ACCELERATED CURING OF NEGATIVE PLATES FOR LEAD/ACID BATTERIES

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Introduction

The level of battery capacity available at low temperatures is predominantly connected with the choice of a suitable expander for the negative plates. The most widely used expanders are lignosulphonates and their salts [1 - 3]. Being surface-active substances, they affect the processes taking place during paste mixing [4, 5], plate formation and charge/discharge, as well as the structure of the active mass [6, 7]. The aim of the present work is to find an additive for the negative plate paste that will increase the cold-cranking ability (CCA) of lead/acid batteries. An important aspect of these studies is to establish the influence of the additive on different stages of the manufacturing process and on other battery characteristics.

Experimental

The studies were carried out on 12 V/55 A h automotive lead/acid batteries. Measurements involving each type of additive were performed on three separate batteries. For comparison purposes, tests were also conducted on batteries produced by traditional industrial procedures using A-72 expander. The paste was prepared as follows:

(i) leady oxide and expander were homogenized by stirring;

(ii) water and H_2SO_4 solution (sp. gr. 1.4 g cm^{-3}) were added and the mixture stirred for 20 min at 35 °C;

(iii) paste density was corrected to 4.2 g cm^{-3};

(iv) automotive-design grids of Pb–6wt.%Sb alloy were pasted.

The amount of the investigated additives introduced into the paste was 0.5% *versus* the leady oxide. Solid additives were mixed with the leady oxide whilst liquid additives were added to either the water or the sulphuric acid solution.

A study was made of the influence on battery performance of over 25 commercially available substances belonging to different groups of com-

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pounds. The effect of each additive on the processes during paste mixing, and during negative plate curing and formation, was also determined.

All studies were performed using positive plates produced under the same manufacturing conditions. The efficiencies of the positive and negative active masses were 50 and 44%, respectively.

The batteries were subjected to initial capacity ($C/20$), CCA and over-charge life tests.

Results and discussion

Establishment of an effective additive

It was found that the additive designated B-88 used together with the expander A-72 has an outstanding beneficial effect on the CCA. Figure 1 provides discharge curves for 12 V/55 A h batteries at −18 °C and a discharge current of 255 A ($4.6 \times C/20$). It can be seen that when 0.5 wt.% B-88 is added to the negative active mass, the CCA increases by ~25% compared with the normal performance. Furthermore, the additive B-88 does not affect the initial discharge voltage (for up to 30 s).

Effect of additive on battery manufacturing process

Paste mixing

It was established that the additive B-88 has no substantial effect on the processes taking place during this stage of battery manufacture.

Plate curing

The optimum conditions for curing negative plates containing B-88 were determined. Changes in the rate of lead oxidation and the CCA measured over the first three cycles were taken as criteria for assessing the
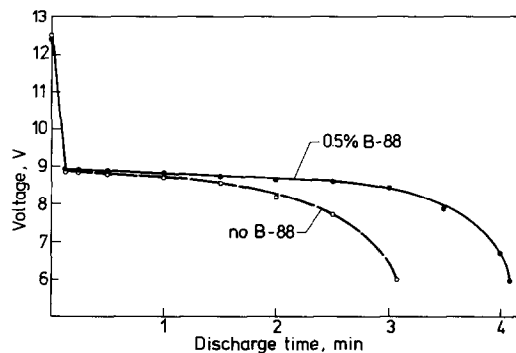

Fig. 1. Discharge curves of 12 V/55 A h batteries at −18 °C and 255 A: − − −, negative plates produced by conventional method using expander A-72; ———, negative plates produced using additive B-88 and expander A-72.
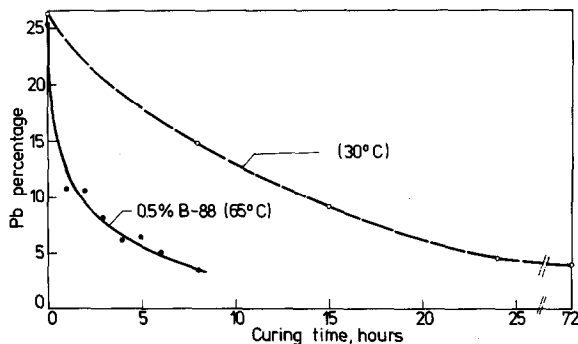
Fig. 2. Change in lead content of paste during curing of negative plates produced by conventional (30 °C) and by new curing conditions (65 °C) with B-88.

efficiency of the curing process. Since curing was performed under continuous air circulation, there was a fairly rapid decrease in the moisture content of the plates. Suitable curing conditions were created by controlling the moisture content according to a cyclogram developed in the authors' laboratories. The influence of temperature on the curing process was studied under these conditions. It was established that the plate energetic parameters exhibit a maximum at about 65 °C.

