

## Technical Note

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### Aspects of lead/acid battery technology

#### 8. Battery oxide

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#### Abstract

The basic component of present-day lead/acid battery active materials is a high metallic lead oxide that is made in attrition mills or Barton pots. The composition of this material dictates the process of plate manufacture and confers to the active materials a particle-to-particle bonding from which stems material strength and service life. The operation and control parameters of attrition mills and Barton pots are described. The level of free lead in the oxide dictates the vigour of the subsequent plate curing reaction and the time interval over which a paste remains usable.

#### Introduction

The basis of present-day lead/acid battery active materials is a high metallic lead oxide made in attrition ('ball') mills or Barton pots. The oxide produced by either method differs in particle shape and, to a certain extent, in basic composition. This oxide, often called in the industry 'grey lead oxide' or 'leady oxide', can vary in colour from blue-grey to yellow-green to yellow depending on the percentage oxidation and average particle size. The material can best be described as a deliberately produced imperfect lead oxide or litharge.

It is this unique composition that dictates the subsequent processes in plate manufacture and confers strength and service life to the lead/acid battery. The composition of the grey oxide is variously defined as the percentage of lead oxide, e.g., 70 wt.% PbO or, conversely, by the percentage of free unconverted lead, e.g., 30 wt.% Pb.

#### Source material — lead

Lead occurs plentifully in the earth, mainly as the ore galena (lead sulfide). The main deposits, most of which have silver as an impurity, occur in the USA, Russian Federation, Mexico, Germany and Australia. The lead metal is extracted by the controlled oxidation of the ore and produces sulfuric acid as a by-product of the refining operation. The lead obtained in this manner contains many impurities; silver,

bismuth, antimony, arsenic and zinc are the main ones. This crude lead is further refined to reduce the impurities to varying levels that depend on the further use to which the lead is to be put.

The attraction of lead for battery making is its relatively low cost and the ease with which it can be processed. It has a high resistance to corrosion; in the presence of highly oxidizing media, the rate of attack can be controlled and relatively precise estimations can be made of the corrosion life. This makes it possible to design grids for positive plates, subject to oxidation conditions, so that the ultimate battery failure is due to one cause only, namely, the mechanical breakdown of the positive grid material.

The physical characteristics of lead can be summarized as follows:

density (at 20 °C) ( $\text{g cm}^{-3}$ )	11.34
melting point (°C)	327
boiling point (°C)	1725
atomic weight	207
tensile strength ( $\text{t in}^{-2}$ )	0.7–1.0
elongation (%)	50
brinell hardness	3–4
resistivity ( $\Omega \text{ cm}$ )	$20.6 \times 10^{-6}$

The low melting point (327 °C) makes the metal particularly easy to melt and subsequently be cast into profile moulds of intricate design. Pure lead is very ductile and, unsupported, will creep under its own weight. The metal is very inelastic with little or no recovery after deformation. Because of this, pure lead is generally not used in the manufacture of pasted-plate lead/acid batteries other than as the starting material from which the grey lead oxide is produced.

There was great conservatism among the older battery technicians as regards to the source of the pure lead. It was even thought necessary to specify the country of origin and to stipulate that the material had to be virgin or primary refined lead. The growing demand for pure lead and lead alloys increased an already heavy load on the lead producers, whilst used batteries created a growing scrap pile of easily reclaimable metal. This led to a large and strategically important secondary lead producing industry whose output exceeded the production of primary lead from the ore.

The amount of metal used in battery manufacture was approximately evenly shared between grid manufacture and that required for the production of battery active materials. This made it realistic to apportion the primary metal to grey oxide production for the active materials and the secondary metal to grid alloys. The secondary metal industry continued to expand to absorb the continual scrapping of used batteries and has now found its way into grey oxide manufacture. Whereas at one time 99.99% virgin lead was the only metal deemed acceptable for oxide manufacture, lead with 99.97% purity made from reclaimed material is used for batteries of the flooded-electrolyte design with no noticeable effect on the market acceptability of the final battery product.

An acceptable quality of pure lead is as follows:

lead:	not less than 99.95%
silver:	0.005%
copper:	0.005%
arsenic:	0.001%
iron:	0.005%
nickel, thallium, zinc, calcium, cadmium, silica and manganese:	total not to exceed 0.01%

### Attrition-mill oxide

This oxide is made by the tumbling of lead balls, cylinders, nuggets and even full ingots of pure lead in a continuously-rotating oxidation chamber. The temperature of the air in the chamber, the feed of lead and the velocity of the air passing through the chamber are adjusted so that the surface of the balls, cylinders, etc., is oxidized and the abrasion from the friction between them rubs away some of the oxide and the unreacted lead to form flattish platelets of the composite.

The ball, cylinder or nugget caster is essentially a furnace that feeds molten lead continuously to a series of simple moulds in the case of the balls, or to an extrusion head that produces lead rod that is then chopped to form nuggets.

The use of cast balls was originally developed not so much because there was any technical virtue in the spherical shape, but rather because spheres roll readily and the task of transferring them into a silo store, and later into an attrition mill, is simple. In practice, however, the balls often deviate from the sphere when the adjustment of the moulds is poor. Maladjustment of the split line of the moulds left ridges on the castings. Depending on the extent of the maladjustment, this defect can become troublesome, especially if the ridges are so irregular and prominent that the free-rolling properly of the castings is destroyed. If dross is allowed to build up in the lead furnace, the multiple moulds become contaminated and irregular-shaped balls are produced.

The successful operation of a caster depends on:

- (i) maintaining the temperature of the lead in the lead furnace at not more than 420 °C;
- (ii) maintaining the extra heat at the nozzle that feeds molten lead to the moulds as low as is consistent with continuous good castings;
- (iii) examining the feed nozzle at regular intervals to prevent an accumulation of lead dross at this point;
- (iv) restricting the temperature fluctuations in the lead furnace to a minimum by regularly feeding lead ingots as soon as the level has fallen by the equivalent of a full ingot, and
- (v) using a large lead furnace so that the cooling effect of melting a complete ingot is small compared with the total heat content of the molten lead in the furnace.

The making of cylinders and nuggets is a less exacting task than making spherical balls that will roll freely. There is generally less down-time associated with machine breakdowns. The feed mechanism for transferring lead cylinders or nuggets to a silo store and, thereafter, to the mill calls for a different operational principle as cylinders will only roll on their axes and nuggets will not roll at all. Generally, cylinders respond to vibratory feeding.

The attrition mill will normally supply the ball, cylinder or nugget casting machine and associated equipment. These should be specified at the same time as the mill. Wherever possible, the objective should be to achieve a minimum handling of the initial ingots. This gives the preference to whole or chopped ingots as the metal feed to a mill. Successful and labour-free operation has been obtained by the installation of power-assisted cutting of whole ingots coupled with the inching forwards of the cut sections at a speed linked to the rate of lead conversion. This minimizes the risk of dross accumulations.

