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MAINTENANCE-FREE INDUSTRIAL LEAD/ACID BATTERIES

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Introduction

Maintenance-free lead/acid batteries are most commonly associated with automotive types, *i.e.*, batteries used to start cars and trucks. This is true with regard to the quantities produced. Such batteries are not significantly different in their design from ordinary ones, they just exhibit a very low water consumption which, in most cases, is achieved by the use of low- and/or non-antimonial alloys.

Industrial batteries are applied to cycling or stand-by service. In respect of such operations, starter batteries have been shown to be unsuitable. Additional precautions must be taken to meet such requirements. Under normal circumstances, maintenance of industrial batteries includes other aspects besides negligible water consumption, and these are discussed below.

General design of industrial batteries

Positive pasted plates

The positive grids used for supporting active material and collecting electric current consist of a frame with a lug at the top and vertical and horizontal spines. Traditionally, the grids are designed mainly with mechanical properties in mind and are produced by simple gravity casting.

Modern design makes use of computer-aided analysis. In principle, this is not necessary as calculation of conductivity-optimized grids is a linear algebraic process. On the other hand, the huge number of crossing points makes such a process very time consuming and, as algorithms are known, the manual work in sophisticated designs is replaced by computer programs.

Advanced technology emerging in F.R.G. uses pressure (die) casting in order to improve the grain structure and to provide corrosion behaviour more similar to that of the tubular design (see below).

Unlike the spongy, negative mass (Pb), the positive mass (PbO_2) shows a grain-like structure that tends to disintegrate mechanically during cycling. The resulting shedding means loss of active material. In order to reduce this effect, the formed positive plates are placed in glass-fibre mats during battery assembly. Modern design of such batteries for stationary applications includes monoblocs of two or three cells, for small sizes, with inter-cell connection

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by welding through the partition wall. Larger cells are still of the single unit type. All sizes are contained in injection-moulded polypropylene cases. The terminal feed-throughs are completely sealed in order to prevent acid spillage.

Positive tubular plates

Tubular plates are well known for their high cycling capability. Each grid consists of vertical spines and a top bar only, *i.e.*, a comb-like structure. In most European countries, casting takes place in special pressure-casting machines; this procedure is also gaining increasing acceptance in other countries. The essential result is a very fine grained structure that avoids the problem of inter-granular corrosion. With this structure, the 'growing' of the positive grid is reduced to a negligible amount. In addition, the total corrosion rate is reduced drastically. Thus, although tubular plates use less grid lead, service life is increased to 1800 cycles compared with 1200 cycles for pasted plates.

The active mass (contained in the tubes around the spines) is based on leady oxide, as in pasted plates. Plate processing includes a pickling stage in dilute sulphuric acid; this takes the place of the curing stage in the preparation of flat pasted plates.

The tubes are made either from glass fibre covered by perforated polyvinyl chloride sheet or from polyester textiles reinforced by synthetic resin. In the tubular design, the active mass is pressed to the spines, so holding the corrosion layer fixed to the metal and inhibiting the access of sulphuric acid to the metal. With this arrangement, the corrosion rate is further reduced and the rate of material shedding is very low.

Role of antimony

Originally, antimony was only used as a hardening agent for the lead. It was not until lead–calcium alloys were used for positive grids (in order to avoid decrease in hydrogen overvoltage with increasing service life) that the additional benefits of antimony were recognized.

It should be remembered that the lead/acid battery is only operable because of the overvoltage of hydrogen at the negative lead electrode. Thermodynamically, lead is not stable in sulphuric acid, but should dissolve with evolution of hydrogen. This reaction is suppressed by the low rate of formation of H_2 molecules from elementary hydrogen. This overvoltage is reduced drastically when elementary antimony (and also other metals) is present as a separate phase on the surface of the active material.

A small amount of antimony is released from the negative-grid alloy, but the main-source originates from the positive grid via its corrosion. Despite the presence of a corrosion layer, especially in tubular plates, the lead dioxide of the mass is capable of absorbing up to 3 wt.% of antimony. With the normal 9 wt.% antimony alloys used in tubular plates, a significant amount of antimony is dissolved in the electrolyte and is transferred (both electrically and by diffusion) to the negative electrodes. There, antimony is reduced partly to the element and partly to stibine gas which is released from the cell.

The benefit of having antimony in the corrosion layer and, with less importance, in the active mass, is that it helps to form a mechanically rigid protection layer with a very small specific surface. Thus, even under severe conditions, the layer will not be discharged to lead sulphate and thereby broken up.