Figure 2 presents the change in lead content of the paste during curing of: (i) negative plates produced by conventional technology (30 °C); (ii) plates containing the additive B-88 and cured under the above optimum conditions (*i.e.*, 65 °C). The lead content decreases considerably faster when B-88 is present in the plates. Negative plates without B-88 were also subjected to curing at 65 °C under the same conditions. It was found that the curve for the lead oxidation is situated slightly above that for plates with B-88, but cracking and partial shedding of the paste was often observed and this rendered the plates unusable. It can be concluded, therefore, that additive B-88 enables the period of the curing process to be reduced to 8 h. There appears not to be any published data or discussion on this effect.

The influence of the new curing cyclogram and B-88 on the pore-size distribution of the cured paste was established. Figure 3 shows data for the paste porosity of negative plates that were cured according to traditional procedures (30 °C) and of plates containing B-88 cured under optimum conditions (65 °C). It can be seen that the new curing conditions result in ∼10% increase in the total pore volume of the cured paste but exert negligible influence on the median pore radius.

BET measurements of both types of negative plates were performed. Values of 0.94 m^2 g^{-1} and 1.15 m^2 g^{-1} were obtained for conventional and B-88 plates, respectively. Evidently, the new curing conditions and B-88 increase the paste specific surface area by ∼20%.

Figure 4 gives electron micrographs of cured pastes produced conventionally (Fig. 4(a)) and with B-88 (Fig. 4(b)). The micrographs clearly show that the new plate curing conditions and B-88 cause the formation of a fine-
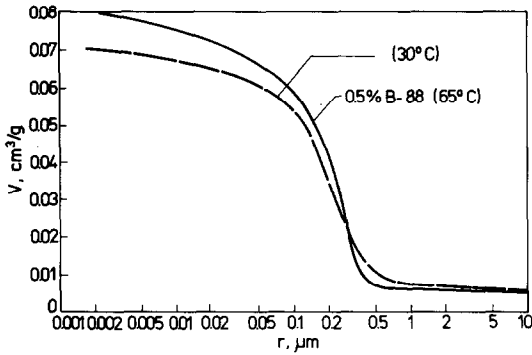
Fig. 3. Pore-size distribution curves of cured pastes prepared with B-88 (65 °C) and by the conventional method (30 °C).
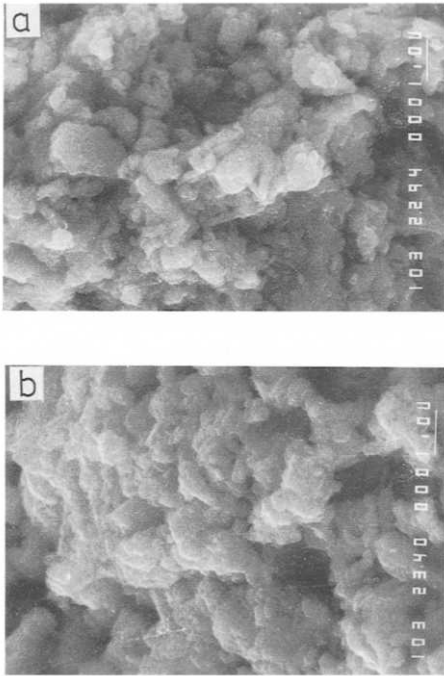

Fig. 4. Electron micrographs of cured pastes produced: (a) by conventional method at 30 °C for 72 h; (b) under the new curing conditions at 65 °C for 8 h with 0.5% B-88. Magnification bar = 1 μm.

grained and more uniform structure. This conclusion is in good agreement with measurements of the specific surface area.

Plate formation
    Plate formation was performed in H_2SO_4 solution (sp. gr. 1.05 g cm^{-3}) at 35 °C and a current density of 5 mA cm^{-2} for 16 h. Paste samples were

taken at regular intervals to determine the $PbSO_4$ content by means of wet chemical analysis.