#### *Operation of attrition mills*

The operation of an attrition mill depends on the chemical interaction between atmospheric oxygen and lead. The latter is raised to a temperature where oxidation

readily occurs and the lead oxide is subsequently removed by the milling action of the sections of lead that are forced to rub against, and hence abrade, each other.

The mill is filled initially with a charge of lead whose weight in modern mills is determined by load cells that continuously monitor the weight in the oxidizing chamber. When the chamber has received its full load, a signal causes the chamber to rotate and the heaters are activated. Simultaneously, air is drawn through the chamber from the outside. As the temperature in the oxidizing chamber rises, the oxygen in the air reacts with the surface of the lead sections and produces a skin of lead oxide. The reaction is exothermic and produces heat in addition to that provided by the heaters. This causes the chamber temperature to rise rapidly and unless checked would result in thermal runaway. Thermocouples within the chamber monitor the temperature and thermostats cut off the external heat when the normal working temperature is reached. Thereafter, a balance has to be maintained between the heat of reaction and the heat losses through the fabric of the mill by conduction, convection and radiation. Some mills have a water-injection system to simplify the task of maintaining an effectual heat balance over a full working day.

The tumbling action of the sections, as the chamber rotates, removes the surface lead oxide, as crude platelets. The air passing through the mill has a dual function: it provides the essential oxygen for the reaction and lifts the abraded oxide up a rising duct to the top of a conical settling chamber. At the entry to that chamber, there is a sudden increase in the cross section which results in the air velocity decreasing to below the value that is required to maintain the particles of lead oxide in suspension. The oxide particles fall under gravity and are passed either to drums or to a collector from where the oxide is fed, usually by screw feed, into a storage silo.

The speed of the air passing through the oxidation chamber is an important control factor. There is a minimum volume of air for each particular output and oxidation level. For example, if the required output was  $300 \text{ kg h}^{-1}$  at an oxidation level of 70 wt.% PbO, the true amount of PbO will be  $210 \text{ kg h}^{-1}$ . The amount of atmospheric oxygen required for the reaction will be:

weight of oxygen:

$$\frac{\text{weight of lead oxide} \times \text{atomic weight of oxygen}}{\text{atomic weight of lead oxide}} = \frac{210 \times 16}{223} = 15.067 \text{ kg h}^{-1}$$

The density of air at normal temperature and pressure (NTP) is such that 22.4 l of oxygen at 760 mm Hg pressure and 273 K weighs 16 g. Thus:

$$\text{volume of oxygen required per hour: } \frac{15.067 \times 1000 \times 22.4}{16} = 21094 \text{ l h}^{-1}$$

A typical oxygen content of air is 21 wt.%. The air required will then be:

$$\text{volume of air required per hour: } \frac{100 \times 21094}{21 \times 1000} = 100.45 \text{ m}^3 \text{ h}^{-1}$$

It is unlikely that NTP conditions will always occur; pressure and temperature will vary throughout the year. Changes in the airflow will have to be made when barometric and temperature conditions change appreciably.

To estimate the order of change in airflow that is required, the gas equation is applied, i.e.:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

where  $P_1$ ,  $V_1$  and  $T_1$  are the initial pressure, volume and temperature, and  $P_2$ ,  $V_2$  and  $T_2$  are the corresponding later values.

Take, for example, a drop in pressure from 760 to 740 mm Hg and a rise in temperature from 15 to 30 °C. The change in the volume of air required is given by:

$$\frac{V_2}{V_1} = \frac{760}{740} \frac{273 + 30}{273 + 15} = 1.04$$

Thus, in order to accommodate the pressure and temperature changes, 4% more air will be required and the airflow in the previous example will need to be increased from 100.5 to 104.5 m<sup>3</sup> h<sup>-1</sup>. If the airflow is not increased, the level of oxidation will fall from 70 to 67.3%. So much depends on the allowable tolerances in oxidation, whether or not changes are made in the mill controls.

The degree of oxidation is only one of the factors determining the suitability, or otherwise, of the final product. Another factor is the average particle size as this determines the total internal surface of the oxide and, thereby, its reactivity. Fine particles provide a greater internal surface area than coarse particles and, hence, a more reactive oxide. Highly reactive oxides can react so vigorously in the paste-mixing operation that the temperature of the process rises to a level where the paste is denatured and battery life is impaired.

Particle-size control must be maintained at all times; especially in the case of programmed paste mixing. Generally, the greater the weight of lead in the oxidation chamber, the greater is the abrading force and the coarser is the particle size of the oxide produced. Coarse particles require a greater air velocity to render them airborne and carry them up to the settling chamber. The skill in operating an oxide mill lies in relating the three variables of temperature, weight of lead in the oxidation chamber and the air velocity.

The essential questions that have to be asked before purchasing an oxide mill are:

- (i) what automatic controls can be fitted to relate the three variables, and, once set, truly control the quality and quantity of the output;
- (ii) what tolerance can be expected from the control system;
- (iii) what is the effect on the final product, and
- (iv) what combination of the three variables will produce the type of oxide as used in the factory; different battery makers have their own preferences for the quality of oxide used based on long-time usage.

The initial determination of the precise mill settings to give that particular oxide is probably the most difficult part of the commissioning process. It is sound practice to require the mill supplier to run the mill for at least 48 h in producing the specified oxide.

#### *Particle size of oxide*

It is important to know the order of particle-size distribution of the oxide — at least initially — since average particle size can be made up in many different ways. The ideal is for the oxide to be comprised mainly of particles that are close to the average, i.e., with few very fine or coarse particles. This is very difficult to achieve. In reality, the particle-size distribution covers a relatively wide spectrum. What has to be avoided is for the oxide to be composed of too great a proportion of very fine particles balanced by very coarse particles, but giving an average size within specification. Such a product suffers from the settling of the coarse particles to the bottom of the

drums or silo with the fine particles floating to the top if the oxide is allowed to stand for extended periods. Storage in drums is more troublesome in this respect than storage in a silo. Drums tend to be stored within a confined space so that they have to be stacked on top of each other. There is a temptation to take from the easier positions in preference to a rigid stock rotation and this results in drums being overlooked and left for long periods before use.

Two empirical tests provide an indication of the average particle size:

(i) *Apparent density*. A measurement of apparent density gives a qualitative guide to the combination of particle shape and size. Originally, the free (zero potential energy) fall of powder was taken as apparent density, this is known as the Scott density. The powder is allowed to fall down a rectangular tube that is fitted with a series of overlapping baffles to destroy the potential energy of the powder and allow the powder gently to collect in the receiving box. The volume of the powder in the box is a measure of the self-packing characteristic of the powder, as determined by particular particle shape and size of the particles. It is difficult to obtain reproducible results and, generally, the equipment is unreliable. The most consistent equipment is the JEL volumeter that is used in the paint industry. This measures the tamped density of the powder. In this method, 150 g of the oxide is placed in a measuring cylinder that is clamped to a table that rests on a cam driven by an electric motor. The amplitude of fall is about 5 mm and a counter control, which can be preset, switches off the motor after the present number of tamps has been completed. The number of tamps (usually about 2000) is set to ensure the oxide has reached a stable density. After this period, there is virtually no heavy compaction. The frequency of tamping is ~100 tamps per min. This type of monitoring is easy to introduce into the oxide mill operation as it can be carried out frequently during a working shift and is not an excessively time-consuming procedure.

