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Failure mechanisms of lead/acid automotive batteries in service in the U.S.A.

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Abstract

Discarded lead/acid batteries were selected at random without regard to brand or condition and these were inspected and tested to determine the causes of failure. Samples were limited to 12-V automotive passenger-car batteries. Their age was determined from the manufacturing code and shipping date. In addition to the cause of failure, information on battery components and construction was also noted. Data are presented showing the principal modes of failure, the effect of geographical location, and the influence of grid alloy on life. In particular, the differences observed between those batteries utilizing calcium alloy for the positive grids and those using antimony alloy are discussed.

Introduction

Periodically, surveys are conducted in the U.S.A. of the failure mechanisms of batteries that have been removed from service. These surveys, the last of which was carried out in 1989, provide very useful information on the cause(s) of battery failure and also allow conclusions to be drawn on the effects of such variables as geographical location and type of battery construction.

In the U.S.A., most batteries built for automobile starting use antimonial alloys for the positive grids and calcium-containing alloys for the negative grids. A sizeable, and growing minority use calcium alloys for both grids. The 1989 survey indicates that approximately 25% of the batteries in service today are made with both positive and negative grids cast from calcium alloy. Although it is recognized that calcium alloys may also contain various amounts of tin and aluminium, for the sake of brevity, these will be referred to generically as calcium alloys.

The reasons why calcium-containing alloys are used by battery manufacturers are well known. These alloys show a higher hydrogen overvoltage than antimonial alloys, resulting in lower water loss during charging, have increased electrical conductivity (see Table 1), and are sufficiently

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TABLE 1

Resistivity of lead alloys

Alloy	Resistivity ($\mu\Omega$ cm^{-1})
Pb	20.65
Pb/Ca	21.9
Pb/2%Sb	22.7
Pb/4%Sb	24.0
Pb/6%Sb	25.2

malleable to be processed by progressive expansion and continuous casting techniques.

On the other hand, they are softer, which can give rise to increased scrap, and are also subject to intergranular corrosion, which can result in grid growth particularly at high temperatures (see Table 2).

These features of calcium alloys permit the construction of batteries having very high cranking currents and low water loss. On the other hand, the susceptibility to enhanced corrosion at high temperatures [1, 2] suggests that batteries made from calcium alloy positive grids will suffer premature failure in geographic areas where summer temperatures are high, or where high under-the-hood temperatures are experienced.

Another significant problem with positive plates made with calcium alloy grids is the so-called 'barrier-layer effect' that results in poor charge acceptance following a deep discharge. In extreme situations, such as where an automobile has been left with its lights on for an extended period, it may be impossible to recharge the battery.

Field surveys of batteries reveal the cause(s) of failure under real operating conditions. In the present study, an analysis was made of effects of new technologies, such as lower antimonial lead and non-antimonial alloys, expanded metal, and the use of envelope separators. Many different modes of failure were detected and analyzed, and these were compared for various

TABLE 2

Rate of ageing of lead alloys

Ageing time (min)	Hardness (Rockwell R Scale)	
	Pb–2.75%wt.Sb	Pb–0.09wt.%Ca–0.3wt.%Sn
0	40	0
10	75	32
20	81	44
40	81	53
60	81	58

geographic regions of the U.S.A. where under-the-hood temperatures varied over a wide range.

This survey was conducted by selecting scrap batteries without regard for brand or condition, except that those that were obviously broken were discarded. Samples were limited to 12-V automotive passenger-car batteries. The age was determined from manufacturing code and shipping date. Since shipping dates were not always available, the manufacturing data was used. The mean difference between manufacturing and shipping dates, for batteries having both codes, was three months.

The batteries were tested in accordance with the procedure outlined in the BCI Battery Service Manual [3]. In addition to the cause of failure, information on battery components and construction was also noted.

The percent of total batteries sampled by group size compares well with the unit sales by group size as reported by the BCI for the years 1985 through 1988 (see Table 3).

The causes of failure were classified into twenty-eight separate categories. These were then summarized into the following six major categories:

- open circuits: includes cell-to-cell, broken straps, and cell-to-terminal
- short circuits: includes plate-to-strap, plate-to-plate (plate fault, separator fault, and sediment/moss related), and hydration
- plate/grid related: includes grid corrosion, paste adhesion, negative shrinkage, soft positive material, sulphation, and dropped/loose plates
- worn out/abused: includes undercharged, overcharged, low electrolyte level, severe terminal corrosion, vibration, and worn out.

TABLE 3

Percent of total batteries sampled by group size compared to BCI reported sales: 1985–1988

BCI group size	Percent of total	BCI unit sales—replacement and OEM (%)			
		1985	1986	1987	1988
24	18	21	18	17	16
74	11	14	11	10	9
70	8	5	8	9	8
24F	7	11	10	10	10
75	6	6	6	7	8
26	6	4	7	6	6
58	5	3	4	6	6
22F	4	3	2	2	1
71	3	5	3	2	1
78	3	3	3	4	4
55	2	1	2	2	2
26/70	2		1	2	5
64	2	2	3	2	2
62	2	2	2	2	2
27	2	2	2	2	1

- serviceable: includes batteries that were still in working condition, either charged or discharged
- broken: includes broken container, broken cover, damaged terminals, external or internal damage, container/cover leakage, and terminal leakage.

Because of difficulties in the interpretation of the mechansim of failure, some overlapping of categories could have occurred. The most likely categories for this are grid corrosion, worn out and abused-overcharged. Because of the similar appearance of the three categories, the technicians performing the analysis had to make their decision on the basis of other factors, e.g., age and external appearance. Another category that requires clarification is plate-to-strap short circuit. Almost all of these were due to grid growth and are therefore life related. The average life before removal from service of 48 months bears this out.

