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A review of soft-lead specifications in the light of the requirements of valve-regulated lead/acid batteries

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Abstract

With the development of valve-regulated lead/acid (VRLA) technology and its concomitant requirements in terms of the quality of the input materials, there is a need to review the status of the present pure-lead specifications as they appear in the majority of national standards for lead. In this paper, four national standards for soft lead are compared with a list of elements that have been identified and reported in the literature as being harmful to the VRLA battery system at impurity levels. None of the four standards is found to limit the presence of all harmful impurities. An alternative specification that meets the needs of VRLA technology as they are currently understood has been proposed. © 1997 Published by Elsevier Science S.A.

Keywords: Valve-regulated lead/acid batteries; Soft-lead specifications; Maintenance-free batteries

1. Introduction

The trend of battery technology towards maintenance-free batteries for automotive applications and valve-regulated lead/acid (VRLA) batteries for the consumer and the industrial end-use sectors is necessitating an increased focus on the quality and purity of the raw material inputs that are used in the manufacture of these products. The purpose of this paper is to assess the suitability of the present, generic, national, soft-lead standards for the production of VRLA batteries, and to open discussions regarding the development of a targetted specification that is suitable for this technology.

2. Background

Maintenance-free and VRLA battery technologies have been developed in response to the desire to remove the need for maintenance during the life of the battery, i.e., to eliminate the need for water addition. For VRLA technology, a corollary to these goals has been the elimination of the risk of leakage and fumes (and, thus, the corrosion of surrounding installation), as well as a greatly reduced hazard in terms of explosion. As a consequence of the successful achievement of these developmental goals, lead/acid batteries now offer, in the form of VRLA designs, full office compatibility. Accordingly, the batteries may be used in applications that have previously been regarded to be the domain of either primary cells or lead/acid's direct competitors such as the nickel–cadmium battery.

An additional opportunity for the deployment of VRLA batteries is potentially provided by the automotive industry's wish to increase the voltage of car electrical (SLI) systems from 12 to 24 or even 48 V. With the likelihood that this will lead to a splitting of the electricity supply into two sources, one for high-rate short-duration loads and one for low-rate loads, there is a strong possibility that the second of these duties will be met by a VRLA battery. This, in combination with the efforts that several companies are putting into the development of VRLA batteries for SLI application, suggests that the technology is likely to be used in an end-use traditionally reserved for the flooded variety.

In order to ensure that high quality VRLA batteries meet the needs of the various end-use applications, careful attention must be paid to: (i) battery design; (ii) the manufacturing process, and (iii) the quality of input materials. Design issues of importance include venting strategy and ensuring that the cell groups that make up the battery

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are under adequate compression. Manufacturing processes that are critical include curing, formation and assembly. Material inputs that will have a critical effect on battery performance include: (i) absorptive glass-mat separators, which must exhibit sufficient spring-back to ensure adequate compression within each cell during the life of the battery; (ii) valves, which must open only at the pressure at which they are designed to open, and then close again; failure to do so may result in cell dry out if they open at too low a pressure; (iii) lead, which in the form of top lead, grid lead and active-material lead is obviously one of the most critical components of the battery.

For lead, the key issue that has to be addressed in terms of VRLA performance is its effect on water loss through electrochemical dissociation during recharging. Dissociation into hydrogen and oxygen gas is the major mechanism by which water is lost from the electrolyte of the battery. Certain elements, even in trace quantities, can cause a lowering of the voltage at which dissociation occurs and, hence, under normal voltage conditions can cause an increase in the rates at which the gases are evolved.

In the VRLA battery, a quantity of oxygen produced at the positive electrode is recombined internally by electrochemical reduction at the negative electrode. Any hydrogen evolved, however, represents a permanent loss of water from the battery. Therefore, whilst it is important that the presence of elements promoting oxygen evolution is controlled, it is equally critical that those elements which promote hydrogen evolution and/or inhibit the reduction of released oxygen at the negative are limited to very low levels. Thus, in order to minimize the maintenance required during service life or, in the case of VRLA batteries, to insure against failure by electrolyte dry-out, it is necessary to construct the batteries from soft and alloyed lead that will limit the extent of water loss via electrochemical dissociation.

3. Developments to date

The major change in terms of lead metal inputs used in the production of maintenance-free and VRLA batteries has been the replacement of antimonial-lead alloys with predominantly, but not exclusively, lead–calcium alloys. This modification in design has occurred in order to exclude the detrimental effect of antimony on the gassing characteristics of the cell, i.e., antimony lowers the hydrogen overpotential at the negative electrode and, thereby, causes an increase in water consumption during the life of the battery. Furthermore, considerable effort has been expended across the industry in the development and refining of calcium alloys that will best meet the needs of VRLA technology. Key areas of concern associated with the use of calcium alloys include: positive grid corrosion; positive grid growth, and premature capacity loss. The main focus of alloy development work, therefore, has been to improve the relevant alloy properties of corrosion resistance and creep strength.

