examination of the perturbation of the lead acid system with FORAFAC additive. However, observations must be carefully interpreted because of differences of voltage evolution at electrodes in VRLA batteries. Cyclic voltammetry carried out in this work will give only
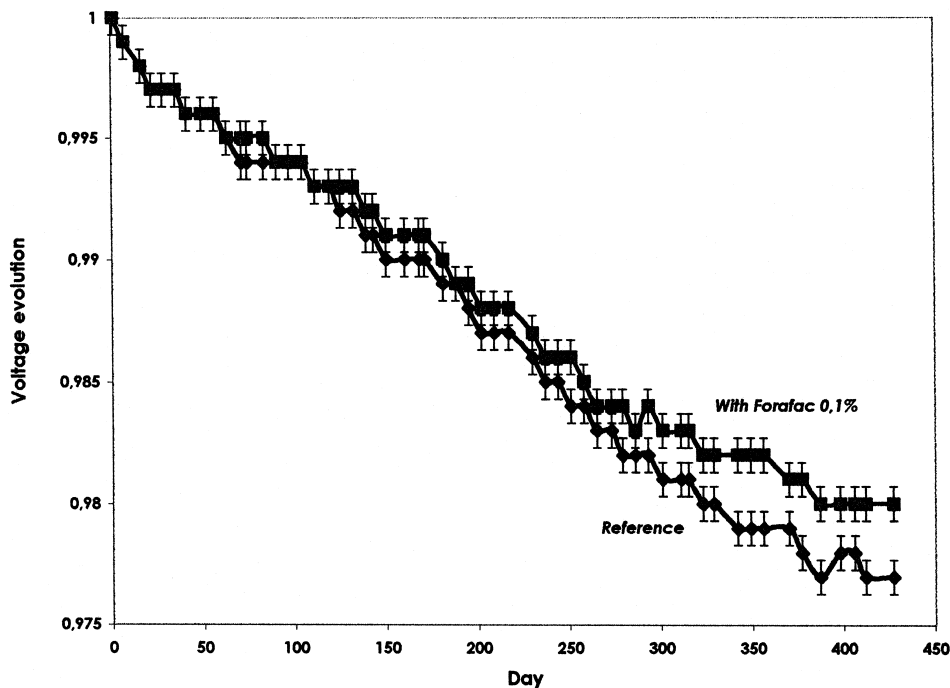

Fig. 5. Self-discharge at 25°C for VRLA 12 V/38 Ah batteries with and without FORAFAC 0.1%.

an indication about the behaviour of the lead system in the presence of FORAFAC.

3. Results

Results of first discharges of C20 or C3 and 2C of batteries are given in Table 1.

It can be observed that a small decrease of initial capacity occurs in the presence of 0.1% of FORAFAC in the battery electrolyte.

Evolution of 2C capacities during accelerated float test are given in Figs. 1 and 2. All the scales have been normalised in order to compare better the evolution of 2C capacities and service life for different battery types. The float duration scale has been normalised with the end of life of the reference batteries without FORAFAC (1 unit corresponds to the time for the reference battery to reach 50% of the initial capacity). Note that the standard service life as already be mentioned, is typically 10 years in the field, but depends on the battery type and on external conditions (temperature).

In Figs. 1 and 2, it is clear that batteries with the FORAFAC additive present longer service life during accelerated float duty. In fact, at the beginning, the 2C capacities are equal or slightly greater than the reference. After a few months, the 2C capacities of the reference batteries decrease substantially, whereas the 2C capacities of the FORAFAC batteries remain high. From these graphs, the life duration with the FORAFAC method is improved by a factor 1.5 to 2.

Fig. 3 represents the evolution of the float currents for the 6 V/10 Ah batteries with arbitrary units (typical float currents for references at 45°C are between 10 and 20 mA for this battery type). This graph shows clearly that float currents are reduced with the FORAFAC method.

Fig. 4 represents the evolution of weight loss of the 6 V/10 Ah batteries. This test is directly related to drying out (including evaporation through the box and gassing through the valve). It can be observed that drying out is significantly decreased with the FORAFAC method.