Batteries were sampled from 24 cities throughout the U.S.A. This provided a very good coverage of different geographical locations and climates (see Fig. 1 and Table 4).

Results and discussion

Examination of the batteries showed that 10.2% were still serviceable, while 4.15% were broken. Plate- and grid-related problems accounted for one-third of all failures. Remaining classifications were: short circuits at 22%; worn-out/abused at 17%; and open circuits at 13.7%. These data are shown in Fig. 2.

Batteries found to still be serviceable had the shortest mean life of 31 months (see Fig. 3). Open circuits averaged 36 months before removal. Broken and damaged was 37 months. Short circuits and plate/grid-related failures both averaged 45 months. Worn-out/abused had the longest mean time before removal of 53 months. When grouped together, the average battery life in the survey was 43 months. When serviceable and broken

TABLE 4

Cities that were used to obtain failed batteries

Phoenix, AZ	Greensboro, NC
Los Angeles, CA	Raleigh, NC
Miami, FL	Lockport, NY
Orlando, FL	Columbus, OH
Tampa, FL	Philadelphia, PA
Atlanta, GA	Pittsburgh, PA
Fort Wayne, IN	Dallas, TX
Baltimore, MD	Houston, TX
Detroit, MI	San Antonio, TX
St. Joseph, MO	Bennington, VT
St. Louis, MO	Seattle, WA
Charlotte, NC	Portland, OR

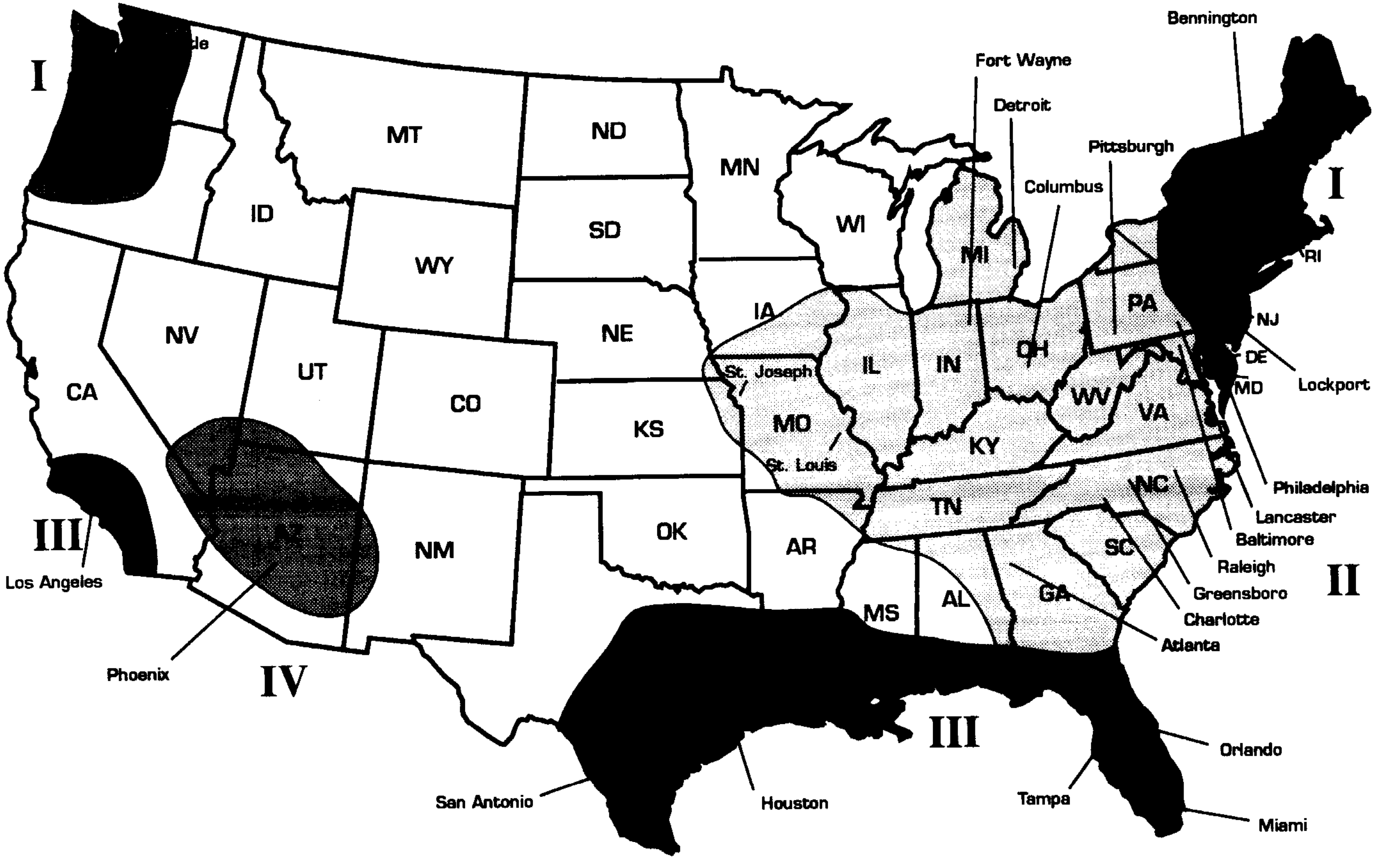

Fig. 1. Locations used in survey of failed batteries.

