Thirteen years' experience with expanded lead-calcium-tin grids for automotive battery plates

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Abstract

During 1977 to 1979, Magneti Marelli decided to develop an in-house expanded-metal grid technology. The metallurgy of lead-calcium alloys for strip production was investigated extensively and a continuous system was developed. Production problems were solved with machinery of proprietary design and in 1979 about a hundred thousand Fiat cars were equipped with hybrid batteries. After about three years of labour and field tests on the integral use of lead-calcium-tin expanded grids, it was decided to convert the whole production (about 3 million batteries/year) to this technology.

Introduction

After decades of very slow development, the 1980s saw new activity in the production methods for automotive batteries. The author's company, as part of the Component Branch of Fiat, embarked upon a new product to comply with car manufacturers' requirements for a smaller and lighter battery, and to improve health and safety in the battery factory. The development of this product is summarized in Table 1.

TABLE 1

The chronological development of expanded grid technology

Industrial feasibility proven by Delco	1971
First plans in Magneti Marelli	1974
Progressive die and pasting test line (strip from St. Joe and Ball Metal)	1976
Continuous casting and milling (Joint Venture with Properzi)	1977
Hybrid battery production. Field test on 100 000 Fiat cars	1979
Production lines installed including strip production (for positive and negative plates) continuous pasting and stacking thermosetting formation	1980 ↓ 1985
New layout for Romano factory (3 million batteries/year)	1988

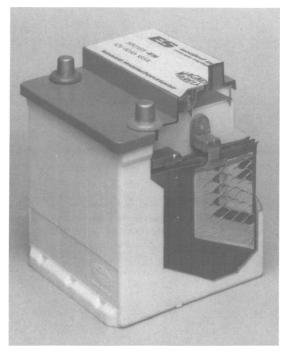


Fig. 1. Battery 34/40 A h, 150/200 A. Size LO-IEC. OEM for Fiat cars.

The product was developed in the early 1980s in the form of a range of batteries based on expanded lead-calcium-tin grids for both positives and negatives. Weight saving was mainly achieved by using a thin grid. The main Fiat car production uses batteries with a lead content of about 5 kg. (Fig. 1).

The dimensions of the diamond pellets were carefully determined by using a programme for the optimization of potential distribution and by field testing to evaluate ageing in real use (Fig. 2).

The negative plates were encapsulated in microporous polyethylene envelopes.

The lead-calcium-tin strip production is based on a proprietary milling system (Continuous Properzi). This has been developed by conducting exhaustive tests on the metallurgical properties, including mechanical quality, corrosion and electrochemistry at the interface with the active material.

The range of starter batteries extends from 34 A h, 6 plates, to 200 A h, 1000 A, in about 20 types assembled with 3-plate dimensions. The -18 °C starting ability test (on car size) gives about 20 A kg⁻¹ (IEC) and 32 A kg⁻¹ (SAE). The water consumption, evaluated according to the International Electrotechnical Commission Recommendation (95-1), is less than 1.5 g A h⁻¹. By comparison, after two years' service, a battery with a 1.8 wt.% antimony grid alloy gives a value of 4 g A h⁻¹. The calcium-based battery can therefore be referred to as absolutely maintenance free.

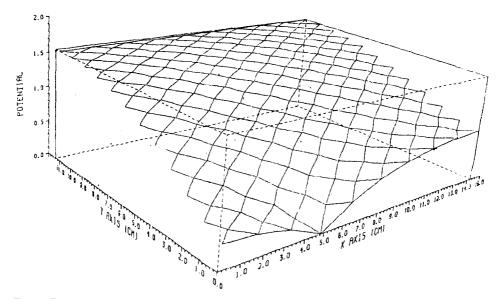


Fig. 2. Determination of voltage drop in a grid.

New technology for continuous production

The following is a description of the main stages of the continuous production line in the Romano Lombardo factory. At present, the output is 3 million batteries per year.

Strip production

The Continuous Properzi system has a capability of 4 million batteries per year (on 3 shifts), Fig. 3. Tests were made with low-antimony content without advantage and with higher cost. The present alloys use a high content of tin in the positive and are the outcome of extensive electrochemical and field tests.

The production commenced with a common alloy both for positive and negative plates, viz., 0.07 wt.% Ca, 0.5 wt.% Sn. Electron micrographs of the strip and grid sections are presented in Figs. 4 and 5. For purposes of comparison, a micrograph of a lead-antimony strip is shown in Fig. 6. Results of field tests (Figs. 7 and 8) showed good performance in taxi duty. This involved some rather deep discharges. Laboratory tests on batteries discharged through a fix resistance (lamp or airport test) showed that the worse conditions for a build up of a barrier layer was at an acid density of 1080 g l^{-1} (Fig. 9).

The beneficial influence of tin was confirmed and a better distribution was achieved by using 0.7 to 0.8 wt.% Sn for the positive and 0.15 to 0.20 wt.% Sn for the negative grid. A more precise curing method was also adopted.

