LEAD INDUSTRIES ASSOCIATION

420 LEXINGTON AVENUE
NEW YORK 17, N. Y.

METALLIC LEAD PRODUCTS DIVISION

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SUBJECT: CORROSION CHARACTERISTICS OF LEAD AND LEAD ALLOYS

To Members of the Metallic Lead Products Divisions

Attached is a copy of the text of an illustrated lecture on the "Corrosion Characteristics of Lead and Lead Alloys" delivered by a staff member of the Association at a special "Short Course on Corrosion," Sponsored by the Case Institute of Technology, the course was held during the week of June 16, 1952 at the Institute in Cleveland, Ohio.

Extra copies are available. Arrangements can also be made to have this or similar lectures on lead delivered before suitable groups..

Very truly yours,

Robert L. Ziegfeld
Secretary

LEAD INDUSTRIES ASSOCIATION
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CORROSION CHARACTERISTICS OF LEAD AND LEAD ALLOYS

by
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More than one-third of the lead consumed each year in America is used primarily for its resistance to corrosion.

The corrosives range from such comparatively inactive media as the atmosphere and potable waters to a host of highly reactive industrial chemicals.

The lead takes such forms as sheet, pipe, cable sheathing, grid metal, castings, coatings, terne plate and such non-metallic applications as red lead - an outstanding metal protective paint pigment.

Table I

U.S. LEAD CONSUMPTION
(1951 - U.S. Bureau of Mines)

	Tons	Percent
Storage Batteries		
** Grid Metal	19[illegible],000	16.8
Battery Oxides	175,000	14.8
** Cable Sheathing	132,000	11.2
Tetraethyl Lead	128,000	10.8
Solder	81,000	6.9
Red Lead and Litharge	71,000	6.0
Calking Lead	46,000	3.9
White Lead and Pigments	38,000	3.2
** Pipe, Traps and Bends	33,000	2.8
** Sheet Lead	31,000	2.6
Alloys	29,000	2.5
Type Metals	28,000	2.4
** Casting Metals	22,000	1.8
** Metal Protective Paints	17,000	1.4
Collapsible Tubes	13,000	1.1
** Terne Metal and Lead Plating	3,000	.3
Others	133,000	11.5
Total	1,178,000 Tons	100.0 Percent

** Used all or in part for corrosion prevention-about 35% of total lead consumed.

* Lead Industries Association, 420 Lexington Ave., New York 17, New York

Lead Specifications

Just as with other metals, the chemical properties of lead are coupled with its composition. Hence the selection of the proper grade of lead for an installation cannot be left to chance. The American Society for Testing Materials has established specifications for various grades of pig lead known in the trade as corroding lead (the purest, for use in pigment manufacture), common lead, acid lead, copper lead and chemical lead. The grade generally used for chemical construction is chemical lead. It contains small percentages of silver and copper which have been found to add to the corrosion resistance of lead and improve its creep and fatigue resistance.

Table II

A.S.T.M. PIG LEAD SPECIFICATIONS

	Corroding Lead	Chemical Lead	Common Lead A	Common Lead B
Ag, Maximum	0.0015	0.020	0.002	0.002
Minimum		0.002		
Cu, Maximum	0.0015	0.080	0.0025	0.0025
Minimum		0.04		
Cu + Ag, Maximum	0.0025			
As, Maximum	0.0015			
Sb + Sn, Maximum	0.0095			
As, Sb + Sn, Maximum		0.002	0.0015	0.0015
Zn, Maximum	0.0015	0.001	0.002	0.002
Fe, Maximum	0.002	0.0015	0.002	0.002
Bi, Maximum	0.05	0.005	0.15	0.25
Lead, by Dif., Minimum	99.94	99.9	99.85	99.73

Corrosion Resistant Alloys of Lead

Antimonial or hard lead is lead generally containing from 1 to 12 percent antimony. Antimony serves to harden and improve lead's physical characteristics up to 120° C; however, its presence lowers the melting point and, while it may not detract from lead's corrosion resistance, seldom does it improve it.

