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METALLIC LEAD PRODUCTS DIVISION

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GENERAL MANAGER

SECRETARY

CHIEF ENGINEER

To Members of the Metallic Lead Products Division:

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

The enclosed section is part of the Eighth Annual Materials of Construction Review. This reprint is also being mailed, as one of our series of Chemical Construction Bulletins, to our mailing list of approximately 1300 chemical construction companies, chemical engineers, chemical engineering professors, and others interested in chemical construction.

Additional copies are available as long as our supply lasts.

Yours very truly,

Robert L. Ziegler
Secretary.



Eighth Annual Materials of Construction Review (1954)

LEAD AND LEAD ALLOYS

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Lead and Lead Alloys



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The lead supply situation continues much as it was last year. Physical and mechanical properties of lead and lead alloys, particularly creep characteristics, have been determined. The effects of purity and additions of antimony, tin, copper, arsenic, bismuth, silver, magnesium, calcium, tellurium, thallium, and silver on the creep characteristics of lead were investigated. New engineering applications of bonded or clad lead linings on steel and copper were described. The performance of lead equipment in the handling of liquid steam and other corrosion was covered along with some applications for lead in modern architecture where resistance to atmospheric corrosion is paramount. Lead continuing to be a means of prolonging the service life of steel equipment exposed to sulfuric acid was described. The use of lead for radiation protection was compared with other possible shielding materials. The technique of using a cartridge powered steel driver for machining sheet lead and steel striping to steel or aluminum vessels has been put to practical use in the field resulting in substantially reduced sheet lead lining erection cost. Corrosion performance and other characteristics of lead-tin alloy coated strip steel were described along with several patents facilitating the manufacture of bonded lead-lined equipment, bonded lead covered pipe, and the lead coating of ferrous objects.

MARKET conditions are such that the users of lead are assured a continuing supply free of government restrictions and at a price competitive with other materials of chemical construction. In fact, the current potential supply of lead is actually in excess of what is being consumed.

Noteworthy technical advancements have been made in the installation of lead, particularly in strapped sheet hangings and in striking lead claddings whereby the corrosion resistance of lead can be combined with the working strength of steel or conductivity plus strength of copper. A number of excellent papers on the behavior of lead and lead alloys in engineering applications have been published.

RESEARCH PROGRESS

Lead Alloys. Hopkins and Thwaites (11) of the British Non-ferrous Metals Research Association laboratories showed that if 99.994% pure lead is used to make a 1% antimonial alloy, no age hardening effect can be produced. In the course of an investigation of the creep and fatigue properties of lead and lead alloys, a binary alloy with 0.85% antimony was extruded from a specially refined billet. Impurities detected in the lead amounted to only 0.0003%. No estimate of oxygen content was made.

After extruding the alloy as rod and aging it at 20° C. no hardening was observed even after 12,000 hours at 173° C. and water quenching. In fact, it did not age harden even after 20,000 hours at 80° C. or 770 hours at 160° C.

According to Hopkins and Thwaites neither the net copper added to amounts of 0.01% to the pure alloy produced any detectable age hardening. On the other hand, as little as 0.001% arsenic caused age hardening to proceed as effectively as it does in commercial alloys. The addition of 0.001% arsenic, moreover, had just as great an influence on the rate of age hardening as had large amounts of 0.02%. The only other element that induced age hardening was silver, but it was possible to produce some hardening by poisoning the specimen.

Brown and Jones (14) of the Naval Research Laboratory in dealing with micro-segregation in antimonial lead alloys were particularly concerned with the effects of microstructure on the corrosion of lead antimony alloys and of nearly pure lead when used as the plates of lead-acid batteries. With as little as 0.01%

antimony, there was pronounced segregation in slowly cooled alloys. Only chill cast alloys showed a normal cast structure and of the chill cast samples only those containing 13% antimony showed 100% eutectic in the microstructure. Slowly cooled alloys, on the other hand, never showed a normal cast structure, whatever the composition.

Research progress in antimonial lead alloys was summarized in two issues of *Metals Industry* by Recorder II (21, 22). The investigations of Hopkins and Thwaites and Brown and Jones were reviewed and correlated with that of previous investigators.

