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Development of a large-sized, long-life, valve-regulated lead–acid battery

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Abstract

For emergency backup of communications and other industrial equipment, the compact and low-maintenance, MSE series, valve-regulated lead – acid battery has mainly been used in place of conventional flooded types. Because of the keen competition in the communications industry, it is becoming more important to reduce battery maintenance and replacement costs. In addition, operations in extreme environments are becoming more common as networks expand. In response to this trend, the new long-life MSE-AT series has been developed. It has twice the life at normal temperatures, i.e., 13 to 15 years, and increased life at high temperatures. This has been attained by improving the negative electrode and separator to reduce the float-charging current, and by using a highly corrosion-resistant alloy for the positive grid. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Alloy; Corrosion; Float charging current; Negative electrode; Separator; Valve-regulated lead – acid battery

1. Introduction

Valve-regulated lead – acid (VRLA) batteries are used as d.c. backup power sources for a variety of applications such as telecommunications, switch gear, and mainframe computer uninterruptible power supply (UPS). The wet cell batteries previously used in these applications, such as the HS, PS and CS type batteries manufactured by Matsushita, have required extensive maintenance, e.g., measurement of acid relative density, periodic replenishment of water, and equalization charging. Space restrictions in numerous remote installations have also limited installation flexibility and have rendered the batteries difficult to maintain. Accordingly, Matsushita has sought to develop a smaller, energy-efficient VRLA battery which is specifically designed for power backup at remote sites.

From 1980 to 1982, the LCR series of VRLA batteries (30 to 100 A h) were developed for a variety of industrial and commercial applications. This small-capacity series had an expected life span of 5 to 7 years. The development of precision manufacturing techniques for this series played an essential role in later, large format, designs of VRLA batteries.

From 1984 to 1987, the MSE series of large VRLA batteries (50 to 3000 A h) were developed with an expected reliable life span of 7 to 9 years. The MSE series shared many of the characteristics of the HS, CS and PS series of wet-cell batteries, but the batteries were smaller and easier to maintain.

In recent years, telecommunications carriers have faced increasing competition. Reducing equipment costs and field service operations are now the key to maintaining profitability. Hence, the demand for higher reliability VRLA batteries with an expected reliable life span of 10 to 14 years to reduce the incidence of service calls and replacement.

Environmental considerations regarding facilities using batteries have also led to the increased use of VRLA batteries which do not normally emit corrosive gas and,

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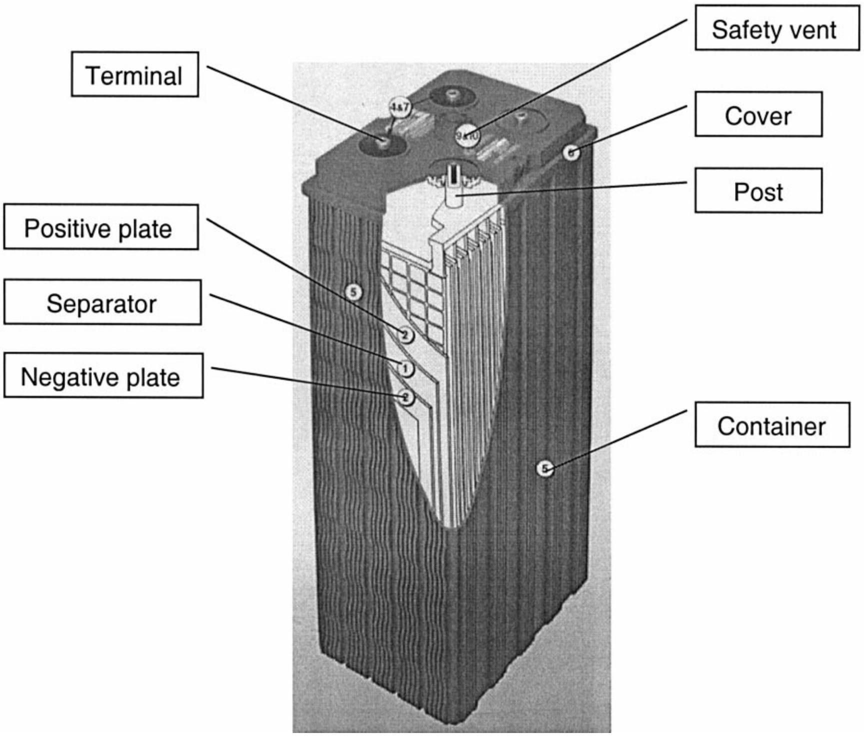


Fig. 1. Construction of MSE-1200AT battery.

thereby, eliminate the need for specially ventilated battery compartments and highly skilled maintenance personnel. There is a particular demand for VRLA batteries which can be used without succumbing to thermal runaway in environments subject to high temperatures.

