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TIN

ITS MINING, PRODUCTION, TECHNOLOGY, AND APPLICATIONS

by

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CONSULTING ENGINEER, NEW YORK

Member, American Institute of Mining and Metallurgical Engineers, American Institute of Chemical Engineers

American Chemical Society
Monograph Series

Second Edition

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GENERAL INTRODUCTION

American Chemical Society's Series of Chemical Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical progress. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the Monographs, Charles L. Parsons, secretary of the Society, Washington, D. C.; the late John E. Teeple, then treasurer of the Society, New York, and the late Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the ACS Series of (a) Scientific and (b) Technological Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successor) of New York.

The Council of the American Chemical Society, acting through its Committee on National Policy, appointed editors (the present list of whom appears at the close of this sketch) to select authors of competent authority in their respective fields and to consider critically the manuscripts submitted.

The first Monograph of the Series appeared in 1921. After twenty-three years of experience certain modifications of general policy were indicated. In the beginning there still remained from the preceding five decades a distinct though arbitrary differentiation between so-called "pure science" publications and technologic or applied science literature. By 1944 this differentiation was fast becoming nebulous. Research in private enterprise had grown apace and not a little of it was pursued on the frontiers of knowledge. Furthermore, most workers in the sciences were coming to see the artificiality of the separation. The methods of both groups of workers are the same. They employ the same instrumentalities, and frankly recognize that their objectives are common, namely, the search for new knowledge for the service of man. The officers of the Society therefore

combined the two editorial Boards in a single Board of twelve representative members.

Also in the beginning of the Series, it seemed expedient to construe rather broadly the definition of a Monograph. Needs of workers had to be recognized. Consequently among the first hundred Monographs appeared works in the form of treatises covering in some instances rather broad areas. Because such necessary works do not now want for publishers, it is considered advisable to hew more strictly to the line of the Monograph character, which means more complete and critical treatment of relatively restricted areas, and, where a broader field needs coverage, to subdivide it into logical sub-areas. The prodigious expansion of new knowledge makes such a change desirable.

These Monographs are intended to serve two principal purposes: first, to make available to chemists a thorough treatment of a selected area in form usable by persons working in more or less unrelated fields to the end that they may correlate their own work with a larger area of physical science discipline, second, to stimulate further research in the specific field treated. To implement this purpose the authors of Monographs are expected to give extended references to the literature. Where the literature is of such volume that a complete bibliography is impracticable, the authors are expected to append a list of references critically selected on the basis of their relative importance and significance.

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Preface to Second Edition

In this second edition the original plan of the book and the viewpoint of treatment of the different sections have been maintained. Since the first edition, the author has been called upon to serve as consultant in connection with ore concentration processes, product application of tin and its alloys in their numerous forms, corrosion of tin plate, conservation of the metal during war periods, as well as its recovery from secondary sources involving detinning, reverberatory smelting of skimmings, drosses, and ashes, the surface application of the metal in plating, and the numerous problems associated with electrolytic tin plate and electrolytic refining.

Many changes in the tin situation have taken place in the last decade Tin smelters have made their appearance in the United States, electrolytic tin plate has grown into an important commercial commodity, improvements in mineral dressing have made available tin from sources formerly discarded; and organized research and development by the tin producers and the Tin Research Institute have added much new information. Intensification of tin recovery from secondary metal sources has caused new ingenuities to be applied Basic metallurgical research has brought forth greater detail on the alloy systems of which tin is a component part. In much of the commercial aspects of tin production and utilization the author was fortunate in having direct contact as a consultant.

The first edition was the subject of a translation into German by W Lidle, appearing under the title "Zinn, Berg- und huttenmanische Gewinnung, Verarbeitung und Verwendung," Verlag von Wilhelm Knapp, Halle (Saale), in 1937. In some sections Dr. Lidle extended the treatment to include German practice of that period. These data are included in the second edition, along with information collected by the technical teams who studied German metallurgy after World War II.

As in the first edition, the author is indebted to a number of men and organizations actively engaged in the tin industries or businesses relating to the production or consumption of tin metal. At various points in the volume these courtesies are acknowledged. The author is indebted to Miss Edna M. Rogers and Frank M. de Santa who painstakingly prepared the manuscript, and to Professor C. H. Mathewson for his helpful criticism of the work before publication.

It is hoped that this volume will be useful to those engaged in the manifold ramifications of tin mining, dressing, production, technology, alloying,

and applications of the metal in its numerous forms. It is also hoped that readers will feel welcome to offer constructive criticism in connection with the production and use of this almost "semi-precious" metal in our national economy.

Munsey Park
Manhasset, New York
December, 1948

C. L. MANTELL

Preface to First Edition

In this monograph the author has attempted to cover the subject of tin in a somewhat comprehensive manner. The history, the physical and chemical properties, and the production, distribution, and consumption of the metal have been treated. The ores and ore deposits, the ore dressing, mining, smelting, refining, and metallurgy represent the distinctly metallurgical sections These have been treated somewhat from the viewpoint of the metallurgical chemist rather than from the viewpoint of the mining engineer. The industrial applications of tin in its simpler forms, as in plating, hot-dipped coatings, foil, and collapsible tubes, are written from the viewpoint rather of the chemist than of the mechanical engineer The section on alloys has been written from the standpoint of the physical metallurgist, and the sections on corrosion from that of the chemical engineer. The chapter on compounds is distinctly chemical. An attempt has been made to gather together the large amount of information, examine the material critically, and present it in usable form. The section on secondary tin has been written from the economic as well as the metallurgical and chemical side The same holds true for detinning of tin-plate scrap. Much of the important data on tin, in the phases either of its production or of its consumption, has been widely spread. This volume is an attempt to gather together as much as possible of the authoritative available information for the use of those in the various fields in which tin finds application.

The author has made free use of a number of references of an authoritative nature pertaining to the various phases of the production of tin from its ores, its smelting, and its commercial applications Considerable information in reference to ores and ore deposits has been obtained from Jones' "Tinfields of the World," on ore dressing from Taggart's "Handbook of Ore Dressing," on alloys from the International Critical Tables and the data sheets of the American Society of Steel Treating, on compounds from Mellor's "Treatise of Inorganic and Theoretical Chemistry;" and on corrosion from the Corrosion Bibliography of the National Research Council.

The author wishes to acknowledge his indebtedness to a number of men and organizations actively engaged either in the tin industries or in other businesses closely connected with the production or consumption of tin metal. Chief among these are E. K. Browne of the American Metal Market of New York, for aid in connection with data on tin marketing; Wil-

liam A. Cowan of the National Lead Company for analyses of various tins, the Malay States Information Agency and the Geological Survey of the Federated Malay States for photographs of tin mines in Malay; Werf Conrad of Haarlem, Holland, and Arthur R. Brown, Ltd., of London, England, builders of dredges, for photographs of tin dredges of various types; the Mining Magazine of London for the use of pictures of the newly opened Penpoll smelter; the American Sheet and Tin Plate Company for illustrations of tinning stacks in the manufacture of tin plate; the Metal Industry of New York for photographs showing the tinning of wire; the Birmingham Iron Foundry for the use of illustrations of rolling mills employed in the manufacture of tin foil, H A Baker of the American Can Company for his cooperation in respect to the application of tin containers for food products; Henry S. Rawdon of the National Bureau of Standards for the loan of photomicrographs of tin scruff; and last but not least, Miss Edna M. Rogers who painstakingly prepared the manuscript, and Andrew M. Hathaway who made the drawings for the many illustrations.

The author is particularly indebted to Dr. J. C. Whetzel, manager of the Research Laboratory of the American Sheet and Tin Plate Co., Pittsburgh, Pa., for his inestimable aid and advice given in connection with his review of this volume in its manuscript form.

It is hoped that this volume may be useful as a reference and as a stimulant to those engaged in the mining, milling, smelting, refining, and alloy founding of tin metal, and to others interested in the manifold applications of tin in industry, in the form either of metal or of its compounds. Criticism will be welcomed at all times and gratefully received. The author will be only too glad to receive suggestions regarding the production and use of this important metal in our national economy.

Pratt Institute C. L. MANTELL
Brooklyn, New York
October, 1928

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Chapter 1

History

Tin, a component of bronze, was used as a metal prior to the dawn of history. It does not follow, however, that prehistoric bronzes were made of metallic tin. Tin does not occur "native" to any extent, although grains of metallic tin occur as a subordinate admixture in some of the gold mines of Siberia, Guiana, and Bolivia. When the unalloyed metal was first introduced can not be definitely ascertained. It is generally believed that tin was employed in the arts in the Grecian age of Homer and the Biblical times of Moses. The metal and some of its alloys were known to Hiram of Tyre and his artificers connected with the building of King Solomon's temple. It is very likely that an early barbarian discovered tin when he attempted to put out or bank his fire with handfuls of black alluvial sand. Perhaps at one time he employed alluvial cassiterite and found, to his surprise the next morning, particles of a bright, shiny new metal.

Primitive Smelting

The most primitive method of smelting tin was that in use in the Bronze Age. The early artificers required the metal to enable them to mix it in varying proportions with copper to make different kinds of weapons and to harden the copper. Socketed axes required 4 to 13 per cent tin, and spear and lance heads 11 to 16 per cent. Gowland came to the conclusion, as a result of a number of analyses of ancient bronze weapons, that the varying tin content was not due merely to chance but to the skill of the smiths of the later Bronze Age. It is thought that the smelting was carried out in trenches lined with clay and filled with brushwood. Above this, small logs of wood were piled. The mass was lighted and as soon as the logs were burning fiercely and the trench full of glowing embers, small quantities of tinstone were thrown upon the fire from time to time. More wood and mineral were added until the required amount of tin had accumulated in the trench. The fire was then allowed to die down or was raked away, and the molten metal ladled into a hole in the ground or into a clay mold near the furnace. It is quite likely that later developments led to the use of a deep hole instead of a shallow pit to confine the fire. Primitive blowers or bellows were introduced and the blast no longer admitted over the edge of the cavity, but through an opening just above the base of the furnace

which was excavated near the edge of a bank of earth Molten tin was allowed to flow out through a tap hole at a point lower than the blast entrance. Further progress was made in later years by erecting small cylindrical furnaces built of clay. The operation of these was more convenient. Most native furnaces are developments along the lines stated.

Early Uses and Sources

Tin metal was not found native by the ancients. They could have obtained it only by extraction from its ores. In alluvial deposits the ore is found near or on the surface, and it gives up its metal more readily than the ores of most metals. The early Britons were acquainted with the slagging operations involved in tin smelting, for many ancient slag hearths are found in Cornwall.

Tin ore occurs in commercial quantities in only a few countries of the world. These were not readily accessible to the Romans or Greeks until after the Caesarian conquest of Britain It appears probable that the metal was scarce and costly. Although more durable than lead or copper, vessels of tin are rarely found among the Greek or Roman antiquities, under conditions where vessels of lead and copper are comparatively common Articles of tin alloys, however, are often found

Moses, in the book of Numbers of the Bible, includes tin in his list of the metals then known. The Hebrew word *bedil* was translated *cassiteros* in the Greek versions, and *stannum* in Latin translations In his "*Historia Naturalis*," Pliny regarded tin as a variety of lead He stated:

"There are two kinds of *plumbum—nigrum* and *candidum* or *album* (*i e* black lead and shining or white lead). The *plumbum candidum* is the most valuable, and it was called *cassiteros* by the Greeks There is a fabulous story told of their going in quest of it to the islands in the Atlantic Ocean, and of its being brought in boats made of osiers covered with hides The *plumbum candidum* occurs as a black sand found on the surface of the earth, and is to be detected only by its weight, it is mingled with small pebbles, particularly in the dried beds of rivers The miners wash the sand, which is then melted in the furnace and becomes converted into *plumbum album* "

Pliny's *plumbum candidum* was no doubt tin, just as his *plumbum nigrum* was lead. Pliny described Roman vessels made of copper and coated with *stannum*, and stated that *plumbum candidum* was esteemed in the days even of the Trojan war. Homer writes of it under the name *cassiteros*.

The history of tin among the ancient peoples may be divided into the period corresponding to the exploitation of tin in Asia, and into a second period corresponding to the importation of the metal from Great Britain by the Phoenicians. Articles of copper and copper alloys found in Mesopotamia, belonging to the period of 4000 B.C., upon analysis show that tin was not used in their manufacture. The oldest bronze objects probably

belong to the period of 3500–3200 B.C. The bronze objects in question, among which are two blades with 12 to 15 per cent tin and a considerable nickel content, were found in the old royal tombs in the town of Ur near the mouth of the Euphrates River. The analysis of an Egyptian bronze mirror belonging to the period of 1600 B.C., showed that tin was present. Bronze seems to have been an Oriental discovery. Tin was used by the Egyptians in 700–600 B.C., as proved by the finding of a strip of tin, free from lead and silver, in the wrappings of an Egyptian mummy of an age not later than 600 B.C. The Chinese bronze industry flourished in 1800–1500 B C., so that tin must have been known in China at that time. The present-day Oriental custom of making coffin lace by the laborious method of hand-beating tin into tin foil, which is to be cut into decorative forms, has its origin in the dim and distant past before the Christian era.

References to the tin trade of the Phoenicians, the Greeks, the Gauls and the Romans are very scanty. Herodotus states that he was not acquainted with the Cassiterides Islands from whence came our tin. In his *"De Bello Gallico,"* Caesar talks of the tin trade, as did Aristotle in his *"De Mirabilibus Auscultationibus,"* and Strabo in his *"Geographica."* Pliny's fabulous story could very well refer to the transport of tin or tin ore from the Scilly Islands and Cornwall by vessels resembling the coracles of the ancient Britons. About 1000 B C. the Phoenicians appear to have worked tin mines in Cornwall, ages before the Roman conquest. They seem to have conveyed there a body of colonists who established an emporium. The metal was also obtained from the inhabitants by barter. They called the Scilly Islands and the shores of Cornwall the Cassiterides, and Dionysius, writing in the beginning of the fourth century, called them Hesperides. In the Bible, Ezekiel refers to the tin commerce of the Phoenicians at Tyre.

The early Greek alchemists called tin *Hermes*; but about 500 A.D. the alchemists called it *Zeus* or *Jupiter*, and represented it by the symbol ♃, which was understood to mean the thunderbolts of the king of the gods. Because tin forms brittle alloys with many metals, it was called *diabolus metallorum*—the devil of the metals. The Latin Geber, in his *"Summa Perfectionis Magisterii,"* probably written about the twelfth century, said:

"I intimate to the sons of learning that tin is a metallic substance which is white, but not pure white; it has a little ring, and emits a creaking sound; it partakes of a little earthiness; and possesses in its root both hardness and softness; it melts rapidly without catching fire, it does not take cupellation—*cineritium et cementum non exspectans;* and it is extensible when hammered. Its vice is that, when alloyed, it makes every metallic body brittle excepting Saturn and pure Sol."

The Spanish tin mines appear to have been abandoned under the government of the Moors. Much of the world's supply of tin about the thirteenth

century came from Cornwall, although the tin mines of Saxony and Bohemia were probably discovered about that time. The Malay States and the East Indies are mentioned as sources of tin by Arabian writers of the eighth and ninth centuries. A number of sixteenth century authors mentioned East Indian and Malacca tin, and many mines at Banka were estimated to have been worked by the Chinese before the seventeenth century. Definite documentary history of the Cornwall mines does not begin earlier than 1156.

The earliest tin-dressing and -smelting operations were applied to alluvial tin deposits. Polwhele, the historian, reported: "The stream tin from St. Austell Moor is of the very purest kind. Without any other management than being washed on the spot, it brings thirteen parts for twenty at the smelting house" Another early reference mentioned the Regis tinstones, from which the metal was obtained after direct heating, the poorer stones being broken up and washed before smelting Evidences of these early preparations for smelting are still to be found in Looe Pool Valley, where

TABLE 1 TIN MINING IN SAXONY AND BOHEMIA (TONS)

PERIOD	SAXONY	BOHEMIA	ANNUAL AVERAGE
1400–1500	31,250	26,250	575
1501–1600	25,000	50,000	750
1601–1700	10,000	10,000	200
1701–1800	15,000	15,000	300
1801–1850	6,400	3,450	100
1851–1900	—	2,460	25

boulders of hard rock show deep holes in which the tinstone was pounded. Similar indentations of rock and the remains of a crude buddle or washing place have been discovered in the Islands of Scilly. Improvements such as the stamp battery were introduced from the Continent early in the sixteenth century. Prior to 1602 tinstone was crushed dry; but about that time a water-wheel-driven wet-stamp battery appears to have been employed. A labor-saving stamping mill was recorded in 1671, and also a shallow trench used to divide the product, evidently according to the rate of fall in water. This operation was termed "trambling" or "buddling" About this time calcination in a square kiln was described. About 1742 only one steam engine was to be found in all Cornwall, but after that time progress was extremely rapid. Stream works were giving way in importance to mine works, and the nineteenth century provided more efficient and automatic mechanisms for dressing with steam power, as well as heavier stamps, stone breakers, classifiers, self-acting calciners and the like.

Pryce classified the ores of Cornish tin as "shode, stream or mine," the

term "shode" apparently referring to lump or gravel-size ore, between mine ore and stream tin in size and situation. Early documentary references, however, described the specific nature of a tin working as a "moor" or "stream" work.

The highest output of tin concentrate on record in the year 1337 was given as 1,328 thousandweight, or about 600 tons, after which the Great Plague ruined the stannaries for some time Such events as the Wars of the Roses, which exerted an adverse effect for a long period, are held partially responsible for the fluctuation in tin output. The advance from 700 tons in the early part of the seventeenth century to 1,500 tons at the end was caused by the general use of the stamp battery introduced in the sixteenth century. During the half century ending 1800, the output varied from 2,000 to 3,500 tons annually.

The history of tin mining in Saxony and Bohemia reaches back to the twelfth century. It is said that the first tin mine was operated as early as the year 1146 in Graupen. In all probability at that time, only the placer ore was mined, which had been created by the weathering of the rocks The Bohemian deposits near Schonfeld and Schlackenwald are said to have been discovered by Cornish miners in the year 1204. The first document from this locality dates from the year 1341. The smelter in Obergraupen was opened in 1379. About the year 1400, the tin mines of Ehrenfriedersdorf and Geyer started to operate—and during the fifteenth century those at Altenberg—and very soon prospered. The Thirty Years War destroyed the industry completely. After the war, the Protestant tin miners who had been expelled from Bohemia started mining operations again, probably first at Zinnwald and Johannegeorgenstadt. The miners, however, did not acquire great prosperity because of the enormous ore discoveries overseas, causing practically a complete stop in mining operations. The growth and decline of the mine can be seen in Table 1 from the production figures according to Neumann.[1]

[1] B. Neumann, "Die Metalle," Halle, 1914.

Chapter 2

Physical and Chemical Properties of the Metal

Although so common and well known, tin is a less abundant element than many of those less familiar and usually ranked with the scarce or rare elements such as cerium, yttrium, lithium, beryllium, titanium, zirconium, and vanadium.

Physical Characteristics

The color of tin is white, with a slightly bluish tinge. When it is compared with nickel, the latter metal is brown in comparison, and with chromium, this substance is definitely blue. Tin is whiter than silver or zinc. Exceedingly thin films of tin transmit various shades of brown when light is caused to pass through the film. The metal has a brilliant luster, and when highly polished has high light reflectivity. The luster depends to a large extent upon the temperature at which the metal is poured when cast If the temperature is too high, iridescent colors may show on the surface as the result of oxide films. If the pouring temperature is too low, the surface is dull. Small amounts of foreign metals such as lead, arsenic, antimony, and iron decrease the luster of tin and impart a yellowish tinge to the metal.

The structure of the cast metal is a mass of crystals. When a bar of tin is bent, it emits a characteristic creaking sound called the "cry" of tin, resulting from mechanical twinning of the crystals during the bending of the metal. Tin metal may lose its coarse crystalline structure by cold working, but grain growth occurs rapidly. If the surface of tinned plate, tin foil, or tin metal in cast form be etched with hydrochloric acid containing a little free chlorine, or with a solution of stannous chloride, attack occurs at the intercrystalline faces. The surface shows patterns resembling the frost flowers on windowpanes in winter. The etched appearance is called *moiré metallique.* Fine dendritic surface crystals of tin may be obtained by casting the metal on a surface of polished steel. In tin plate the intercrystalline boundaries are shown by fine grooves or channels which result from the method of manufacture, during which the plates are drawn from a bath of molten tin and allowed to drain. More fusible impurities are forced, by the crystallization of the tin, to the intercrystalline junctions, after which the still fluid impurities drain off, leaving minute channels.

The fine grain structure obtained by quenching molten tin in water is not affected by annealings over long periods at temperatures below the melting point. If, however, so-called "block tin" should have its crystalline structure extremely subdivided by severe compression or working, it can be caused to recrystallize at 150°. Tin crystals sometimes show lines which are due to stresses set up during rapid growth.

Cold-rolled tin shows a tendency to recrystallize at ordinary temperatures immediately after rolling. If annealing be carried out at 170° to 180°, secondary recrystallization occurs. In this case the smaller crystals grow at the expense of their neighbors. The resultant metal has a coarse crystalline structure. If rolled once again and allowed to stand, the primary crystals which form are larger than before, but about the same size as those produced by annealing at temperatures up to 150°.

Single crystals of tin have been made by a number of investigators. Mark[1] and his coworkers found that when a tin crystal is elongated to a wire and heated at 150° for three minutes, the wire is disrupted by recrystallization which begins at the ends, growing at the rate of approximately one mm. per second. The orientation of the new crystal in reference to the old one is such that the width of the wire is not changed on elongation Tammann and Mansuri[2] stated that coalescence of the grains of powdered tin occurs by recrystallization at 142°.

The physical properties of tin are given in Table 2 on page 17.

Allotropic Forms. Tin is one of the few metals which have sufficient dignity to be subject to a "disease." Many workers have observed that ordinary tin changes into a gray powder when exposed to extremes of cold. Medallions, coins and antiques in museums acquire a surface crust of powdery gray tin which gradually grows, seemingly self-catalyzed, until complete disintegration results. This is the "tin pest" or "disease" of the museums. Krause[3] stated that Aristotle[4] refers to the change tin undergoes when subjected to extreme temperatures. Erdman[5] in 1851 noted structural changes in organ pipes. He thought them to be the effect of vibration. Fritzsche[6] described the disintegration of pig tin. After exposure to the Russian winter of 1867–8, when the temperature during January fell as low as −38° C., some blocks of Banka tin had disintegrated to granular cystalline pieces and coarse powder. A large number of workers have noted the same effect. Gowland[7] referred to the change in an old

[1] Mark, Polanyi, and Schmid, *Naturwiss.*, **11**, 256 (1923), *Z. Physik*, **32**, 684 (1925).
[2] Tammann, and Mansuri, *Z anorg. Chem.*, **126**, 119 (1923).
[3] Krause, *Prometheus*, **11**, 701 (1900).
[4] Aristotle, "De Mirabilibus Aucultationibus."
[5] Erdman, *J Prakt Chem* (1), **52**, 428 (1851).
[6] Fritzsche, *Mem Acad St Petersburg* (1), **7**, 15 (1870).
[7] Gowland, *Archaeologia*, **56**, 13 (1899).

vessel, consisting of 94 35 per cent tin, 5.06 per cent lead, traces of iron and copper, 0 59 per cent oxygen and carbon dioxide, in the following words:

"The extraordinary molecular change which the metal of this vessel has undergone is of more interest to the physicist and metallurgist than to the antiquary The metal is not much oxidized, yet it is so exceedingly brittle that it can be easily broken with the fingers The effect of time upon it has resulted in a complete alteration of its molecular structure, the mass of the alloy being converted into an agglomeration of crystals, and to this its brittleness is due On smelting and casting a small fragment I found that the crystalline structure disappeared and the metal regained its original toughness"

When tin or a tin alloy is affected by tin pest, gray colored spots appear and the metal becomes brittle Expansion occurs so that the product occupies a greater volume than the unaffected tin. The expansion produces pustule-like or nodular excrescences at the affected points. Transformation extends radially outward from the spots until the whole mass is infected. The metal then rapidly breaks down to a brittle powder. The disease is infectious and can be propagated by inoculation. Transformation can be begun by contact between a grain of the powder and a piece of sound metal. The metal becomes sick in an analogous manner to that of the human organism when attacked by pathogenic bacteria. Once infected, the whole mass is in danger. Powdery gray tin shows the same analysis as that of the ordinary white metal. In other words, gray tin is an allotropic modification of the elemental metal. Cohen and Van Eijk[8] showed that tin pest is due to the enanthiomorphic change of ordinary white tetragonal tin into gray tin If white tin be powdered, mixed with some gray tin, and kept at a low temperature, say −50° C., for a few days, the entire mass changes to gray tin, and conversely, gray tin changes to white tin by warming the mass on a water bath Measurements of the potential difference of the two forms of tin in a cell with stannous chloride as electrolyte give a zero value at 18° C., at higher temperature the gray form is the positive pole, and at lower temperature, the white. The transition temperature is 18° C. Consequently, when the ordinary metal is kept below 18° C., it is metastable, and before equilibrium can be reached it must change into the gray form. As Cohen and Inouye[9] expressed it, white tin under ordinary conditions is in a metastable state; but under ordinary atmospheric conditions, the change is exceedingly slow. The rate of change is accelerated by lowering the temperature, reaching a maximum at about −50°, and thereafter diminishes as illustrated by Fig. 1. Janecke[10] observed the change through an extended interval of temperature about 20° and 600 atmospheres

[8] E. Cohen, and C. Van Eijk, *Versl. Akad. Amsterdam*, **8**, 36, 102 (1899); *Z. Phys. Chem.*, **30**, 601 (1899).

[9] Cohen, and Inouye, *Chem. Weekbl.*, **6**, 881 (1909).

[10] Jänecke, *Z. phys. Chem.*, **90**, 257, 313 (1915).

pressure. Stepanoff[11] studied the rate of transformation of gray and white tin.

The following table shows the rate (in mm. per 10 hr.) at which the transformation of tin spreads from centers inoculated with the gray modification at −10° C., and how it is affected by small quantities of other metals [12]

Kahlbaum tin	0 0205
Kahlbaum tin + 1% lead	0 0075
Kahlbaum tin + 0 1% bismuth	0 002
Kahlbaum tin + 0 5% bismuth	0 0000
Kahlbaum tin + 0 1% antimony	0 001
Kahlbaum tin + 0 5% antimony	0 0000
Banka tin	0 0125
Banka tin + 2% cadmium	0 0095

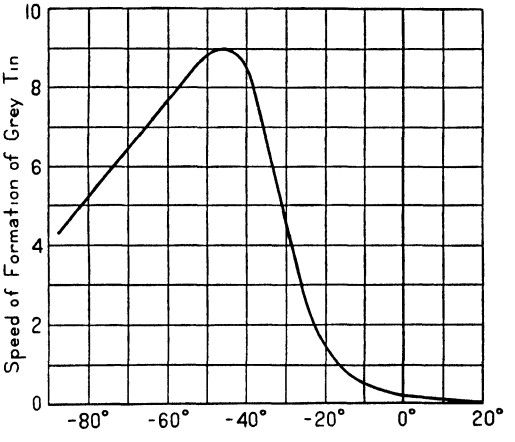

FIGURE 1
Relative speeds of transformation of ordinary tin to gray tin at different temperatures

Hasslinger[13] stated that a tinned iron vessel showed a crystalline, brittle surface after it had been kept at 16 to 45° C. for two years. He inoculated other masses of tin with small portions of this crystalline metal. These were transformed in a similar manner, the affected area increasing 3 to 5 mm. in diameter daily. No difference could be noted between experiments at 7°, 19° and 37° C. When tin foil was inoculated, the change extended through the thickness of the foil. The crystalline tin preserves its appearance up to near the melting point, but becomes normal after melting and again solidifying. Cohen[14] showed that the structural change of the worked

[11] Stepanoff, *Ann. Inst Phys Chem.* (*Leningrad*), **2**, 500 (1924).
[12] G. Tammann, and K. L. Dreyer, *Z. anorg. allgem. Chemie*, **199**, 97 (1931)
[13] Hasslinger, *Sitzb. Akad. Wien*, **117**, 501 (1908), *Monatsh.*, **29**, 787 (1908).
[14] E. Cohen, *Chem. Weekbl.*, **2**, 450 (1905); **6**, 625 (1909), *Trans. Faraday Soc* , **7**, 122

metal consists in a recrystallization process, the result of which is the formation of larger tin crystals from smaller ones; and that the various forms of mechanically worked tin are in a metastable condition with reference to unstrained tetragonal tin above 18° C., and also with reference to gray tin below 18° C The so-called *moiré metallique*, which results when tin plate is etched by means of hydrochloric acid and potassium chlorate, corresponds with the recrystallized tin, and this can be used to start the change in other samples of tin plate.

Bijl and Kolkmeijer[15] showed from their x-ray studies of gray tin that it crystallizes in the cubic system. Its space-lattice is of the diamond type with an edge of unit cube $a = 6.46$ Å units.

"Tin pest" might have been responsible for the death of Scott and his comrades on the ill-fated South Pole expedition in 1911–1912 [16]

In the depots or cachés laid out along the route to the Pole, there were tin cans containing petroleum or kerosene for the oil stoves. These cans were on top, to be reached first when opening a depot. When Scott was going back, one depot after the other was found to contain more or less empty oil cans and food saturated with oil Thus the explorers, downhearted after having found that Roald Amundsen had reached the Pole some weeks before them, were deprived of heat and nourishment, which might perhaps have sustained their strength and lives [17]

The cans presumably were soldered with pure or too pure tin solder which did not stand the extreme Antarctic cold, but turned into powder.

In the Scandinavian countries, sticks of solder are sometimes found (probably of normal 50-50 per cent composition) which do not run properly and seem to contain the gray powder allotropic form of tin intercrystallinely.

The importance of tin solders in radio receivers, canned goods, and other merchandise carried to all parts of the world, and particularly where severe cold seasons are encountered, warrants more detailed attention to the occurrence of tin pest and its prevention.

In low-temperature equipment, such as that handling liquefied gases such as nitrogen, oxygen, hydrogen, helium and air, tin and tin solders are to be avoided as joining agents.

There has been considerable acceptance that tin exists in a number of allotropic forms. At low temperatures, the stable form is gray cubic, or *alpha* tin, which changes at 18° C. to *beta* tin, the ordinary white tetragonal

(1911), *Z Elektrochem*, **18**, 616 (1912), **19**, 23 (1913); *Z. phys. Chem*, **33**, 57 (1900), **35**, 588 (1900), **36**, 513 (1901), **48**, 243 (1904), **63**,625 (1908); **68**, 214 (1909).

[15] Bijl, and Kolkmeijer, *Chem. Weekbl.*, **15**, 1264 (1918), *Proc. Acad. Amsterdam*, **21**, 405, 494, 501 (1919).

[16] Private communication from Kaye Weedon, Engineer, Oslo.

[17] L. Huxley, Editor, "Scott's Last Expedition," Vols. I and II, London, 1914, in which are found accounts of the leaking cans.

form [18] A number of workers have indicated that beta tin supposedly suffers transformation at 161° C. to a so-called rhombic, brittle or gamma tin This, in turn, at 232° C. passes into the molten state. Mason and Pellissier[19] critically studied all the previous work and concluded that no valid crystallographic evidence exists for rhombic or any other gamma tin. Careful investigations, based on x-rays and physical properties, have failed to find any evidence for gamma tin.

Back-reflection powder x-ray photographs of pure tin at several temperatures between 25° and 200°, and at atmospheric pressure, show no indication of any structure but that of tetragonal beta tin It appears that the so-called gamma or rhombic tin was rhombic tin sulfide impurity in tin metal.

In an article concerning the allotropy of tin, Tammann[20] presented a pressure-temperature diagram in which rhombic tin was allotted a definite field of stability on the basis of some of the earlier work Further, he stated that the transformation into rhombic tin can lead to cracks and fissures on hot-rolling or pressing Stolba[21] had previously shown that at about 200°, tin, like other metals near their melting points, becomes brittle enough to be pulverized in a mortar, but Smits[22] attributed this hot-shortness to a modification stable above 200° Greaves and Jones[23] found a change of direction of the impact-temperature curve (no more marked than in copper at 120° to 200°) at 190°.

Homer and Plummer[24] in a study of the embrittlement of tin at elevated temperatures, demonstrated the marked influence of very small amounts of impurities on the temperature above which brittle fracture occurs. They also confirmed the linear hardness-temperature relationship previously found by Sauerwald,[25] in contradiction of earlier work by Ludwik [26]

Nishikawa and Asahara,[27] in an early x-ray study of the recrystallization of several rolled metals, found no radical change in the diffraction patterns of white tin (purity not stated) at high temperatures, and concluded that no transformation occurred Murphy,[28] using sensitive measuring methods

[18] Cohen, "Physico-Chemical Metamorphosis," New York, 1926, *Proc Kon Akad Weten Amsterdam*, **40**, 746 (1937), **41**, 462, 860 (1938) (Also many other publications)

[19] C W Mason, and G E Pellissier, Jr , *Trans Am. Inst. Mining Met. Engrs., Inst Metals Div* , **133**, 280–93 (1939)

[20] G Tammann, *Z Metallkunde*, **24**, 154 (1932).

[21] In the book by Elam, "Distortion of Metal Crystals," p. 156, Oxford, 1935.

[22] Smits, *Proc Acad Amsterdam*, **15**, 676 (1912).

[23] R H Greaves, and J A Jones, *J. Inst. Metals*, **34**, 85 (1925).

[24] C E Homer, and H. Plummer, *J Inst. Metals*, **64**, 169–208 (1939).

[25] F. Sauerwald, *Z Metallkunde*, **16**, 315 (1924).

[26] Ludwik, *Z. phys Chem* , **91**, 232 (1916).

[27] Nishikawa, and Asahara, *Phys. Rev* , **15**, 38 (1920).

[28] A. J. Murphy, *J. Inst. Metals*, **35**, 107 (1926).

and "Chempur" tin, found no arrest in the heating or cooling curves for tin between 20 and 232° C. Electrical resistance-temperature curves over this temperature range also showed no inflections. Hanson and Pell-Walpole,[29] in agreement with the findings of Murphy, discovered no evidence of the allotropy of tin at elevated temperatures.

The most conclusive research concerning the alleged high-temperature allotropy of tin was conducted by Matuyama.[30] The following impurities were reported for the tin used: 0.01 per cent zinc, 0.008 per cent lead and a trace of cadmium. No breaks were found in the electrical resistance-temperature curve, the differential dilatation-temperature curve, the differential thermal analysis curve, and the thermoelectromotive force-temperature curve. Even more convincing evidence of the absence of any high-temperature allotropy of tin was provided by the identity of good x-ray powder patterns taken at room temperature and at 220 to 223° C Furthermore, x-ray patterns of a 4 per cent cadmium alloy (a small amount of cadmium is supposed by some to accelerate the transformation to gamma tin) taken at room temperature and at 152° to 163° C. were also identical

Homer and Plummer's[31] review of the evidence regarding gamma tin discussed in considerable detail much of the work mentioned above and showed how discontinuities in physical properties can well be due to impurities.

Mechanical Properties. Tin metal is soft. It can be readily cut with a knife, but when filed it chokes the teeth of the tool. On the von Moh scale it shows a hardness of 1.8 as compared to 1.5 for lead and 2.5 for gold The metal is slightly hardened by hammering

Pell-Walpole[32] found that in cold-rolled material an increase of 60 to 100 per cent in tensile strength is observed as the number of grains in the cross section increases from 1 to about 20 or 30. Elongations are constant over this range. A further reduction in grain size produces only a slight increase in tensile strength, but elongations increase rapidly. He found that the tensile strength increases continuously with the number of grains in small chill-cast ingots consisting entirely of columnar grains. The increase is 50 to 100 per cent for an increase in the number of grains from 2 to 60. He found that the calculated true stress varies continuously with grain size The variation of the hardness of tin with temperature is discussed under the manufacture of tin foil.

Tin is most ductile in the neighborhood of 100° C., and at about 200° C it can be pulverized in a mortar. Its tensile strength is low, being about 1 ton per square inch. When bars of tin are subjected to repeated bending, heating of the metal occurs as the result of friction of the crystals.

[29] W. T. Pell-Walpole, and D. Hanson, *J. Inst. Metals*, **56**, 165 (1935).
[30] Y. Matuyama, *Science Repts. Tôhoku Imp. Univ., First Ser.*, **20**, 649 (1931)
[31] C. E. Homer, and H. Plummer, *J Inst Metals*, **64**, 169–208 (1939).
[32] W. T Pell-Walpole, *J Inst Metals*, **69**, 131–46 (1943).

The most marked lines in the spark spectrum of tin, as shown in Fig. 2, are the orange yellow line 6453, the yellow line 5799, the yellowish green 5632β, the green lines 5589, 5563, and 5331, and the indigo blue line 4525α. The vapor of tin is not luminescent under the influence of cathode rays.

The electrical conductivity of tin is about one-seventh that of silver. The electrical resistance varies considerably with temperature. The values are plotted in Fig 3, in micro-ohms per centimeter cube. The resistance of tin decreases normally with falling temperature down to –269.2° C , or 3 8° K , when the resistance suddenly becomes immeasurably small and the metal becomes an excellent conductor Tin shows marked volume changes

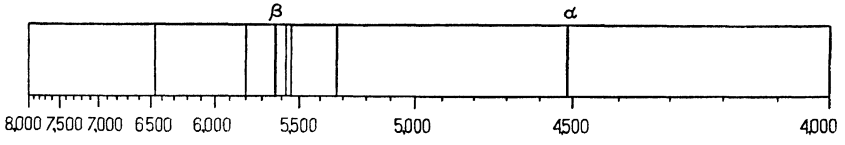

FIGURE 2 Spark spectrum of tin

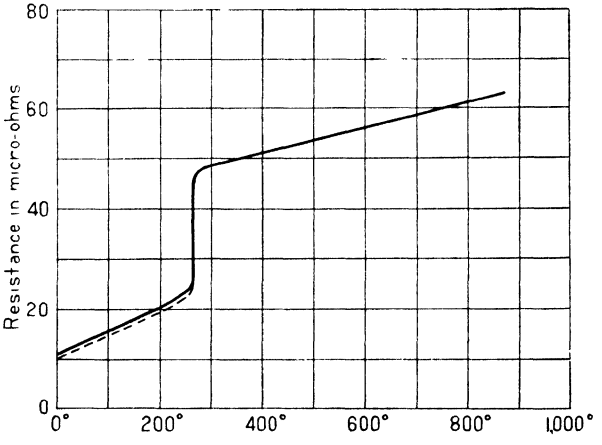

FIGURE 3 Electrical resistance of tin

during melting or freezing. The dilatometer readings of the volume change of tin during melting are plotted in Fig 4 Conversely, the specific volume of tin varies markedly with temperature, and the fluidity increases in an almost parallel line The change in volume in cc. per kilogram of weight with increase in temperature is plotted in Fig. 5. For those physical properties not specifically discussed, the reader is referred to Table 2 at the conclusion of this chapter.

Chemical Characteristics

Tin metal is not affected by hydrogen. Considerable work in the literature seems to indicate the possibility of the occurrence of tin hydrides,

but if they are formed they are very readily decomposed. The metal is but little affected by air at ordinary temperatures, even in the presence of moisture, but gradually acquires a superficial tarnish Tammann[33] estimated that to form the first visible layer of oxide coating on tin metal in dry air would take 36 x 10^8 years. Tin is readily oxidized by air at elevated temperatures, with the formation of its oxides When the metal is heated to near its boiling point, it burns in air with a pale, white flame. At ordinary temperatures it is appreciably affected by moist oxygen. In this chapter we will attempt to confine ourselves to the purely chemical

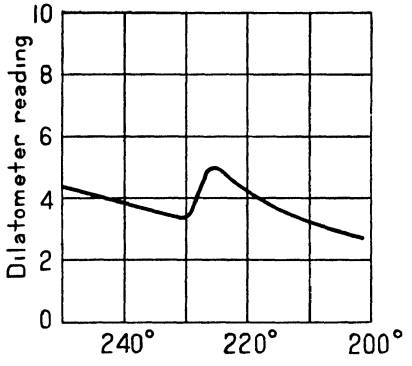

FIGURE 4
Volume change of tin during melting.

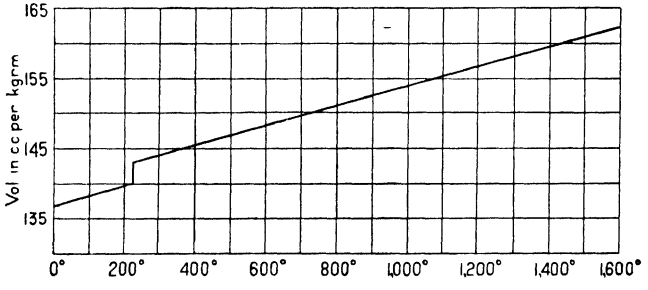

FIGURE 5 Specific volume of tin

reactions of tin and discuss its corrosion in more detail elsewhere The halides unite directly with tin, forming stannic salts Dry chlorine reacts with tin at room temperatures.