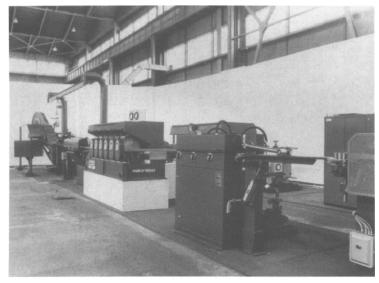


Fig. 3. Continuous Properzi strip production system.



Fig. 4. Strip section of Pb-0.07wt.%Ca-0.5wt.%Sn alloy (×160).

At present, data is being collected on battery life. The results are showing a distribution in life centred on 45 months.

The strip expansion is achieved by using a progressive die of in-house design at a speed of about 12 m min^{-1} (Fig. 10). Five lines can be operated by one man plus one supervisor per shift. The strip is coiled to match more easily the pasting procedure. It is worth noting that the two men are





Fig. 5. Grid node (a) $\times 12$; (b) $\times 50$.



Fig. 6. Strip section of Pb-1.8wt.%Sb-0.15wt.%As-0.2wt.%Sn alloy (×160).

unskilled, while the casting of thin low-antimony grids requires some skill and/or sophisticated controls for the moulds. New and faster machines are under development to match the paster. These run at twice the speed of the present equipment.

Continuous pasting line

The pasting line produces plates at a speed of 25 m min^{-1} . A rotary cutter divides the plates before they enter a flash drying oven with special

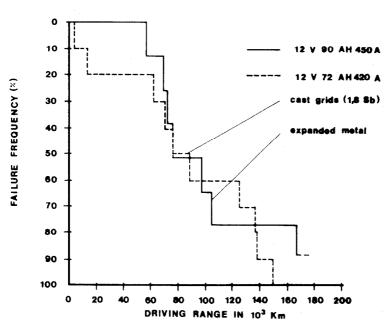


Fig. 7. Failure mode in taxi duty (km).

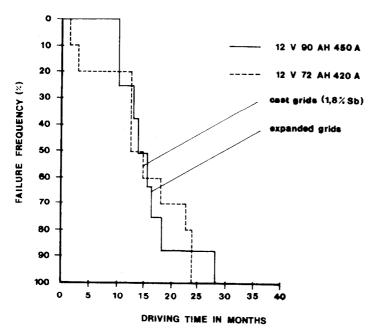


Fig. 8. Failure mode in taxi duty (time).

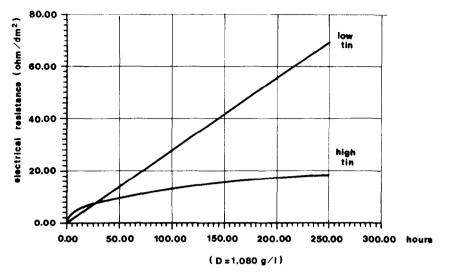


Fig. 9. Resistance of barrier layer.

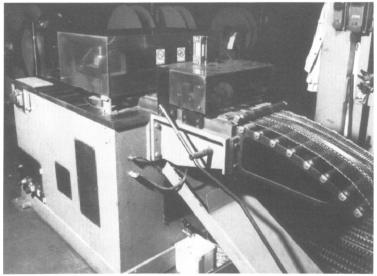


Fig. 10. Strip expansion (progressive die).

protection against over-drying. the plates are then stacked automatically in 4 pallets of 8000 plates. Monitoring of weight is made in real time with a radioactive isotope system.

Curing system

Chambers with controlled temperature and humidity produce excellent curing in 32 h (Fig. 11). The enveloped plates are grouped together with



Fig. 11. Curing chambers temperature and humidity are controlled on preset values.

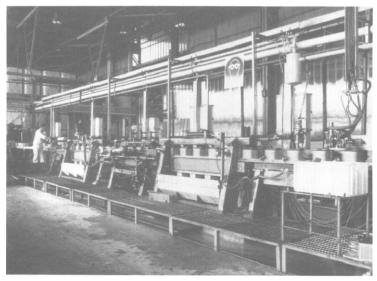


Fig. 12. Dumping and refilling line.

cast-on-strap machines (different designs for small and big groups). The batteries are assembled on automatic lines. Leakage current is checked and the internal resistance and voltage applied are monitored on a CRT display.

After formation (using cooled, low density acid), the battery acid is dumped and refilled twice to reach an even final gravity without a further mixing charge. A high-current test is automatically made and values are recorded for each battery. Each line treats 2500 batteries/shift (Fig. 12).

Conclusions

The new technology has resulted in savings in both cost and scrap. In addition, lead dust levels in the ambient and external air, as well as in the effluent water, have all been lowered below the stringent mandatory requirements.

Car manufacturers (Fiat, Iveco, Renault, Peugeot, Seat) are very satisfied with the weight reduction and reliability of the batteries. The overall production cost is more than 20% less than that for an equivalent cast-grid battery.

Finally, the average life, after 10 years of field experience, is longer than that of a low-antimonial grid battery.