(ii) *Acid absorption test*. This gives an approximate guide to the wetted surface area of the oxide. The latter, in turn, depends on the number of particles and their individual surface area. The finer the material and the flatter the platelets, the greater is the acid absorption value. The test is complementary to the apparent density test and the two together give a good description of the oxide and determine whether or not the oxide has differed from previous batches. It is not a test which can be expected to be carried out by the mill operators as it calls for trained laboratory staff. The test consists of weighing a 50 g sample of the oxide into a 500 cm<sup>3</sup> flask to which is added an accurate 100 cm<sup>3</sup> of sulfuric acid of 1.100 sp. gr. The flask and contents are shaken vigorously for 10 min and then stood for 5 min. The clear liquid is decanted to a dry filter. From the filtrate, 25 g is titrated with 1 M KOH. The difference in the concentration of the acid before and after shaking with the oxide sample indicates the degree of absorption. The acid absorption is expressed as the change in weight (mg) of sulfuric acid per gram of oxide.

Typical values from three different makes of attrition mill are as follows: (A) 120 to 150; (B) 150 to 250, and (C) 200 to 280. The oxide from mill A tended to be coarse and suitable for traction and low discharge-rate batteries. The oxide from mill B was much finer and was suitable for batteries required to give good high discharge-rate performances at low temperatures. The oxide from mill C was also suitable for high rates, but tended to be more difficult to control during the paste mixing.

The value of acid absorption data is the advance information that is provided to quality control staff on: (i) the possible temperature variations that may occur subsequently in paste mixing, and (ii) how to dispose of 'out of specification' oxide without upsetting the quality of the paste mixing and the finished plates.

Whilst it is helpful to have early knowledge of the true particle-size distribution of the oxide, such determinations require specialized equipment or recourse to sedimentation measurements that are time consuming. Generally, such determinations are needed perhaps once to certify that the oxide from a new mill is truly similar to the previous product. Thereafter, routine tamp density and acid absorption tests are adequate to give assurance that the product is acceptable.

### *Specifying an oxide mill*

The following information should be given to the supplier when seeking quotations for new mills:

- (i) type of oxide required, i.e., acceptable ranges of oxidation percentage, tamp densities and acid absorption values;
- (ii) output of oxide per 24 h that conforms to the specifications in (i);
- (iii) whether the mill is to be run continuously or intermittently; this will affect the output for a particular size of mill;
- (iv) maximum time acceptable from starting up to reaching oxide of the stated specification; this dictates the order of 'out of specification' oxide that has to be worked away in an approved manner and is particularly important with intermittent working;
- (v) whether the oxide is to be stored in drums or silos, and
- (vi) what types of feed lead are acceptable, i.e., balls, cylinders, nuggets, chopped ingots or whole ingots; all, other the last, will require ancillary equipment to prepare the form of lead feed.

The degree of oxidation and the tamp density will determine the output from a particular mill. The lower the oxidation level, the higher will be the hourly yield. The latter determines the mill operating economics. The time taken from starting up until oxide is obtained to the required specification determines how much 'out of specification' oxide will be made. If this can be kept to a low level, say less than 5% of the starting day's output, the material can be easily segregated and blended in small proportions with good oxide without upsetting the subsequent paste mixing and finished plate quality. This is only possible where the oxide is collected in drums. Where the oxide is directed to silos, segregation is not possible and the creation of substandard oxide has to be kept to very low quantities.

The decision whether or not to store in silos in preference to drums is based on economic grounds and depends on the amount of capital available. The use of drums will always introduce an extra cost factor in the running costs of oxide production. There are problems associated with silo storage due to the further oxidation that occurs after the oxide has been made. The large amount of oxide in a silo, with its lower heat conduction and radiation characteristics, tends to attract higher temperatures than the smaller amount of oxide in the relatively larger mass of a drum. In other words, the greater relative surface area of the drum produces greater conduction and radiation losses.

It is particularly important when using an attrition mill with a silo store that: (i) an adequate amount of metal is used in the mill fabric to conduct heat away rapidly, and (ii) the external form of the mill is conducive to good radiation. As the oxide passes from the oxidation chamber to the final silo, it is necessary to extract heat so that the final temperature within the silo is safe and there is no danger of internal burning.

There have been real problems in a number of installations where there has been insufficient conduction and radiation to prevent very high temperatures from occurring, even to the extent of thermal runaway. This introduces unacceptable safety risks. In

some installations, separate cooling in addition to that from the mill itself has been found necessary. This not only introduces an extra complication, but also an extra cost factor. When seeking quotations for attrition mills with silo storage, it is advisable to place a total requirement for mill and silos with the same supplier and to stipulate the maximum temperature that will be permitted in the silo.

### *Setting up an attrition mill*

Each design of mill has its own particular characteristics so that, included in the negotiated purchase price, there should be a contingency sum of money to cover the commissioning of the mill by the supplier's own engineers. In those contract clauses that relate to the commissioning, the full characteristics of the oxide and the steady mill outputs should be repeated in order to avoid any misunderstanding as to the precise meaning of the term 'commissioning'. It is inadequate to demonstrate that the mill, as set up, produces an oxide somewhere near the specified quality and the yield approaches the target and then to intimate that the further work required to achieve the full requirements is simply a matter of a little adjustment and experience with working the mill. The task of equating the three variables of temperature, lead feed and airflow to arrive at stable output conditions can be a slow and difficult task to one not experienced in the handling of mills. It is equally insufficient to demonstrate that the mill is controlled over 24 h and from it to state the settings are correct for continuous running. A minimum of 48 h continuous running with oxide within the specification and the output up to target is considered reasonable. The pattern of tamp density, percentage oxidation and acid absorption over that period will demonstrate the mill stability.

If it is not possible for the supplier's engineers to commission the mill, the next best approach is to request the supplier to arrange a visit to a company using an identical mill. The purpose of the visit will be, first, to confirm that another maker has consistently produced oxide to specification and at the required yield. The second objective will be to obtain the approximate weight of lead in the chamber, the operating temperature and the airflow conditions to give the type of oxide specified, together with some guidance of the least and the most sensitive of the control parameters. The person who visits the other maker should concentrate on the shop supervision personnel as well as the engineering maintenance staff so that the shop floor obtain knowledge first hand and not by transmitted information that may, or may not, be accurate.

Commissioning should begin using the acquired information so that the techniques the other firm found effective can be capitalized. There are many people who look on such a procedure as somewhat degrading and a reflection on their professional competence, but if it brings the time and cost of commissioning down and speeds up the acceptance into full production it will have well repaid the action. Pride in one's own unaided effort can be a very costly business.