According to Baisch,[34] a chlorination curve of tin is shown in Fig. 6 and a volatilization curve of tin chloride is shown in Fig 7

Fluorine does not react with tin at low temperatures, but at 100° it forms stannic fluoride. Tin is feebly attacked by hydrofluoric acid, slowly dis-

[33] G Tammann, *Rec. Trav. Chim. Pays-Bas*, **42**, 547 (1923).

[34] Baisch, "Method for the Working up of Tin, Hard Slag and Liquation Dross," Thesis, Aachen, 1929.

solved by dilute hydrochloric and more rapidly by hot concentrated hydrochloric acid, with the formation of stannous chloride and the evolution

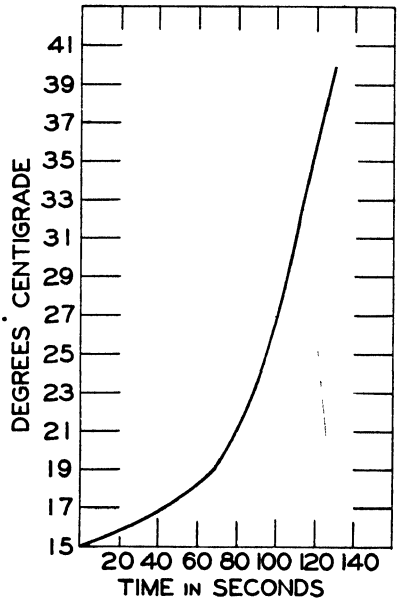

FIGURE 6
Chlorination curve of tin.

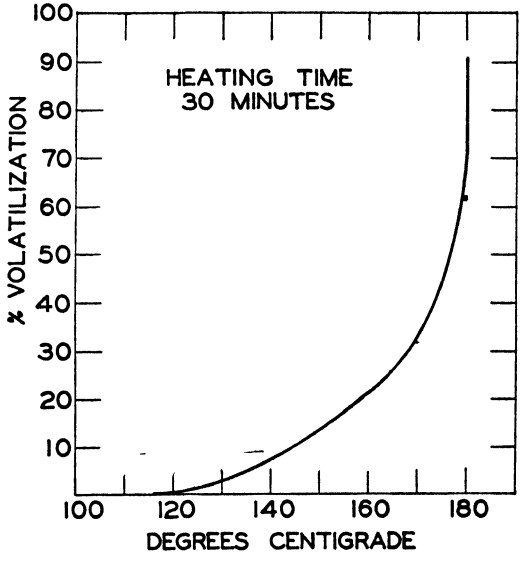

FIGURE 7
Volatilization curve of tin chloride.

of hydrogen. The reaction is accelerated by the presence of small amounts of platinic chloride, or when tin is in contact with copper, antimony, silver, lead, or platinum metal. Hot hydrobromic or hydriodic acid also readily

dissolves tin. Alkali hypochlorites react on tin, forming an oxychloride with the evolution of oxygen. Chloric acid dissolves tin without the evolution of hydrogen, but with the formation of stannic chloride.

Tin unites directly with sulfur when a mixture of the two elements is heated. Hydrogen sulfide does not ordinarily act readily on tin at ordinary temperatures, but at 100° to 400° it forms stannous sulfide. Over appreciable time periods, hydrogen sulfide tarnishes tin. Ammonium sulfide attacks tin more readily than does hydrogen sulfide When tin is fused with sodium sulfide, stannous sulfide is formed. Sulfuryl chloride and sulfur monochloride, S_2Cl_2, both attack tin. Sulfur dioxide reacts with the metal with the formation of stannous sulfide Dilute sulfuric acid does not readily react on tin in the cold, but the action is accelerated by the presence of oxygen. Calvert and Johnson[35] found that when the acid concentration is increased to a concentration corresponding to H_2SO_4 $6H_2O$, the attack is more evident The presence of chlorides in sulfuric acid markedly affects the solution of tin in that acid. A mixture of one volume of sulfuric acid, two volumes of nitric acid, and three volumes of water, according to Bassett,[36] dissolves tin in the cold, with the evolution of very nearly pure nitrous oxide and the production of a clear solution of stannic sulfate. Tin reacts vigorously with selenium and tellurium when a mixture of the two is heated.

Tin does not form a compound by direct union with nitrogen It is oxidized by hot nitric acid to hydrated stannic oxide or stannic acids, which see.

The soluble salts of tin are few. Those which are commercially important are the chlorides, acetates, sulfates, and oxalates. All of them show tendencies to hydrolyze. Tin in its compounds is amphoteric. This phase of its action is discussed in greater detail under the tin compounds.)

Physiological Action. The physiological action of tin has been the subject of widespread study. The number of authentic cases wherein tin and its salts have been poisonous is very low, being almost nonexistent The stannous salts are believed to be only very slightly toxic, but the stannic salts somewhat more so. The rarity of tin poisoning, contrasted with the extended use of the metal for cooking vessels and in tin cans for preserving food, shows that the attendant risks are small. There are no special pharmaceutical preparations of tin or its compounds, although sometimes tin has been recommended for tapeworm. Micheels and de Heen[37] remarked that a stimulating action on germinating wheat is effected by colloidal tin Gimel[38] found that one part of stannous chloride in 10,000 has a favorable effect on the alcoholic fermentation of yeast.

[35] Calvert, and Johnson, *J. Chem. Soc* , **19**, 435 (1866).
[36] Bassett, *Chem News*, **53**, 172 (1886)
[37] H Micheels, and P. de Heen, *Bull. Acad Belg* , 119 (1907).
[38] Gimel, *Compt. rend.*, **147**, 1324 (1908)

TABLE 2 PHYSICAL PROPERTIES OF TIN

			AUTHORITY
Abrasion*			
Copper		0 67	
Cadmium		1 10	
Magnesium		1 27	
Lead		1 27	
Tin		1 33	
Antimony		2 93	
Zinc		3 40	
Bismuth		14 73	Honda and Yamada (1)
Absorption Coefficient, for β-rays (M)		M/D = 9 46	Crowther (2)
Absorption Coefficient, for γ-rays (M), from			
Radium		M/D = 0 281	
Uranium		M/D = 0 341	
Thorium-D		M/D = 0 236	
Mesothorium		M/D = 0 305	Russell and Soddy (3)
Absorption of Hydrogen by Molten Tin			
at 400° C	0 440 cc	gas per 100 g	
553° C	0 575		
704° C	0 705		
798° C	0 935		
900° C	1 405		
1005° C	1 465		Iwasê (4)
Absorption Index†			
at 2570 Å		2 98	
3470 Å		2 20	
4250 Å		3 55	
4360 Å		3 44(liquid)	
4680 Å		4 44	
5020 Å		4 58	
5330 Å		4 41	
5460 Å		3 08(liquid)	
5880 Å		4 03	
5890 Å		3 55	
6300 Å		3 30	
6680 Å		3 53	International Critical Tables (5)

* The values given represent the coefficient of relative wear, based on the weight of metal removed by a cast-iron disk revolving in contact with it When the coefficient of friction = 0.3 and the friction work = $1\ 5 \times 10^{-4}$ h p , the weights (in grams) of metal removed per h p per minute are as shown

† The absorption index, k, is given by $J_x = J_0 e^{-4\pi nkx/\lambda}$ where J_0 and J_x are the intensities of parallel light at two planes within the substance, the planes being perpendicular to the direction of propagation of light and separated by the distance x, λ is the wave-length of incident light *in vacuo*, and n is the refractive index

TABLE 2. PHYSICAL PROPERTIES OF TIN (*Continued*)

		AUTHORITY
Atomic Entropy (cal. per deg., at 25° C)	11 17	Lewis, Gibson and Latimer (6)
Gray tin at 25° C.	9 23	Lewis, Gibson and Latimer (6)
Atomic Heat (g -cal per g -atom per °K.)		
White tin at		
10 °K	0 45	International Critical Tables (7)
20 °K	1 05	International Critical Tables (7)
22 4°K	1 27	Lange (11)
40 °K	2 97	International Critical Tables (7)
56 7°K	4 06	Lange (11)
60 °K	4 13	International Critical Tables (7)
79 8°K	4 64	Bronsted (8)
87 3°K	4 87	"
100 °K	5 38	International Critical Tables (7)
101.1°K	5 40	Lange (11)
188 °K	5 91	Schmitz (9)
194.9°K	6 20	Bronsted (8)
200 °K	6 20	International Critical Tables (7)
256 4°K	6 37	Bronsted (8)
273 °K	6 39	"
	6 4014	Jaeger and Bottema (10)
286 3°K	6.27	Lange (11)
288 1°K ..	6 49	Bronsted (8)
293 °K	6 4564	Jaeger and Bottema (10)
300 °K	6 44	International Critical Tables (7)
323 °K	6 5470	Jaeger and Bottema (10)
333 °K.	6 57	Schmitz (9)
373 °K	6 7195	Jaeger and Bottema (10)
423 °K.	6 9187	" "
463 °K.	7 0973	" "
473 °K.	7.1447	" "
505 °K	7.3033	" "
(extrapolated)		
Gray tin at		
10 °K.	0.36	International Critical Tables (7)
15.5°K. ..	0.599	Lange (11)
20 °K.. . ..	0.85	International Critical Tables (7)
31.5°K..... ...	1.675	Lange (11)

TABLE 2 PHYSICAL PROPERTIES OF TIN (*Continued*)

		AUTHORITY
40 °K.	2.13	International Critical Tables (7)
60 °K.	3 14	International Critical Tables (7)
79 8°K.	3 80	Bronsted (8)
87 3°K.	4 07	"
92 5°K.	4 42	Lange (11)
100 °K.	4 68	International Critical Tables (7)
194 9°K	5 66	Bronsted (8)
200 °K	5.83	International Critical Tables (7)
256 4°K	5 88	Bronsted (8)
273 °K.	5 90	"
283 7°K.	6 13	Lange (11)
288 1°K	5 91	Bronsted (8)
300 °K	6 18	International Critical Tables (7)
Atomic Heat of Fusion	1712 Cal	Richards (12)
Atomic Radius	1 40 Å	Pease (13)
Atomic Refraction	18 6–27 0	Gladstone (14)
Average Compressibility (β at 20°)	1 9 × 10^{-6} per megabar at 300 megabars pressure	Richards (15)
	1 89 × 10^{-6} at atmospheric pressure	Adams, Williamson and Johnston (16)
	1 64 × 10^{-6} at 10,000 megabars pressure	Adams, Williamson and Johnston (16)
Boiling Point (°C.)	2260	Smithsonian Physical Tables (17); International Critical Tables (18)
	2270	Greenwood (19); Mott (20); Ruff and Bergdahl (21)
	2440	Van Laar (22)
Bulk Modulus (at 18° C.)	5400 kg /mm ^{2}	Grüneisen (23)
Capillary Constant a^2 at 226° C.	17 87 sq. mm.	Siedentopf (24)
247° C.	15 74 sq. mm.	Hagemann (25)
346° C.	15.77 sq. mm.	"
398° C.	15.83 sq. mm.	"

TABLE 2. PHYSICAL PROPERTIES OF TIN (*Continued*)

		AUTHORITY
in air, at		
878° C	15 87 sq. mm	Drath and Sauerwald (26)
900° C.	15 86 sq mm	Drath and Sauerwald (26)
1000° C	15 74 sq mm	Drath and Sauerwald (26)
1050° C	15 69 sq mm	Drath and Sauerwald (26)
in hydrogen,		
3 9° C	15 45 sq mm	Hogness (27)
Change of Electrical Resistance in a Transverse Magnetic Field, (percentage increase)		
at 11,000 gauss field strength and 22° C	0 00304	International Critical Tables (7)
at 22,700 gauss and room temp	0 0093	Patterson (28)
at 20,300 gauss and room temp	0 0074	"
at 11,000 gauss and −253° C	1 13	Onnes and Hof (29)
at 300,000 gauss and temp liquid air	23	Kapitza (30)
at 300,000 gauss and room temp	2	"
Change of Specific Heat on Melting, (g-cal per g per °C)	0 00624	Wust, Meuthen, and Durrer (31)
	0 0047	Iitaka (32)
Compressibility, Cubical (in mm²/kg. × 10^6) at		
−190° C, pressure within elastic limit	210	Gruneisen (33)
15 2° C. and pressure within elastic limit	310	"
18° C. and pressure within elastic limit	190	"
20° C and 1 02–5 09 kg/mm² pressure	186	Richards (34)
20° C and atmospheric pressure	185	Adams, Williamson and Johnston (16)
20° C and 102 0 kg/mm.² pressure	161	Adams, Williamson and Johnston (16)
Compressibility, Linear (in mm²/kg × 10^6) at		
30° C, ⊥	60 22	Bridgman (35)
∥	67 19	"
75° C., ⊥	61 44	"
∥	69 56	"
Critical Pressure	650 atmospheres	Van Laar (22)
Critical Temperature	3730° C	Van Laar (22)
Crystal Structure		
White tin		
crystal system	tetragonal	International Critical Tables (18)
lattice constants	a = 5 824 Å	
	c = 3 165 Å	International Critical Tables (18)

TABLE 2. PHYSICAL PROPERTIES OF TIN (*Continued*)

		AUTHORITY
	a = 5 824 Å	
	c/a = 0 5415	Shinoda (36)
	a = 5 8194 Å	
	c = 3 1753 Å	Stanzel and Weerts (37)
Gray tin		
crystal system	cubic	International Critical Tables (18)
lattice constant	a = 6 46 Å	International Critical Tables (18)
molecules per unit cell	8	International Critical Tables (18)
calculated density	5 8	International Critical Tables (18)
Cubic Expansion		
Metal near melting point	$0\ 0_3114$	Vincentini and Omodei (38)
Liquid near melting point	$0\ 0_4689$	Vincentini and Omodei (38)
400–700° C , d_4 = 6 97	$0\ 0_6105$	Bornemann and Siebe (39)
232–396° C , d_4 = 7 01	$0\ 0_6106$	Hogness (27)
232–988° C , d_4 = 6 98	$0\ 0_6126$	Omodei (40)
232–1600° C , d_4 = 6 98	$0\ 0_6100$	Day, Sosman and Hostetter (41)
232–1600° C , d_4 = 6 99	$0\ 0_6114$	Vincentini and Omodei (42)
9–72° C	$0\ 0_47$	Kopp (43)
Diffusion Coefficient (k) per sq cm /day)		
Sn into Hg at 10 7° C.	1 53	Von Wogau (44)
Sn into Hg at 15° C	1 22	Guthrie (45)
Sn into Au at 500° C	4 65	Roberts-Austen (46)
Pb into Sn at 260° C	1 23	Merz and Brennecke (47)
Pb into Sn at 500° C.	3 18	Roberts-Austen (46)
Ag into Sn at 550° C.	4 14	" "
Zn into Sn at 310° C	3 11	Merz and Brennecke (47)
Effect of Pressure on Melting Point (rise per kg./cm.^{2})	0 0022° C	Tammann (48)
	0 003159° C.	Adams and Johnston (49)
Elastic limit	0 1 ton per sq. in	Coe (50)
Pressed and annealed	0 16 kg per mm^2	"
Elastic Limit for Critical Plasticity		
Annealed at 100° C.	0.08 kg. per mm^2	Coe (50)

TABLE 2 PHYSICAL PROPERTIES OF TIN (*Continued*)

		AUTHORITY
Elastic Modulus (kg. per sq. mm) .	4148	Wertheim (51)
	5407	Voigt (52)
Observed value	4170	Stuart (53)
Calculated value .	4130	"
Cast	1700	Hess (54)
Cast	5540	Gruneisen (23)
Rolled	4100	Hess (54)
Rolled	4768	Kiewiet (55)
Electrical Conductivity		
Ag = 100	14 01	Becquerel (56)
at −183° C	294,000 mhos	Dickson (57)
−78° C	114,000 mhos	"
0° C.	76,600 mhos	"
20° C.	86,900 mhos	International Critical Tables (18)
91 45° C. ..	54,800 mhos	Dickson (57)
176° C	42,300 mhos	"
Solid at melting point	44,900 mhos	Vassura (58)
Liquid at melting point	21,100 mhos	"
358° C.	19,800 mhos	Muller (59)
860° C.	15,400 mhos	"
Electrical Resistance (in micro-ohms per cu. cm)		
at −197 1° C.	3 399	Dewar and Fleming (60)
−81 9° C	8 788	" "
−44 2° C	10 667	" "
0° C	13 048	" "
20° C.	11 4	International Critical Tables (18)
225° C. ..	22 00	Northrup and Suydam (61)
m.p. (solid)	22 00	Northrup and Suydam (61)
m.p. (liquid) . .	47 4	Northrup and Suydam (61)
300° C.	49.44	Northrup and Suydam (61)
400° C..... . .	52 00	Northrup and Suydam (61)
500° C.....	54 62	Northrup and Suydam (61)
600° C...	57 22	Northrup and Suydam (61)
700° C.	59.88	Northrup and Suydam (61)
750° C...	61.22	Northrup and Suydam (61)

TABLE 2 PHYSICAL PROPERTIES OF TIN (*Continued*)

		AUTHORITY
Electrochemical Equivalents		Roush (62)
Stannous 2		
mg per coulomb	0 61503	
coulombs per mg	1 62595	
g per amp -hr	2 21409	
amp -hr per g	0 45165	
lb per 1000 amp -hr	4 88124	
amp -hr per lb	204 866	
Stannic 4		
mg per coulomb	0 30751	
coulombs per mg	3 25190	
g per amp -hr	1 10705	
amp -hr per g.	0 90330	
lb per 1000 amp -hr	2 44062	
amp -hr per lb	409 732	
Elongation, per cent		
Pressed and annealed	86	Coe (50)
Cast in metal mold	55 on 10 cm	Nightingale (63)
Emissivity		
Radiating capacity, tinned sheet iron, 50° C	0 04	
Tin, bright, 50° C	0 04	
Hall Effect ($R \times 10^6$) at field strength		
11 3,		
−270 3° C	9 8	Onnes and Hof (29)
−268 85° C	2 6	" "
4, room temp	−2	Hall (64)
5 0, room temp	−3 6	von Ettinghausen and Nernst (65)
10 5, room temp.	−4 1	Rathjen (66)
Hardness, on		
Von Moh scale	1 8	Rydberg (67)
Brinell scale,		
at 17° C	4 02	Sauerwald and Knehaus (68)
67° C	3 35	Sauerwald and Knehaus (68)
117° C	2 75	Sauerwald and Knehaus (68)
166° C	2 14	Sauerwald and Knehaus (68)
216° C	1 66	Sauerwald and Knehaus (68)
226° C	1 52	Sauerwald and Knehaus (68)
231° C	1.43	Sauerwald and Knehaus (68)

TABLE 2. PHYSICAL PROPERTIES OF TIN (*Continued*)

		AUTHORITY
cast	5 2	Coe (50)
annealed at 100° C	5 0	"
cast	4 0– 4.2	Rose (69)
rolled at −25° C	13 0	"
same after 30 min at −20° C	14 0	"
same after 30 min at 0° C.	13 0	"
same after 1½ hr at 14° C	10.0–10 5	"
same after 20 hr at 13° C.	6 5– 6 6	"
same after 24 hr at 15° C	4 5	"
rolled at 15° C	9 5–10.0	"
same after 97 days at room temp	4 5	"
same after 217 days at room temp.	4 2	"
heated to 50° C and quenched	8 6	Rose (69)
heated to 100° C and quenched	5 2	"
at 16° C	5 66	Ludwik (70)
63° C	3 87	"
125° C	2 25	"
163° C	1 46	"
229° C	0 64	"
purest standard cast tin	5 4	Gueterbock and Nicklin (71)
hammered, polished and annealed at 100° C , 10 hr 12 8–13 4° C	5 65	Hargreaves (72)
28° C	5 05	"
cast in metal mold	4 6	Nightingale (63)
Heat of Formation of Ions (g -cal per g -atom)		
Sn 2	2390	International Critical Tables (7)
Sn 4	−960	International Critical Tables (7)
Heat of Fusion	14 252 cal.	Person (73)
	6 67 kilo-joule per g -atom	Glaser (74)
		Awbery and Griffiths (75)
	14 6 g -cal per g.	Pionchon (76)
	14 05 g -cal per g	Robertson (77)
	14 3 g -cal. per g.	Guinchant (78)
	14 4 g -cal per g	Smithsonian Physical Tables (17)
Heat of Recrystallization		
For 50 per cent deformation.	6 5 cal.	Van Liempt (79)
For 100 per cent deformation	13 0 cal.	"
Heat of Transformation,		
White → gray tin	4.46 g.-cal. per g.	International Critical Tables
Beta → gamma tin	0.02 g.-cal. per g.	Werner (80)

TABLE 2 PHYSICAL PROPERTIES OF TIN (*Continued*)

		AUTHORITY
Heat of Vaporization	85 55 cal	Van Liempt (81)
Hydrogen Overpotential (volts) at c d (milliamp per cm ^{2})		
0	0.2411	Knobel, Caplan and Eiseman (82)
0 1	0 3995	Knobel, Caplan and Eiseman (82)
1	0 8561	Knobel, Caplan and Eiseman (82)
2	0 9469	Knobel, Caplan and Eiseman (82)
5	1 0258	Knobel, Caplan and Eiseman (82)
10	1 0767	Knobel, Caplan and Eiseman (82)
50	1 1851	Knobel, Caplan and Eiseman (82)
100	1.2230	Knobel, Caplan and Eiseman (82)
200	1.2342	Knobel, Caplan and Eiseman (82)
500	1 2380	Knobel, Caplan and Eiseman (82)
1000	1 2306	Knobel, Caplan and Eiseman (82)
1500 ..	1 2286	Knobel, Caplan and Eiseman (82)
	0 73	Centnerszwer and Straumanis (83)
Internal Pressures (megabars, or 10^6 dynes per sq cm)	68,700	Traube (84)
Ionic Susceptibility, Sn 4	−30 3	International Critical Tables
Izod Impact Strength (ft -lb) cast in metal mold	14 2	Nightingale (63)
Linear Expansion Coefficient, White tin		
−183° to 15 8° C	0 0.2257	Gruneisen (85)
−163° to 18° C (99 9% Sn)	0 0.16	Cohen and Olie (86)
0° to 100° C.	0 0.2296	Matthiessen (87)
8° to 95° C.	0 0.2033	Smithsonian Physical Tables (17)
10° to 90° C	0 0.209	Fizeau (88)

TABLE 2 PHYSICAL PROPERTIES OF TIN (*Continued*)

		AUTHORITY
18 7° to 100 4° C	0 0,2703	Gruneisen (85)
20° C.	0 0,214	Smithsonian Physical Tables (17)
20° to 232° C.	0 0,23 to 0 0,24	Cohen and Olie (86)
		Vincentini and Omodei (42)
Gray tin		
−163° to 18° C.	0 0,53	Cohen and Olie (86)
Single crystals,		
∥ 20° C.	0 0,305	Bridgman (35)
⊥ 20° C.	0 0,1545	"
∥ 34° to 194° C	0 0,458	Shinoda (36)
⊥ 34° to 194° C	0 0,257	"
Linear Velocity of Crystallization,		
cm per min	9	Czochralsky (89)
cm per min max value	200	Tammann and Rocha (90)
Maximum Load in Tension, annealed tin (tons)	1 31	Coe (50)
Melting Point (°C)	231 9	National Bureau of Standards, 1919
500 atm pressure	232 26	Adams and Johnston (91)
750 atm pressure	233 09	Adams and Johnston (91)
1000 atm. pressure	233 89	Adams and Johnston (91)
1490 atm. pressure	235 47	Adams and Johnston (91)
2000 atm pressure	237.18	Adams and Johnston (91)
Modulus of Rigidity (kg per mm ^{2})	1726	Voigt (52)
	1543	Kiewiet (55)
15° C.	1530	Horton (92)
15° C.	1350	Sutherland (93)
14° C.	1683	deHaas and Kinoshita (94)
17° C.	1765	deHaas and Kinoshita (94)
−194° C.	2315	deHaas and Kinoshita (94)
−200° C.	2418	deHaas and Kinoshita (94)
−270.34° C.	2455	deHaas and Kinoshita (94)
−270.76° C.	2561	deHaas and Kinoshita (94)

TABLE 2 PHYSICAL PROPERTIES OF TIN (*Continued*)

		AUTHORITY
Photoelectric Threshold	3620 Å	Richardson and Compton (95)
	3180 Å	Hamer (96)
Beta (tetragonal)	2740 ± 10 Å	Goetz (97)
Gamma (hexagonal)	2820 ± 10 Å	"
Liquid	2925 ± 10 Å	"
Plasticity (in C G S units)		
19° C , 0 197 kg /mm ^{2}	0 79 × 10^{-23}	Shoji and Mashiyama (98)
54° C., 0 130 "	2 15 × 10^{-23}	Shoji and Mashiyama (98)
70° C., 0 058 "	6 15 × 10^{-23}	Shoji and Mashiyama (98)
94° C., 0 055 "	8 32 × 10^{-23}	Shoji and Mashiyama (98)
Plasticity Number		
Copper = 49 3	3 5	Edwards and Herbert (99)
Plasticity, Critical (stress)		
Chill-cast and pressed,		
calculated on original section (kg /mm ^{2})	2 83	Coe (50)
calculated on enlarged section (kg /mm ^{2})	1 70	"
reduction in length at critical stress (%)	32 2	"
Annealed at 100° C ,		
calculated on original section (kg /mm ^{2})	3 31	"
calculated on enlarged section (kg /mm ^{2})	2 03	"
reduction in length at critical stress (%)	34 3	"
Poisson's Ratio	0 33	
Pressure Coefficient of Electrical Resistance,		
at 0° C	−0 0$_5$92	Beckmann (100)
at 0–12,000 kg /cm ^{2},		
0° C	0 0$_5$9204	Bridgman (101)
25° C.	0 0$_5$9280	"
50° C	0 0$_5$9357	"
75° C.	0 0$_5$9434	"
100° C.	0 0$_5$9510	"
Single crystals (resistivity) at 0° C.		
‖ to *c*-axis	0 0$_4$1096	Bridgman (35)
⊥ to *c*-axis	0 0$_4$1028	"
Pressure Coefficient of Linear Expansion,		
Extruded tin, $-d\alpha/\alpha dp$ =	1 92 × 10^{-5}	Bridgman (102)
Cast tin, $-d\alpha/\alpha dp$ =	1 19 × 10^{-5}	"
Reflecting Power (per cent)		
λ = 1.0μ .	. 54	
2.0μ.. .	61	
4.0μ ...	72	

TABLE 2 PHYSICAL PROPERTIES OF TIN (*Continued*)

		AUTHORITY
7 0μ	81	Coblentz (103)
10 0μ	84	
12 0μ	85	"
Reflectivity (per cent)		
Wave-length in Å		
1060	54 0	Coblentz (103)
1710	59 3	
2500	33	Coblentz and Stair (104)
3000	38	" "
3060	68 6	Coblentz (103)
3500	45	Coblentz and Stair (104)
3960	71 7	Coblentz (103)
4000	52	Coblentz and Stair (104)
4500	60	" "
5000	67	" "
5240	76 7	Coblentz (103)
5500	72	Coblentz and Stair (104)
6000	73	" "
6750	80 3	Coblentz (103)
8020	83 2	"
9380	87 0	"
10490	87.0	"
12030	86.9	"
Refraction Equivalent $(M\text{-}1)/D$	0 1686	Haagen (105)
Refractive Index		
for λ = 589 (sodium light)	1 48	Drude (106)
for wave-length in Å		
2570	1 12	International Critical Tables
2750	1 12	International Critical Tables
2980	1 04	International Critical Tables
3250	0 98	International Critical Tables
3470	1 01	International Critical Tables
3610	0 91	International Critical Tables
3980	0 68	International Critical Tables
4250	0 70	International Critical Tables
4360	1 18(liquid)	International Critical Tables
4470	0 72	International Critical Tables

TABLE 2. PHYSICAL PROPERTIES OF TIN (*Continued*)

		AUTHORITY
4680	0 70	International Critical Tables
4800	0 71	International Critical Tables
5020	0 78	International Critical Tables
5330	0 89	International Critical Tables
5460	1 73 (liquid)	International Critical Tables
5790	1 77 (liquid)	International Critical Tables
5880	1 12	International Critical Tables
5890	1 48	International Critical Tables
6200	1 25	International Critical Tables
6300	1 66	International Critical Tables
6680	1 42	International Critical Tables
Shear Strength		
Rate of loading 2 54 mm per min , chill cast	2 02 kg /mm ^{2}	Nightingale (63)
Shrinkage on Solidification (per cent)	2 8	Endo (107)
	2 7	International Critical Tables
Single Electrode Potential (volt)	<0 192	Wilsmore (108)
	0 146	Noyes and Toabe (109)
	0 1359	Prytz (110)
Specific Gravity		
White tin	7 3	Homer and Watkins (111)
at 1° C	7 285	Endo (112)
15° C	7 286	Cohen and Goldschmidt (113)
15° C	7 2984	
21° C	7 30	Wigand (114)
226° C	7 184	Smithsonian Physical Tables (17)
pressed for 3 weeks at 20,000 atm	7 292	Spring (115)
pressed for 6 weeks at 20,000 atm.	7 296	"
Gray tin ...	5 75	Homer and Watkins (111)

TABLE 2. PHYSICAL PROPERTIES OF TIN (*Continued*)

		AUTHORITY
at 1° C	5 765 ± 0 001	Endo (112)
18° C	5 751	Cohen and Olie (86)
−163 3° C	5 768	" "
Liquid tin		
at 232° C	6 98	Pascal and Jouniaux (116)
250° C	6 982	Day, Sosman and Hostetter (41)
263° C	6 961	Matuyama (117)
270° C	6 957	"
281° C	6 947	"
300° C	6 943	Day, Sosman and Hostetter (41)
318° C	6 918	Matuyama (117)
319° C	6 95	Hogness (27)
348° C	6 893	Matuyama (117)
362° C	6 99	Hogness (27)
379° C	6 869	Matuyama (117)
396° C	6 89	Hogness (27)
412° C	6 847	Matuyama (117)
442° C	6 825	"
466° C	6 805	"
496° C	6 785	"
500° C	6 814	Day, Sosman and Hostetter (41)
527° C	6 762	Matuyama (117)
550° C	6 745	"
577° C	6 730	"
700° C	6 695	Day, Sosman and Hostetter (41)
900° C	6 578	Day, Sosman and Hostetter (41)
1000° C	6 518	Day, Sosman and Hostetter (41)
1200° C	6 399	Day, Sosman and Hostetter (41)
1400° C	6 280	Day, Sosman and Hostetter (41)
1600° C	6 162	Day, Sosman and Hostetter (41)
t	7 01−0 00074 (*t*-232)	Hogness (27)
Specific Heat		
White tin	0 0514	Dulong and Petit (118)
at −223° C approx	0 0286	Dewar (119)
−203.5° C	0 0385	Smithsonian Physical Tables (17)
−193° C	0 0390	Bronsted (120)
−186 7° C	0 0422	Smithsonian Physical Tables (17)

TABLE 2. PHYSICAL PROPERTIES OF TIN (*Continued*)

		AUTHORITY
−150° C	0 0450	Smithsonian Physical Tables (17)
−100° C	0 0483	Smithsonian Physical Tables (17)
− 50° C	0 0512	Smithsonian Physical Tables (17)
−182 to 15° C	0 0499	Tilden (121)
0° C	0 05363	E H. Griffiths and E Griffiths (122)
0° C	0 0536	Smithsonian Physical Tables (17)
0 to 21° C	0 05417	Wigand (114)
0 to 100° C	0 055	Regnault (123)
15 to 180° C	0 0577	Tilden (121)
18 to 100° C	0 0556	Schubel (124)
18 to 200° C	0 0582	"
24 to 100° C	0 05453	Waterman (125)
25° C	0 0548	Smithsonian Physical Tables (17)
97 6° C	0 05690	Griffiths and Griffiths (122)
100° C	0 0577	Smithsonian Physical Tables (17)
t(0 to 100° C)	0 0534 + 0 0000348t	International Critical Tables (7)
t(0 to 200° C)	0 0525 + 0 000052t	Smithsonian Physical Tables (17)
Gray tin		
at −196 to −253° C	0 0286	Dewar (119)
−193° C	0 0319	Bronsted (120)
20 to −188° C	0 0502	Richards and Jackson (126)
0 to 18° C	0 05895	Wigand (114)
8 to 13° C	0 0493 ± 0 0002	Cohen and Dekker (127)
Molten tin	0 0637	Spring (128)
at 250 to 350° C	0 0637	Person (129)
1100° C	0 0758	Smithsonian Physical Tables (17)
Specific Refractory Power	19 89	Haagen (105)
Specific Susceptibility*		
White tin	+0 02 × 10^{-6}	Owen (130)
at 20° C	+0 027 × 10^{-6}	Honda (131)
221° C	+0 027 × 10^{-6}	"
236° C	+0 013 × 10^{-6}	"

* Magnetic susceptibility per unit volume, k, is the ratio of the intensity of magnetism of a substance to the intensity of the magnetizing field Specific susceptibility, or susceptibility per unit mass, λ, is equal to k/density

TABLE 2. PHYSICAL PROPERTIES OF TIN (*Continued*)

		AUTHORITY
240° C ..	$-0\ 023 \times 10^{-6}$	"
348° C.	$-0\ 036 \times 10^{-6}$	"
Gray tin	$-0\ 255 \times 10^{-6}$	Owen (130)
	$-0\ 35 \times 10^{-6}$	Honda (131)
Specific Volume		
White tin,		
at 20° C	0 1395	Hess (132)
Liquid tin,		
at 263° C	0.14365	Matuyama (117)
270° C.	0 14374	"
281° C.	0 14394	"
318° C.	0.14454	"
348° C.	0 14508	"
379° C.	0 14558	"
409° C. . . .	0.1462	Bornemann and Siebe (39)
412° C.	0 14605	Matuyama (117)
442° C.	0 14651	"
448° C	0 1468	Bornemann and Siebe (39)
466° C	0 14694	Matuyama (117)
474° C.	0 1486	Bornemann and Siebe (39)
496° C	0 14739	Matuyama (117)
523° C.	0 1479	Bornemann and Siebe (39)
527° C.	0 14788	Matuyama (117)
550° C	0 14827	"
574° C.	0 1486	Bornemann and Siebe (39)
577° C	0 14859	Matuyama (117)
602° C.	0 1490	Bornemann and Siebe (39)
648° C.	0 1499	Bornemann and Siebe (39)
675° C.	0 1501	Bornemann and Siebe (39)
704° C	0 1506	Bornemann and Siebe (39)
Stopping Power for α-Rays	3 37	Bragg (133)
Surface Tension,		
dynes per cm ,		
in vacuo, at		
melting point	580	Matuyama (134)
247° C.	539 8	Hagemann (25)
250° C.	575	Matuyama (134)
271° C.	538.0	Hagemann (25)
300° C.	566	Matuyama (134)
346° C.	534.8	Hagemann (25)

TABLE 2. PHYSICAL PROPERTIES OF TIN (*Continued*)

		AUTHORITY
350° C.	557	Matuyama (134)
350° C	524	Coffman and Parr (135)
398° C.	533 9	Hagemann (25)
400° C	545	Matuyama (134)
450° C	536	"
500° C	525	"
550° C	516	"
600° C	506	"
in air, at		
melting point	662	"
259° C	652	"
299° C	649	"
325° C	640	"
347° C	627	"
352° C	633	"
364° C	633	"
399° C	616	"
418° C	616	"
878° C	508	Drath and Sauerwald (26)
900° C	506	Drath and Sauerwald (26)
1000° C	497	Drath and Sauerwald (26)
1050° C	492	Drath and Sauerwald (26)
in hydrogen, at		
250° C	550	Bircumshaw (136)
300° C	544	"
300° C	526	Hogness (27)
350° C	522	"
400° C	537	Bircumshaw (136)
400° C	518	Hogness (27)
450° C	514	"
500° C	510	"
600° C	526	Bircumshaw (136)
800° C	510	"
964° C	514	Bircumshaw (137)
t	531-0 080(t-232)	Hogness (27)
in carbon monoxide, at		
750–910° C	480	Smith (138)
in hydrocarbon gas, at		
250° C.	532	White (139)
mgs per mm.	598 to 681 2	Quincke (140)
Temperature Coefficient of Electrical Resistance* (α)		

* The variation of electrical resistance with temperature is given by $R_{t'} = R_t(1 + \alpha(t' - t))$, where α is the temperature coefficient.