Labberg (19) surveyed the relationship between the melting point of various antimonial alloys and the temperature at which creep begins. The various means by which creep resistance can be increased are reviewed. Studying the effect of alloying additions on lead alloys showed that antimony and bismuth in the order of 0.1% each affect the creep resistance of lead unfavorably or not at all. The more favorably reacting metals include tin, magnesium, and calcium which are dissolved by lead only in quantities of less than 0.1%. The improvement in creep with copper is remarkable, requiring less than 0.005%. The paper is of the review type and does not represent an original investigation.

Goffin (20) investigated the influence of thallium additions on the creep of lead. Variations in creep characteristics with thallium concentrations of 0.5%, 0.5 to 2%, over 2%, and 68.5% are plotted.

Laine (18) conducted tests both at constant internal pressure and at constant hoop stress on lead and lead alloys in the form of pipe. The results provided some indication of the effects of alloy additions, grain size, and prior deformation on fracture, ductility, and creep of lead and lead alloys. Some alloy additions, notably antimony (0.26%) and tellurium (0.01%), appear to promote considerable embrittlement at slow creep rates.

Atkinson and associates (1) described the creep and fatigue characteristics of a new arsenical tin-copper-lead alloy used for cable sheathing.

Alloys
for
Cable
Sheathing
and Antimony

0.01%
Antimony
0.01%
Tellurium
0.01%
Copper
0.01%
Tin
0.01%

At a given stress the creep rate for this alloy is lower than for a commercial copper-lead alloy. The creep rate at hoop stresses below 250 pounds per square inch is not greatly affected by variations in lead treatment which produce a tensile strength in the range between 32,000 and 37,000 pounds per square inch. Addi-

lead steel is extensively employed. In piling the cost differential between lead and other materials is generally in favor of lead; a factor influencing its selection as a construction material.

ADVANCEMENTS IN TECHNOLOGY

One of the most interesting and practical developments in the lead chemical construction field of recent years was in its preliminary stages last year and briefly described as such in last year's review for Lead and Lead Alloys (30). It involved the use of a cartridge powered steel driver for anchoring sheet lead and steel strapping to steel or concrete vessels. Since this time, the technique has been used in the field and has proved to be a real innovation substantially reducing sheet lead lining construction costs. Strapped lead linings may be erected considerably faster and better than by customary drilling and luting techniques. The method also eliminates the serious risk of scaffolding on the outside of large tanks. The first of several similar articles describing the use of the steel driver on lead linings appeared in the *Corrosion Forum* section of *Chemical Engineering* (8).

While the use of bonded lead lining or cladding has in many cases replaced the strapped sheet type of lead lining in chemical construction, because a cladding more effectively combines the strength of steel with the superior corrosion resistance of lead; nevertheless there are many applications where the extra expense of a bonded lead lining is not warranted and where a strapped lining will do the job just as effectively. For this reason strapped lead linings are still regarded as an important method of lining lead in chemical construction and any developments making such installations easier or more economical are especially significant. The cartridge powered steel driver is such a development. It is used for securely anchoring steel straps to a lead lined steel vessel without drilling and matching bolt holes or for fastening sheet lead to concrete without requiring other time-consuming and expensive methods.

Planning in the application of the cartridge powered steel driver, the Remington Arms Co., (17, 28) in cooperation with the Lead Industries Association, arranged with a number of lead fabricators to test the new device under actual service conditions. More than Remington's own, Inc., (29) has entered the field and has contributed several additional innovations.

In general, the cost reductions compared with customary fastening technique have been about 60%, largely the result of lowered labor costs. For example, the Lone Star Lead Construction Co. in Houston, Tex., installed a lead lining in a 24-ft tank without having to erect scaffolding on the outside. With the steel driver all the work was done from the inside in less than half the time normally involved. On one job, Knapp Mills, Inc., of Long Island City, N. Y., estimated 500 hours for installing bolted straps, but with the steel driver the time was reduced to 150 hours.

The thickness of strapped lead lining commonly being fastened is through 1/2-inch steel strap, plus 1/2-inch lead lining plus 1/2-inch steel shell although a newly developed tool has successfully driven fastenings in 1-inch steel tank walls. There is evidence that the thickness of the lead is more or less unimportant since it appears to behave more as a lubricant for the steel shell than as an impediment. Tests on the strength of the steel have shown that the normal tank-type steel will continue to hold long after a 1/2-inch steel shell had not and bolts would have failed by shearing.

Ports of the steel protruding through the outside of the steel tank can be stripped off with a torch, cut off with a special bolt cutter, or covered by a steel firing strip hammered over them.