If it is decided that the commissioning will be conducted in-house, the contract should include the provision by the supplier of detailed instructions for setting up and routine running with, if feasible, fault finding charts and probable remedial actions. The instructions should be carefully checked and used for the commissioning. If found sketchy and devoid of detail, the procedure should be rejected and final payments should be frozen pending clarification. It is a common mistake to think it presumptuous to ask for, and insist on receiving, such detailed information. It is not only right but a duty to one's company.



The following is the procedure for commissioning a new mill:

(i) Set the charge of lead in the oxidation chamber to the recommended load figure and, if the mill has a sensing device that passes back weight information to an automatic feed, set this to the same load figure.

(ii) Start the motor that rotates the oxidation chamber and open the airflow control to approximately one-quarter of the anticipated working airflow.

(iii) Commence heating up the chamber and as the temperature rises increase the airflow accordingly so that the temperatures of both the air and the chamber simultaneously reach the approximate working value given by the suppliers.

(iv) When the working temperature is attained, cut back the external heating until the chamber temperature remains substantially stable.

(v) Check that the temperature sensors are in agreement and are operating correctly.

(vi) Check that the airflow controls are maintaining a stable input of air by reference to the water-pressure gauge.

By this time, a steady output of oxide will be appearing at the collector drum or feed to the silo. From now onwards, it is necessary to monitor the oxide characteristics at regular intervals.

#### *Monitoring the mill output*

The main objective is to maintain a reasonably consistent oxide under continuous production. In the past, when oxide mills were manually controlled, there were large variations in the oxide from time to time although, in bulk terms, the product on average was reasonable. This led to the practice of the paste-mixing operator first keeping a close watch on the condition of the slurry that was formed when the initial water was fed into the dry powder and then, as the amount of water approached the normal specified quantity, deciding when to stop the addition in order to compensate for oxide variations. The judgement was based on experience and depended on a visual assessment of the slurry condition or consistency. This crude control was acceptable given the relatively low performances demanded in the past from batteries and provided that the paste-mixing operative was thoroughly experienced. It did provide some compensation for the large variations then occurring in the oxides. As the demand for increasing cold-start voltages and reserve capacities of automotive batteries grew, so a much greater control over the oxide and the subsequent paste became inevitable and human judgement was inadequate if the minimum specified performances were to be regularly achieved. A feedback control to the mill will serve to stabilize the output but, without good regular maintenance, there is often the risk of malfunctioning. In view of this, it is equally important with manually-controlled mills to keep a regular check on product quality.

It is known that during starting up a mill, and before the oxidation chamber and airflow have been stabilized substandard oxide will be produced. It is necessary to know the quantity and the degree to which this product differs from specification. Grey oxide is an expensive component and it is uneconomical to scrap the substandard oxide. It has to be blended with good oxide and, therefore, it is essential to know the amount that can be mixed with acceptable oxide without upsetting plate performance.

A simple method of monitoring oxide quality is to employ a daily oxidation and acid absorption chart. Samples of oxide are taken several times during the first two hours from starting up and the corresponding oxidation level is determined. The percentage oxidation is plotted against time. It is normal for the early samples to be low in oxidation. If drummed, the drums should be numbered in sequence and the

drum numbers marked on the oxidation plot at the time when the oxide was produced. The oxidation level will continue to change until the mill stabilizes. The number of drums with oxide below specification can be interpolated from the curve. These drums should be set aside from the good oxide and blended away in a disciplined manner. It is common practice to blend one in ten good drums although some firms use as much as one in five. This could lead to increased product variation.

The record of percentage oxidation does not give a complete understanding of how the oxide produced will behave when converted into plates. Some knowledge of its reactivity is needed. The same samples of oxide must be be evaluated for reactivity (acid absorption) and the results plotted against percentage oxidation over a complete 24-h period.

Figure 1 shows the suggested percentage oxidation chart and Fig. 2 the 'scatter chart' of acid absorption against oxidation. In the latter, the plots for mill A are lightly distributed about a mean and thus indicate that mill A has stabilized and that the output is predictable on the basis of percentage oxidation. The plots for mill B are random and show that the mill has not stabilized and that the bulk oxide so produced will throw up problems of control of texture in the mixed paste. The scatter diagrams of acid absorption and percentage oxidation are simple charts but are informative, particularly where the paste mixing is programmed.

Where a factory has a number of oxide mills of differing design, the grey oxides produced will be distinctive of each mill. For example, a particular factory had H & D, Berger and Uranio mills. These produced oxides with respective acid absorption values of 120 to 150, 150 to 250 and 180 to 260. In such situations, there are difficulties in maintaining a uniform blend of oxide to ensure that the resultant paste mixes are consistent in texture and density. Wherever possible, mixed mills should be avoided since it is not possible to ensure that there is always the same mix of oxides.

A sampling point should be provided when silo storage is adopted. When sampling from drums, the sample should be taken well down the drum. If available, a special sampling tool should be used that can remove oxide over a band below the surface. The reason for this procedure is that the drum is not normally filled to the top and the surface oxide will be in contact with atmospheric oxygen. Over a period of time, this oxygen will be extracted from the air and the percentage oxidation at the top of

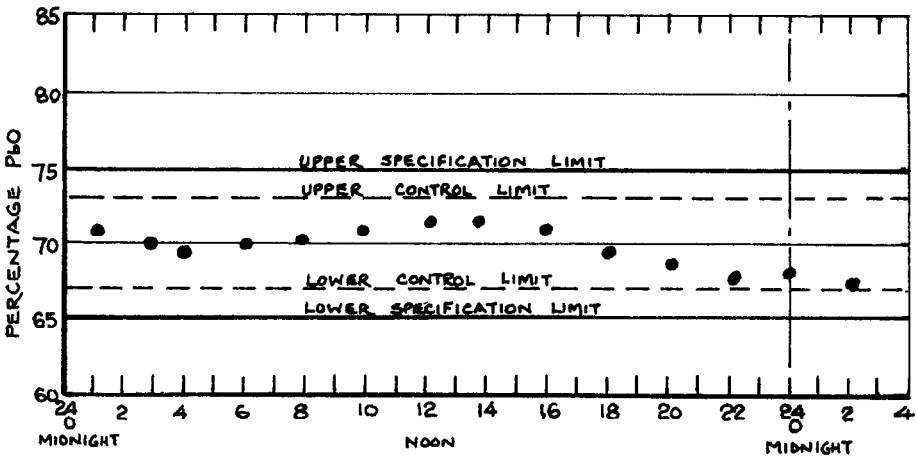


Fig. 1. Daily control chart for lead oxidation.

