

## Short Communication

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# Changes in the morphology and structure of positive active material of starter batteries as a consequence of their use in vehicles

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### Abstract

The changes in the structure, morphology and composition of the positive active mass of lead/acid starter batteries under normal use in vehicles were investigated. The softening of the active mass as a function of the service life of the batteries was clearly seen on the basis of the methods of analyses used in this study.

### Introduction

The pastes for conventional pasted lead/acid battery plates are prepared by mixing incompletely oxidized lead powder (leady oxide) with water, sulfuric acid and sometimes additives. The battery plates are produced by applying the paste containing lead sulfates, lead oxides and metallic lead into a lead alloy grid. The pasted plates are then subjected to curing and drying procedures during which the metallic lead particles are oxidized, the active mass/grid contact as well as the mechanical strength of the active mass are improved and water is evaporated from the plates. After curing, the plates are electrochemically charged for the first time ('formed') in sulfuric acid solution. This converts the lead compounds of the active mass to lead dioxide ( $\text{PbO}_2$ ) on positive plates, or to metallic (sponge) lead on negative plates. Lead sulfate ( $\text{PbSO}_4$ ) is formed on both plates during discharge [1–3].

In addition to the reversible charge/discharge reactions, some irreversible reactions take place, especially in the positive plates during service, limiting the lifetime of a lead/acid battery. There are two major causes of the limited lifetime of lead/acid batteries: (i) anodic corrosion of the lead alloy grid and (ii) softening and shedding of the active material. Both processes change the structure of the positive plate and, hence, the performance of the battery in an unfavourable way during the cycle life [4].

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Positive lead/acid battery active material has been investigated, at various stages of production, from the partially oxidized lead powder manufacture through to the electrochemical formation of the finished plates. In order to develop positive plates with a higher stability and thus batteries of improved performance, the nature of the grid/active mass interface and the interparticle bonding in the active mass, as well as the mechanism of the charge and discharge reactions, have been investigated. Crystallographic and compositional changes in the active material have been studied by microscopy, X-ray diffraction and wet-chemical methods.

In the laboratory tests, electrochemical phenomena and changes in phase composition and morphology in the lead/acid battery electrodes have usually been investigated under cranking conditions. The behaviour of the electrodes might be different at a low rate of discharge [5] and, in practice, the service life of a starter battery is composed of both periods of high rate discharge/charge due to the cranking and those usually of a lower rate discharge/charge due to a variable use of accessories. In addition, there is always more or less vibration present when driving a vehicle.

Many comprehensive laboratory investigations on positive active masses have been reported [6–8]. However, very little has been published on SLI battery field tests where the positive active masses of batteries are monitored during real use in vehicles. Although simulated cycling, shaking and capacity tests carried out in laboratories, combined with characterization of active masses give valuable and useful information about the active masses and batteries, there is still at least a slight uncertainty about the correlation between the laboratory test conditions and the practical conditions. Therefore, by using field tests, where the battery is subjected to all practical conditions simultaneously for a sufficiently long time, the final applicability of the laboratory test results to the real-life systems can be seen. In spite of the fact that it is difficult to evaluate the effects of different parameters on the active mass in the field test, they might, however, provide a battery manufacturer with the most desired information.

The aim of the present study was to use the starter batteries in actual service and monitor the changes in structure and morphology of the positive active mass periodically by some widely used analytical methods. The batteries monitored were installed in cars of the same make and model, and the daily use of the cars was expected to be rather similar. The length of the monitoring period of this study was two years.

## Experimental

The test batteries were 60 Ah starter batteries with low antimony grids. The annual mileage of the batteries are given in Table 1.

One third of the batteries were tested and characterized immediately after production, a second third after one year's use and the last third after two years use in the vehicles. With the first third, however, some further charge/discharge cycling was needed after formation to remove the basic lead sulfates from the active mass and to render the paste more appropriate for the charge/discharge process. The increase of the DIN  $C_{20}$  capacity by approximately two Ah indicated the completion of that procedure.

The capacity (DIN  $C_{20}$ ) measurements were performed on all batteries investigated. One half of the cells in the batteries subjected to monitoring tests were charged and the second half were completely discharged. The differences in the structure and morphology of the active mass were expected to be most easily observable at the two extreme charging stages of the plates.

TABLE 1

DIN  $C_{20}$  capacities of the test batteries as a function of time in use

Age (annual mileage)	DIN $C_{20}$ capacity (Ah)
New (0 km)	72.1
New (0 km)	72.9
Used 1 year (23000 km)	69.8
Used 1 year (26000 km)	70.7
Used 2 years (21000 km)	69.7
Used 2 years (37000 km)	69.6

After charge/discharge the positive plates of the batteries were removed from the batteries and handled according to the procedure of Rand [9] prior to the analysis. The positive active mass was obtained from 12 grids (3 cells, 4 grids per cell). The mass particles were gently ground to a powder for the analyses.

The X-ray powder diffraction analyses were carried out on a Siemens D500 powder diffractometer. The identification of the crystalline phases in the positive active masses prior to the quantification was performed with the help of the JCPDS (Joint Committee on Powder Diffraction Standards) reference data. The quantification of the crystalline phases was done by PEAKS [10], a routinely used quantitative X-ray powder diffraction PC program.

