Short communication

Control of vital chemical processes in the preparation of lead-acid battery active materials

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Abstract

Chemical reactions occurring during the processing of positive and negative active material of lead-acid batteries have a significant impact on the performance and life of the product. Understanding and control of these chemical and electrochemical processes will result in batteries which consistently meet vehicle requirements.

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1. Introduction

A casual visitor to a modern automotive lead-acid battery factory is understandably impressed by the multiple lines of high speed automated equipment turning out component parts and assembling and testing intermediate and final product. However, much of the science and technology involved in the manufacture of consistent high performance, long life vehicle batteries is chemical or electrochemical in nature and as such is invisible. In particular, the chemical reactions vital to preparation of positive and negative active material must be understood and controlled. Various process parameters have a profound impact on the composition and crystal structure of active material during oxide manufacturing, paste mixing, plate flash drying, curing and formation.

2. Lead oxide

The basic raw material used in the preparation of lead-acid battery positive and negative active material is lead monoxide—commonly known as "leady litharge", "grey oxide", "lead dust" or simply "battery oxide". The material as produced by the two most common processes—ball mill and Barton pot processes consists of finely divided particles of two polymorphs of PbO (tetragonal and orthorhombic) and 20–30 wt.% metallic lead. The fine particles of unoxidized metallic lead are uniformly

dispersed throughout the material and act as the fuel in the subsequent plate curing reactions.

Physical and chemical characteristics of the oxide as determined in the manufacturing process are among the earliest harbingers of the resulting battery's performance and life.

Oxide produced by the ball mill and Barton pot processes while similar in some regards vary from each other in several key aspects. The origin of the differences can be explained by studying the reactors in which the material is produced.

Observation of the flow diagrams or visiting the actual factories in which ball mill and Barton oxide is produced can be overwhelming. The variety and size of the equipment and control panels as well as the noise and heat in the actual factory can be impressive. The majority of the equipment in such an installation however consists of preparation, classification, storage and transfer devices of a material handling nature. Focus from a process/material control standpoint should be on the reactor—Barton pot or ball mill.

Barton pot (Fig. 1): Ultrapure molten lead is carefully metered by pump or gravity feed valve into the Barton pot reactor. Inside the reactor is a rotating paddle near the reactor bottom. When the molten lead inventory in the pot reaches the level of the paddle, small droplets of lead are splashed up into an airstream which is drawn through the upper portion of the reactor. The airstream is trifunctional (source of oxygen, cooling, conveyance/separation) and therefore requires precise velocity control. The oxide produced is conveyed out of the reactor by the air stream into particle size classifying and separation devices such as upsweep ducts, settling tanks, cyclones and baghouses.
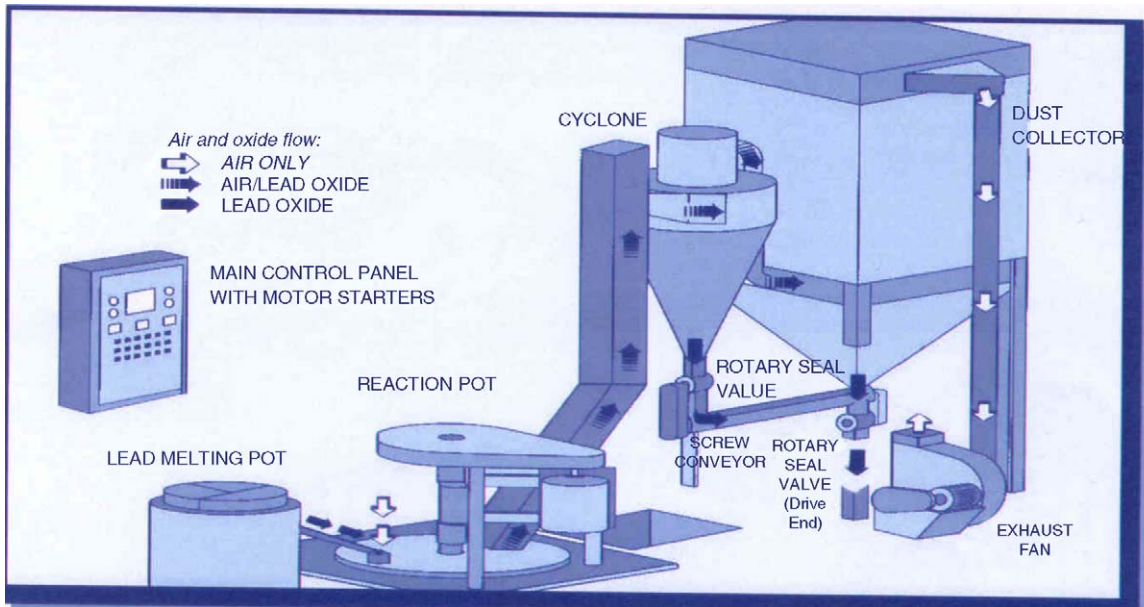
Fig. 1. Barton oxide system. *Source:* Eagle Oxide Services.