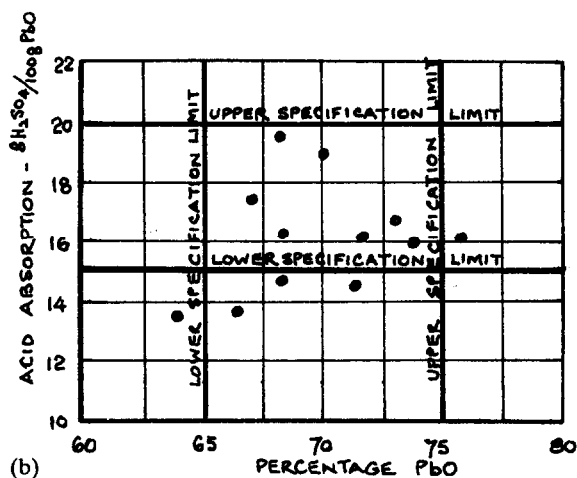
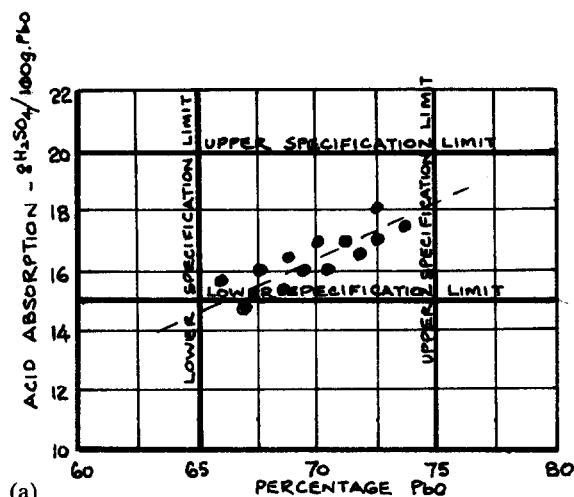


Fig. 2. Scatter diagrams of acid absorption and percentage oxidation. (a) mill A, and (b) mill B.

the drum will be increased. Figure 3 shows the way in which the percentage oxidation can vary throughout the depth of a drum with standing, even though the drum has been sealed with a cover and clamping band.

It is almost impossible to control the rate of oxide production to match the daily usage and, in consequence, drums will be in store for variable periods of time. This could lead to variable oxide being fed to the paste mixers. It is good practice to hold the drums in bond for at least one week before passing them to the mixing department as, in that time, the oxidation reaction will have been completed and the oxide will have stabilized.

Since the percentage oxidation will always increase and not decrease, it is preferable when operating an oxide mill to err on the lower side of the production percentage oxidation tolerance rather than to work close to the top of the tolerance.

Drums of oxide should be stored in a dry atmosphere even though the drums may be sealed. The oxide as it is fed into the drums will be hot and as it cools, air

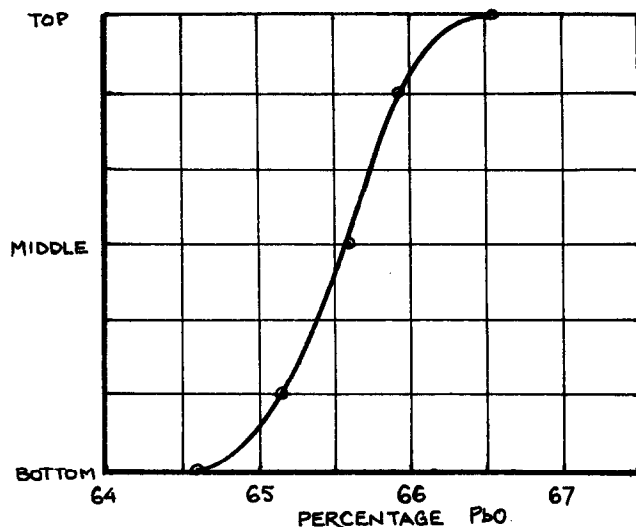


Fig. 3. Effect of entrapped air on the further reaction of the oxide in a drum.

will be drawn into the sealed drums. If the air has an appreciable moisture content, the water in the air will be absorbed by the oxide. Later, when the drums of oxide are emptied into a paste mixer, the absorbed water will increase the total water in the paste. The extent to which this can upset paste mixing can be appreciated by the fact that 1 wt.% of water in the oxide will be equivalent to 10 l of water in a 1000 kg mixing of paste. As many automotive paste mixes call for 80 to 100 l of initial water, the absorbed water from the damp oxide constitutes a major increase in the total water and the resultant paste texture can be very different from that intended. For this reason, more than the extra cost of handling drums, the adoption of a silo store for the oxide as it is produced from the mill is always to be preferred.

### Barton-pot oxide

The Barton-pot method of making grey oxide has been very popular in the USA because it is claimed to be simpler in plant design, more rapid in attaining stability, and lower in manufacturing cost.

There are differing views concerning the use of the oxide direct from the pot. The oxide particles have a roughly spherical shape and many operators claim that pastes made from such powders lack the good particle-to-particle cementation bonds that are typical of attrition mill oxides. The good cementation with the latter oxides is alleged to stem from interlocking of the rough platelets that are formed by the tumbling action of the lead charge in the oxidation chamber. Some operators, wishing to retain the lower operating costs of the Barton-pot process and yet not to lose the alleged cementation in the pastes, have introduced a hammer-milling process between the production stage and the storage of the oxide either in drums or in a silo. The object of hammer milling is to flatten the roughly spherical particles into platelets so that they more closely resembling the shape of attrition-mill oxides.

Hammer milling is a noisy and environmentally-troublesome process and is frowned upon by the health authorities. In the author's opinion, the curing process is the key

process in producing strength and particle-to-particle cementation in plates. With an efficient and well-controlled cure, both the attrition-mill and Barton-pot methods will produce oxide that is suitable for all types of batteries.

#### *The Barton-pot process*

A Barton pot comprises a lead pot, a molten lead feed, a reaction pot, and an airborne lift to the cyclone collector. These are shown diagrammatically in Fig. 4.

The molten lead is contained in a standard lead pot, or furnace, of the type that is normally used to feed casting machines. A lead pump takes molten lead from below