By contrast, batteries made from lead–calcium or other antimony-free alloys should not be subjected to deep-discharge. Under such conditions, a lead sulphate layer is formed immediately adjacent to the lead spines that cannot be converted back to lead dioxide under normal charging procedures. Also, other effects such as sudden death (*i.e.*, loss of capacity) in stationary batteries under usual float conditions is found to occur, and special procedures have been devised to avoid such failures in lead–calcium batteries.

Given such experience, most manufacturers of automotive batteries have made strenuous efforts to meet battery-performance specifications by the use of low-antimony alloys. The same is true for industrial batteries of the low-maintenance type. Wherever possible, similar alloys have been used to achieve high reliability without the precautions required for maintenance-free batteries.

Special aspects of modern design

State-of-the-art

With any new modification, the well proven properties of the traditional lead/acid design should be maintained; these are:

— high reliability
— long service life in cycling and stand-by operation
— good charge acceptance
— high round-trip efficiency
— simple check for state-of-charge
— low price.

The disadvantages of the lead/acid system should be eliminated or reduced, these are:

— acid contamination of the environment
— corrosion of terminals and connectors.

Within technical limits, there are means to eliminate the above disadvantages. Such means are frequently used in cells with liquid electrolyte and are obligatory in recombination-type cells. For example, heat sealing of lids to containers has been standard for many years. For perfect sealing between the poles and the lid, O-ring gaskets are pressed on a machined shoulder of the pole bolt by means of a polypropylene ring. This ring is fixed by two half-rings inserted into a groove in the bolt. Sealing to the polypropylene lid is made by injection moulding polypropylene into the gap, which melts to the ring and to the lid. The electrical conductivity of the terminal bolts is improved by the inclusion of copper inserts.

Inter-cell connectors are screw-type, flexible cable connectors with plastic heads; gaskets ensure that any acid spilled accidentally is not retained in the connection area, thereby giving rise to corrosion.

Low-maintenance batteries

The inclusion of ceramic-filter vent plugs in low-maintenance batteries not only prevents the flash-back of any external sparks into the cells, but also reduces acid fumes to a negligible level, and allows for hydrometer access and topping up without plug removal. With this development, the modern stationary battery installation no longer requires a tiled floor and walls, and acid-proof clothing is not necessary for the maintenance staff. The situation is similar with cycling batteries. Customers request acid circulation and cooling in order to minimize the charging time without affecting service life. Such features are now available, together with higher energy density, *e.g.*, CSM technology [1]. By virtue of these new aspects, there has been even further improvement in the general advantages of the lead/acid battery compared with other systems, namely: measurement of state-of-charge; charge acceptance; round-trip efficiency. Reliability and service-life improvements are even more remarkable, as such batteries undergo much heavier loads compared with older types.

Maintenance-free batteries

Recombinant-electrolyte technology (the basic part of maintenance-free industrial batteries) relies on the development of an overpressure in the cell. Thus, rigid containers must be used with the larger cells, *i.e.*, styrene acrylonitrile or thick-walled polypropylene.

For different reasons, the utilization of the active material is significantly smaller both in the absorptive glass-mat and in the gelled electrolyte types, *i.e.*, based on the same weight, the capacity is 15 - 20% lower. The gel is formed from the liquid acid by the addition of precipitated silica. The filling and charging process is somewhat complicated and starts with discharged plates and acid of low specific gravity (s.g.), mixed with silica. Labour and energy-consuming conditioning cycling is required to activate the recombination process.

The absorptive-mat batteries require an expensive separator made from a mixture of standard and microfine glass-fibres. Plate thickness, plate pitch, and separator thickness must be adjusted exactly in order to obtain the correct pore diameter and volume. The amount of electrolyte is also critical. Cell height is restricted due to limited capillary forces; these maintain the electrolyte in position.

Comparison of low-maintenance and maintenance-free technologies

Maintenance-free batteries are more expensive than low-maintenance types. This is not only true with regard to the purchase price, but also if service life is taken into consideration, see Table 1.

TABLE 1

Comparison of low-maintenance (LM) and maintenance-free (MF) industrial batteries (Prices in Deutsche Mark: 1 U.S.$ = 1.90 DM.)