Coarse particles are returned to the Barton pot for further size reduction. A secondary grinding process such as a hammer mill is frequently used to enhance uniformly and break up oxide agglomerates. A small stream of water is frequently injected into the reactor to assist in controlling reaction temperature and to promote production of the tetragonal polymorph of PbO.

Ball mill (Fig. 2): Unlike the Barton process, the ball mill process is solid state—the feed stock consists of pieces of lead (pigs, shot, etc.) and the reactor is operated at temperatures below the melting point of lead. In the process, pieces of ultrapure lead are conveyed into a rotating ball mill. The lead pieces serve as both the feed stock for the reaction and the grinding media. Heat is generated by attrition and the exothermic oxidation of the surface of the lead pieces. An airstream, similar to that in the Barton process provides the oxygen, assists in cooling and conveys the appropriate size particles out of the reactor. Product
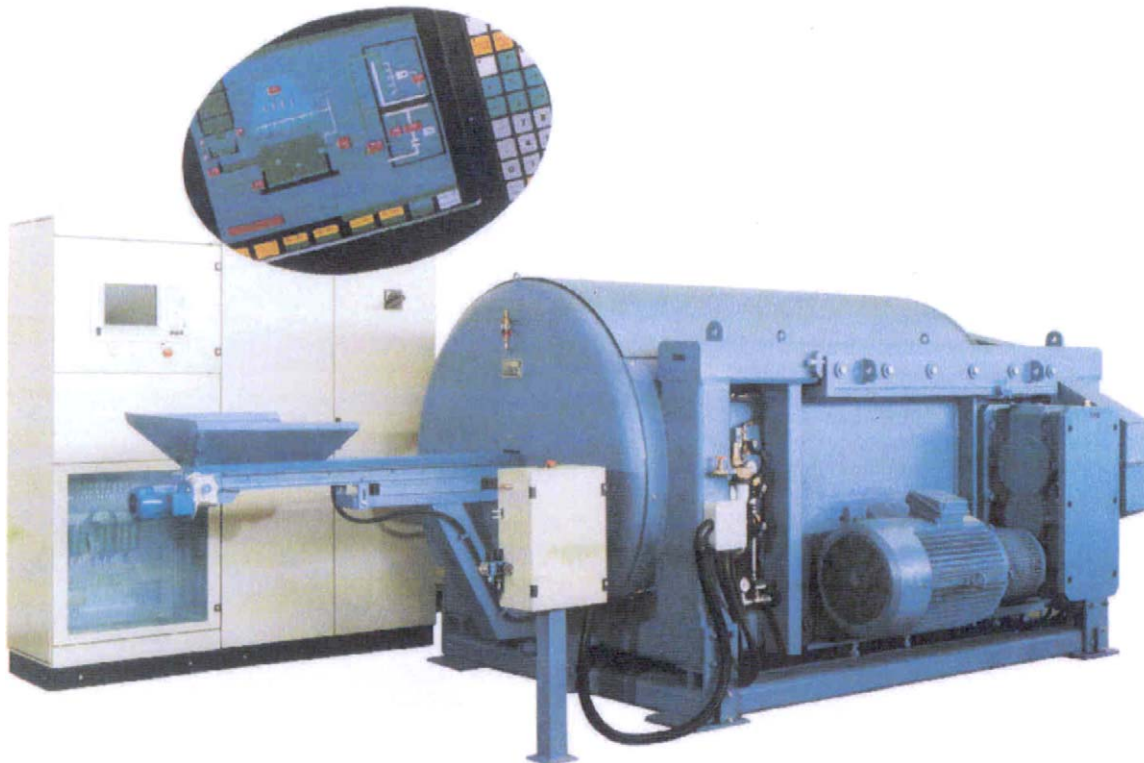