Tellurium-lead is chemical lead to which has been added approximately 0.04 percent tellurium. Tellurium retards grain growth and therefore increases fatigue resistance. Corrosion resistance is comparable to chemical lead.

In plating operations, particularly chromium plating, an alloy of lead with about 7 percent tin is occasionally used as the tank lining. Recently a proprietary lead alloy was perfected especially for use as a chromium plating tank lining. The alloy containing small percentages of silver and tellurium promotes the formation of an adherent protective film of chromates in chromic acid much as the lead sulphate film which forms in contact with sulphuric acid.

In the battery industry, grid metal is usually composed of 7 to 12 percent antimony and 0.25 percent tin. The connecting lugs on top of the battery are a similar alloy with less antimony. Some newer alloys exhibit greater corrosion resistance in the presence of the sulphuric acid electrolyte without sacrificing strength. They contain small amounts of silver to replace part of the antimony content. Some also contain tellurium.

Another interesting development in the battery field is the use of calcium-lead grid metal. Pure lead plus no more than 0.1 percent calcium has performed remarkably well as grid metal in stand-by battery installations.

In cable sheathing, new arsenical lead alloys have demonstrated greatly improved fatigue and creep resistance characteristics.

Protective Coating

Lead is normally chemically reactive but like aluminum, magnesium and chromium, it is blessed with a natural protective coating that forms on contact with a corrosive. Upon mechanical injury the environment generally permits self-healing of the coating.

The rate of reaction of a metal in a corrosive environment depends largely upon the character of the products of corrosion; their solubility, permeability and adherence to the surface of the metal. Lead, for instance, owes its excellent resistance to sulphuric acid to the formation of a tightly adherent, impermeable film of lead sulphate which is practically insoluble in sulphuric acid solutions. But when the temperature is raised or the concentration increased above 96 percent, then the rate of solution of the lead sulphate also increases until the use of lead in these ranges becomes marginal.

By the same token if the sulphate film is ruptured or disturbed such as by excessive vibration, abrasion or high velocity, the corrosion rate will also increase. If other chemicals are present which react with lead sulphate and, in effect, remove it or alter its beneficial characteristics, that too will raise the corrosion rate. Nitric acid is an example of a corrosive which reacts with lead to form a soluble salt and is also capable of reacting with lead sulphate to reduce its function as a protective coating. Obviously where lead linings are protected by a brick lining or a Karbate liner the protective film will not be disturbed.

A chemical plant installed a completely enclosed lead lined vessel for handling hot, dilute sulphuric acid. The vessel was in operation for a short period when it was discovered that corrosion was taking place at an accelerated rate above the liquid level. Resistance of the lead to the liquid was excellent, but resistance to the vapors left something to be desired. The problem was eliminated by simply raising the level of the liquid to the top of the vessel just long enough to enable a lead sulphate film to develop. The vessel was then put back into normal operation and no more corrosion took place in the vapor zone.

The point to bear in mind is that in order for lead to demonstrate its corrosion resistance it must first have a protective film. In the case of corrosives which, in themselves, do not readily form a protective film and will not dissolve lead sulphate, it is often possible to make the lining corrosion proof by swabbing the lead with dilute sulphuric acid or, if possible, filling the vessel with it for a short period of time in order to establish a protective sulphate film. At 70° F in 25 to 35 percent sulphuric acid chemical lead will form a complete sulphate film in from 9 to 10 hours. Under the same conditions 9 percent antimonial lead forms a sulphate film in from 1 to 1½ hours.

Corrosion Rate Interpretation

The common systems of indicating corrosion rate are inches penetration per year (IPY) or milligrams weight loss per square decimeter per day (MDD). Either of these can be somewhat misleading in the case of lead since best performance is usually judged on the basis of the lowest corrosion rate. This situation is especially true in chemical construction where, for mechanical reasons, lead linings are used in thicknesses generally of 3/16 inch or more. Greater thickness has an obvious advantage when considering service life because with equal rates of penetration, a thicker lining can be expected to give a longer service life than some other corrosion resistant lining of thinner construction.