In a typical strapped sheet lead-lined steel vessel, the use of the steel driver eliminates the drilling of the strap and shell, an operation requiring about 12 minutes after marking, and the strap operation which takes about 2 minutes, making a total of 14 minutes for each bolt. Strip applies to the creation of the necessary staging and equipment so that the operators can have

proper leverage for drilling. Steel driving, on the other hand, takes approximately 2 minutes per hole for loading the gun and shooting the rivet after the strap, making a total of only 4 minutes per hole or a time saving of more than 70%. Furthermore, marking time can be cut considerably because in driving studs, it would not be necessary to adhere to a specific spacing. Studs can be driven virtually at random.

Spiral "button nuts" 2 inches in diameter have been patented which eliminate the strapping as such and can be tightened down against the lead with a spanner wrench. Of course, the steel button must be in turn covered with lead to prevent corrosion.

Metallizing or the spraying of metals, such as paint is sprayed, has gained considerable recognition as a means of improving the corrosion resistance of the less expensive but more readily corroded metals. An application where sprayed lead was used to particular advantage was described (17). It was concerned with steel battery boxes used for supporting lead-acid storage batteries where, because of the moisture and electrolyte, unprotected steel became severely corroded in a short time. By metallizing with approximately 0.03 to 0.05 inch of lead, sufficient corrosion resistance was provided to enable steel to be used successfully. The article points out, however, that because of its porous nature, metallized or sprayed lead does not successfully serve as a substitute for sheet lead or bonded lead.

The shielded arc welding technique has been extended in one instance to the welding of lead flashings. A fabricator (31) of lead vent pipe flashings noted that shielded arc welding required production costs to one quarter the cost of methods previously used. Flashings were welded on a production line basis at an average speed of 20 inches per minute employing an electrode operated at 30 amperes. It produced smooth, uniform welds in lead while eliminating post-welding cleaning steps. However, so far as can be determined, no attempts have been made to apply this type of lead welding to commercial applications in the chemical process industries. Tests that have been conducted indicate definite shortcomings that may be overcome in the future.

Rambell (30) emphasized the superior corrosion resistance of lead-iron alloy coated strip steel. Referring to the 85% lead and 15% tin alloy deposited on strip steel from a recently developed fluoroborate solution, he pointed out that strip steel thus coated offers several important fabricating advantages. The coating acts as a lubricant thus reducing wear on dies and forming rolls, its presence substantially reduces post-fabrication plating costs, and it offers excellent weldability. The paper is well illustrated with photographs of the coating operation.

Several British publications described a continuous lead coating machine designed and recently installed by the Fraser and Chalmers Engineering Works of the General Electric Co., Ltd. (4, 25). The machine is being used by a chemical producer and has a capacity of 10 tons of pipe per hour. The machine comprises 25 moulds, each holding 2 pigs of 34 pounds each. The moulds form a continuous train around the truck of the machine somewhat like the chain on a sprocket drive.

NEW PATENTS

Patents were applied for by Knapp Mills, Inc., covering a new method for extruding a bonded lead covering on copper or steel pipe (19). The company reports that the new process is being used to make tubes and rods in small diameters.

After bonded lead tanks are assembled from lead-lined sheet sections and field welded, the welded area must be clad with lead. Since the upright and girth seams are in a difficult position, the work of lead-lining these areas has been tedious and expensive. Patents (18) have been applied for by Knapp Mills, Inc., covering a "walking mold" which makes a lead cladding over a steel mold. The use of this device reportedly simplifies the cladding technique and decreases the cost of this phase of the work.

October 1954

INDUSTRIAL AND ENGINEERING CHEMISTRY

2089

Small improvements claimed for this alloy include good ductility at both high and low stress, freedom from age hardening, and adequate tensile strength.

Reversing the use of lead and lead alloys in the field of chemical construction, Leach (14) illustrated the improved creep characteristics of silver-copper-lead (0.016% each) over high purity (99.99%) lead.

Physical Property	Alloy, %	Days
Yield strength	2.5	100
Tensile strength	2.5	100
Creep	2.5	100
Lead	2.5	100
Silver-copper-lead	2.5	100
Lead	2.5	100
Silver-copper-lead	2.5	100
Lead	2.5	100
Silver-copper-lead	2.5	100
Lead	2.5	100
Silver-copper-lead	2.5	100
Lead	2.5	100
Silver-copper-lead	2.5	100

What is termed silver-copper-lead in Great Britain is approximately equivalent to chemical lead in the United States. Chemical lead, according to ASTM Specification B23, contains 0.02 to 0.002% silver and 0.04 to 0.08% copper with a lead content of 99.90%.