The new MSE-AT series has, therefore, been developed in answer to the need for a series of batteries with specifications identical to the previous MSE series, but with more than twice the expected life span. The ability to withstand high temperatures has also been enhanced.

2. MSE series valve-regulated lead – acid batteries

The MSE-1200AT (2 V, 1200 Ah) battery, which is representative of the MSE-AT series, is shown in Fig. 1. In

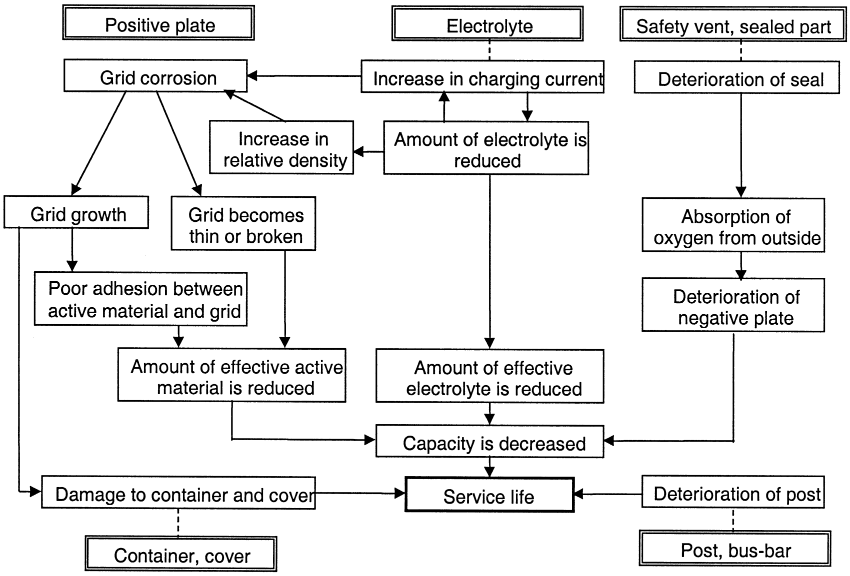


Fig. 2. Deterioration mechanism of VRLA batteries.

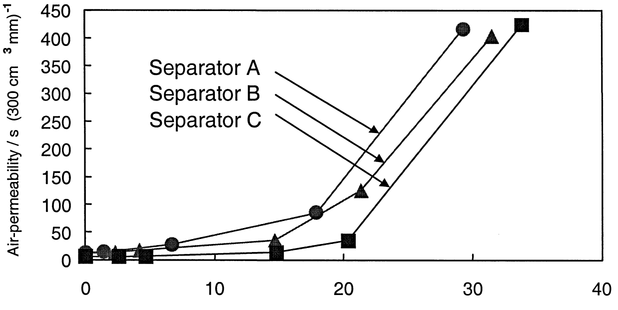


Fig. 3. Air-permeability of separators.

this battery, the positive and negative grids are produced from a lead–calcium alloy. The electrolyte is absorbed in separators which are made from non-woven sheets of spun glass. The case is sealed and fitted with a low-pressure, safety relief valve with a built-in flame arrestor. The battery can be placed vertically or horizontally with no loss of capacity or life.

3. Battery components subject to deterioration and their improvement

Based upon an analysis of field studies, the components of a MSE series battery that are subject to deterioration are shown in Fig. 2. Although deterioration of the negative electrodes due to loss of air-tightness was observed, the rate of deterioration was so slow that the problem was considered to be unimportant. More importantly, MSE series batteries which are charged to the rated capacity via either float or trickle charging are subject to oxidation of the positive grids. There follows deterioration of the contact between the active material and the grid due to loss of conductance and/or grid growth. These factors, in turn, cause loss of active material which reduces the discharge capacity and life of the battery.