Corrosion rate as weight loss can also be misleading in the case of lead since this metal has the highest density of any commonly used corrosion resistant metal. This means that what might appear to be an excessive corrosion rate expressed in weight loss of lead could actually be a very nominal rate in terms of volume loss.

It is obvious then that when comparisons are being made between various corrosion resistant materials, the corrosion rate data should be carefully interpreted.

Chemical Corrosion and Corrosion Products

Lead is somewhat unusual among the metals in that it is amphoteric; it reacts with alkalies to form plumbates as well as with acids to form lead salts.

Generally speaking, lead can be assumed to have good resistance to neutral solutions where lead carbonate and possibly oxide are corrosion products. It has fair resistance to alkaline solutions in which these are soluble. Experience has shown that lead is commercially resistant to chromic, sulphuric, sulphurous and phosphoric acids; that it is subject to corrosion at somewhat higher rates by hydrochloric and hydrofluoric acids and that it is susceptible to being strongly corroded by acetic, formic and nitric acids. Also nitrate salt solutions are moderately corrosive whereas carbonate solutions are not.

Determining the cause of corrosive attack is simplified in the case of lead because of the easily discernible and usually characteristic corrosion product. For example, when lead is attacked by alkalies, hydrated-red monoxide of lead is usually the corrosion product. Occasionally a white plumbate of lead will form. When lead is subjected to electrolytic action as in stray current corrosion, the attack is typified by a crystalline metallic appearance. In the presence of sulphides, the characteristic black lead sulphide color is apparent. Sulphuric acid results in a light gray patina of lead sulphate. Carbon dioxide in solution as well as other carbonate-forming cations produce a characteristic white lead formation.

The Old Dutch White Lead Process for making basic lead carbonate provided the clue to solving this incident: A lead sheathed cable housed in underground redwood conduits was being badly corroded forming a white corrosion product. Investigation disclosed that rotting of the redwood in the presence of moisture produced carbon dioxide and acetic or a similar organic acid which proceeded to convert the lead to basic carbonate white lead just as in the Old Dutch Process.

The problem was solved and further corrosion of the sheath prevented by introducing into the manholes dry ammonia gas to neutralise the acid and stop the reaction until repairs could be effected.

Effect of Concentration

When observing the reactions of lead in various chemical environments, contradictions in its behavior become apparent. In the high ranges of concentration, the rate of corrosion of lead in sulphuric acid, for example, increases as the concentration of the acid increases. On the other hand, the rate of corrosion of lead in nitric acid decreases as the concentration is raised. The explanation is simple enough. Sulphuric acid, as mentioned earlier, forms lead sulphate which is practically insoluble in dilute sulphuric acid. However, its rate of solution increases with increasing acid concentration.

Table III

Solubility of Lead Sulphate in Sulphuric Acid Per Hundred Grams at 17 to 18.5° C					
% H_2SO_4	98.11	98.94	100.01	101.13(5% SO_3)	105.05(15% SO_3)
g $PbSO_4$	.54	1.34	4.21	3.54	8.23

The opposite is true with nitric acid. The lead nitrate which forms on contact with nitric acid is readily soluble in the water present in dilute nitric acid. As the concentration of the acid increases, less water is present and consequently less lead nitrate is dissolved. Therefore, concentrated nitric acid in the range of 52 to 70 percent by weight has little effect on lead at room temperature. Acetic and hydrofluoric acid and sodium bisulphate parallel nitric acid in their reaction with lead.

Lead satisfactorily resists hot sulphuric acid of all strengths up to 85 percent with temperatures up to 220° C. The reaction of lead with sulphuric acid is typical of its reaction with chromic, sulphurous and phosphoric acids.

Effect of Temperature

The rate at which a chemical reaction proceeds is geometrically proportional to the temperature. It follows then that an increase in the temperature of the corrosive almost invariably means an increase in the corrosion rate. The importance of determining the temperature range of the corrosive before selecting the material of construction cannot be emphasized too strongly.

Mixed Corrosives

With mixtures of corrosives it is a general rule that lead will react with each of the constituents in the mixture as it would normally in the unmixed state.