Fig. 5 represents the evolution of self-discharge at 25°C of 12 V/38 Ah batteries (average of three reference batteries and three batteries with 0.1% FORAFAC). This
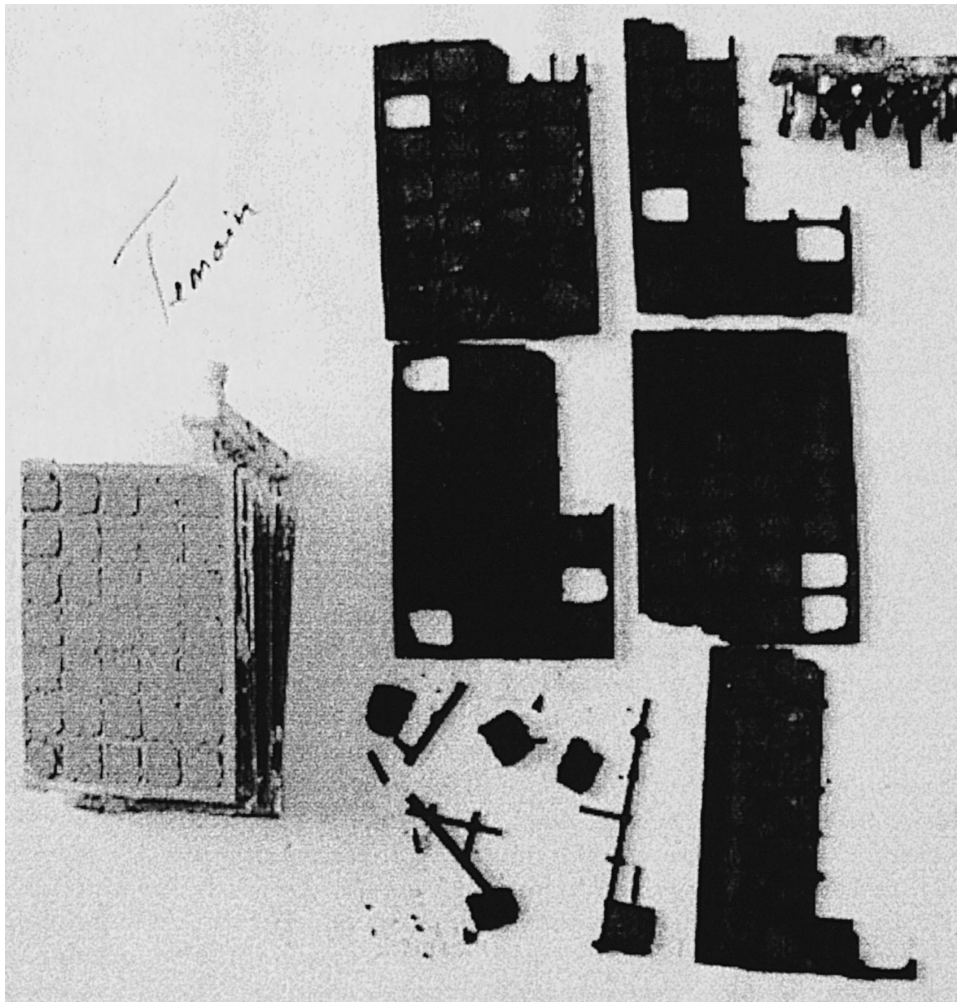

Fig. 6. Photograph of one battery group from reference battery after 1 unit of accelerated floating test at 45°C.
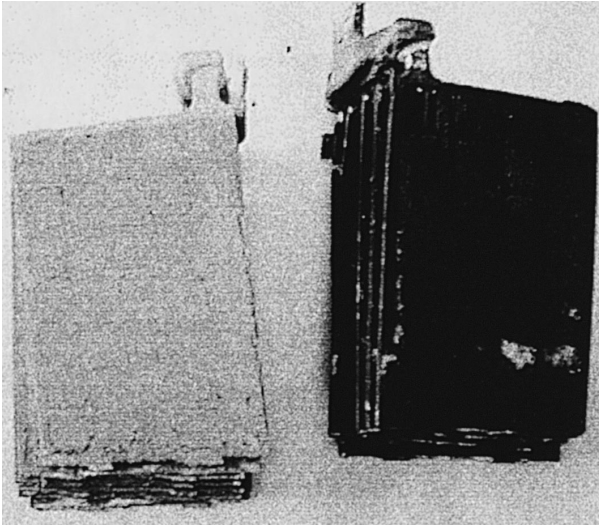
Fig. 7. Photograph of one battery group from battery with 0.1% of FORAFAC in electrolyte after 1 unit of floating test at 45°C.