A great deal of success has been achieved in the area of corrosion resistance via the inclusion of low levels of additional alloying elements such as silver. At the same time, improvements in creep resistance and a delay in capacity loss has been effected by adding high levels of tin, namely, up to 2.5 wt.%. Much effort has also been put into the identification of alloys that will join effectively the high melting-point, calcium grid alloys — either via conventional plate burning or via cast-on strap.

4. Soft-lead specifications for VRLA batteries

Despite the fact that there has been considerable research that has identified a number of specific elements which exert a deleterious effect on the gassing perfor-

Table 1
National soft-lead specifications as they currently stand (maximum ppm) [a]

Element	National standards AS 1812–1975 9999	ASTM B29-92 Refined pure	BS 334–1982 Type A	DIN 1719–1986 Pb99.99
Ag	10	25	25	10
As	10	5	5	10
Bi	5	25	5	5
Cd	10	NS	5	NS
Co	[b]	NS	NS	NS
Cu	10	10	30	10
Fe	10	10	30	10
Ni	[b]	2	10	NS
S	10	NS	5	NS
Sb	10	5	20	10
Sn	10	5	10	10
Te	NS	1	NS	NS
Zn	10	5	20	10

[a] NS = not specified.

[b] Co + Ni < 10 ppm.

Table 2
Impurity elements that exert a deleterious effect on the performance of maintenance-free and VRLA batteries

Element	Deleterious effect	Ref.
Arsenic	Increases oxygen evolution at positive electrode	[2]
	Increases hydrogen evolution at negative electrode	[5,6]
Antimony	Greatly increases hydrogen evolution at negative	[2,4,6]
Cobalt	Greatly increases oxygen evolution at positive	[2,3]
	Greatly inhibits oxygen recombination at negative	[5]
	Greatly increases hydrogen evolution at negative	[3,5,6]
Chromium	Marginally increases oxygen evolution at positive	[4]
	Greatly inhibits oxygen recombination at negative	[5]
Nickel	Increases oxygen evolution at the positive	[2–4]
	Marginally inhibits oxygen recombination at negative	[5]
	Greatly increases hydrogen evolution at negative	[3–6]
Tellurium	Greatly increases hydrogen evolution at negative	[2,5,6]

mance of batteries, a review of the major national standards for soft-lead, as provided in Table 1, reveals that the results of this work are generally not reflected in present soft-lead specifications [1]. Thus, VRLA battery manufacturers continue to quote generic specifications such as 99.99 and 99.97% which may no longer meet the needs of their particular technology. In order to determine whether or not these specifications are appropriate for VRLA battery production, it would perhaps be pertinent to review some of the research that has been undertaken during the past 10 to 15 years on the effects that minor impurities exert on the gassing characteristics of positive plates, as well as the gassing and recombination characteristics of negative plates during recharge.

5. Review of the literature

The research considered in this review involves investigations of the effect of additions of impurities made to either the electrolyte or the active material. The effects have been measured using methods that include linear potential scan, potential step, and collection of gases evolved. The levels of impurities tested range from 4 through to 1000 ppm. The findings are summarized in Table 2.

Most interestingly, the review has found that where more than one team has conducted tests on a particular impurity, there is extremely good agreement between results achieved and reported. Given that the primary aim is to identify and exclude elements that both enhance hydrogen evolution and inhibit oxygen reduction, key findings include:

- cobalt, antimony and tellurium greatly increase hydrogen evolution at the negative electrode
- nickel also increases hydrogen evolution but not to the same degree
- cobalt and chromium strongly inhibit oxygen reduction at the negative

It should be noted that cobalt also strongly enhances oxygen evolution at the positive. In addition to these elements that have been clearly identified as harmful, there are a number of other hitherto unexamined elements which, it is believed, may be harmful to battery performance. These include molybdenum, selenium and vanadium [1].

On the other hand, elements that have been shown to be beneficial to VRLA batteries include:

- bismuth, which has been demonstrated by several researchers to increase cycle life and reduce overall gas build-up via improved oxygen reduction at the negative; note, Manders et al. [7] have reviewed a comprehensive list of investigative work that has identified the benefits associated with the addition of bismuth to batteries
- tin, which has also been shown [5] to enhance oxygen reduction at the negative
- cadmium, which has been demonstrated [3] to decrease hydrogen gassing at the negative
- zinc, which has been demonstrated [3,4] to reduce hydrogen gassing at the negative

6. Discussion

The majority of the current, generic, soft-lead specifications (as listed in Table 1) has evolved around battery technologies that are based on antimonial grid alloys. In these cases, antimony in the positive and negative grids dominates the performance of the battery, and minor impurities are of little significance. Furthermore, rather than aiming to reflect the needs of the battery industry (or any other end-use industry for that matter), the elements and levels specified by these generic specifications are more a reflection of the refining and analytical capabilities of lead producers. For batteries employing antimonial-alloy grids, the use of soft lead which is in compliance with the majority of generic specifications results in adequate performance. In the context of the greater demands of mainte-

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[1] One exception to this general rule should be noted. As reported by Prengaman [1], a review of the *ASTM B29* soft-lead standard in 1992 went some way towards providing for the needs of new battery technology via the inclusion of what is referred to as the 'Refined Pure' specification, a copy of which is provided in comparison to equivalent BS, DIN and ASTM standards in Table 1.

