A LOOK TO THE FUTURE OF LEAD PRODUCTS

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INTRODUCTION

The usage of many lead-based products has been greatly diminished and some have been completely substituted during the past three decades. These products include paints based on lead, lead-based anti-knock compounds as gasoline additive for automobile, lead glazes for pottery, solder for various applications such as sealing the seams of steel cans, automobile body solder, soldering pipe connections for potable water systems, sealing copper radiators, lead pipes, lead-based metal bearings, lead sealants such as for drain pipes or for wine bottles, chemical tank linings, ammunition, and power and electrical cable sheathing.

In most cases the application was eliminated or the products were substituted due to environmental pressures associated with the dispersive and toxic nature of lead in order to minimize the potential exposure of lead. The anti-knock additives in gasoline were banned because lead terminated the functionality of the catalytic connectors on automobiles, which were employed to improved air quality. Most lead bearing solder materials for steel cans and potable water systems were substituted because of a potential leaching of lead from these products. Mainly to reduce vehicle weight copper radiators have been replaced by aluminum. Roller bearings replaced lead bearings, plastic/aluminum composites replaced lead cable sheaths, plastic pipes replaced tile drain lines, and lead tank linings have been replaced by stainless steels. Steel shots are now used for waterfowl hunting and leaded steels are being replaced with bismuth containing alloys.

PRODUCT DEVELOPMENT

The successful substitution of lead based products is mainly driven by applying materials with lower toxic properties, and advanced mechanical properties such as less weight, or increased strength. Very often these materials are also manufactured with new production methods resulting in lower production cost. In addition, they restrict the release of lead to the environment. In the new millennium lead-based products will consist only of lead products with a definite purpose. The criteria for these products will be:

- needed throughout the economy
- cost effective
- readily recycled
- not readily substituted
- packaged to limit exposure to lead
- have longer life and use lower amounts of lead
- offer significant advantages over competitive materials.

Product development in the new millennium will focus on only a few product areas at already existing application categories. Some governments around the world wish to ban all lead products or at least limit the application of lead to the currently used products. Therefore, it will be virtually impossible to introduce new lead products. How can an industry perform good product research and development when there are no new products?

The lead products in the future require special unique properties of lead, which enable it to compete with other materials. The special characteristics are protection and electrochemical.

Protection

One of the unique properties of lead is the capability to collimate and absorb x-rays and other damaging radiation. Therefore, it will find significant use in protecting the population from radiation. Applications are and will continue to be in containers for radioactive isotopes, shielding in nuclear power and medical treatment facilities. In the form of lead oxide glasses it will be employed in cathode ray tubes, TV picture tubes, computer screens, and transparent shielding to protect users of these products from ionizing radiation. The degradation process of PVC products due to ultraviolet radiation or the exposure to other natural environmental processes will be virtually prevent by means of lead stabilizers. Lead sheet will continue to be used as waterproofing where long lifetimes are required.

For each individual application, continued product development will result in improved properties as well as the most optimum amount of lead for each shielding material. Improved stabilizers will permit the use of lower amounts of lead while still imparting the same beneficial properties. And finally, means must be developed to recycle the lead shielding materials particularly those in TV and computer screen glasses. In many lead products, process development to recycle these products will be as important as product research to improve the product.

Electrochemical

Lead is able to exist in three different states (metal, ion with +2 charge, and ion with a +4 charge). Because of this unique property it is used not only as electrochemical anodes to electroplate other metals from sulfuric acid solution but also serves as anode, cathode, and active material in lead acid storage batteries. Storage batteries represent over 70% of lead usage worldwide and over 80% of lead usage in the United States.

Batteries and anodes for electrowinning are two of the unique successes of lead product development efforts. The development of novel processes and products, which use these newly improved old products, can be attributed to these efforts.

Anodes

Insoluble lead-based anodes have been used for electroplating of zinc, copper, nickel, cobalt, and other metals from sulfuric acid for many years. Over the past 20 years the performance of these anodes have been dramatically improved as seen in Table I.

Table I - Performance of Anodes in Copper and Zinc Electrowinning Systems

EW Process	Date	Anode Thickness (mm)	Anode Life (Life)	Current Density (A/m^2)
Copper	1980 2000	10 - 15 mm 6 mm	.5 - 2 8 - 10	180 300
Zinc	1980 2000	12 - 18 mm 9 mm	1 - 2 6 - 8	380 550

The performance of the new lead anode products have enabled new copper SX-EW processes to grow from a very small percentage of the copper market in 1980 to a significant market share in 2000 with significantly lower production costs than conventional copper production methods and similar copper cathode purity. Product research has been responsible for the development of new rolled lead-calcium-tin alloy materials with unique grain structures which are extremely corrosion resistant for anodes. This has enabled the anode thickness to be reduced by a factor of two while the average life has been increased by a factor of at least five, even as the current density was almost doubled.

New lead-calcium-silver-alloy zinc electrowinning anodes have given longer life with thinner anodes at higher current density. The lead anodes offer significant cost, life, performance advantages over conventional anodes. The lead anodes offer scrap value to recyclers and are much more cost effective than non-lead competitive electrowinning anodes. Much of the development of electrowinning anodes has been the result of new product development aimed at improvements in lead acid battery technology. For lead to be competitive in a toxic/regulatory environment it must offer dramatic improvement over the old product. For lead to continue to be considered a viable product in the new millennium the product must use less material, have a longer life, and offer greatly improved performance than the current product. Lead electrowinning anodes are an excellent example of the "new" old products.