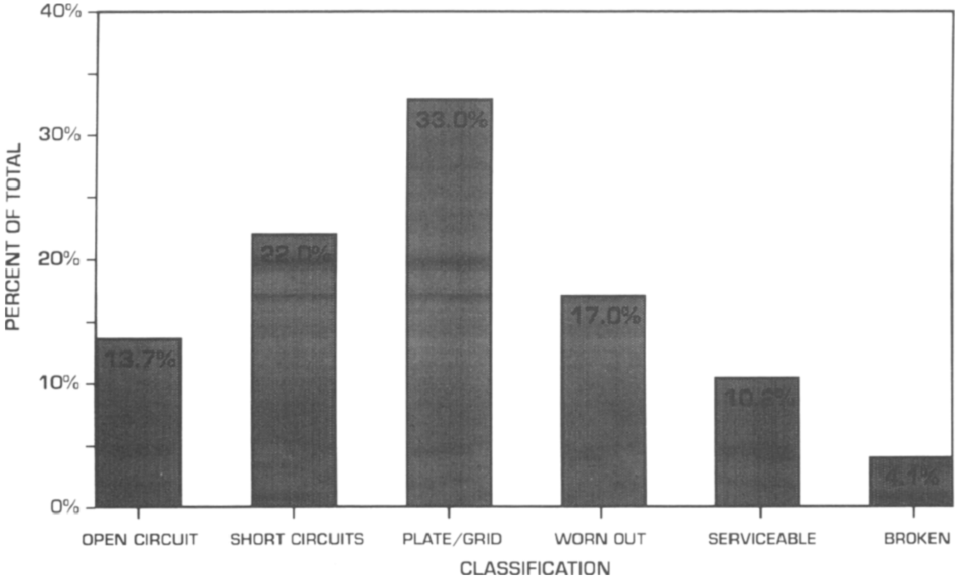

Fig. 2. Why batteries were returned: 1990 survey.

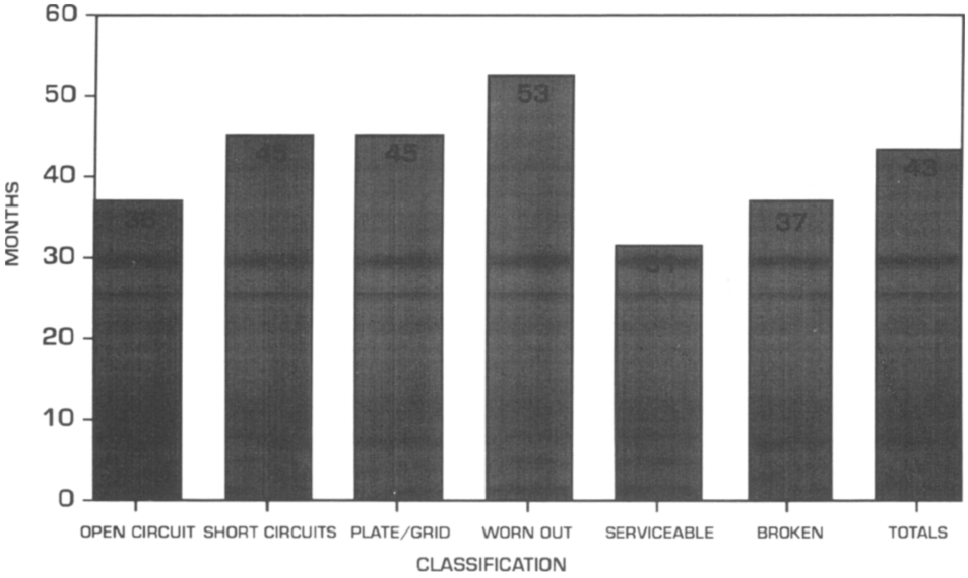

Fig. 3. When batteries were returned: 1990 survey.

containers and covers are removed, it is 44 months. This is an increase of 10 months over a similar survey conducted in 1982.

Open circuits dropped by 1% between surveys, viz., 13.7% compared to 14.7% in 1982. At the same time, the mean life increased by seven months from 29 to 36 months (see Fig. 4).

Short circuits increased from 14.5% to 22.0%. This is probably due to the increased incidence of grid growth which, in turn, results from the increased population of batteries utilizing calcium alloys. The life before failure increased from 27 to 45 months, or 1.5 years longer (see Fig. 5).

Plate/grid-related failure increased slightly from 30% in 1982 to 33%. But, again, the mean time before failure increased by almost one year, viz., 45 months compared with 35 (see Fig. 6).

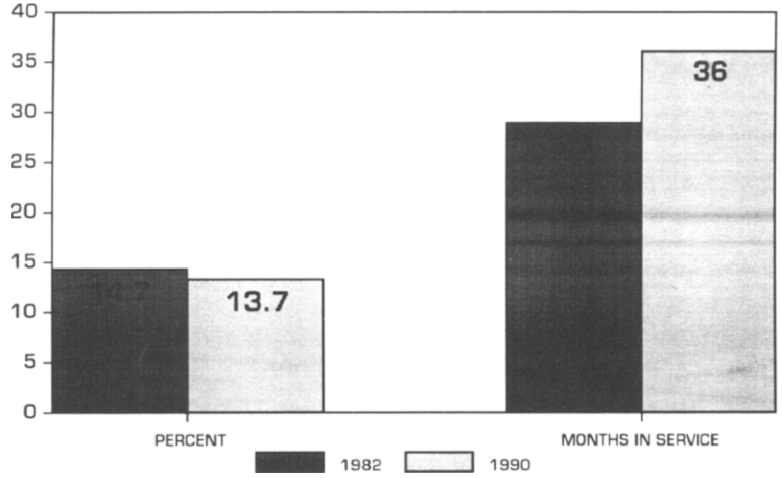

Fig. 4. Open circuits: 1990 vs. 1982.

