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Reliability of lead–calcium automotive batteries in practical operations

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Abstract

In order to reach a statistically sound conclusion on the suitability of maintenance-free, lead–calcium automotive batteries for practical operations, the failure behaviour of such batteries has been observed in a large-scale experiment carried out by Mercedes Benz AG and Robert Bosch GmbH in different climatic zones of North America. The results show that the average failure behaviour is not significantly different to that of batteries from other manufacturers using other grid alloy systems and operated under otherwise identical conditions; the cumulative failure probability after 30 months is 17%. The principal causes of failure are: (i) early failure: transport damage, filling errors, and short-circuits due to the outer plates being pushed up during plate-block assembly (manufacturing defect); (ii) statistical failure: short-circuits due to growth of positive plates caused by a reduction in the mechanical strength of the cast positive grid as a result of corrosion; (iii) late failure due to an increased occurrence of short-circuits, especially frequent in outer cell facing the engine of the vehicle (subjected to high temperature), and to defects caused by capacity decay. As expected, the batteries exhibit extremely low water loss in each cell. The poor cyclical performance of stationary batteries, caused by acid stratification and well-known from laboratory tests, has no detrimental effect on the batteries in use. After a thorough analysis of the corrosion process, the battery manufacturer changed the grid alloy and the method of its production, and thus limited the corrosion problem with cast lead–calcium grids and with it the possibility of plate growth. The mathematical methods used in this study, and in particular the characteristic factors derived from them, have proven useful for assessing the suitability of automotive batteries.

Keywords: Lead–calcium batteries; Automotive batteries; Reliability

1. The problem

The last few years have seen a constant reduction in the antimony contained in the grids of both the negative and positive electrodes of automotive batteries supplied with new vehicles. This raises the question as to the viability of replacing the hybrid battery, in general use at present, by a completely antimony-free unit. The basic question is as follows: to what extent do the weak points revealed by laboratory tests (incomplete recharge after total discharge, capacity decay after cyclical use, etc.) limit the practical suitability of absolutely maintenance-free lead–calcium batteries? As laboratory tests can only give a very incomplete picture of practical operation, and most standardized tests have been designed for the comparison of antimony batteries [1], the question as to the risk involved in the use of lead–calcium batteries can only be answered satisfactorily by a well-supervised, large-scale practical experiment. Thus, the aim of a large-scale experiment of this kind is to reach the soundest possible conclusion on the reliability of lead–calcium batteries in practical operations.

As expected, the problem is difficult to solve. In contrast to the standardized bench-life tests, there are as yet no battery characteristics for the purposes of measurement and comparison. The period taken for the battery to sink below the 50% mark of its possibility of survival [2] is often used as a measure of reliability. In the case described here, the vehicle manufacturer and the battery producer together chose methods of running the experiment and of assessing the results.

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The large number of batteries tested guaranteed a statistically sound conclusion, and the comparability of the results was ensured by means of strictly defined test conditions, as well as clearly defined mathematical values taken from the theory of reliability.

2. The experiment

The North-American market was chosen as the test field. This region allowed central observation of a sufficiently large number of batteries for the period of the experiment. Moreover, the accompanying conditions with regard to vehicle type, engine and electrical fittings were almost identical for all batteries. Finally, the very differing climates to be found in the North-American market made it also possible to study the effects of the average electrolyte temperature on the suitability of batteries for practical operations.

2.1. Batteries examined

A total of about 40 000 batteries, manufactured by various European companies and with a *C*/20 capacity of 62 Ah and a cold-cranking test current of 280 A, was examined between 1988 and 1992. Of these, 7429 batteries from three delivery lots totalling 10 088 batteries were of the lead–calcium type. The others were of the lead–antimony or of the hybrid type. Table 1 shows the characteristics of their design, as well as the deadlines and the unit numbers of the delivery lots of lead–calcium batteries.

