LEAD INDUSTRIES ASSOCIATION, INC.
292 MADISON AVENUE
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SUBJECT: ANNUAL ARTICLE IN INDUSTRIAL AND ENGINEERING CHEMISTRY

To Members of the Lead Industries Association, Inc.:

We are attaching a copy of the annual article on new developments in lead which we prepare annually for Industrial and Engineering Chemistry, which appeared in the April, 1962 issue under "New Uses for Lead."

Additional copies are available free of charge in quantities up to 25 and at our cost of $2.50 per hundred for larger quantities.

Very truly yours,

R. L. Zimmerman

Executive Vice President

RLZ:mk
Enc.

Look Ahead with Lead

NEW USES FOR LEAD

For most common materials there is one major property, or perhaps a few related properties that account for the major use. Not so with lead. Few materials have as wide a spectrum of uses based on as many different properties

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Because of a great diversity of useful properties, lead has been able to maintain a stable market in the last decade, despite the relentless influx of new materials to compete with lead in architecture, cable sheathing, chemical construction, paints, and other uses. Some markets have dwindled under this attack but new uses have sprung up to take their places.

Total lead consumed in 1961 has been estimated at about 1,005,000 tons, which compares to a lead usage of about 1,151,000 tons in 1951 (see table). Not included in the 1961 figures are perhaps 20,000 to 25,000 tons of fabricated lead products that are imported. This influx has been due to a loophole in the lead import quotas established in 1958. The quotas cover pig lead imports but not fabricated products. Cable sheathing alloys and white lead house paints have been the major losers to new materials in this last decade. But this loss has been replaced in large measure by increased use of tetraethyllead antiknock additives. These in turn are finding competition from other compounds.

Consumption of sheet and extruded lead products in chemical construction has remained about constant over the 10-year period (i.e., an estimated 23,000 tons in 1961, compared to 21,000 tons in 1960 and 25,000 tons in 1951). This does, however, represent a net loss to other materials when the growth of the chemical industry is taken into account. Two other products that have experienced substantial net uses in the last decade are ammunition—the popular appears to be hunting pellets and caliking lead. Caliking lead has grown not only because of increased construction but because of a swing away from substitute materials. Collapsible tubes is another product that has been growing. The introduction of fluoride-containing toothpaste has served to

CONSUMPTION OF LEAD IN THE UNITED STATES

(Tons of contained metal)

	1951	1960	1961
White lead	25,700	11,600	11,200
Red lead and litharge	75,700	74,900	72,200
Storage batteries	393,900	393,200	392,200
Cable covering	139,900	60,400	59,200
Construction	65,700	45,700	44,000
Tetraethyllead	127,500	163,800	166,000
Ammunition	51,300	43,600	44,000
Foil	2,800	3,700	2,800
Bearing metal	33,700	20,700	17,000
Solder	65,400	60,000	55,000
Type metal	33,700	28,200	25,000
Caliking	43,800	66,500	71,000
Other uses	167,200	85,700	81,000
	1,151,000	1,021,200	1,005,000

Source: U.S. Bureau of Mines Statistical Data

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increase the use of lead collapsible tubes from 8,000 tons in 1960 to over 11,300 tons in 1961. The fluoride compounds are apparently corrosive to lead's major competitor in this field, aluminum.

Some applications that are expected to make significant contributions in the next decade are covered here.

Sound and Vibration

Lead, both as sheet metal and as a component of fabricated composite materials, is finding increasing use in sound and vibration control. Such composites have been brought to wide scale commercial use in the past year. The most widely used are dispersions of lead powder in vinyl sheet, with or without fabric backings. Some silicone and epoxy formulations loaded with powdered lead or lead ore are also used. In addition, many new materials, chiefly plastics in the vinyl, epoxy, and polyethylene-polypropylene families, have been loaded with lead or lead compounds to form new composites suited for special use.

Three general areas of usefulness have been found for lead in this field:

Antivibration mountings
Sound barriers
Sound and vibration-damping materials

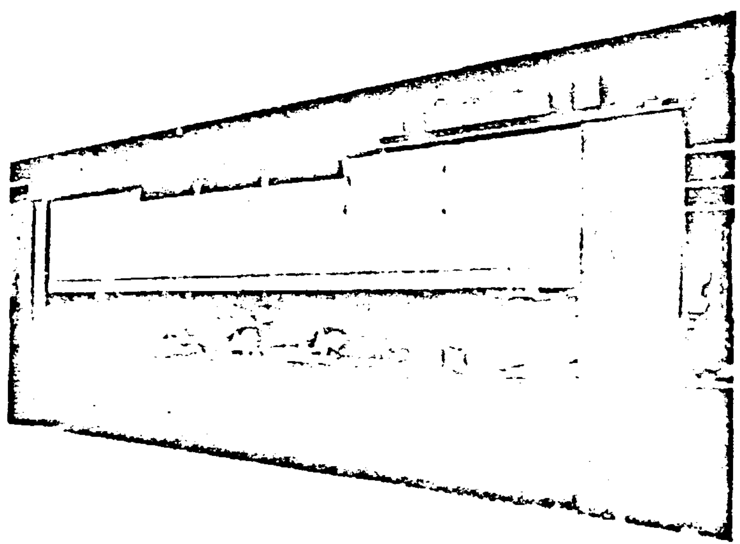
Antivibration pads, most frequently made of alternating layers of lead and asbestos, were used in the foundations or footings of several prominent buildings during the year. The best known and most illustrative example is probably the new Pan American Building being erected over Grand Central Terminal in New York. Here, heavy street and rail traffic under and around the base of the building leads to serious vibration problems. To keep such ground-borne energy out of the steel structure of the building, more than 600 various size lead and asbestos pads, 1 inch thick, have been placed between the steel and its footing. Research is in progress to determine the attenuation mechanism of the pads. Estimates of vibration transmission at various frequencies and static loading will also be confirmed.