The formation proceeds in two stages [8, 9]. In the first stage, basic lead sulphates and lead oxide are reduced to form a skeleton of lead dendrites. $PbSO_4$ crystals are also formed. These processes take place in neutral or weakly alkaline medium whereby the plate potential is lowered. During the second stage of plate formation, the $PbSO_4$ crystals are reduced to fine lead crystals that are located on the surface of the lead skeleton. The process proceeds in acid medium and the electrode potential is higher. The changes in the negative-plate potential, and the $PbSO_4$ content in the paste during formation of plates produced by both types of technology, are presented in Fig. 5. The data reveal that between the second and sixth hours the $PbSO_4$ content is approximately equal for the two types of plates, and that the new curing conditions and B-88 increase the duration of the first formation stage. The formation is completed within 12 h and 14 h for conventional and B-88 plates, respectively. This slowing up of the negative-plate formation by 2 h does not affect the total duration of the battery formation process since the corresponding positive plates treated under the same conditions require 16 h for formation.

Undesired intensive evolution of hydrogen during formation commences when the negative plate potential exceeds 1200 mV *versus* the Hg/Hg_2SO_4 electrode. Figure 5 shows that this process starts 2 h later for plates containing B-88.

Determination of optimum B-88 content in the paste

A series of batteries with plates containing different amounts of B-88 was produced. Tests were performed to determine both the ampere-hour capacity at the $C/20$ discharge rate and the CCA. The results are presented in Fig. 6.

With the increase in the B-88 content, $C/20$ rises, exhibits a maximum in the range 0.1 - 0.3% B-88, and then declines to an approximately constant
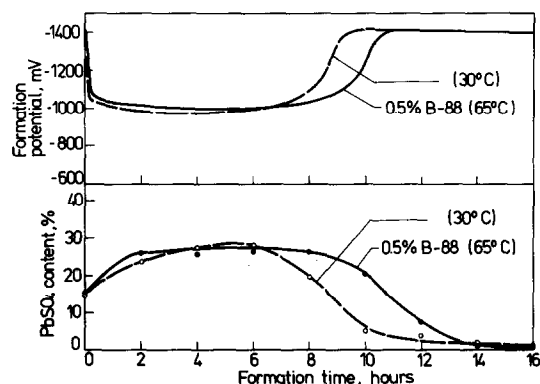

Fig. 5. Change of potential (*vs.* Hg/Hg_2SO_4) and $PbSO_4$ content in paste during formation of new (65 °C cure, B-88) and conventional plates. Current density, 5 mA cm^{-2}.
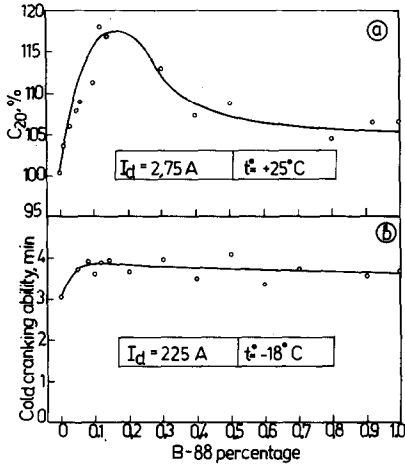
Fig. 6. Dependence of: (a) $C/20$ capacity and (b) CCA on B-88 content in the negative paste for 12 V/55 A h batteries.

value that is higher than that obtained for batteries made without B-88. The CCA increases by ~25% for B-88 contents between 0.05 and 1 wt.% and remains virtually unaffected by higher B-88 concentrations. It is considered that the optimum B-88 content in the negative plate paste is between 0.2 and 0.5%.

Overcharge life tests

Automotive batteries produced by traditional (30 °C) and by the new technology (65 °C) were subjected to overcharge tests according to the 'VAZ-FIAT' standard. The results demonstrate that batteries containing B-88
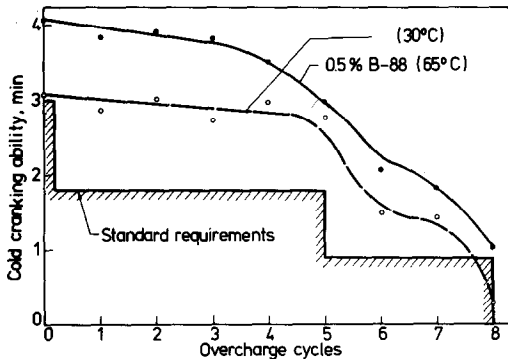

Fig. 7. Change of CCA during overcharge life tests of 12 V/55 A h batteries at −18 °C and 255 A. Each cycle comprises: 110 h overcharge at 0.15 × $C/20$ A and 40 °C; 24 h at open circuit and 40 °C; 24 h cooling at −18 °C; CCA determination. VAZ-FIAT standard requirements are shown.

maintain a higher performance than conventional types over the total period of service (Fig. 7). It appears that B-88 batteries meet more adequately the standard requirements and have higher energy and power reserves.

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