Table 1
Details of lead–calcium automotive batteries examined in survey

PbCa battery type 056219 with the following characteristics	
+/− plate ratio	6/5
+/− active material ratio (dry, formed)	1.3
Acid-to-mass ratio	>0.67
+ and − grid alloy	Pb–Ca–0.3wt.%Sn
Plate strap alloy	Pb–3.5wt.%Sb
Thickness of PE envelope separator (mm)	1.0
Thickness of + and − plate (mm)	1.8
Theoretical thickness of plate group (mm)	31.8
Cell width at bottom (mm)	30.5
The three delivery lots comprised a total of 10 088 batteries	
Lot 1 (Nov. 1988)	2861 units
Lot 2 (Jan. 1989)	3219 units
Lot 3 (Mar. 1989)	4008 units
Of these 7429 were observed in North America[a]	
The observed period extended for 48 months from the date of manufacture	

[a] For the failure questionnaire see Fig. 1.

2.2. Experimental conditions

The number of batteries (vehicles) to be observed were divided into the following areas:

New York Washington	3075
Jacksonville	1065
Chicago	1200
Houston	637
San Francisco	750
Los Angeles	702

The vehicles observed were medium-size Mercedes passenger cars with 2.6 and 3.0 l gasoline engines of the same type. All vehicles were equipped with electricity-powered, air-conditioning systems and were equipped with the same electrical fittings. The vehicles were shipped from Europe to the USA under identical conditions, with battery connected and consumers of rest current switched on. The storage time before initial operation of the vehicles varied from 2 to 7 months. Outliers were registered for up to 20 months. The possibility of a considerable current drain in the showrooms prior to initial operation cannot be ruled out.

2.3. Battery diagnosis

Battery failure was diagnosed in 2 stages:

(i) at the end of 3–4 months after installation;

(ii) at the end of about 30 months following the date of manufacture.

Diagnosis was carried out according to the following procedure.

(i) The data relevant to battery failure were determined from the questionnaire (Fig. 1).

(ii) Level and density of the electrolyte in the cells was measured.

(iii) The battery was charged using 14 V and left to stand for 24 h.

(iv) The acid density in the cells was again measured.

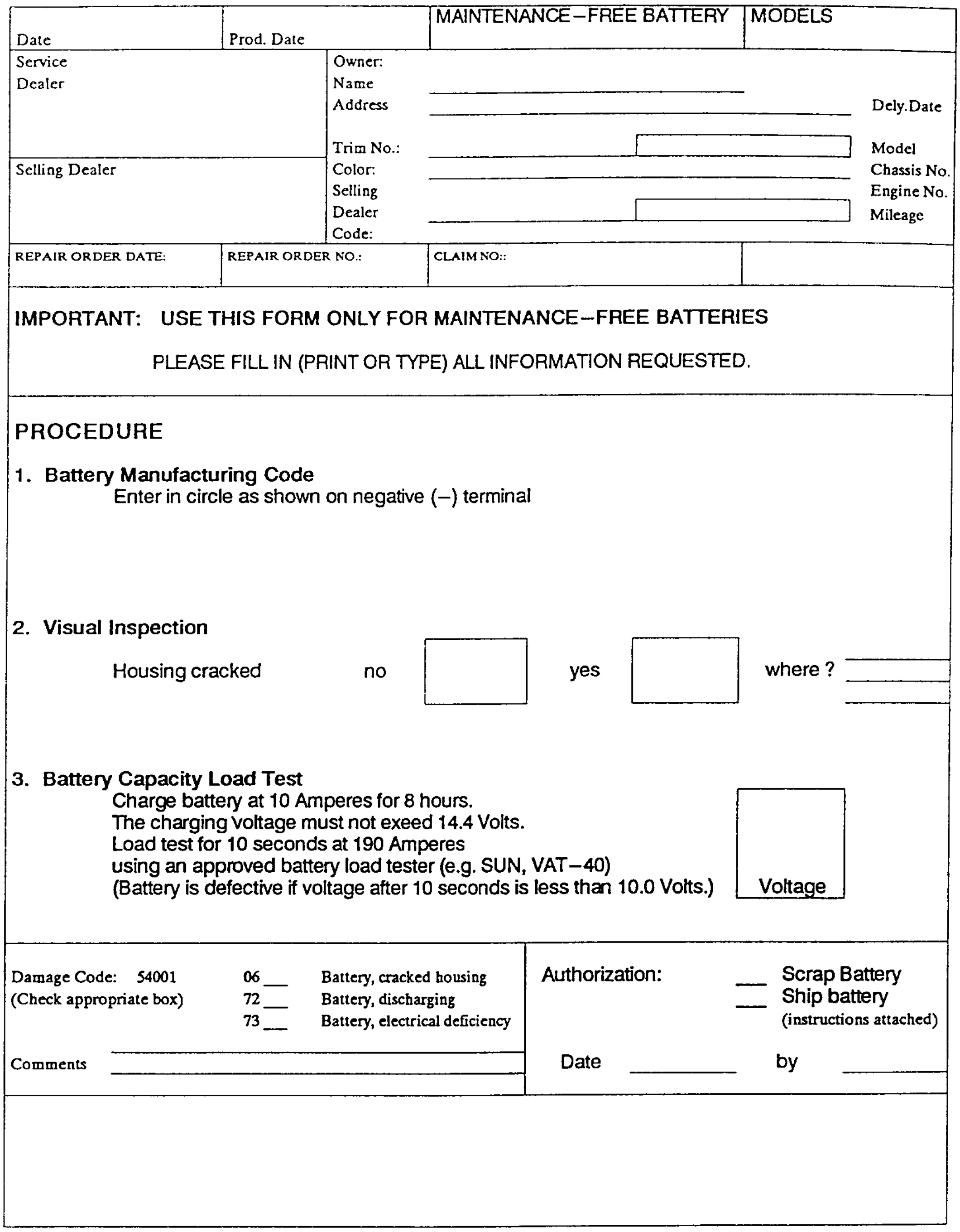
(v) Battery power was tested by means of a maximum-current discharge using 180 A for 15 s at room temperature.