Some use of these pads has been made in mounting such vibration sources as cooling towers ([illegible]), printing presses ([illegible]), and others. Behavior of lead-asbestos pads in such applications is not so well understood as it is in building foundations, chiefly because of the lighter static loadings usually involved.

Research to date indicates that small pads may begin to attenuate appreciably vibration in the frequency range above 100 cycles per second. Higher frequencies are more effectively blocked than low ones so that, at 300 cycles per second and above, 5% or less of the original vibration would pass through the pad.

The most difficult obstacle to the use of small pads on chemical plant equipment is a prior determination of the frequencies to be blocked. A fan with a shaft speed of 1200 r.p.m., for example, might be thought to have most of its vibration in the region of 1200 r.p.m. or 20 cycles per second. Allowing for, say, six blades on the fan, this peak might be thought to fall in the 120 cycle-per-second range. Yet actual measurements on such a fan showed the peak to be in the 150 to 300 cycle-per-second band. Furthermore, the vibration in the 300 to 600 band was as intense as that in the 75 to 150 cycle-per-second band. Under these conditions, lead-asbestos pads would be expected to supply appreciable attenuation. Research is continuing in this area.

The use of sheet lead as a sound barrier has been



Lead-loaded plastic sheet can be used for sound control in flexible room arrangements. The vertical [illegible] is provided when the sheet is lowered by a [illegible] roller.

explored and lead has been found to possess a unique combination of density and structural limpness which gives it the highest sound transmission loss of any common building material. It has been found (24), for example, that lead foil, 0.008 inch thick, is acoustically equivalent to $\frac{1}{4}$ inch of fir plywood; $\frac{1}{4}$ inch of lead is equivalent to a standard plastered wall with gypsum lath and $\frac{1}{2}$ inch of sand plaster on each side of wire truss studs.

By incorporating finely powdered lead in plasticized vinyl sheet, a highly flexible material is obtained which also has a high sound transmission loss. Various proprietary formulations of this material have found use in quieting aircraft, office equipment, noise sources in the plant (*A0*), and architectural applications (*A4*). Tests of various configurations of sheet lead and common building materials for prefabricated acoustic panels have also shown great promise.

Leaded plastic materials for sound damping are less well known generally. Their development and predominant use has been in classified military projects. Generally speaking, this group of materials is made up of a soft plastic matrix, commonly epoxy or vinyl but sometimes silicone, with powdered lead or lead ore dispersed through it. Common loadings are 65 to 85% lead by weight. The newest development is a paint based on an elastomer to produce the same sort of finished system. The mechanism of sound damping by such systems is not well known though, viscoelastic shear is thought to be largely responsible for the damping.

Thermoelectricity

Thermoelectricity appears to be a growing use for lead. Despite the very energetic research for new and better materials, and the discovery of some, lead telluride today is still the most efficient material in the temperature range of power generation (between 500° and 1200° F.).

Though not ready to compete with conventional sources of prime power yet, significant commercial markets still exist for these exotic power packages even today. Commercial uses can be separated into two classes: auxiliary power from waste heat sources, and power packages for areas remote from power lines.

The first demonstration of a remote power source was the Snap III built by Minnesota Mining & Manufacturing Corp. It provided 7% conversion efficiency with relatively light weight and no moving parts. Some Snap III's have recently been built and are being placed in service.

One of the early commercial uses of lead telluride for remote power is by Northern Illinois Gas Co. After many months of testing, this company has a 10-watt thermoelectric generator in actual service protecting 8000 feet of 16-inch diameter steel pipe. Installed at the end of two gas mains in LaGrange, Ill., the unit is powered by burning gas from the gas mains. Predicted operating costs for the thermoelectric generator (using the company's product—natural gas) should be about $3.00 per year for one generator, compared to an electric bill of about $5.90 per year for equivalent service. Northern Illinois Gas now uses about 100 rectifiers in its cathodic protection program running an annual electric bill of about $10,000.00.

The future for thermoelectric power is bright. With conversion efficiencies of 8 and 9% today, continuing research will almost certainly improve efficiencies to over 10%. Some responsible sources are even suggesting that 20% will be achieved in the foreseeable future.