graph shows that self-discharge is slightly improved with FORAFAC.
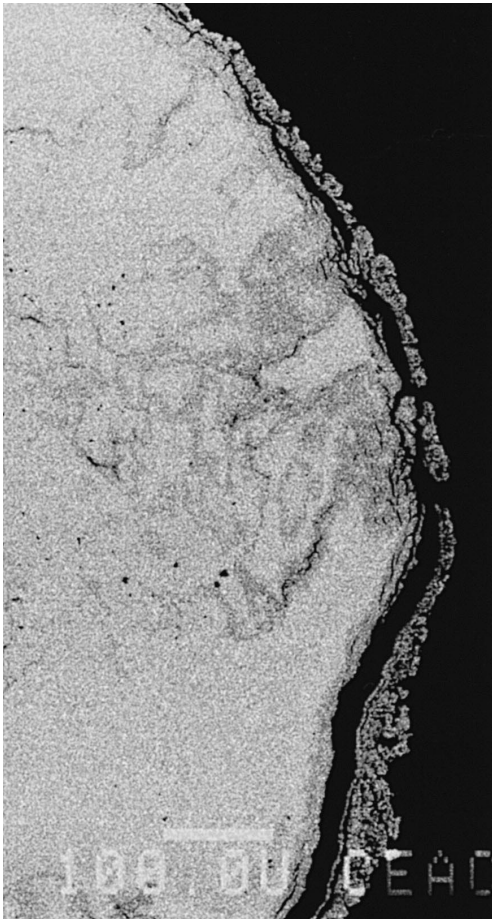

Fig. 8. SEM photograph of positive grid section from reference battery after 1 unit of floating test at 45°C.
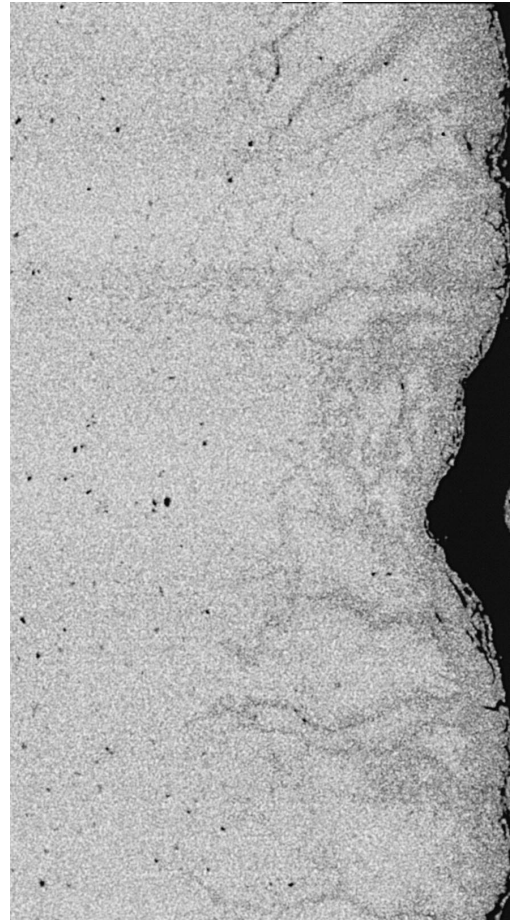

Fig. 9. SEM photograph of positive grid section from battery with 0.1% of FORAFAC in electrolyte after 1 unit of floating test at 45°.

In order to better understand the FORAFAC mechanism, one reference 6 V/10 Ah battery and one 6 V/10 Ah battery with FORAFAC were dismantled at the same time (when the reference reached 50% of its initial capacity).

No valve malfunction, excessive drying out or short circuits were observed for either battery. Rest voltages were good for all cells. However, it was observed that the reference battery showed large corrosion at the positive plate groups and it was impossible to maintain the group integrity when plate groups were removed. A photograph of a typical plate group from the battery reference is

Table 2
Quantification of crystalline phases for active materials after float duty ($\pm 5\%$)

PEAKS quantification percentage	α-PbO	β-PbO$_2$	β-PbO	PbSO$_4$	Pb
Positive Reference	27	73	–	–	–
Positive FORAFAC	23.5	76.5	–	–	–
Negative Reference	–	–	64	–	36
Negative FORAFAC	–	–	41	–	59

Table 3
Crystallite size phases for β-PbO$_2$ after float duty ($\pm$9%)

WINEL β-PbO$_2$ crystallite size (Å)	h,k,l	
	1,1,0	0,1,1
Positive Reference	758	707
Positive FORAFAC	790	778

presented in Fig. 6. Fig. 7 presents the same view, but for battery with FORAFAC.