Thus, the focus of the present investigation has been to extend the effective life of the battery by suppressing the charge current which causes corrosion of the positive electrodes, and to find a more corrosion-resistant alloy for use in positive grids.

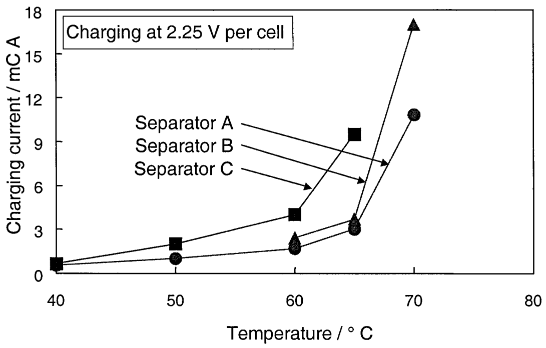


Fig. 4. Trickle charge current with different separators.

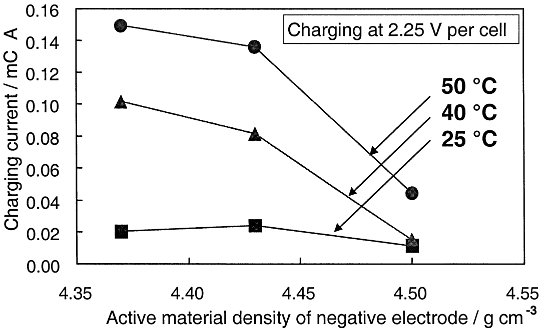


Fig. 5. Relationship between charging current and active-material density of negative electrode.

3.1. Reducing trickle charge current

The following reactions occur in conjunction with the flow of trickle charge current.

(i) Oxidation of positive electrode:

$$H_2O \rightarrow 1/2\,O_2 + 2H^+ + 2e^- \qquad (1)$$

(ii) Diffusion of oxygen; oxygen spreads throughout the separator.

(iii) Oxygen recombination at the negative electrode:

$$Pb + 1/2\,O_2 + H_2SO_4 \rightarrow PbSO_4 + H_2O \qquad (2)$$

$$PbSO_4 + 2H^+ + 2e^- \rightarrow Pb + H_2SO_4 \qquad (3)$$

To suppress the charge current, attention was focused on features (ii) and (iii), which are relatively easy to control. Thus, investigations were made of means to control the diffusion of oxygen through the separator, and to

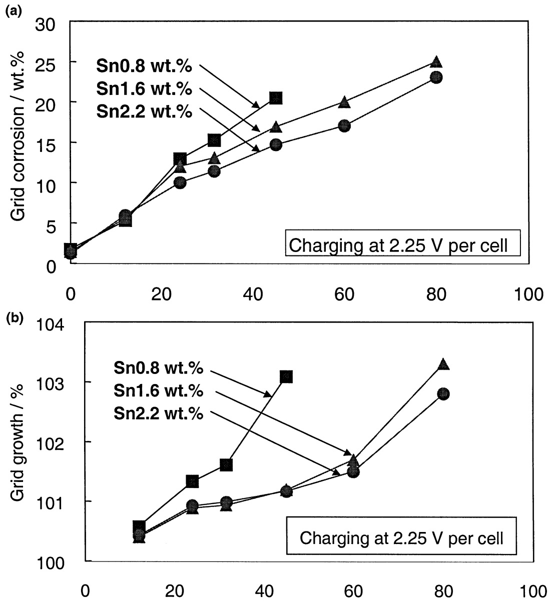


Fig. 6. (a) Positive grid corrosion loss and (b) positive grid growth as a function of trickle charge period.

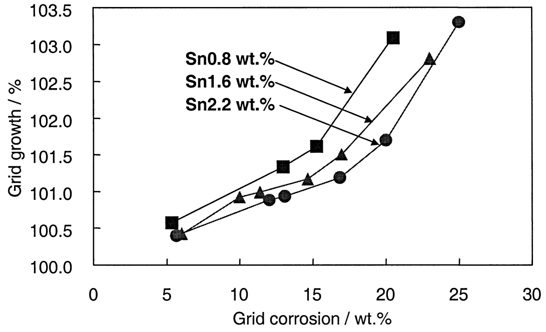


Fig. 7. Relationship between positive grid growth and weight loss.

control the reduction reaction at the negative electrode. Advanced materials technology for the suppression of trickle charge current is important because it helps to extend the life of the battery. This is especially true for large-sized, VRLA batteries and helps to prevent thermal runaway, a phenomenon often encountered when batteries are operated at high temperatures.

