Chapter 10
Lead

10.1 Introduction

Lead (Pb) has been known since ancient times, as its use from the 7th to the 5th millennia B.C. is now a well established fact. Since the dawn of civilization, lead has served for the conveyance of water. The bath erected by the Romans in the city of Bath was lined with sheet lead and it is claimed that it is still supplied with water through the original lead pipes which were installed nearly 2000 years ago. In later years the use of lead was extended to include roofing, as witness many churches and cathedrals of the Norman period. Since that time lead has been called upon to serve many other purposes where corrosion resistance is needed.

Reverberatory furnaces for lead smelting were used until late in the 1800s. The process consisted of a roast-reduction, oxide and sulphide formed by roasting the ore was reduced by unaltered sulphide. Slag contained 40% lead and this was dealt with in the slag hearth, a modified, small blast furnace. Such a method was prevalent in the UK, Europe and elsewhere until superseded by the blast furnace, which now produces a majority of the world's lead.

10.2 Sources

Lead is produced from ores, and it occurs in the form of various minerals; galena (PbS) is the most common ore of lead and zinc. Other minerals are anglesite ($PbSO_4$) and cerussite ($PbCO_3$). Galena is associated with ZnS, FeS, Cu_2S, SiO_2, other impurities (Bi, As, Sb) sulphides and precious metals (mainly Ag). Ores are generally of a complex variety, chief lead associates being zinc, copper and silver. Content of zinc often exceeds that of lead.

10.3 Extraction of Lead

Lead sulphide, at the temperature ordinarily reached in practice, is not reduced by carbon or carbon monoxide; and consequently lead sulphide ore must be roasted for smelting. Furthermore, the presence of too much sulphur in the ore charge would tend to throw an undue proportion of the lead into the matte and render the subsequent recovery of the metal difficult. Since most lead ores contain small amounts of copper, every effort is made to concentrate this in the form of a matte. On the other hand, there should be only a small amount of this matte; hence the necessary of regulating the sulphur content carefully by means of preliminary roasting. In principle, roasting lead ores differs only slightly from roasting of copper ores. It should be noted that galena (PbS) is much more easily fused than most copper minerals, and consequently the temperature must be more carefully regulated.

Flow diagram of extraction of lead is shown in Fig. 10.1. Method of lead extraction from galena involves the following stages:
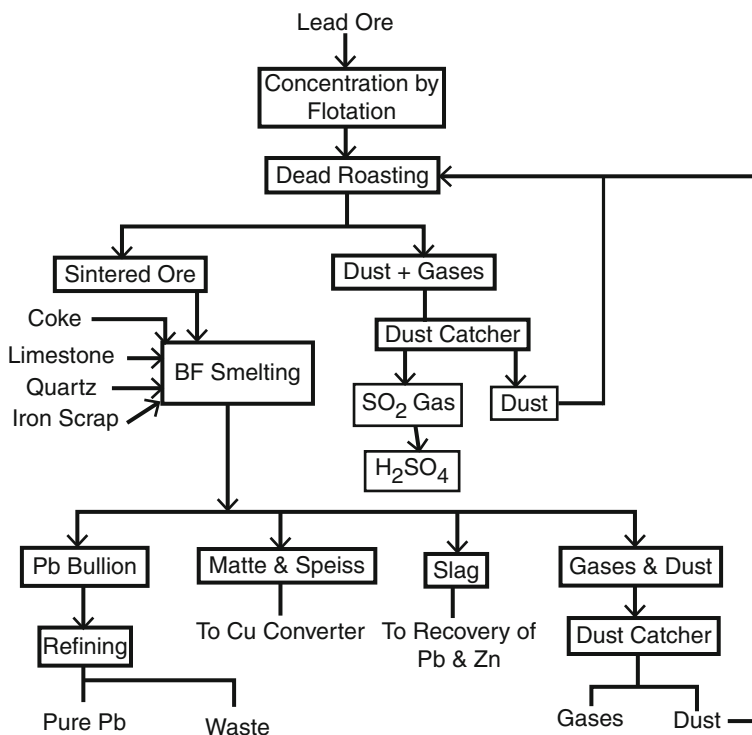

Fig. 10.1 Flow diagram of extraction of lead

(1) Concentration.
(2) Dead roasting.
(3) Smelting.
(4) Refining.