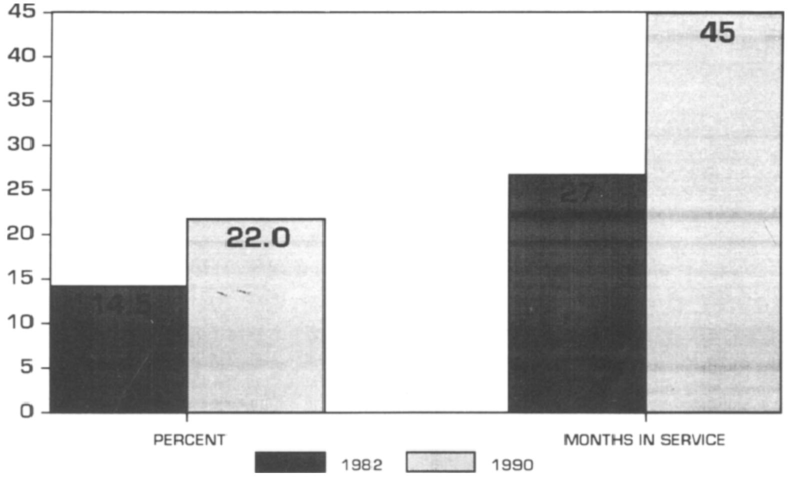

Fig. 5. Short circuits: 1990 vs. 1982.

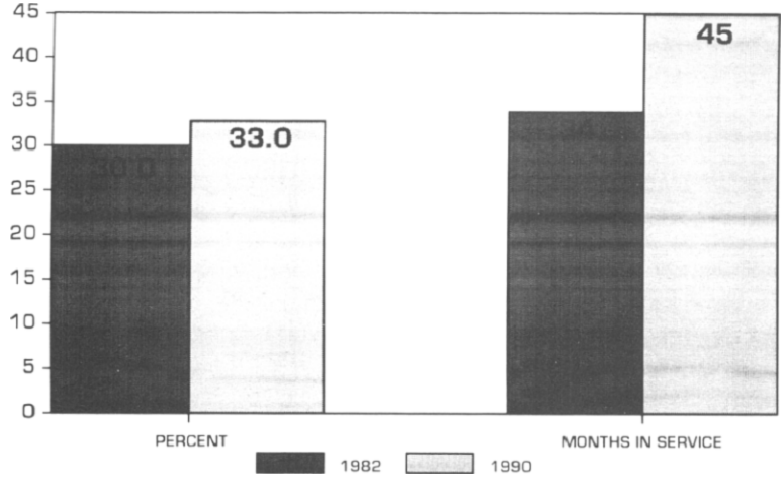

Fig. 6. Plate/grid related: 1990 vs. 1982.

Figure 7 shows that the category of worn-out/abused remained almost constant at 17.0% compared with 17.2%. Life increased five months to 53 months.

Serviceable product life was 31 versus 20 months and had only 10.2% of the total compared to 16.0% in 1982 (see Fig. 8).

The average life of those batteries that were found to be broken or damaged increased from 30 months to 37 months, while the percentage found in this category fell from 8 to 4.1 (see Fig. 9).

Differences in battery life as a result of the choice of antimonial alloys or calcium alloys for the postive grids would be expected to show up at high

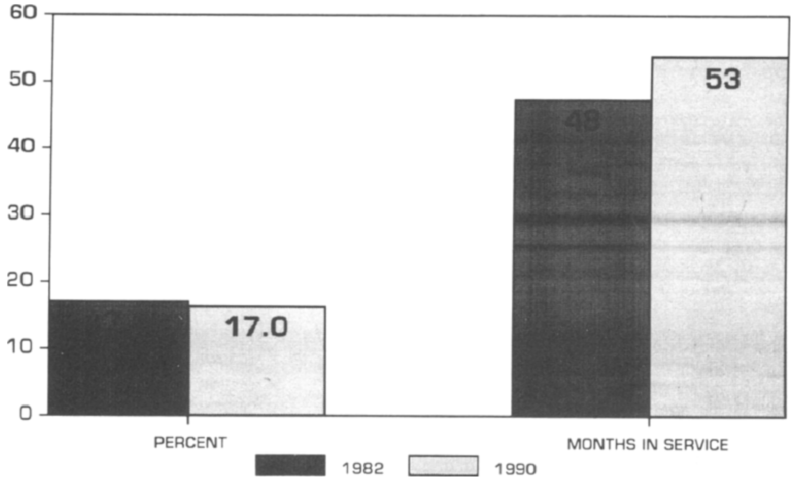

Fig. 7. Worn out/abused: 1990 vs. 1982.

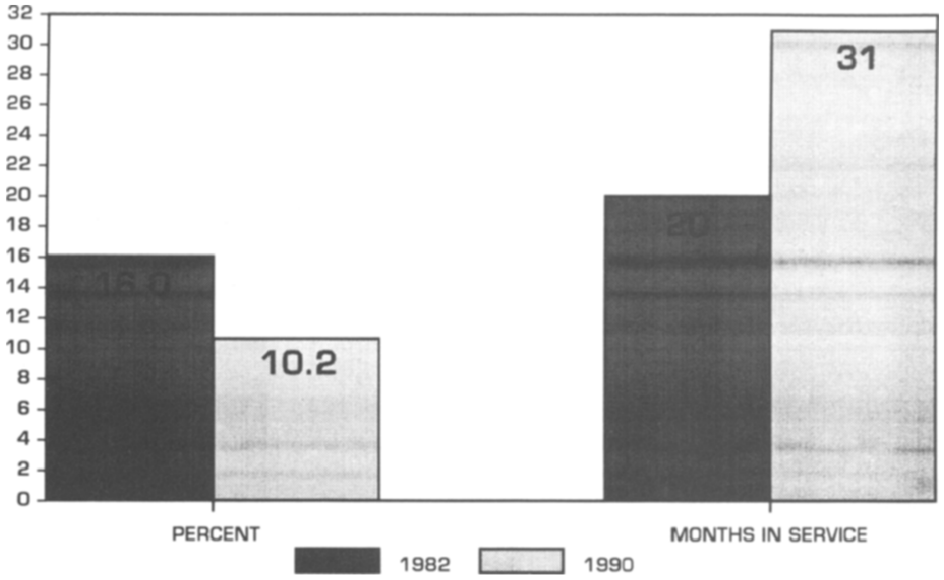

Fig. 8. Serviceable: 1990 vs. 1982.