(vi) After opening the battery: the cell voltage was measured; cells conspicuous respect to defect in grids, active material, separators and plate straps were examined by visual means; the cause of failure was determined.

3. Results

3.1. Battery failure as a function of age and climate

The method of the mathematical theory of reliability for non-repairable components was used in order to



Date	Prod. Date	MAINTENANCE–FREE BATTERY	MODELS
Service Dealer	Owner: Name ______ Address ______ Trim No.: ______ ☐		Dely.Date Model
Selling Dealer	Color: ______ Selling Dealer ______ ☐ Code:		Chassis No. Engine No. Mileage
REPAIR ORDER DATE:	REPAIR ORDER NO.:	CLAIM NO.:	

IMPORTANT: USE THIS FORM ONLY FOR MAINTENANCE–FREE BATTERIES

PLEASE FILL IN (PRINT OR TYPE) ALL INFORMATION REQUESTED.

PROCEDURE

1. **Battery Manufacturing Code**
   Enter in circle as shown on negative (–) terminal

2. **Visual Inspection**
   Housing cracked no ☐ yes ☐ where ? ______

3. **Battery Capacity Load Test**
   Charge battery at 10 Amperes for 8 hours.
   The charging voltage must not exeed 14.4 Volts.
   Load test for 10 seconds at 190 Amperes
   using an approved battery load tester (e.g. SUN, VAT–40)
   (Battery is defective if voltage after 10 seconds is less than 10.0 Volts.)
   ☐ Voltage

Damage Code: 54001 (Check appropriate box)	06 ___ 72 ___ 73 ___	Battery, cracked housing Battery, discharging Battery, electrical deficiency	Authorization: ___ Scrap Battery ___ Ship battery (instructions attached)
Comments ______			Date ______ by ______

Fig. 1. Failure questionnaire form.

assess and compare failure behaviour. Due to the cumulative effects of several parameters, it was necessary to check the plausibility of the resulting curves and characteristics of

- standing time before initial operation
- charging state during standing time
- age of the battery
- total mileage of the vehicle
- influence of the climatic zone

The statistical material to be interpreted was also affected by the behaviour of the client and of the service staff with regard to reporting cases of battery failure and, in particular, by the decrease in warranty claims on completion of the agreed pro-rata periods.

3.1.1. *Mathematical description of failure behaviour*

The failure rate $\lambda(t)$ has proved to be especially useful in the assessment of the failure behaviour of technical components and systems. Multiplied by the time interval dt, it is a unit of the probability with which batteries $N(t)$ intact at time t will fail during the time interval $t \rightarrow t + dt$. That is:

$$\frac{dN(t)}{N(t)} = -\lambda(t)\, dt \qquad (1)$$

In general, technical systems show an increased failure rate at the beginning of their lifespan (early failure, manufacturing defects). The following phase is characterized by statistical failure with an approximately constant failure rate. At the end of the lifespan of the system, wear and fatigue cause a renewed increase in the failure rate. This pattern is known as a Weibull distribution.