10.3.1 *Concentration*

The theoretical lead contents of lead sulphide is 86.8%, but actually lead contains much less in ore. Zinc and other sulphides are separated by flotation. Lead ore is concentrated by flotation; lead is enriched up to 60–80%. Silver almost invariably follows the lead into the concentrate, remaining with it during smelting; it is finally recovered during the refining operation.

10.3.2 *Dead Roasting*

The main object of the roasting of lead concentrate is to eliminate or carefully control the percentage of sulphur in the ore. It is done in a Dweight-Lloyd sintering machine. During roasting, the temperature (at 800°C) must be carefully controlled because, above 800°C, PbS tends to fuse. This machine not only eliminates sulphur to a large extent but also produces a sinter with required properties, such as strength and porosity, for the subsequent blast furnace operation. Sulphur is reduced from 16–18% to 1–2%. The flue gases contain 1–3% SO_2 depending upon the nature of the charge and operating conditions.

Galena ore was first roasted at a temperature below the fusion point in order to promote formation of oxide and sulphate.

$$2PbS + 3O_2 = 2PbO + 2SO_2 \tag{10.1}$$

$$2FeS + 3O_2 = 2FeO + 2SO_2 \tag{10.2}$$

At lower temperatures, sulphates can be formed:
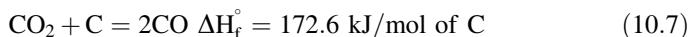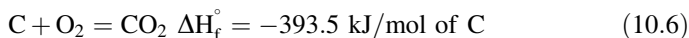
$$PbS + 2O_2 = PbSO_4 \tag{10.3}$$

Fe_2O_3 and SiO_2 are always present in raw materials, hot Fe_2O_3 and SiO_2 act as catalysts to promote the oxidation of the sulphur dioxide to trioxide and that may react with lead oxide to form the lead sulphate.

$$2SO_2 + O_2 = 2SO_3 \tag{10.4}$$

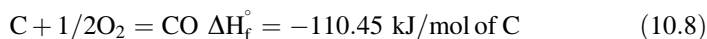$$PbO + SO_3 = PbSO_4 \tag{10.5}$$

10.3.3   Smelting

A blast furnace (BF) is used for smelting of lead ore sinter. This BF is smaller than one used for smelting copper or nickel. Height of BF is 8 m, top diameter is 3 m and stack height is 5 m. Coke, acting as fuel and reducing agent, is charged (10%) along with sinter from sintering machine; limestone and quartz (10%, act as flux), and iron scrap (1%, to reduce lead losses in the slag) are also charged in BF. Cold blasts of air are blown in through tuyeres (15–20 numbers) around the bosh to burn coke and oxidize the carbon (which is present in coke), producing the required amount of heat. The major portion of the heat is furnished by the combustion of coke, because all the sulphur which is desired to be eliminated has been oxidized in the earlier roasting operation. The bosh is water-cooled to ensure that the bosh temperature and the temperature of the outgoing gases remain low. This is to reduce the loss of lead due to vaporization (boiling point is 1737°C).

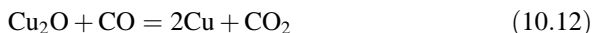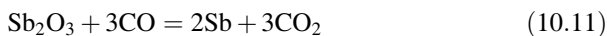Burning of coke at tuyeres region:

$$C + O_2 = CO_2 \; \Delta H_f^\circ = -393.5 \; kJ/mol \; of \; C \tag{10.6}$$

$$CO_2 + C = 2CO \; \Delta H_f^\circ = 172.6 \; kJ/mol \; of \; C \tag{10.7}$$

Overall reaction: $2C + O_2 = 2CO$

or

$$C + 1/2O_2 = CO \; \Delta H_f^\circ = -110.45 \; kJ/mol \, of \, C \tag{10.8}$$