		MF	LM PzS	LM CSM
Tubular traction batteries				
Price[a] per kW h:				
C/5 rate		348	311	279
C/2 rate		465	397	341
Cycles 80% DOD, 30 °C		1200[b]	1500	1500
Price, DM/kW h discharged:				
C/5 rate		0.36	0.26	0.23
C/2 rate		0.48	0.33	0.28
Cycles per week (5 d)		4	10	10
Topping-up		—	weekly	weekly
Check cell voltage		weekly	monthly	monthly
	MF tubular	MF flat plate	LM tubular	LM flat plate
Stationary batteries				
Price[c] per kW h:				
C/10 rate	408	426	364	381
C/1 rate	902	844	746	754
Cycles 80% DOD, 30 °C	1200[b]	600[d]	1200	1000
Life (stand-by, years)	12	9	20	12
Price per kW h (*C*/1 rate):				
stand-by (annually)	75	94	37	63
discharged (cycle)	0.75	1.41	0.62	0.75
Topping-up	—	—	3 years	2 years
Check cell voltage	monthly	monthly	6 months	6 months

[a]Full battery with inter-cell connectors, container and — except MF — topping-up system.
[b]Maximum value cited.
[c]Cells and inter-cell connectors.
[d]Average of experimental and claimed data.

Further restrictions are necessary for the charging conditions. For example, this reduces the number of cycles per day from two (in practice) to one (hopefully), and does not allow for full utilization of the panel power in solar application.

On the other hand, maintenance-free batteries can be operated in any position. They do not create any hazards involving acid fumes, exhibit five-times longer shelf life, and may be shipped, without risks of acid leakage, in a fully charged and operable state.

What is the meaning of "maintenance free"? For car batteries the answer is very simple. A daily check is made for operational performance, *i.e.*, when the owner cranks the engine. Low rotation is easily detected and any defective battery is replaced. From time to time, the car is taken to a garage for service, where — if the staff does the job correctly — the battery is cleaned.

The service cost will be 1% lower in the case of a maintenance-free battery, as the latter will not require water addition.

The performance of a stationary battery cannot be monitored daily. But as in past practice, the battery should be checked for correct trickle-charge voltage of each cell and cleaned if necessary. Such a procedure is essential for maintenance-free batteries as acid level and s.g. cannot be measured, and one defective cell can ruin the whole battery by increasing the trickle-charge current above the acceptable value. Assuming such a voltage check is made every 15 min for a 24 V battery, this procedure amounts to 30 h over 10 years of service life. A low-maintenance battery would require 31.5 h of service; the extra time originating from the need to replenish the cells with water.

In the F.R.G., maintenance-free batteries have secured 1% of the traction-battery market and 3% of the stationary-battery market. Primary, nickel/cadmium and maintenance-free lead/acid batteries compete for the appliance market; traditional lead/acid batteries have never been used in this area. Maintenance-free batteries are also finding niche markets, *e.g.*, computer back-up, small fork-lift trucks, etc.

HAGEN maintenance-free batteries

Stationary batteries

The HAGEN compact battery, with pasted positive plates and liquid electrolyte, is regarded as a 'low maintenance' type. The most important aspects of this system are: (i) acid-proof, heat-sealed containers; (ii) acid-proof safety pole; (iii) topping-up interval about 3 years. The HAGEN Drysafe compact with fixed electrolyte is the maintenance-free version. This type is available in 6 V monoblocs of 18 A h to 192 A h, and 4 V monoblocs of 224 A h to 256 A h. The recombination is based on the use of absorptive glass-mat separators.

Both the reinforced containers and lids are injection moulded high quality polypropylene. The wall thickness of 5 - 6.5 mm provides the containers with a high stability; this ensures that the elements are kept tight together and that an internal pressure of 0.1 bar is maintained. Safety vents are built into the lids as protection against overpressure resulting from incorrect charging conditions.

Traction batteries

Strong, positive tubular plates, together with 'high load', optimized, negative pasted plates, are the basic design criteria for HAGEN supra F traction batteries. The grids are pressure-cast from special non-antimonial alloys, and a gelled electrolyte is employed. The cell is hermetically sealed by heat-sealing the lid to the container and to a safety pole. A safety vent in the cell lid is included for protection against overpressure due to incorrect charging.

Fully insulated, screw-type cable connectors are used for inter-cell connection.

Conclusions

For most applications, by virtue of their high price and limited freedom of operation, maintenance-free batteries will not be preferred to corresponding low-maintenance types. As most of the maintenance operation of modern batteries is concerned with ensuring proper charging, tightly fixed connectors, and cleaning, the advantage of not having to add water is not a serious argument in favour of maintenance-free batteries. An exception to this may lie with small batteries, where battery care cannot be exercised or causes real problems and thus demands a high priced, problem-free battery. However, the market is increasingly being taken over by primary lithium systems. By virtue of their high energy density, extremely long shelf-life, and reasonable price, lithium batteries are becoming extremely competitive with their lead/acid counterparts.

Reference

1 R. Kiessling, *J. Power Sources, 19* (1987) 147.