TABLE 2. PHYSICAL PROPERTIES OF TIN (*Continued*)

		AUTHORITY
at −100 to 0° C.	0 00509	Dewar and Fleming (141)
0 to 100° C.	0 00440	Dewar and Fleming (141)
18 to 100° C.	0 00465	Jager and Diesselhorst (142)
20° C.	0 0042	Bureau of Standards (143)
−80 to 230° C	0 004359	International Critica Tables
232 to 1000° C	0 000565	International Critical Tables
Single crystals at 0–100° C (resistivity),		
‖ to *c*-axis	0 00447	Bridgman (35)
⊥ to *c*-axis	0 00469	"
Temperature Coefficient of Thermal Conductivity† (α)		

† The variation of thermal conductivity with temperature is given by $k_t = k_0 (1 + 10^{-3}\alpha t + 10^{-6}\beta t^2)$ The values of the coefficient α are given

at −170 to −100° C	−1 54	International Critical Tables
−100 to 18° C	−1 0	International Critical Tables
0 to 100° C	−0 8	International Critical Tables
0 to 100° C	−0 69	Smithsonian Physical Tables (17)
0 to 232° C	−0 47	Brown (144), Konno (145)
232 to 500° C.	−0 66	Brown (144)
232 to 500° C	−0 20	Konno (145)
Temperature of Transformation.		
White → gray tin	18° C	Cohen (146)
Beta → gamma tin	203 3° C	Werigin, Levkojev and Tammann (147)
	170° C.	Cohen and Goldschmidt (148)
	202 8	Smits and deLeeuw (149)
	168	Werner (80)
Temperature of Transition	13.2° C.	Homer and Watkins (111)
Tensile Strength	1 ton per sq. in.	
Pressed and annealed (kg /mm.²)	2.06	Coe (50)
Pure standard cast tin (kg./mm.²)	1 89	Gueterbock and Nicklin (71)

TABLE 2. PHYSICAL PROPERTIES OF TIN (*Continued*)

				AUTHORITY
Cast in metal mold (kg./mm²)			1 48	Nightingale (63)
Rolled .			2 5	
Annealed			1.7	
Thermal Capacity (g.-cal per g) at				
0 to 232° C.	$0\ 0533t + 0\ 1375(0\ 01t)^2$			Schwarz (150)
232 to 600° C	$14\ 14 + 0\ 0572t$			"
Thermal Conductivity,				
Ag = 100 .	31 2			Despretz (151)
at −174° C.	0 195	abs	units	Lees (152)
−170° C.	0 195	"	"	"
−170° C.	0 19	"	"	Jakob (153)
0° C.	0 155	"	"	"
0° C.	0 1528	"	"	Lorenz (154)
0° C. (weighted mean of best determinations)	0 157	"	"	International Critical Tables (7)
15° C	0 1528	"	"	Kirchhoff and Hausemann (155)
18° C	0 153	"	"	Wiedemann (156)
25° C.	0 1575	"	"	O'Day (157)
27° C	0 157	"	"	Lees (152)
50° C.	0 1428	"	"	Brown (144)
100° C	0 1423	"	"	Lorenz (154)
102° C	0 1404	"	"	Brown (144)
108° C	0 151	"	"	Konno (158)
125° C	0 149	"	"	"
200° C	0 145	"	"	Jakob (153)
209° C	0 143	"	"	Konno (158)
209° C.	0 1297	"	"	Brown (144)
291° C.	0 0752	"	"	"
292° C.	0 081	"	"	Konno (158)
347° C.	0 767	"	"	Brown (144)
417° C.	0 079	"	"	Konno (158)
498° C.	0 078	"	"	"
Thermoelectric Effects, thermo-e.m.f (microvolts), one junction at 0° C., other at				
−203 8° C			−4.40	Dewar and Fleming (159)
−100 9° C			−2 60	Dewar and Fleming (159)
−64 2° C			−2.40	Dewar and Fleming (159)
−11.7° C			−0.80	Dewar and Fleming (159)
−2° C.			0.00	Dewar and Fleming (159)

TABLE 2. PHYSICAL PROPERTIES OF TIN (*Continued*)

		AUTHORITY
12 4° C.	0 50	Dewar and Fleming (159)
50 5° C.	3 40	Dewar and Fleming (159)
100 1° C.. .. .	5 70	Dewar and Fleming (159)
Torsion Modulus (g per sq cm.)		
Hammered tin,		
at 0 to 20° C.	109×10^6	Sutherland (93)
Pipe tin	157×10^6	"
at 15° C.	135×10^6	"
Trouton's Constant	34 34	Van Liempt (81)
Valency Attraction	$\sqrt{A} = 38$	Van Laar (160)
Vapor Pressure (mm)		
at 991° C .	$0\ 5 \times 10^{-4}$	Harteck (161)
1010° C	10^{-3}	Johnston (162)
1076° C	$2\ 1 \times 10^{-4}$	Harteck (161)
1127° C	$6\ 5 \times 10^{-4}$	"
1130° C	10^{-2}	Johnston (162)
1161° C	$8\ 5 \times 10^{-4}$	Harteck (161)
1270° C	10^{-1}	Johnston (162)
1440° C	1	"
1660° C	10	"
1850° C	50	"
1940° C.	100	"
1970° C.	99	Greenwood (163)
2005° C	126	Ruff and Mugdan (164)
2045° C	178	" "
2100° C.	266	Greenwood (163)
2160° C	372	Ruff and Mugdan (164)
2190° C	485	" "
2195° C	502	" "
2260° C	760	Johnston (162)
2270° C	760	Greenwood (163)
2270° C.	755	Ruff and Mugdan (164
1950 to 2270° C $\log_{10} p = 9\ 643 - 52\ 23 \times 328/T$		International Critical Tables
— $\log p = -14450T^{-1} + 7\ 85 + \log_{10} 4\ 6$		Hildebrand (165)
Velocity of Crystallization (mm per min)	90	Czochralsky (166)
Velocity of Sound Through Tin (meters per sec)	2640 4	Masson (167)
	2490	Gerosa (168)
	2643	Stierstadt (169)
Viscosity, n (poises)		
at 240° C	0 0191	Stott (170)
255° C.	0 0116	Arpi (171)
260° C	0.0182	Stott (170)

TABLE 2. PHYSICAL PROPERTIES OF TIN (*Continued*)

		AUTHORITY
280° C.	0 0174	Stott
280° C	0 01678	Pluss (172)
296° C	0 01664	"
300° C.	0 0167	Stott (170)
301° C	0 01680	Sauerwald and Topler (173)
308° C.	0 0108	Arpi (171)
320° C	0 01593	Sauerwald and Topler (173)
320° C.	0 0160	Stott (170)
340° C	0 0154	"
351° C	0 01518	Sauerwald and Topler (173)
357° C.	0 01421	Pluss (172)
360° C.	0 0103	Arpi (171)
360° C.	0 0148	Stott (170)
380° C.	0 0143	"
389° C.	0 01311	Pluss (172)
396° C.	0 0100	Arpi (171)
400° C.	0 0138	Stott (170)
420° C.	0 0133	"
440° C.	0 0129	"
449° C.	0 01257	Sauerwald and Topler (173)
450° C.	0 01270	Sauerwald and Topler (173)
454° C.	0 0094	Arpi (171)
460° C.	0 0125	Stott (170)
480° C.	0 0122	"
500° C.	0 0118	"
507° C.	0 0092	Arpi (171)
520° C	0 0115	Stott (170)
536° C	0 0090	Arpi (171)
540° C	0 01125	Stott (170)
560° C	0 0110	"
580° C	0 0107	"
600° C	0 0105	"
604° C	0 01045	Sauerwald and Topler (173)
606° C.	0 01041	Sauerwald and Topler (173)
620° C	0 01025	Stott (170)
640° C	0 01005	"
660° C	0 00985	"
680° C.	0 00965	"
700° C	0 00945	"
720° C.	0 0093	"
740° C.	0 00915	"
745° C.	0.00913	Sauerwald and Töpler (173)

TABLE 2 PHYSICAL PROPERTIES OF TIN (*Continued*)

		AUTHORITY
750° C	0.00905	Sauerwald and Topler (173)
760° C	0 0090	Stott (170)
780° C	0 00885	"
800° C	0 0087	"
Volume Change on Fusion and Solidification (per cent) at 232° C	2.7	Bornemann and Siebe (39); Endo (174), Topler (175)
Volume Susceptibility, White tin	$+0.364 \times 10^{-6}$	Wills (176)
	$+0\ 31 \times 10^{-6}$	Clifford (177)
X-ray Emission spectrum (characteristic), wave-lengths in 0 001 Å	4063.3	International Critical Tables
	3781 8	International Critical Tables
	3601 08	International Critical Tables
	3592 18	International Critical Tables
	3377 92	International Critical Tables
	3336 3	International Critical Tables
	3298 9	International Critical Tables
	3262 2	International Critical Tables
	3167 9	International Critical Tables
	3149	International Critical Tables
	3149 3	International Critical Tables
	3142 6	International Critical Tables
	3134 7	International Critical Tables
	3114 4	International Critical Tables
	3108 1	International Critical Tables
	3077 4	International Critical Tables
	2994 93	International Critical Tables

TABLE 2. PHYSICAL PROPERTIES OF TIN (*Continued*)

		AUTHORITY
	2972 3	International Critical Tables
	2968 5	International Critical Tables
	2827.3	International Critical Tables
	2771 3	International Critical Tables
	2769 3	International Critical Tables
	493 96	International Critical Tables
	489 48	International Critical Tables
	435 06	International Critical Tables
	434 40	International Critical Tables
	424 85	International Critical Tables
	424 3	International Critical Tables
Yield point (kg /mm ^{2})		
Pure standard cast tin	1 20	Gueterbock and Nicklin (71)
Chill cast tin	1 04	Gueterbock and Nicklin (71)

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Chapter 3

Production, Distribution, and Consumption

Tin Supplies of the World

Tin is one of the rarest of the base metals and at the same time one of the most indispensable Before World War II, the world's annual production of tin metal was 163,000 to 176,000 tons, of which the United States annually imported and consumed more than 50 per cent This tin metal was valued at well over $100,000,000 annually The production of tin in terms of tons of 2,240 pounds for the years 1925 to 1945 is given in Table 3 for mine production and in Table 4 for smelter production. These represent primary tin Secondary tin recovered in various forms amounts to approximately 32,000 gross tons per year in the United States America's primary tin production before World War II was negligible, while ore production was not of importance.

Several smelters were operated during World War I, but were driven out of the field by English competition, cheaper English labor, and more favorable freight rates

Figure 8 illustrates graphically the normal peacetime sources of tin in the various countries of the world during the period between World War I and World War II The illustration shows that Federated Malay States, Bolivia, and Indonesia (Netherlands East Indies) produced approximately three-quarters of the world's supply of tin In the Straits Settlements there were two principal smelters of tin, the Straits Trading Company and the Eastern Smelting Company. It was the habit of these smelters to sell daily against their intake of ores, either by disposing of the metal directly or by "hedging" it on the London Metal Exchange. Bolivian ores were largely shipped to England or the European Continent Banka tin is a product of Indonesia (Netherlands East Indies), the name originating from the island of Banka. Prior to World War I, it sold at bimonthly auctions (about 2,500 tons each auction) in Holland. From World War I up to the time of World War II it was disposed of by private tender in Batavia, Java. Billiton tin was largely, if not wholly, smelted in the Straits, and came out as Straits tin. As such it was sold presumably as produced, chiefly to London dealers or hedged on the London Metal Exchange. Some ores from Banka were also smelted in the Straits, as well as the ores from Siam, China, Australia, South Africa, Nigeria, and Bolivia. Except for

TABLE 3 World Mine Production of Tin*

(Long Tons)

Country	1925–29 Average	1939	1940	1941	1942	1943	1944	1945
Australia	2,830	3,067	3,501	3,494	2,931	2,635	2,540	2,500[a]
Belgian Congo	967	8,964	12,482	16,190	16,191	17,480	17,326	17,077
Bolivia[b]	37,169	27,211	37,940	42,199	38,293	40,312	38,720	42,487
Burma	2,228	8,536	5,500[a]	[c]	[c]	1,000[a]	500[a]	200[a]
China	7,085[b]	10,422[b]	6,249[b]	8,000[a]	7,000[a]	5,000[a]	3,000[a]	1,500[a]
Malay States								
Federated	54,606	49,525						
Unfederated	2,206	1,994	85,384	78,000[a]	15,000[a]	15,000[a]	10,000[a]	2,000[a]
Straits Settlements	25	206						
Netherlands Indies	33,266	27,755	43,193	51,000[a]	10,000[a]	15,133	6,069	843
Nigeria	8,319	9,427	12,012	15,000[a]	12,500[a]	12,654	12,500	11,500[a]
Portugal	625	1,486	1,721	2,330	2,670	3,460	1,800[a]	600[a]
Thailand (Siam)	8,204	17,325[b]	17,447	16,250[a]	12,000[a]	7,000[a]	5,000[a]	3,000[a]
Union of South Africa	1,174	482	518	463	508	526	506	500[a]
United Kingdom	2,658	1,633	1,620	1,509	1,363	1,359	1,289	993[a]
Other Countries	2,048	7,622	8,663	5,622	6,493	4,964	5,526	2,983
Total	163,000	176,000	236,000	240,000	125,000	127,000	105,000	87,000

* "Minerals Yearbook, 1945," Bureau of Mines, U S Dept of Interior, Washington, D C , 1947.

[a] Estimated

[b] Exports

[c] Estimate included in total

TABLE 4 WORLD SMELTER PRODUCTION OF TIN*

(Long Tons)

COUNTRY	1925–29 AVERAGE	1939	1940	1941	1942	1943	1944	1945
Argentina	—	1,080	881	768	709	552	500[a]	500[a]
Australia	2,952	3,294	3,544	3,656	3,024	2,565	2,442	2,400[a]
Belgian Congo	—	2,124	7,832	11,818	13,963	11,068	10,000	10,000[a]
Belgium[a]	720	3,100[b]	[c]	[c]	[c]	[c]	[c]	500[a]
British Malaya	88,855[d]	81,536[d]	126,945[b]	125,000[a]	10,000[a]	15,000[a]	5,000[a]	2,500[a]
Canada	—	—	—	29	553	347	231	379
China	7,080[e]	10,850	13,000[a]	10,000[a]	7,910[f]	4,349[f]	2,160[f]	1,000[a]
Germany[g]	3,444	7,000	3,000	3,000	4,000	5,000	4,000	[c]
Italy	—	146	330	72	228	[c]	[c]	[c]
Japan	606	2,000[a,b]	2,500[a]	[c]	4,000[a]	[c]	2,000[a]	1,000[a]
Mexico	[c]	90	116	150	320	395	286	160[a]
Netherlands	1,000[h]	14,600[a]	2,967	[c]	[c]	[c]	[c]	[c]
Netherlands Indies[e]	14,749	13,941	22,035	23,000[a]	8,000[a]	12,000[a]	3,000[a]	500[a]
Norway	[c]	283	206	98	48	23	27	[c]
Portugal	2[i]	30	781	1,481	2,381	3,058	373	182
Spain	—	138	112	86	99	121	515	590
Thailand (Siam)	113[j]	[c]	[c]	[c]	[c]	[c]	[c]	7,000[a]
Union of South Africa	—	—	33	143	535	862	1,150	1,000[a]
United Kingdom[a]	45,800	37,400	[c]	40,000	30,000	31,026	25,000[a]	28,000[a]
United States[k]	—	—	1,391	1,839	16,168	21,489	30,884	40,475
Total (estimate)	165,000	177,600	227,000	225,000	109,000	118,000	105,000	98,000[a]

* "Minerals Yearbook, 1945," Bureau of Mines, U S Dept. of Interior, Washington, D C , 1947

[a] Estimates

[b] Yearbook of American Bureau of Metal Statistics

[c] Data not available; estimate included in total

[d] Exports plus difference between carry-over at end and beginning of year

[e] Exports

[f] Unoccupied China

[g] Includes production of some secondary tin

[h] Estimated production in 1929

[i] Average for 1926–27

[j] Average for 1926–28

[k] Including tin content of ores used direct to make alloys

some refined tin marketed by China and Australia to the extent of some 10,000 to 15,000 tons per annum, the balance of the output from the last-named countries was shipped in the form of ores or concentrates to English, German, or other smaller Continental smelters Cornish production was all taken by British smelters. All the tin, as is the case with Straits, was sold concurrently against ore purchases or hedged on the London market Before 1930 the Penpoll smelting group of the Anglo Oriental Mining Corporation, the London Malayan Tin Trust, Limited, and the Tin Selection Trust, Limited, became a factor in the tin production of the world Their tin is marketed under the name of Penpoll

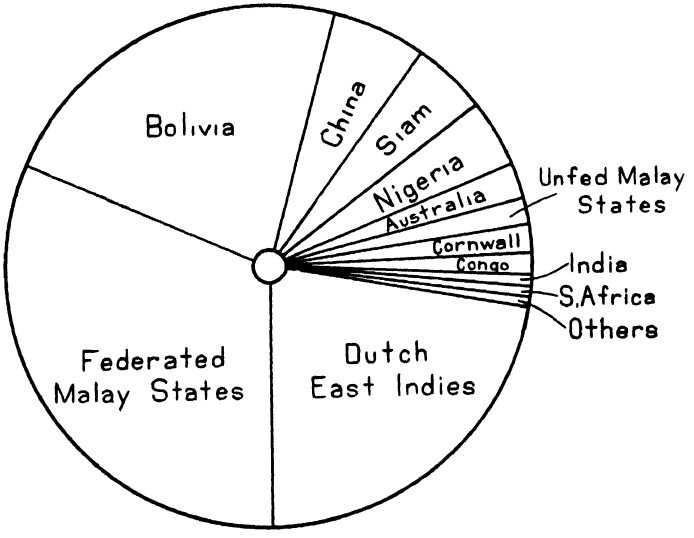


FIGURE 8 World's production of tin in 1927, apportioned by countries of origin

Brokers, dealers, merchants, and manufacturers all resorted to the same tactics as the smelting companies. This hedging practice caused a large volume of business on the London Metal Exchange As a result, there was a large business in options, of which the "put" and the "call" of tin, the buyers' option to double as well as the sellers' option to double greatly enlarged the turnover and insured a ready market within a reasonable price range, even when transactions were on a large scale for the disposal of tin on the London Metal Exchange. Prices in other countries, both consuming and producing, irrespective of the monetary unit in which they were quoted, were all based on the London price per ton in pounds sterling, converted at the current rate of exchange.

In the period of 1930 to 1940, various forms of international tin controls, buffer stocks, production quotas and agreements were in operation to

regulate the price of tin and prevent violent market fluctuations. During World War II, after the fall of Singapore, Malaya, Burma, and Indonesia (Netherlands Indies) into the hands of the Japanese, the Western World lost its major sources of ores and tin United States tin smelters were established, with dependence mostly on Bolivian ore. After World War II ended, political conditions in the Far East, as well as enemy damage to installations, made the return of production capacity slow and at times insecure. It also brought the United States smelters into world markets for tin ore to be smelted in the United States World War II brought governmental control of the tin ore purchases, the smelting and the allocation of metal as to its end use As a result of tin shortages, substitutes and replacement materials were developed, normal percentages of tin in many alloys were lowered to as great an extent as possible, other metals were substituted for tin, electrolytic tin plate with lower weight per base box became important, and recovery of tin from secondary sources was stimulated and intensified

Principal Uses

Before 1930, about 38 per cent of the tin consumed in the United States went into the manufacture of tin plate This contained 1 5 to 1 7 per cent of tin. America has often been termed the home of the tin can, where it is estimated that we consume and destroy a can per person per day throughout the year in our consumption of canned food products alone Before 1930 the value of tinware produced in the United States annually was more than $260,000,000, the production of some 240 plants

The United States has more automobiles than any other country in the world We consume an average of 7 5 pounds of tin per car produced

Before 1930 nearly 90 per cent of the American consumption went into four main channels: tin- and terne plate, solder, Babbitt, and brasses and bronzes. About 35,000 tons were used for tin- and terne plate Sixty per cent or more of this tin plate went into tin cans More than 28,000 tons entered into solder manufacture, an alloy of lead and tin, whose manifold uses are well known. More than 22,000 tons were used for Babbitt and machinery bearing metals, without proper bearing metals our modern machinery age would be seriously hampered Brass and bronze—particularly ornamental bronzes—high-strength and corrosion-resistant metals consumed 16,750 tons of tin per year Tin oxide (an important constituent of bathtub enamels and similar products, opaque glasses, ceramic glazes), tin chemicals, and other minor uses of the metal consumed nearly 15,400 tons of tin per year.

Since 1930, from 45 to 50 per cent of the virgin tin in the United States is consumed in the manufacture of tin- and terne plate

Table 5 gives the tin consumption of the United States by uses from 1928 on.

Since World War II, the major tin-consuming industries taking more than 90 per cent of the tin were the same as before 1930—namely, tin- and terne plate, solder, Babbitt, brasses and bronzes Because of the large amount of electrolytic tin plate with lower percentages of tin, the average percentage of tin in all tin plate is approximately two-thirds that of the 1930 period. Average tin contents of solder are much lower than before World War II

Collapsible tubes, which in the 1928 to 1940 period consumed of the order of 3,500 tons of tin per year, after World War II were taking about one-seventh of this amount This use is largely in tin-coated lead tubes, with a very little in pure tin tubes for special medical and pharmaceutical applications.

Tin chemicals and tin oxide were important consumers of tin, but competitive materials for ceramic applications, opacifiers in enameled metalware which were satisfactory and cheaper, as well as the loss of the tin chlorides markets with the disappearance of silk and the competition of nylon, have brought the consumption after World War II to less than one-tenth of the 1928 figure.

Type metal as a consumer of tin is largely of the secondary metal variety, requiring virgin metal only to the extent of making up losses and metal not recovered from drosses, ashes, and slags

Virgin tin is required for tinning and retinning of articles such as milk cans, dairy equipment and food processing equipment. Being an essential use, the tin demands have been steady over a twenty-five year period, of the order of 2,500 to 3,000 tons per year.

Military and naval demands during World War II caused a sharp increase in the amount of tin for bronzes and brasses.

Seemingly every year more tin is consumed than the total amount imported plus that which is recovered from secondary sources. The difference between this figure and the consumption is apparently accounted for by drafts on stocks.

A part of this unaccounted-for metal may be attributed to the short service rendered by the finished article and the rapidity with which it finds itself in the melting pot. Thus, metal may be reused several times during the year. The accumulated free stocks of tin are never high.

Babbitt and bearing metals, brasses and bronzes, castings, white metal, and type metal are the only applications for tin serving a short period that allow the metal to be reused, but even these cause considerable losses. The metals used in tin- and terne plate, foil, collapsible tubes, chemicals, and similar uses are dissipated largely for all time.

TABLE 5 CONSUMPTION OF TIN IN THE UNITED STATES

Consumption of primary and secondary tin by products (tin content). Reported by U S Bureau of Mines, in gross tons

	1928	1930	1936		1937		1938		1939		1940	
			Primary	Secondary	Primary	Secondary	Primary	Secondary	Primary	Secondary	Primary	Secondary
Tin plate	27,053	27,753	33,750	—	39,221	—	23,545	—	36,640	—	38,764	—
Terne plate			369	943	382	1,015	264	743	317	1,137	455	1,058
Solder	13,874	11,407	12,068	6,682	12,026	7,832	7,590	5,208	9,578	7,701	10,222	8,797
Babbitt	8,150	5,438	5,070	1,609	4,501	2,272	2,893	1,264	3,850	1,598	4,473	3,173
Bronze	4,324	3,499	3,559	2,631	3,712	2,784	2,334	1,598	3,385	3,051	5,444	9,216
Collapsible tubes	2,864	3,826	3,556	—	3,571	†	3,427	—	3,507	†	3,512	†
Tinning	2,636	2,814	2,377	13	2,585	67	1,738	35	2,165	172	2,455	265
Foil	5,068	3,061	1,645	43	1,456	4	2,283	†	2,001	†	1,713	—
Chemicals*	4,246	3,268	209	1,346	171	1,331	166	910	167	288	52	330
Pipe and tubing	†	†	1,401	82	1,278	18	948	†	606	†	661	†
Tin oxide	1,183	666	969	361	793	411	547	444	651	359	651	506
Type metal	411	223	253	919	221	1,140	134	978	149	990	84	1,048
Galvanizing	†	†	1,016	—	997	†	792	—	1,028	—	963	—
Bar tin	730	74	656	84	652	174	456	213	1,100	241	1,000	91
Miscellaneous alloys	629	306	418	62	482	24	938	19	404	45	353	11
White metal	802	1,117	358	9	374	33	390	44	466	42	953	83
Miscellaneous	2,399	1,996	558	34	506	97	371	202	569	221	659	252
	74,369	65,448	68,232	14,818	72,928	17,202	48,116	11,658	66,583	15,845	72,324	24,830
Total	74,369	65,448	83,050		90,130		59,774		82,428		97,154	

* Other than tin oxide

† Included in miscellaneous

TABLE 5. CONSUMPTION OF TIN IN THE UNITED STATES (*Continued*)

	1941		1942		1943		1944		1945		1946‡
	Primary	Secondary	Primary	Secondary	Primary	Secondary	Primary	Secondary	Primary	Secondary	
Tin plate	44,854	—	28,522	—	21,684	42	24,968	—	26,080	—	27,051
Terne plate	917	1,129	339	543	100	334	510	230	493	248	
Solder	18,084	10,141	7,228	6,696	5,292	7,384	8,786	4,841	10,930	3,399	17,255
Babbitt	7,495	3,104	3,195	2,904	3,217	4,536	5,790	2,996	4,144	3,684	6,833
Bronze	10,067	13,103	10,646	17,009	11,180	18,575	13,768	19,327	9,093	17,972	22,305
Collapsible tubes	4,233	212	1,048	51	282	309	283	242	515	44	898
Tinning	3,987	145	2,764	251	2,690	324	2,771	370	2,390	202	2,230
Foil	4,292	—	576	—	227	145	226	92	181	64	238
Chemicals*	280	690	36	210	112	299	34	259	196	448	118
Pipe & tubing	1,325	†	143	18	82	118	230	32	204	89	324
Tin oxide	995	495	84	47	—	—	—	—	—	—	—
Type metal	287	1,528	40	1,113	28	1,053	49	1,302	10	1,281	1,378
Galvanizing	863	104	82	—	4	—	—	—	—	—	—
Bar tin	1,526	607	601	121	685	276	1,092	167	963	131	†
Misc alloys	480	137	558	256	360	566	417	707	378	228	†
White metal	2,463	98	83	156	90	55	19	86	65	151	†
Miscellaneous	938	116	343	24	220	61	213	162	—	—	1,756
	103,086	31,609	56,288	29,399	46,253	34,077	59,156	30,813	55,642	27,941	80,386
Total	134,695		85,687		80,330		89,969		83,583		80,386

* Other than tin oxide.

† Included in miscellaneous.

‡ Estimate of both primary and secondary.

Tin-plate scrap from container manufacturers is the raw material for the detinning companies producing tin chlorides, which was formerly their major product, stannates, tin oxides, tin chemicals and metal. The chlorides were used for the "weighting" of silk and in textile printing and dyeing, but with the departure of silk from the market during World War II, much of the tin chloride market also disappeared. The use of stannates in tin electroplating provided a market for this product of detinning There is considerable recovery of solder from "sweating" old or junked automobile radiators, as well as recovery of tin-containing bearing metals from scrapped machinery.

Census reports state that fire extinguishers and sprinkler systems consume 5,000 tons of tin per year in peacetime, and refrigerators some 2,500 tons of virgin tin in the form of solder.

Aluminum foil in many industries has successfully replaced tin foil for wrapping various products This replacement has caused a decreased consumption from 5,000 tons per year in 1928 to only essential uses of one-tenth as much in the World War II years

Price

Tin has been the medium of a vast amount of speculation, particularly on the London Metal Exchange. The price of tin for 165 years is plotted in Fig. 9, in British pounds sterling per long ton War conditions have noticeably affected the price, causing it to fluctuate markedly

Secondary Tin. In the United States there is an appreciable and important secondary metal business This is the outgrowth of what was originally a group of operations concerned with the handling of junk, but which, under better technical control, is converting scrap metals into materials of qualities almost equal to that of the virgin materials and constantly endeavoring to reclaim for reuse metals and products which have outlived their usefulness in their original form. Figure 10, giving the production of secondary tin in the United States, shows the influence of the secondary metal business on the tin production, or rather, the business of preparing tin metal to add to the available supply, the source of the metal being not ores but old metals, drosses, ashes, and tin-containing residues. The curve shows a steady upward trend with the exception of the period from 1920 to 1922, which was one of marked industrial depression following the overproduction resulting from World War I.

As a consequence of the secondary metal development, there is a market for scrap tin, either as elemental tin metal or in alloys, drosses, ashes, or any other combined form. Scrap tin prices, as shown in Fig. 11, more or less follow the prices of the virgin metal but are lower by the amount or necessary cost incidental to recovery of the tin metal from the form in which it is bought by the secondary metal dealer.

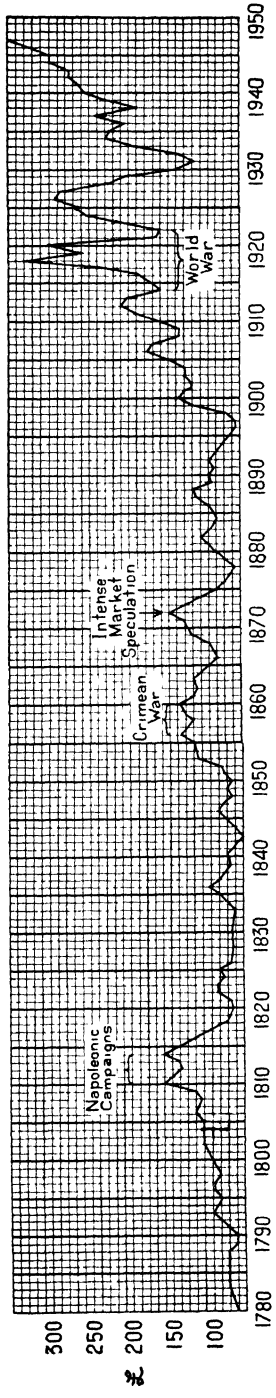


FIGURE 9 Graph showing average prices of tin metal per ton (2,240 lbs.) for the years 1780–1947

Future of Tin. One other aspect of the tin situation is a continual emphasis placed upon the belief that the known tin resources of the world are comparatively limited. The public is constantly being reminded that a tin famine is sure to arrive in the none too distant future. This undoubtedly has a sentimental bullish effect on the market. However, the officials of the largest tin-consuming companies in the United States have no misgivings as to the future adequacy of the supply either of tin or of any of the other metals. Whatever the needs may be, they will be met

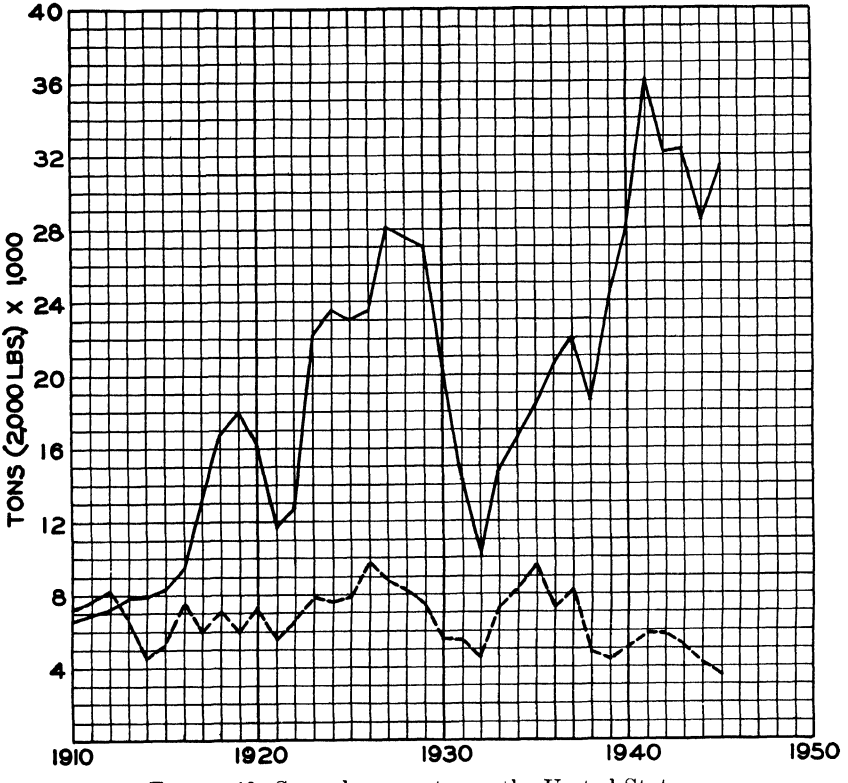


FIGURE 10 Secondary pig tin in the United States
(—— *recovered in alloys*, - - - - *secondary pig tin*)

Even if these predictions were acceptable, it must be pointed out that they are based upon present knowledge of the technique of mining and smelting. South America and other countries of the world, not yet fully explored, possess millions of tons of low-grade tin ore which thus far have no commercial value. Sooner or later developments in technical knowledge will make them workable and their treatment commercially necessary and profitable. Cornwall, England, whose mines were thought almost entirely worked out, passed through a revival stage as a result of high tin

prices and the discovery of new valuable lodes at lower levels through the sinking of deeper shafts.

In Yunnan, China, the forests surrounding the tin smelters have disappeared as a result of charcoal manufacture. Charcoal is used there as a smelting fuel. Ore-dressing methods can be greatly improved throughout all of China.

Since 1930 the technical branch of tin mining in Bolivia has been intensively studied. Mines improved the recoveries of the tin value of their ores. The Bolivian government interests itself in bettering tin mining prac-

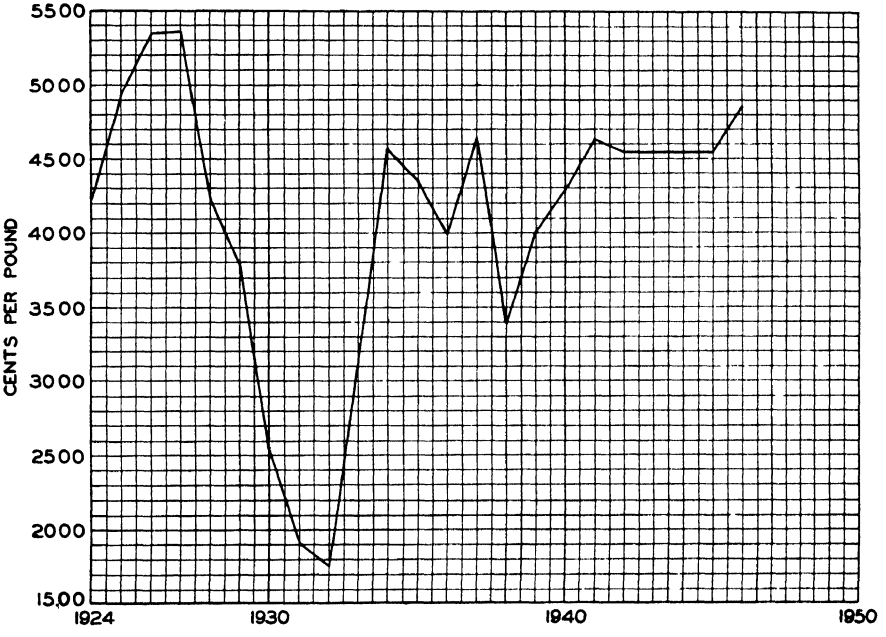


FIGURE 11 Scrap tin prices.

tice, as export duties on tin concentrates bring a large proportion of the governmental revenue.

When attempts are made to create a tin shortage artificially, there is always a great impetus toward the development and use of substitutes. Experience shows that consumers will adopt almost any kind of expedient to retain their independence. World War II emphasized not only lower tin-content tin plate, but also the "tinless" can for packaged products, which year by year will be of greater importance, a tin shortage would bring it into prominence with great speed.

Antimony oxide can be and is used to replace part or all of the tin oxide used for enamels. Aluminum foil has made serious inroads on its tin com-

TABLE 6 TYPICAL TIN ANALYSES

	Sn	Sb	As	Pb	Bi	Cu	Fe	Ag	S	Co	Ni + Co	OTHER ELEMENTS
American Electrolytic	99 928	0 002	0 002	nil	0 042	0 026	trace					
Banka	99 983	0 0101	trace	0 0001	—	—	0 0064					
Banka	99 950	0 007	nil	trace	nil	0 018	0 045	nil	trace			
Billiton	99 960	0 006	nil	nil	nil	0 023	nil	nil	nil			
Billiton	99 934	0 018	0 018	0 019	0 001	0 003	0 007					
Billiton	99 93	0 031	0 004	0 025	nil	0 003	0 007					
Capper Pass												
Chempur	99 9918	0 0031	0 0001	0 0025	0 0004	0 0004	0 0016	nil	0 0002	nil		
No 1	99 9895	0 0055	0 001	0 0008	0 0001	0 0005	0 0025	—	0 00025			
Cornish												
Refined	99 880	0 012	0 006	0 014	trace	0 046	0 003	—	0 017	—		
Refined	99 820	0 022	0 030	0 065	0 010	0 034	0 005	—	—	—	0 014	
Lamb & Flag	99 321	0 174	0 034	0 068	trace	0 205	0 040	—	0 044			
Lamb & Flag Common	99 180	0 139	0 080	0 440	0 020	0 118	0 008	—	—		0 015	
Dutch Lamb & Flag (99 5%)	99 530	0 185	0 079	0 152	0 007	0 038	0 009					
Dutch Lamb & Flag	99 05	0 526	0 075	0 280	0 005	0 055	0 009					
Eastern Smelting Co	99 907	0 003	0 035	0 024	0 009	0 003	0 008		0 008		0 003	
German Lamb & Flag	99 080	0 150	0 080	0 500	0 060	0 080	0 050					
Th Goldschmidt												
No. 1	99 860	0 004	nil	0 102	nil	0 043	trace	nil	trace	—		
No 2	99 460	0 015	nil	0 425	nil	0 069	trace	nil	trace	—		
No 3	99 150	0 122	0 046	0 143	0 112	0 352	0 007	0 006	trace	—		
Hawthorne Refined	99 891	0 010	0 029	0 028	0 004	0 028	0 010	—	—	trace		
Hawthorne	99 8600	0 0153	0 0228	0 0368	0 0097	0 0276	0 0178	trace	—	0 0015		Zn trace; Ni 0 0020; Mn trace
Irvine Bank	99 580	0 062	0 034	0 221	0 025	0 126	0 002	0 018	0 004			
O. T Lempriere & Co.	99 880	0 011	0 016	0 019	0 012	0 026	0 020	nil	trace	0 008		
Longhorn 3 Star	99 880	0 037	0 020	0 020	0 004	0 025	0 004	0 0005	0 005		0 005	Cd trace

Mellanear												
99 9%	99 915	0 013	0 008	0 037	0 007	0 009	0 004	—	—	—	0 007	
Refined	99 827	0 028	0 025	0 065	0 013	0 022	0 005	0 002	—	—	0 013	
Lamb & Flag	99 190	0 160	0 060	0 160	0 350	0 060	0 020	—	—	—		
Metal & Thermit Refined	99 978	0 006	trace	0 0055	0 0005	0 0009	0 009	nil	nil	nil	nil	Cd nil
Metal & Thermit Electrolytic	99 971	0 005	trace	0 012	included with Pb	0 001	0 011					
Mt. Bischoff	99 847	0 015	0 015	0 042	0 001	0 017	0 063					
Mt. Bischoff	99 795	0 015	0 063	0 037	0 005	0 035	0 042	trace	0 008			
Murex Refined	99 895	0 020	0 023	0 036	0 006	0 012	0 008	—	trace	—	—	Zn trace
Penang	99 939	trace	0 013	trace	nil	0 016	0 028	nil	0 004			
Penang (E S Coy)	99 904	0 002	0 035	0 028	0 008	0 008	0 008	nil	0 005	—	0 002	Cd nil
Penpoll												
Special Refined	99 9309	0 019	trace	0 0256	0 0015	0 0102	0 0087	trace	—	0 0041		
Refined	99 800	0 118	0 054	0 041	0 007	0 052	0 004	0 009	0 007			
No 1	99 720	0 118	0 054	0 041	0 007	0 052	0 004	0 009	0 007			
No 2	98 710	0 569	0 042	0 546	0 055	0 103	0 007	0 015	0 004			
No 3	99 300	0 325	0 056	0 212	0 050	0 088	0 002	0 021	0 009			
Lamb & Flag Common	99 158	0 190	0 078	0 386	0 019	0 129	0 006	0 012	—	—	0 017	Cd 0 005
P.K M A	99 89	0 01	0 02	0 05	0 015	0 005	0 003	0 0005	nil		0 001	Cd nil
Redruth	99 160	0 176	0 053	0 177	0 017	0 0445	0 041	0 006	0 008	0 012		
Rodonko No. 1	99 265	0 10	0 04	0 50	0 20	0 15	0 015					
Rodonko No 2	97 638	—	0 135	1 810	0 145	0 185	0 052				0 034	
Singapore	99 870	0 008	0 045	0 034	0 003	0 052	0 003	0 006	0 005			
Straits Trading Co	99 895	0 004	0 031	0 029	0 007	0 025	0 009	—	—	—	trace	
Sutton, T. & Sons	99 550	trace	0 022	0 342	0 015	0 045	0 010	trace	nil	trace		
Tulip	99 871	0 046	0 028	0 028	0 003	0 015	0 009					
Tulip	99 870	0 073	0 011	0 029	0 001	0 008	0 008					
Union Minière du Haut Katanga	99 966	—	0 006	0 012	trace	0 013	0 003					
U.S Specification S-14 (Grade A)	99 80*	0 04†	0 05†	0 05†	0 015†	0 04†	0 015†	0 001†	0 01†		0 01†	Cd 0.001†

TABLE 6. TYPICAL TIN ANALYSES (*Continued*)

	Sn	Sb	As	Pb	Bi	Cu	Fe	Ag	S	Co	Ni + Co	OTHER ELEMENTS
Vulcan												
Electrolytic	99 9958	0 0008	—	trace	—	0 0004	0 003					
American Refined	99 9907	0 0012	trace	0 0021	0 0002	0 0009	0 0048	0 0001				
3-Star	99 890	0 029	0 014	0 038	0 003	0 019	0 002	trace	0 003		0 002	Cd nil
Williams, Harvey & Co												
No 1	99 860	0 015	0 040	0 004	0 005	0 047	0 003	nil	0 006			
No 2	99 560	0 166	0 037	0 162	0 007	0 050	0 005	trace	0 013			
No 2-a	99 350	0 245	0 065	0 223	0 015	0 042	0 016	trace	0 013			
No 3	99 200	0 300	0 037	0 396	0 007	0 100	0 013	0 014	0 006			
No 4	99 941	0 011	0 022	trace	0 001	0 020	trace	trace	0 005			
Wing, Hong & Co												
No 1	99 343	0 031	0 040	0 434	0 007	0 052	0 010	trace	0 011		0 072	
No 2	98 662	0 039	0 035	1 035	0 012	0 134	0 014	trace	0 011	0 058		
No 3	95 280	0 381	0 050	3 995	0 020	0 106	0 026	0 018	0 008	0 116		
Yunnan Tin Corp , Refined	99 870	trace	0 056	0 044	0 0056	0 010	0 014	0 0004				
Yunnan Tin Corp	99 17	0 01	0 04	0 61	0 03	0 13	0 003	0 0009	nil	nil		Ni 0 001; Mn nil

* Minimum

† Maximum.

petitor, almost completely capturing this market. With manufacturing costs reduced, aluminum collapsible tubes followed the same trend.

The United States, the largest consumer of tin, seemingly does not face a "hold up" by foreign producers of this important commodity. When it appears that consumption might equal or exceed production, new technical methods, plant modernization, utilization of lower-grade ores, and better mining methods will make available greater supplies of this "semi-precious" metal

Parsons[1] points out how low the price of tin can go without squeezing income to the point at which it is deemed more profitable to shut down dredges or curtail production than to produce at normal maximum capacity Over a long period the earnings of many of the tin companies are not unusual when they reach 50 per cent per annum, and dividends have ranged from 15 to 75 per cent per year Before the interruptions of World War II there was a trend in the Indonesian (Netherlands East Indies) mines to install larger and better gravel pumps. In Bolivia, mining and ore-treatment operations have been reorganized. In Nigeria, and particularly in Malaya, bigger and better dredges equipped with efficient classifying and jigging machinery were put into productive operation, some displacing older and less efficient dredges and others starting operations on deposits where dredges have never been used Now, after World War II and the return of peacetime stabilization and removal of political disturbances, tin should follow the sequence analogous to the well-known progress in the mining, milling, smelting, and producing of other nonferrous metals.