Fig. 2. Ball mill oxide system. *Source:* Sorema USA.

Table 1
Typical oxide properties

	Unground Barton	Ground Barton	Ball mill
Acid absorption (mg g^{-1})	140–185	180–200	260–290
Apparent density (g in^{-3})	25–30	21–25	18–22
Metallic lead (wt.%)	18–28	18–28	25–35
Orthorhombic PbO (%)	10–35	10–35	0
Median particle decimeter (μ)	6–10	2–6	2–6

collecting equipment typically consists of a classifier (returning the coarse fraction to the reactor) a cyclone and baghouses. In addition to the process airstream external waterspray on the shell of the reactor is sometimes used for temperature control.

The lead feed stock for either process must be very pure—whether primary or secondary lead. Some metallic contaminants (i.e. antimony) are known to accelerate the lead oxidation reaction while others (i.e. silver) retard it. Metallic contaminants in the oxide and the resulting active material become readily available to poison cells causing increased gas generation [1]; grid corrosion or self-discharge.

Motor load on the Barton pot paddle drive or the ball mill motor is typically used to control reactor inventory by metering lead feed rate.

Oxide characteristics: The chemical assay of oxide made by the Barton and ball mill processes may be identical, i.e. 75% PbO, 25% Pb, but further chemical, physical and microscopic analysis reveals significant differences between the two. These differences have a profound impact on handling of the material, subsequent processing and performance of the active material which it ultimately becomes.

Typical property ranges of oxide produced by the two processes are given in Table 1.

Test methods for the first three listed attributes are Battery Industry standards, orthorhombic PbO is determined using an internal standard, semi-quantitative X-ray diffraction technique and particle size using a Coulter Counter is reported as "equivalent spherical diameter" which because of particle shape has more direct meaning for Barton than ball mill particles.
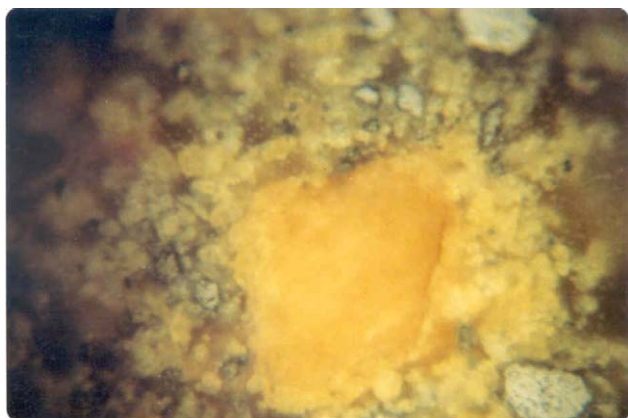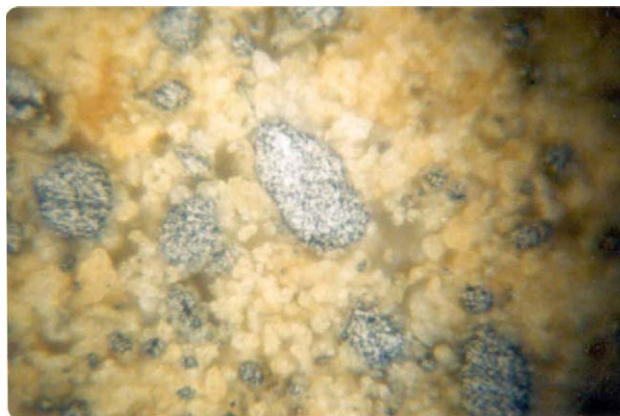

Fig. 4. Hammer-milled Barton oxide.