The presence of some sulphuric acid will usually enhance the performance of lead with corrosives such as hydrochloric acid or phosphoric acid. "Impure" phosphoric acid containing some sulphuric acid is definitely easier to handle in lead than the purest grades, as shown in Table IV.

Table IV

LEAD VERSUS PURE AND CRUDE PHOSPHORIC ACID

Phosphoric Acid	Concentration	Temperature	Corrosion Rate, IPY
Pure	42%	15° C	0.0198
Crude*	42%	15° C	<0.0001

* Contains traces of sulphuric acid.

Stress Corrosion

Lead has a relatively high linear coefficient of thermal expansion - approximately three times that of steel. Therefore when lead is used in a corrosive environment in such a manner that it is under stress then stress corrosion in the form of more or less severe intercrystalline etching will be evident. Stress corrosion has been encountered when lead is subjected to severe cyclic temperature changes, or to continuing vibration. Stresses induced by lead's own weight also occasionally contribute to the stress corrosion of improperly supported sheet lead, lead pipe and cable sheathing.

Stress corrosion can be eliminated by either (1) removing the source of stress or (2) counteracting its effect by using thicker lead, increasing the strapping of a sheet lead lining, using a bonded lead lining, or installing brick lining over the lead to provide mechanical, thermal and chemical protection.

Stress corrosion characteristics may vary with different alloys of lead. Antimonial lead and tellurium chemical lead, for example, may be work hardened and age hardened to a certain extent. The latter has a higher resistance to fatigue than unalloyed chemical lead because the tellurium acts as a grain growth inhibitor.

Corrosion by "Green" Concrete

Sometime ago in Baltimore, the lead sheathing in an underground power line conduit was being corroded to white lead carbonate. When it was determined that the seepage was limewater, corrosion was stopped by introducing carbon dioxide gas from cylinders into the manholes. The gas precipitated the free lime as calcium carbonate, thereby converting it from the hydroxide which attacks lead to the carbonate which does not.

When lead is to be used in direct contact with freshly poured concrete, any corrosion which might take place because of calcium hydroxide plus oxygen and moisture being present can easily be avoided by coating the lead with asphaltum paint. For example, sheet lead safe pans in shower stalls should always be painted with asphaltum to protect the metal from the free lime in the "green" concrete until it has had time to convert to carbonate.

Galvanic corrosion, so far as lead is concerned, is seldom encountered. In acid solutions iron is anodic to lead; hence when coupled to lead the lead is protected from corroding. In alkaline solutions, however, the reverse is true and the corrosion of lead is accelerated.

Under certain conditions where it is not possible to use lead equipment throughout lead has been known to cause the galvanic corrosion of nickel-chrome-moly alloys such as Worthite. In sulphuric acid lead ordinarily remains anodic to Worthite, but in the absence of any oxygen or air in solution, lead takes on a heavy coating of lead sulphate which is more noble than lead itself. Under these special conditions Worthite becomes anodic to lead bringing about galvanic corrosion of the Worthite.*

If the wetted area of the lead in a deaerated, hot sulphuric acid environment is very much greater than the wetted area of Worthite such as a pump in a lead system involving tanks and piping, then the galvanic current density acting on the anodic Worthite may be of considerable magnitude resulting in corrosion of some or all of the pump parts.

Fortunately this condition exists only in the rare instances when the sulphuric acid is deaerated either by physical or chemical means and the anodic area is much smaller than the cathodic area. A mixture of sulphur dioxide with sulphuric acid at elevated temperatures also may "activate" Worthite, or similar alloys, by a preferential oxidation of the sulphur dioxide rather than the available oxygen going to form the protective oxide film, or layer of absorbed oxygen, which keeps the nickel-chrome-moly alloys more noble than lead sulphate.