Propaganda of long ago that tin production could not be greatly increased is exploded, for it has increased and there has been much progress in the technique. The working of alluvial deposits has been extended to leaner gravels, for with the improved dredging equipment and the use of gravel pumps, facilitated by operations passing into strong hands with command of capital, a half pound of tin per cubic yard is workable against one and a half pounds formerly.

The marginal producers whose costs are above the average, such as the operations of the Chinese who, according to the best estimates, contribute about 45 per cent of the Malayan production by hand mining, are discussed by Parsons:

"It is argued in some quarters that lower prices will cause a decided shrinkage in output from this source On the other hand, consider the following view of the situation The miners are there on the ground, their position is like that of a farmer with a single money crop They are not particularly concerned with conserving the world's supply of tin nor with the depleting of their own ore reserve They are sure of a market at some price for all the concentrate they can produce, if they work harder than they have been working they can produce more tin, thereby

[1] A. B. Parsons, *Eng. Mining J.*, **125**, 685 (1928).

offsetting the effects of lower prices and still maintain their income. Perhaps the cost of production is high, but labor is the one big item in the cost, and if no other means of earning a living is at hand, the average Chinese is likely to dig tin for whatever he can get. Incidentally, there has been a trend toward the purchase of large modern gravel pumps among the Chinese, so that it is probable that many of them can produce more cheaply than ever before. To conclude that a decline in the price, say to forty cents, would seriously affect Chinese production appears to be unwarranted."

Marketing

Marketwise, tin is by far the most mysterious of the familiar metals. It is notable that those most fully posted frankly state that virtually they know almost nothing about it. It is impossible to measure closely the influence of price upon production, but the influence upon consumption is a more open matter.

Qualities of Commercial Tin. Two important classes of tin are commodities in the United States. These are commonly known, according to the specifications of both the London and the New York Metal Exchanges, as standard or Straits tin, and 99 per cent tin. On contracts calling for standard tin, Straits, Australian, Banka, Billiton, American Electrolytic, and English Refined tin were deliverable at contract prices. Other virgin refined tins also fell into this class, provided they assayed not less than 99.75 per cent tin. On contracts calling for 99 per cent tin, any brand of tin assaying not less than 99 per cent of the metal and approved by the Exchange was good delivery.

Tins are sold by brands which are either indicative of the origin of the ore from which the tin was smelted or else are indicative of the smelter, carrying his name or trademark The tins from alluvial ores when made by straight pyrometallurgical methods are purer, while those from vein ores are generally poorer Table 6 gives tin analyses of a large number of brands on the market.

The selling and buying of tin metal are regulated by contracts of the various exchanges. These contracts are very specific as to general conditions, deliveries, and methods of making shipment. Ordinarily, no delivery of less than five tons is valid.

Chapter 4

Ores and Ore Deposits

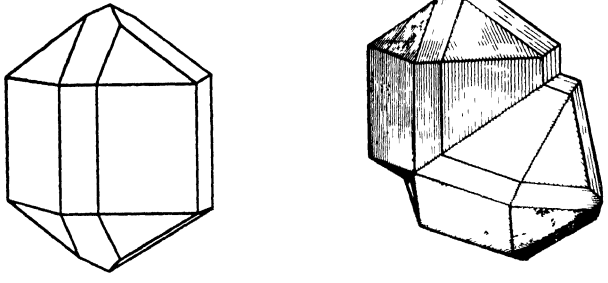
Characteristics of Tin Ores

Cassiterite, or tinstone, is the only mineral that is an important source of tin. This mineral is frequently called "tin ore" The use of the term should be restricted to the ore containing the mineral, and not, in addition, to the concentrates of the mineral obtained from the ore or from stanniferous alluvial deposits There is a general misuse of the term tin ore in the Malay Peninsula and adjacent localities, particularly where most of the mineral is obtained from secondary stanniferous deposits The term, cassiterite, is exclusively used in mineralogical, geological and other scientific writings. It is unfortunate that it is not more frequently used when referring to the occurrence of the mineral on an economic scale

Tinstone is a convenient old English term deserving more frequent use. Tinstone is a dioxide of tin, or stannic oxide When chemically pure, as in the rare transparent variety, it has a metallic content of 78 6 per cent tin This transparent species is found in the Tipuani River in Bolivia Frequently, however, the crystals and grains contain appreciable amounts of impurities, chiefly iron and tantalum The impurities are in the mineral itself We are for the present unconcerned with the usual impurities found in tinstone concentrates Ainalite is a variety of cassiterite containing almost 9 per cent of tantalum pentoxide. Tinstone usually has a deep brown or black color with an adamantine luster Several other colored varieties are known, among them red ruby tin, yellow rosin tin, and yellow wax tin; the names in each case are descriptive of the mineral's appearance. Separable tin, tooth tin and needle tin, as a result of their acute ditetragonal pyramidal crystalline form, receive their names from their crystallographic appearance. Wood tin is a compact variety of cassiterite composed of radiating fibers resembling dry wood. Toad's eye tin is a similar variety on a smaller scale in which the fibers appear to resemble the eye of a toad. Stream tin is water-worn tinstone. Float tin is sometimes employed to describe the cassiterite occurring in soil derived from the weathered surface of a mineralized area.

The crystals of cassiterite belong to the tetragonal system. Common forms are tetragonal prisms terminated by tetragonal pyramids Figure 12 shows the structure of well-formed crystals. Twin crystals are common,

one modification known as the kneecap twin being more prevalent. Well defined crystalline forms readily recognizable are more frequently absent than present. Cassiterite also occurs massive and as grains, often in reni form shapes with radiating fibrous structure such as wood tin. It is brittle and has a subconchoidal fracture. The broken surfaces are frequently un even with a resinous appearance. Cassiterite is about as hard as ordinary steel, having a value of 6 to 7 on the Von Moh mineralogical scale. Its specific gravity varies in different varieties from 6 4 to 7 1, which is un usually high for a mineral with a non-metallic luster. The high specific gravity of tinstone is one of its fortunate characteristics. It is about two and one-half times as heavy as quartz sand (specific gravity 2 65), two and one-third times as heavy as tourmaline (specific gravity 3), and about one and one-third times as heavy as ilmenite (specific gravity 4 5 to 5), mag



Ordinary crystal *Knee-cap twin*

FIGURE 12. Crystals of cassiterite.

netite (specific gravity 4 9 to 5 2), and hematite (specific gravity 4 5 to 5.3). It is frequently associated with these minerals. Its higher specific gravity makes it readily separable by panning, by sluice boxes and shaking tables.

Cassiterite is ordinarily considered infusible. When the finely powdered mineral is treated with the blowpipe on charcoal with a mixture of sodium carbonate and charcoal powder, it gives a globule of tin with a coating of white tin oxide. Fusion mixtures of cyanides readily reduce tinstone to the metal. If the mass resulting from the fusion of the mineral with sodium carbonate be moistened with cobalt nitrate and again strongly heated, a characteristic blue-green color is produced Cassiterite is practically insoluble in almost all chemical solutions or mixtures of such solutions, a characteristic which is not shared by stannic oxide artificially prepared in the chemical way.

Stannite is an ore of tin of lesser importance than cassiterite. It is a

sulfide of tin, copper and iron, sometimes known as tin pyrites or bell-metal ore. Its chemical composition is sometimes expressed by the formula $Cu_2S \cdot FeS\ SnS_2$, with zinc usually present in varying quantities. The tin content varies from 22 to 27 per cent with about 29 per cent of copper, 13 per cent of iron, and 30 per cent of sulfur. Crystals are rare, but when they do occur are found to be of the cubic system The color of the mineral is steel gray when pure, but the usual variety is frequently iron black, sometimes bronze or bell-metal color, and occasionally with a bluish tarnish The presence of an admixture of copper pyrites causes the mineral to assume a yellowish color. Stannite has a metallic luster and gives a blackish streak. Its specific gravity is 4.3 to 4 5—being considerably less than cassiterite—with a hardness of 4 on the Von Moh scale. When heated in an open tube it gives off sulfur. When treated by the blowpipe on charcoal, it eventually fuses to form a brittle, metallic globule. The reactions for iron and copper are given by the roasted mineral with borax. It is only in Bolivia that stannite has been proved to occur in quantities of economic importance. In some of the old Cornish mines its appearance and working are only sporadic. Stannite is an unstable mineral. It is thought that probably most of the tin oxide known as wood tin is of secondary origin after stannite.

A few grains of native metallic tin have been reported to occur in one or two tin fields. Investigations of such occurrences have generally shown them to be nothing more than ancient smelted products, such as the Jew's house tin occasionally found in Cornwall. Irregular rounded grains of native tin have been reported from some of the gravels of the Aberfoil and Sam Rivers of New South Wales. It is probable, however, that this so-called native tin was a thin film of the metal on the surface of tinstone grains owing to the natural reduction in the presence of dilute sulfuric acid from decomposing pyrite and a metal. This reaction is discussed under the field test for tinstone. It is believed that tin does not occur native.

Cylindrite has been found in Bolivia in sufficient amount to justify special ore-dressing methods for milling it. It owes its name to the cylindrical shell-like fragments into which it cleaves. It is a complex lead-tin-antimony sulfide, its composition being represented by the formula $Pb_6Sb_2Sn_6S_{11}$. Its color is blackish lead gray, its luster metallic, its streak black. Its specific gravity is lower than cassiterite but higher than that of stannite, being 5.42, but it is softer than either of the other minerals, being 2.5 to 3 on the Von Moh scale. It is often associated with stannite and cassiterite in veins along with franckeite, sphalerite, pyrite, proustite and quartz. A typical highgrade specimen of cylindrite is a compact lead-gray mixture of sulfides which are soft and dirty the hands. The cy-

lindrical shells of cylindrite are prominent on the broken surface of the ore.

Another complex sulfide of tin is *franckeite*, which is similar to cylindrite except that it has perfect cleavage in one direction. It is a blackish-gray to black mineral with a metallic luster. It is generally associated with cylindrite. Its composition is represented by the formula $Pb_5Sb_2Sn_2S_{11}$, containing therefore a smaller percentage of tin than cylindrite. Its specific gravity is higher than cylindrite, being 5.5, and its hardness is approximately the same as the latter mineral, being 2 75 on the Von Moh scale. Franckeite often occurs massive with imperfect radiated and foliated structure. It is found in veins in Bolivia associated with the same minerals ordinarily found with cylindrite.

There are a number of other sulfide minerals containing tin, most of which, however, are rare. They are *canfieldite*, *teallite* and *plumbostannite* The borates, *nordenskioldite*, *hulsite* and *paigeite*, also contain tin *Stokesite* is a tin silicate which exists only as rare specimens of considerable scientific interest. Certain tourmaline hornfels rocks from Ear Mountain in Alaska contain a coal-black mineral which seems to resemble the associated granular tourmaline. This material, however, is a magnesium-iron-tin borate of low tin content, being approximately 10 per cent

Tests for Tin. Although cassiterite can be readily recognized in coarse grains or larger fragments because of its high specific gravity, its unusual hardness, color and adamantine luster, these physical characteristics are not sufficiently reliable in identification of the mineral when it occurs as small water-worn grains in alluvial deposits.

A useful field test for tinstone depends upon the fact that stannic oxide is cathodically reducible by hydrogen. The field test consists of placing the grains in contact with zinc or iron in a solution of a cold dilute non-oxidizing mineral acid such as hydrochloric or sulfuric acid The hydrogen, evolved as a result of the action of the acid on the zinc at the contact surface between the grain and the metal, reduces the stannic oxide, leaving a thin film of metallic tin as a gray coating over the grains of the mineral. If the small pieces of the mineral be washed and then rubbed between the fingers or on a piece of soft fabric, the bright silver-white surface of metallic tin is produced. No other mineral is affected in a similar manner by hydrogen reduction. Serious mistakes involving considerable sums of money have been made by mistaking grains of such minerals as wolframite, ilmenite, zinc blende, rutile, zircon, tourmaline, garnet, hematite, etc., for tinstone. Tinstone may occur pseudomorphous with a number of minerals such as tantalite, columbite, and rutile. Table 7 (from Jones[1]) shows the physical characteristics of those minerals which may be taken for tinstone.

[1] W. R. Jones, "Tinfields of the World," London Mining Publications, Ltd., 1925.

TABLE 7 MINERALS OFTEN MISTAKEN FOR TINSTONE

MINERAL	SPECIFIC GRAVITY	HARDNESS	CRYSTAL FORM	TEST
Tinstone, SnO_2 (cassiterite)	6 8 to 7 1	6 to 7	Tetragonal pyramids or prisms	See text
Zinc blende, ZnS	4 0	3 5	Cubic system, in tetrahedrons	The encrustation on charcoal when heated with cobalt nitrate, gives grass-green color. Sulfuretted hydrogen evolved with HCl
Ilmenite, FeO TiO_2	4 7	5 5	Tabular, trigonal	Gives a yellow solution with potassium bisulfate, which turns violet when reduced with tin.
Wolframite, (FeMn) WO_4	7 5	5 5	Tabular crystals, monoclinic	Cleaves easily into thin flakes Fused mass is decomposed with hydrochloric acid and when heated with tin gives a blue solution
Hematite, Fe_2O_3	4 9 to 5 3	5 5 to 6 5	Rhombohedron, reniform, other forms	Become magnetic on heating Red streak
Rutile, TiO_2	4 2	6 5	Like cassiterite	Fused with potassium bisulfate it gives a solution which when reduced with tin has a violet color
Zircon, ZrO_2SiO_2	4 7	7 5	Prisms with pyramids, tetragonal	Almost always shows good crystal forms
Tourmaline, borosilicate of Al, etc	3 1	7 5	Prisms with pyramids, trigonal	Generally appears like an aggregate of black needle-like crystals Breaks easily, and can be panned off as easily almost as quartz grains.
Garnet, $3R'' OR_2'' O_3 3SiO_2$	3 7 to 4.0	7 5	Dodecahedron, cubic	Can be panned off easily, being only a little more than half the weight of cassiterite
Axinite, borosilicate of Al and Ca	3 3	6 5	Flat crystals, triclinic	Intumesces in blowpipe flame
Tantalite (Columbite), niobate and tantalate of iron and manganese	5 3 to 7 3	6	Orthorhombic	Gives a dark-red to black powder and streak.

Types and Geology of Tin Deposits

Tinstone occurs in nature in two types of deposit, the first of a primary nature, being veins, and the second of secondary origin as alluvial or placer and detrital deposits. Those not occurring *in situ* as in veins are conveniently termed secondary stanniferous deposits. Jones[2] stated:

"By far the greatest amount of the world's supply of this mineral has been derived originally from stanniferous veins of quartz and pegmatite traversing granite, schists, phyllites and slates, and it is also derived from veins of aplite, quartz-porphyry, greisen and other granite modifications traversing the rocks named above, and occasionally in veins traversing quartzite, limestone and other rocks. The term "granitic rocks" is conveniently used to embrace the quartz, pegmatite, aplite, quartz-porphyry, greisen, etc., which occur in veins or dykes, for they are modifications of granite, and represent the residual and more acid part of the parent granite magma. Tinstone is also found disseminated through granite and adjacent rocks, but such occurrences are rarely workable as ore bodies, although they may have contributed a good deal of tinstone to neighboring secondary stanniferous deposits.

The bulk of the world's supply of tinstone is obtained at present from stanniferous alluvial and eluvial deposits derived from mineralized areas in their immediate neighborhood. It is an interesting and significant fact that *not in a single tinfield in the world has tinstone been found "in situ" except near granite or granitic rocks,* and it has not been found in alluvial or eluvial deposits except where these have been derived from mineralized areas in which granite or granitic rocks are known to occur."

Tin as an element forms less than 0.001 per cent[3] of the igneous rocks in the earth's crust. Only a small fraction of the earth's granite masses is stanniferous. It is thought that there are no exceptions to the rule that primary tin deposits occur in or near an acid igneous rock such as granite or related rocks like granite-porphyry, quartz-porphyry, aplite, pegmatite or quartz. These rocks generally occur as veins traversing granite and metamorphosed rocks of sedimentary origin, as illustrated by schists, phyllites, slates and quartzites, and metamorphosed limestone in some tinfields.

While it is true that tinfields occur in connection with acid igneous rocks, the converse is not true, for there are extensive areas of granitic rocks which contain no tin minerals. In Pahang in the Federated Malay States, the Benom and the Main Range of the Peninsula run approximately parallel, only about twelve miles apart. Tin mining is extensively done in the Main Range, while the Benom Range has failed to show the existence of any tin deposits in it. Mica, muscovite, and lepidolite are

[2] *Ibid.*

[3] F. W. Clarke, and H. S. Washington, *U. S. Geol. Survey*, Prof. Paper No. 127, (1924).

abundant in the Main Range but absent in the Benom chain, while hornblende, widely distributed in the Benom granite, is rare in the Main Range.

The economically important primary tin deposits occur in the infillings of fissures. It is thought that the position and shape of the veins were determined by pre-existing fissures which were enlarged as they became infilled with magma under pressure The fissures probably occurred during the later consolidation phases of the granite magma When formed, they were filled with the residual and more acid differentiation products of the parent magma during the final stages of the igneous intrusion Mineralizing gases and carriers for tin and other metals, such as borates, fluorides, sulfides, arsenical compounds and related products in the residual magma, probably formed the metalliferous compounds and the related minerals now found in the veins resulting from the fissure infilling. Most authorities agree that the carriers of tin minerals were in the gaseous state A minority believe that mineralizing liquids played the more important part The magma must have been in a very fluid state during its intrusion into the fissures as well as under great pressure

Stanniferous veins are generally more common on the margins of granite masses where the fissuring is more pronounced The greater portion of the world's supply of tin minerals is obtained from granite contact lodes.

The discussion of tinfields will be subdivided into what are now considered the various metallogenetic tin provinces,[4] or the areas where primary tin deposits were formed at the same period of mineralization. Chronologically in respect to their discovery and working on a considerable commercial scale, these are the tinfields of (1) the west of England, Brittany and the Erzgebirge, (2) Burma, Siam, the Malay States and Indonesia (Netherlands East Indies), (3) Bolivia, (4) Nigeria, and (5) Australasia, in reference to which it is not certain that all the tinfields there may be grouped in one province.

European Metallogenetic Tin Province. Rastall points out that the tinfields of the west of England and of Brittany form detached portions of a single geological unit, while the tinfields of Saxony and Bohemia in the Erzgebirge are of a very similar type belonging to the great mountain systems of Central Europe. The tinfields of Portugal and Spain form part of an ancient plateau consisting of paleozoic rocks strongly folded by the same type of convulsions as gave rise to the geological units in Brittany and the Erzgebirge.

Cornwall is now practically the only source of tinstone in Great Britain and Ireland, although a small amount comes from that part of the mineralized area which extends into Devonshire. The history of tin mining in

[4] Rastall, "Geology of the Metalliferous Deposits," Cambridge University Press, 1923.

Cornwall dates back to prehistoric times. The mineralized areas are either in the granite or on the margins of the granite, or in the metamorphosed sedimentaries nearby. Nearly all of the tin ore in Cornwall and Devon occurs in lodes in the infillings of fissures in the granite and in the adjacent sedimentaries. At times the country rock may be extensively altered, making it impossible to distinguish the walls of the lode In certain sections of Cornwall, particularly at East Pool, no normal granite is seen except at a considerable distance from the lode, as a result of silicification. Such alteration is also common in parts of the Malay Peninsula. Irregular bunches or masses of ore may occur where the lode widens out.

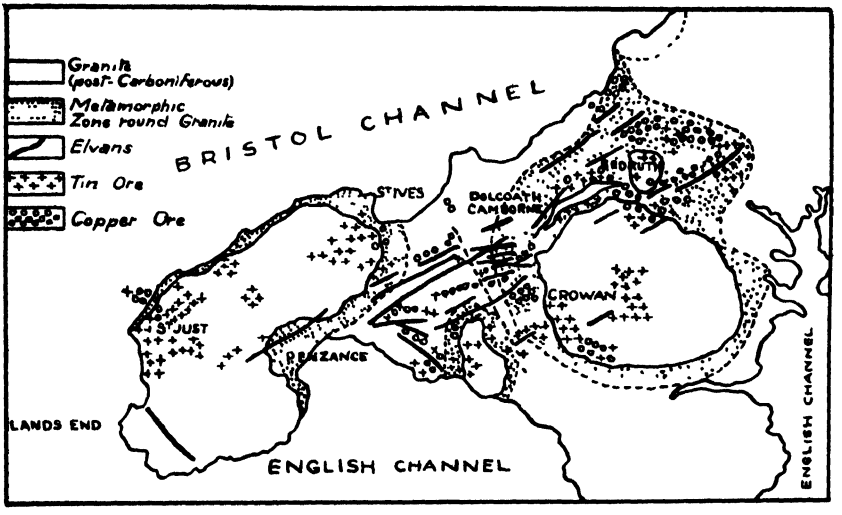


FIGURE 13 Geological map of West Cornwall showing the relation of the ores to the granite (*Jones*)

The relation of the Cornwall tin mines to the granite is shown in Fig 13. The minerals are distributed vertically in the tinfields with a certain regularity. Jones believes that "there is sufficient accumulated evidence to point very strongly to the conclusion that such distribution is intimately related to the temperatures and pressures of formation of these minerals Those of the highest temperature of formation, like tinstone, occur towards the bottom of the metalliferous depth zones." Figure 14 shows the vertical distribution of mineral zones in Cornwall as given by Dewey.[5]

The highly mineralized area of Camborne and Redruth produces about 95 per cent of the total output of Cornwall. Tin and copper minerals were probably obtained from Land's End during the Bronze Age. In 1907 all alluvial working for stream tin ceased, and only a few tin and

[5] Dewey, Pres. Address, Geol. Assoc., Feb., 1925, p. 129.

copper mines have worked intermittently since. There is a rich group of copper and tin lodes in the parish of St. Just and a smaller group near St. Ives, both close to the northern margin of the Land's End granite.

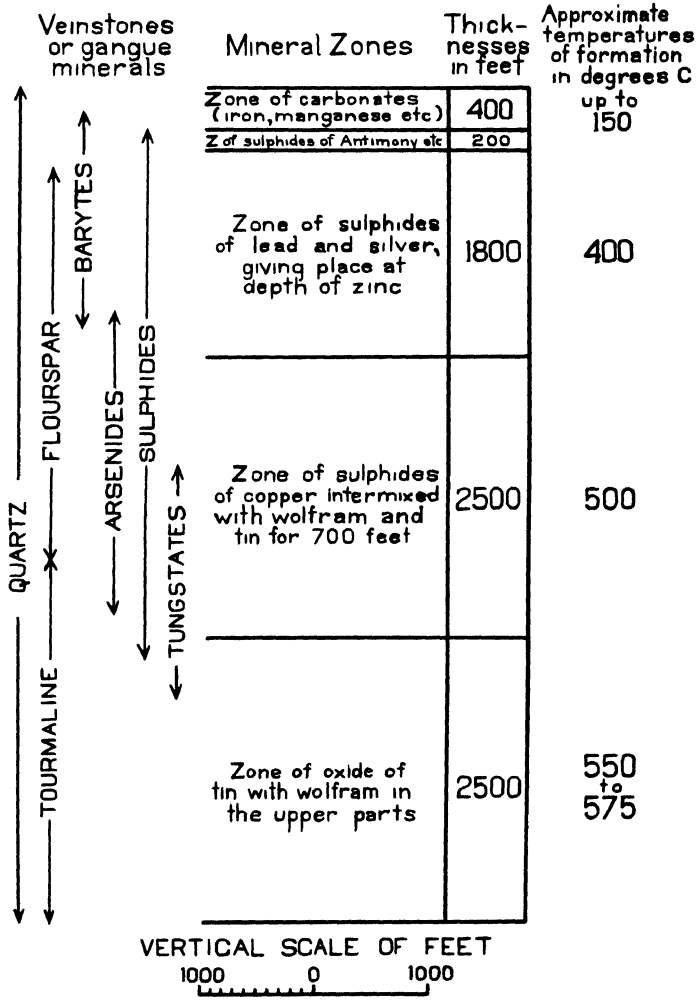


FIGURE 14 Diagram showing the vertical distribution of mineral zones in Cornwall

No economically important deposits of tinstone occur in Scotland, Ireland, France or Holland.

Situated in the same metallogenetic province are the Erzgebirge tin deposits in Czechoslovakia and Germany. These deposits have been worked for tinstone for the last eight centuries. The principal rocks of the highlands extending along the boundary of Saxony and Bohemia

are gneisses, schists and phyllites. Tinstone is mined in the Altenberg-Zinnwald district, at Sadisdorf, Altenberg, Zinnwald and Graupen. The workings at Altenberg are confined to the small granite stock intrusive in granite-porphyry and traversed in different directions by innumerable minute stringers of tinstone so thin as to be almost invisible. The adjacent rock is mineralized The percentage of tin in the rock varies from 0 1 to 0.9 per cent, with an average of 0.3 per cent, carrying a bismuth content of 0.002 per cent. It is only because of the peculiarly favorable conditions

[FIGURE 15. Map showing the chief tin and tin-tungsten fields in Spain and Portugal (*Jones*)

that it is possible to work the deposit profitably. The Erzgebirge deposits are more important historically than as tinstone producers.

Associated with wolframite, tinstone occurs in a mineralized belt extending with numerous breaks from the northwest of Galicia in northwest Spain through the provinces of Pontevedra and Orense to the northeast of Portugal, and as far southwards as the mountain ranges of Sierra da Estrella. The position of the chief tin and tin-tungsten fields in Spain and Portugal is given in Fig. 15. These fields belong to the same metal-

logenetic province as those of Cornwall, Saxony and Bohemia. Spain produces very little tinstone, the average being about 20 tons in terms of metallic tin per year. Practically the whole Portuguese output, about 400 tons a year, comes from shallow stanniferous alluvial deposits in the Gaia Valley near Belmonte.

Italy has no important tinstone deposits.

While it is known that tinstone occurs in the Trans-Baikal province, in the Urals, in the Russian Empire and in Finland, only a portion of the deposits have been worked on a small scale. At Pitkaranta in Finland, veins traversing metamorphosed limestone and schist have been worked for iron and copper ore, tinstone and silver. Their production is small.

Asiatic Metallogenetic Tin Province. The chief tin-producing part of Asia is a mineralized belt which is continuous through Lower Burma, Lower Siam, the Malay States into the islands of Singkep, Banka and Billiton in Indonesia (Netherlands East Indies). This intensively mineralized metallogenetic tin province produces more than half of the world's total annual production. The location of the fields is given in Fig. 16.

Tin mining is in operation in every one of the Federated Malay States—Perak, Selangor, Negri Sembilan, Pahang—and each of the Unfederated Malay States—Kedah, Perlis, Kelantan, Trengganu and Johore. So extensive is the mineralization in and near the granite of the Peninsula that it is stated that it would be difficult to find any stream having its source in the Main Mountain Range that did not contain in its bed a certain amount of tinstone. For a long period of years Perak has remained the chief tin-producing state in British Malaya. The Kinta district in the center of the state is the chief producer. A typical mine is shown in Fig 17. This district, only 36 miles long and 25 miles wide in its maximum width, is estimated to be the source of about 50 per cent of British Malaya's output. In the Gopeng Consolidated Mines in the Kinta district, the detrital deposits worked carry 1.25 to 1.4 pounds of tinstone to the cubic yard, while in the mines of the South Perak Tin Dredging Company the alluvial deposits handled carry about 0.73 pound of tinstone to the cubic yard.

The alluvial and residual placers of the Malayan deposits account for 94 per cent of the total output. Of the remaining 6 per cent, the Pahang Consolidated Company, Ltd., produces nearly all of it from lode mining The placers are on the west side of the Peninsula, covering large areas, and are virtually continuous for some 200 miles. The richest of the placer deposits are of the residual type and are known as "contact mines." Dredging, begun in 1912, has increased until it now accounts for upwards of 20 per cent of the total production. The ground has been carefully prospected and the richest spots mined. The ground available for dredging consists of old Chinese tailings too low to work by hand methods. It is thought that areas set aside for agriculture contain valuable placers. In

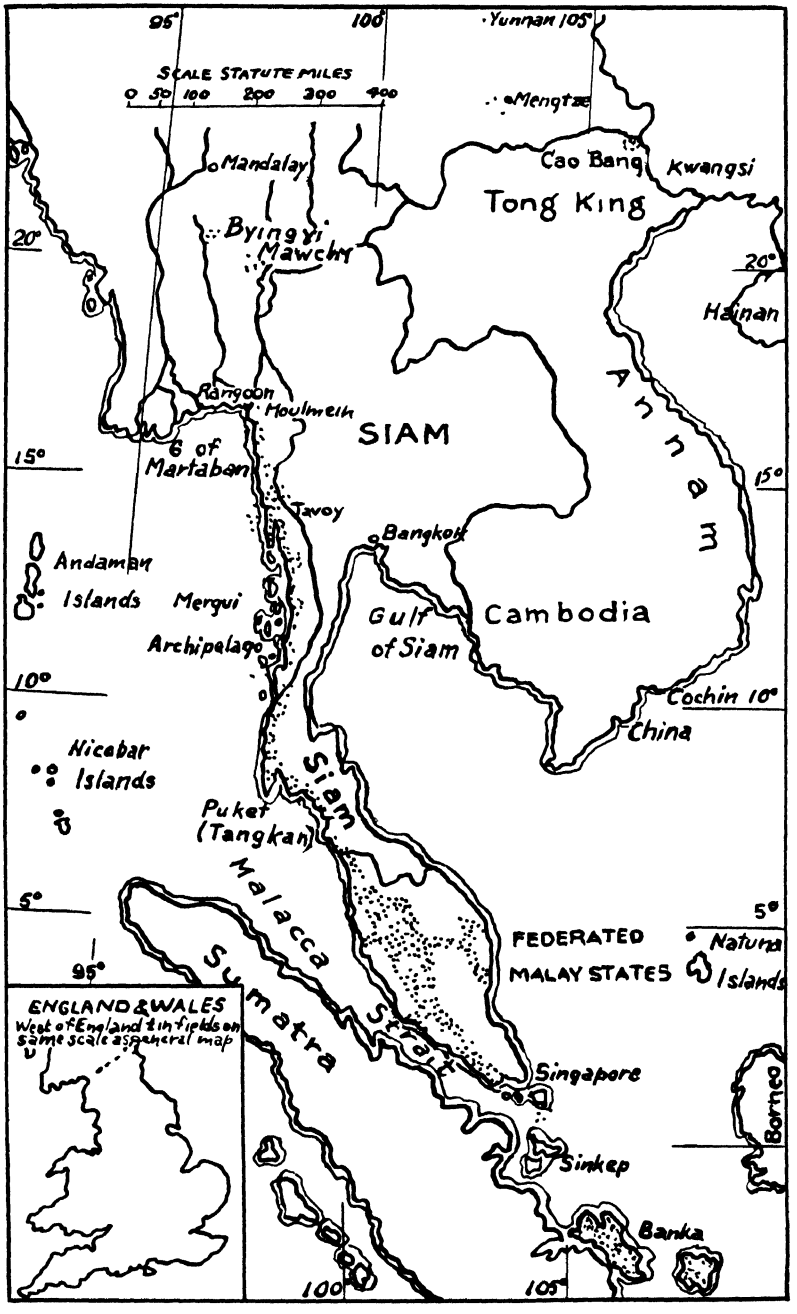


FIGURE 16. Map showing tinstone-wolframite fields of Malaya, Indonesia, Siam, Burma and the Yunnan fields of China (*Jones*).

the Gopeng mine the deposits consist of decomposed schists and phyllites, varying in thickness from about 50 to over 120 feet, that have in many places become disorganized owing to their subsidence on the metamorphosed underlying limestone. There are many extremely large open-cast workings. The Tronoh mine in the western part of the Kinta district formerly obtained the bulk of its tinstone from an enormously large open-cast mine at the foot of a hill composed of schists, granite and granitic intrusions. The limestone rock at the foot of the hill had been dissolved to form a trough about 1,900 feet long, 500 feet wide, and about 150 feet deep. As this trough was being formed, the eluvial deposits on the steep

(Courtesy Pacific Tin Consolidated Corp.)

FIGURE 17. Chin Fatt Kongri Mine.

flanks of the hill kept slipping down. Stanniferous eluvial and alluvial deposits to the extent of about four million cubic yards occurred in the trough. The sinking movement had caused concentration of the tinstone in exceedingly rich patches. When Tronoh Mines was the largest producer of tinstone of the world, no machinery of any kind except for pumping water was employed. The mine was worked by thousands of Chinese coolies who carried the tin-bearing ground to the surface in baskets suspended from shoulder sticks. Formerly, under certain circumstances, many mines in the Malay Peninsula could be worked more economically by hand labor than by machinery. Tin mining in loose ground, however,

has been revolutionized by the use of gravel pumps and bucket and suction cutter dredges.

The state of Selangor produces about 25 per cent of the total output of the Federated Malay States. The geological structure of the tin-mining areas is similar to that previously described in the Kinta district. In South Selangor tinstone *in situ* has been worked on a small scale in hundreds of places in the foothills. The decomposed surfaces of the mineralized granite, schists, and phyllites have been removed and the mineral recovered in sluice boxes after hydraulicking.

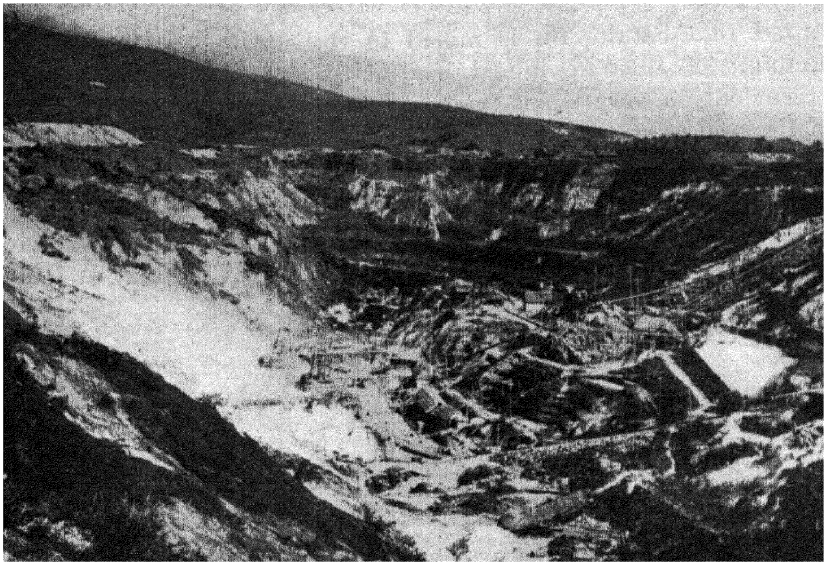
(Courtesy Geological Survey, Federated Malay States)

FIGURE 18. A mine near Lahat.

Some of the Malay mines are shown in Figs. 18 and 19. In Fig. 18, the large mass of rock on the right of the picture is crystallized limestone.

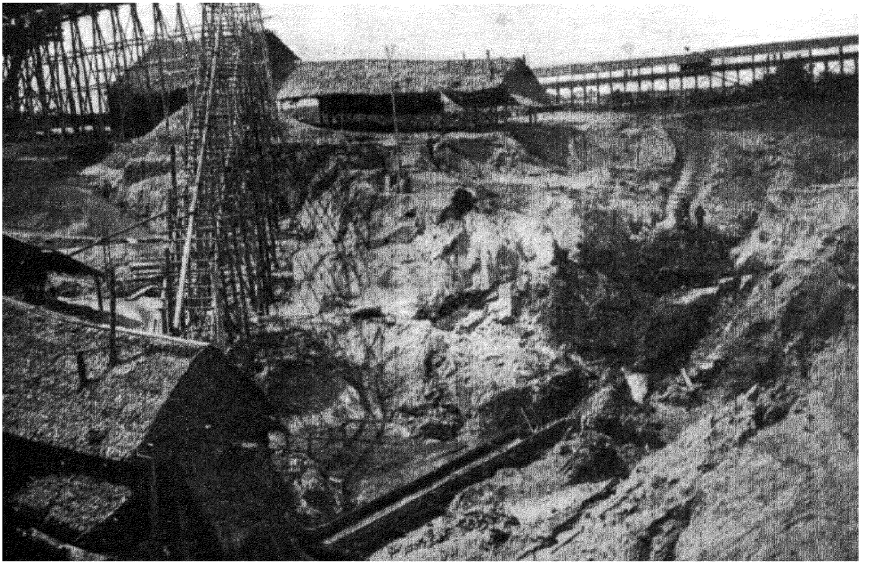
In Fig. 20 the cap of the tin-bearing pipe is shown shortly after it had been uncovered. Figure 21 shows this extraordinarily rich tinbearing pipe in the crystalline limestone. It is now worked to the depth of several hundred feet.

It is a popular belief in the United States and Europe that there are many large tin mines in the Straits Settlements. "Straits tin" is known the world over. People who are not interested in mining have taken it



(*Courtesy Geological Survey, Federated Malay States*)

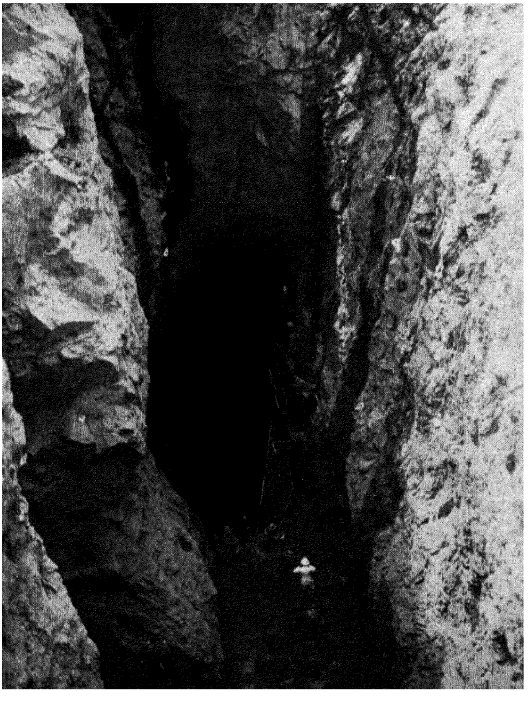
FIGURE 19. The North Mine in Lahat Ltd.'s property.



(*Courtesy Geological Survey, Federated Malay States*)

FIGURE 20. The Beatrice Mine.

for granted that Straits tin is mined in the Straits Settlements. The total amount of tinstone mined in the Straits Settlements, however, would form only a very small fraction of the output of even one of the smaller tin mines in the Malay States. Practically the whole output of tinstone concentrates from the Malay States is smelted at Singapore and Penang in the Straits Settlements. Two of the larger tin-smelting companies in the world are the Straits Trading Company at Singapore and Penang, and its subsidiary the Eastern Smelting Company at Penang.



(Courtesy Geological Survey, Federated Malay States)

FIGURE 21. The Beatrice Mine, near Ipoh.

Tin mining on a very small scale has been carried on in Malacca and at times in the Dindings.

Almost the entire production of tinstone in Siam comes from the western side of that narrow part of the country lying between Lower Burma and the Malay States, where it forms part of the Malay Peninsula. The tinfields of Siam form part of the mineralized belt that runs parallel to the granite ranges previously described as continuous through Lower Burma, Lower Siam, the Malay States and Indonesia (Netherlands East Indies).

Stanniferous alluvial deposits are worked by bucket dredging in the neighborhood of Renong and as far southward as the island of Puket, about halfway between Victoria Point, Lower Burma, and the northern boundary of the state of Kedah in the Malay States The Tongkah Harbor Tin Dredging Company works stanniferous alluvial deposits in the shallow harbor of Tongkah. The dredges work from near the shore to a few miles out at sea The shallow water covers a coarse sand containing well-rounded grains of tinstone derived from the mineralized area forming the seashore Jones[6] stated that part of the flatland on the shore had been worked. The main street of the small town of Tongkah had also been dredged.

Almost all the tin mines in the Indian Empire are restricted to Lower Burma where the chief producing centers at present are in the Tavoy and the Mergui districts. The stanniferous areas are worked by bucket dredging and gravel pumps The deposits are largely alluvial. The tin and tungsten localities in Burma are shown in Fig 22 In the Tavoy district all but a few of the mines produce mixed wolframite-tinstone concentrates varying in their tin content from below 1 per cent tin and over 70 per cent WO_3, to those carrying over 20 per cent tin and in exceptional cases to well over 40 per cent. No wolframite chemically free from tin is known to occur in the whole district. The Tavoy Tin Dredging Company works the chief alluvial stanniferous deposit at Hindu Chaung The average yield of recent years has been 1.21 pounds of tinstone per cubic yard

Except during the period of Japanese occupation during World War II, Indonesia (Netherlands East Indies) contributes about 23 per cent or more of the world's supply of tin. The continuation of the mineralized belt of the Malay States extends through the islands of Singkep, Banka and Billiton in Indonesia (Netherlands East Indies). For a long period of years these small islands have alternated with Bolivia as the second largest tin-producing areas. Whereas almost the whole of the Bolivian yield is obtained from lode mining, practically the total output of the Netherlands East Indies is from alluvial and detrital deposits The island of Banka produces about two-thirds of the tin shipped from the Netherlands East Indies, and Billiton nearly all the remainder, with the exception of about 2 5 per cent from Singkep. Banka's production is about as large as the combined outputs of Siam, China and Nigeria The Billiton and Singkep areas contain considerable reserves but their total is probably only a fraction of those of Banka. The tinstone concentrates are high grade The impurities have been decomposed and removed by percolating waters They therefore offer no difficulty in smelting and refining the metal The

[6] W. R Jones, "Tinfields of the World," London, Mining Publications, Ltd , 1925

deposits have been derived from the weathering down of the mineralized areas in granite and in schists and phyllites near the granite margins.