The appearance of positive plate groups from the reference battery shows that corrosion is strong and preferentially located near the lugs where the current densities are higher. Moreover, active material is often disconnected from the grid—likely due to corrosion (leading to poorer interface adhesion). The positive plate group from the battery with FORAFAC shows remarkable integrity in comparison with the reference battery and active material was not disconnected from the grid after the group was removed.

The negative groups seem to be identical, but closer examination reveals a higher expansion for the negative

mass of the reference battery and a more metallic aspect for the negatives plates from the battery containing FORAFAC.

Corrosion was investigated on a grid section from the centre of the positive plates. In Fig. 8, SEM presents the grid corrosion layer from the reference plate. In Fig. 9, SEM presents the grid corrosion layer from a plate with FORAFAC at the same magnification. Corrosion at the centre of both plates is not very developed, but it is observed that the corrosion layer is more homogeneous for the plate with FORAFAC. Penetrating corrosion is observed for both samples, but the penetration depth is more developed for the grid coming from the reference battery.

Tables 2 and 3 present the results of the X-ray diffraction analysis of active materials from the reference plates and from the plates with FORAFAC. Table 2 presents quantification of crystalline phases using the PEAKS software.

No differences are observed between the materials with or without FORAFAC in the quantification of crystalline phases, except the lead content of the negative material, which is higher for the plate with FORAFAC. However,
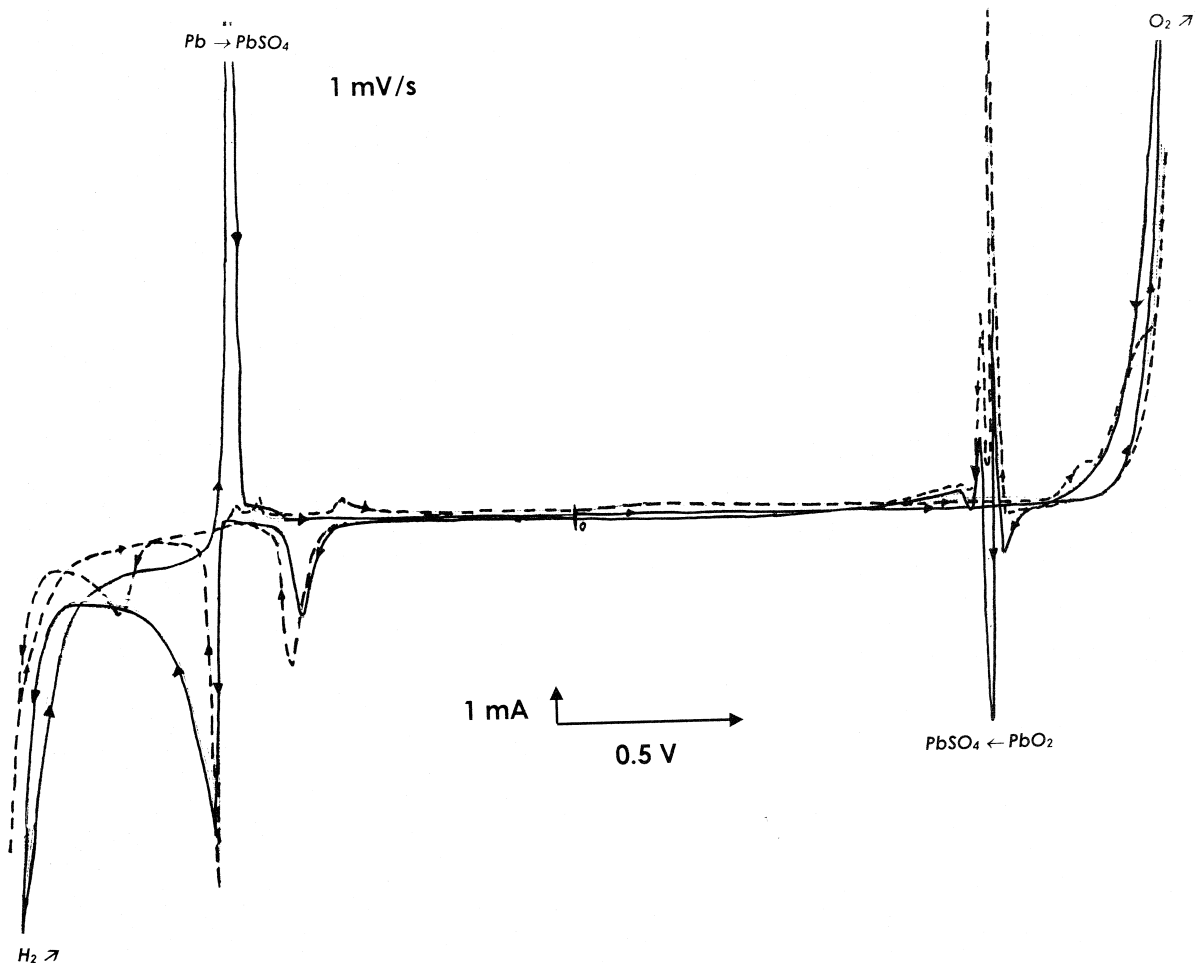