Galvanic corrosion of the nickel-chrome-moly alloys can be eliminated by simple re-aeration of the sulphuric acid and cooling, if necessary, to the permissible temperature range for the alloy. It is also possible to reverse the potentials by adding minute amounts of an oxidizing agent such as nitric acid, sodium chromate, copper sulphate or ferric sulphate to the de-aerated sulphuric acid. Where such measures are impracticable the Worthite may be insulated from the lead through the use of rubber hose or other suitable plastic or porcelain insulators or insulated flanges. An obvious solution to the problem is to use cast hard lead or lead lined steel pumps and valves, and thus avoid dissimilar metal contact.

Bacterial Corrosion

The possibility of bacterial corrosion of lead sheaths in underground ducts is currently under investigation. Corrosion products in the slime often found in underground cable ducts have been tested with hydrochloric acid and the presence of lead sulphide indicated. There is strong evidence that bacteria are a factor in lead sheath corrosion under certain circumstances. The circumstances remain to be defined but it is reasonable to expect bacteria to be found in submerged ducts where there is likely to be an absence of oxygen.

* Worthite becomes anodic to lead in 50 percent sulphuric acid that has been deaerated by raising the temperature to 260° F.

WHY LEAD'S CORROSION RESISTANCE IS USED

Chemical Construction

Lead is naturally soft and although occasionally used alone, more often it is supported by an external framework of wood or steel. Frequently, steel or wooden vessels are lined with loose sheet lead fastened at intervals with lead covered steel straps.

Another method of lining vessels with lead is to bond the lead directly to the shell of the steel vessel. This is known as bonded or homogeneous lead lining. The bond may be accomplished by means of a thin solder film between the lead and the steel; or by bonding the lead directly to the steel.

The direct bond is usually accomplished by first preparing the surface of the steel vessel by shot blasting or pickling, and then fluxing with molten zinc-ammonium chloride, stannous chloride or other proprietary fluxes. The lead is then poured on or melted and bonded to the steel by hand using lead burning bars and torches. Sometimes, in the case of regular shapes, this is followed by rolling to compress the lead. While more expensive as a result of the labor involved, bonded or homogeneous lead lined vessels are finding wider acceptance in industry today because by this method the corrosion resistance of lead can be combined with the greater physical strength of the steel shell. Higher operating temperatures more prevalent in industry today, require this type of lining. Bonded lead linings permit heat transfer through the walls as in jacketed vessels. They also resist lifting of the lead lining when lined vessels are used under vacuum.

In many processes, lead pipe coils inside the vessel are used for cooling purposes and occasionally for heating with steam or hot water. For use with steam pressures exceeding 50 and up to 150 pounds steam pressure or where good heat transfer is vital, lead covered copper or steel coils are preferred. Here again, as in a bonded lining, the greater strength of copper is combined with the corrosion resistance of lead.

Lead pipe and conduits are used to a great extent for conducting corrosive liquids and fumes. Where the lead pipe is suspended it is common practice to either lay it in a trough or better still, use lead lined cast iron or steel pipe. This consists of ordinary pipe in which is placed a lead pipe expanded by hydraulic pressure to fit snugly or bonded with the aid of solder.

Lead in Plumbing

Lead for many years has been used in household and industrial plumbing. It is used to conduct drinking water from the cast iron water mains in the street to the house. Inside the house, it is used in the form of pipe for waste, lead traps beneath basins, tubs and showers, lead bends on water closets and occasionally as vent pipe. In practically all cases, the lead pipe is joined by wiping with solder.

A surprisingly large amount of lead is also used in conjunction with cast iron water mains and soil pipe which is used to conduct waste to the sewer or for venting purposes. Here it serves as a calking material to form a water-tight seal between the sections of pipe. Usually the lead is melted and poured into the joint and then calked with special tools. Sometimes if it is impractical to use molten lead, lead wool is used instead. Because of its self-weldability lead wool is easily consolidated or calked into a solid water-proof mass.

Architectural Applications

Architecturally, lead also sees considerable service, most prominently as a roofing and flashing material. Here its corrosion resistance and pleasing gray color are the chief advantages. It is also used for gutters, statues, spandrels, leaded glass windows and other ornamental devices. Lead coated copper is occasionally used for roofing and flashing purposes.

