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SUBJECT: NINTH ANNUAL MATERIALS OF CONSTRUCTION REVIEW (1955)

Attached is a reprint of the section on lead and lead alloys prepared by the Lead Industries Association and published in the September 1955 issue of "Industrial and Engineering Chemistry," official publication of the American Chemical Society.

The section is part of the Ninth Annual Materials of Construction Review. Additional copies are available as long as our supply lasts.

Yours very truly,

Robert L. Ziegfeld

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Secretary

LIA10077

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Lead and Its Alloys

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[illegible] lead supply continued plentiful and at a reasonable price. The American Society for Testing Materials Committee B-2 on Nonferrous Metals and Alloys has approved revisions of ASTM Standard Specifications for pig lead (B 29-46). The revision involves a reduction in the number of grades specified inasmuch as some now listed are no longer commercially available (1).

Research Progress

High Purity Lead. Several research papers were published last year on the subject of high purity lead. Fagnani (11) described the production and application of superpure lead, along with its physical and chemical properties. Applications included the chemical industry, lead-acid batteries, and others.

Hughes (18) evaluated the various methods of preparing high purity lead and, based on analytical results, described a combination of procedures that result in lead of extremely high purity. The method involves the electrolytic displacement of bismuth and other elements from lead salt in solution by treatment with lead metal, supersaturation of numerous impurities on lead sulfide, conversion to metal, and final vacuum distillation.

De Souza Santos (37) showed how refined lead of 99.99+% is being manufactured in Brazil. Purity requirements, composition of lead bullion, sequence of refining operations, description of equipment used, sampling, chemical analyses, and composition of the refined lead were all given.

Davey (5) described the desilverizing of lead bullion, going into the theoretical aspects of the silver-lead-zinc system and the fundamental bases of various desilverizing procedures.

Kemmer (18) described several processes for the production of lead alloys and crude soft lead in Germany, along with techniques for the removal of copper, tin, and antimony.

For certain specialized experimental work involving radioisotopes and radiation detection equipment, commercially purified leads which may contain minute traces of radium-decay series elements can introduce indications of radioactivity, harmless for all common purposes and undetected by conventional devices but of high enough radioactivity to upset extremely sensitive detectors. To alleviate this situation, the Atomic Energy Commission at the Oak Ridge National Laboratories has asked the Lead Industries Association for its assistance in a cooperative research program, the purpose of which will be to evaluate all of the commercially available leads as to the presence of detectable trace radiation. It is anticipated that such factors as geological age, proximity of ore deposits to uranium minerals, methods of refining, and presence of "Thorium" and other radioactive contaminants will all have a bearing on the investigation.

Physical Characteristics of Lead. Douglas and Dever (10) measured the heat content relative to 0° C. of a sample of 99.9+% lead at ten temperatures to 900° C. and derived the heat of fusion and the heat capacity of the solid and liquid from the data. The heat capacity, entropy, heat content, and free energy are tabulated at intervals over the range of 2.5° to 1800° K.

Zavaritsky (51) determined the heat capacity and resistance measurements for lead and aluminum wires. Measurements at temperatures ranging from room to near melting point were determined for each metal. The author showed that both heat capacities and temperature coefficients of resistance increased in temperature in such a way as to suggest that they are influenced by a single activated process rather than by impurities.

Some measures of sound velocity in single crystal specimens of lead and particularly the effect of cold work surfaces on ultrasonic echoes were given by Kemmer (18).

Bordoni and Nuovo (3) determined the dissipation of elastic waves in lead at high temperature. The damping of extensional vibrations in lead was measured in ranges from 10 to 40 Kc. for temperatures between 300° and 600° K. by means of electrostatic methods.

Mantsch (25) described the determination of oxygen content in lead by the hydrogen reduction method and others.

McKeown (24) described an accelerated method of determining the endurance limits of lead and lead alloys using a standard fatigue specimen and Wechsler-type machine.

Advances in Lead Physical Metallurgy. Sumee and Jones (36) reported on the role of inverse segregation and redistribution of minute atoms in the freezing of hypereutectic lead-antimony alloys. They show that there are possible harmful effects in storage battery grids caused by the concentration of antimony in the surface of the alloys. The effect appears to be caused by interdendritic flow of multi-motion alloy having near-eutectic composition to the cap left between the mammoth crust and the mold face during solidification.