Optical microscopy is useful in further defining the differences between the materials. Fig. 3 is a photomicrograph of unground Barton oxide, Fig. 4 is the same material after subsequent grinding in a hammer mill. Fig. 5 is a photomicrograph of ball mill oxide. All micrographs are at approximately 500×. The scale in all of the micrographs is 1 cm = 16 μm.

The oxide and metallic lead particles produced by the molten-lead Barton process are roughly drop-like or spherical in configuration, while those produced by the solid state attrition ball mill process are long, flat and flake-like.

The particle size, shape and surface area of ball mill oxide yield a material which is highly reactive chemically and electrochemically—important characteristics in further processing. The metallic lead particles contained in ball mill material are long, thin and relatively easy to oxidize in the curing process. Barton oxide metallic lead particles are spherical and become larger in diameter and more difficult to oxidize as the proportion of metallic lead in the material is increased. As a result, the specified limits of metallic lead in ball mill material can be higher without fear of incomplete oxidation in curing.

The orthorhombic crystal form is the high temperature stable polymorph of PbO. It occurs mainly when the molten-lead Barton reactor is operated at very high through-put rates or when the internal walls of the reactor become fouled with oxide and incapable of adequate heat transfer. Virtual absence of orthorhombic
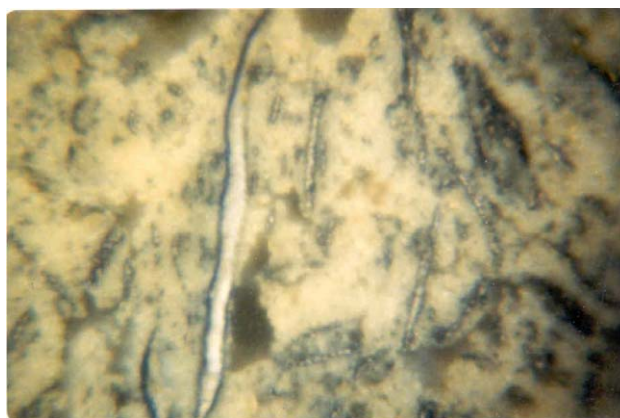

Fig. 3. Un-ground Barton oxide.

Fig. 5. Ball mill oxide.

PbO is assured in ball mill material because of lower operating temperatures. Minimizing orthorhombic PbO ($\leq$15 wt.%) should be the goal of any oxide system as it eliminates one variable in subsequent processing, i.e. paste mixing. Positive plates made with high orthorhombic PbO content oxide require more ampere-hour to convert to PbO_2 in formation than identical plates made with tetragonal PbO oxide. In the absence of X-ray diffraction equipment and technique, the two polymorphs can be identified roughly by color—tetragonal PbO is reddish brown while orthorhombic PbO is yellow.

The spherical shape of Barton oxide particles allows the material to be more easily transported in bulk than the flat, fine particled ball mill material. Ball mill oxide is prone to "shelf" and "rat hole" in storage hoppers and because of its high reactivity it is also more prone to self ignite in storage hoppers. These factors should be fully understood and accommodated for when designing an oxide system.

In carefully controlled experiments with all other variables being equal, ball mill oxide electrodes outperform Barton oxide electrodes by approximately 5% on reserve capacity and cold cranking tests.

3. Paste mixing

Preparation of paste for application to grids is a process typically done in batches of approximately 1 t or more. Various paste mixing machines are available and while they are universally referred to as "mixers" perhaps a more descriptive term would be "controlled reactor" (Fig. 6). Paste preparation begins with the blending of oxide with other appropriate dry ingredi-

ents (fiber, negative expander, etc.) followed by the addition of a measured quantity of water. Negative expander is an additive which is designed to maintain an open and porous structure in the formed negative material (sponge lead). It typically consists of carbon black, barium sulfate and a lignin derivative [2]. The water serves to wet the oxide particles in preparation for the introduction of the other main reactant, dilute sulfuric acid. Acid is carefully metered into the mix and exothermically reacts with the oxide to form a basic lead sulfate—typically tribasic lead sulfate hydrate. Typical sulfate levels in a paste mix range from 15 to 20% depending on desired final paste density. Maintaining consistent peak temperatures is very important in the production of reproducible paste mixes. Likewise, the final or drop temperature of the mix should be low enough to maintain consistency of the batch during pasting. If properly controlled the resulting paste will have the desired consistency, density, moisture content and temperature for use in the pasting process.