Reduction of lead oxide and other oxides are done by counter current motion of carbon monoxide gas at BF:

$$PbO + CO = Pb + CO_2 \tag{10.9}$$

$$As_2O_3 + 3CO = 2As + 3CO_2 \tag{10.10}$$

$$Sb_2O_3 + 3CO = 2Sb + 3CO_2 \tag{10.11}$$
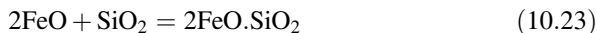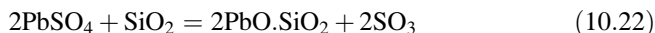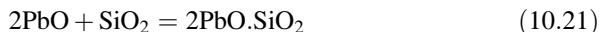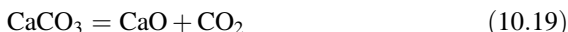
$$Cu_2O + CO = 2Cu + CO_2 \tag{10.12}$$

The iron oxide is also reduced by CO, and this iron together with scrap iron (which is added as part of the charge) is also reacted with lead sulphide and lead oxide.

$$FeO + CO = Fe + CO_2 \tag{10.13}$$

$$PbS + Fe = Pb + FeS \tag{10.14}$$

$$PbO + Fe = Pb + FeO \tag{10.15}$$

Metallic lead is also formed by the interaction between lead sulphide and oxide or sulphate; as well as by direct reduction by carbon.

$$2PbO + PbS = 3Pb + SO_2 \tag{10.16}$$

$$PbSO_4 + PbS = 2Pb + 2SO_2 \tag{10.17}$$

$$2PbO + C = 2Pb + CO_2 \tag{10.18}$$
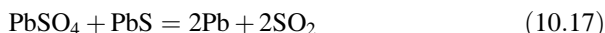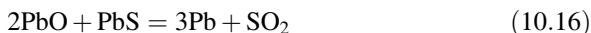
As the temperature approaches 900°C, the limestone of the charge is decomposed; liberating lime, which is united with the silica and other gangue materials present in the system, to form a slag.

$$CaCO_3 = CaO + CO_2 \tag{10.19}$$

$$\text{Slag formation: } CaO + SiO_2 = CaO.SiO_2 \tag{10.20}$$

$$2PbO + SiO_2 = 2PbO.SiO_2 \tag{10.21}$$

$$2PbSO_4 + SiO_2 = 2PbO.SiO_2 + 2SO_3 \tag{10.22}$$

$$2FeO + SiO_2 = 2FeO.SiO_2 \tag{10.23}$$

As atmospheric oxygen plays an important role in the reduction, enriching the air blast with 2% oxygen has increased output by about 15%, as well as saving in coke and smoother operation. Another important factor in securing efficiency lies in the production of a suitable slag, which depends upon the rate of smelting and recovery of lead and silver. In order to secure fast running, a satisfactory separation of the metal and slag must take place, and to ensure this, certain requirements of the slag are necessary as follows:

(1) Low specific gravity, for the greater the difference in density between it and the metal or the matte, the more rapid and complete the separation.
(2) Low melting point, for to flow freely from the furnace, slag must be completely molten.
(3) A slag may have a low melting point and low density, yet if viscous in nature, separation of metal and slag will not be clean, the slag carrying away entrained metal.

Blast furnace slag consists essentially of iron and calcium silicates containing: 18–35% SiO_2, 30–38% FeO, 10–20% CaO, 2–4% Pb plus small amounts of alumina, magnesia, sulphur, etc.
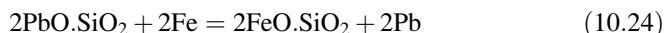
Iron scrap in the charge serves as follows:

(a) It helps in reducing any residual lead sulphide left unroasted during the sintering.

$$PbS + Fe = Pb + FeS \qquad (10.14)$$

(b) It combines with silica present in the charge to form $2FeO.SiO_2$, which lowers the melting point of the slag, to increase fluidity at operating temperature.