Tiedema and Burgers (34) studied precipitation in lead-tin alloys and confirmed with x-ray photographs of aging single crystals of lead-tin alloys the fact that the rate of decomposition is maximum at definite undercooling. The precipitation process is discontinuous and accompanied by recrystallization. For slow rates of precipitation the resulting fine grained material showed the texture to be related to the orientations of the original single crystal lattice.

Margerie and Farrer (35) investigated the titanium-lead system in the region 0 to 55% lead and from 500° C. to liquidus temperatures.

Creep Characteristics. Dullieu (9) issued a progress report on an investigation of creep, fracture, and bending of ornamental lead alloys for cable sheathing conducted in cooperation with the Edison Research Committee of the Commonwealth Edison Co. and the Department of Theoretical and Applied Mechanics of the University of Illinois.

In tensile-creep tests of ornamental alloys, just as for other lead and lead alloys, at stress of 300 lb. per sq. inch or less, there seem to be three well defined stages: a preliminary stage during which creep starts at a relatively high rate and diminishes in rate as the stage proceeds; a stage during which the creep may remain nearly constant, diminishes gradually at a greatly reduced rate for several thousand hours, or gradually increases for a long period; and a third stage during which the creep rate increases, the specimen tends to "neck down," and final fracture occurs. The creep rate during the second stage, which is the minimum creep rate during the entire test, is usually taken as the index of creep resistance of the metal. Low creep rate means high creep resistance.

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Creep deformation in lead alloys results from the combination of two mechanisms: creep within the grains, which occurs as crystallographically directed slip, or translation; and plastic flow at the grain boundaries. At higher stresses creep deformation which precedes failure is more a result of slip, whereas with the lower stresses reported in the creep tests, grain boundary flow becomes the major mechanism of deformation. The alloying constituents tend to form a mechanical lock with the grains, retarding slip due to stresses below certain limits. Failure then takes place at the grain boundaries.

Dendritic (coring) structures (that form appreciable alpha and eutectic areas) in lead moderately enhance the creep resistance of lead. Under the influence of heat and stress, unless the alloy is artificially aged, precipitation takes place and a higher creep rate is observed. If the precipitation is discontinuous highly localized boundary flow leads to early fracture. Evenly dispersed particles of metallic or of stable intermetallic compounds greatly enhance the creep resistance of lead.

The presence of other metals in lead retards recrystallization. Arsenic gives the lead an extremely fine grain size and also retards recrystallization. When recrystallization does occur the grains are small in comparison to other alloys of lead. The self-annealing tendency of arsenical lead is a slow recrystallization spread over a long period of time. The excellent creep properties of the arsenical leads at lower temperatures (110° F.) are due to the ability of these materials to retain considerable work hardening from the lead press. At the higher temperatures (above 110° F.) some recovery and slow recrystallization take place which increase the creep rate and lead to greater elongation.

Multiple strip bending machines operating at 110° F. with 10-min. and 1-hr. cycles were used to measure the bending resistance of a longitudinal strip cut from sheathing. In the range of strains commonly met in service (0.3 to 0.5%), the superiority in bending resistance of the arsenical leads was demonstrated. Alloys prone to discontinuous precipitation have poor bending resistance to this range of strains. Slightly overaged alloys are more resistant to bending. Some of the alloys that tended to lose ductility under low stress conditions had good bending resistance to the range of strains. Very good bending resistance was obtained with both copper-bearing and tellurium-bearing arsenical leads in which the arsenic content was slightly higher than the tin content.

Stopping of the press during extrusion affects the creep properties of the sheathing. Even if the sheathing is quenched some distance from the die block, a section of the sheathing may become overaged due to slow cooling near the die block. The creep resistance of this section is lower and failure occurs here. For an inch or two before the press mark the sheath is not cooled as much and receives a more severe quench when the press is started. This section is slightly overaged but more nearly to the point of maximum creep resistance.