3.1.1. Separator

To suppress the diffusion of oxygen, a study was made of the relationship between this phenomenon and the diameter and density of the spun glass fibres. Evaluation of the speed of diffusion through the separator was achieved by measuring the time required for 300 cm^3 of air to pass through the thickness of the separator, i.e., a technique based on JIS P8117 (Gurley Method).

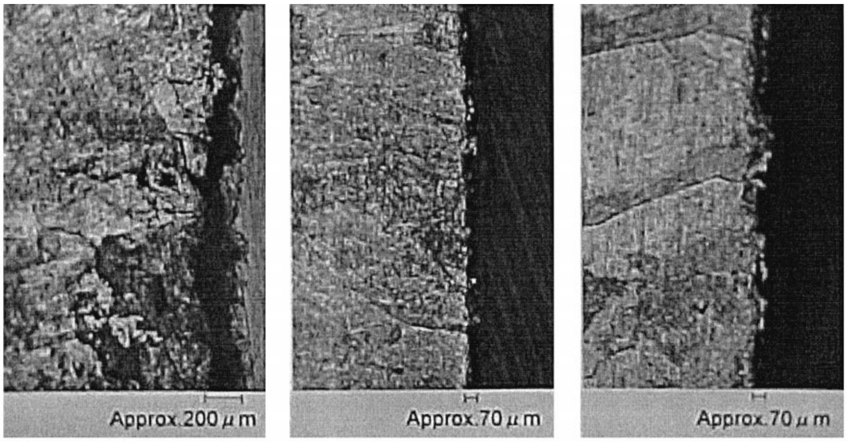
The resistance to the passage of air in different types of separator is shown in Fig. 3. The corresponding trickle currents are presented in Fig. 4. Separator A demonstrated the highest resistance to the passage of air and was able to suppress the trickle current. The performance of this separator was particularly good in regions where the recharge current on the high-temperature side was large, in other words where the evolution of oxygen was highest. Therefore, Separator A was adopted and specifications were established that would prevent adverse effects from oxygen recombination, absorption of liquid, and loss of elasticity.

3.1.2. Composition of negative electrode

In order to restrict the trickle charge current to as low a value as possible, the active material in the negative electrode was changed, the apparent density was enhanced, and the reaction surface area was reduced. These changes resulted in an increase in the charge voltage. Fig. 5 shows the relationship between the apparent density of the active material of the negative electrode and charging current during trickle charge. Raising the apparent density of the active element is one way of suppressing the trickle charge current. Thus, it was decided to use a negative electrode with an apparent density of 4.50 g cm^{-3}; this value is within the range which does not compromise electrical discharge qualities.

3.2. Improving resistance to corrosion in positive grid

Materials used in the positive-grid alloys of VRLA batteries include: arsenic, silver, cadmium, and numerous other materials which are intended to improve resistance to corrosion. Considerations of loss of electrolyte, environmental concerns, as well as production costs and methods, focused attention on a lead–calcium–tin alloy. This alloy has long been the subject of research in terms of determining the optimum weight percentages of calcium and tin. In recent years, the amount of tin has exceeded 1 wt.%. In attempts to extend cycle-life, a series of batteries with varying amounts of tin in the positive grids was fabricated. In the course of accelerated life-testing, these positive



(a) Sn: 0.8 wt.%
Corrosion: 9.4 %
Growth: 101.1 %

(b) Sn: 1.6 wt.%
Corrosion: 7.2 %
Growth: 100.4 %

(c) Sn: 2.2 wt.%
Corrosion: 7.0 %
Growth: 100.4 %

Fig. 8. Cross-sections of positive grids.