Fig. 10. Cyclic voltammetry of lead acid system without FORAFAC (————) and with FORAFAC (— — — —) at 0.1% in electrolyte $d = 1.28$.

this observation cannot be viewed or significant because of air oxidation after removal of the plates from the batteries.

Table 3 presents the calculation of the crystallite size of β-PbO_2 calculated with the method developed by Zaninotto [5].

Taking into account the accuracy of this calculation (about 10%), it is not possible to differentiate the crystallite size for the two cases.

Fig. 10 presents cyclic voltammetry carried out in order to assess the mechanism of operation of FORAFAC. Cyclic voltammetry performed in this work will give only a broad indication about the behaviour of the lead system in the presence of FORAFAC. The full line represents the evolution of current with voltage scanning without FORAFAC in the electrolyte. The dotted line represents the current evolution with the presence of 0.1% of FORAFAC in the electrolyte.

Fig. 10 shows that FORAFAC at 0.1% in the electrolyte leads to only a small increase of overvoltages at the positive and at the negative potentials. A significant effect is observed at the potential of reduction $PbO_2 \rightarrow PbSO_4$ ($+1.12$ V/ESS). The corresponding current peak is strongly reduced with the presence of FORAFAC. On the negative side, a similar effect is observed; the current peak corresponding to the oxidation $Pb \rightarrow PbSO_4$ (-0.9 V/ESS) is strongly reduced with the presence of FORAFAC. Some negative effects concerning the formation of α-PbO_2, the reduction $PbSO_4 \rightarrow Pb$ and the Pb/PbO evolution in corrosion layers are also observed, but these phenomena must be carefully interpreted.

4. Discussion

Results obtained show that addition of FORAFAC at 0.1% in the electrolyte of VRLA AGM batteries leads to a major improvement of service life during accelerated float tests (graphs 1 and 2). It appears that the use of FORAFAC leads to high capacities during service life and plays a beneficial role in terms of corrosion (photos 3 and 4), water consumption (Fig. 4) and self-discharge (Fig. 5).

Shi et al. have recently reported [6] that anionic surfactant FC99 which is very similar to FORAFAC 1033D can play affect the surface tension of the electrode/electrolyte interface and that PbO_2 crystals become smaller during cycling, giving more porosity and more capacity to the positive electrode. In our study, we have not observed modification of the PbO_2 crystal size (Table 3), but intensive cycling tests with FORAFAC have not been performed.

For float application, it seems preferable to consider the action of FORAFAC from the point of view of electrochemical passivation. This view has to be confirmed in the future by deeper studies concerning the evolution of materials at the grid/active matter/electrolyte interfaces.

During float, the float current I_{float} can be considered as being decomposed of a number of parts as indicated in the following formulae:

$$I_{\text{float}} = i_{\text{corr}}^+ + i_{\text{self}}^+ + i_{O_2 \nearrow}^+ = i_{\text{rec}}^- + i_{\text{self}}^- + i_{H_2 \nearrow}^-$$

with

i_{corr}^+ = corrosion current at the positive
i_{self}^+ = self-discharge current $PbO_2 \rightarrow PbSO_4$
$i_{O_2 \nearrow}^+$ = oxygen gassing current at the positive
i_{rec}^- = oxygen recombination current at the negative
i_{self}^- = self-discharge current $Pb \rightarrow PbSO_4$
$i_{H_2 \nearrow}^-$ = hydrogen gassing current at the negative.