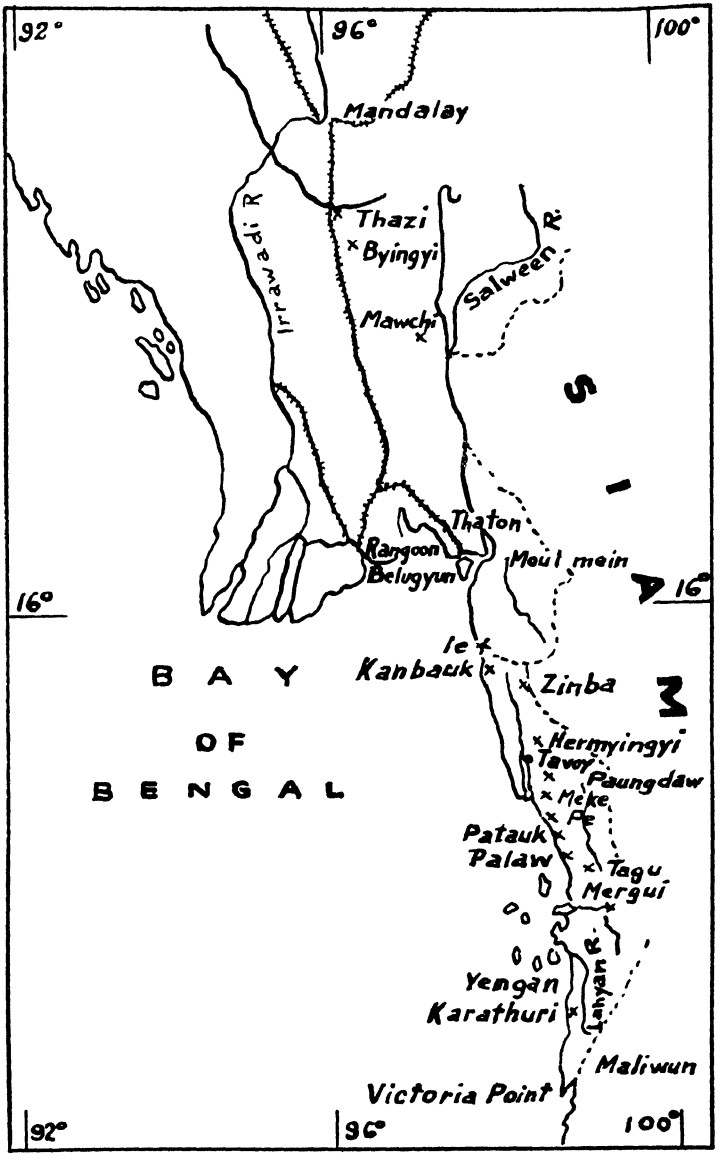


FIGURE 22 Map showing tin and tungsten localities in Burma (*Jones*)

No tinstone deposits of importance occur in Sumatra. The only important deposits of tin in French Indo-China are in association with wolframite in the provinces of Tonkin and Laos. Decomposed stock works and detrital

deposits are worked open-cast. When a plentiful supply of water is available during the rainy season, the rich deposits yield large profits The important alluvial deposits are those at Beau-Site and St Adele

Tinstone occurs in the Chinese provinces of Yunnan, Kwangsi, Hunan, Kwangtung and Fukien The tinfields extend over large areas The chief producing center is about thirty miles west of the treaty town Mengtze in Yunnan. In normal years about 93 per cent of the total production of China comes from Yunnan, 4 per cent from Kwangsi and 3 per cent from Hunan. The tinstone occurs in alluvial deposits in large solution cups and troughs resting on a limestone bedrock The alluvium is of a dark brown argillaceous nature, highly ferruginous The deposits appear to be similar to certain stanniferous alluvial workings in the Malay States The mining methods are primitive. No machinery of any kind other than native pumps worked by hand or foot is used. The overburden is dug out manually and carried to the surface in shoulder-stick baskets where the tinstone is concentrated in small sluice boxes Many of the mines in the Hunan and Kwangsi Provinces, such as shown in Fig 23, are small and are worked by native labor. In the Fu Chuan district the tin deposits are all alluvial and detrital, scattered over a granite range for a distance of thirty miles The ground worked carries about 3 pounds of tinstone per cubic yard Very little tin is produced in the Kwangtung and Fukien Provinces, although tinstone is known to occur there

Tinstone is mined in Satsuma Province in Japan, where it occurs in quartz veins intrusive in metamorphosed sedimentaries, phyllites, and slates. Some of the lodes carry as high as 3 per cent tin Stanniferous alluvial deposits are known to occur in the vicinity of Takayama and Hirukawa in Mino Province, where the stanniferous gravels occur as beds on the river banks.

Bolivian Metallogenetic Tin Province. While in the Malay States, Indonesia (Netherlands East Indies), Siam, China and Nigeria the bulk of the production is obtained from stanniferous alluvial and detrital deposits, practically all the Bolivian tinstone production is from primary or vein deposits. For the period between 1905 and 1920, Bolivia was second only to the Federated Malay States as a tin-producing area It was second again in 1922 but third in 1923, being superseded by Indonesia (Netherlands East Indies) Bolivia produces from 22 to 25 per cent of the world's tin production The mineralized areas of Bolivia consist of a high plateau or tableland nearly 500 miles long and over 100 miles wide, about 12,500 feet above sea level. The tin mines are at elevations of about 12,000 to nearly 20,000 feet, mines at the higher elevations being in a rugged snow-clad country where conditions are severe The chief tin-mining centers are shown in Fig 24. The tinstone deposits are the most widely distributed of all the mineral wealth of Bolivia. They are worked throughout the extent of the Cordillera Real Mountains and their southern extension from

the north of La Paz to the southeastern end of the department of Potosi. About 90 per cent of the total production comes from ten producing centers. Tin mining in Bolivia is of comparatively recent origin, although the tin deposits have been known for several hundred years. Little tin is obtained from placers, but this class of mining is being developed. In the period around 1925 approximately 70 per cent of the tin production of Bolivia came from the Llallagua and La Salvadora mines of the Patiño Company. The mineralized area containing tin is large. Development work has been confined to the accessible localities. The output of many

(Courtesy Malay States Information Agency)

FIGURE 23. Chinese Mine at Kongsi.

mines is limited to high-grade ores in order to meet transportation charges. Judged from the character of the deposits in the accessible localities, relatively large bodies of low-grade ore will become productive when transportation facilities are improved. Because of the topography of the tin-bearing areas, the development of transportation will be gradual.

The ten most important producing centers from north to south are Araca, Oruro, Machacamarca, Huanuni, Llallagua, Uncia, Potosi, Sala Sala, Chocaya, and Chorolque. The most important of these is the department of Potosi. The type of country in Potosi is shown in Fig. 25. Davy[7] stated that the mines of Milluni, Huayna, Potosi, Araca, Choque-

[7] Davy, "Ore Deposition in the Bolivian Tin-Silver Deposits," *Econ. Geol.*, **15**, 463 (1920).

tanga, San Enrique, Mallochuma, Quimsa Cruz, and Santa Vela Cruz are grouped along the west and south border of the granite area. All the rest,

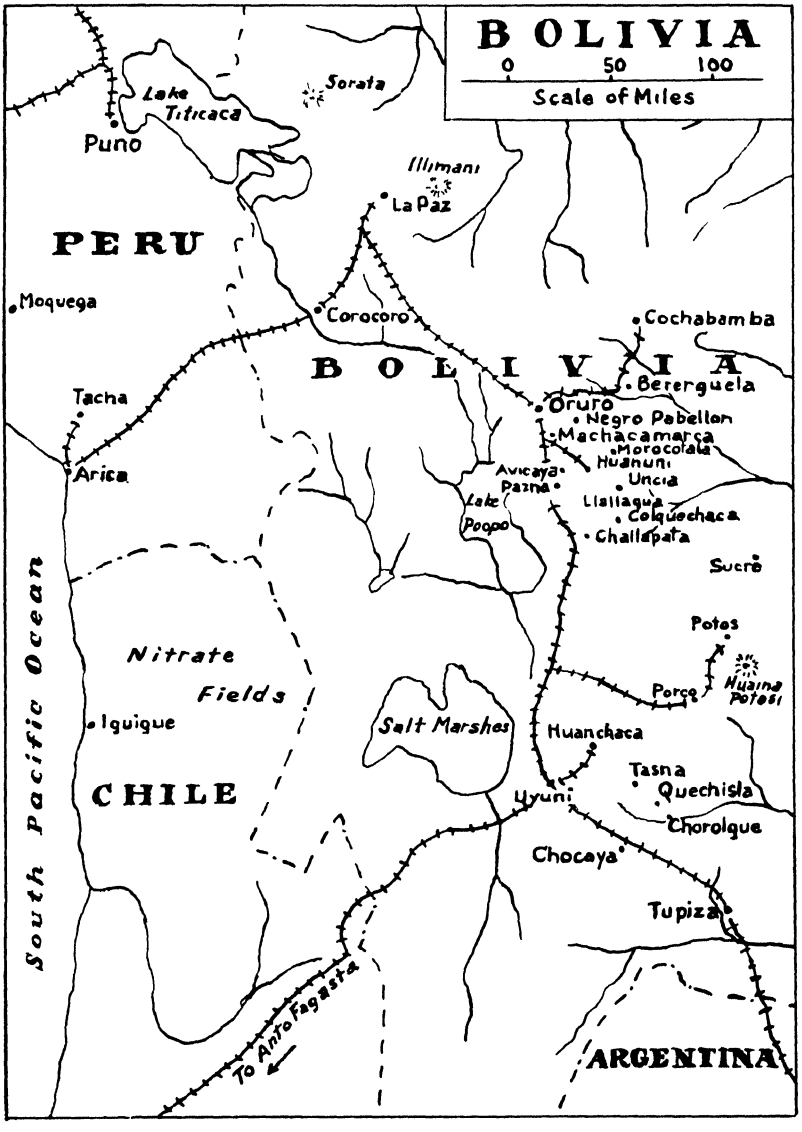


FIGURE 24. Map showing chief mining centers in Bolivia

including Oruro, Negro Pabellon, Llallagua, Uncia, Avicaya, Potosi, Porco, Pulacayo and many others, are found in or about intrusions of quartz-porphyry or related types of acid igneous rocks, with the excep-

tion of one or two occurrences where the workings have not, so far, exposed igneous intrusions. Granite outcrops in small areas near Potosi and may be at no great depths beneath the surface in many other places, especially

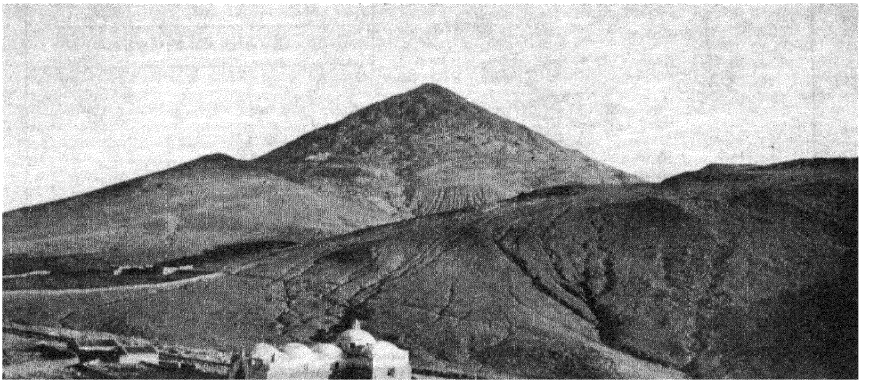


FIGURE 25. The Potosi tin area in Bolivia.

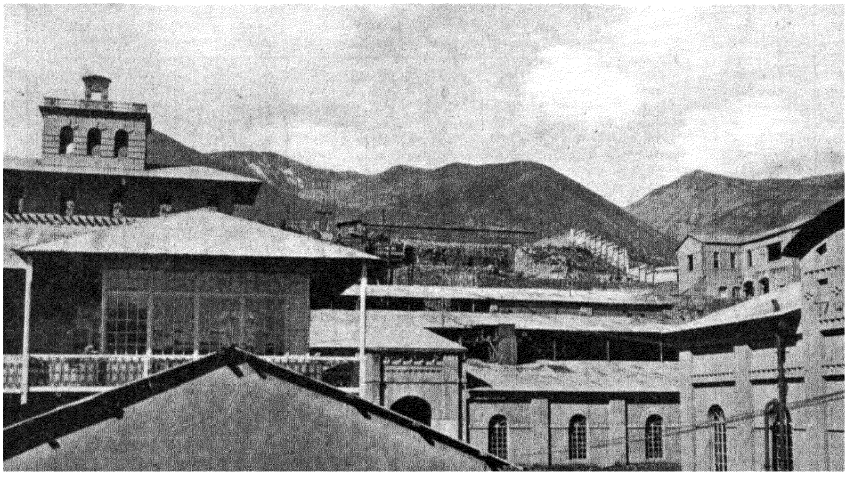


FIGURE 26. Tin mine near Oruro, Bolivia.

in the vicinity of Uncia, Llallagua and Avicaya, where the deposits have similarities to the Bolivian tin deposits in or about the granite itself. Although the silver veins worked at Potosi carried tinstone, the old Spanish miners rejected it as rubbish. Its value was not recognized until about the

middle of last century when it was first mined at Huanuni, in Oruro, and smelted in small charcoal furnaces similar to those which are still used in some of the tin-mining areas. A tin mine near Oruro is shown in Fig. 26.

All Bolivian tin deposits occur in comparatively small veins which often penetrate deep beneath the surface in various formations such as granite, porphyry and sediment minerals, and whose structure therefore is subject to great changes. It is difficult to estimate the reserves of an ore deposit properly. From an economical viewpoint, Pilz[8] divided the veins into pure tin-ore veins and silver-tin-ore veins, which to some extent takes into account the occurrence of the veins partly in granite, partly in liparite and dacite, and the shales and quartzites which they penetrate. The tin veins usually carry, in addition to tinstone and occasionally stannite, sulfide ores such as pyrite, pyrrhotite, copper pyrites, arsenopyrites, zinc blende, molybdenites, bismuthites, galena, and antimonite. In the silver-tin veins, tetrahedrite, jamesonite are also found, and in some deposits around Poopo and Colquechaca, cylindrite, franckeite, teallite, canfieldite, and argyrodite Tungstenite also has been found in many tin-ore veins. The matrix of the deposits is quartz, tourmaline, fluorspar, mica, bitter spar, siderite and barite. Topaz occurs somewhat less frequently.

The Uncia group and the adjoining Llallagua Company's mine have been at times the large producers of tinstone. Bismuth is produced as a by-product The grade of the ore worked is about 9 per cent tin. The average grade of ore milled was about 6 per cent metallic tin; there is a tendency toward a lower figure with the metal at a high price. Labor in all but the highest grades is native—that is, either mestizo or indian. The efficiency of the miners and laborers is moderate. The labor supply varies much in different parts of the country.

Chile and Peru produce little tinstone, although they export large quantities of the mineral which has been mined in Bolivia. Tinstone deposits in Peru are known to exist.

Nigerian Metallogenetic Tin Province. The occurrence of tinstone and smelting methods were known to the natives in Western Bauchi in Nigeria before European occupation. The tin deposits are distributed over an extensive area, well over 10,000 square miles. The important deposits, however, occur in Bauchi Province. The bulk of the output of tinstone in Nigeria is from secondary stanniferous deposits. These alluvial and detrital deposits are of varied types, owing to the different conditions during different geologic times under which they were formed. Some accumulated before the elevation of the plateau in which they are found and have remained in their original area of deposition. Others have been removed and redeposited by streams forming and reforming and changing their channels. Still other deposits result from the denudation of part of the

[8] Pilz, *Z. prakt. Geol.*, **33**, 15 (1925).

ore bodies after the uplifting of the plateau. These are now found in the present river beds and the flats on the river banks. Hollows or pockets filled with rich stanniferous gravels occur in the channels of the rocky streams. Sharp angular tinstone in quantities of economic importance occurs on the weathered outcrops of stanniferous quartz, pegmatite veins and other mineralized rocks. Falconer[9] stated that the minerals most commonly associated are topaz, ilmenite, magnetite, rutile, zircon, monazite, garnet, and more rarely, columbite, wolframite, corundum and gold. Raeburn[10] considered the important stanniferous terrace deposits at Jemaa as alluvium deposited by the river which has subsequently eroded its bed. Tinstone occurs free from impurities when concentrated. Streambed deposits are widely distributed over Nassarawa The tinstone here has been derived from weathered mineralized granite.

One of the factors which limits Nigerian production is a small quantity of water during most of the year, water being important in the working of the secondary deposits by the usual methods.

No important deposits have been found in either the Gold Coast or Nyasaland.

Practically the whole output of tinstone of the Belgian Congo comes from a mineralized belt about 250 miles long in Katanga on the northwest face of the rugged plateau of Monte Mitumba The mountains are composed of mica schists, tourmaline-bearing quartzites and slates. The tinstone occurs in quartz and pegmatite veins in detrital and alluvial deposits. The greater portion of the output has so far been obtained from shallow alluvial and detrital deposits

Tinstone deposits have not been worked in Portuguese East Africa. There has been successful working of the detrital deposits in Southwest Africa. The tinstone is sporadically scattered through pegmatite in large grains and crystalline masses.

Rhodesia produces little tinstone concentrates, although a number of veins and alluvial deposits are known.

In the Union of South Africa there are many ancient workings in places in the Transvaal where tinstone was formerly smelted by the natives. The Cape Province, Transvaal, and Swaziland outside of the Union produce tinstone concentrates. Cassiterite is known to occur in Natal. The Transvaal tinfields are those of the Waterberg in the northwest and the eastern Transvaal tinfields near the borders of Swaziland. They are secondary stanniferous deposits derived from the many large pegmatite veins traversing the granite. The tinfields occupy the eastern and southern margins of a geological basin, the central portion of which is composed of

[9] Falconer, *Geol. Survey of Nigeria*, Bull. No 1 (1921).

[10] Raeburn, "The Tinfields of Nassarawa," *Geol. Survey of Nigeria*, Bull. No. 5 (1924).

sandstones and conglomerates. Feldspar is frequently and intimately associated with the cassiterite in red granite.

Australasian Tin Deposits. Tin is known to occur in various parts of the Australian continent, in Tasmania and in New Zealand. Of the Australian states, Victoria has the lowest and New Wales the highest output.

The geographic distribution of cassiterite in New South Wales is very wide. The important tinfields are those in the neighborhood of Emmaville and Tingha. Here it occurs in lodes, in stock works and alluvial deposits. The chief tinfields of New South Wales, Queensland, Victoria, Western Australia and Northern Territory are shown in Fig. 27 The greatest bulk from the Tingha district is from alluvial deposits. In many sections of Australia the lack of water is a handicap in mining stanniferous gravels No large lode mines are known in Australia. An important tinfield in Queensland is the Herberton, its production being about one-third from lode mining and two-thirds from alluvial gravels Cameron[11] stated that the greater part of the lodes traverse coarse graywackes[12] and quartzites. The granite is a biotite granite and in places a hornblende granite Occasionally tinstone occurs in grains disseminated through the unaltered granite and porphyry The associated minerals are topaz, fluorite, tourmaline, and in some lodes wolframite, bismuthine, antimonite, galena and chalcopyrite

The chief mineralized areas of Victoria are in the northeastern part of the state Tasmania has been one of the chief producers of tin in Australasia The greater part of the tinfields are confined to the northern half of the island. Tasmania claims to have produced the largest individual mass of tinstone known. Three-fourths of the whole mass of the Gormanstown nugget, which weighs about 1,900 pounds, is said to be tinstone. An interesting mine in Tasmania is that of Mt Bischoff Situated toward the top and on the flanks of a mountain about 2,600 feet high, it has been worked as an open quarry Lodes of the usual type occur, traversing quartz porphyry and slate The Queen lode varies from 8 inches to 18 feet in width and has been traced for a length of over 3,000 feet along its strike at an average width of 3 feet It is said to carry between 1 and 2 per cent of tinstone over a considerable distance Stanniferous alluvial deposits have been worked at Cox Bight in the southern division of Tasmania. In the western division of Tasmania transport is a very serious difficulty.

No stanniferous deposits of economic importance have been discovered

[11] Cameron, "Report on the Herberton Tinfields," Department of Mines, Queensland, 1904.

[12] Sandstone, usually of gray color, containing particles of other rocks and minerals in addition to quartz and feldspar

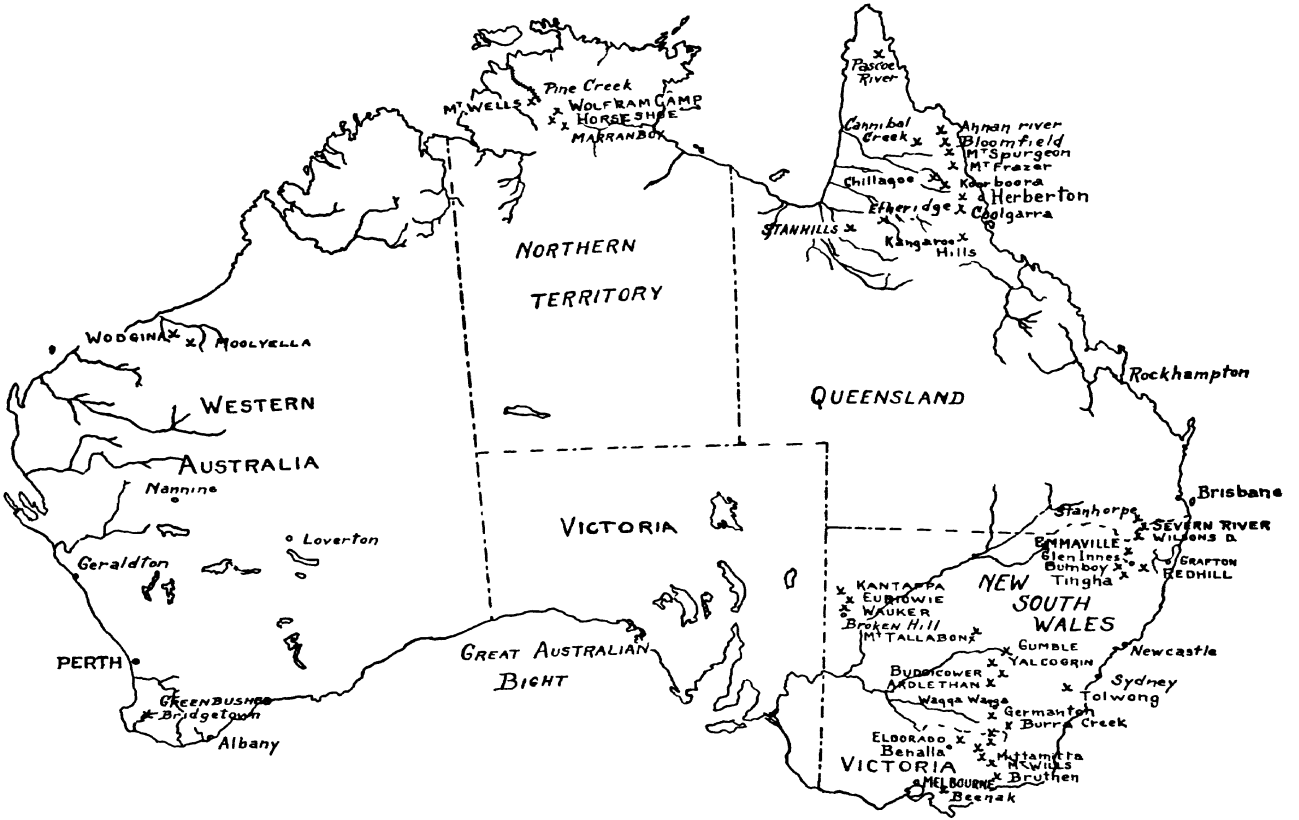


FIGURE 27. Map showing the chief tinfields of New South Wales, Queensland, Victoria, Western Australia and Northern Territory

in South Australia, and the occurrence of cassiterite in New Zealand is of only scientific interest.

Deposits Unrelated to Any Metallogenetic Tin Province. Tin mining has been conducted in Mexico since the Aztec period The mineral was smelted by the Indians on a small scale before the advent of the Spaniards Tinstone is widely distributed, being found in the states of Durango, Jalisco, Guanajuato, San Luis Potosi, Queretaro, Aguas Calientes, Coahuila and Sonora It occurs in veins traversing rhyolites with porphyritic quartz and feldspar. It is often found disseminated through the country rock in the neighborhood of the veins Tinstone is often found in the form of wood tin Nodules weighing as much as 25 pounds with radiating structure have been found The associated minerals are chalcedony, opal, calcite, iron and manganese oxides, fluorite, topaz, wolframite and bismuth minerals Stanniferous alluvial and detrital deposits occur in Aguas Calientes

Promising occurrences of cassiterite have been found in British Honduras The deposits appear to have been derived from a mineralized area of granite ranges

Tinstone in North America. Tinstone has been found in many of the states of the United States, but in no locality in paying quantities Prospectors in the western parts of the country have stated that cassiterite is often found in the mountain stream gravels California at one time produced small amounts of tinstone. Cassiterite occurs in narrow quartz veins and as replacements of granite in Virginia The ore bodies have been found disappointing in both size and metallic content Periodically reports are received of "tin mines" in North and South Carolina The tin areas have been examined by the United States Government, which reported that "the conclusion is irresistible that tin ore does not exist in this belt in sufficient quantities to permit of a commercially successful operation" Small amounts of cassiterite have been mined from veins and disseminations in granite in Texas and smelted locally

Hess[13] stated that there are tin deposits in the Black Hills of South Dakota, in pegmatites and in quartz They occur in shoots and are nowhere equally disseminated The shoots of profitable tin-bearing rock are ordinarily of small cross section and of uncertain length and depth Their occurrence in narrow dykes necessarily means that in general they can be worked only on a small scale at each place It was reported at one time that an ore body containing 2 per cent of tinstone had been found Stanniferous alluvial deposits were discovered in New Mexico in 1918

Wood tin was found in 1916 in North Lander County, Nevada, in narrow

[13] Hess, "Tin, Tungsten and Tantalum Deposits of South Dakota," *U S Geol Survey*, Bull No. **380**, 131–63.

veinlets associated with specular hematite, chalcedony, quartzite and tridymite

Occurrences of tin of academic interest have also been found in Alabama, Connecticut, Georgia, Idaho, Maine, Massachusetts, New Hampshire, Washington and Wyoming.

Practically the only commercial production of tin from the United States and its territories is from Alaska where cassiterite grains are recovered incidental to hydraulic gold mining and dredging. The known tin deposits of Alaska indicating any future importance are situated in the extreme western part of Seward Peninsula Ear Mountain, Buck Creek Cape Mountain and Lost River have been mined for tinstone on a small scale The tinstone occurs in small veins and in alluvial deposits

Cassiterite occurs in a few places in Canada but none of the deposits is of economic value In Lunenburg County, Nova Scotia, the mineral is found in a quartz vein traversing granite, associated with chalcopyrite, wolframite and zinc blende. It has also been reported as occurring in granular quartz schists in some localities in British Columbia Microscopic crystals have been reported in the gneisses of the graphite area of the Buckingham district

The North American continent to date has shown no tin-bearing mineralized areas

Chapter 5

Mining and Ore Dressing

Mine Working

Detrital deposits on hillsides are the most easily and cheaply worked sources of tinstone when sufficient water is available and where mine tailings can be readily disposed of into lower-lying areas Ground sluicing shifts the loose stanniferous deposits into trenches where the swiftly flowing water carries away the lighter materials, leaving the heavier minerals behind. It is practiced in some mines situated on steep hillsides in Malay, Siam, Indonesia (Netherlands East Indies) and Nigeria Ground sluicing in a modified form is used in many mines to break up the ground, allowing it to float to lower levels from whence it is elevated by gravel pumps or by hydraulic lifts. In very steep places the ground is broken into steps The water is made to run in shallow trenches dug at various heights in the working face It is desired to make as much use as possible of the water and the force of gravity. Low-grade deposits cannot be worked economically by any other method It may be profitably handled by laborers working on hillsides where the rock is decomposed to the depth of several feet With a plentiful supply of water, a coolie will shift several cubic yards a day Damage is always done by the mine tailings

When cassiterite occurs in loose ground or in gravel free from much clay, panning is sometimes used to concentrate the mineral The pan is a large rounded shallow dish, frequently made of wood, in which, by a swirling movement, water is made to carry away the lighter minerals The method has the advantage that it is simple and can be applied where alluvial deposits are small or sparsely distributed

The discussion will be divided into three classes of mine working The first is the open-cut mining of alluvial and detrital deposits, second, dredging of alluvial deposits; and third, lode mining.

Open-Cut Mining

The principal methods of working open-cut mines are by benches or with inclines, gravel pumps, or by hydraulicking and hydraulic elevators Working by benches is used in mining large flat alluvial deposits to 50 to 60 feet deep. The mining face is carried in benches Light trestles across the pit provide the shortest possible level distance to the dump. The maxi-

mum height of the benches is limited, by the danger of caving, to about 20 feet. The overburden is stripped and carried, usually by hand or wheelbarrows, over trestles to the back of the pit. The stanniferous earth is carried to the top in baskets to the washing troughs. The stacked overburden is kept as close as possible to the working face Drainage of the pit is by gravity when possible or by pumps when necessary. All digging is done in the Malay States by a combination pick, mattock and shovel called a "*changkol*" Open-cut mines using only hand methods in moving earth generally advance the faces in a fairly straight line. The overburden and tailings from washing are dumped in the worked-out pit.

Inclines are used extensively in the deeper mines up to 200 feet along granite limestone contacts They are often used in other large open cuts to depths of 50 to 60 feet to hoist the waste to the dumps and to elevate the stanniferous earth to the washing plants Pits are worked in various ways They may be advanced in benches, in which case stanniferous earth is loaded in cars on the floor of the pit and trammed by hand to the foot of the incline At times stripping is handled by cars Open pits on contact deposits are usually long and relatively narrow. In flat alluvials pit faces are fairly straight, as in bench working Basins or pockets of stanniferous earth, occurring too low in the bottom of the pit for convenient car loading, are worked by being carried in baskets to the washing troughs on the pit floor

Gravel-pump mining usually involves hand work to break the material from the bank, ground sluices to carry the material to a sump, pumps to elevate the materials, and washing troughs for concentration Impounding dams are usually built around the tailings storage area, the water running back into the pit and through ground sluices along the base of the working face Clays and sands are broken down into ground sluices with hoes or bars The face slopes are kept steep enough so that material slides to the sluices by means of gravity The gravel-pump method is applicable over widely varying conditions in different types of deposits It requires a delivery of the entire overburden and the stanniferous earth or "karang" to the sump in the pit floor Working faces are thus continuous from the floor to the surface and assume a roughly circular shape around the sump as a center The entire bank is elevated by the pump and must be stored in the tailings piles at the end of the washing troughs The recovery of over 75 per cent of the tin content in ground sluices is rare. Gravel-pump methods provide cheap breaking up of ground, raising of the material at a fairly low cost, with delivery of the earth to the washing troughs well puddled and with the correct ratio of water for washing

The large percentage of clay and sand and small percentage of coarse gravel, combined with a necessity for puddling of the clay, make Malayan tin deposits more favorable for successful gravel-pump operation than most

gold placer deposits. The pumps can handle up to 25 per cent solids, but this pulp is too thick for the washing troughs.

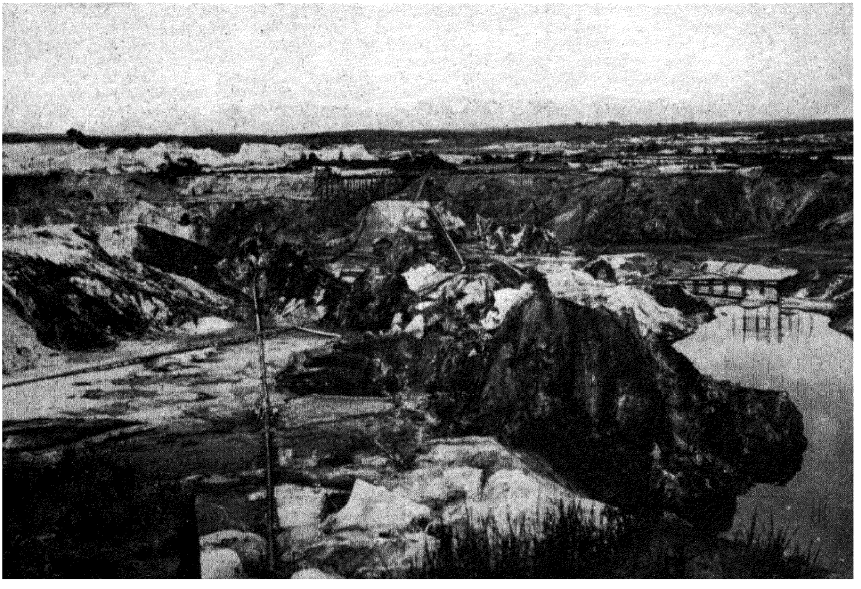
Hydraulicking and hydraulic elevators are used under the same general conditions in tin mining as in the working of gold placers, except that the washing is done in ground sluices or washing troughs. The water is impounded in reservoirs or diverted from streams and conducted in ditches, flumes and pipes to an elevated point above the deposit, and thence to the

(Courtesy Malay States Information Agency)

FIGURE 28. Hydraulic monitors.

working face through pipes. A monitor, much like a large fireman's jet, is attached to the end of the pipe by a reducing fitting. Monitors in use in a tin mine are shown in Fig. 28. A powerful jet of water issues from the nozzle. A three-inch jet under a pressure of 170 pounds per square inch has a potential energy of about 340 horsepower at the nozzle. Such powerful jets break down the toughest deposits rapidly. The important hydraulic tin mines work alluvial deposits that lie too low for gravity disposal of tailings. Hydraulic elevators or large gravel pumps then elevate the material to washing troughs located high enough to allow space for the disposal of tailings. Raising the broken ground by hydraulic elevators is

popular in those localities where sufficient water under natural pressure is available and where dumping areas exist at convenient distances from the mine. The hydraulic elevator consists of a jet of water under a natural pressure of from 60 to 200 pounds, which is caused to shoot out of a nozzle set in a cast-iron frame, up a pipe set parallel to the upward direction of the jet of water. The suction resulting from the rapid passage of the water in the pipe elevates the broken ground from the sump. At the Gopeng mine,



(Courtesy Geological Survey, Federated Malay States)

FIGURE 29. Part of the Gopeng Consolidated Company's mine, in 1921.

shown in Fig. 29, ground is broken, elevated, and treated by means of hydraulic elevators.

In general, the large percentage of fine materials in the banks, absence of coarse boulders, and the necessity for puddling the clayey materials are much more favorable conditions for hydraulic elevators than are found in most gold placers. Hydraulicking and hydraulic elevators in combination have the advantages of completely puddling the material, lifting a high percentage of solids, and employing only small amounts of labor.

Washing Devices. Simple hand washing devices are important in the industry. Panning has been described. The average operator handles 1.25 cubic yards of sandy material per 8 hours. For final concentration,

operation of the pan is the same as for making rough concentrate, but the work is slower.

Sluice boxes vary widely in different localities. The lanchute is coffin-shaped. Material enters near the top, being puddled first if necessary. As the sands pass down the box, a coolie rakes them with a hoe. The volume of water to that of sand is about 10 to 1, the grade 1 to 16, recovery of tinstone about 90 per cent, and the work of a man per shift about 12 cubic yards of well-puddled material.

Clay puddling is often necessary. In small-scale work it is done with hoes in lanchutes, and in larger-scale working by stage treatment in small open pits. About 60 per cent by volume of water is added to the stan-

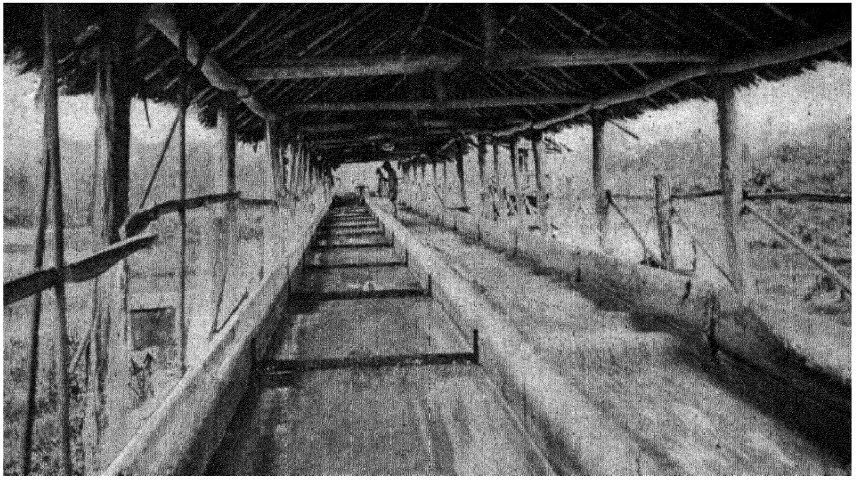


FIGURE 30. Sluice boxes or palongs.

niferous earth on the pit floor. The resultant pulp is scooped across the floor to the foot of one of the banks, in the face of which is a series of small basins. Coolies at each puddle dip the pulp from one puddle to the next, and finally to the lanchute on the surface. In larger workings, power-driven drag machines are used with half-inch discharge screens, the openings of which are maintained by the use of a water jet. The usual method, however, is by high-speed box puddlers which are similar to log washers. These machines have a large capacity but do imperfect work. When hydraulic elevators or gravel pumps are used, clay puddling is eliminated as these machines do this work effectively.

Ground sluices are extensively used in mountainous districts and in hydraulic mines. With a slope of 4 to 8 degrees, their capacity is about 2

cubic yards per hour per foot of width. The recovery is often less than 50 per cent. They are cleaned up either by panning the material in the bottom or by digging it out and concentrating it in a lanchute. The sand in the sluice is allowed to form its own riffles and eddies No blocks or stops are used

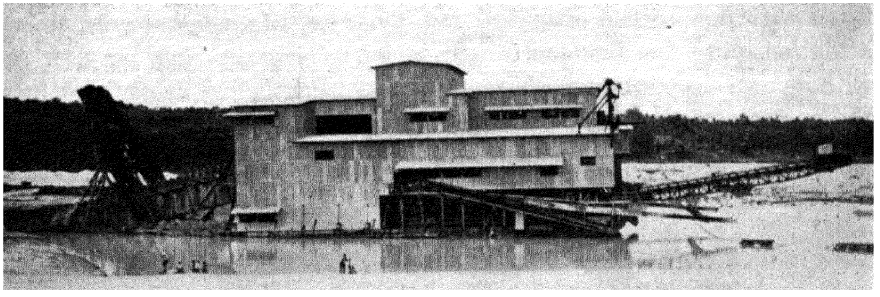
Most of the Malayan tin is recovered in long wooden sluice boxes called "palongs," such as shown in Fig 30 The typical size is 120 feet long, 4 feet wide, with a 3-degree slope Transverse baffles, usually 10 to 12 feet apart, are used The palongs are either single or in sets of two or more side by side, roofed for protection from the weather, and supported on trestles to give them sufficient height for discharge on tailings Their capacity is about one and one-half cubic yards per hour per foot of width The water feed is about 8 to 1 The material flowing through is stirred manually. As heavy sands accumulate, additional baffles are inserted Cleanups, usually daily, are effected by streaming down with a small section of clear water The final concentrates carry 15 to 30 per cent cassiterite These are shoveled into buckets and carried to the tin sheds where they are brought up to standard grade in lanchutes It is stated that palongs save about 80 per cent of the tin delivered to them Water-worn cassiterite is easy to recover, but angular grains are difficult to save Lumps of clay cause serious losses Slight overloading causes heavy loss

Dredging

The first Malayan dredge was started in 1912 Dredging is the most important method of working alluvial and detrital deposits Dredges allow profitable exploitation of low-grade deposits unworkable by hand The principal factors affecting their design for tin mining are absence of boulders, small size of grains of cassiterite, and large amounts of clay The dredges are of two general classes according to their method of digging bucket dredges and suction cutter type These are again subdivided as to their method of recovery of the tinstone into sluice and classifier-jig varieties Tin dredges in the Malay States may dredge 50 feet below water level Some units have capacities of nearly 4,000 cubic yards per day They are of the table type with tinstone-saving tables and a tailings elevator Figure 31 shows a bucket cutter dredge of the Malay States Tin Ltd in operation in the field Dredges smaller in size have been used to a limited extent in Cornwall Figure 32 shows a small dredge of the bucket type with sluice tables

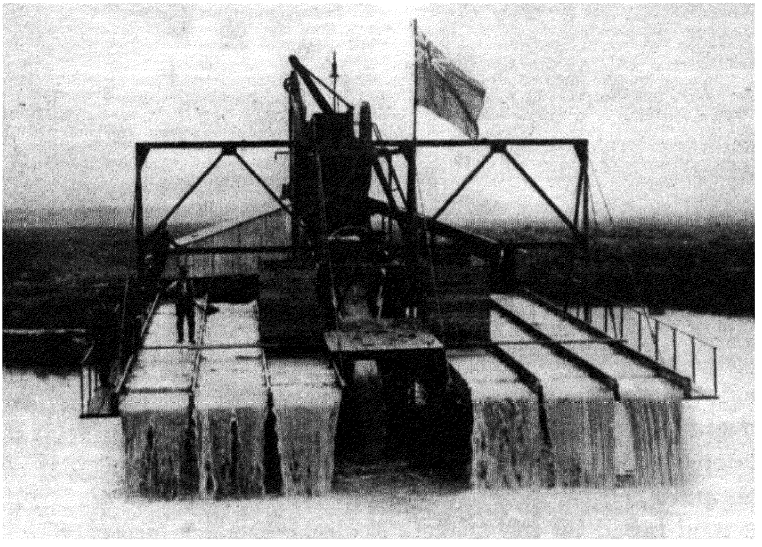
Dredging for tinstone consists of mechanically breaking up and elevating low-lying stanniferous deposits and of treating the elevated deposits The concentrates are retained and the tailings discharged over the end of the dredge. The elevated solids pass into a downward-sloping and revolving steel cylinder or trommel with a powerful jet of water playing on the

solids during their passage through the trommel. Balls of clay and larger pebbles pass out of the mouth of the screen. The broken solids are forced by the jet of water through the screen holes into the recovery system.