Lead Acid Batteries

Lead acid batteries are the bright spot in lead product development. Since 1970 the percentage of the lead market occupied by lead acid batteries has risen from 28% in 1960 to over 73% in 1999. The lead market has risen primarily as a result of the dramatic increase in production of lead acid batteries even as other lead products declined or disappeared. The lead consumption has risen from 3,260,000 tons in 1960 to over 6,000,000 tons in 1997. Batteries increased from just under 1,000,000 tons to 4,400,000 tons per year. The lead acid battery is readily packaged for recycling and the amount of recycled lead production increased dramatically from under 1,000,000 tons in 1960 to over 3,000,000 tons in 1999.

Much of the improvements in lead acid batteries have been the result of lead product development aimed at improving the performance of the lead acid battery. Novel battery grid alloy materials have led to process changes which resulted in significant decreases in cost to produce the batteries. The process changes not only decreased production costs but also increased productivity and at the same time decreased worker exposure to lead.

In 1975 at the U.S. Super Bowl the Sears die-hard battery started several cars simultaneously on a frozen lake in Wisconsin. Table II shows how typical lead-acid starter battery performance has improved between 1975 and 2000.

Table II - Lead Acid Battery Performance

Year	Weight (Kg)	Cold Cranking Amps
1975	21	450
2000	15	750

The performance of the battery has been almost doubled while the weight of the battery has been reduced by over 30%. The resultant battery product has been improved by a factor of 2.5 times. The improved performance and reduced material consumption has resulted in reduced lead consumption per battery. The improved performance combined with improvement in productivity due to new lead battery alloys and lead materials have resulted in a decrease in cost to the consumer for automobile starter batteries in 2000 compared to 1975.

The major improvement has been the replacement of lead antimony alloys with lead-calcium-tin alloys. The new alloys are more conductive and significantly more corrosion resistant than the alloys which they replaced. In addition, the new alloys permitted the construction of maintenance-free batteries which do not require the addition of water during the expected life of the battery. The new alloys permitted dramatic changes in the battery grid and plate manufacturing process from handling individual grids and plates to continuous processes where battery parts are produced at high speeds. The continuous processes reduced worker exposure to lead in battery manufacturing. The maintenance-free batteries, because of the sealed construction, reduced consumer exposure to the acid electrolyte in the battery further enhancing the environmental appeal of the modern automobile battery.

Automobile batteries have also been designed for recycling. The secure case permits return of the failed battery to the recycler without unique environmental problems. Lead recyclers have developed processes to recover virtually all the lead values in the battery for return to new battery production. In addition, the battery cases and acid have been also recycled to usable products. Lead acid batteries represent the highest recycling rates of any commercial product. Rates of 95-97% have been achieved in the late 1990's.

The greatest growth area for lead products is in sealed valve-regulated lead acid batteries (VRLA). In these batteries the electrolyte is contained in a gel or the separator between the plates, and gases generated upon charging are recombined within the battery. The totally sealed batteries can be utilized in any orientation and virtually any location and have found use in telecommunications and uninterruptive power sources for hospitals, computer systems, and emergency systems. VRLA batteries are also used for power conditioning, remote area power storage such as from solar or wind power generation, and are being specially developed for electric vehicle and/or hybrid electric vehicles. Much of the research and development for these new battery systems particularly for EV and HEV service has been funded by the Advanced Lead Acid Battery Consortium (ALABC).

Lead product development efforts have been devoted to the development of new lead alloys to reduce the rate of corrosion, improve the conductivity between the grids and active material, and constrain the active material to increase life. Lead product development efforts for batteries are also aimed at improved oxides for the active materials leading to improved material utilization. Process development to improve the purity of lead from recycled batteries is also a major factor in improving the life of VRLA batteries.

Because of the development of extremely corrosion-resistant, extremely strong battery grid materials, new manufacturing methods have been developed to produce much thinner grid materials which not only decrease weight but also improve the performance of the active material. The new lead alloy grid materials are resistant to corrosion and degradation at elevated temperatures making them ideal candidates for extending the life of new batteries operating in hot, severe climates where battery life is extremely short today.

These new alloys have permitted significantly different battery designs. New battery designs such as thin metal fail batteries using grids as thin as 0.05 mm offer significant improvements in power compared to conventional designed batteries using grids of 1-2 mm thick. A 12-V battery of the new design weighs about 3.5 kg and delivers 1000 amperes while the conventional design weighs 15 kg and delivers only 750 amperes. New battery designs using the newly developed grid materials are being developed to compete with exotic battery chemistries for use in hybrid or electric vehicles.

Product development in the new millennium means not only developing your own material, but also assisting the customer who produces the ultimately used lead containing materials. The assistance requires even more knowledge of the customer's process and leads to a partnership between lead product producer and lead consumer in batteries. The lead product development engineer in the new millennium must be as (or more) knowledgeable about the user's process than the customer.

CONCLUSION

Lead products have decreased significantly over the past 30 years. The remaining lead containing products offer special advantages over competitive products with regards to performance, cost, life, and recyclability. The major areas where lead products remain are those of security and electrochemical. These few remaining lead-based products have dramatically expanded lead usage by serving customer needs at the same time reducing environmental exposure of a toxic metal by extremely high recycling rates. Product development in the new millennium is not only development of improved products, but also a partnership with customers to improve their productivity as well as produce lead-based products which are readily recycled.