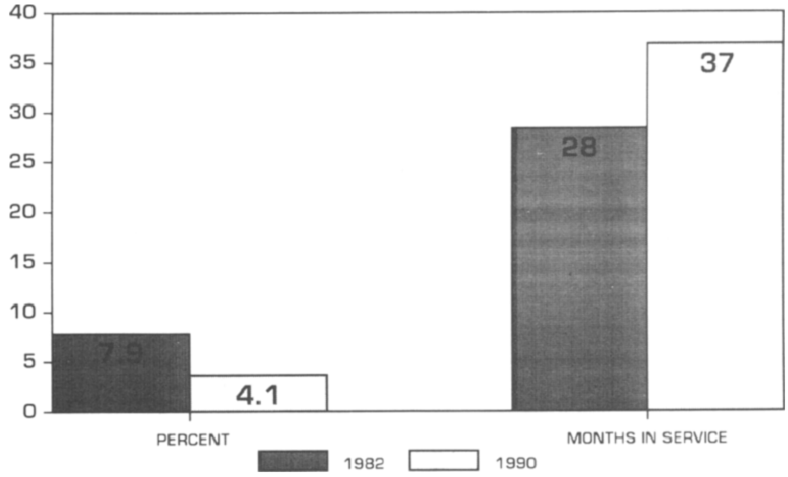

Fig. 9. Broken/damaged: 1990 vs. 1982.

temperatures. For this reason, it was decided to explore in more detail the effect of temperature on battery life. Modern vehicles designed with low hood profiles to reduce drag also reduce the amount of air being taken into the battery compartment. This increases under-the-hood temperatures, which, when combined with high ambient temperatures, can result in reduced battery life.

Battery age to failure collected from cities where 50 or more samples were obtained is compared in Table 5 with climatological data from the 1988

TABLE 5

Comparison of battery life to climatological data

Location	Average age from manufacture	Annual mean temperature	Average no. of days	
			>90 °F	<32 °F
Bennington, VT	55	47	27	143
Portland, OR	56	54	17	32
Seattle, WA	54	53	3	18
Atlanta, GA	40	62	59	50
Charlotte, NC	48	60	55	48
Greensboro, NC	48	57	45	90
Raleigh, NC	48	58	51	79
Columbus, OH	46	52	43	138
St. Louis, MO	47	57	65	93
St. Joseph, MO	49	55	6	115
Miami, FL	39	77	95	0
Orlando, FL	39	72	85	0
Tampa, FL	41	72	100	1
Dallas, TX	42	66	104	47
Houston, TX	40	69	112	21
San Antonio, TX	40	70	121	24
Los Angeles, CA	38	63	6	0
Phoenix, AZ	31	76	190	4

National Oceanographic and Atmospheric Administration summaries. Little correlation is found between the average age when removed from service and the number of days with temperatures minima less than 32 °F (Fig. 10). The correlation coefficient is calculated as 0.605. On the other hand, when the average age is compared with the number of days with temperature maxima greater than 90 °F, a higher correlation is apparent (−0.717), Fig. 11. A better correlation is seen when age is compared with annual mean temperature for that location. The correlation is −0.873 (Fig. 12).

These comparisons verify previous knowledge: higher temperatures, not lower, shorten the life of a battery. If batteries can be protected from higher temperatures, longer life can be expected.

As noted earlier, batteries were sampled from 27 cities. These were grouped, by climate and similar age, into four major areas with similar ages and characteristics. The average life before removal from service varies from a high of 52 months in the northwest and northeast to a low of 31 months in the desert southwest (see Table 5 and Fig. 13). All categories, except serviceable, follow this pattern of the longest life in the northwest/northeast and the shortest life in the desert southwest.

As shown in Fig. 14, open circuits averaged from a high of 45 months down to 25 months. The percent of total failures was in inverse proportion with the age. Open circuits were 8.2% of the total in area I and 19.1% in area IV.