(*Courtesy Pacific Tin Consolidated Corp.*)

FIGURE 31. Malay States Tin Ltd. Dredge No. 6.



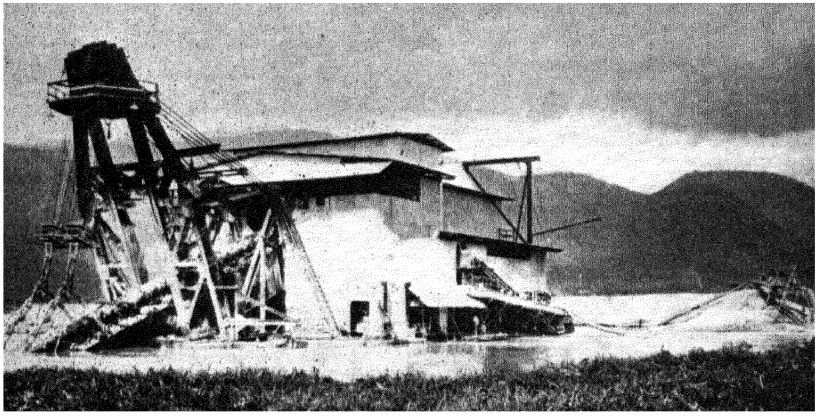
(*Courtesy Werf Conrad, Haarlem, Holland*)

FIGURE 32. Small bucket-type dredge at work in Cornwall.

Many dredges have close-connected buckets ranging from 5 to 12 cubic feet capacity. Experience in working large properties shows that the economical size is about 9 cubic feet with an output of 130,000 cubic yards

per month. Some of the earlier dredges had open-connected buckets of 10 to 12 cubic feet. A typical dredge in operation is shown in Fig. 33.

The difficulty encountered is not in raising the material but in treating it when raised. The tinstone-saving tables required are of such large area that very large pontoons were necessary. Many of the later dredges are fitted with jigs instead of tables, and it has been found that with skilled attention quite fine tinstone can be saved. Generally each jig is driven with its own electric motor, the concentrates from the jigs being taken from the spigots by chutes to a sump. From there they are delivered to a "cleanup" jig or jigs. The jigs are built of steel with four to eight cells



(Courtesy Pacific Tin Consolidated Corp.)

FIGURE 33. Dredge No. 3, Kampar.

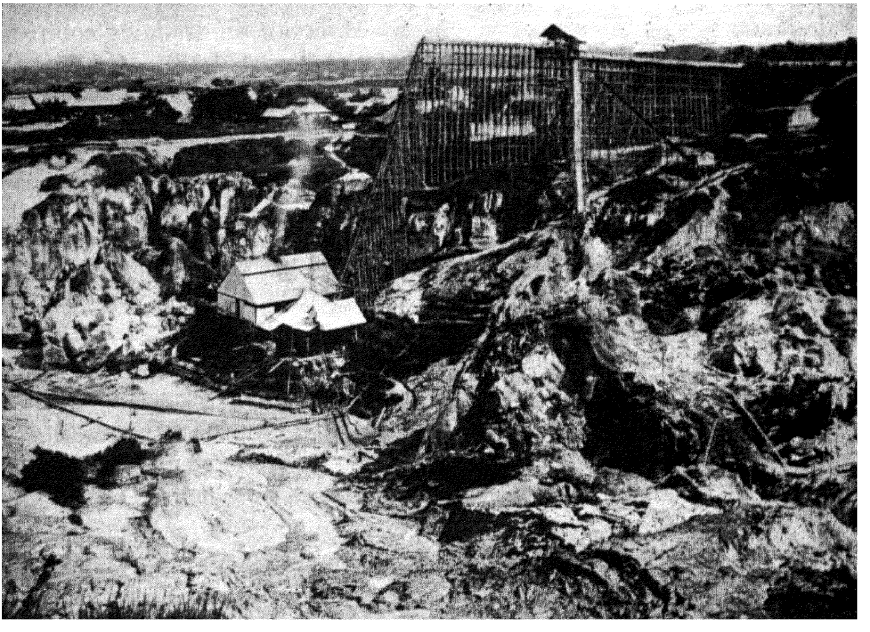
after the style of the old "Harz" type, but varying in design according to the experience of the different designers.

The floating pontoons range from 140 feet to 200 feet long, and from 40 to 60 feet beam. They must be built to withstand the enormous stresses encountered. The dredging depth ranges from 40 to 60 feet, but dredges are now under construction to dig to 100 feet and over.

The spoil raised by the buckets is discharged into a revolving screen supplied with water at a high pressure. The stones pass through the screen and are discharged astern by a tail chute or by a tailings conveyor. The finer material that passes through the perforations of the screen is led to the tables or jigs for treatment. Steam is generally the power used, with water tube boilers to burn wood or coal. In Malaya the "Rawang" coal is burnt on chain-grate stokers, the boilers also being fitted with superheaters. Several companies have electrified their dredges with a

power supply from a central water-power station. It is not considered economical to build a special generating station for less than four dredges.

The water used for washing the material in the screen and tables or jigs is supplied by centrifugal pumps, the quantity varying from 11,000 to 18,000 gallons per minute. The jig-saving dredges require less water. The buckets are of cast steel with manganese steel cutting lips. The later dredges have manganese steel cast buckets with renewable manganese steel cutting lips, the bucket chain being connected by nickel-chrome steel



(Courtesy Pacific Tin Consolidated Corp.)

FIGURE 34. Suction dredge and elevating gear at Seng Loong Mine at Ampang.

pins. The open-connected bucket is generally of the "built up" type with manganese steel pins.

The suction cutter dredge differs from the usual bucket type in the manner of elevating the ground. A rotating cutter and a powerful gravel pump do the work of the buckets. The cutter is ordinarily of the propeller type, being in some cases over four feet in diameter. It is mounted at the free end of a long flexible steel shaft. When the cutter blades rotate under water, they break up the ground against which they are pressed. The broken ground falls into a large orifice connected by a steel pipe to a power-

ful gravel pump mounted on the dredge proper A suction dredge operating in the Malay States is shown in Fig. 34 For specific details and greater information on dredges, their construction and operation, the reader is referred to mining engineering texts.

The advantage of dredging is that low-lying deposits in swampy or very wet ground can be worked at a lower cost per cubic yard than by any other method. Extensive low-grade areas not previously economically workable have been treated with success by dredging.

Dredging for tin is normally the cheapest form of mining, provided care is taken that the property is properly prospected and tested and the dredge is designed to suit the property. Many Malayan tin dredging companies have paid a 25 per cent dividend for a number of years Ground that contains 1 katti of tin ($1\frac{1}{3}$ pounds) per cubic yard is considered rich Most companies are paying well on lower values than this With dredging practice it has been prophesied that areas as low in tin content as one-quarter pound tinstone per cubic yard may eventually be profitably dredged

After World War II, dredges were built to work 7,000 hours per year and excavate 4,000,000 cubic yards of alluvial deposit They are equipped with an endless chain of 128 alloy-steel buckets carried on the digging ladder These buckets weigh 4,000 pounds each and discharge their load at the rate of 270 cubic feet a minute into a large revolving screen where the bigger pieces of rock are eliminated. Then powerful streams of water carry the sludge over a series of jigs until the tin ore is eventually separated out, concentrated, and prepared for shipment to the smelter

Each dredge is a self-contained powerhouse and pumping station The water requirements of over 2,000,000 gallons per hour would supply the needs of a city of over a quarter of a million inhabitants Twelve thousand kilowatts are generated by supercharged diesel engines directly coupled to generators Elaborate systems of automatic relays and safety devices are fitted, and indicating and recording apparatus facilitates rapid and centralized control The pilot house is 43 feet above deck level and the highest point of the dredge some 75 feet above deck is approximately the height of an eight-story building. The dredges are about 220 feet long and 100 feet wide, have a displacement of about 4,000 tons and are sufficiently seaworthy to withstand their long sea journey of almost half the circumference of the globe.

Lode Mining

Where the country rock is much decomposed and the tinstone veins are narrow, the ground may be mined by the methods used for detrital and alluvial deposits. Pegmatite and quartz veins are usually more resistant to weathering agencies than most surrounding minerals and rocks. Often

in tropical climates the country rock can be readily broken down by hand labor, whereas the lode itself may require blasting Narrow stanniferous veins may be worked through the weathered zone in this manner

In undecomposed rock, breakdown in the working face is accomplished by drilling and blasting The broken rock is hauled to the surface and to the mill where it is usually crushed in rock breakers or jaw crushers, then pulverized by stamp batteries or grinding mills Often hand picking is practiced between the jaw crushers and the stamp battery The ore-dressing flowsheets which follow give the treatment of various types of ores in considerable detail

Ore Dressing

Flowsheets of Various Mines

Ore-dressing methods of tin-bearing materials will differ widely, depending upon their type and source The simplest dressing flowsheet is shown by those concentrates from Malayan alluvial deposits Bolivian vein deposits are of several different varieties and degrees of complexity Separation of the cassiterite is easy in the simple oxidized ores where quartz feldspars and iron oxides are the accompanying minerals Concentration of the cassiterite from the complex sulfide ores is difficult not only because pyrite, chalcopyrite, bornite, arsenopyrite, wolframite, bismuth and silver compounds, galena and sphalerite are the accompanying minerals, but because the mines are inaccessible and progress is slow. Cornwall vein ores are low grade, more or less complex The cassiterite is finely dispersed The ore-dressing methods differ greatly from those in Bolivia Most of the flowsheets are antiquated The various procedures for ore dressing of tin minerals will be discussed as well as one of the best examples of tailings reworkings

In a typical flowsheet of a Malay placer tin plant, coarse material is removed on a screen. Relatively large amounts of low-grade concentrates are made in sluices. This concentrate is often cleaned up by hand on small film sizing tables and hand jigs. The gravel or stanniferous earth is excavated by the mining methods previously described (either open-pit mining, hydraulicking or dredging). On dredges, a revolving stone screen with one-half to three-quarter inch holes is ordinarily used for sizing and disintegrating In hydraulic mining, a sluice grizzly does this work. In open-pit mining, the disintegrator resembles a log washer. In some cases it consists of a horizontal pan in which the earth and gravel are stirred and raked by rods set in revolving radial arms The oversize from the sizing mechanism goes to waste; the undersize to sluices where separation is made into tailings, containing probably 10 to 15 per cent of the tinstone in the original feed, and concentrate. The sluices or palongs have been described under washing devices.

The concentrates, depending upon their rate of accumulation, are collected at intervals from several hours to a week. The feed of pulp is diverted, the concentrates washed down with clear water and gathered by shoveling. Crude concentrates run 10 to 50 per cent cassiterite, the balance being ilmenite, iron ores, pyrite, black sand and other heavy minerals.

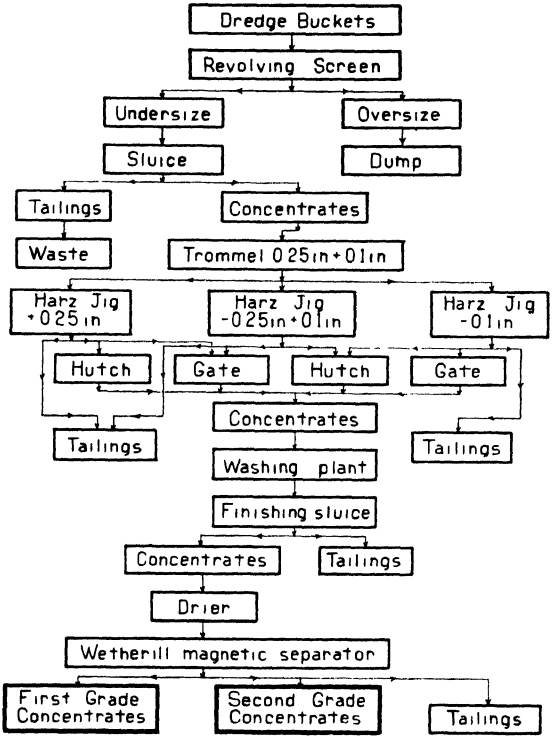


FIGURE 35 Flowsheet of a placer tin dredging plant in southern Europe (*Portuguese American Tin Co*)

The concentrates go to the cleaning sheds for further treatment in lanchute sluices These are 10 to 12 feet long, 9 to 10 inches deep, converging from 3 to 5 feet at the head end to about 15 inches at the discharge end. Water is supplied the full width at the head end over a 6- to 7-inch high weir board. At first the lanchutes are operated with a fairly strong stream of water, while coolies hoe the material to remove the bulk of the sand tailings These ordinarily run about 0.1 per cent tin Weak streams of water are then used to collect the coarse portions of the concentrates at one end of the sluice. This coarse rough concentrate is jigged by hand in sieves, 12 inches in diameter, 3 inches deep, with apertures of 60 to 80

mesh, into concentrates for the market and middlings returned to the sluice for reworking The material remaining in the lanchute after coarse concentrates are removed is further washed with a heavy stream, at the same time being hoed up the slope, giving fine concentrates for the smelter and middlings to be reworked The fine concentrates run 70 to 76 5 per cent tin

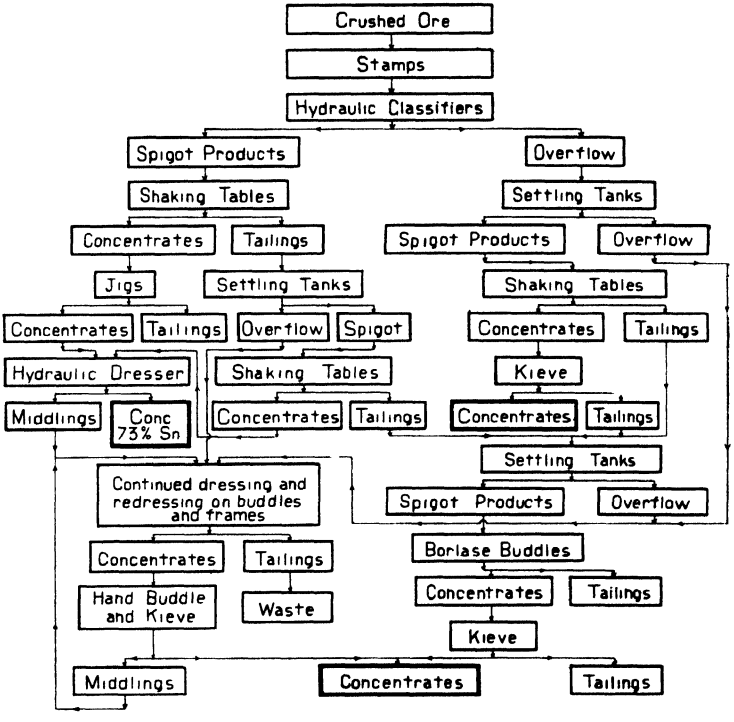


FIGURE 36 Flowsheet of a Tasmanian plant (Anchor Mine)

Ore dressing of tinstone from alluvial deposits involves no crushing It is essentially two-stage sluicing with hand jigging of coarse-finishing sluice concentrate

In a placer tin dredging plant in Southern Europe, Harz jigs are used in addition to sluices The simplified flowsheet is given in Fig 35 [1]

As an example of the treatment of simple low-grade ores, the simplified flowsheet of a Tasmanian plant working a cassiterite in granite deposit where the mineral is finely disseminated (50 per cent passes 200 mesh) is given in Fig. 36.[2] The ore runs 0 10 to 0 16 per cent, the tailings 0 03 per

[1] *Eng Mining J.*, **104**, 1109 (1917)
[2] *Mining Sci Press*, **109**, 65 (1914).

cent, the concentrates 68 to 73 per cent tin The recovery is 70 to 75 per cent. The ore dressing consists essentially of gravity concentration by repeated roughing of roughly classified products. Repeated cleaning of concentrates is practiced Middlings are retreated without regrinding

Treatment of Complex Tin Ores. The complex tin ores fall into four general classes The first includes Bolivian sulfide ores low in lead and

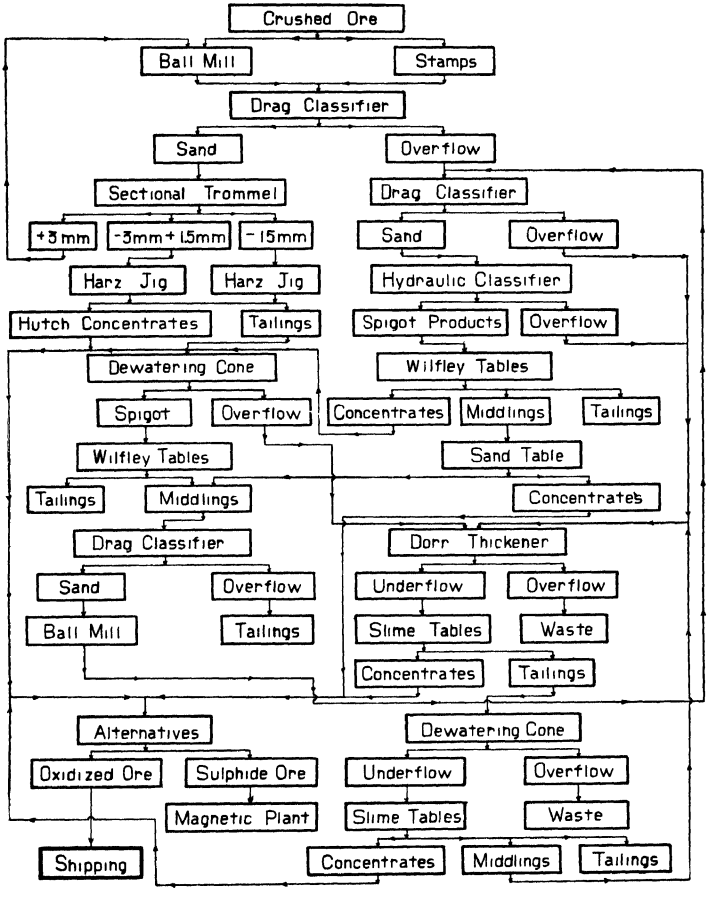


FIGURE 37. Flowsheet of Avicaya mill

silver but carrying no other metals of economic value As examples the flowsheets of the Avicaya mill, Pazna District, Bolivia, the Llallagua magnetic plant, the Santa Ana unit of Oploca, the Victoria plant of Patiño Mines near Catavi, as well as Bolivian flotation practices are given The ores of the second class are the same as the first but carry high silver values and economic amounts of gold, lead and copper. As an example, the flow-

sheet of the Machacamarca, Bolivia mine, Socavon de Oruro is given. Cornish ores containing workable quantities of tungsten and arsenic constitute the third class, represented by the flowsheet of the East Pool mine The ores of the fourth class are complex tin, tungsten and lead minerals, worked for all three metals, as represented by the Butler mine in New South Wales

Class I. Avicaya mill, Bolivia The ore is partly oxidized, being cassiterite with a siliceous and iron oxide gangue, and partly cassiterite and pyrite in quartz with chalcopyrite, other sulfides, feldspar and tourmaline. The average ore runs 5 per cent tin, concentrated to 60 to 65 per cent from the oxidized portions and 50 to 55 per cent from the sulfide

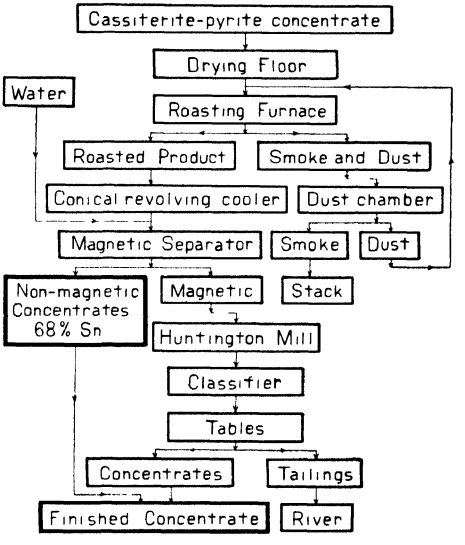


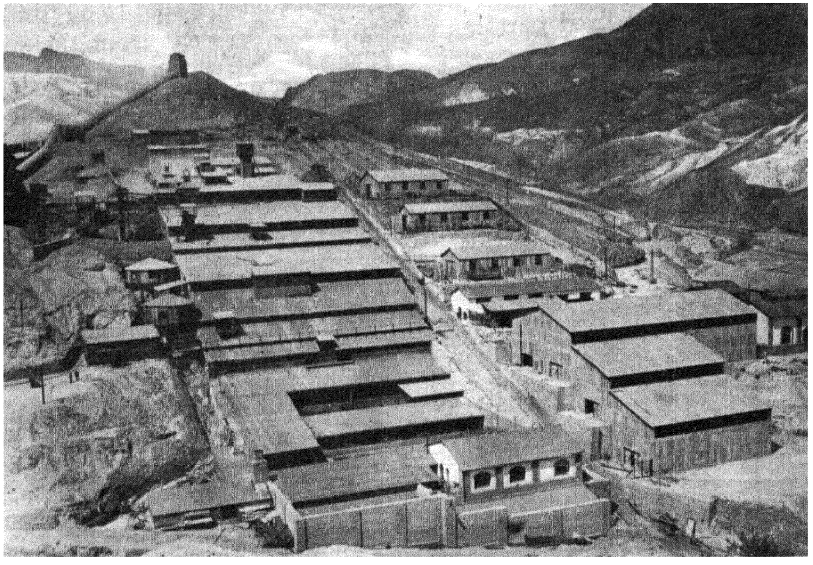
FIGURE 38 Flowsheet of Llallagua magnetic plant

parts The tailings run less than 1 per cent tin The flowsheet,[3] given in Fig 37, shows fine grinding, step gravity concentration beginning at 3 mm particles Repeated treatments of fine sand are made, giving concentrates for magnetic separation (omitted with the oxidized ore) and middlings for regrinding and further concentration.

At the Llallagua magnetic plant[4] (Fig 38), the ore is a cassiterite arsenical pyrite from the gravity concentration mill similar to the one just given above. The tin recovery is 93 to 95 per cent with a concentration ratio about 2 to 1. The concentrate, mostly smaller than 1 mm size, is roasted to render it magnetic in a five-hearth furnace, similar to the McDougall,

[3] *Ibid.*, **114**, 774 (1917), **115**, 343 (1917)
[4] *Eng. Mining J*, **100**, 513 (1915)

until the sulfur content is lowered from 25 to 27 per cent to 10 to 12 per cent. The sulfur oxidation furnishes the necessary heat. The roasted concentrate, running 33.3 per cent tin, 12.76 per cent sulfur, 29.3 per cent iron (feed was 31.8 per cent tin, 25.0 per cent sulfur, 24.5 per cent iron), is then cooled, wet, and magnetically separated into a nonmagnetic concentrate running 68.05 per cent tin, and magnetic tailings, which are reground and then classified into tin concentrate and waste tailings. The final concentrates run about 68.67 per cent tin, 4.75 per cent iron and 3.58



(Courtesy Cia. Minera y Agricola Oploca de Bolivia)

FIGURE 39. General view of Santa Ana concentrator. Capacity 250 tons tin ores per 24 hours.

per cent sulfur, with small amounts of nickel, copper, bismuth, lead, zinc, silver, TiO_2, WO_3, lime and silica. The tailings run about 3 per cent tin.

An example of a Bolivian concentrator, the Santa Ana 250-ton unit, of Cia. Minera y Agricola Oploca de Bolivia at Chocaya, is shown in Fig. 39.

As an example of a Bolivian tin ore-dressing plant, Fig. 40 gives a flowsheet of the Victoria ore-dressing plant of the Patiño Mines and Enterprises Consolidated Inc., near Catavi, Bolivia. The ore which comes from the company's various mines is crushed, washed in drums and shaking sieves and separated according to grain size. The ore of more than 3-inch grain size passes into a sorting conveyor which retains all ore with less than 0.5

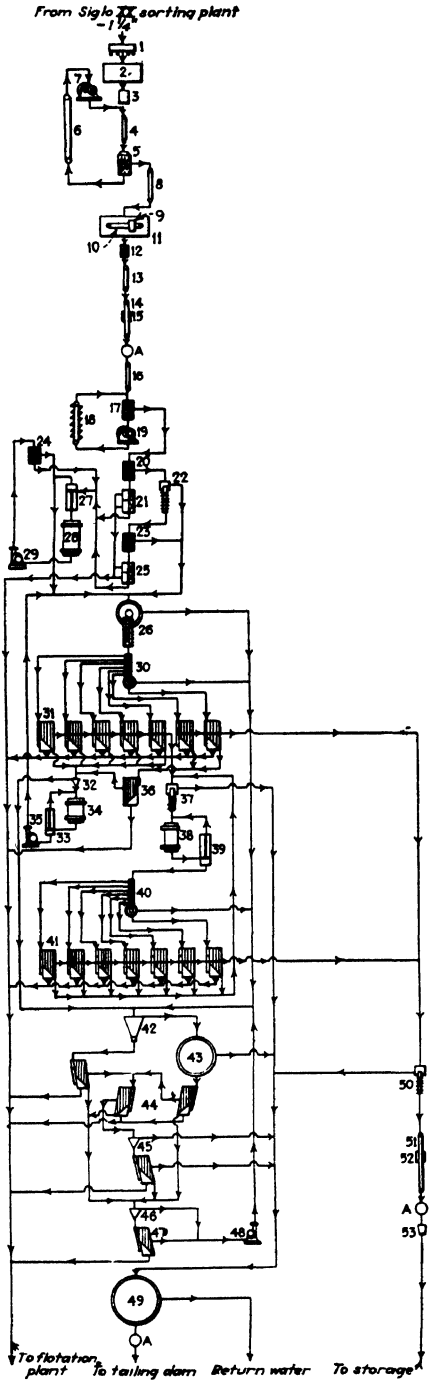
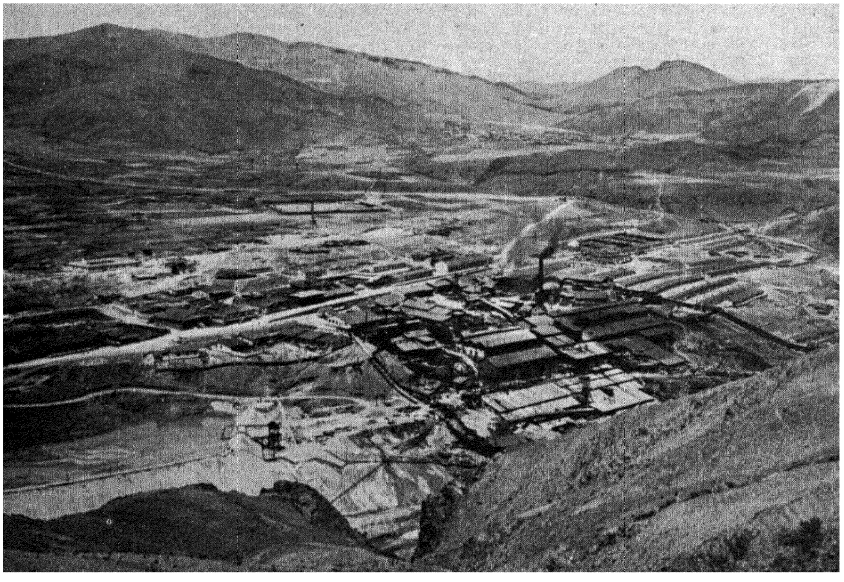


FIGURE 40 Flowsheet of Victoria plant after completion of remodeling

1 35-metric-ton cars
2 2,500-metric-ton bin
3 Eight chute feeders
4 Two variable-speed conveyor belts
5 Four 48x90-in trommels 20-mm x 2-in slots
6 One 24-in conveyor belt
7 Two 57x20-in rolls
8 One 24-in conveyor belt
9 One 24-in conveyor belt
10 One distributor
11 3,100-metric-ton bin
12 Five 18-in apron feeders
13 Two 20-in conveyor belts
14 One 20-in conveyor belt
15 One Merrick weightometer
16 Two 16-in conveyor belts
17 Eight 6-mm vibrating screens
18 Two 16-in elevators
19 Four 42x16-in rolls
20 Eight 3-mm vibrating screens
21 12 coarse jigs, 3-6 mm
22 Four 10-in drag belts
23 Eight 1-mm vibrating screens
24 Eight 1-mm vibrating screens
25 Twelve fine jigs, 1-3 mm
26 Two bowl classifiers
27 Six Dorr duplex classifiers
28 Six 5x10-ft rod mills
29 Twelve 3-in pumps
30 Six hydraulic classifiers
31 Deister Plat-O tables
32 Two dewatering cones
33. Two duplex classifiers
34 Two 5x5-ft ball mills
35 Two 3-in pumps
36 Four Deister tables
37 Two drag belts
38 Four 5x10-ft rod mills
39 Four duplex classifiers
40 Four hydraulic classifiers
41. Deister Plat-O tables
42 Eight cones
43 Eight thickeners
44 Forty-six Deister - Overstrom tables
45 Sixteen thickening cones
46 Three thickening cones
47 Three re-treatment tables
48 Two 2-in pumps
49 One 75-ft thickener
50 Three 12-in drag belts
51 One 16-in conveyor belt
52 One weightometer
53 One aerial tramway
A Automatic samplers

per cent tin. The next step is to reduce the ore to a $1\frac{1}{2}$-inch grain size in a cone mill. The ore, together with the smaller grain sizes recovered earlier, is stored in a 2,500-ton bunker from which it is withdrawn in 35-ton lots to the dressing plant. The procedure can be seen in the illustration. From the Victoria ore-dressing plant, the concentrates of every grain size pass on to the flotation plant. They are then made into uniform grain size and flotated; this process brings about only the separation of the pyrite. Inasmuch as a concentrate with a tin content of 62 per cent may



(*Courtesy Patiño Mines & Enterprises Consolidated Inc.*)

FIGURE 41. A general view of the reduction plant at Catavi with the 20th Century tin mine in the background.

contain no more than 4.5 per cent SiO_2 and 1.5 per cent Al_2O_3 without causing a penalty deduction, an attempt is made in the table and settling operations to obtain a concentrate which is as free as possible from silicon and aluminum oxide.

A general view of the concentration and reduction plant at Catavi with the 20th Century tin mine in the background is shown in Fig. 41.

Barnitzke[5] reported on a process using reducing gases instead of air in flotation. A number of suggestions are found in the patent literature.[6]

[5] J. E. Barnitzke, *Metall u. Erz*, **25**, 621–4 (1928).

[6] *German Patent 427,649*; *U. S. Patent 1,628,046*; *British Patents 292,832* and *311,239*.

Handy and Beard[7] suggested flotation in the presence of an alkaline electrolyte, that is, a solution of an acid salt in sodium carbonate (copper sulfate) a collector such as oleic acid and a depressant such as sodium silicate Gerth[8] also has investigated this method of separation of tin-stone from quartz matrix

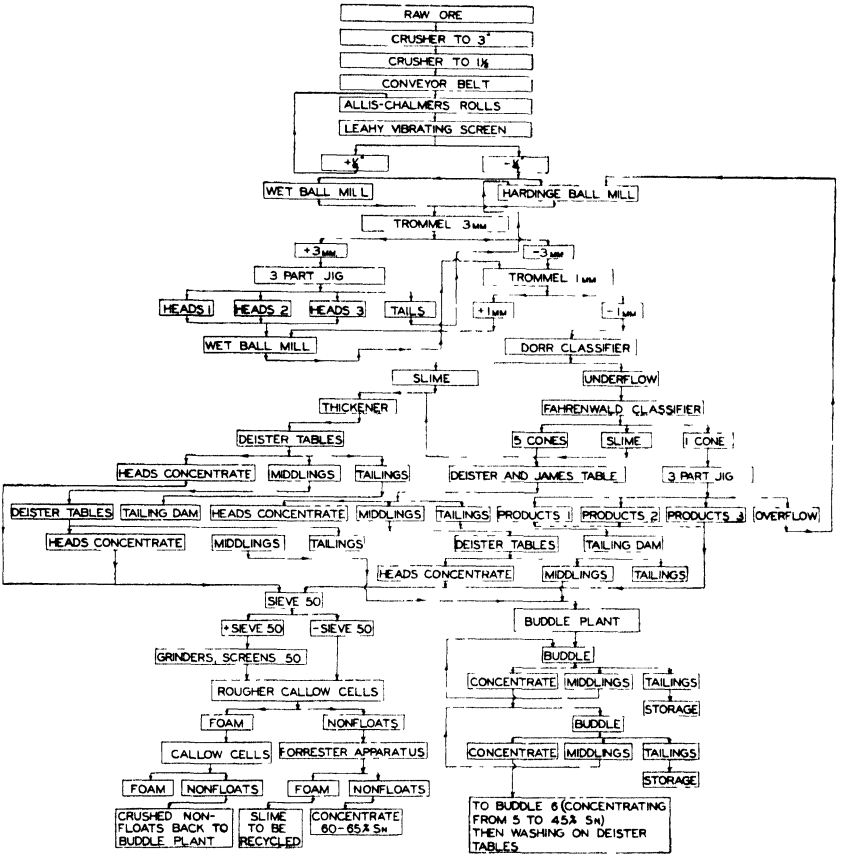


FIGURE 42 Flowsheet of ore dressing process in Bolivia

The dressing of Bolivian ores is given in the flowsheet (Fig. 42). The plant has a mean capacity of 200 to 300 tons per 24 hours It is interesting to note that the tin concentrates which remain in the flotation residue are subjected to another wet treatment on "shaking tables.'

Gau and Jameson[9] gave the flowsheet of Leeuwpoort Tin Mines, Ltd.,

[7] Handy, and Beard, *U. S Patent 1,737,717*

[8] G Gerth, *Metall u Erz*, **27**, 527 (1930)

[9] **W. J Gau, and J I Jameson, Third (Triennial) Empire Mining and Metallurgical Congress, South Africa, 1930.**

Warmbaths, South Africa, involving concentration by tables and thickeners, roasting of pyritic concentrates, further concentration by magnetic separation and flotation.

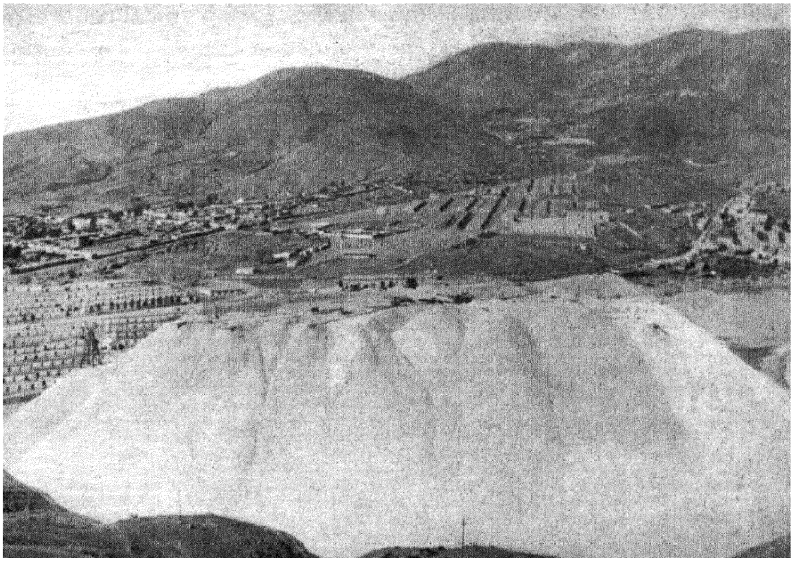
Gaudin and coworkers reported on flotation studies on Bolivian ore. Gravity separation did not recover more than an average of 50 per cent of the tin mined in Bolivia. Flowsheets were suggested for Canutillos involving leaching with salt and sulfur dioxide;[10] for Oploca[11] ore by the following steps: (1) Grind to 95 per cent minus 200 mesh in nonmetallic mill. (2) Float sulfides with xanthate at natural pH (about 4.0). (3)

(Courtesy Patiño Mines & Enterprises Consolidated Inc.)

FIGURE 43. View of the sink and float plant which partially conceals the parallelly-situated old crushing and picking plant. A portion of the partly reworked old Siglo XX dump is visible at the extreme right center.

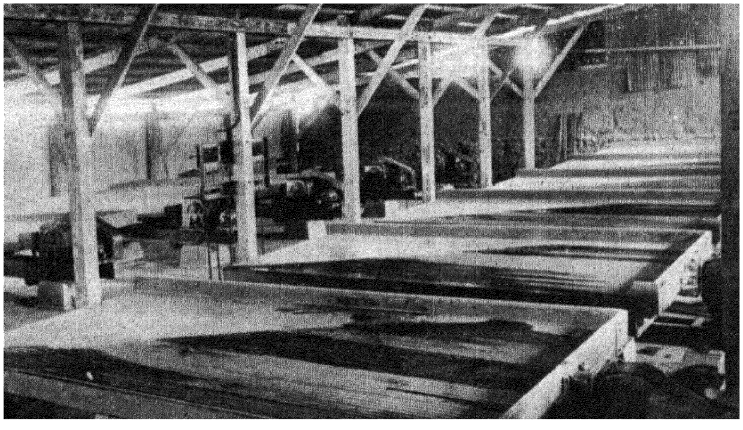
Float cassiterite at pH about neutral, using oleic acid, a hydrocarbon oil, and Calgon. (4) Regrind cassiterite rougher concentrate. (5) Leach reground product with acid and wash to remove dissolved iron. (6) Float leach residue at pH about neutral with minute quantities of same reagents as step 3; for Colquiri ore[12] involving crushing and grinding so that 75 per cent passes through 200 mesh, effecting sulfide flotation with copper sulfate, ethyl xanthate and pine oil, thickening and effecting tin concentration by soap flotation with retreatment of rejects; and for Sañ José ore[13] with selective flotation following fine grinding.

[10] *Eng. Mining J.*, **147**, No. 10, 54–9 (1946).
[11] *Ibid.*, No. 11, 72–3 (1946).
[12] *Ibid.*, No. 12, 68–72 (1946).
[13] *Ibid.*, **148**, No. 3, 70–2 (1947).



(Courtesy Patiño Mines & Enterprises Consolidated Inc.)

FIGURE 44. View of the Siglo XX dump which gives an indication of the tonnages available for retreatment in the sink and float plant. At the time this photograph was taken only the picking plant was in existence. A portion of it can be seen in the background of the dump. The present dump is larger.



(Courtesy Patiño Mines & Enterprises Consolidated Inc.)

FIGURE 45. Centenario. Concentrating tables.