Leach illustrated with photomicrographs that joining lead by welding results in the formation of a cast lead structure at the junction and that therefore the practice of hammering the welds to bring about recrystallization can be recommended as a means of improving the strength of this type of joint.

Lead. Lucas and Lane (15) carried out a series of tests on the yield strength of pure lead in compression as part of a general investigation of hot rolling in which cold lead was used as a model for hot steel. The variation of the yield stress of pure lead in uniaxial compression with temperature, strain, and strain rate was described. Experiments were designed to test the accuracy of the results. The average coefficient of friction between the platens and specimen was measured for lubricated and unlubricated compression, and its dependence on strain rate was demonstrated. The effect of previous strain rate history on the yield stress was also discussed.

The cause and prevention of "barreling" of compression test specimens were discussed. By machining conometric grooves 0.02 in. deep in each end of the specimen and lubricating, barreling can be entirely eliminated. Too few grooves resulted in barreling and too many entangled so much so that the ends of the specimen were played outward. The optimum was 32 grooves per inch radius.

Metallurgy published detailed abstracts of a German symposium devoted to the hot deformation of metals; the original papers were published in German in *Metall*. A paper by Hoffmann (16) was devoted to the hot and cold forming of lead and the determination of the oxygen content of lead by means of the hydrogen reduction method. He emphasized the dependence of oxygen solubility in lead on temperature.

Frank and Thomas (7) starting with a 4.5-inch diameter billet of pure lead, extruded it at room temperature to form a 1.5-inch diameter rod by using three extrusion rates: 0.1, 0.74, and 5.15 inches per minute. Metal extrusion was studied experimentally at various strain rates. Factors influencing extrusion, and directions for the improved extrusion process with a sharp-edged die were determined. The flow pattern was investigated with respect to extrusion rate and pressure effects. All characteristics were determined on a cross-section plane using a step-wise extrusion method.

The rate of denaturation of lead sulfide into metallic lead at high current densities in alkaline and weak acid solutions was studied by Ralsberg (17) at the Naval Research Laboratory. The cause of this phenomenon is the formation and subsequent decomposition of a volatile unstable hydride of lead, PbH₂.

ENGINEERING APPLICATIONS

A development of Kapp Mfg. Inc. involved the successful commercial production of lead plate heaters and direct gas-fired tube type immersion heaters (18). The latter is constructed of lead bonded to steel or copper. Although the melting temperature of lead is 621° F., direct gas-fired immersion heaters are able to operate successfully because of the conductive heat transfer that takes place between the lead and steel or copper when the lead is properly clad.

The use of lead in liquid steam condensing systems such as those employed in most public water works is described and illustrated in some detail in *Lead*, (19) a publication of the Lead Industries Association. Methods and equipment employed at the Wyandotte water works in Michigan, serve to illustrate the advantages of lead for handling liquid steam, a chemical corrosive to most materials of construction.

One advantage of lead brought out in this particular case was that a concrete vessel that had been deteriorated from other service was readily restored to usefulness by lead lining with 10-in., 4% antimonial sheet lead supported by a lead-covered steel strap. Three-inch lead pipe and other lead fittings were used as fill-ins and for carrying the liquid steam to the evaporating unit. Methods of using dry steam instead of liquid and desludging it as the pressure in a lead-lined tank that could double as a storage tank were also cited.

Flawger (8) described the use of lead as a corrosion resistant material in chemical equipment citing reasons for its high corrosion resistance. He especially illustrated and gave examples of applications of lead in the German chemical industry.

For many centuries lead has been recognized as an important metal in architecture where it served in a dual role—it provided protection to the buildings through its resistance to atmospheric corrosion, and it provided aesthetic advantages, architecturally speaking. How lead is used in architectural architecture is illustrated with drawings and photographs in *Lead* (19) with specific reference to a new private dwelling recently constructed in Randolph, Vt. Lead is used as a flashing strip and gravel cap around the ridge of the flat roof, as a flashing around all structures extending through the roof such as vent pipes, dormers, and chimneys, as a flashing around a parapet wall, and as a capping protecting the tops of two large chimneys.