$$2FeO + SiO_2 = 2FeO.SiO_2 \qquad (10.23)$$
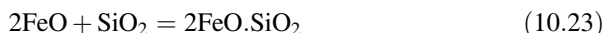
(c) It lower the lead losses in slag i.e. it recover lead from slag.

$$PbO + Fe = FeO + Pb \qquad (10.15)$$

$$2PbO.SiO_2 + 2Fe = 2FeO.SiO_2 + 2Pb \qquad (10.24)$$

At the same time, the sulphur is joined with the copper and iron present to form a matte. At the temperature of about 1000°C, the matte and slag are completely liquefied, coming down to the hearth; where they are separated into the layers according to the specific gravities. In certain cases neither matte nor speiss is formed. If the charge content low sulphur any copper present, that goes with the lead, there is no formation of matte. Production of speiss is closely allied with the amount of arsenic and iron present in the blast furnace.

$$As_2O_3 + 8FeO + 11C = 2Fe_4As + 11CO \qquad (10.25)$$

If low in arsenic or antimony, no speiss is formed. If there is an unduly high amount of arsenic, a speiss may form, but ordinarily arsenic content is low enough to be absorbed by the matte or metal. Hence, products of blast furnace are lead bullion, matte and speiss, and slag. Due to difference in specific gravities it gives four distinct layers as follows:

(1) 1st layer: Slag (specific gravity of 3.6, contain: FeO, SiO_2, CaO, MO).
(2) 2nd layer: Matte (specific gravity of 5.2) contains sulphides of copper and other elements (Cu_2S. PbS, CaS, FeS).
(3) 3rd layer: Speiss (specific gravity of 6.0) contains compound of arsenic (if arsenic is present in the charge), Fe_4As and impurities.
(4) 4th layer: Lead (specific gravity of 11.0), it is also called *base bullion*.

Lead (or base) bullion contains 92–99% Pb, 0.1–7% Cu, 0.05–0.8% Ag, < 0.05% Au, up to 1.5% Zn, As, Sb; up to 0.3% Bi and Fe. Presence of

impurities has adverse effect on properties, e.g. As and Sb make the lead metal very hard. Lead bullion contains greater part of the impurities in mechanical suspension (rather than in alloy form) due to their higher melting points than lead's.

10.3.4 Refining

Flow sheet for refining of lead bullion is shown in Fig. 10.2. The steps of refining are as follows:

(1) Drossing and skimming.
(2) Softening of lead bullion.
(3) Desilverization.