Patiño Mines & Enterprises started a sink and float plant (**Fig. 43**) operating on the Siglo XX dump shown in Fig 44 Typical concentrating tables of the gravity separation type are shown in Fig 45 (Centenario)

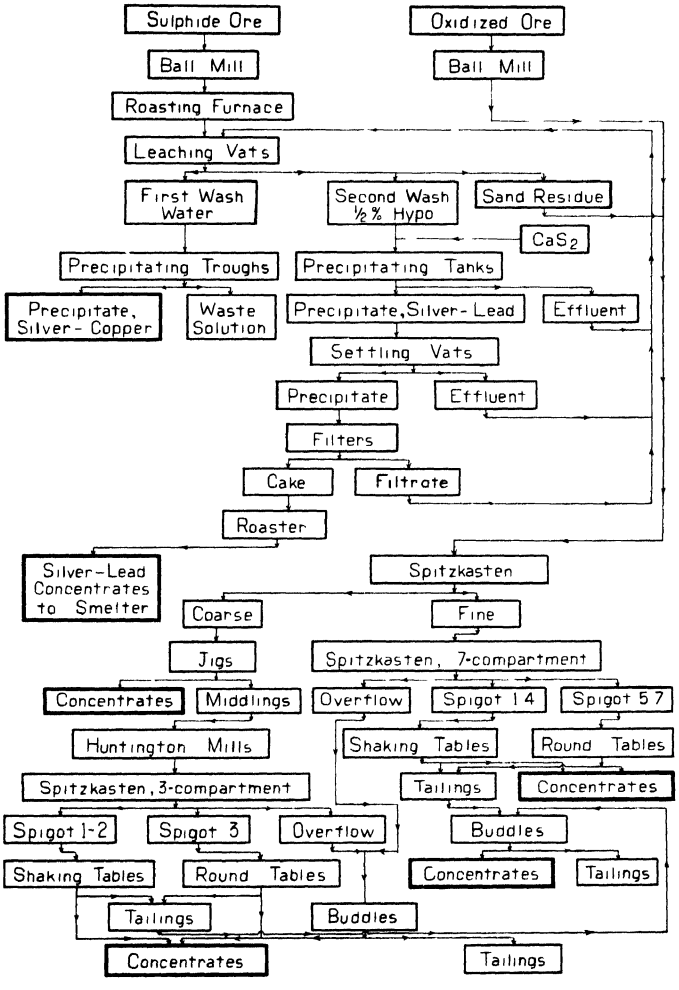


FIGURE 46 Flowsheet of Socavon de Oruro

Class II As an example of the second class of complex ores, the flowsheet[14] is given in Fig 46 of Socavon de Oruro from which the ore is a complex sulfide and oxide mineral containing tin, silver, gold, lead, copper, iron, antimony and arsenic in a siliceous gangue The original ore runs 3 to 10 per cent tin with 39 ounces of silver per ton Fine grinding is

[14] *Mining Mag.*, **6**, 301 (1912)

practiced in screen-discharge ball mills in the dry way. The sulfide ore is roasted and leached in two stages to recover silver, gold, copper and lead. This is followed by gravity concentration of the leaching-plant tailings. In roasting, the sulfur is reduced from 30 to 3 per cent with chloridization (4 per cent sodium chloride) on the last hearth of the three-hearth roasting furnace. The concentrates from the jigs and sand tables run better than 60 per cent tin, while those from the slime tables run 30 to 60 per cent and from the buddles[15] less than 30 per cent. Round tin-concentrating buddles are illustrated in Fig. 47.

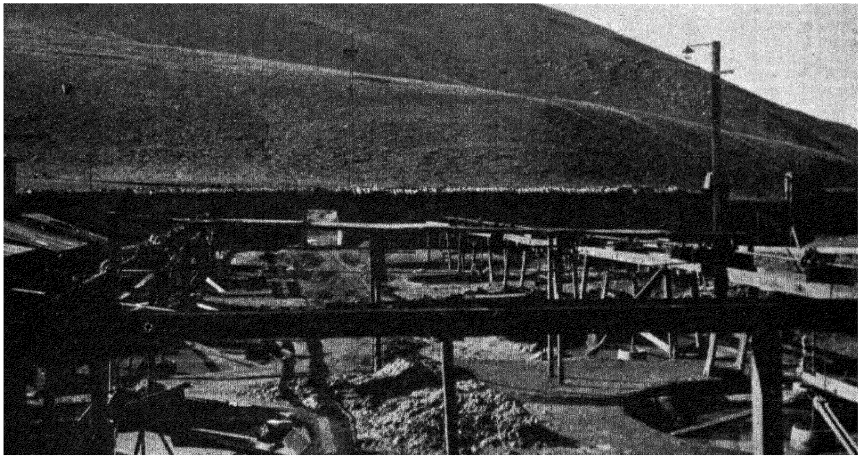


FIGURE 47. Round buddles for tin concentration, in Bolivia.

Class III. The third class of ore is exemplified in the dressing methods of the East Pool mill[16] in Cornwall, given in Fig. 48, where a complex mixture is found containing finely disseminated cassiterite along with wolframite, arsenopyrite and chalcopyrite in a siliceous gangue. The ore runs 0.5 to 1 per cent tin, 0.5 to 1 per cent As_2O_3 and 0.25 to 0.5 per cent WO_3. The recovery is about 60 to 70 per cent tin. Coarse crushing and gravity stamps are used, followed by gravity concentration to reject rocky tailings. The rough concentrates are roasted to recover arsenic and make iron magnetic. This is followed by a leaching treatment to reduce the iron

[15] These are stationary washers in which the slope is so gentle that the ore gradually builds up until a bed 10 or 12 inches deep has accumulated. The washing is then stopped and the products cleaned out. The building up of the sands is regulated by adjusting the tailboards which prevent the ore from rolling off the table. They are made convex conical, concave conical, and rectangular.

[16] *Mining Mag.*, **6**, 115 (1912).

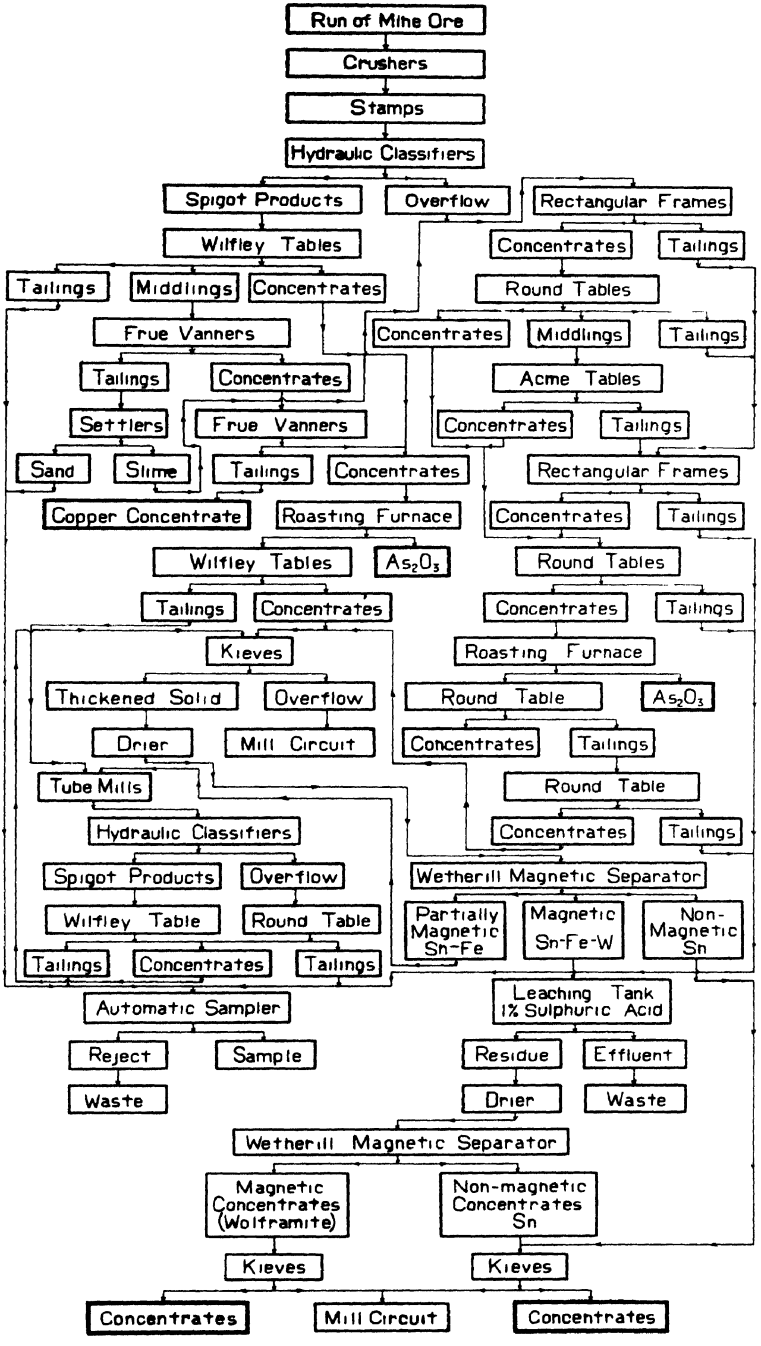


FIGURE 48. Flowsheet of the East Pool mill.

content, and a two-stage magnetic separation to separate tin and tungsten Notwithstanding the usually very fine dissemination of the cassiterite, regrinding of tailings is not practiced As a result, practically no tin not freed in the primary grinding is saved.

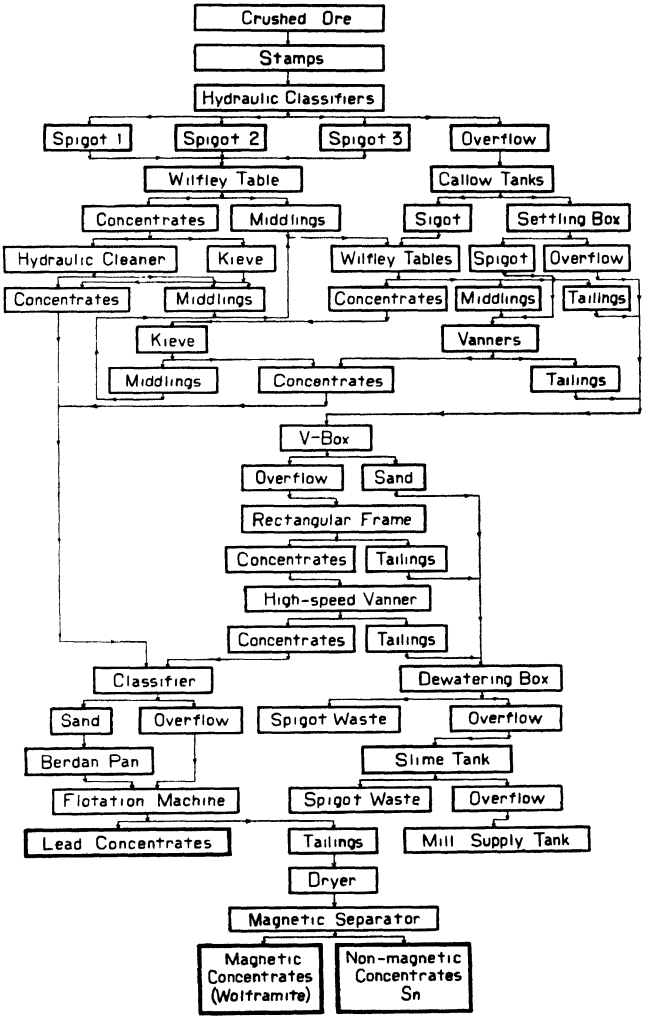


FIGURE 49. Flowsheet of the Butler mine

Class IV. The fourth class of complex tin ores may be exemplified by the flowsheet[17] of the Butler mine in New South Wales, given in Fig. 49, where a complex tin-tungsten-lead ore is worked. The recovery is about

[17] *Eng Mining J.*, **106**, 530 (1918).

80 per cent of tin, 68 per cent WO_3 and 64 7 per cent of the lead. Jaw crushers and gravity stamps break up the original material, followed by collective gravity concentration on tables, vanners and frames This is coupled with flotation of gravity concentrate to separate the lead Tin and tungsten are separated magnetically from the flotation tailing

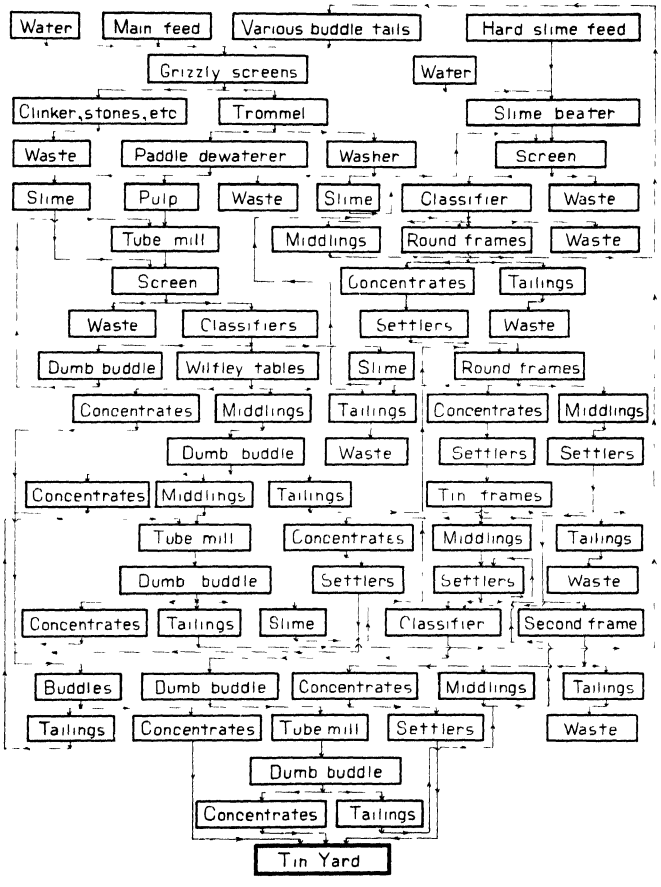


FIGURE 50 Flowsheet of the Treskillard Minerals in Cornwall

Treatment of Tailings. As an example of practice for the recovery of tin from tailings running only 0 6 per cent tin, the flowsheet[18] of the Treskillard Minerals in Cornwall is given in Fig 50 The large tonnage of tailings stacked by the old Grenville, West Frances, South Frances, and West Basset mines, in Cornwall, is treated. A recovery of about 75 per cent has been obtained, or over 9 pounds of tin concentrate (54 per cent metal)

[18] *Eng. Mining J.*, **124**, 773 (1927)

per long ton of material treated. No novel tin-concentrating appliances are used. The apparently crude appliances used for the concentration of tin ores are susceptible of fine adjustment and delicate work Efficient concentration and minimum loss of metal are obtained by separate treatment of products of varying degrees of grade and of coarseness All products alike in grade and size of particles, irrespective of origin, must be treated together Stress is laid on the importance of classification In general, a machine that is delicately adjusted for one class of product will not treat any other class efficiently

Thorough classification begins immediately after the primary grinding by tube mills The discharge goes through a series of classifiers and then to Wilfley tables where each pair of tables treats only material supplied by its own classifier These tables make a head which goes for final treatment to the tin yard, where the heads from each pair of tables are buddled separately Before being reground, the Wilfley middlings are buddled. This buddling yields a small amount of high-grade head and a small tailing, suitable for return to the primary grinding circuit.

The secondary fine grinding of tailings in this flowsheet is particularly to be noted as well as the very efficient use of the buddle It is stated that total treatment costs are about 16 cents per long ton of ore treated It is obvious that this type of plant requires highly skilled operation and close supervision

Sale of Concentrates

The purchasing of tin concentrates by the smelters is chiefly done by contract, usually on an annual basis, calling for delivery of a certain definite tonnage, although some of the smelters make a practice of buying small parcels whenever offered for sale Usually 96 to 98 per cent of the tin content of the concentrates is accounted for, depending on the kind of ore. The concentrates must run ordinarily at least 60 per cent tin. Bolivian tin concentrates, or "barilla," usually contain 58 to 70 per cent tin, while those from the alluvial deposits, especially the Straits, contain 70 to 76 per cent tin, the balance being slag-forming constituents. The tin in Straits concentrates is easily reduced with the production of a resultant metal of high purity, while the treatment of the Bolivian concentrates is extremely complicated.

The procedure involved in calculating the amount of the payment for the ores differs somewhat with the different individual smelters. In some cases payment for all the tin is made, the smelting losses and other factors being taken care of in the treatment charge. The value of the tin is usually determined by taking the average of the prices ruling on the London Metal Exchange for "spot" and "three months standard" tin as quoted during the second calendar month after the shipment is made. This means

that if a shipment be made on January 14th, the liquidation would be made as per the average of the quotations for the month of March

The returning charge and final settlement for the ore is made in pounds sterling The rate of exchange in recent years has been an important factor in governing the net returning charge. Therefore, to offset fluctuations in the rate of exchange and to stabilize the returning charge, the value of the pound sterling may be fixed for the duration of the contract All transactions are based on a ton of 2,240 pounds.

The concentrates are nearly all purchased on a 60 per cent tin basis For each unit (1 per cent, or 20 pounds per short ton, 22 4 pounds per long ton) or fraction thereof above or below 60 per cent, the returning charge is reduced or increased at the rate of x shillings per unit The net returning charge varies The basic price for standard tin is generally taken and the returning charge is increased or decreased at a fixed rate for each pound sterling the settlement quotation is above or below the basic price One per cent of sulfur is allowed free and is penalized at the rate of y shillings per unit or fraction thereof over 1 per cent

Five per cent of iron is allowed free and is penalized at the rate of y shillings per unit or fraction thereof over 5 per cent. The usual splitting limits on assays are as follows: tin 0 5 per cent, sulfur 0 2 per cent, iron 0 2 per cent.

The undesirable constituents, such as lead, copper, arsenic, antimony, and bismuth, are not penalized specifically, but an increased treatment charge is made to cover costs occasioned

A somewhat different ore purchase contract is employed in connection with the American Texas City smelter where the concentrates are acid-treated in preparation for smelting It is to be noted that payment is for "insoluble tin."

Deliveries are to be in 10 long-ton lots or greater Lots containing less than 10 tons would be subject to a deduction of a fixed charge per lot to cover the extra cost incident to sampling and analysis of such small lots.

The price would be A cents per pound of insoluble tin contained in the ores less the following treatment charges, unit deductions to cover smelter losses, and penalties for impurities:

The treatment charge would be B dollars per long ton of concentrates assaying 60 per cent insoluble tin, with a decrease of C dollars per ton for each 1 per cent of tin above 60 per cent and an increase of D dollars per ton for each 1 per cent of tin below 60 per cent, down to 40 per cent. For concentrates assaying below 40 per cent tin, the treatment charge would be $(B + 20D)$ dollars plus E dollars for each 1 per cent tin below 40 per cent. Material containing less than 18 per cent tin would be subject to rejection.

The unit deduction would be one unit for concentrates containing 64

per cent tin, increased by 0.025 unit for each 1 per cent tin content below 64 per cent.

The impurity penalties are as follows·

	% FREE	CHARGE FOR EXCESS	MAXIMUM CHARGE PER TON
Antimony	0 2	3 00 *F* dollars per unit	—
Arsenic	0 4	2 50 " " " "	—
Copper	0 2	3 00 " " " "	—
Lead	0 2	3 00 " " " "	10 00 *F* dollars
Bismuth	0 2	3 00 " " " "	—
Zinc	3 0	1 00 " " " "	—
All above, fractions *pro rata*			
Sulfur	4 0	1 00 " " per ton up to 8 per cent	
		1 50 " " per ton above 8 per cent	

Representative samples of materials must be submitted to determine their suitability for treatment Payment is made for each shipment after weighing, sampling, and analysis of the ore or concentrates at the Texas City smelter.

Chapter 6

Metallurgy

Tin Production

When considered from the viewpoint of world annual output, tin is one of the rarest metals Its annual production is exceeded by that of iron, copper, lead, zinc, aluminum, magnesium, probably by that of the ferroalloys of manganese, chromium, and silicon, and possibly by the world production of sodium, while it exceeds only the output of such common metals as nickel, antimony, mercury, tungsten, molybdenum, silver, gold and the precious metals.

The only American book on tin metallurgy prior to 1925 is that of Henry Louis—"Metallurgy of Tin " In his preface in 1911, Louis said.

"This little work is in the main a reprint of a monograph on the metallurgy of tin, published originally in *Mineral Industry* for 1896, Vol V Authentic information on the subject of tin smelting is somewhat scarce, and as the above-mentioned volume has long been out of print, it was decided to issue the monograph as a separate work, incorporating in it as much recent information on the subject as was obtainable The small amount of new matter is due to two reasons first, the unprogressive character of tin smelting, which continues from decade to decade with comparatively little change, and, secondly, the profound degree of secrecy observed by tin smelters, who are extremely anxious to keep to themselves any modifications or improvements in processes These two facts, the slow advance of the industry and the secretive habits of those engaged in it, are related as effect and cause "

Until the World War I period, the chief improvements in practice originated in the Pulo Brani Works of the Straits Trading Co at Singapore, Straits Settlements, Federated Malay States. These works produced 30,000 to 50,000 tons per year. There is no doubt that they constitute one of the main reasons why tin metallurgy has not kept pace in any measure with that of other common metals Tin is by far the rarest It must be remembered that several individual copper, lead, and zinc plants produce more than 100,000 tons a year, close to the total annual tin production. When metallurgical operations are conducted on a small scale, they are more likely to be surrounded with secrecy. In consequence,

improvements come slowly, and ancient methods survive with surprising tenacity.

Special Treatment of Ores

Tin concentrates are the product of open-cut mining, hydraulic sluicing, gravel-pump operation, or dredging when applied to alluvial deposits, or lode mining in conventional fashion.

Ore-dressing methods are relatively simple when pure oxide ores are handled, but increase in complexity as the ore complexity increases

It is often necessary to treat specially the tin concentrates from some localities so as to remove objectionable metallic impurities, with the object of making them more suitable for smelting and the production of a purer final metal. Concentrates from vein deposits such as Bolivian ore may require extensive preparation before smelting. Concentrates from alluvial sources require relatively little pretreatment.

Although the literature on tin ores, smelting and metal purification is not abundant, because of a small number of plants, technical references are available Louis[1] described ore reactions and smelting in shaft and reverberatory furnaces, Jones[2] extensively described ores and the tin mines of the world from the geologic and mining viewpoint, Hallett[3] reviewed world practices in the metallurgy of tin, Mantell,[4] as a result of intensive experimental work and collection of data from original sources, augmented the technical literature Mantell and Lidle[5] further increased the available information in reference to secondary smelting and tin recovery from nonmineral sources, Fink and Mantell[6] described their studies of gaseous reduction, leaching, smelting, metallic reduction, treatment of Bolivian concentrates, and electrolytic refining in relation to winning of tin from impure Bolivian vein ores

There are a number of general methods, which may be broadly classified into: (1) roasting followed by further mechanical separation of minerals that have been physically broken away from the cassiterite as the result of the process or altered in such a manner, *e g* , as change in specific gravity,

[1] H Louis, *Mineral Ind* , **5**, (1896), "Metallurgy of Tin " New York, McGraw-Hill Book Co , Inc , 1911.

[2] W. R. Jones, "Tinfields of the World," London, Mining Publications, 1925

[3] R L Hallett, in Liddell's "Handbook of Nonferrous Metallurgy," Chap 42, New York, McGraw-Hill Book Co , Inc , 1926

[4] C L Mantell, "Tin, its Mining, Production, Technology and Applications," *Am Chem Soc , Monograph* **51**, New York, Reinhold Publishing Corp , 1929

[5] C L Mantell, and W Lidle, "Zinn, Berg-und huttenmannische Gewinnung, Verarbeitung und Verwendung," Halle (Saale), Verlag von Wilhelm Knapp, 1937

[6] C G. Fink, and C L Mantell, *Eng Mining J.*, **124**, 686–91, 967–72, 1052–4 (1927), **125**, 201–6, 325–8, 452–5 (1928), Dissertation for Ph D degree, Columbia University, New York, 1928

to make them more amenable to further mechanical concentration; (2) roasting under controlled conditions followed by leaching with water or acid solutions; (3) heating with sodium salts such as soda ash, sodium chloride, salt cake, etc , followed by leaching; (4) metallic impurity removal by oil flotation when the impurities are present as sulfides. These will be discussed rather briefly.

When calcined at a red heat, cassiterite is unchanged but many of the associated minerals of metals other than tin are altered. Much of the sulfur and arsenic and some of the antimony are volatilized. The volatile products, particularly arsenious oxide, are sometimes collected either in bag houses, Cottrell installations or other dust-collecting equipment. The roasted concentrates contain tin oxide, oxides of iron, zinc, bismuth and copper, lead sulfate, small quantities of more or less unaltered sulfides, tungsten compounds and minor amounts of other minerals.

According to the type and quantity of the impurities, oxidizing, reducing, or chlorinating roasting is applied. If the ore is of a grain size which is not sufficiently small for roasting and leaching, it is brought to a suitable grain size of the order of 1.5 mm. in a ball mill.

Roasting is done in furnaces of many varieties, either of a hand-rabbled reverberatory variety or in multi-hearth mechanical furnaces or those of the rotating cylinder type. The last named are made with a heavy steel or cast-iron cylindrical shell 30 to 40 feet long and 4 to 6 feet in diameter, lined with firebrick. In appearance they are somewhat similar to cement kilns Coal or oil is used as fuel, the burners being located at the discharge end. The fixed-hearth, revolving-rabble-type furnaces such as the Wedge, Herreshoff, MacDougall, Ridge, Pearce turret, Merton and related kinds are also used. Multiple hearths are usually employed, the top hearth being sometimes used as a drier. The furnace capacities are about a ton of tin concentrates per hour with a fuel consumption of 100 to 300 pounds of coal per ton of concentrates. The material to be roasted is usually crushed to pass a quarter-inch screen Roasting temperatures are from 550° to 650° C

Roasting is often followed by leaching with water or acid solutions to remove the products made soluble by the roasting process.

The leaching is usually done in wooden vats with mechanical stirrers. A German plant used spherical leaching vats with spheres of about 10 feet diameter, mounted rotary, and with an acid-proof lining of rubber and stone. Charging and discharging are done through an aperture of $1\frac{2}{3}$-feet diameter which can be rigidly closed The capacity of the sphere is about 7.2 cubic yards. The leaching liquid is concentrated hydrochloric acid; if the ore dissolves easily, it may be diluted up to four times its original volume. The amount of acid to be added usually depends upon the ore content of soluble iron. Some ores are leached twice. The treatment

lasts from 6 to 8 hours for simple leaching, and up to 12 hours for double leaching. The leaching is done under a steam pressure of 15 to 30 pounds per square inch. The leached ore is separated from the acid over a suction filter and washed with hot water Leaching under pressure and increased temperature is stated to be more efficient and gives better removal of impurities, particularly iron.

The roasting and leaching methods have the disadvantage that insufficient antimony is removed Antimony may occur as antimony tetroxide (Sb_2O_4) which is not volatile and is insoluble in acid.

According to a process developed by Zinnwerken Wilhelmsburg,[7] antimony which is present in this form can be removed by transforming it into the soluble trivalent form by means of reducing additions Solid ferrous sulfate or highly concentrated iron chloride solutions are used as reducing agents. The acid consumption increases on account of the necessary multiple leachings. Other lower metal oxides and suitable metals also may be used. By this method the antimony can be removed up to a few tenths of one per cent and up to a few hundredths of one per cent, if required.

The leach does not contain any appreciable amounts of tin. If the recovery of the dissolved metals is worth-while, they are precipitated with scraps of sheet iron Larger amounts of bismuth are precipitated as bismuth oxychloride by dilution with water In the case of silver-bearing ores, occasionally a leaching with sodium thiosulfate is introduced.

Tungsten-bearing tin concentrates are sometimes heated with sodium carbonate or sodium sulfate at 600° C , to form sodium tungstate. Excess sodium salt is avoided, otherwise some of the cassiterite will be converted to sodium stannate The sodium tungstate is soluble in water and is leached from the treated concentrates, recovered from the leached liquors by evaporation, and purified for the market This method has been used in a number of localities. Hand picking of tungsten materials is generally used to remove them from the concentrates before smelting

When the concentrates carry considerable quantities of sulfides, a chloridizing roast, followed by leaching, is sometimes used This method is often employed on Bolivian silver-tin ores and silver-tin-lead concentrates. When the sulfides are roasted with salt (NaCl) in an oxidizing atmosphere, sodium sulfate and the chlorides of the metals are formed with no attack on the tin oxide. Many of the chlorides are volatile Bismuth, lead, arsenic, antimony and silver may be thus partially removed in the form of fume. The chloridizing roast is usually followed by suitable leaching and washing in wooden vats, in some cases fitted with filter bottoms. The furnaces for the chloridizing roast are similar to those used for dead roast-

[7] *German Patent 472,515.*

ing, with the exception that 1 to 5 per cent of salt (NaCl) is mixed with the concentrates before they are charged into the furnace.

Most common metal sulfides are easily separated from oxide ores by oil flotation. While this method has not been extensively used in preparing tin ores or concentrates for smelting, it is known that the process may be applied and may assume considerable importance in the future.

Outline of Metallurgical Methods

Practically the only source of primary tin is the stannic oxide ore, cassiterite. The winning of tin from its ores consists essentially of causing the conversion of the stannic oxide, SnO_2, to elemental tin. This can be accomplished in a variety of ways, only one of which is now in commercial use and of present economic importance.

Stannic oxide can be reduced by carbon at fairly high temperatures. Cassiterite can be reduced to tin metal by certain reducing gases, such as hydrogen and carbon monoxide; commercial gases containing these or mixtures of them, or at a lessened rate by hydrocarbons and gasified oils

The possible metallurgy of tin naturally falls into several subdivisions by following through the analogy of other nonferrous metals:

(1) Reduction and removal of oxygen by carbon and related solid reducing agents.

(2) Reduction and removal of oxygen by gaseous reducing agents.

(3) Leaching of the ore (as in the case of copper) with direct separation of the metal from the leaching liquors.

(4) Converting stannic oxide to a soluble form and decomposing the compounds formed

(5) Solution and decomposition in a fused salt bath (as the Hall process for aluminum).

(6) Electrolytic reduction at the cathode in aqueous solutions.

(7) Reduction of cassiterite by metals.

(8) Combinations of these methods or combinations of parts of them, such as leaching with acids in advance of roasting or smelting, or preliminary roasting followed by leaching and then by carbon smelting.

The most common commercial method is the first in the classification, that of reduction by solid carbonaceous material. The second, that of gaseous reduction, has manifold advantages in specific locations. In one American tin smelter, acid treatment or leaching of the ore for the removal in a selective manner of some of the impurities prior to smelting is followed.

The reduction of tin from its oxide is not difficult. Reduction takes place readily at fairly high temperatures in the presence of reducing agents such as coal, culm, or coke. The required temperature for smelting is determined principally by the composition of the slags that are formed. The smelting temperature must be sufficiently high to keep the slags fluid,

and allow the reduced tin metal to settle and collect in the bottom of the furnace

Inasmuch as the smelter has only one ore to deal with, the metallurgy of tin is comparatively simple. Its reduction in practice is almost invariably accomplished with the aid of carbonaceous materials. Several complications occur, however:

(1) The temperature of reduction is so high that the oxides of other metals, present in a greater or lesser degree, are reduced at the same time. These metals may produce undesirable and troublesome tin alloys. The iron-tin alloy, "hardhead," is an example

(2) Tin oxide is amphoteric Unless conditions are carefully regulated, the furnace linings are attacked. Siliceous acid linings cause tin silicates to be formed, basic linings of lime or magnesia result in losses as stannates. The great difficulty in tin smelting is caused by the fact that tin oxide readily combines with silica to form tin silicates During the smelting of the concentrates mixed with flux and fuel, a considerable amount of tin invariably combines with silica and goes into the slag in the form of readily fusible tin silicates mixed with other more or less complex silicates that make up the slag. On the other hand, if an extremely basic slag is used, tin oxide will act as an acid and enter the slag The slag components must be nicely adjusted It is desired to produce slags of as low a tin content as possible, as the principal loss in tin smelting is in the tin carried off by the slags The making of low-tin slags, however, is not of the greatest importance in the primary smelting of tin concentrates.

(3) Tin metal at elevated temperatures is more fluid than is mercury at ordinary temperatures It finds the most minute openings for escape and soaks into the porous refractories of furnaces to an amazing degree.

(4) The slags produced contain appreciable quantities of tin. This metal must be recovered. Slags require further treatment also; there may even be treatment of successive slags for their tin content. Part of the tin in the slags is mechanically retained as "prills," or small metallic globules Unduly large amounts of metal go into the slag, which may run 10 to 25 per cent tin.

Smelting Furnaces

Smelting furnaces used for tin are of two types,—the blast or shaft furnace, set vertically, and the reverberatory furnace, set horizontally. The blast furnace is much older, being in most general use in the early industrial life of tin smelting. Treatment in reverberatories did not come into use until well along in the eighteenth century Full development of the reverberatory method did not occur until about the middle of the nineteenth century.

In its simplest form, the blast furnace consists of a short vertical shaft,

circular, square or rectangular in cross section, and of moderate height. Charcoal is used as a fuel in alternate layers between the layers of concentrates. Air is supplied by a blast, almost invariably cold, through tuyeres located a little way from the bottom of the furnace.

Pryce[8] stated that the reverberatory furnace was introduced into Cornwall for tin smelting with fossil fuel in the beginning of Queen Anne's reign (about 1705), but up to that time the shaft furnace, or "blowing house" as it was called, with charcoal as a fuel, had always been used Primitive furnaces still exist and are operated in the Far East, even as crude as the pre-Roman method of digging a hole in the ground and throwing tinstone on a charcoal fire excited by a bellows.

Pryce[9] described Cornish practice as follows:

"The Cornish tin-miner took his cleaned stream tin to the blowing house, paying the owner of the house twenty shillings for every tide or twelve hours, for which the blower was obliged to deliver to the Tinner, at the ensuing coinage, one hundred pounds gross weight of white Tin for every three feet or one hundred and eighty pounds of Stream Tin so blown, which is equal to fourteen pounds of Metal for twenty of Mineral, clear of all expense "

"The furnace itself for blowing the Tin is called the Castle on account of its strength, being of massive stones cramped together with Iron to endure the united force of fire and air This fire is made with charcoal excited by two large bellows, which are worked by a water-wheel, the same as at the iron forges They are about eight feet long and two and a half wide at the broadest part. The fire-place, or castle, is about six feet perpendicular, two feet wide in the top part each way, and about fourteen inches in the bottom, all made of moorstone (*i e*, granite) and clay, well cemented and cramped together. The pipe or nose of each bellows is fixed ten inches high from the bottom of the castle, in a large piece of wrought Iron, called the Hearth-Eye The Tin and charcoal are laid in the castle, stratum super stratum, in such quantities as are thought proper, so that from eight to twelve hundredweight of tin, by the consumption of eighteen to twenty-four sixty-gallon packs of charcoal, may be melted in a tide or twelve hours' time Those bellows are not only useful for igniting the charcoal, but they throw a steady and powerful air into the castle, which, at the same time that it smelts the Tin, forces it out also through a hole at the bottom of the castle, about four inches high and one and one-half inches wide, into a moorstone trough six and one-half feet high and one foot wide, called the float, whence it is ladled into lesser troughs or moulds each of which contains about three hundred pounds of Metal, called Slabs, Blocks, or Pieces of Tin, in which size and form it is sold in every market in Europe, and on account of its superior quality is known by the name of Grain Tin, which brought a price formerly of seven shillings, that is further advanced, the last two or three years, to ten or twelve shillings per hundred more than Mine Tin is sold for, because it is smelted from a pure Mineral by a charcoal fire, whereas Mine Tin is usually corrupted with some portion of Mundick [pyrite], and other Minerals,

[8] Pryce, "Mineralogia Cornubiensis," p. 282, 1778.
[9] *Ibid.*, p. 136.

and is always smelted with a bituminous fire, which communicates a harsh, sulphureous, injurious quality to the Metal."

In the Far East, particularly in China, fairly pure cassiterite is smelted in very crude small blast furnaces. No definite slag practice, except a rule of thumb one, is followed. The tin metal produced is usually of poor grade. Many of the furnaces consist of bamboo cylindrical forms, lined with clay

When tin ores from Cornwall became a factor in England, shaft furnaces were built of stone and brick and operated with positive-pressure blowers for the draft Figure 51 shows an old Cornish "tin castle," reproduced from the 1832 edition of Karsten's "System of Metallurgy "

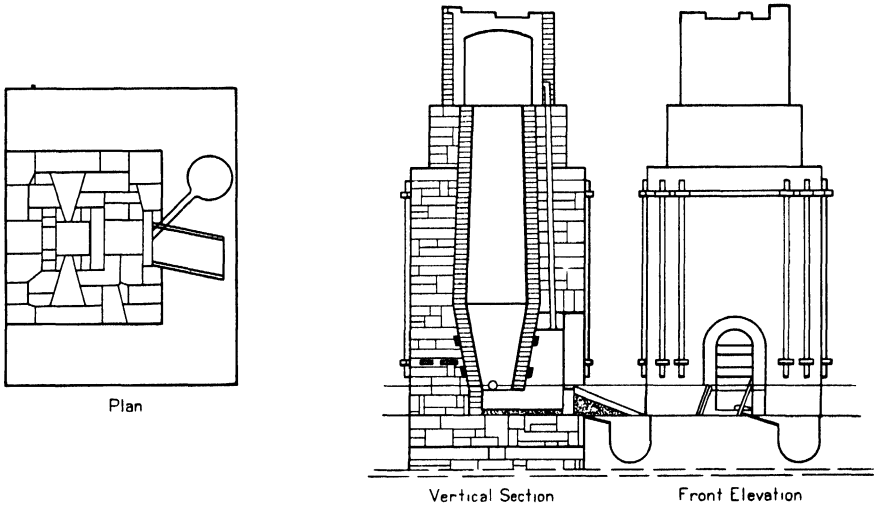


FIGURE 51 An old Cornish "tin castle "

Modern steel-shell, brick-lined blast furnaces, with water cooling, are used all over the world for tin smelting. Practice in operation is similar to that employed for other metals, although tin shaft furnaces are built with somewhat lower shafts, to operate with comparatively low blast pressures. Coke is the usual fuel. Brick "settlers" or fore-hearths are sometimes used to collect liquid slag and tin metal as they are tapped from the furnace. The slag usually overflows from the settler to the slag pots. These are removed and the molten slag poured into water to granulate it, or it may be allowed to freeze and then be broken up mechanically.

Metallic tin is tapped from the bottom of the settler at intervals and run off into cast-iron molds The tin pigs ordinarily need refining, which is usually done by thermal methods.

Typical Smelting Practices

There are three stages in the smelting of tin ores or concentrates: (1) reduction, or tin smelting proper; (2) cleaning the slags and furnace linings and recovery of tin from them; and (3) refining the impure tin.

Inasmuch as, in general, they represent three different practices as a function of locality, fuels, types of ores, and increasing difficulty of treatment, descriptions will be given of eight smelters. The first is that of the Straits Trading Co. at the Pulo Brani Works at Singapore, Straits Settlements, Federated Malay States, where the ores are relatively pure because of their alluvial origin. The second is that of the Eastern Smelting Co.; the third, that of Cornish practice, the fourth, the Penpoll smelter; the fifth, that of American practice, which involves electrolytic refining; the sixth, that of the Longhorn tin smelter in Texas, where acid treatment of ores to prepare them for smelting is an important part of the operation; the seventh, German practice related in character to that of the Longhorn smelter; and the eighth, Canadian practice involving electric-furnace smelting of tin materials separated as a minor constituent of base metal ores.

It is to be noticed that the first two—that is, Straits Trading and Eastern Smelting—deal with relatively pure ores; the English smelters with pure alluvial ores and mixtures of lode or vein ores, coupled with dross and secondary material at times. The American practice, however, deals with Bolivian ores, thought of as being the most difficult to treat because of their complexity and metals other than tin.

Pulo Brani Works. One of the most eminent smelters in the world was the Pulo Brani Works of the Straits Trading Co. This plant is on an island off Singapore, Straits Settlements. The following discussion relates to the situation before the Japanese seizure of Singapore in World War II; restoration was made when peace returned.

A process and tonnage flowsheet of the operation is given in Fig. 52. Reverberatory smelting furnaces are used, a special feature of the furnace being the water vault. The lower part of the furnace foundation, below the ground line, is built so as to form a water tank the full length of the hearth and the length of the holding kettle. An 8-foot depth of water is maintained. Any tin leaking through the furnace bed or through joints drops into the water and is thus granulated, this material is collected periodically. As it is impossible to prevent leakage of so mobile and easily fusible a metal as tin, this water vault presents to the smelters a satisfactory method of handling leakage and recovering the metal.