Paste density in particular has a profound impact on battery performance and life. Paste prepared from Barton oxide typically has better flow characteristics than that made with ball mill oxide. The reactivity and high surface area of ball mill oxide ties up the liquids more completely than the less reactive Barton material.

Minium, Pb_3O_4 is added to positive paste mixes by some manufacturers, in the order of 5–25%, to enhance the conversion to PbO_2 in the formation process. Some work has also been done on developing tetrabasic lead sulfate crystals in the paste mix through temperature modification and seeding [3,4].

4. Pasting and flash drying

While no significant chemical reactions occur in the pasting and flash drying processes some points which impact battery performance are worthy of discussion.

4.1. Pasting

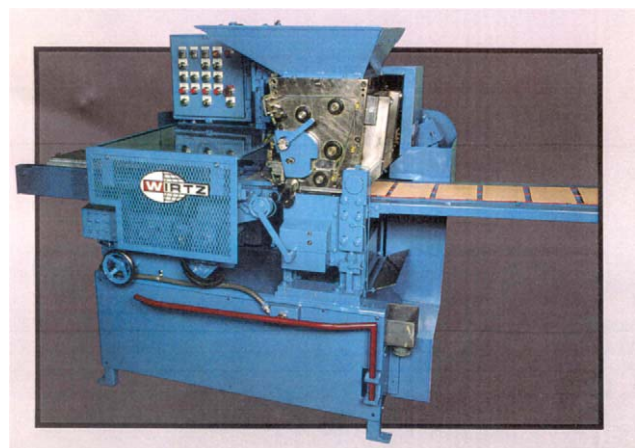Various models of two types of pasting machines are available—belt pasters and fixed orifice pasters (Fig. 7).

Fig. 6. Oxmaster paste mixer. *Source:* Wirtz Manufacturing.

Fig. 7. Fixed orifice paster. *Source:* Wirtz Manufacturing.

As the name implies a belt paster applies paste to a lead alloy grid panel or continuously cast and punched or expanded strip which is supported by and transported on a cloth belt. The process is quite forgiving, accepting grids with less than perfect thickness control and paste with certain inconsistencies. The flexible belt beneath the pasting hopper however can result in significant variation in pasted plate weight as well as very little wrap-around to the bottom side of the grid.

In fixed orifice pasters, grid panels or continually cast, expanded or punched strip of lead alloy are fed between two steel orifice plates which are at a fixed dimension from each other. The process is less forgiving in that grids must be of the proper thickness and paste must flow consistently. The result however, is exceptionally uniform paste weight control and consistently flat plates with the grid centered in the paste facilitating formation and enhancing electrical performance and life.

Until the fixed orifice pasting process was perfected relatively minute differences such as the ball mill versus Barton oxide performance advantage could not be documented because it was lost in the "noise" of imperfect paste weight control.

4.2. Flash drying

Following pasting, plates are passed through a flash drying oven to remove the moisture from the surface so that they can be stacked for curing without sticking together. Even more important than the moisture removed from the surface is the moisture retained in the interior of the paste which is vital to the subsequent curing reactions. Paste moisture content after flash drying should be about 10% by weight.

5. Curing

Plate curing also called chemstetting, hydrosetting and conditioning, consists of a series of chemical reactions which strengthen and dry positive and negative plates making them suitable for assembly into cells and for formation.