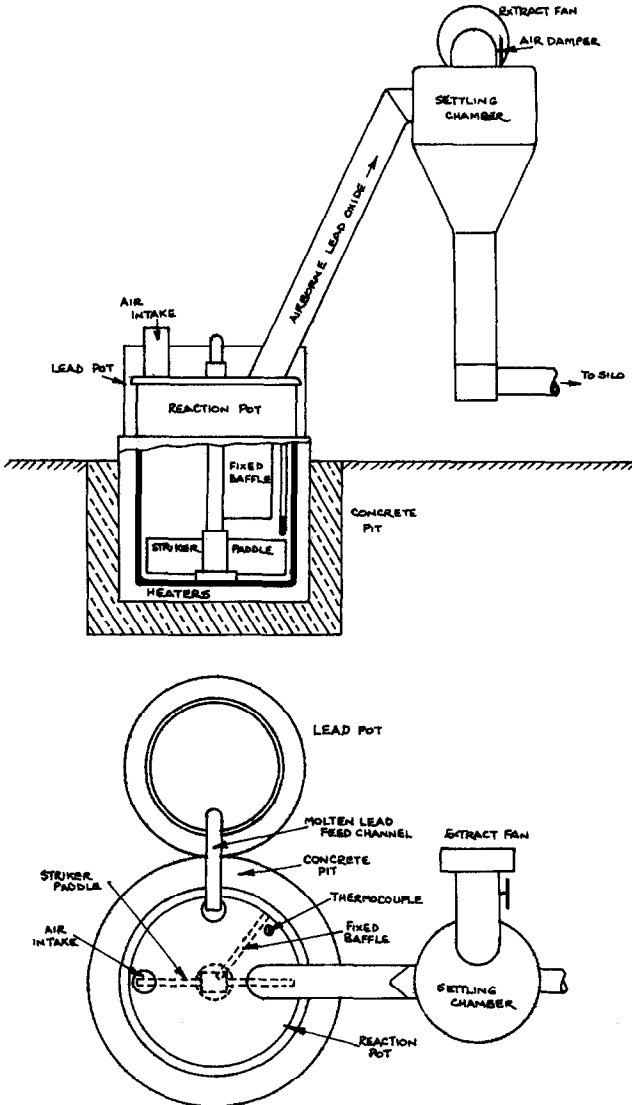


Fig. 4. Schematic of a Barton pot.

the surface of the metal to avoid dross inclusions. The pump delivers the molten metal to a feed channel, that is separately heated, to raise the temperature of the lead stream to that necessary for the oxidation reaction to occur.

In many installations, the reaction pot is sunk into the ground for the surrounding earth to act as an excellent heat insulator that will give the pot greater stability of temperature. The reaction pot is provided with a molten-lead entry port that directs the fine stream of molten lead to a position that is approximately one-third down from the top of the pot. Heating elements, usually gas fed, are sited both around the periphery of the reaction pot and below the pot in order to enable metal in the bottom of the pot to be rapidly heated to the oxidation temperature. A pyrometer element is fitted in the pot for temperature control. Within the reaction pot, a striker paddle is mounted vertically on a thrust bearing and driven at around 150 rpm. A fixed baffle is positioned at an angle to the molten lead entry port. A guard plate, mounted above the entry port, prevents splashes of molten metal from travelling upwards. Air is drawn through an entry port (located at  $\sim 120^\circ$  to the molten lead feed) and passes across the molten metal in the reaction pot to a withdrawal port at  $\sim 120^\circ$  to the entry port.

The amount of lead drawn from the lead pot, where the temperature is thermostatically controlled, is regulated by a calibrated valve on the feed channel. Within the reaction pot, the striker paddle slowly rotates and churns up the molten lead in order to break up the stream of molten lead that is entering the pot. Small particles of molten lead are thrown off into the path of the air currents that pass over the molten lead bath in the bottom of the reaction pot. These particles, due to the temperature within the reaction pot, are at a temperature of 343 to 398 °C. At this temperature the particles are rapidly oxidized, become airborne, and pass up the inclined duct that leads to the cyclone settling chamber. The withdrawal port and outlet duct are set at  $\sim 30^\circ$  to the vertical. Once the oxide enters the cyclone, it loses velocity and ceases to be airborne. It then falls to the bottom of the settling chamber from where it is withdrawn into drums or is screw fed into a silo. The degree of oxidation and the yield of oxide is determined by the size of the stream of molten lead that enters the reaction pot, the temperature within the reaction pot, and the velocity of the air stream that passes through the reaction pot. These are basically the same three variables as for the attrition mill.

Once a Barton pot has been commissioned, there will be a mass of lead at the bottom of the pot that will freeze when the pot has been shut down. This must be melted first to free the striker paddle before the process can be restarted. Once the bottom lead has been melted, molten lead from the lead pot is added until the striker paddle is more or less covered. The temperatures of both the molten metal entering the reaction pot and the reaction pot itself are then adjusted in accordance with the type of oxide required. When these temperatures have been reached, the striker paddle is started. Air is then drawn through the reaction pot and oxide is collected from the lower end of the settling chamber.

#### *Estimation of oxide quality*

The oxide quality depends on achieving a balance between the reaction-pot temperature and air speed. The following data typical for Barton pots are given in Table 1.

Once the oxidation reaction occurs, heat is evolved and little or no pot heating is then required. The rate of airflow provides a secondary control on the pot and metal temperatures and the particle size. An increase in the airflow tends to depress

TABLE 1  
Barton-pot oxide quality

Pot temperature (°C)	Colour of oxide	Approximate particle size (μm)
371	greenish-brown	2 (tetragonal)
427	reddish-brown	3 (tetragonal)
482	greenish-yellow	9 (tetragonal)
>482	yellow	(orthorhombic)

TABLE 2  
Barton-pot oxides: percentage oxidation vs. pot temperature

Pot temperature (°C)	PbO (wt.%)	Approximate particle size (μm)
371	58	2
427	71	3
482	85	9

the pot temperature and lower the degree of oxidation, and vice versa. The skill in operating a Barton pot lies in maintaining the right balance of temperature of the input lead and the rate of airflow. In one particular combination of airflow and input lead temperature, the following relationships between percentage oxidation and pot temperature were met and given in Table 2.

#### *General experience with Barton-pot oxides*

Globally, the experience with operating Barton pots has been varied. Some operators are able to set easily the airflow and lead-pot temperatures and then quickly adjust the lead feed to achieve the desired oxidation. Thereafter, the control parameters remain substantially constant. Most operators seem to agree that Barton pots require continuous attention, otherwise the percentage oxidation is variable and there is the danger of thermal runaway. The more sophisticated pots incorporate a feedback-control circuit that is based on the sensing of the temperature in the reaction pot and using this to modulate the airflow to maintain the required balance of parameters. These pots tend to be stable and to produce a constant oxide.

With the simplest Barton pots, considerable reliance is placed on using the current taken by the motor that drives the striker paddle as a control parameter. The ammeter in the motor-supply circuit reflects the mechanical loads imposed on the paddle by the conditions in the reaction pot. The fluid resistance of the molten metal is controlled by the temperature of the lead. Every time leady material falls from the cover of the reaction pot back into the pot, it shows up as a movement of the ammeter pointer away from the norm.

Most operators stress the importance of easy movement of the airflow control in order to enable small changes to be made without undue effort. Some operators concentrate on the control of airflow by baffles on the uptake duct to the collector chamber. These change the airflow over the lead in the reaction and, thereby, it is

claimed that a smoother control can be obtained in this way. All these points indicate that a detailed record of the effect of any imposed change should be kept and, from these data, the best routine should be deduced for the particular pot design. Operating the pot by reference to an instruction book is not likely to result in equivalent results from a number of units of similar design. Rather, each has its own peculiarities and requires investigation. Where there has been careful and well-documented commissioning, however, the Barton-pot process has been shown to be both economical and capable of running for long periods with low maintenance costs.