The specific surface area and particle size distribution of the positive active masses were measured on an ASAP 2400 BET instrument and Sympatek Rodos light-scattering equipment, respectively. Electron microscopic studies of the active masses were carried out by a JEOL JSM-840A scanning electron microscope.

## Results and discussion

### *Capacity measurements*

Prior to the other analyses, the batteries were subjected to the capacity (DIN  $C_{20}$ ) measurements. The capacity results are given in Table 1. There was a slight decrease in the average capacity of the batteries as a function of service life. The loss of capacity is caused by breaking of the current transportation routes and formation of the paste particles which cannot participate in the charge/discharge process. This is a consequence of 'pulsing' – the expansion and contraction of the active material during cycling, due to the density differences of lead sulfate and lead dioxide.

### *Phase composition by X-ray diffraction*

After the preparation procedure described in the experimental chapter, the charged and completely discharged active masses were subjected to X-ray powder diffraction analysis to analyse the phase composition of the masses. The phase composition was calculated from the diffraction peak intensities by the PEAKS program, and the results have been given in Table 2. The completeness of the charge/discharge reactions can be estimated from the relative phase composition.

The results in Table 2 show that the lead sulfate content of the discharged active masses decreased as a function of the service life of the battery. This means that

TABLE 2

The phase composition of charged and completely discharged positive active masses of the test batteries after different service life; concentrations are given as wt.%

Age (condition)	PbSO <sub>4</sub>	β-PbO <sub>2</sub>	α-PbO <sub>2</sub>
New (discharged)	93.7	6.3	traces
New (discharged)	91.3	8.7	traces
Used 1 year (discharged)	81.6	18.4	traces
Used 1 year (discharged)	85.0	15.0	traces
Used 2 years (discharged)	71.5	28.5	traces
Used 2 years (discharged)	78.2	21.8	traces
New (charged)	1.2	98.8	traces
New (charged)	1.5	98.5	traces
Used 1 year (charged)	7.4	90.2	2.4
Used 1 year (charged)	5.4	94.6	traces
Used 2 years (charged)	14.6	85.4	traces
Used 2 years (charged)	10.3	89.7	traces

either the discharge proceeded further in new plates than in used plates or the crystallite size distribution/crystallinity of the phases changed dramatically as a function of the use. The X-ray diffraction results for the discharged masses also show that the tetragonal lead dioxide content of the positive active mass increased as a function of the service life of the battery.

Orthorhombic lead dioxide was identified both in charged and discharged active masses, but the relative diffraction peak intensities of this phase were too low to obtain any numerical concentration values from calculations by the PEAKS program. Only one charged active mass, which had been in use for one year, had a significant amount of orthorhombic lead dioxide. That mass contained 2.4% of α-PbO<sub>2</sub>.

The composition of the charged masses indicated the growth of the content of lead sulfate which cannot be transformed to lead dioxide during charge as a function of the service life of the batteries. The completeness of the charge/discharge was checked by measuring the density of the electrolyte solution of the batteries.

#### *The specific surface area and particle size distribution*

The active masses were also analysed by both a BET surface area and a particle size analyser. The results obtained are given in Table 3. The specific surface areas of both charged and discharged active masses increased as a function of service life of the batteries. Also, the size below which 50 population per cent of the particles existed, increased as a function of the service life both in charged and discharged masses. The particle size in Table 3 is consistent with the density differences of PbO<sub>2</sub> and PbSO<sub>4</sub>, i.e., PbSO<sub>4</sub> having a lower density gives a greater particle size. Therefore, the softening process of the plates is also evident on the basis of these results. The higher surface area of charged active masses is due to the crystallite morphology of PbO<sub>2</sub> having much more convoluted surface than PbSO<sub>4</sub>.

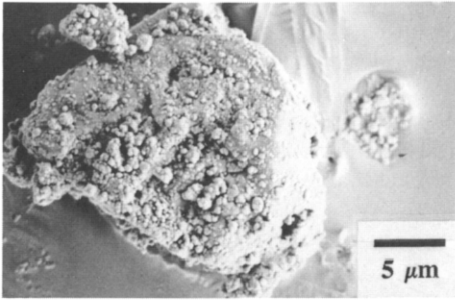
#### *Scanning electron microscopy*

The active masses were analysed by scanning electron microscopy (SEM) in order to find some changes in their morphology. The increasing porosity of active masses as a function of service life can be clearly seen in Fig. 1, which shows the SEM

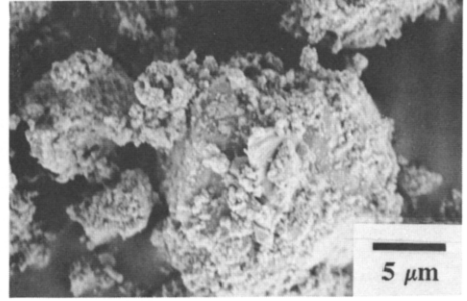
TABLE 3

Specific surface areas (SA) and particle size distributions (given as a size below which 50% of the particle population existed) of charged and discharged positive active masses of the test batteries as a function of service life