The cumulative failure probability is obtained by solving the differential equation, Eq. (1), i.e.,

$$\frac{N_0-N(t)}{N_0}=1-\exp\left(-\int_0^t \lambda(v)\,\mathrm{d}v\right) \tag{2}$$

where N_0 describes the number of components originally involved in the experiment.

The differentiation of Eq. (2) with respect to t supplies the distribution density function of the probability of failure, namely

$$\frac{\mathrm{d}N(t)}{N_0}=f(t)\,\mathrm{d}t=\lambda(t)\exp\left(-\int_0^t \lambda(v)\,\mathrm{d}v\right)\mathrm{d}t \tag{3}$$

which, in the case of a constant failure rate, is simplified to form the well-known exponential relationship

$$f(t)=\lambda\exp(-\lambda t) \tag{4}$$

The difference between the distribution density function and the failure rate is that the former puts the number of batteries that failed in the time interval $t\rightarrow t+\mathrm{d}t$ in relation with the number of batteries present at the beginning of the experiment. Thus, in contrast to the distribution of the failure rate, the density function towards the end of the lifespan of the battery is a follows

$$\lim_{t\rightarrow\infty} f(t)=0 \tag{5}$$

In addition to the effect of the age (t) of the battery on its failure behaviour, it is necessary for two other parameters to be taken into account, the standing time (τ) of the battery before initial operation and the mileage (s) of the vehicle. All three variables are not independent statistically, but linked via the running performance (ν) of the vehicle, i.e.,

$$\nu=\frac{s}{t-\tau} \tag{6}$$

Typically, the running performance of passenger cars is distributed skew-symmetrically, with a noticeable maximum frequency at small powers.

In order to interpret the results achieved by statistical means, it is necessary to put the failure mechanisms typical for batteries in relation to the following parameters: (i) age of the battery; (ii) mileage of the vehicle; (iii) standing time of the battery before initial operation of the vehicle.

We can then expect the following.

(i) the failure rate $\lambda_E(t)$ of early failure resulting from manufacturing defects is higher and is distributed similarly for relatively new batteries and for vehicles with low mileage.

(ii) The corrosion of grids, suspension lugs and plate straps, caused by the standing time in vehicles prior to initial operation and with consumers of rest current $\lambda_\tau(t)$ switched on, increases dramatically with the duration of total discharge and, thus, is independent of the later operation time or mileage.

(iii) In contrast, plate growth caused by progressive corrosion $\lambda_C(t)$ mainly increases with the age of the battery. The mileage of the vehicle has negligible effect [3]. Corrosion occurring during the standing time is considered as prior damage.

(iv) Grid corrosion caused by overvoltage $\lambda_0(t)$ is increased by high mileages, but is of secondary importance with regard to detrimental effects and frequency (distribution of running performance of vehicle).

(v) Capacity deterioration $\lambda_{Cap}(t)$ due to failure of the positive active material (shedding), hardening of the negative material, and extreme loss of water were only caused by high mileages during the observation period of 3–4 years.

(vi) With the exception of early failure, all failure mechanisms mentioned here are, as expected, accelerated by high mean electrolyte temperatures.

3.1.2. Reliability analysis of batteries tested

Fig. 2 gives the curves of the following functions for technical components and systems: $\lambda(t)$ according to Eq. (1); $F(t)$ according to Eq. (2); $f(t)$ according to Eq. (3). The data supply characteristic values of the following parameters:

(i) failure rate for early failure $\lambda(t\rightarrow 0)$;

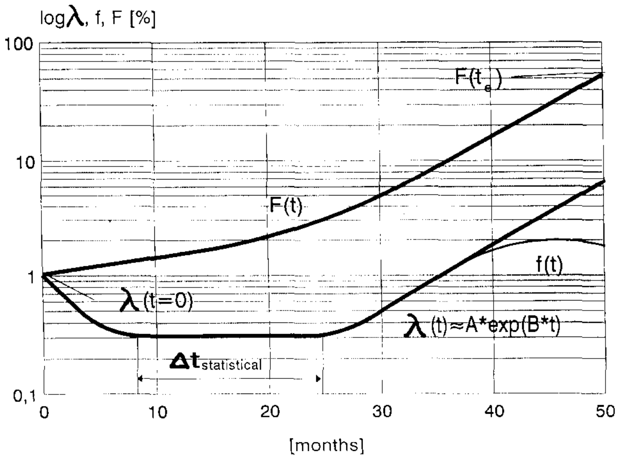


Fig. 2. Time dependence of $\lambda(t)$, $F(t)$ and $f(t)$ functions.