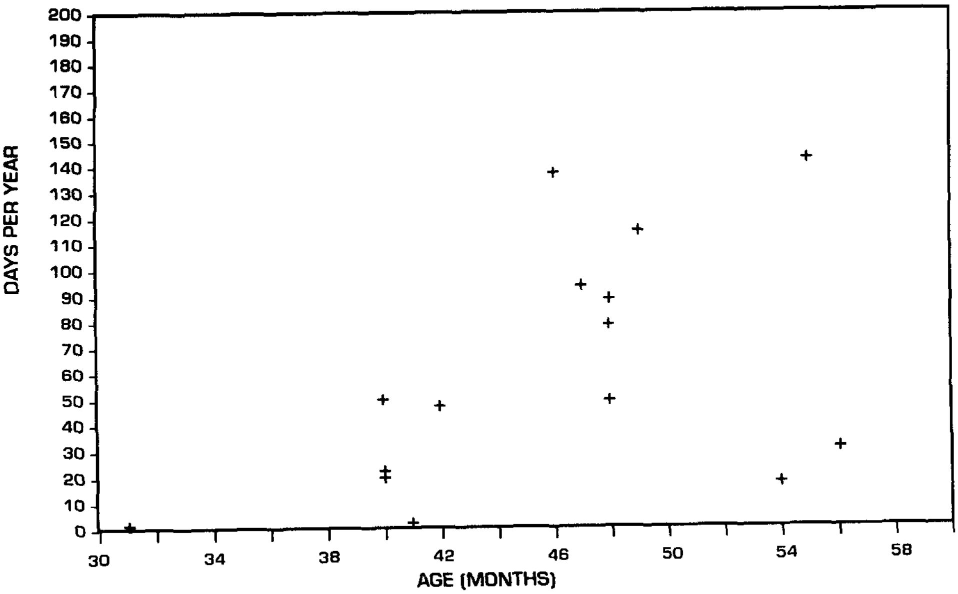

Fig. 10. Age vs. average days < 32 °F.

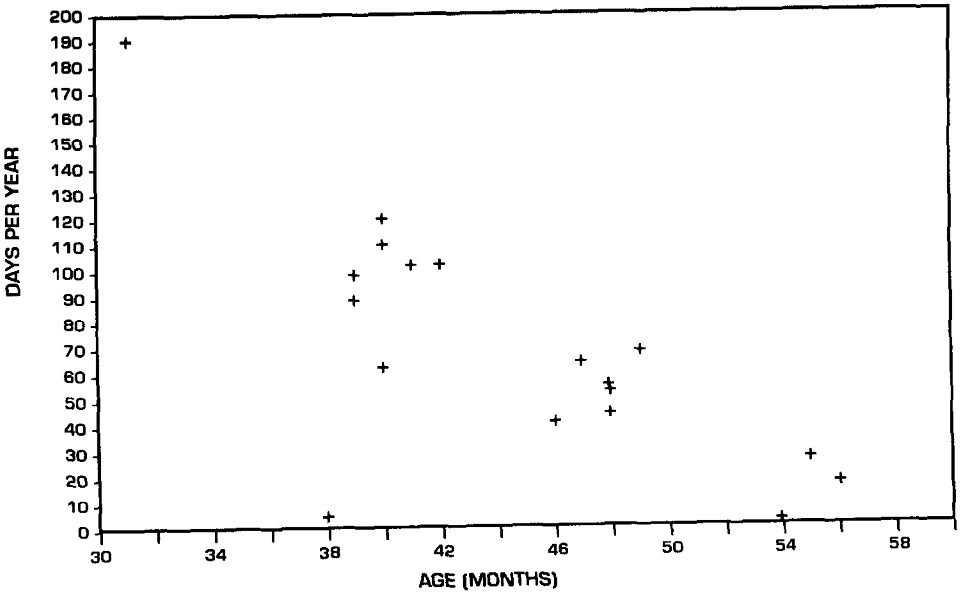

Fig. 11. Age vs. average days < 90 °F.

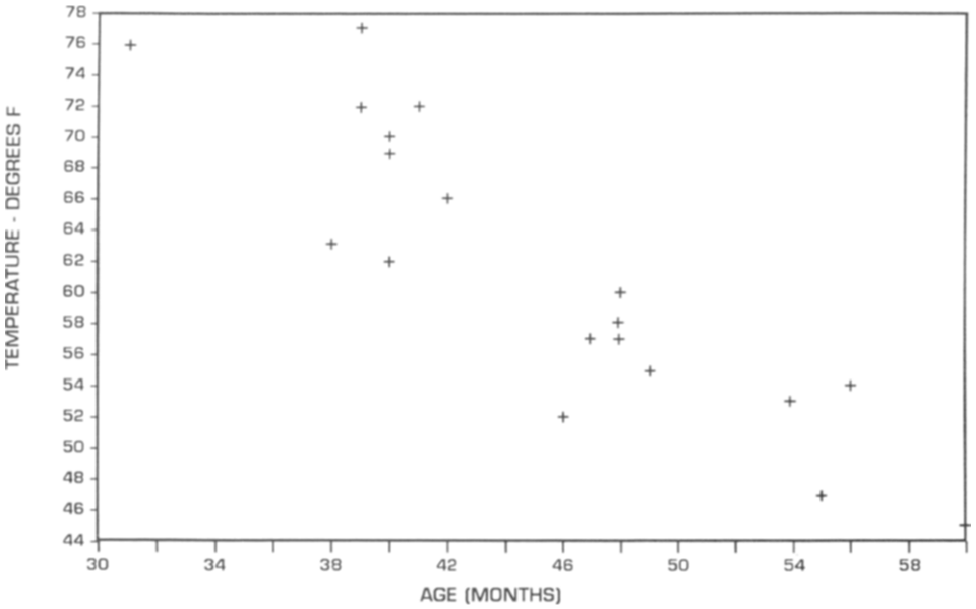

Fig. 12. Age vs. annual mean temperature.

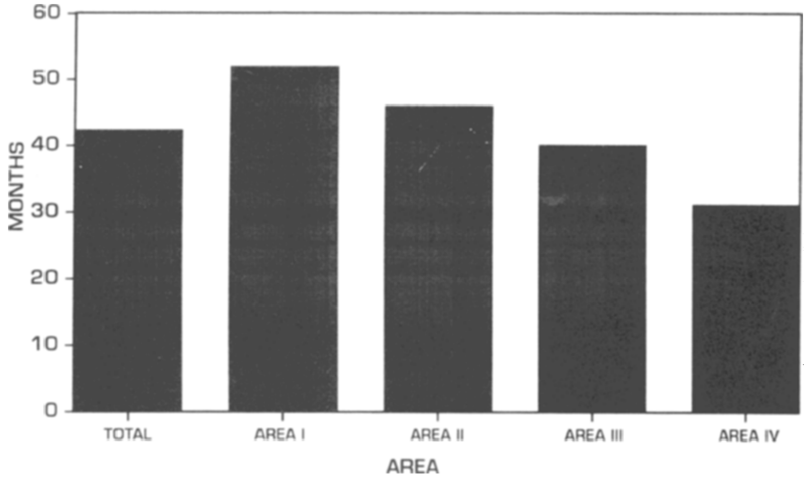

Fig. 13. Age when removed from service: by area.