KEMPTON H. ROLL, technical director of the Lead Industries Association, has been our review author for Lead and Lead Alloys since 1952. Roll, a metallurgical engineer, attended Carnegie Institute of Technology, received the degree of B.E. from Yale University and M.S. from the Polytechnic Institute of Brooklyn. He is past regional chairman of the National Association of Corrosion Engineers for their 1954 meeting, he will serve as general conference chairman. Roll holds memberships in A.S.T.M., ACS, AATM, AIChE, AIME, SAE, and is vice chairman of the New York Section of the American Society for Metals.

Brook (*4*) demonstrated the effect of grain size on creep rate and the effect of stress and grain boundary sliding on two similar specimens of lead containing 0.5% tin. One specimen tested at a stress of 300 lb. per sq. inch, creep 51% in 13,000 hours, whereas the other specimen tested at 500 lb. per sq. inch creep only 11% in the same time. The author attributed the surprising drop in creep rate at the higher stress to recrystallization which occurred during the test.

Hopkin and Thresher (*14*) continued their work on the creep and fatigue properties of lead and lead alloys investigated the effects of some constitutional factors. Because of the number of factors at work it was too difficult to [illegible] results in a quantitative way. Qualitative generalizations only were attempted.

Pelley, Drayton, and Watkins (*5*) assigned to the British Non-ferrous Research Association took out a patent on a process for lead coating ferrous and ferrous metals. This invention [illegible] that control of [illegible] of lead on base metals. [illegible] as a measure of the [illegible] discovered that a specific [illegible] to low than 15° on the [illegible] The investigators performed a [illegible] system forms no plate [illegible] be coated. Any type of [illegible] lead or lead-base alloy may be [illegible] this system. The presence of arsenic, silver, or bismuth in the lead appears to have little or no effect on the coating characteristics of the nickel-lead. The nickel may be added to the molten lead in the form of metallic nickel or as a nickel-lead hardener. The metals to be coated are prepared in the usual manner by first degreasing and pickling using hot 10% sulfuric acid for the latter. Copper was pickled by dipping in ferric sulfate or chloride solutions. After pickling the metal is fluxed with aqueous zinc chloride or zinc-ammonium chloride. According to the patent the lead coatings are smooth, continuous, and relatively free from pores. The inventors declare that no other method of lead coating by hot dipping hitherto employed gives coatings so free from porosity in the case of iron, steel, and copper. The coatings are ordinarily from 0.001- to 0.002-inch thick and are not destroyed by subsequent working of coating even above the melting point of lead.

New Grid Alloys. One of the reasons storage batteries wear out in service is corrosion of the lead-antimony positive grids. To compensate for this, there has been a trend toward reduction of the antimony content of grid alloys as a means of increasing battery life. Roberts (*28*) found that by substituting small percentages of silver and arsenic for some of the antimony content, service life was increased materially by improving the resistance of positive grids to corrosion.

Common battery grid alloys contain from 6 to 12.5% antimony. According to the patents by adding between 0.45 and 1.25% arsenic, the antimony content can be lowered to between 4.5 and 6.5%. By adding silver in the order of 0.04 to 0.6% in addition to the arsenic and antimony, the battery life due to lowered grid metal corrosion is not only increased but the evolution of undesirable stibine and arsine gases is reduced. Figure 1 shows how the service life of a lead-acid battery is influenced by the presence of arsenic and silver of varying percentages in the grid alloy.

Corrosion Characteristics

Roll (*23, 24*) summarized the principal applications and significant characteristics of lead and lead alloys as used in the chemical process industries, in the form of a series of two reference sheets published by the American Institute of Chemical Engineers. The first covered the grades and forms in which lead is employed in chemical construction, including its characteristics, properties, and common types of construction. Lead valves, castings, fittings, and sheet construction are detailed. Heat treatment, weldability, temperature limitations, and mechanical and physical properties are also given. The second reference sheet was devoted principally to the corrosion characteristics of lead and lead alloys. It included tabulated data showing the performance of lead with commercially used acids and alkalies, salts, gases, organic materials, and others.

Kato (*17*) reviewed the corrosion characteristics of lead, and

Porcelain enameled aluminum . . . possible by low fusing temperature of lead frits

partially the exposure of corrosion of lead in neutral, acid, and alkali solutions. Surface reactions were detailed.