(ii) length of the period Δt_{stat} for statistical failure ($\lambda(t) \approx$ const.);

(iii) constants A and B for the empirical representation of the failure rate curve in the stage of late failure;

(iv) value for the cumulative failure probability at the end of the observation period ($F(t_e)$).

The curves of the functions λ, f and F for the six climatic zones are given in Fig. 3(a)–(f). The following conclusions are drawn:

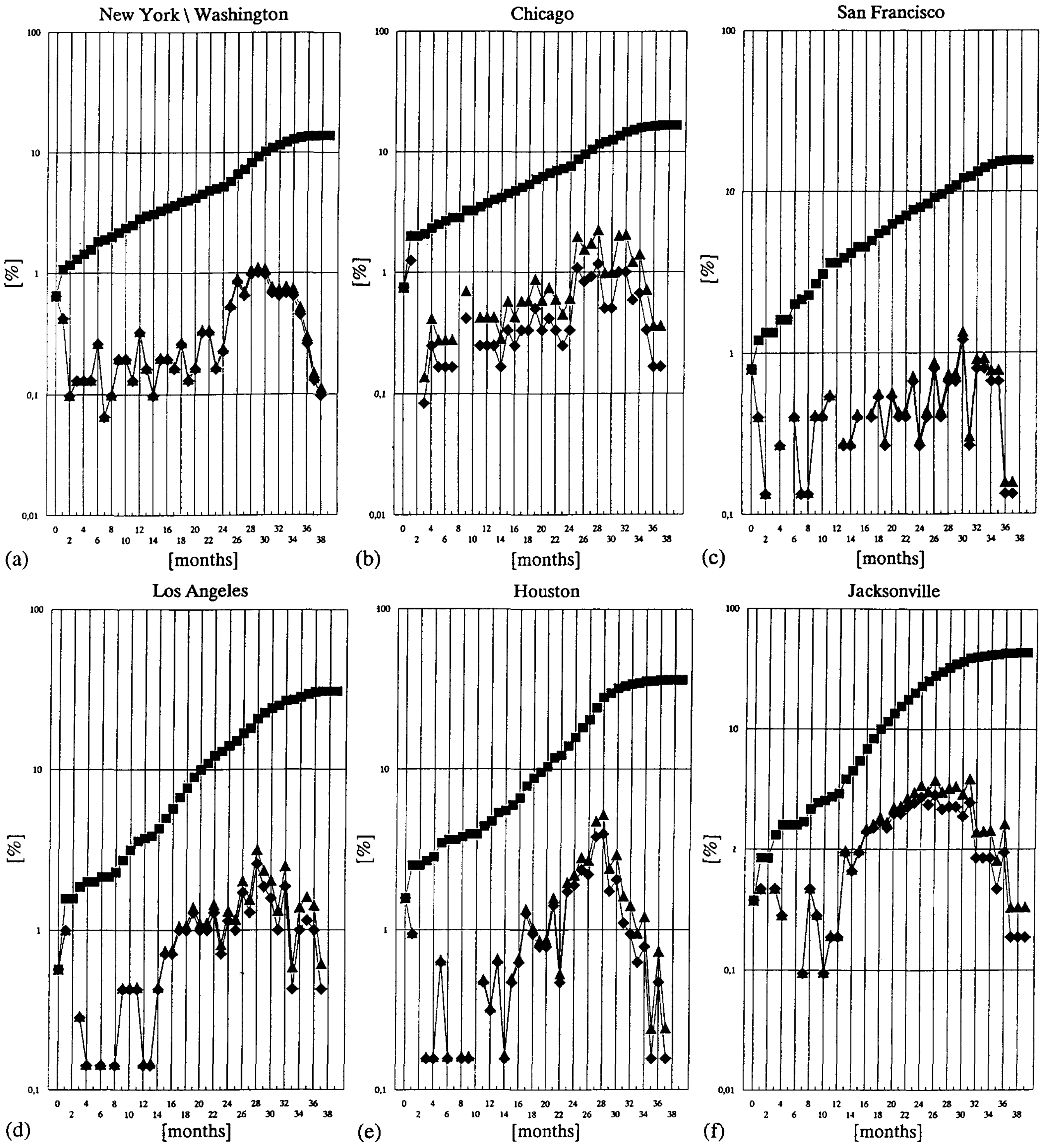


Fig. 3. Time dependence of $\lambda(t)$ (▲), $F(t)$ (■) and $f(t)$ (◆) functions for: (a) New York/Washington; (b) Chicago; (c) San Francisco; (d) Los Angeles; (e) Houston; (f) Jacksonville.

Table 2
Characteristic values for failure behaviour of lead–calcium batteries

Parameter	Location						All batteries
	Washington/ New York	Chicago	San Francisco	Los Angeles	Houston	Jacksonville	
λ_0 (%)	0.6	0.7	0.8	0.6	1.5	0.5	0.7
λ_{stat} (%)	0.15	0.35	0.3	0.3	0.3	0.4	0.2
Δt_{stat} (m)	18	18	18	8	8	8	14
A λ_{late} (%)	0.00715	0.0286	0.0223	0.151	0.185	0.21	0.0728
B (m^{-1})	0.173	0.144	0.129	0.099	0.10	0.12	0.112
F(30) (%)	10	12	12	25	30	35	17

(i) the curves show considerable discontinuities in the initial phase;

(ii) the period of statistical failure is relatively short;

(iii) in the phase of late failure, the function $\lambda(t)$ falls again approximately after the 30th month.

These phenomena can be explained as follows.

(i) The low number of warranty claims made by service staff regarding statistical failure caused the discontinuities in this phase, especially in climatic zones where few of the batteries used in the experiment were located.

(ii) The field of statistical failure was reduced by a considerable number of batteries that suffered prior damage during transport and the subsequent storage time, an assumption confirmed on opening the batteries after about 4 months.

(iii) The decrease in the failure rate occurring after about 30 months could have been caused by the decreasing number of claims as the warranty periods (pro-rata system) ran out and by the disqualification of batteries with prior damage. Otherwise, the functions show the expected curves, and the climatic zone in particular is shown to have a considerable effect.