Wherever there is a demand for red lead, the Barton-pot can produce litharge readily in a form that is suitable for roasting. In these circumstances, it is worthwhile considering the addition of a red-lead furnace to the Barton-pot. This furnace will accept not only litharge, but all the out-of-specification grey oxide and convert it into red lead. This arrangement has the benefit of avoiding a decision on what to do with the out-of-specification oxide. By taking that oxide out of the bulk stock of grey oxide, the remainder is highly suitable for programmed paste mixing.

#### *Purity of grey oxide*

There is always the hazard in setting maximum permissible impurity levels of either erring on the side of ultra purity or relaxing too much for the more demanding types of batteries where life is of paramount importance. The permissible impurity levels recommended by two organizations are compared in Table 3.

Experience over many years with all types of batteries suggest that, whilst the impurity levels recommended by organization B are generally acceptable for automotive use, there are real doubts concerning their use for either traction or stationary battery applications. For general use for all types of batteries, the compromise level of maximum impurities given in Table 4 is preferred.

For flooded-electrolyte batteries, no significant loss of performance or life has been found when the grey oxide has been made from secondary or recycled lead, instead of from refined virgin lead of ultra purity (99.99 wt.%). It is recommended that the lower limit of pure-lead quality should not be less than 99.95 wt.%.

TABLE 3  
Impurity levels for Barton-pot oxide

Impurity	Maximum impurity level (wt.%)	
	Organization A	Organization B
Silver	0.003	0.010
Bismuth	0.050	0.100
Copper	0.003	0.010
Antimony	0.002	
Arsenic	0.000005 (total)	0.005 (total)
Tin		
Iron	0.020	0.020
Cadmium	0.003	
Total of all other impurities	0.010	



TABLE 4

Maximum impurity levels for general-purpose Barton-pot oxide

Impurity	Maximum impurity (wt.%)
Silver	0.005
Bismuth	0.050
Copper	0.005
Antimony	0.005
Arsenic	0.001
Tin	0.005
Iron	0.020
Cadmium	0.003
Total of all other impurities	0.010

### Economics of manufacture of grey oxide

In the conversion of pure lead into lead oxide, the lead combines with atmospheric oxygen to form the PbO/Pb powder that is called grey oxide. The oxygen is free of cost and, in the process, the weight of the grey oxide produced will be greater than the weight of the lead precursor. For example, if the oxide produced is one with 70 wt.% PbO and 30 wt.% Pb, the weight of grey oxide produced from 1 t of lead will be  $\sim 1.04$  t.

A typical attrition mill that produces about 40 t per 168-h week can be controlled by one operator comfortably, even if the grey oxide is collected in drums. A typical power demand for this size of mill is  $\sim 200$  kWh per t of oxide produced. This figure reduces as the size of the mill is increased so that a mill producing 80 to 100 t per 168-h week requires 120 kWh per t of oxide.

All mills require regular maintenance. Thus, when estimating the running cost of a mill, it is realistic to increase the labour element by roughly 20% to cover this factor.

In deriving the first estimate of the manufacturing cost of oxide per t and the order of capital cost recovery, care must be taken not to base the estimations on the mill working 168 h every week, year-in and year-out. This never happens in practice. It is necessary, therefore, to ask the following questions:

(i) Can all the output of the mill be absorbed fully in production? If not, make an allowance for the proportion of time the mill will not be working. This is not a simple proportion based on a comparison of actual time envisaged with the theoretical 168 h, but is something less to compensate for starting up and shutting down.

(ii) If all the output from the mill can be absorbed in the normal factory practice, how will the paste-making processes be maintained in the event of a mill breakdown?

(iii) If a lien is established on an outside supplier to supply a fixed amount of oxide per week on the understanding that the supply will be increased when required to cover breakdowns, what effect has this regular supply on the ability to run the mill fully through the working week?

(iv) If the regular supply from an outside source is the balance between the factory demand and the full mill output, what allowance must be made for minor disturbances? A factor of 85% effectiveness is reasonable for a well-maintained mill.

### Stability of grey oxide

When grey oxide is first produced it is in an unstable state and, in the presence of atmospheric oxygen, the oxidation reaction will continue. This instability is more pronounced for oxide of finer particle size. The effect of this instability is more marked when the oxide is stored in drums. A number of factors assist the further reaction, i.e.:

(i) Drums are rarely filled completely and this leaves a volume of air in the free space under the lid.

(ii) Drums are usually transported from the mill area to a separate storage area, and then from that area to the paste mixers. During this movement, oxide is shaken up with the result that more of the powder is exposed to atmospheric oxygen and entrapped air is released so that the oxide settles and occupies less volume than before. When the heat of the further reaction has been dissipated, more air is drawn into the drum.

(iii) The lid of the drum rarely, if ever, forms a tight seal and as the original air in the drum is denuded of its oxygen, fresh air is drawn into the container.

By contrast, in the situation where the grey oxide is stored in a silo, further oxidation is confined to the air held between the particles of material. Thus, the magnitude of this secondary oxidation is less than in the case of storage in drums. The effect of this increase in percentage oxidation is shown as a decrease in the reactivity of the oxide in the presence of water and sulfuric acid during the paste-mixing operation. In order to have a stable oxide for paste mixing when using drums, it is advantageous to hold a stock of about two weeks usage.

The order of average percentage change in powder weight when standing in drums for periods of up to 60 days is shown in Fig. 5. The weight change is brought about by the further oxidation. The four curves refer to oxides made in different mills. The same oxides showed losses over the same period of around 18% in acid absorption for the initially most reactive, and around 11% for the least reactive. The change in

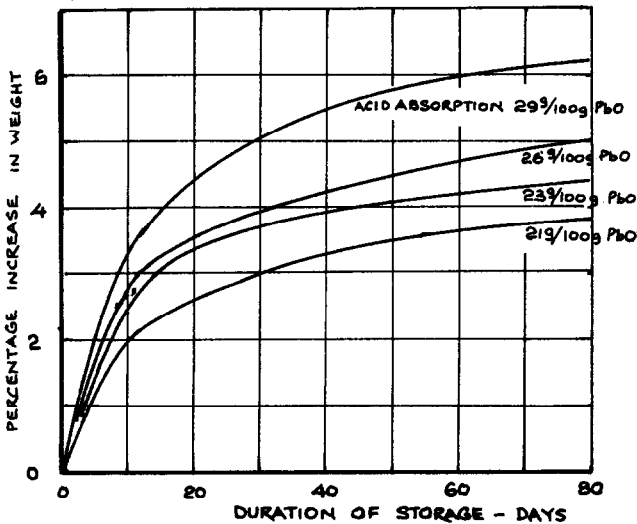


Fig. 5. Typical increase in the weight of grey oxide during storage in drums at 15 °C.

water reactivity (i.e., the rate of rise of temperature in contact with water) is more spectacular ranging from a reduction of 70% in the case of the most reactive sample to 50% for the least.

