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**DISCUSSION ON THE PROPERTIES AND MANUFACTURE OF  
LEADY OXIDE**

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**Topics under discussion**

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● Effect of Humidity . . . . .	143
● Relative Benefits of Barton-pot and Ball-mill Oxides . . . . .	143
● Oxide Blending. . . . .	144
● Apparent Density and Reactivity . . . . .	145
● Role of $\beta$ -PbO. . . . .	145
● Back-up for Oxide Plants . . . . .	146

## EFFECT OF HUMIDITY

*Question: What is the effect of high humidity (as experienced in many Asian countries) on the production and handleability of leady oxide as well as on the maintenance requirements of the oxide processing plant?*

**K. H. BROCKMANN**

Humidity acts as a catalyst for the production of leady oxide, that is, it speeds up the oxidation of the lead particles. Thus, high humidity will increase productivity, especially when making litharge. Given this effect, it is important to monitor humidity when running oxide plants automatically — a dramatic change in ambient humidity or temperature will require a resetting of the control parameters of the process.

Humidity presents no special maintenance problems to oxide plants. It is a simple matter to protect the electronic control systems from extremes in environmental conditions.

**A. RYDER**

The Chloride Group also has not experienced any particular humidity-related difficulties in leady oxide production.

## RELATIVE BENEFITS OF BARTON-POT AND BALL-MILL OXIDES

*Question: It is generally agreed that Barton-pot oxide is more suitable than ball-mill oxide for tubular-plate industrial batteries, but why do so many automotive battery manufacturers around the world also prefer Barton-pot oxide?*

**A. RYDER**

The choice of Barton-pot oxide for automotive batteries appears to be simply a matter of following a whim or fashion. At various times, the Chloride Group has opted for either Barton-pot or ball-mill oxide. In our former industrial battery factory at Over Hulton, both types of oxide were used and in some instances were mixed together. Despite this, it has generally been the tradition at Chloride to use ball-mill oxide for both automotive and industrial batteries, especially when plates are subjected to natural (*i.e.*, ambient temperature) curing conditions. In recent times, with the trend towards more controlled methods of curing, including processing at elevated temperature, the predilection for ball-mill oxide does not seem to be so important.

The cost of the machinery is a significant factor. The relative costs of the two oxide-making processes certainly favour the Barton pot. There is an approximate 'two-thirds rule'. For example, compared with the Chloride Type 8 oxide mill, a Barton pot consumes two-thirds as much power, occupies two-thirds the space, and is two-thirds the price. Thus, if there is indeed no effect of oxide manufacturing route on battery performance, it makes economic sense to choose a Barton pot. Nevertheless, to re-emphasize my opening remark, the selection of one method for making battery oxide over the other is not so much based on the physicochemical superiority of a given oxide variety, but rather on the personal preference of the plant operators — there are 'pot men' and there are 'mill men', and in many cases never the twain shall meet.

**K. H. BROCKMANN**

There is a clear difference of philosophy in different parts of the world concerning the decision of battery manufacturers to install a Barton pot or a ball mill. Where there is a British or Japanese influence, ball mills are favoured. Conversely, practice in the

U.S.A. leans towards Barton pots. As D. W. H. Lambert of CBS Batteries suggests, this difference in tradition may reflect a 'not-invented-here' syndrome.

A large battery manufacturer in the F.R.G. divided oxide production approximately equally between the Barton-pot and ball-mill processes. Then, on 15 February 1988, a sudden decision was made that Barton pot alone was to be used until the year 2000. No reasons were given.

A. M. HARDMAN (from the audience)

The Chloride Group has carried out an exhaustive programme of tests in order to determine whether there is any difference in electrical performance between automotive batteries made with Barton-pot oxide and those made with ball-mill oxide. No detectable difference in behaviour was found. More importantly, experience has shown that Barton pots are extremely difficult to operate and, therefore, ball mills are installed in most of the Group's factories.

I. G. MAWSTON

In my experience, the difference between Barton-pot oxide and ball-mill oxide is akin to the difference between Coke and Pepsi!

## OXIDE BLENDING

Question: *Is it possible to combine the acclaimed beneficial properties of Barton-pot oxide and ball-mill oxide by blending the two varieties of oxide?*

K. H. BROCKMANN

At present, Heubach and Lindgens supplies the battery industry with both ball-mill oxide, called Type HBS 1, and Barton-pot oxide, called Type HBS IV. Intermediate mixtures of the two oxides are sold under the brand names HBS II and HBS III. In addition, a number of clients are buying blends of ball-mill oxide with red lead and/or litharge.

Question: *Can the Mawston model for battery-paste calculations take into account differences in the relative amounts of the two PbO modifications in the leady oxide, especially when mixtures of Barton-pot oxide and ball-mill oxide are used?*

I. G. MAWSTON

The model does not consider that any particular phase is formed at any given time. It is important to realize, however, that  $\alpha$ -PbO and  $\beta$ -PbO have different reactivities, i.e., different acid absorption values, and this determines whether the mix, as formulated, actually reaches the calculated point on the triangular phase diagram. In my opinion,  $\beta$ -PbO reacts faster than  $\alpha$ -PbO.