Short circuits follow the same age trend, see Fig. 15. A high of 54 months down to 32 was observed. All areas had close to the same proportion, ranging from 18.9% to 24.5%.

Plate- and grid-related failures ranged from 56 to 36 months. The percent of total revealed no relationship between areas, ranging from a low of 26.1% up to 42%, see Fig. 16.

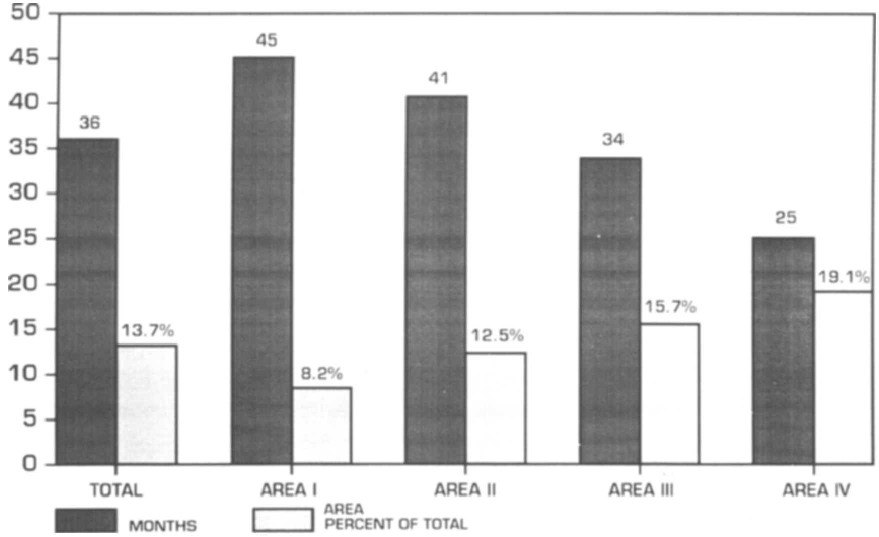

Fig. 14. Open circuits: by area.

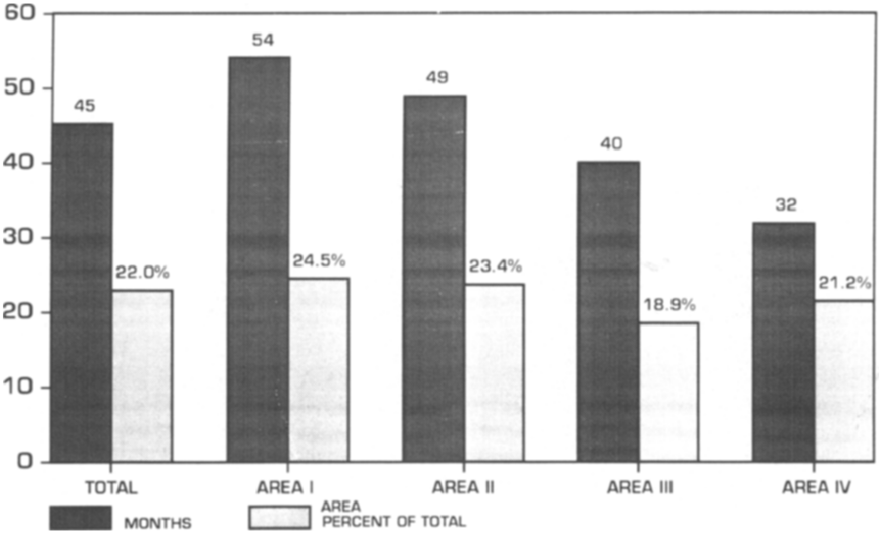

Fig. 15. Short circuits: by area.

Worn-out/abused ranged in age from 62 months down to 27 months. Again, no relation between areas is noted in the percent of total, ranging from a low of 3.2% up to 22.5%, see Fig. 17.

With regard to construction, 70% of the batteries analyzed had accessible vents, with the remainder being non-accessible. The percent of serviceable product in these categories is virtually the same, indicating there is no problem with checking of the product.

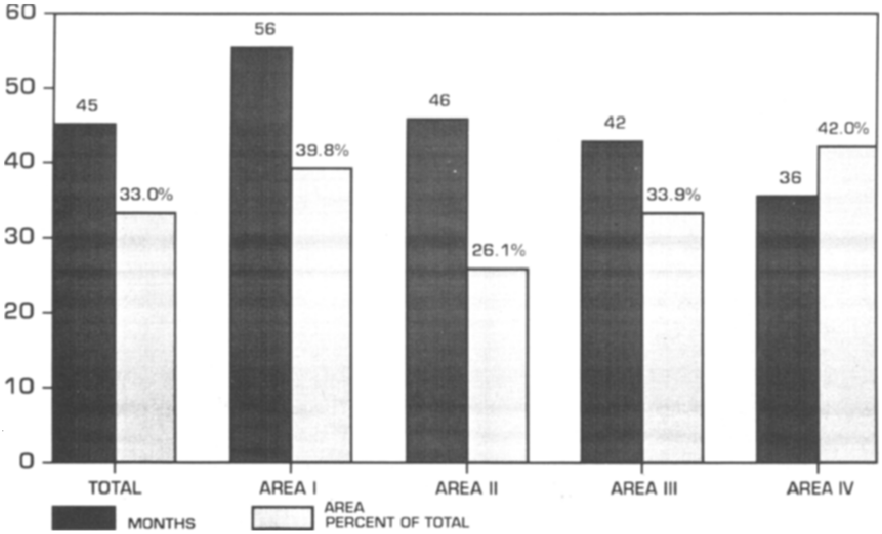

Fig. 16. Plate/grid related: by area.

