

## BACKGROUND ASPECTS OF LEADY OXIDE PRODUCTION

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### Battery oxide

The basic starting material for lead/acid battery plates is generally referred to as 'leady' or 'grey' oxide. This material is prepared by reacting a lead feedstock with oxygen in either a Barton pot or a ball mill, and usually comprises about one-part unreacted fine lead particles (so-called 'free lead') and three-parts lead monoxide ( $\alpha$ -PbO and  $\beta$ -PbO). A small amount of red lead ( $Pb_3O_4$ ) can also be produced, but battery manufacturers generally prefer to add this oxide from a separate source. The blending (or indeed complete substitution) of leady oxide with red lead is particularly popular in the preparation of tubular positive plates.

### Barton-pot process

In the Barton-pot approach to making battery oxide, lead is melted, forced into a spray of droplets, and then oxidized by air at a regulated temperature (330 - 400 °C). Any accumulated bulk molten lead is broken up again into droplets by a revolving paddle that directs the lead against a fixed baffle arrangement inside the pot. By careful control of the:

- pot temperature
- paddle rotation speed
- rate of air flow
- size of operating load (determined by the rate of solid or molten lead feed)

battery oxide of the desired chemical composition and particle-size distribution can be obtained. Some manufacturers, however, pass the Barton-pot oxide through an additional milling stage that aims to produce finer particles with greater reactivity.

### Ball-mill process

The alternative means for preparing battery oxide — the ball-mill process — involves tumbling lead balls, cylinders, billets or entire ingots in a rotating steel drum through which a stream of air is passed. The heat gen-

erated by friction between the lead pieces is sufficient to start oxide formation. This reaction generates more heat and thus allows the lead particles that are rubbed off by the abrasion to be converted to leady oxide of the required composition. As with the Barton-pot method, the relative amounts of the oxide constituents can be controlled by manipulation of the operational parameters governing the oxide-making process, namely:

- mill temperature
- mill speed
- flow rate and temperature of the air stream
- amount of mill charge

### Phase composition of leady oxide

The ball-mill drum is usually cooled (either with water or by forced-air flow) and, as a result, the oxidation takes place at a much lower temperature ( $\sim 180^\circ\text{C}$ ) than in a Barton pot. This difference in operation causes a corresponding difference in the relative amounts of free-lead,  $\alpha$ -PbO and  $\beta$ -PbO produced by the two processes. In general, the conversion of lead to oxide is lower for the ball-mill process, *i.e.*, the material has a higher free-lead content than the Barton-pot variety. The transition temperature at which the  $\alpha$ -polymorph converts to the  $\beta$ -polymorph is around  $480^\circ\text{C}$  and, therefore, the latter will be formed in appreciable amounts only when using the Barton-pot method.

It has become a tradition within the battery industry to set a limit of  $\sim 15$  wt.% for the  $\beta$ -PbO content of Barton-pot oxide [1]. Control of the relative proportions of the two polymorphs of PbO is important in flat-plate manufacture as there are documented claims [2 - 4] that the polymorphs promote the formation of different basic lead sulphate compounds during the subsequent plate-curing process, *i.e.*,

- $\alpha$ -PbO favours the development of 3BS
- $\beta$ -PbO gives 4BS

In turn, these sulphate phases strongly influence the performance characteristics of battery plates during charge/discharge service [5].

Rather surprisingly, there has been little systematic study of the effect of differing  $\beta$ -PbO content on plate behaviour. In general, industry has accepted the 15 wt.% limit without question. Furthermore, it is unclear whether this restriction has arisen either because experience has shown that the presence of higher percentages of the  $\beta$ -polymorph in leady oxide is symptomatic of poor (temperature) control of Barton pots, or because there is genuine evidence (albeit empirical) that excessive amounts of the polymorph are harmful to plate performance. In terms of the initial capacity, recent studies in the CSIRO laboratories have shown [6, 7] that the  $\beta$ -PbO content exerts little effect when plates are cured at ambient temperature (*i.e.*,  $25^\circ\text{C}$ ). By contrast, there is a marked increase in both the initial and the maximum values of the capacity when plates are subjected to high-tem-

perature (*i.e.*, 95 °C) curing and are prepared from oxide containing 20 wt.%  $\beta$ -PbO. The improvement in performance is related to the presence of an open and porous, yet very strong, reticular structure in both the cured and formed states. This structure allows greater acid penetration, and hence increased utilization of the plate material, while the cross-linking of the particle network helps to preserve the mechanical integrity of the plate during the stresses of charge/discharge cycling. The former observation suggests that the problems of low initial capacity and inferior charge acceptance that are commonly experienced with high-temperature-cured plates (*i.e.*, plates containing 4BS) may be ameliorated by closer control and optimization of the  $\beta$ -PbO content of the starting battery oxide, either through regulation of the oxide-making process itself (principally the temperature of operation) or through blending with independently manufactured  $\beta$ -PbO.