Table 1
Specifications of VRLA batteries

Model	Nominal voltage (V)	Capacity (A h)		Width (mm)	Height (mm)	Total length/ depth (mm)	Weight (kg)
		8 h	1 h				
MSE-150AT	2	150	95	106	170	365	12
MSE-250AT	2	200	127	106	170	365	15
MSE-300AT	2	300	191	150	170	365	21
MSE-500AT	2	500	284	182	228	368	32
MSE-560AT	2	560	302	160	183	580	39
MSE-640AT	2	640	325	160	183	580	44
MSE-720AT	2	720	365	194	183	580	48
MSE-800AT	2	800	406	194	183	580	53
MSE-960AT	2	960	487	245	183	580	62
MSE-1040AT	2	1040	528	245	183	580	66
MSE-1120AT	2	1120	568	281	183	580	71
MSE-1200AT	2	1200	609	281	183	580	75
MSE-1360AT	2	1360	690	328	183	580	88
MSE-1440AT	2	1440	731	328	183	580	93

grids were removed and examined for corrosion and grid growth. The results are presented in Fig. 6(a) and (b). Clearly, less corrosion is observed and grid growth is limited as the percentage of tin is increased. Using these data, and comparing them with the corrosion and grid growth of various alloys, as shown in Fig. 7, it is found that even when the corrosion is not changed, alloys with larger percentages of tin exhibit less grid growth.

Cross-sections of corroded positive grids are shown in Fig. 8. It is seen that corrosion advances rapidly as the tin content is lowered. Therefore, it is concluded that the larger the percentage of tin in the grid alloy, the greater the effect in resisting corrosion. Thus, an alloy with 1.6 wt.% or more tin has been adopted.

4. Characteristics of new MSE series batteries

4.1. Specifications

The specifications for the 10 VRLA batteries in the new MSE-AT series (150 to 1440 A h) are listed in Table 1. A photograph of the batteries is presented in Fig. 9.

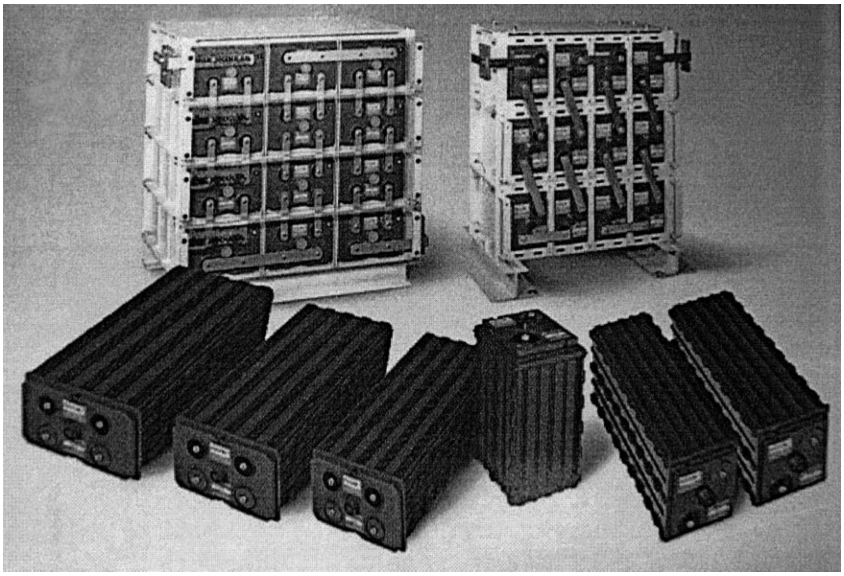


Fig. 9. Appearance of new MSE-AT series.

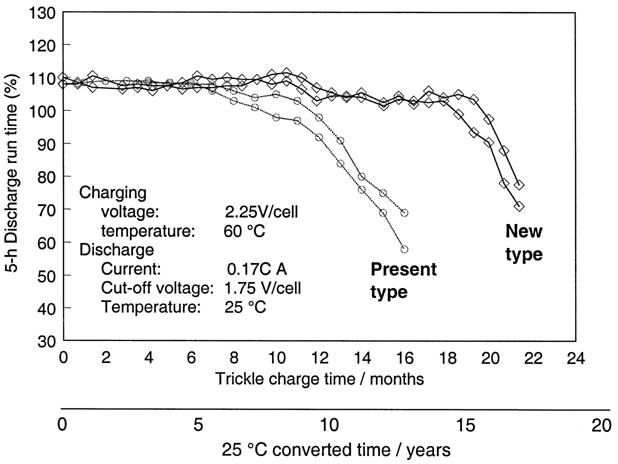


Fig. 10. Accelerated life test of MSE battery at 60°C.