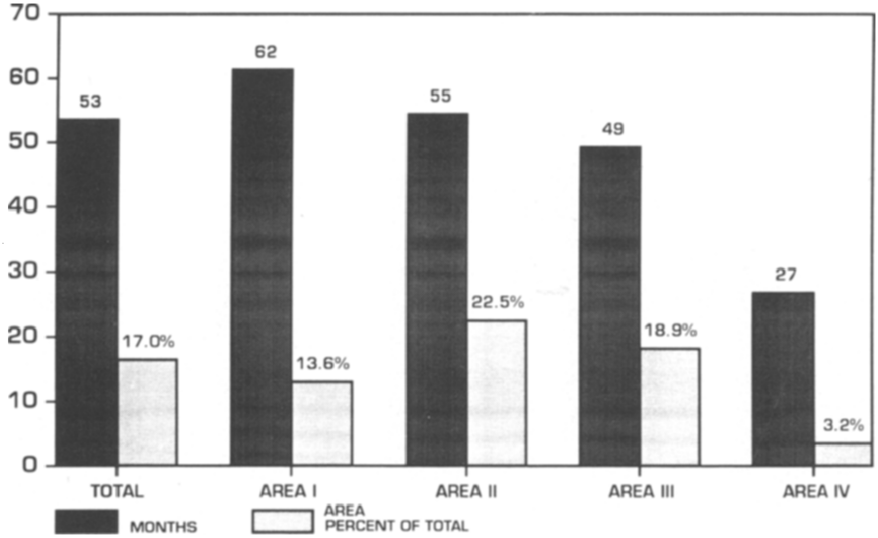

Fig. 17. Worn out/abused: by area.

A total of 70% of the batteries had both positive and negative cast grids; 25% had both expanded positive and negatives, while 5% were mixed, Fig. 18. It can reasonably be assumed that the majority of batteries with cast positive plates were manufactured from antimonial alloys, while those with expanded positive grids were made from calcium alloys.

Significant differences in the cause(s) of failure were observed between the two classes of construction. For example, the most common cause of

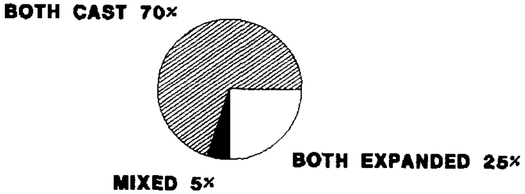

Fig. 18. Grid types.

failure of batteries with antimonial positive grids was corrosion, while for batteries with calcium positive grids it was growth. The percentage of total failures caused by these two conditions is given in Table 6.

Since the present principal cause of failure in batteries in the U.S.A. is corrosion of the positive grids, this suggests that the most fruitful line of research to further increase battery life will be the development of grid alloys that have improved corrosion resistance. Further improvements in grid production technology that would yield improved grain structure and uniformity will also lead to improved life.

One of the most important questions that can be addressed from the data obtained in this survey is that of life expectancy of batteries utilizing positive grids made from antimonial or calcium alloys. In addition, conclusions can be drawn concerning the effect of temperature on their life.

Table 7 presents the average life to failure of batteries utilizing cast positive grids (which can be assumed to be antimonial alloy with a high degree of certainty), and those utilizing expanded positive grids which will almost certainly be made from calcium alloys. In interpreting the data, it should be pointed out that the population of batteries with cast positive and expanded negative grid construction was low compared with those where both grids were either cast or expanded, therefore the data for this type of construction may not be statistically significant.

TABLE 6

Percentage of total battery failures attributable to corrosion (C) and grid growth (G)

	Region							
	I		II		III		IV	
	C	G	C	G	C	G	C	G
Cast/cast	50	3	33	6	39	3	47	2
Cast/expanded	30	15	42	0	67	0	64	0
Expanded/expanded	5	76	8	57	16	44	6	85

TABLE 7

Average age to failure of batteries with various alloy combinations (months)

	Region			
	I	II	III	IV
Cast/cast	57	49	40	32
Cast/expanded	53	39	34	37
Expanded/expanded	56	54	48	34

The data show that the difference in the average age to failure for batteries made from antimonial or calcium positive grids is not appreciably different. Surprisingly, perhaps, both types are affected equally by temperature, despite the reported acceleration of the corrosion of calcium alloys at elevated temperatues.

This survey did not include a study of such important characteristics as water loss and deep-discharge recovery. One would expect that batteries utilizing antimonial positive grids would lose water at a more rapid rate than those with calcium positive grids because of antimony transfer to the negative plate and its effect of reducing the hydrogen overvoltage. Batteries with calcium alloy positives might be expected to experience deep-discharge recovery problems because of the barrier layer effect. The observation that there is no difference in life between the two types of construction may indicate that the growing use of low-antimony alloys has resulted in a reduction of water loss during charging and that the use of calcium alloys containing tin has reduced the problem of deep-discharge recovery.

Clearly the data in this survey show that from an applications and durability standpoint, little difference will be seen in batteries utilizing either antimonial or calcium positive grids. Both antimonial and calcium positive alloys have been improved to the point that the alloy type has little bearing on life. Grain structure and uniformity appear to be the key to achieving longer life.

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