Plates entering the curing process should contain approximately 20 wt.% metallic lead, 10% moisture the balance being made up of lead monoxide and tribasic lead sulfate. Oxidation of the metallic lead particles, an exothermic reaction which requires moisture, occurs within the plate and the resulting heat drives the moisture from the plate. A photomicrograph (1 cm = 16 μm) of a partially oxidized particle of metallic lead is shown in Fig. 8. The rate at which the oxidation reaction of lead occurs is dependent on the moisture content in the paste. At high and very low moisture contents, the reaction rate is slow but in the range of approximately 5–8% moisture the oxidation proceeds rapidly. No change in the tribasic lead sulfate occurs unless a temperature of approximately 140 F (60 °C) is exceeded during positive plate curing resulting in conversion to large crystals of tetrabasic lead sulfate. Difficulty in converting such crystals to lead dioxide in the formation process was described in a pervious paper [5]. Coarse crystals of tetrabasic lead sulfate frequently form quickly encapsulating unoxidized particles of metallic lead (Fig. 9) thus preventing them from oxidizing. Conversion from tribasic lead sulfate to tetrabasic lead sulfate during curing is inhibited by
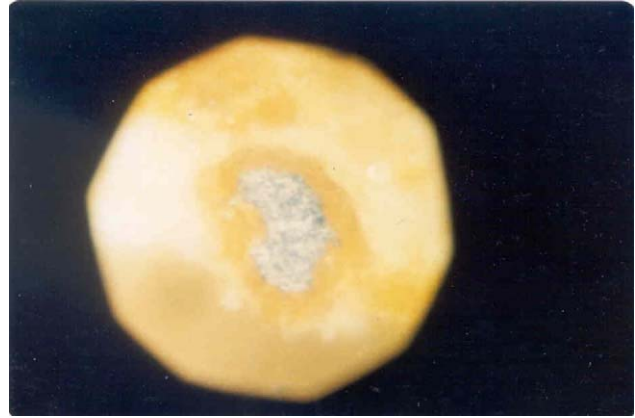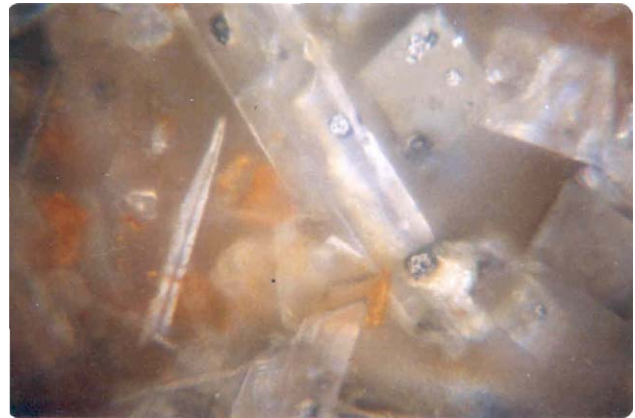

Fig. 8. Partially oxidized free lead particle.

Fig. 9. Coarse crystals of tetrabasic lead sulfate.

the ligin in negative paste and therefore only occurs in positive pates.

Control of the curing reactions requires immediate placement of the stacked plates in a humidified chamber (80–100% humidity) at about 120 F (49 °C) for 16–24 h followed by placement in a drying chamber to complete the drying process.

Cured plates should contain no more than 4% moisture and 4% metallic lead—preferably less than 2% of each. Conversion of any remaining particles of metallic lead in the positive mass to lead dioxide in the formation process is difficult at best and metallic lead particles in the negative mass possess significantly less surface area for discharge after formation than the mass formed from oxidized particles. Corrosion of the surface of the grid wires during curing provides a strong bond between the grid and the paste.

6. Formation

A sequence of important mechanical operations: enveloping, stacking, cast-on strap, through-partition-weld, cover heat seal, etc., are employed to assemble the cured positive and negative plates into batteries. The next chemical process is formation of the active materials.