In *Lead*, a publication of the Lead Industries Association, case histories of several lead- and lead-alloy equipment at high temperatures were described (*11*). One of the equipment [illegible] Monel-lined lead and the other a 13% chromium steel, was in lead pipe lines and valves [illegible] of sulfuric acid brine. The metals were subjected to sulfuric acid, chlorinated organics, and some hydrochloric acid and operated at 300° F. Another vessel, protected with a brick and lead lining, was handling 25% sulfuric acid and was hot at 120° F. and after 13 years service was in perfect condition. The metals [illegible] C. have been in service for about 6 years [illegible]

The [illegible] of Corrosion Engineers (*12*), through the work of Technical University in Delft, published the replies to a questionnaire relating to practice used in making corrosion surveys on underground lead-sheathed cables. Information was presented on testing [illegible], instrumentation, criteria and materials, along with recommendations based on replies from 22 companies and Examinations Commission.

Hoover (*13*), speaking at the 37th Annual Meeting of the Lead Industries Association, discussed the outlook for lead in chemical processing. He pointed out the need to encourage the use of bonded lead equipment where lead physical limitations are at a minimum and cost is still in line with competitive materials. The use of bonded lead has increased from between 1500 and 1800 tons per year 5 years ago to between 3000 and 3500 tons per year at present.

Klinger (*14*) reviewed the manufacture and application of bonded lead linings for the handling of sulfuric acid.

Corrosion by Liquid Lead. In conjunction with studies of the suitability of liquid metals for high temperature heat transfer systems, an investigation was made by Gangler (*15*) to determine the resistance of 13 ceramics and cermets, 13 refractory metals, and 9 high temperature alloys to attack by lead-bismuth eutectic alloy (44.5% Pb and 55.5% Bi) in a dynamic system at temperatures of 1500° or 2000° F. With the exception of zirconium carbide all the ceramics and cermets were resistant to attack by the molten alloy at 2000° F. Of the thirteen refractory metals only arc-cast molybdenum sulfided resistance to lead-bismuth at 2000° F. All nine high temperature alloys had poor resistance at 1800° F.

Cathcart and Manly (*6*) described a satisfactory new testing technique devised for comparing the corrosion characteristics of a series of metals in liquid lead, one of several dynamic liquid metals used as coolants in nuclear reactors. The apparatus is reported to be simple, easy to construct and relatively inexpensive and apparently affords a means of studying metals such as chromium and molybdenum which could not be screened adequately by more conventional techniques. The apparatus and test results are detailed.

Metal Protective Paints. The Red Lead Technical Committee of the Lead Industries Association developed five new formulations for the protective coating of metal, weathered, or treated new galvanized surfaces, according to a preliminary report by Cherry (*7*). Prior work on red lead paints specifically suited to [illegible] treated steel has been limited. The present formulations are the result of 2 years of exposure tests. Three of these are for one-coat applications; two are for use under a topcoat. The paints are versatile in that they serve as primer and corrosion paints for galvanized surfaces which are already rusted from weathering or they serve as protective coatings for new galvanized metal that has been properly treated. Testing of the new formulations is continuing and a full report by the Committee is expected some time next year. Detail formulations for five different systems are given in Red Lead Technical Letter No. 2 published by and available from the Lead Industries Association.

Porcelain Enameled Aluminum. Considerable activity has taken place in the application of porcelain enameled aluminum, a new material made possible by the low fusing temperatures of lead frits (*16*). In addition to expanding use for [illegible] and certain wall construction, new uses of porcelain enameled aluminum reported during the year [illegible] combustion tile, train announcement signs, storm sashes, [illegible] of New York City subway cars, airport runway markers, and just about to come on the market are concealed aluminum ceilings—e.g., roofing utensils where outsides are porcelain enameled coated.

Enfield and Horton (*43*) described the supply picture of lead, reported in detail where and how the metal is mined, its treatment at concentrating mills, smelters, and refineries, and the importance of secondary lead. Lead reserves were also discussed as well as semifabricated and fabricated forms with particular reference to solid-type bearings, storage batteries, and red lead primers for railroad use.

Engineering Advances

Zahn (*45*) showed how casting quality can be improved through better permanent mold techniques. Defects in the casting of storage battery grids caused by solidification stresses, segregation effects, and impurities of hot metal by mold ejectors were eliminated through redesign of the grid and better casting control.