D. A. J. RAND

Recent studies in the CSIRO laboratories on a number of Barton-pot oxides from different manufacturing plants suggests that reactivity increases with increasing  $\beta$ -PbO content but decreases with increasing  $\alpha$ -PbO content. These findings support the views of Mr Mawston. As I mentioned in the opening paper of this Oxide Clinic, the importance of  $\beta$ -PbO in determining the processing characteristics and performance of battery plates is still not fully understood or exploited. Present information indicates that both the chemical and the physical features of  $\beta$ -PbO influence its reactivity. For example, it is possible to prepare forms of  $\beta$ -PbO with very high surface area compared with  $\alpha$ -PbO [1]. On the other hand, it has been argued [2] that the nucleation and growth rates

of  $\text{PbSO}_4$  are faster on the surface of  $\beta\text{-PbO}$  because of the large number of crystal-lattice defects contained within the polymorph.

## APPARENT DENSITY AND REACTIVITY

Question: *What is the significance of the apparent density and reactivity (acid absorption value) of leady oxide on battery performance?*

I. G. MAWSTON

There are many parameters that relate to battery oxide (*e.g.*, apparent density, acid absorption, water absorption, surface area, etc.) and an equally large number of parameters that relate to paste mixing (*e.g.*, quantities of water and sulphuric acid, mechanics of mixing, temperature, etc.). At present, however, there are no simple and accurate guidelines for optimizing these two sets of parameters, and their inter-relation, in order to achieve the best paste formulation. Nevertheless, if a given oxide has a low bulk density and a high acid absorption value, then less sulphuric acid will be required to produce a paste of the required density (say  $3.9 - 4.0 \text{ g cm}^{-3}$ ) than for an oxide with a high bulk density and a low reactivity. Thus, bulk density and acid absorption measurements are useful and assist manufacturers in preventing the addition of excess acid during the paste-making stage so that the formation of harmful species, such as mono-basic lead sulphate, is avoided.

Question: *Given that an acid absorption test takes longer to perform than a bulk density measurement, is there a relationship between the two parameters so that bulk density can be taken as the first line of control of an oxide plant?*

I. G. MAWSTON

Unfortunately, the relationship between acid absorption and bulk density appears to be mystical. Determination of the relationship, if any, would be extremely valuable. This is especially important given the fact that the acid absorption value changes with ageing of the oxide in the storage bunker. Acid absorption is also extremely difficult to determine with a good degree of repeatability; it is very sensitive to the skills of the technician performing the test.

D. A. J. RAND

Studies of the change in phase composition of leady oxide with storage time have shown [3] that there is: (i) a significant decline in the free-lead content; (ii) a corresponding large increase in the  $\alpha\text{-PbO}$  content; (iii) a relatively small increase in the  $\beta\text{-PbO}$  content, leading in the case of ball-mill oxides to an overall decrease in the ratio of  $\alpha\text{-PbO}$  to  $\beta\text{-PbO}$ ; (iv) a decrease in the amount of amorphous material. Since oxide reactivity depends on the  $\alpha\text{-PbO}:\beta\text{-PbO}$  ratio, it is not surprising, therefore, that acid absorption values vary with storage time, and not necessarily in a consistent manner. Such features must obviously be taken into account when formulating paste mixes otherwise battery performance could be seriously affected.

## ROLE OF $\beta\text{-PbO}$

Question: *In addition to leady oxide composition, do not plate formation parameters such as temperature and current density also influence the initial capacity?*

D. A. J. RAND

It is quite correct that the conditions of formation will also influence the initial capacity of plates. Factors that enhance the  $\alpha\text{-PbO}_2$  content (*e.g.*, low acid sp.gr., high

temperature) cause a corresponding reduction in the plate capacity. This is because the electrochemical activity of  $\alpha$ -PbO<sub>2</sub> is less than that of  $\beta$ -PbO<sub>2</sub>. Taking all other parameters into consideration, however, it still appears that there is a relationship between the proportion of  $\beta$ -PbO in the starting leady oxide and the resulting plate capacity.

Question: *What is the influence of  $\beta$ -PbO on plate cycle-life?*

D. J. A. RAND

The level of  $\beta$ -PbO found to give optimum initial capacity (*i.e.*, 20 wt.%) does not adversely affect the charge/discharge performance of battery plates, but whether such a composition promotes a significant increase in deep-discharge service life has still to be resolved.

## BACK-UP FOR OXIDE PLANTS

Question: *Given that microprocessors do fail occasionally, how important is it to have manual back-up systems on automatic oxide plants, especially in less-industrialized countries?*

A. RYDER

In discussing the Chloride Type 8 oxide mill, specific mention was made of operational difficulties when using hi-tech plant in countries where servicing facilities are lacking. The problems are compounded by the fact that battery manufacturers usually want the latest in technology — it is extremely difficult to have accepted machinery that the customer perceives to be second best. The fact that this machinery may not be ideal for the given situation often does not enter into the calculation. Such situations occur not only in less-developed countries, but also in places such as Eastern Europe where there are central buying organizations that are not strong technically but follow a philosophy of buying the latest model. In summary, battery manufacturers should concentrate more on selecting equipment to suit the job and should always take into consideration the availability of back-up and servicing facilities.

## References

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