4.2. Cycle-life

Results of accelerated life-tests of MSE series and new MSE series batteries are shown in Fig. 10. Improvements in the active material of the negative electrode and the separator have helped suppress trickle recharge current, and the adoption of a new corrosion-resistant positive electrode grid alloy has resulted in a doubling of the conventional life to 13 to 15 years with greatly enhanced reliability.

4.3. Resistance to thermal runaway

The rapid growth of small remote sites has placed additional requirements on VRLA batteries which are required to operate in extreme environments. For example, batteries have to be installed in or near other electrical loads or rectifiers, which thus increases exposure to high temperatures.

Oversized VRLA batteries are particularly susceptible to thermal runaway, which occurs when high temperatures cause the charge current, which is accompanied by the oxygen-recombination reaction, to rise. This results in more heat being generated which, in turn, causes a larger charge current. There are various ways of controlling the charge current with respect to temperature, but this can increase equipment costs.

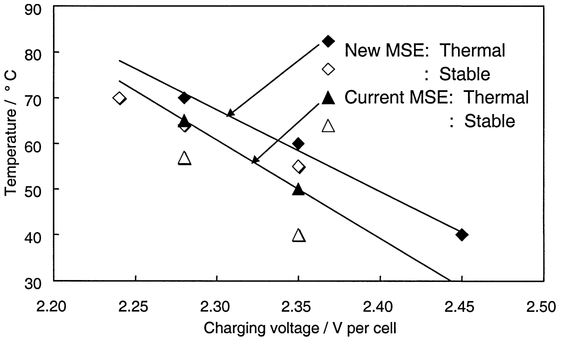


Fig. 11. Thermal runaway limit of MSE series batteries.

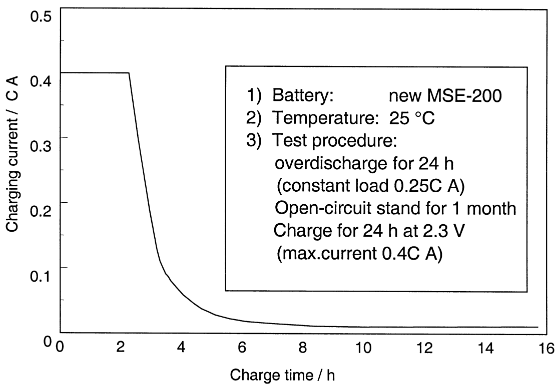


Fig. 12. Charge-acceptance after extended overdischarge.

By suppressing the trickle charge current, not only is the life span of the battery increased but the generation of heat by the battery is also reduced. The result of this reduction is increased resistance to thermal runaway.

A comparison of the thermal runaway limit for both the new and present MSE series relative to the ambient air temperature and float charge current is given in Fig. 11. Three MSE series batteries were connected in series for the test. The thermal runaway limit was determined as the point where the battery temperature and charge current continued to rise successively. The new MSE-AT series batteries have a standard charge of 2.23 to 2.25 V and the thermal runaway limit is increased by approximately 5°C compared with that of conventional MSE batteries.

4.4. Recovery of fully-discharged batteries

When used as emergency power sources, the batteries are sometimes deeply discharged and sometimes can pass before they can be recharged. Lead – acid batteries are said to be particularly vulnerable to deep discharge. Lead – calcium – tin alloys which have more tin help prevent loss of conductivity in the positive grids. Thus, batteries with these grids are capable of being recovered even after being deeply discharged. The charge characteristics for the batteries after complete discharge are shown in Fig. 12. Even when left uncharged for more than 30 days, the batteries can still be successfully recovered.

5. Conclusions

New MSE series batteries have been developed and have a life expectancy of 13 to 15 years, i.e., twice the life of the earlier version. The key design factors are:

(i) suppression of the float charging current which causes corrosion of positive grids;
(ii) a more corrosion-resistant alloy for use in positive grids.

As the world approaches the 21st century, and the ‘age of information,’ the need for reliable emergency power is increasing. The application of advanced materials and manufacturing technologies to MSE VRLA batteries will produce the life and reliability that the market expects.

Further reading

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