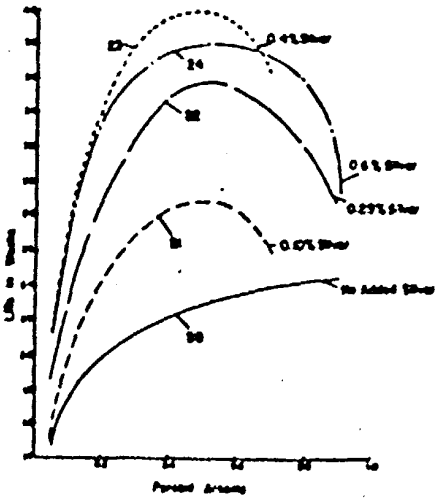

Figure 1. Effect of silver and arsenic in grid metal on service life of lead-acid storage batteries

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Lazarus (20) described the use of rubber molds and centrifugal casting techniques in the production of precision dimensional lead castings. Standard hot chamber machines are used in the die casting of lead with the single difference that dies are not hardened.

Voll[illegible] (41) described the applications of lead in the pulp and paper industry in Germany, [illegible] covering the properties of hard lead alloys used in [illegible], [illegible] and [illegible]. [illegible] strength, creep, and corrosion.

[illegible] (39) covered current applications of lead in Italy, [illegible] plumbing, [illegible], and [illegible].

New developments in lead smelting techniques were described in [illegible] (42), based on the [illegible] lead smelter, [illegible]. The developments include improved [illegible] pelletizing of the flux and lead concentrate, and [illegible].

Fishman and Kenner (23) developed a simple, rapid method for determining lead in lead drosses by Versenate titration.

New Publications

The Ramset Division of Olin-Mathieson Chemical Corp. released a booklet (32) describing lead linings in a variety of applications installed by the Ramset Fastening System; in common, it is the use of a powder charge to seat a specially designed fastener. The booklet is devoted solely to lead lining techniques, including lining heavy- and thin-walled steel tanks, wood tanks, concrete tanks, x-ray laboratory and storage rooms.

The Lead Industries Association has released three more in the series of *Lead Chemical Construction Bulletins*. *Bulletin No. 11* is reprinted from the lead section of the *Chemical Engineering* 16th Biennial Materials of Construction Report (6). The editors commented that despite the developments of competing materials, the applications of lead continue to grow due to its inherent characteristics and experience from long and varied use. Lead is more than holding its own.

Bulletin No. 12 reprints the Lead and Lead Alloys Section of the 5th Annual Materials of Construction Review (1954) which appeared in INDUSTRIAL & ENGINEERING CHEMISTRY (36).

Bulletin No. 13 reprints the Lead Reference Sheets, Parts 1 and 2 from *Chemical Engineering Progress* (33, 34).

A concise listing of the types and uses of lead clad and coated materials, together with frequent textual remarks, is included in *Materials & Methods Manual No. 111* on clad and precoated metals (27). Lead plated copper and steel, lead clad copper and steel, copper and steel hot dipped in lead, and terne metal are covered.

The *Materials & Methods* Materials Engineering *File Facts* (26) featured the physical and mechanical properties, fabricating properties, corrosion resistance, available forms, and uses of both soft and hard lead.

To provide a complete guide to the selection and installation of drainage systems in chemical laboratories, the Lead Industries Association released a 5-page "Suggested Specifications for Chemical Laboratory Drainage Systems." Specifications for materials, joints and connections, hangers, and supports are included. Specifically treated are laboratory waste and vent piping, traps, sinks, and [illegible], troughs, safe pans, and neutralizing basins.

Sheet lead is commonly used as a safe pan under tile or masonry shower stalls and in industrial applications where seepage of either water or corrosives is involved. Since no masonry surface is entirely impervious to seepage, the lead beneath the tile serves as a collector for liquids which manage to penetrate the surface. The Lead Industries Association published a "Suggested Specification for Lead Shower Pans" in 1954. The specification recommends the use of 4-lb. sheet lead turned up at least 6 inches on all sides. Detailed directions are given for forming the pan and preparing it before laying in the concrete.

Copies of either publication may be obtained free of charge by writing to the Lead Industries Association, 420 Lexington Ave., New York 17, N. Y.

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