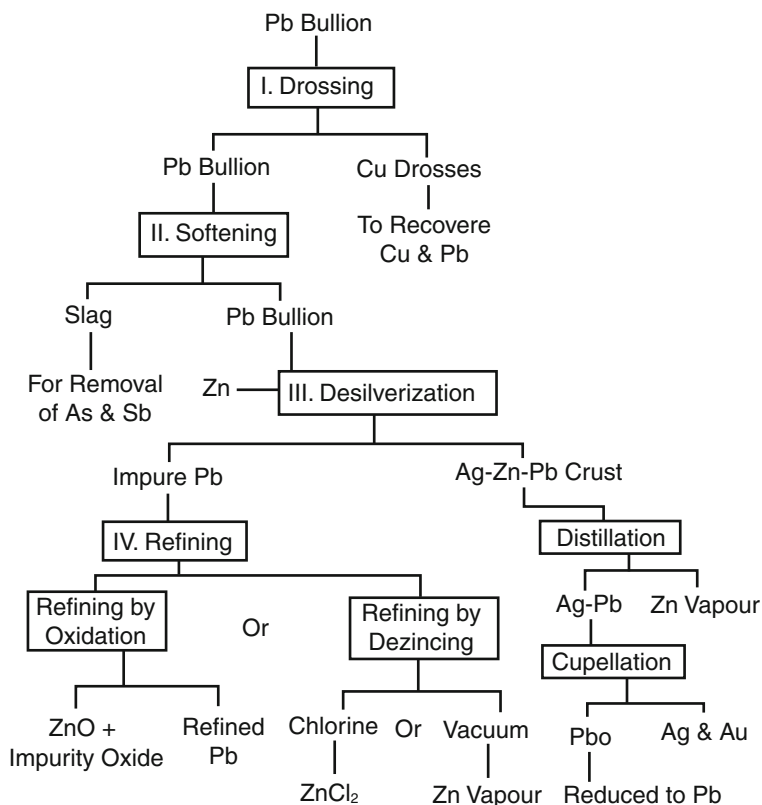**Fig. 10.2** Refining of lead bullion

10.3.4.1 Drossing and Skimming

Drossing is a process of oxidation and liquation. The lead bullion as it leaves the blast furnace well holds the greater part of the impurities in mechanical suspension (rather than in alloy form); and possessing a higher melting point than lead, a lowering of the temperature results in the insoluble oxidized impurities rising to the surface as a dross which can be removed by skimming. The bullion is held at a temperature just above the melting point of the alloy (370–380°C) under the oxidizing atmosphere for a period of about 2 h; during which a dross consisting copper, sulphur, arsenic and lead rises to the surface. This product (copper skimmed) is removed from the furnace for further treatment. Sometimes sulphur is also added into the drossing kettle to eliminate copper as sulphide, copper content is reduced to 0.005%.

10.3.4.2 Softening of Lead Bullion

The drossed bullion, still containing 1–1.5% impurities consisting of arsenic, antimony and tin, is treated in a softening furnace maintaining strong oxidizing condition. The temperature of the bath is raised to about 650°C and air is passed freely to the furnace so that oxidizing conditions may prevail. The lead, arsenic and antimony are oxidized to their respective oxides and form a litharge slag. If tin is present, it also joins this slag; the bath is held at that temperature for about 12 h, during which time nearly all the arsenic, antimony and copper can be removed. Bismuth cannot be removed from the lead by oxidation

10.3.4.3 Desilverization

At the third stage, desilverization is done to lead bullion by addition of zinc. Silver dissolves in all proportions in lead and zinc, with more affinity for the latter. In addition to silver, zinc has affinity for copper and gold, and these two have greater affinity than for silver. Hence the elimination of copper is needed in the drossing and softening operations. Lead and zinc, on the other hand, are only soluble to a very limited extent in each other. Thus, at the melting point of lead, zinc dissolves 0.6%, and lead in zinc to about 1.5%. When zinc is mixed with molten lead bullion and allowed to stand, a separation takes place; the lower layer contains lead with 0.6% Zn; and upper layer of zinc with 1.5% Pb and all silver. Now impure lead, containing 0.6% Zn and a small amount of impurities, is further refining by two methods

(a) Refining by oxidation at 750°C for the removal of zinc. Refined lead, contains 99.98% Pb, is casted.
(b) Refining by dezincing method, there are also two methods: by chlorination to form $ZnCl_2$; by vacuum at 540°C to form zinc vapour.

After third-stage desilverization, the Ag–Zn–Pb crust (consists of 30–60% Pb, 20–50% Zn and 25% Ag) is getting. This is then distilled at 1100°C to separate zinc vapour and Ag–Pb. Cupellation is done in a small furnace, melting the silver containing lead and exposing it to a blast of air whereby the lead and other metals present are oxidized and slagged off. Since silver does not have any affinity for oxygen, it remains on the hearth. By cupellation (oxidation) of Ag–Pb, PbO and silver, gold is separated. Further lead is recovered by reduction of PbO.

10.3.4.4   Electrolytic Refining

In the electrolytic refining process (Fig. 10.3) anodes are made from the lead bullion of blast furnace. Cathodes are thin sheets of pure lead supported on copper bus bars in a cell containing a solution of lead fluosilicate in hydrofluosilicic acid (H_2SiF_6). Lead is dissolved by the electrolyte from the anode and deposited on the cathode, the impurities (such as bismuth etc.) remaining behind (on the anodes).