In general, there are easements in the operational control of paste mixing by allowing drummed powders to stand for periods of the order of two weeks before use. This is because the initial rise in temperature in the paste mixer is lower and, consequently, the final temperature is reduced. This is particularly relevant in the case of programmed paste-mixing where the water and acid additions are constant irrespective of oxide condition. The stored and stabilized oxide produces a cooler paste that will have a longer shelf life in production.

In the case of silo storage, where the oxidation changes are not so marked, the powder taken from the silo bears a closer resemblance to the samples taken from the mill for routine analysis. If a choice of storage is possible, silo storage is always to be preferred.

### **Routine mill operation**

The analysis of mill samples presents a problem to mill operators where wet-analysis methods only are available. This is due to the time interval before results are fed back to the mill from the laboratory. By that time, the mill could have drifted out of oxidation control. In these situations, the operator must rely on the simple observation that the colour of the oxide matches the colour of a sample of oxide of an acceptable quality that is kept in a transparent sealed container. This is a crude test and relies on the skill of the operator but, with experience, the control can be quite good. It is important to view the sample in the container from the same angle each time and to keep the container outside surface clean. Operators can be fallible and, from time to time, it is necessary to confirm the accuracy of their visual assessment if confidence in the product is to be assured. It is wise to maintain a running chart that shows the manner in which the product varies from day to day. By inserting on the charts the operators names, one soon builds up an understanding of each operator's skill and attention to the task. The nature and consistency of the grey oxide is a prime factor in controlling battery performance and life. It is good management to identify and retain those operators who demonstrate they have both an interest and a flair for operating an oxide process.

The recommended day-to-day charts are based on routine checking of selected drums, where these are used, e.g., every fifth or sixth drum in strict rotation or, where silo storage is used, routine sampling at relatively precise intervals throughout the working day. The percentage oxidation, tamp density and acid absorption are plotted as in Fig. 6 in time sequence with the operator's name. Preferably, the chart is displayed alongside the mill so that the results are open to inspection by both operator and shop supervisor. A good operator will ask questions initially about the scatter of results. By exploiting these questions, it is possible to give a training session, on an informal basis, that is directed towards increasing the operator's job satisfaction in what could otherwise be a somewhat tedious and uninteresting occupation.

### **Choice of grey oxide characteristics**

Either type of process, attrition mill or Barton pot, can be regulated to produce percentage oxidations that range from 50 to >90%. This is achieved by changing the

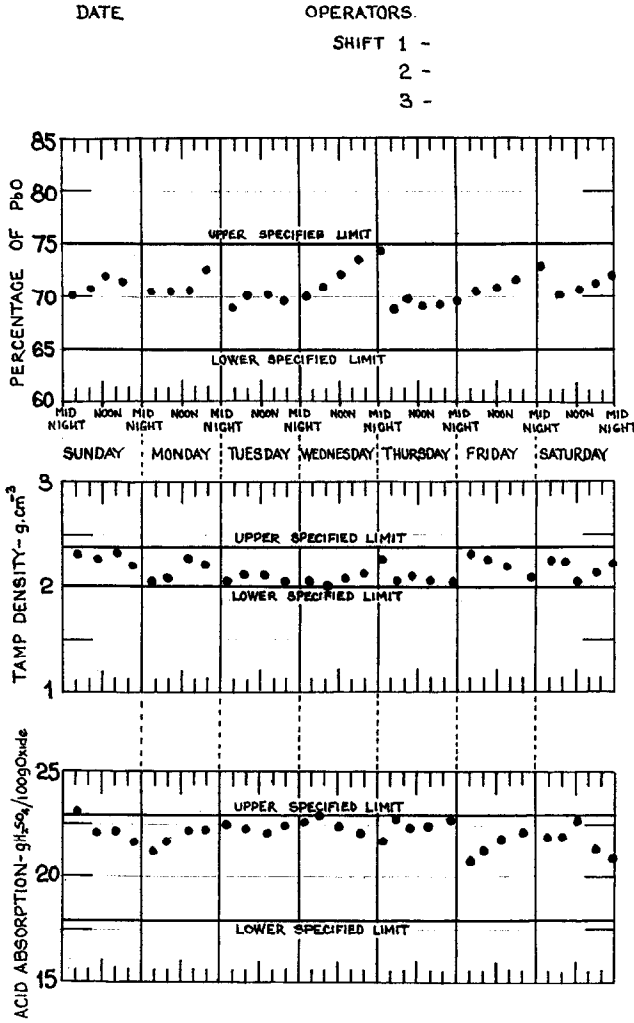


Fig. 6. Oxide mill routine control chart.

weight of the lead charge and the throughput of air in attrition mills, or the feed of molten lead and throughput of air in Barton pots. The temperatures of the reaction chamber or the reaction pot will vary with these parameters because the oxidation reaction is exothermic and, once started, is self-sustaining. The fineness or coarseness of the powder is the result of the interplay of these parameters.

In general, low air velocities favour finer oxides and so does a decrease in the weight of the charge in the attrition-mill chamber. High yields go with low oxidation percentage, and vice versa.

The choice of oxidation level and average particle size is a compromise that is influenced to some extent by the type of paste mixer used and the type of battery to be manufactured. Coarse oxides are generally less reactive than fine oxides. Temperatures in the paste mixer will be lower when using coarse oxides, and there

is less danger of the paste setting rapidly during the mixing procedure. Such oxides do not produce the highly-developed internal surface area that is needed for high cold-start performances and, therefore, tend to be restricted to traction batteries. Fine oxides produce hotter pastes and with some paste mixers where there is only limited cooling there is the risk of the development of unacceptable temperatures during mixing and, consequently, of the finished paste becoming denatured, a condition often referred to as 'burning'. When this occurs, the paste is gritty and difficult to spread and the subsequent curing reaction is usually restricted.

The vigour of the curing reaction is dependent on the amount of free lead that is present in the paste, together with the temperature and moisture. Low-oxidation oxides tend to cure more vigorously than high-oxidation oxides; they also tend to set more rapidly both after mixing and while standing prior to use. Some firms have employed oxides of 50% oxidation, but this is an exception. In such cases, the manufacturers rely on the paste being used rapidly to avoid premature setting. There are firms who use oxides with as high as 80% of lead oxide and these have no problem of premature setting, but need to achieve consistently low free-lead levels after curing to ensure good cementation in the cured plate. The majority of manufacturers favour a percentage oxidation between these extremes, and 65 to 70% PbO is common. The tendency is for coarse oxides to be used for industrial (i.e., traction and stationary batteries) and fine oxides for automotive batteries. This does not mean that fine oxides cannot be used for industrial batteries, but rather that they are not essential.

The acid absorption levels must be high in order for automotive batteries to meet the high cold-start performances that are common to modern battery requirements. For industrial batteries, however, values of 120 to 150, are adequate. Here again, this does not mean that oxides with higher acid absorption values cannot be used for industrial batteries, but that they are not essential.