Considering that FORAFAC is a stable anionic surfactant, the molecules can absorb on the positive electrode surface which is positively charged during float. In that case, it is possible to assimilate the FORAFAC layer adsorbed on the positive plate as a very thin passivation layer which can make the exchanges at the electrode/electrolyte interface more difficult; in other words, the positive electrode is more stable against self-discharge, oxygen gassing, and subsequently, against corrosion.

Further, as was shown in Section 3, the cyclic voltammetry experiment (Fig. 10) seems to show that the presence of FORAFAC reduces slightly positive gas evolution, but reduces also the self-discharge transformation $PbO_2 \rightarrow PbSO_4$. For these reasons, the $i_{O_2 \nearrow}^+$ and i_{self}^+ currents are decreased. The i_{corr}^+ current is reduced due to a smaller activity of the oxygen species at the positive electrode. Thus, less oxygen (gas) is produced at the positive and the recombinant current i_{rec}^- at the negative will also be reduced.

In the mechanism of the interaction of FORAFAC with electrodes, the possibility for the FORAFAC molecule to adsorb on the negative during discharge cannot be eliminated. In that case, it is possible that a small quantity remains adsorbed on the negative and can play a similar role on negative to that observed at the positive. Shi et al. [7] have discussed the role of FC99 perfluorinated additive at the negative. They have reported that when FC99 is used at a concentration of 40 ppm, a dense hydrophobic layer is formed by the adsorbed molecules and the hydrous sulphate ions of the bulk solution are prevented from approaching the surface. The consequence is that the formation process of $PbSO_4$ is suppressed. These observations are in accordance with the present work. The voltammetry study (Fig. 10) shows clearly that the transformation $Pb \rightarrow PbSO_4$ (-0.9 V/ESS) is strongly reduced in the presence of FORAFAC.

One conclusion of this discussion is that the summation of small effects due to interaction with the FORAFAC layer gives a sensible reduction of the total float current I_{float} in the battery (Fig. 3). Therefore, all the parasite reactions, like corrosion and drying out during float, are reduced.

Furthermore, an important point is that the adsorption of FORAFAC at the positive during float could give a

more homogeneous distribution of potential at the electrode/electrolyte interface. Thus, very active positive electrochemical sites should be preferably inhibited by FORAFAC molecules. This can reduce excessive overgassing and penetrating corrosion as is observed in the metallographic grid section (photo 4).

Of course, the FORAFAC passivation should not be too important in order to avoid problems in battery chargeability and reduced capacity as can be understood with the first capacities shown in Table 1. This is one reason why the FORAFAC concentration in the electrolyte must be low (0.1%). Another reason to keep the FORAFAC concentration low is to limit the cost of this new battery technology.

5. Conclusion

Results obtained in this study show clearly that the addition of FORAFAC 1033D at 0.1% in the electrolyte of standby VRLA AGM batteries leads to a major improvement of the service life of such batteries during accelerated float tests at 45°C. Batteries containing FORAFAC show a remarkable electrical behaviour during the test. The life duration of standby VRLA lead acid batteries with this method could be improved by a factor 1.5 to 2. A good influence of FORAFAC has been also observed on water consumption and on self-discharge.

Complementary analysis including corrosion measurements, XRD and cyclic voltammetry studies seems to indicate that the FORAFAC molecules can absorb on the positive electrode surface during float. In that case, it is possible to envisage the FORAFAC layer adsorbed on the positive plate as a very thin passivation layer leading to a better stabilisation of the positive electrode. Therefore, float currents are reduced and all the parasite reactions like corrosion and drying out during float are reduced. This passivation is very weak, but it permits the failure of batteries to be strongly delayed without decreasing their performance in discharge.

The use of the FORAFAC method appears to be a very promising solution in order to improve the behaviour of batteries for standby applications.

Moreover, this method could be useful for applications at high temperatures when corrosion is the critical factor leading to shorter service life. Another way could be to use the FORAFAC method for the purpose of increasing the specific energy of batteries by the use of thinner grid collectors and correspondingly thinner plates, giving better active mass utilisation.

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