Superiorities of Lead-Calcium Alloys for Storage Battery Construction *

RECENT investigations, conducted at the Bell Telephone Laboratories and elsewhere, have demonstrated that the lead-antimony alloys almost universally employed in storage cell construction are far from ideal for the purpose from the electrochemical standpoint. It has been shown that *in the course of normal operation* of the present type cell, antimony is leached out of the positive electrode, passes through the solution and deposits on the negative, where it promotes "local action" and self-discharge. Also, it has been demonstrated that stibine is generated in perceptible amounts by the present type battery on over-charge.

The continued use of lead-antimony alloys for over fifty years has been due primarily to their desirable metallurgical and physical characteristics and the fact that other equally satisfactory alloys of lead have not been available. Electrochemical theory indicates that for use in storage cell construction, lead should be alloyed only with metals *electronegative* to it. The alloying constituents should have little tendency to diffuse or segregate at the normal operating temperatures reached in a cell. The resulting alloy should be considerably stronger than lead, easily cast, and resistant to electrolytic corrosion. It should also have high electrical conductivity and small solidification and thermal contraction.

As a result of a comprehensive investigation of lead-calcium alloys in connection with cable sheathing materials, data were accumulated at the Bell Telephone Laboratories which suggested the use of certain of these alloys for storage battery grids and plates. Tests have been conducted to determine the value of this suggestion, and with very promising results.

In the course of the cable sheath studies, the thermal equilibrium diagram of lead-calcium alloys containing a very small percentage of the calcium component was determined and is illustrated in Fig. 1. This diagram shows that the amount of calcium soluble in solid lead

* Digest of Two Papers: "The Electrochemical Behavior of Lead, Lead-antimony and Lead-calcium Alloys in Storage Cells" by H. E. Haring and U. B. Thomas, and "Some Physical and Metallurgical Properties of Lead-calcium Alloys for Storage Cell Grids and Plates" by E. E. Schumacher and G. S. Phipps. These papers are, being presented before the Convention of the Electrochemical Society in Washington, October, 1935, and published in the *Transactions* of the Society.

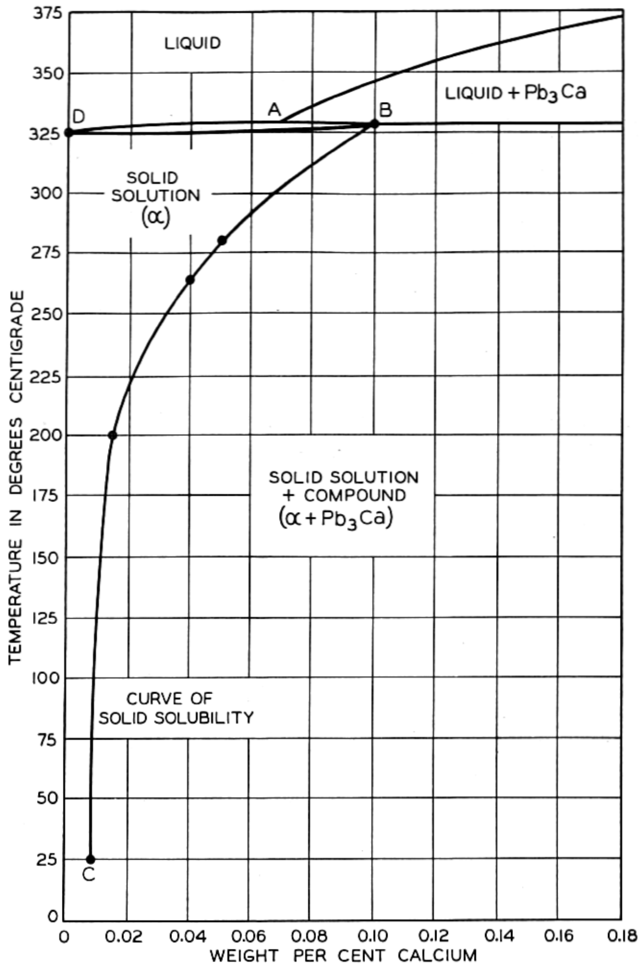

Fig. 1—A partial equilibrium diagram of the system lead-calcium, according to Schumacher and Bouton.

varies continuously from 0.10 per cent at 328° C. to about 0.01 per cent at room temperature. Moreover, when the 0.10 per cent alloy is cooled below 328° C., the calcium precipitates out of the solid solution in the form of Pb_3Ca. This precipitation, while a gradual process, can be hastened by suitable heat treatment. Physically, the effect of the Pb_3Ca molecules highly dispersed throughout the body of the alloy is to strengthen and harden it very materially. Thus, the alloy with a calcium content of 0.10 per cent has a tensile strength of around 8,000 pounds per square inch, a value comparable to that reached by the lead-antimony alloys most generally used in storage battery construction. It has been found, furthermore, that at ordinary temperatures no decrease of tensile strength occurs with age. This maintenance of strength is probably related to the low rate of diffusion of the hardening constituent Pb_3Ca which, being a large and stable molecule, does not diffuse readily in the matrix. The electrical conductivity of this lead-calcium alloy is approximately 20 per cent greater than that of lead-9 per cent antimony, a factor of importance in securing uniform distribution of current when large currents are drawn from a battery.

Experimental cells of both Planté and Fauré (pasted) types have been constructed and are being subjected to a variety of tests. To date, forty-two cells of the starting and lighting type have been pasted, assembled, formed and cycled. This investigation has progressed sufficiently to make it quite evident that the behavior of a complete cell can be predicted with a high degree of accuracy if the electrochemical properties of the structural alloy are known. It has been definitely established that when the negative electrodes of lead-calcium cells of the starting and lighting type (previously subjected to 100 charge-discharge cycles) are charged and allowed to stand one month, they lose only 4 to 5 per cent of their charge as compared to 20 to 25 per cent for lead-antimony cells similarly treated. The efficiencies of lead-calcium cells have been found to be superior to those of lead-antimony cells. No undue corrosion of lead-calcium grids has been observed.