Piezoelectricity

In 1955, a particular mixture of lead zirconate and lead titanate, calcined together, was discovered to be an excellent piezoelectric material (*1B*). A number of commercial modifications of this original material have been made. Called *PZT* in the trade, this material has a high coupling coefficient electromechanical coupling efficiency and a very high operating temperature. Curie points as high as 600° F. have been reported.

Today *PZT* is finding a rapidly increasing market. One important use has been in ultrasonic cleaning equipment (*2B*).

Another use in test is in electrostatic gas-filtering systems. Using pressure supplied by the rotating fan shaft, chunks of *PZT* can maintain a high electrostatic charge on the filtering screens. Varying voltages can be applied to successive screens by varying the pressure on the crystals.

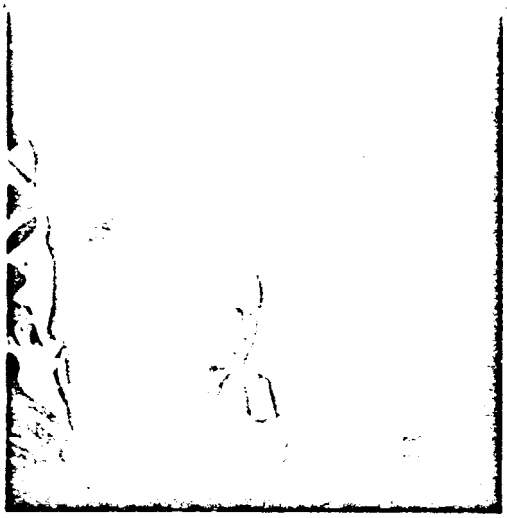
Recent research at General Telephone and Electronics Labs., Bayside, N. Y., has developed a flat panel of *PZT* sheet stock coated with an electroluminescent phosphor that will create a simple image (*3B*). Possibility of a picture frame television screen is obvious.

Corrosion

Corrosion of soft lead in boiling sulfuric acid over a range of concentrations has been studied by Holdstein and Pelzel (*2C*). Discrepancies that have been observed in the corrosion rate for 50 to 80% H_2SO_4 can be explained, according to the authors, by a passivation of lead because of anodic polarization. The authors have correlated three specific ranges of potential with weight loss.

Tests were carried out by Schmeling and Roschenbleck to clarify the electrochemical phenomena during the formation of surface films on lead (*4C*). Starting with the premise that pores in the protective coatings are responsible for pitting, potentiostatic and galvanostatic measurements were made on the behavior of lead in electrolytes known to form protective coatings. The

AUTHORS. *Sid Turner, a graduate Metallurgist, was a staff member of the Lead Industries Association, Inc., at the time this article was written. His chief interest with LIA was the use of lead and lead chemicals in the CPI. Bruce Fuder, a graduate Chemical Engineer, is a staff member with LIA. His chief interest is the devel pment of improved leaded plastics and elastomers for sound control.*



The flat panel of PZT sheet steel coated with an electroluminescent phosphor shown being inspected here may be the forerunner of television screens hanging from a wall-like picture

effects of chloride ions and corrosion products were studied as well as the structure, deformation, and surface condition of the lead.

Use of lead anodes for impressed current cathodic protection systems for steel immersed in water has been advancing steadily. A new automatic control system has been developed which provides the right amount of current through the anode at all times (*1C*).

Ceramics

Research on high pressure high temperature polymorphism of lead oxides were carried out at Penn State University by White and others (*2D*). The common oxides were examined at up to 60,000 atm. and from 100° to 500° C. Unusual metastability and inversion characteristics of the massicot phase were examined in detail. PbO₂ (rutile structure) was transformed at pressures in excess of 13,000 atm. at 300° C. to an orthorhombic form, according to the authors.

Volatility of lead at process temperature is a subject of much interest in ceramic operations, due to the difficulty of controlling composition. Hirayama has reported the volatility of binary lead silicate and lead borate melts containing more than 7% of lead oxide at reduced pressures (*1D*). At comparable temperatures, the volatility of the binary lead silicate melt is higher than that of the lead borate of corresponding PbO to boron ratio. The volatilization of PbO appears to be diffusion controlled.

Pigments and Paints

In the past decade or so many of the long-standard paint formulations have been revised because of a revolution in vehicles. For the most part, established anticorrosion coatings based on red lead have survived in their original or in modified forms. A number of these formulations, based on red lead, have been tested under various conditions and the formulations of the best 24 have been published (*1E*).

One innovation of the past few years has been the commercialization of lead pigmented paints where the active lead pigment is coated over the surface of microscopic carrier particles of silica. These paints, said to be pigmented with basic lead silicochromate, have passed through the manufacturers' testing phase and are now in use or under test by several state highway departments and others.

Research was also started on water-based lead-bearing paints for use on both metal and wood surfaces. Though the program is far from complete, there is definite promise in this area.

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