Table 2 sums up the characteristic statistical values supplied by the curves. The rate of early failure was above average in Houston only. The failure rate, which was virtually independent of the time ($\lambda_{stat} \approx$ const.) was only below average in Washington/New York, and in Jacksonville it was slightly below the unweighted mean value. The climatic zone had, however, a noticeable effect on the length of the period for statistical failure. This was 18 months for cooler climates, but only 8 months for the warmer zones.

The same results apply for the constants of the empirical equation

$$\lambda(t) \approx A \exp Bt \qquad (7)$$

in the phase of late failure. The A values for the cooler climates are almost an order of magnitude lower than those for the other regions. The B values are all of the same magnitude, a fact that points to similar failure mechanisms, but they show that, in the cooler zones, initial low failure rates are compensated for in the later phase, or that the reporting behaviour of the dealers was 'correct' over a long period. The cumulative failure probability as a unit of the reliability of the component 'battery' after 30 months (beginning of the bend in $\lambda(t)$) is very high, with values between 10% (Washington/New York) and 35% (Jacksonville). These values show that the failure behaviour of batteries is considerably more dependent on the accompanying conditions than on the mechanical or electrical components. This conclusion was confirmed by the representation of the characteristic functions for all lead–calcium batteries, which showed less variation (Fig. 4).

Compared with data from the European and American home markets, and regardless of the negligible differences in the characteristic values of the failure rates (Table 1), the probability is relatively high that about 17% of the batteries would have failed after 30 months. This demands a change in the technical and logistical conditions concerning batteries for export vehicles.

3.2. Diagnosis of battery failure

3.2.1. Assessment of early failure

After about 4 months, a sub-class of 8 batteries from a total of 18 that were complained about were examined as to the cause of failure. The principal cause was not a problem specific to lead–calcium batteries but was due to total discharge of the battery followed by a long standing time or manufacturing defects. Interpretation of the questionnaire described in Fig. 1 gave the following picture.