### Physical characteristics of leady oxide

In addition to differences in phase chemistry, Barton-pot and ball-mill oxides also exhibit dissimilarities in particle size and morphology. The free-lead particles are elongated (or 'flaky') in ball-mill oxide, but roughly spherical in Barton-pot material (see Fig. 1). The greater surface area of the free-lead particles in ball-mill material increases the rate of secondary oxidation during storage, that is, ball-mill oxide has a shorter shelf-life than its Barton-pot counterpart. On the other hand, this feature enables paste made from ball-mill oxide to be cured faster (note, oxidation of free lead is the driving force in curing). It is also claimed that ball-mill oxide provides plates with greater mechanical strength and higher initial electrical capacity.

The Barton-pot process produces the larger oxide particles. As a consequence, Barton-pot oxide is less prone to aggregation and therefore easier to handle. This property also provides the oxide with good flow characteristics and thus favours its use in tubular-plate production. By contrast, plates filled with ball-mill oxide tend to exhibit poor uniformity in weight and a lower packing density. Currently, considerable interest is being shown in the development of granular oxide for tubular plates [8, 9]. This material is manufactured from leady oxide using only sulphuric acid as a binder. The granular oxide is free flowing and non-dusting. The latter property is particularly advantageous given the increasing pressure on battery manufacturers to minimize the health and environmental hazards associated with the filling of tubular plates. It has still to be decided, however, whether the granular-oxide approach is superior overall to the alternative 'clean' filling procedures that are based on wet-slurry filtration and paste-injection techniques.

### Reactivity of leady oxide

The larger size of the Barton-pot oxide particles also results in the material having a lower reactivity with sulphuric acid (*i.e.*, a lower 'acid absorp-

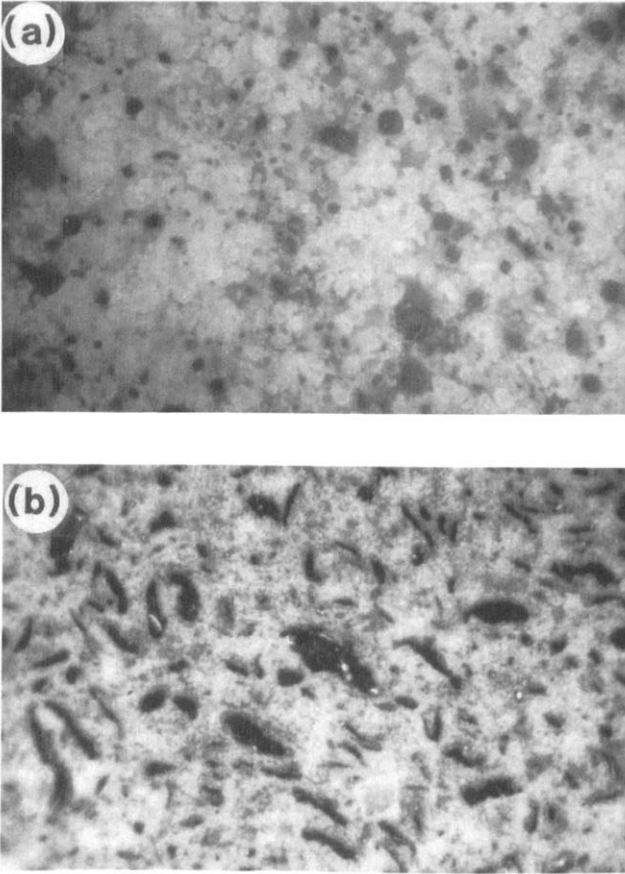


Fig. 1. Optical micrographs of (a) Barton-pot oxide and (b) ball-mill oxide ( $\times 260$ ). Dark spots are particles of free lead.

tion value') than ball-mill oxide. Naturally, this factor is particularly important in the manufacture of flat plates, as differences in reactivity will necessitate modifications to paste formulations and will cause variations in paste properties. In general, it is claimed that the mixing and application of battery paste is easier when using Barton-pot oxide.

#### Manufacturing costs of leady oxide

Finally, what of the economics? Although a Barton pot is considered to be more difficult to control, the equipment is less capital intensive, produces more oxide per unit space, and consumes less energy than a ball mill. Indeed, these economic features are often the main determinant in choosing between the two methods for manufacturing leady oxide.

## Which leady oxide is best?

The state-of-play between Barton-pot and ball-mill oxide is summarized in Table 1. It should be emphasized that very little experimental evidence has been published in support of the assertions listed in this Table. The purpose of the Oxide Clinic held at the Third Asian Battery Conference is to debate in depth the relative advantages and disadvantages of Barton-pot oxide *versus* ball-mill oxide and to attempt to reach a valued consensus of opinion on which is the best material to use in the manufacture of a given type of battery plate.

TABLE 1

Claimed advantages/disadvantages of Barton-pot and ball-mill leady oxides

Parameter	Barton pot	Ball mill
Economics	lower initial cost	greater energy
Operation	higher output per unit space harder to control	lower maintenance
Oxide	easier to handle longer shelf life	more consistent in quality more reactive
Flat plates		faster curing stronger material higher initial A h
Tubular plates	easier filling higher density	

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