Table 3
Proposed specification levels of critical elements and elements of concern for lead used in the production of VRLA batteries (maximum ppm) [a,b]

Element	Proposed specified levels	Currently Specified Levels			
		AS 1812–1975	*ASTM B29–92*	*BS 334–1982*	*DIN 1719–1986*
		9999	Refined pure	Type A	Pb99.99
Ag	10	10	25	25	10
As	1	10	5	5	10
Ba	10	NS	NS	NS	NS
Co	1	[c]	NS	NS	NS
Cr	5	NS	NS	NS	NS
Cu	10	10	10	30	10
Fe	5	10	10	30	10
Mn	3	NS	NS	NS	NS
Mo	3	NS	NS	NS	NS
Ni	2	[c]	2	10	NS
S	10	10	NS	5	NS
Sb	1	10	5	20	10
Se	1	NS	NS	NS	NS
Te	0.3	NS	1	NS	NS
V	4	NS	NS	NS	NS

[a] NS = not specified.

[b] Ba has been included due its generally acknowledged detrimental effect on positive-plate shedding.

[c] Co + Ni < 10 ppm

nance-free and VRLA batteries, however, research of the type reviewed earlier has demonstrated that generic specifications such as 99.99% are inadequate. This is due to the fact that such specifications erroneously elicit focus on the lead content, rather than on the actual elements that make up the 0.01% maximum of impurities and the levels at which they individually occur.

Whilst research has identified that impurities such as As, Co, Cr, Ni, Sb and Te are harmful to VRLA batteries, many national soft-lead standards fail to specify elements such as Co, Cr, Ni and Te. Where the last four elements are specified, it is usually at inappropriately high levels. In the case of elements such as Sb and As, which have always been included in generic standards due to the fact that appreciable amounts often occur in the concentrates or scrap feed used in the production of soft lead, the levels at which they are specified are an order of magnitude higher than those levels that are regarded as being of concern. Conversely, elements that have been clearly demonstrated to be beneficial to battery performance (e.g., as bismuth) are always limited to levels well below those that can actually improve battery performance.

7. Proposed soft-lead specification for VRLA batteries

From the above discussion, it would seem there is a need to develop a soft-lead specification that adequately addresses the needs of the VRLA battery. In developing such a specification, it is first necessary to consider what would be a critical level for certain elements based on the research to date. Unfortunately, experimental evidence of the exact critical level of each of the harmful elements — both those which have been identified and those which are suspected — is unavailable. Therefore, the selection of each of the thresholds must be an exercise in informed prudence.

Second, the selection of a specification needs to be made in the knowledge of what is currently viable in terms of the analytical capability of lead suppliers. In other words, the specification must reflect:

- the known effects of certain impurity elements
- the yet to be confirmed effects of a number of additional elements suspected as being harmful
- the practical limitations of current analytical techniques

After lengthy deliberation, Pasminco has arrived at a proposed soft-lead specification for VRLA batteries that is considered to reflect accurately both the requirements of battery manufacturers and the limitations of affordable and appropriate analytical techniques. This specification is provided in Table 3 in comparison with current generic specifications.

As stated earlier, Sn, Bi, Cd and Zn have been demonstrated to be at the very least inert of the elements and, in some situations, are in fact beneficial to modern battery systems. Thus, the current limitations on these elements in the generic specifications are in need of review. It is for this reason that they have not been included in the proposed specification.

8. Conclusions

It is the belief of the authors' Company, Pasminco, that the generic specifications for soft lead as represented by most national standards are no longer appropriate for certain lead-consuming industries, especially in the case of VRLA batteries. This belief is founded on three key points:

1. present generic specifications either totally exclude or fail to limit ao a sufficient extent elements that have been identified by several researchers as being seriously harmful to VRLA batteries;
2. the specifications also fail to limit elements that are suspected of being harmful, and
3. the specifications impose limits on elements that have been demonstrated by a large number of researchers to be beneficial to VRLA batteries.

It is proposed, therefore, that new soft-lead specifications be adopted that reflect both the needs of each particular end-use and the limitations of current analytical procedures. A specification to reflect adequately the requirements of the unique technology of VRLA batteries has thus been submitted for consideration.

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