Lead is used also for anchoring objects to masonry. An old method to attach an object to stone or masonry is to drill a hole, place a bolt in the hole and then pour molten lead around it. Today lead anchor bolts are available which have cast lead plugs as an integral part. When the lead is compressed, it expands between the bolt and the inside of the masonry thereby forming a secure anchor.

Electrical Applications

In the electrical industry, the chief use for lead and also the greatest consumer of lead is the storage battery. Storage batteries contain on the average, 25 pounds of recoverable lead. This includes both the lead alloy used for making grids as well as the lead oxides used on the battery plates.

Also in the top third of the lead consuming industries is the manufacture of cable sheathing. A sheath for cable whether telephone or power, must be (1) corrosion resistant to the atmosphere and soil waters, (2) flexible enough to be coiled on reels, unreeled and drawn through conduits and, (3) it must be able to be extruded to form a continuous sheath around the wires in a cable.

In certain applications copper wire is coated with lead before being covered with rubber insulation because the sulphur compounds in some rubbers attack copper and, vice versa, copper affects some insulating materials adversely. The presence of a lead coating eliminates any reaction between the copper and rubber.

The utility of lead is materially extended where electrical conductivity is important by bonding it to copper, steel or other metals with good conductivity.

Plating

In the plating industry, particularly chromium, copper and nickel plating, lead is used as a tank lining material, as an anode, and for heating coils. It is used for two reasons here: (1) Because lead is normally resistant to attack from the acid electrolytes used in plating these metals, and (2) because any corrosion products that might be formed do not affect the plating operation or the final appearance of the plate. A more recent development in this industry is the anodizing process in which a cold electrolyte is used. Lead pipe and lead covered copper or steel pipe coils are used to cool the anodizing solutions by means of circulating brine or freon and the tanks themselves are lead lined.

Lead Coatings

A number of objects are coated with lead containing less than 3 percent tin plus some silver and antimony by the process known as "hot dipping." This is somewhat similar to hot dip galvanizing. Terne plate is used quite extensively in industry. It is made in the same manner as hot dip tin plate except that instead of

pure tin, an alloy of lead and 15 to 25 percent of tin is used. Large quantities of sheet steel are terne plated and used in making paint cans, gasoline tanks for automobiles and other metallic containers requiring corrosion resistance as well as for architectural applications where its affinity for paint is used to advantage.

Lead and its alloys are cathodic to iron and copper when applied as coatings. An local action at discontinuities in the coating may be prevented by applying red lead or some other corrosion inhibiting paint to the surface. In most cases, small pinholes in lead coatings become self-sealed with corrosion products which prevent further pitting action.

From a practical viewpoint, the solution to pinhole corrosion is to increase the thickness of the coating to the point where pinholes are absent. In the case of lead coated copper this involves increasing the coating weight from 12-15 lbs. per 100 sq. ft. to 20-30 lbs. per 100 sq. ft.

SUPPLY OUTLOOK

The lead supply situation cannot be ignored whenever discussing any of lead's applications. Despite predictions made twenty years ago that we would have no lead today, lead is still plentiful and its continuing supply is assured for many years to come. The recent drop in price is a fair indication of this fact. New mines have been opened and most of the old ones have not, as yet, hit bottom.*

Lead is fortunate among metals in that the bulk of its uses are recurring. That is, after being used it can be salvaged and returned to the market as secondary metal ready for re-use. This is particularly so in the case of industries utilizing lead for its corrosion resistance. Storage batteries and cable sheathing, the two largest consumers of lead in this category, are prime examples of recurring uses.

Lead's applications cover a multiplicity of industries which utilize one or more of its many characteristics. It is a metal that has been around for a long time and one which will certainly continue to find considerable use in the changing technology of modern times.

The Lead Industries Association is always willing to cooperate without obligation in the solution of problems involving lead. Inquiries should be addressed to 420 Lexington Avenue, New York 17, New York.

* There is a saying that "old mines never die." For example, Mine LaMotte located in Southeastern Missouri was first discovered by a man in Fernando DeSoto's party in the early Sixteenth Century. It has been producing lead since that time and today is still one of the important lead producing mines in Southeastern Missouri.