Dilute sulfuric acid electrolyte is introduced into the dry unformed cells of the battery reacting with the lead compounds
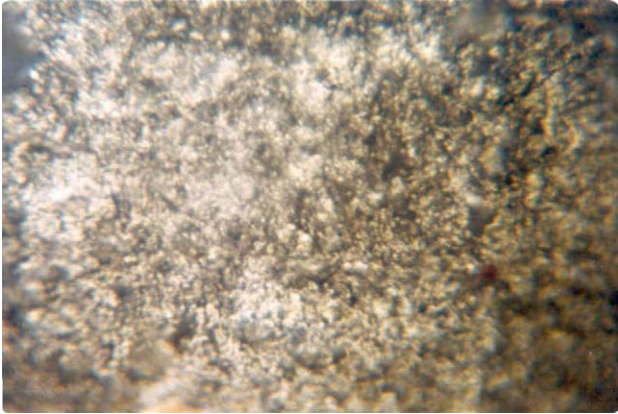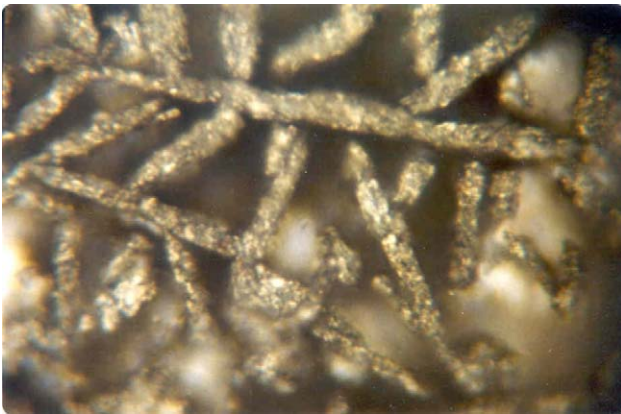
Fig. 10. Low temperature formed NAM.

Fig. 11. High temperature formed NAM.

in the pasted plates to form lead sulfate. The exotherm resulting from this reaction can result in significant elevation of the battery's temperature prior to the start of formation or charging. Techniques such as chilling of the fill acid are frequently used to reduce the thermal impact of this initial reaction.

Formation involves the introduction of electrical energy into the battery, electrochemically changing the bivalent lead compounds in both plates. The positive material is oxidized to PbO_2 and the negative material is reduced to Pb. Poor electrical conductivity of the unformed paste and inefficient electrochemical conversion result in much of the current being wasted in gas and heat generation particularly early and late in the formation process.

High temperatures during formation (>170 F (77 °C)) have been shown to have a marked irreversible negative impact on a battery's electrical performance. The microstructure of negative active material in particular is affected by the temperature at which it is formed. Figs. 10 and 11 are photomicrographs (1 cm = 16 μm) of negative active material (NAM) formed at 40 F (5 °C) and 200 F (93 °C), respectively. The low temperature formed material is finely divided and porous with very high sur-

face area. The material formed at elevated temperatures shown at the same magnification appears as coarse, dendritic crystals of lead with relatively low surface area. The elevated temperature during formation has negated the advantageous effects of the expander which was blended into the negative paste mix. Since positive active material tends to form more rapidly and completely at elevated temperatures, a compromise in maximum formation temperature, about 140–170 F (60–77 °C), must be established to optimize formation of both electrodes (140–170 F, 60–70 °C).

Two forms of PbO_2, alpha and beta have been identified. The relative proportion of the two forms can significantly impact battery performance and life. Composition of unformed paste and formation parameters are among the determinants of the PbO_2 form attained.

Electrical performance (reserve capacity, 20 h capacity, cold cranking, etc.) of batteries formed at elevated temperatures is significantly lower than that of similar product formed under controlled temperature conditions.

Methods of controlling temperature during the formation process include spraying water or blowing air on the exterior surface of the product or perhaps the most effective method—formation in a bath of circulating water.

7. Conclusion

Without minimizing the significance of the important mechanical and metallurgical aspects of lead-acid battery manufacturing, we have traced the development of active material from a chemical process standpoint. Understanding of and control over the many vital chemical processes involved in the conversion of ultrapure lead into consistently high performing, long lived positive and negative active material is essential to successful battery manufacturing.

Control of the various process parameters allows the Product Engineer to design batteries with a "sharp pencil" confident of predicted consistent performance and life.

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