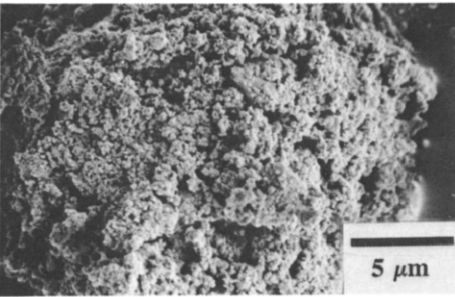
Age (condition)	SA (m <sup>2</sup> /g)	size (μm) < 50% population
New (discharged)	0.84	23.0
New (discharged)	1.06	23.2
Used 1 year (discharged)	1.91	28.0
Used 1 year (discharged)	1.38	27.6
Used 2 years (discharged)	2.05	28.4
Used 2 years (discharged)	2.12	29.1
New (charged)	3.63	31.1
New (charged)	3.78	31.6
Used 1 year (charged)	4.24	31.4
Used 1 year (charged)	4.04	32.4
Used 2 years (charged)	4.21	33.6
Used 2 years (charged)	4.52	34.7



(a)

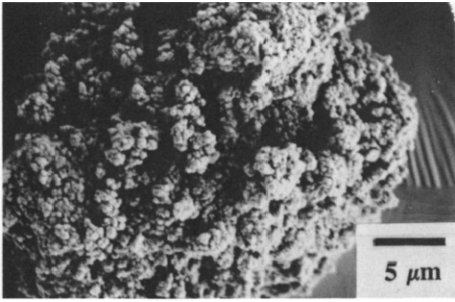


(b)

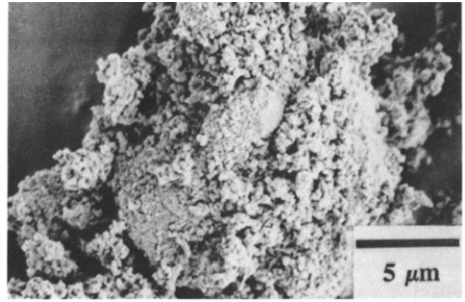


(c)

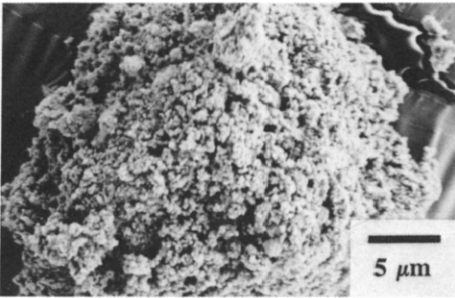
Fig. 1. Scanning electron micrographs of discharged positive active masses of the test batteries as a function of service life: (a) new battery, (b) battery used 1 year, and (c) battery used 2 years.



(a)



(b)



(c)

Fig. 2. Scanning electron micrographs of charged positive active masses of the test batteries as a function of service life: (a) new battery, (b) battery used 1 year, and (c) battery used 2 years.

pictures of discharged masses. The change in porosity of the charged active masses as a function of the service life of the batteries (Fig. 2) is also evident, although the change can be more clearly seen in the case of discharged masses.

## Conclusions

The softening process of the positive active masses causes a gradual disintegration of the mass from the plates and the loss of the capacity. However, the decrease in the DIN  $C_{20}$  capacity as a function of service life was lower than one would have expected. This can be, at least, partly explained by the fact that the increase of porosity of the active mass as a function of the service life of the test batteries compensated for the influence of the formation of the electrochemically-inert active mass particles due to the breaking of the current transportation routes in the active mass structure.

## References

- 1 C.F. Yarnell and M.C. Weeks, *J. Electrochem. Soc.*, **126** (1979) 7–11.
- 2 E.J. Taylor, G.A. Shia and D.T. Peters, *J. Electrochem. Soc.*, **131** (1984) 483.
- 3 N.E. Bagshaw, R.L. Clarke and B. Halliwell, *J. Appl. Chem.*, **16** (1966) 180.
- 4 R.V. Biagetti and M.C. Weeks, *Bell Syst. Tech. J.*, **49** (1970) 1305–1319.
- 5 K. Julian, *J. Power Sources*, **11** (1984) 47–61.

- 6 D. Pavlov and N. Kapkov, *J. Power Sources*, 31 (1990) 189–201.
- 7 K. Harris, R.J. Hill and D.A.J. Rand, *J. Electrochem. Soc.*, 131 (1984) 474–482.
- 8 K. Harris, R.J. Hill and D.A.J. Rand, *J. Power Sources*, 8 (1982) 175–196.
- 9 D.A.J. Rand, R.J. Hill and M. McDonagh, *J. Power Sources*, 31 (1990) 203–215.
- 10 A.M. Foxworthy and R.J. Hill, *PEAKS: a program for quantitative X-ray diffraction phase analysis of lead/acid battery materials*, CSIRO/Pasminco Metals, Melbourne, Australia, 1989.