An interesting historical observation is brought out in the article—sheet lead was used in the ancient Hanging Gardens of Babylon to protect the famous structure from damage due to evaporation and to retain the moisture necessary for the gardens. Fox (6) of Brookhaven National Laboratories discussed the use of lead in nuclear shielding.

The use of lead for shielding in the γ -ray region is 10 to 100 times as effective as an equal weight of iron and even more effective than other materials, but as compared to about 3 M.P.V., there is very little distinction between lead and iron.

Although the use of lead is more economical in the γ -ray region than at the higher energy levels, lead always has the advantage of greater density and hence is preferable where there are space limitations, such as in steam powered submarines or airplanes. One of the major uses of lead and one that promises to be still greater in the future is in the construction of containers for storing and shipping radioactive materials and for handling them in laboratories. For example, the current requirements for Brookhaven National Laboratories are about 1,000 tons of lead to which can be added 300 additional tons annually, all of it is used for handling radioactive materials.

Whitlock (20) of Rensselaer and Poyer, New York, discussed the use of lead as a corrosion resistant material in chemical construction. In the metal recovery field, the most lead is used where the processes have been in use for longer periods and more is known regarding the best materials of construction. In wet process metallurgical operations, brick and lead-lined and lead-

A U. S. patent (85) was issued covering a new method of lead coating ferrous articles. The process involves first electroplating a thin coating of tin between 0.00003 and 0.00018 inch and then heating the tin plated article to 650° F. to melt and transform substantially all of the tin to a continuous layer of iron-tin alloy. Finally the article is dipped in a molten bath of substantially pure lead.

NEW PUBLICATIONS

The Federated Metals Div. of the American Smelting & Refining Co. released a brochure (5) consisting of a comprehensive compilation of data on lead and lead products. Beginning with a description of lead's use as a construction material, the brochure gives the grades of lead used, characteristics and specifications of sheet, pipe, and special fittings including flanges, solid lead valves, and lead-lined valves. Lead welding and construction techniques are also described and illustrated with photographs and line drawings of recommended construction methods for sheet lead and bonded lead-lined installations and for heating and cooling coils. In addition there are handy reference tables and data on lead's behavior with various corrosives along with the important chemical, physical, and mechanical properties of lead and lead alloys.

The National Lead Co. published a brochure showing in considerable technical detail the applications of lead in the chemical industry with special emphasis on its excellent corrosion characteristics (21). Production techniques for all the common lead products, including sheet-lead equipment, pipe, coils, valves, fittings, pumps, lead-lined pipe and lead die castings, are described and illustrated. Cast lead and lead-lined valves are especially featured with exploded detail drawings, photographs, and mechanical specifications. Other lead products such as acid recovery equipment and lead bricks used in radiation protection are included in the brochure.

The St. Joseph Lead Co. published a similar booklet on lead (32). Essentially a reference brochure on the properties and applications of lead and lead alloys, the St. Joseph publication also goes into some detail on the use of these materials in architecture, chemical construction, plumbing, radiation protection, cable sheathing, ammunition, solder, bearings, type metal, batteries, tetraethyllead, paint, and glass.

The Lead Industries Association, under the guidance of last year's Review, released three more in its series of Lead Chemical Construction Bulletins. Bulletin No. 3 is a flow chart showing the manufacture of high purity sulfur dioxide from reactor gases (6). The process is based on the absorption and subsequent stripping of sulfur dioxide in demethylamine and makes considerable use of lead chemical construction. For example the absorption towers are constructed of 12-B, 8.5% antimonial lead covered in cup-type construction, the solution collectors are entirely of 65-B lead, and the stripping tower is of lead bonded or clad steel. Various counter-current lead pipe heat exchange coils are illustrated and described.

Bulletin No. 2 repeats the Lead and Lead Alloys portion of the Seventh Annual Materials of Construction Review (1953) which appeared in *INDUSTRIAL & ENGINEERING CHEMISTRY* (20).

Bulletin No. 10 describes the use of the stud driver in the construction of lead linings.

The Interstate Commerce Commission (17) formulated and published amendments to their regulations for the transportation of explosives and other dangerous articles that became effective December 31, 1953. Some changes of interest to the chemical industry cover the transportation of phosphorus oxychloride, phosphorus trichloride, and thiophosphoryl chloride as well as new include tank motor vehicles when the tanks are lead-lined.

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