Finding a suitable electrolyte in which to carry out the electrolysis for refining of lead is a problem. Most of the salts of lead when electrolyzed give rise to side reactions, since the anion, when discharging, is about oxidation, lead peroxide is deposited at the anode. The salt chosen must be readily soluble and the solution must have high conductivity; otherwise excessive electrical energy will be consumed in overcoming the resistance of the electrolyte. Electrolyte consists of a solution of lead fluosilicate in hydrofluosilicic acid. It is formed by the action of hydrofluoric acid on pure silica, resulting in hydrofluosilicic acid which is combined with lead to form lead fluosilicate ($PbSiF_6$).
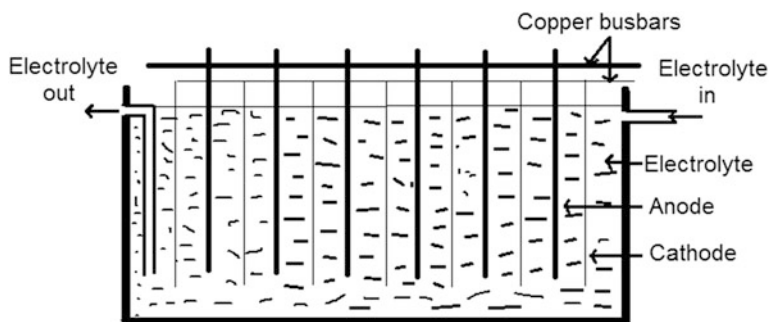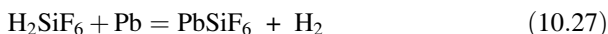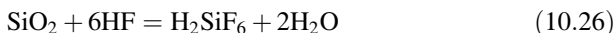
$$SiO_2 + 6HF = H_2SiF_6 + 2H_2O \tag{10.26}$$

$$H_2SiF_6 + Pb = PbSiF_6 \ + \ H_2 \tag{10.27}$$

**Fig. 10.3**   Electrolytic refining of lead

The electrolyte contains 7–10% lead, 10–15% total hydrofluosilicic acid with 5–10% free hydrofluosilicic acid. The composition of the electrolyte necessarily influences the efficiency of the operation, for as the conductivity is dependent upon the presence of hydrogen ions, an increase in the free acid content will increase the number of hydrogen ions with a consequent decrease in the resistance to the current. The presence of fluosilicate increases the resistance, and thus to ensure an electrolyte of minimum resistance it is necessary to have adequate free acid present.

10.4 Properties

The atomic weight of lead is 207.21. Although lead is one of the heaviest of metals (specific gravity: 11.37), it is also one of the softest of the commercial metals. Lead's low melting point (327°C) makes for easy casting. Its boiling point is 1750° C. The low tensile strength (1.575 kg/mm^2) limits its usefulness. For water-carrying purposes, its tensile strength is less important than its creep strength. Metals which are subjected to a steady load stretch slowly in the course of time (especially at high temperatures). This slow stretching or yielding is known as creep. The internal water pressure on pipes exerts a steady load and hence the wall thickness of the pipe must be of sufficient strength to resist continuously any creep tendencies. Lead can easily be rolled for sheets production, and extrusion is used for pipes. The process of joining lead, without use of soldering material, is known as lead burning. The edges of the material to be joined are melted together by means of a small flame, extra lead being added as necessary. Lead burning is invariably used in chemical plumbing. Joins in pipe work, lead to lead, or lead to brass are also carried out. Softness of lead is influenced by impurities.

Corrosion resistance of lead to the action of acids, alkalis and many other compounds promoted its wide use in the protection of chemical apparatus at the time when stainless steels and plastics were still unknown.

In nitric acid, lead dissolves vigorously according to reaction:

$$3Pb + 8HNO_3 = 3Pb(NO_3)_2 + 2NO + 4H_2O \tag{10.28}$$
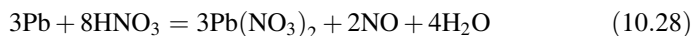
and at a lesser rate in concentrated acid as compared to a slightly diluted one, because of a poor solubility of $Pb(NO_3)_2$ in a strong acid.