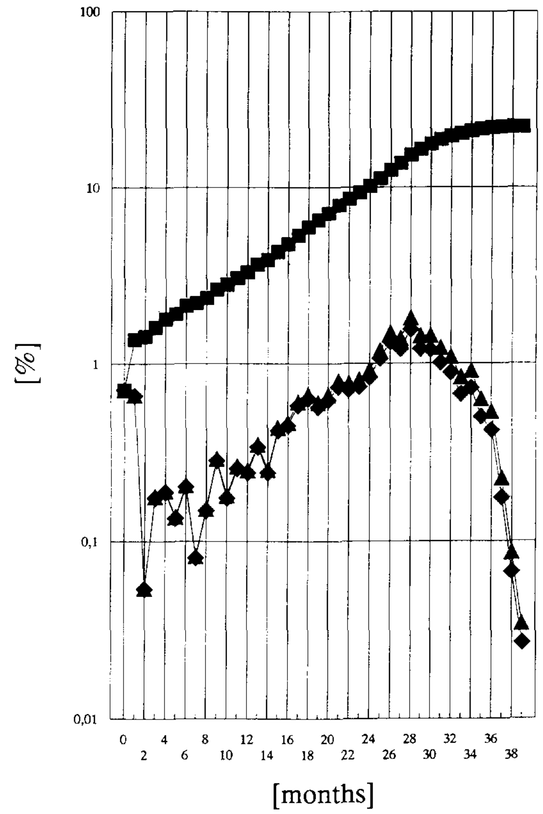


Fig. 4. Time dependence of $\lambda(t)$ (▲), $F(t)$ (■) and $f(t)$ (◆) functions for all lead–calcium batteries in the survey.

• Average time of operation (weeks) Range (weeks)	16.5 10–22
• Average mileage (km) Range (km)	70 0–131
• Complaint from the dealer	7 batteries
• Complaint from the customer (19 weeks, 2500 km)	1 battery

The diagnosing procedure described above yielded the following results:

• No defects (probably negative charging balance)	2 batteries
• Corrosion at low acid density (after total discharge)	4 batteries
• Manufacturing defects (plate assembly, incomplete filling with acid)	2 batteries

3.2.2. *Assessment after about 30 months*

The picture with regard to deterioration had changed completely since the first examination. Now the main cause of failure was grid corrosion, particularly in the outer cell, which faces the engine of the vehicle and is this subjected to the highest temperatures. A more precise analysis showed that very little erosion corrosion had taken place, for the bars of the grid were still of the original thickness. In contrast, the grid had broken into fragments, a fact which points to so-called stress-corrosion cracking.

The task of the manufacturer is thus to produce grids of more mechanical strength and, possibly, to tolerate small amounts of erosion corrosion.

The assessment of 12 questionnaires (Fig. 1) led to the following results.

• Average standing before sale (months)	5
• Average age of battery (months)	30
• Average mileage (km)	30 000–80 000

- One battery with a standing time of 13 months and a mileage of only 9000 km was assessed separately.

The diagnosing method, used on 12 batteries, has the following results.

• No defects (probably negative charging balance)	1 battery
• Short-circuit due to grid growth (corrosion) (5 batteries of which in outer cells facing the engine)	8 batteries
• Separator defect (manufacturing defect)	1 battery
• Completely sulfated	1 battery
• Cause not clear	1 battery

These results are in complete agreement with those given in Ref. [4].

4. Discussion of the results

The planning, supervision and conditions of the experiment ensured a high degree of validity of the results. The conclusion to be drawn from this large-scale experiment is equally clear. Statistically, the reliability of maintenance-free batteries with lead–calcium alloys manufactured in 1989 is comparable with that of other average automotive batteries.

After elimination or reduction of the frequent causes of battery failure, the vehicle export business should also be able to give good service to its customers with lead–calcium batteries. Some of the changes that have already been introduced include: (i) safer battery manufacture; (ii) lead–calcium alloys that prevent intercrystalline strain-corrosion cracking in cast positive grids by means of finer grain and higher mechanical strength; (iii) the interruption of the rest current during the transport and storage of vehicles.

The methods of characterizing battery reliability that were used in this study have proved to be of practical value. Now that the development and manufacture of different battery systems have reached a very high standard, the derived characteristics can help to compare their behaviour in specific cases.

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