10.5 Applications

In addition to resistance to corrosion by water and weathering, lead also exhibits non-corrosiveness in contact with many mineral acids, hence its extensive use in storage tanks for sulphuric acid. Soft lead (containing 99.99% Pb) is used where

lead of high purity is necessary. Antimony and arsenic are often added to the lead to impart hardness for special purposes in chemical plant equipment and lead shots.

The presence of small amounts of other metals in lead modifies and improves certain properties. Addition of 0.003–0.005% each of silver and copper results in an increase in tensile strength of 15%, together with better creep and fatigue resistance. These improved properties are used in pipes for conveying water under pressure; due to these improvements, thickness of the pipe can be reduced. Sn−Cd−Pb alloy is formed of 1.25–1.75% Sn and 0.2–0.3% Cd; it possesses improved creep resistance and tensile strength, but also increased resistance to fatigue under service conditions of vibration. Lead when alloyed with 0.05–0.1% tellurium has the property unique among lead alloys of being amenable to work hardening. By reason of this property, the material strengthens very appreciable when subjected to stress, becoming both tougher and stronger.

The important industrial alloys are those formed by lead with tin, antimony and copper; and, according to their application, these alloys can be classified as follows: bearing metal, antimonial lead, solders.

1. Bearing metal: Various types of bearing metals are available: (a) lead base babbitt; (b) alkali hardened lead bearings; (c) bearing bronzes.

   (a) Lead base babbitt: The term *babbitt* (named after Isaac Babbitt who invented a high tin-bearing alloy in 1839) is generally used to include alloys ranging in composition from 90% or more tin with no lead to 80% lead and less than 5% of tin. The lead base babbitt metals are based on the lead-antimony-tin system and like the tin base babitts have a structure consisting of hard crystals in a relatively soft matrix. The nature of the hard crystals and the matrix depends upon the tin content, and most of the alloys in commercial use fall into one of the two classes. First, those containing 12–18% Sb and up to 5% Sn in which the crystals consist of an antimony-rich solid solution; and second, those containing about the same amount of antimony but with 10–12% Sn. In these alloys the primary phase is SbSn.

   (b) Alkali hardened lead bearings: This class of alloy has been developed as a substitute for high tin alloys rather more for economic than technical reasons. The best known is Garman *Bahnmetall* which contains small amounts of alkali metals (0.6% Na, 0.7% Ca, 0.04% Li) as hardening elements. Another of these alloys is *Satco* containing 0.5–0.75% Ca, 1.5–2.0% Sn, with remainder lead.

   (c) Bearing bronzes: The addition of lead to 10% tin bronze improves the bearing properties and enhances the pressure tightness of the castings. The amount of lead added varies between 5 and 25%, the more heavily leaded bronzes being used where lubrication may be deficient, the lead itself serving in some degree as a lubricant. An important class of copper-lead alloys containing up to 30% lead and only small quantities of tin has been developed for the bearings of diesel and aircraft engines and for other heavy duty purposes.

2. Antimonial lead: The addition of antimony to lead confers the necessary strength and hardness needed in many industrial applications such as chemical plant equipment, battery plates etc. The hard lead, comprising 8–12% Sb, may be machined and screw threaded.

3. Solders: The use of tin-lead alloys to join metals was known some 2000 years ago. Tin and lead are miscible in all proportions and practically the whole range of soldering alloys from 5% to 95% Sn finds use in various industries. The characteristics of solders depend not so much on the mechanical properties as on such physical qualities as wetting ability and penetrative power. Without wetting of a metal surface by a solder there can be no soldering action but only a mechanical anchorage. The molten solder wets or adheres when it leaves a continuous permanent film on metal surface. Wetting is greatly assisted by the ability to alloy as shown by the contrasting behaviour of lead in the manner of solder. Lead when applied to iron or copper fails to wet them but effects joining merely by penetrating and solidifying.