Straits practice is summed up in the following operation: Alluvial concentrates are smelted with carbonaceous material to produce "ore metal" and "rich slag" high in tin. The rich slag is smelted with the aid of coal and scrap iron to produce "rough metal" and "poor slag." The "poor slag" is smelted for prills, producing "hardhead" and another low-grade

slag, which is sent to the dump "Hardhead" and the rough metal, together making the "slag metal," are refined, the dross returning for reprocessing, the refined slag metal joining the "ore metal" The total metal recovered from the concentrates is refined by liquation, poling, or tossing It is stated that in continuous operation 97 to 98 per cent of the

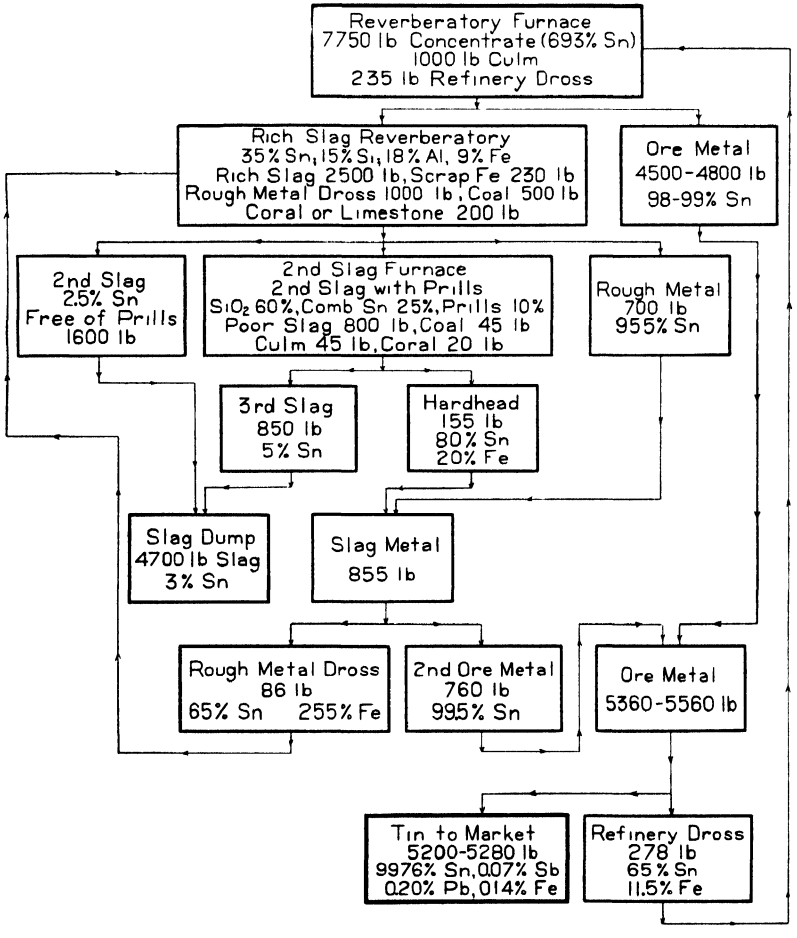


FIGURE 52 Flowsheet of Straits practice

metal present in the original concentrates is recovered The iron consumption amounts to about 5 per cent of the tin produced, and the coal consumption 25 to 30 per cent. Concentrates run from 65 to 70 per cent or better in tin. They are of alluvial or "stream" origin, thus being very pure.

Penang. The practice of the Eastern Smelting Co. in Penang, Straits

Settlements, is described in *The Mining Journal* (London, Jan 25, 1930) as follows:

On arrival at the works all arsenical and sulfur-bearing ores are first roasted at a low temperature in a large mechanical roasting furnace to eliminate the deleterious impurities, arsenic and sulfur. The roasted ore is then sent to the smelting furnaces, together with the clean ores, as received

The smelting furnaces in use by Eastern Smelting Company, Ltd , are large regenerative oil-fired reverberatory furnaces The charge, consisting of ore, clean or roasted, anthracite for reduction, crushed limestone for fluxing purposes and various by-products formed in the smelting operations, passes through the charge mixing plant, and is then hoisted to the furnace charging floor, whence it is fed to the furnaces and levelled down The oil flame is then turned on, and the charge is worked for a period of seven to twelve hours. At intervals the charge is rabbled (stirred) with long-handled iron rabbles.

The reduction of the ore commences in a short time, and tin is drawn off almost continually during the working of the charge.

At the end of the working period the taphole is opened, and the resultant slag, together with the remaining portion of the reduced tin, is drawn off, the tin into a kettle or a float and the slag into a granulating pit

The crude furnace tin produced is then sent to the refinery, and the rich slag is sent to a second slag-smelting furnace. Here the slag is mixed with further anthracite, limestone and occasionally scrap iron, and treated similarly to an ore charge, with the exception that no tin is tapped during the working of the charge, the whole of the products being drawn off in the final tapping. The products of the slag-smelting furnaces are a rich tin-iron alloy, which is returned to the ore-smelting furnaces, and a slag, low in tin, which is discarded

All furnaces are coupled to a fume- and dust-collecting plant, which recovers the fine particles of tin and tin oxide carried off with the spent furnaces' gases, the oxide collected being returned to the ore furnaces.

The crude tin drawn off from the furnace is usually impure, and contains different metals—*e.g.*, iron, copper, lead, antimony, arsenic, and bismuth As these impurities detract from the market value of the tin, it is necessary to remove them by a process of refining, which consists of liquidation and "boiling" of the tin. The ingots of crude tin are melted down in a furnace at a low temperature, and the molten tin is allowed to run into a large iron pot or kettle, the less easily fusible metals remaining behind on the bed of the furnace. The tin which collects in the kettle is kept molten during the "boiling" by means of a fire underneath.

The boiling consists of releasing a stream of compressed air from a pipe well below the surface of the molten metal. By this means every portion of the mass of metal is brought into contact with the air, the foreign metals

and a portion of the tin being oxidized and collecting as a foamy mass on the surface of the metal The molten mass is then allowed to stand for some time to allow the heavy impurities to settle to the bottom After this the scum is skimmed off, and the refined tin poured into molds.

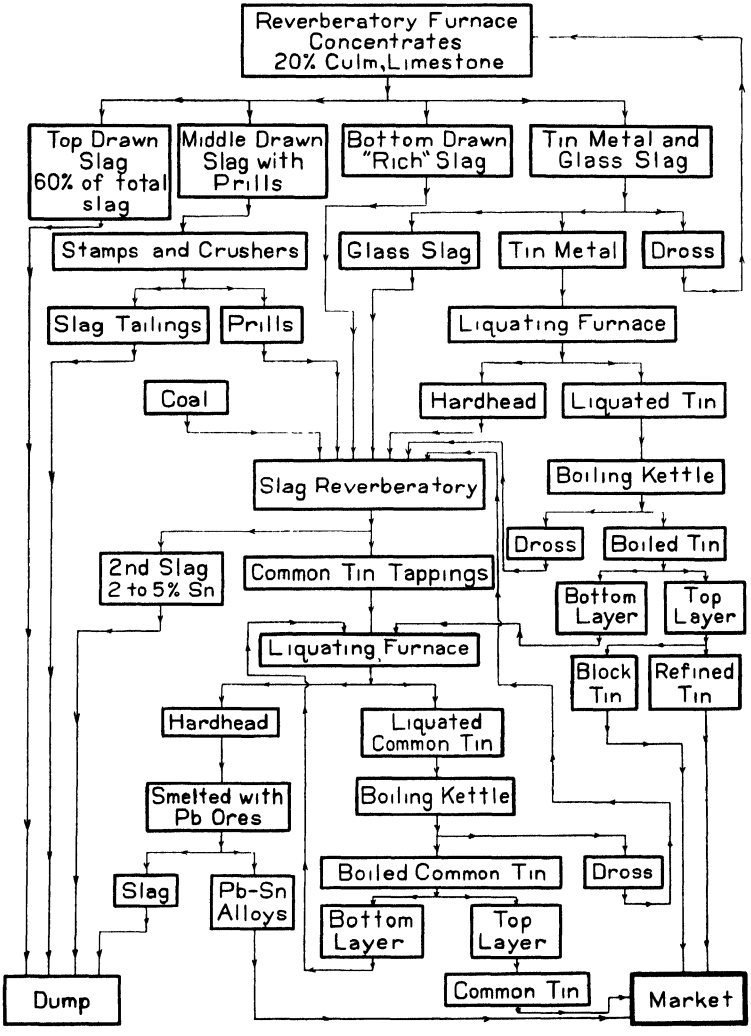


FIGURE 53 Flowsheet of Cornish practice.

Cornish Practice. Cornish practice is shown in the second flowsheet (Fig. 53). It differs from Straits practice in that ordinarily iron as raw material is not used to replace tin in the slags as a method of recovery. The slags are subdivided to a greater extent and a greater number of

varieties of tin are produced. Cornish smelters have to use Bolivian vein ores, diluted with alluvial concentrates. Furnace liquation is used in Cornwall more often in the treatment of the impure tin metal produced Concentrates are mixed with 15 to 20 per cent of culm, a small amount of lime as a flux, and often some slags, drosses, or other tin-bearing products from other stages of operations. The materials are mixed and dampened before they are charged into the furnace Furnace temperatures are of the order of 1200° to 1300° C. After rabbling and settling, about two-thirds (the upper two-thirds) of the slag is withdrawn and sent to the dump Another portion is reworked by stamping and crushing for prills. The slag tailings go to the dump, the prills being reworked with the remainder of the slag, which contains appreciable tin in the combined form.

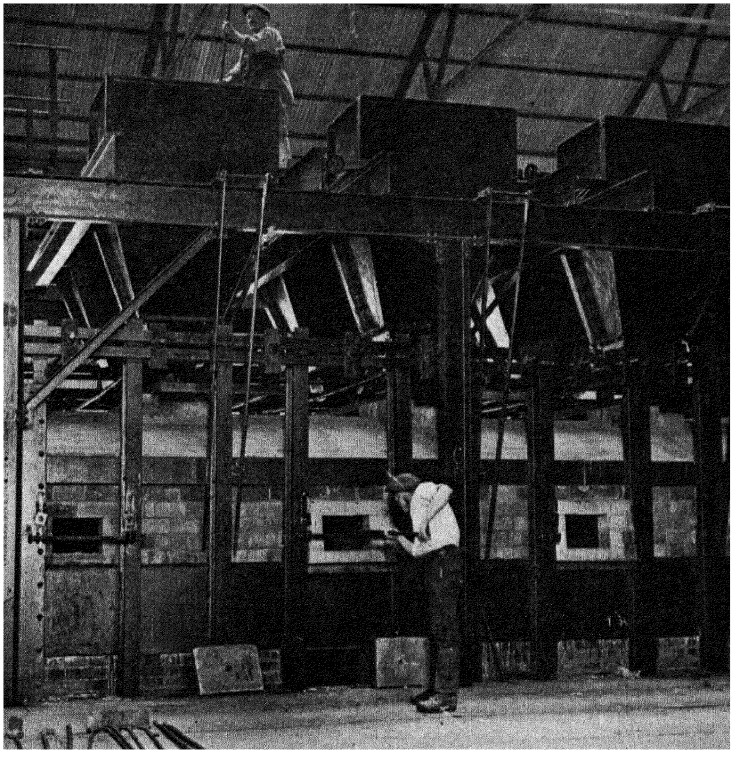
Tin metal from reverberatory smelting is cast into molds, the "glass" slag with it being removed and sent to the slag furnace. The cast tin is liquated, the hardhead going to the slag furnace for reworking. The liquated tin is "boiled" by poling with billets of green wood or admitting air under pressure, and the heavy impurities are allowed to settle out The top layers of the boiled tin are cast into molds, and, depending upon the purity of the metal, sold as refined tin or as block tin. Drosses return to the concentrate-smelting furnace for reworking, the lower layers from the boiling kettle are mixed with the metal recovered from the slags and other products. The slags containing appreciable tin, the prills, hardhead, and glass slags are treated with some culm in the slag reverberatory The resultant slags, running from 2 to 5 per cent of tin, are discarded. Metal tappings from the furnaces are cast into molds and sent to the market as common tin. The bottom layers are returned to the slag reverberatory furnace, along with the drosses, for reworking, and the hardhead produced from liquation is either discarded or smelted with antimony or lead ores to produce antimony, tin, or lead-tin alloys, which can be disposed of as such.

Penpoll Smelter. As a modification of the Cornish practice, many mechanical changes and variations were introduced at the Penpoll smelter.

Reverberatory smelting of tin concentrates dates back to the early part of the eighteenth century, when reverberatory furnaces were introduced into Cornwall. They have increased in favor, for they are adaptable not only for primary smelting, but also for slag treatment to recover tin Reverberatory furnaces produce somewhat cleaner slags in the primary smelting, as well as in the resmelting of the first-run slags. The operations are more readily controlled in reverberatories than in blast furnaces. The reverberatory is particularly suited to the smelting of fine tin ores and concentrates because of the lower dust losses. The furnaces are constructed of firebrick and vary greatly in size. Hearths on the largest ones

are approximately 30 feet long and 12 feet wide. The firebox is at one end and the flue and stack connection at the other.

Figure 54 shows one of the most modern tin reverberatories, one of those at the Penpoll smelter at Bootle, England. The fuel is long-flamed bituminous coal, although oil is sometimes used. For the larger furnaces, 8- to 12-ton charges are typical. The usual charge consists of tin concen-



(Courtesy The Mining Magazine, London)

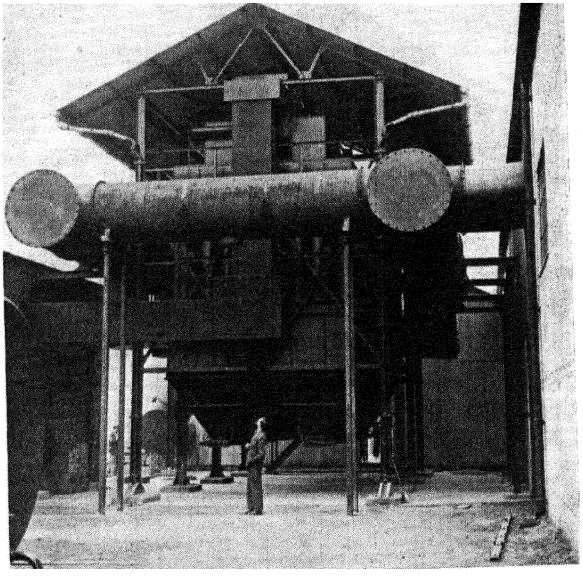
FIGURE 54. Tin-smelting reverberatories at Penpoll.

trates with 15 to 20 per cent of anthracite screenings, small amounts of slag-making materials such as sand and limestone, old slag and refinery by-products. Premixing of the charge constituents is accomplished usually outside the furnace. The process is entirely a batch operation.

The smelting time of the larger furnaces is usually 10 to 12 hours, at temperatures of 1200° to 1300° C. Relatively large amounts of tin are allowed to go into the slag, as such practice tends toward the production

of metal containing a minimum amount of impurities. After the batch is smelted, the practice of handling the fluid slags and tin is the same as in blast-furnace operations. Reverberatory-furnace slags usually run 10 to 25 per cent tin. Rabbling in the furnace is accomplished with iron hoes attached to long iron handles, which are operated through the side doors of the furnace. The stirring is usually done as completely as possible.

Tin-smelting reverberatory furnaces are constructed of firebrick, having a hearth sloping toward the taphole which is usually placed at about the center of one side of the furnace and low enough to drain the furnace com-



(Courtesy The Mining Magazine, London)

FIGURE 55. The Lodge electrostatic dust collector for flue gas at Penpoll.

pletely. The roofs are of arch construction, of the same type as that generally employed in metallurgical works for this kind of smelting unit. Charging is done through several holes in the roof. Some type of dust-collecting equipment is usually found on the flue end of a smelting system. A modern dust collector, as shown in Fig. 55, is often of the electrostatic precipitation type.

Maurer Plant. Refining tin by furnace methods is at best an imperfect operation, for large quantities of impurities cannot be separated. The quality of the metal produced depends very largely on the original purity of the concentrates.

American tin-smelting practice, when plants existed in the United States

for the treatment of foreign tin ores before World War II, was more advanced than any others developed at that time. In 1903, R. T. White built a plant for the International Tin Co. at Bayonne, N. J., to smelt Straits of Malacca (Malayan) concentrates. The British Government then placed a 40 per cent *ad valorem* export duty on tin ores to other than British smelters. The plant failed, owing to lack of raw material at a price that would allow the enterprise to continue. In 1915, tin shortages in the United States and the availability of Bolivian vein ores again made possible the establishment of tin smelters.

The flowsheet of the Maurer plant of the American Smelting and Refining Co. is given in Fig. 56. This plant treated Bolivian ores exclusively. The material termed "ore" was a concentrate containing between 55 and 65 per cent of tin, with arsenic, antimony, iron, copper, tungsten, bismuth, lead, and sulfur as impurities. The ore was given a preliminary roast in a Wedge furnace, to drive off sulfur by oxidation and antimony and arsenic by volatilization. The ore from the Wedge furnace was mixed with blast-furnace dust (recovered in the baghouse) in a mechanical mixer. It passed on to a Dwight and Lloyd sintering machine, where it was sintered with lime and sometimes silica. Lime was added to the sinter charge to protect the grate bars of the machine and also for fluxing the sulfur remaining in the ore. The sintered ore passed to the blast furnace, where it met drosses from various operations, coke, and the fluxes or slag-forming materials.

Special care had to be taken in proportioning the slag to prevent it from being too basic, as under such condition the tin compounds in the ore formed stannates and were lost in the slag; and not too acid, because under that condition tin silicates formed and were similarly lost.

The best proportions of the slag components were found to be 38 to 40 per cent silica, 22 to 28 per cent iron oxide (FeO), and 38 to 40 per cent lime, magnesia, and alumina. An average slag in good tin-smelting practice was about 33 per cent silica, 28 per cent iron oxide, and 28 per cent lime. Finished slags were of about the percentage composition: SiO_2, 35, FeO, 18; CaO, 28; Sn, 2.8 to 2.5; and the remainder, MgO and Al_2O_3.

Very good slags, metallurgically speaking, were 3:4 sesquisilicates.

In the blast furnace the stannous oxide, when produced, acted as a basic constituent, whereas the stannic oxide acted as an acid one. It is interesting to note at this point that the stannous sulfide was volatile at 1075° C., whereas the temperature of the blast might go as high as 1400° C.

In practically all plants the first slag produced from the blast furnace contains such large quantities of tin that it must be retreated practically as if it were an original ore. At the Maurer (New Jersey) plant it was claimed, however, that better than 90 per cent of the tin in the original ore was recovered and that there was little volatilization of tin compounds.

In the Maurer flowsheet, the blast furnace produced a crude tin, which

went to the liquating furnace, and a high-tin slag, running 6 to 10 per cent tin, which was sent in the molten condition to the slag reverberatory Fumes from the blast furnace were collected in the baghouse, re-

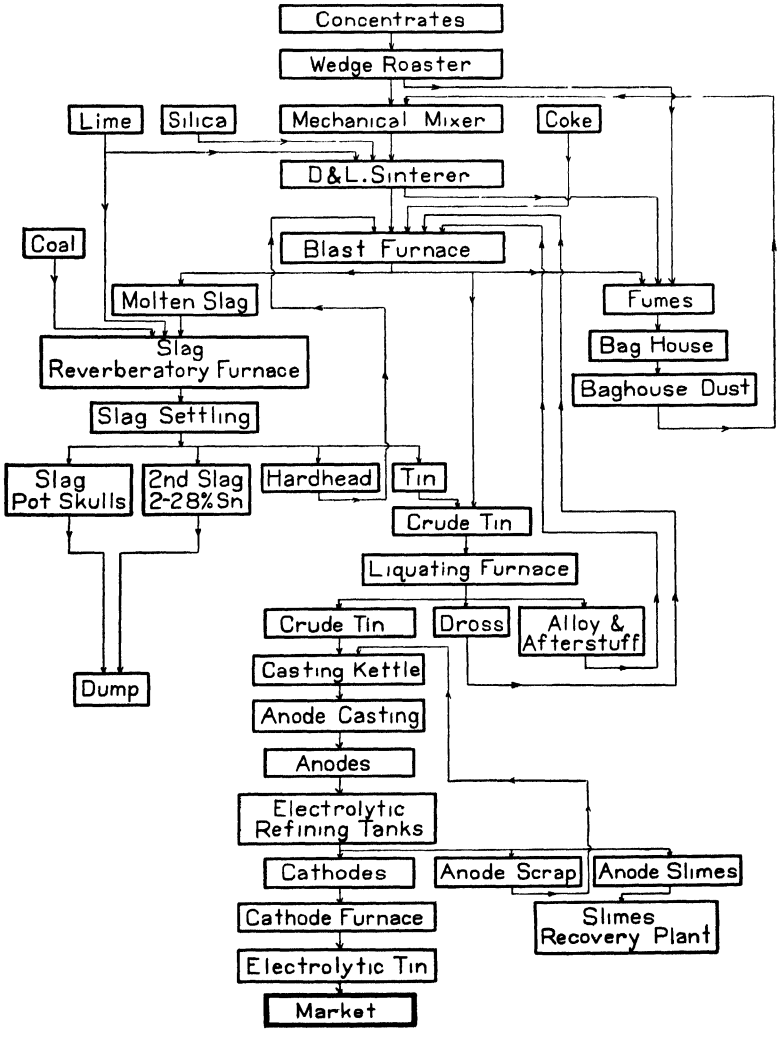


FIGURE 56 Flowsheet of Maurer American practice.

turning to the process by mixing and sintering with fresh ore. The slag, at 1100° C., was raised to about 1300° in the slag reverberatory and treated with lime and coal. It was then settled. Tin metal produced was either sent to the liquating furnace, joining the tin from the blast furnace, or placed in the casting kettle for casting into anodes. The slag from the

reverberatory, containing 2 0 to 2.8 per cent tin, was sent to the dump. Slag-pot skulls went to waste Iron-tin alloy or hardhead was returned to the blast furnace.

The crude tin from the blast furnace was liquated and then cast into anodes on a continuous anode-casting wheel Dross, alloy, and scrap were returned to the blast furnace The anodes were sent to the electrolytic refinery and refined in a manner almost identical with that for copper, using lead-lined tanks and a sulfate-fluosilicate electrolyte. The product, ready for market, was 99 8 per cent tin

The anode slime, which, in the refining, in contradistinction to copper refining, clings to the anodes, was washed from the anode scrap and worked up for bismuth, and in some cases for arsenic, antimony, lead, and other constituents Anode scrap was returned to the anode furnace for recasting into anodes.

Electrolytic tin was lower in impurities than any of the foreign brands of tin It was claimed that an average of three-fourths of a ton of slag was produced per ton of 60 per cent concentrates smelted The tin loss in slags was 1 5 to 2 5 per cent of the tin Electrolytic refining losses were 10 pounds per ton of 97 per cent tin anodes refined Tin recoveries were of the order of 94 to 97 per cent of the metal originally charged as concentrates

Longhorn Smelter. The Longhorn tin smelter, in Texas, operates a processing method on Bolivian ores which is in many ways a modification of that used by the Billiton Company at the Arnhem smelter in Holland

As described by the plant management, the process used is as follows:[10]

The Longhorn smelter is constructed for handling all grades of tin compounds from the pure alluvial concentrates to the lowest grades of primary ores, and the treatment process depends upon chemical composition and physical properties. For the pure alluvial ores, which contain only small amounts of silica and iron and traces of other metallic impurities, a simple two-step reduction process in reverberatory furnaces is adequate to yield a high-grade metal at a high recovery. The greater part of the primary ores and concentrates from Bolivia contain, however, base metals in such quantities that reverberatory smelting would yield a low-grade metal whose use would be limited. In addition to the base metals such as arsenic, antimony, copper, lead, and bismuth, these ores contain excessive sulfur, which must be eliminated before reverberatory smelting can be used. The iron content is often too high for direct smelting, and in the low grades of Bolivian ores the percentage of silica is also high. The complexity of the flowsheet is illustrated in Fig. 57.

Upon arrival, the ore is weighed, sampled, and stored in piles according to the required treatment. Most of the ore comes under the classification

[10] *Mining and Met*, **24**, 198 (1943)

in which the silica content is less than 10 per cent. It is calcined, with or without the addition of a reducing agent or common salt, the iron and other impurities thus becoming readily soluble in hot hydrochloric acid.

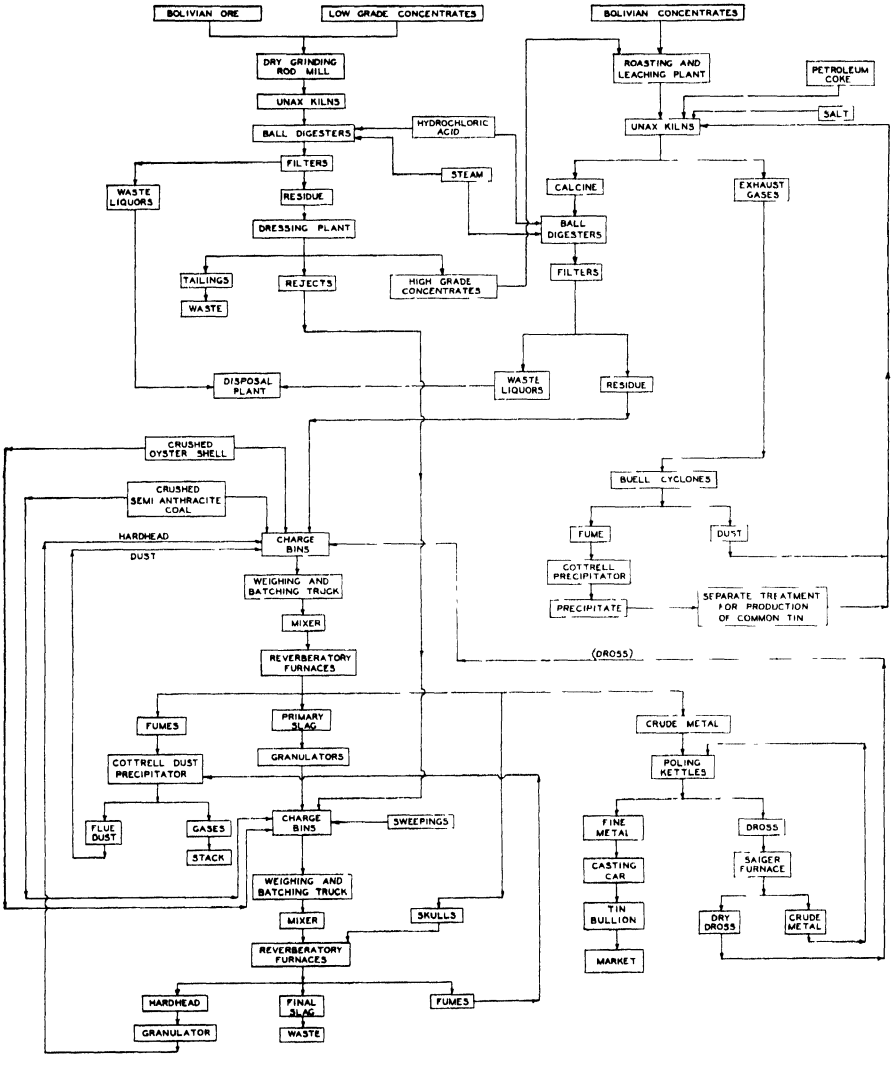


FIGURE 57. Flowsheet of Longhorn smelter.

The calcining is carried out in Unax kilns. These special kilns are provided with water-cooled cylinders in which the hot calcined ore is cooled to room temperature, with the exclusion of air to prevent reoxidation.

The extreme fineness of the ore causes dust losses in the kilns; most of

this dust is precipitated in Buell cyclones directly connected with the kilns, and the precipitate is immediately returned to the kilns. The cooled gas is further treated in a Cottrell installation, where the remaining dust is precipitated together with the fumes. The precipitate from this installation runs high in antimony and arsenic, and is therefore treated separately. The calcined material from the kilns is leached in digesters with hot hydrochloric acid. These are of spherical design and have a rubber lining protected from heat and abrasion by two layers of acid-proof brick. Steam, necessary to ensure the desired leaching temperature, is supplied through one of the hollow trunnions. The spheres rotate slowly, so that the ore is agitated continuously, and a high elimination of impurities is obtained. Leaching time depends upon the amount of impurities and varies between 4 and 8 hours. The capacity of the digesters depends upon the specific gravity and the iron content of the ores treated and ranges between 8 and 11 tons per batch.

Leaching is followed by filtering of the chloride solution on Nutsch filters. After having been washed with diluted acid, the residues are of such purity that subsequent treatment in reverberatory furnaces will yield a metal of at least 99 80 per cent tin.

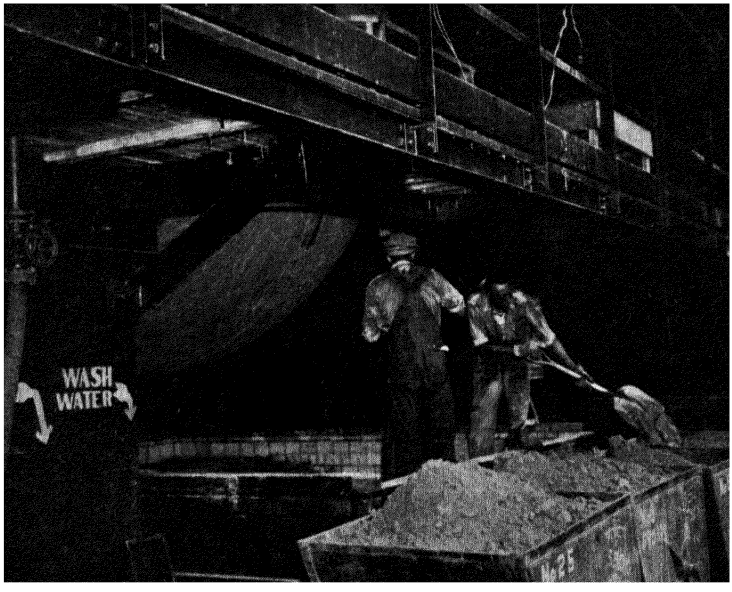
Medium- and low-grade ores generally contain excessive amounts of gangue and iron compounds. They can be divided into two groups. In the first, the percentage of base metals is so low that direct smelting will yield a hardhead from which pure metal may be produced The gangue and iron compounds are carried off in the slag together with a small amount of tin. The other group, in which metallic impurities are too high, will not yield a clean hardhead by smelting, and a roasting and leaching process, as already described, must be used first. Generally these ores become free-milling after this treatment, so that the residues yield high-grade concentrates on jigs and tables in the dressing plant.

If the dressing-plant concentrates still contain excessive amounts of base metals, they are retreated in the roasting and leaching plant, yielding a high-grade residue, ready for smelting. The tailing of the dressing plant can sometimes be discarded directly, but usually it pays to recover the tin by smelting to a final slag with a low tin content and a hardhead from which common tin can be recovered.

Smelting of all concentrates and clean residues is done in two steps in reverberatories fired with natural gas. In the first step, known as ore smelting, the amount of reducing agent is limited, so that metallic tin practically free of iron is obtained. After this operation, the slag still carries considerable tin. In the second operation, the primary slag is further reduced to a low tin content in the final slag. To obtain the desired results, a great amount of iron is reduced simultaneously, forming an alloy with

the tin, called hardhead. This hardhead, usually containing over 80 per cent tin, is treated simultaneously with the ore in the first operation, whereby the iron acts as a reducing agent.

The metal produced from the primary smelting is tapped in floats and transported to poling kettles in which the metal is refined by means of steam. After stirring and skimming, it is ready for casting. A certain amount of the tin volatilizes and is carried with the exhaust gases to the Cottrell installation, where it is precipitated and from which it is returned into the reverberatory furnaces.



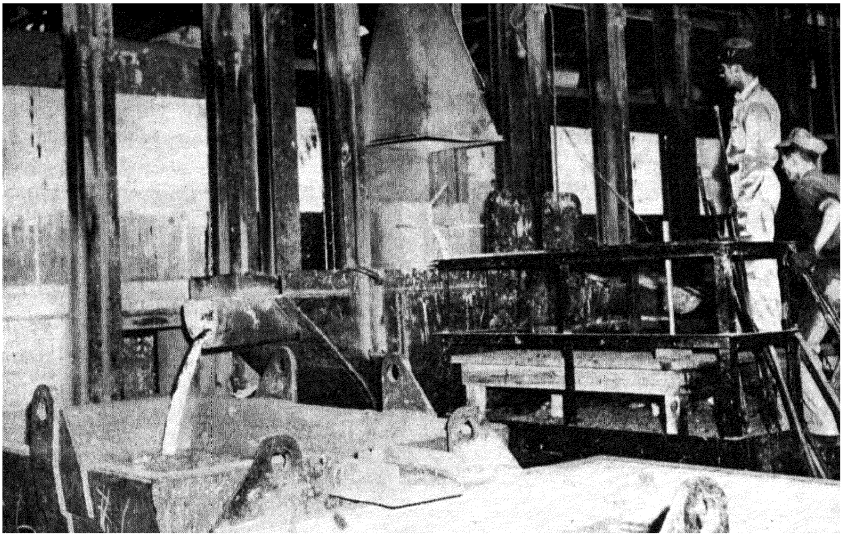
(Courtesy Office of War Information)

FIGURE 58. Discharging leached ore from ball digesters, Longhorn tin smelter.

Tin's high price and scarcity warranted the construction of an extensive dust-precipitation plant, from which the recovery will be better than 99 per cent. Further tin losses appear in slags containing about one per cent tin. In the leaching process, a small percentage of the tin is converted into tin chloride, which currently is not recovered, though treatment of the waste solution, by which the metallic impurities and tin will be precipitated, is contemplated.

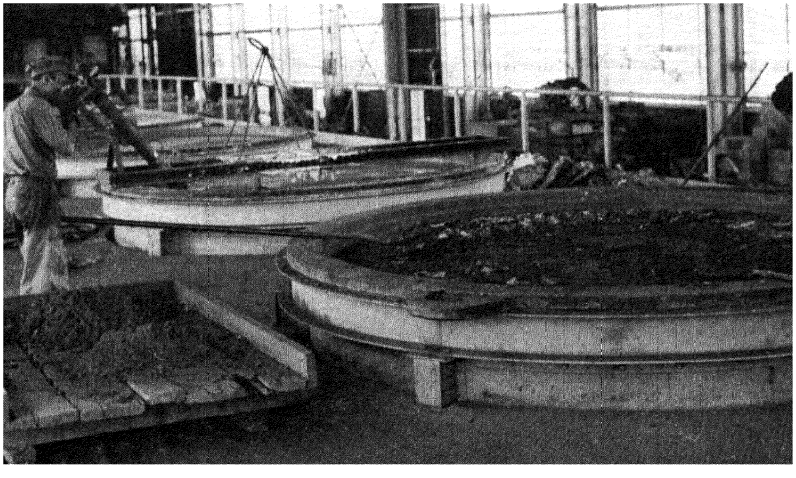
Some of the operations at the newest tin smelter in the world are shown in Figs 58 to 61.

German Practice. The Gruson Works of the Fried. Krupp Company



(Courtesy Office of War Information)

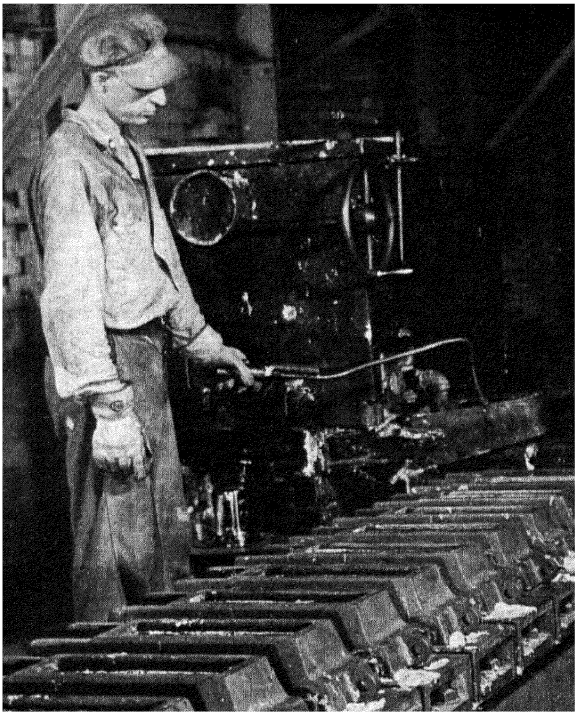
FIGURE 59. Tapping reverberatory furnaces and discharge of liquid tin into "settlers," Longhorn tin smelter.



(Courtesy Office of War Information)

FIGURE 60. Poling kettles for treatment of crude metal from reverberatory furnaces, Longhorn tin smelter.

in Magdeburg-Buckau, Germany, investigated the profitable melting of complex Bolivian tin ores, particularly those which contain zinc, lead, or antimony. The method was developed by Johannsen[11] from the revolving process. The basic principle is the volatilization of tin from tin slag, ores of low tin content, and complex tin ores, and collection of the fume as tin oxide which is reduced in the usual manner. The process is effected in a



(Courtesy Office of War Information)

FIGURE 61. Casting pure tin into blocks for bars, Longhorn tin smelter.

revolving tubular furnace which is lined with firebricks and which has at its discharge end an oil or coal-dust burner. The furnace used in the experiments was 53 feet long, with an outer diameter of 4 feet and an inner diameter of 3 feet. The energy requirements were 6 to 8 horsepower. The furnace had a capacity of 12 to 14 metric tons per 24 hours, and a fuel oil consumption of 2 to 6 per cent of the ore processed.

When the revolving method, which is generally used for the dezincing of zinc-bearing ores, was transferred to tin ores, an incomplete removal of

[11] Johannsen, *German Patent 525,687.*

tin resulted A slag of the composition 10.4 per cent tin, 27 65 per cent FeO, 35 0 per cent SiO_2, and 5 5 per cent CaO still contained 2 to 4 5 per cent in aftertreatment in the revolving furnace at 1160 to 1200° C. following mixture with 25 per cent coke dust This corresponds to a tin volatilization of 75 to 85 per cent The process was therefore changed in such a manner that the tin was volatilized not as metal vapor, but as the more readily volatile tin sulfide which was converted into tin oxide and sulfur dioxide in the oxidizing atmosphere over the ore This was done by adding sulfur-containing substances When 10 per cent pyrite was added, the volatilization of tin from the slag was increased to 94 to 96 per cent, while the tin content of the poor slag was reduced to 0 5 per cent

The process can be applied with equal success to sulfidic tin ores of low content and complex tin ores A tin ore with 9 5 per cent tin, 35 0 per cent iron, 38 per cent sulfur, and 9 2 per cent silicon dioxide was mixed with 10 per cent comminuted coke and the mixture treated in a revolving furnace which required 5 to 7 per cent coal dust for additional heating The residual slag had 0 05 to 0 2 per cent tin, which corresponds to a volatilization of 98 to 99 5 per cent The collected tin oxide contained 70 per cent tin, small amounts of lead, antimony, and arsenic, and had a sulfur content of 1 per cent

A complex sulfidic tin ore of the composition 22.0 per cent zinc, 4 2 per cent lead, 5 0 per cent tin, 19 per cent sulfur, 10 per cent iron, and 29.0 per cent silicon dioxide was treated in the revolving furnace at 1150° C The residue contained 0 3 to 0 5 per cent tin, 0 3 to 0 6 per cent lead, 25 to 27 per cent zinc. The volatilization of the tin amounted to 86 to 92 per cent, that of the lead to 90 to 94 per cent, while 89 to 91 per cent of the zinc remained in the residues.

The tin oxide obtained by the revolving treatment can be freed from its content of arsenic, a part of its lead, and a small part of its antimony by sintering at 1150 to 1200° C , which causes an increase in tin oxide concentration

In the case of many complex ores, a part of the tin is volatilized When a complex tin ore with 14 to 15 per cent tin, 7 5 per cent lead, 17.3 per cent zinc, and 14.8 per cent sulfur was processed, an oxide was obtained which contained about 35 per cent tin, 13 per cent lead, and 14 per cent zinc, and a residue with about 0 1 to 0.2 per cent tin and about 24 per cent zinc remained

The tin smelter of the Berzelius Metallhutten Company, Ltd , in Duisburg-Wanheim, reduces mixed oxides in a revolving tubular furnace [12] This furnace differs from the Krupp furnace in that it is constricted on the discharge end, thus causing the formation of a sump where the separated

[12] *German Patents 572,253* and *585,628*

metal collects, while the slag flows off on top of the metal Heating by oil or coal-dust burners is on the discharge end and is adjusted in such a fashion that the hottest zone of the furnace is just above the metal sump, the temperature decreasing toward the charging end of the furnace. The charge consists of the mixed oxide, coal, and soda and is continuously fed into the furnace The reduction of the metal oxides takes place at first without melting of the charge, during which process a considerable part of the reduced metal is already separated and flows toward the sump on the discharge end of the furnace. The nearer the charge approaches the discharge end, the more it assumes a crumbly dough-like character and

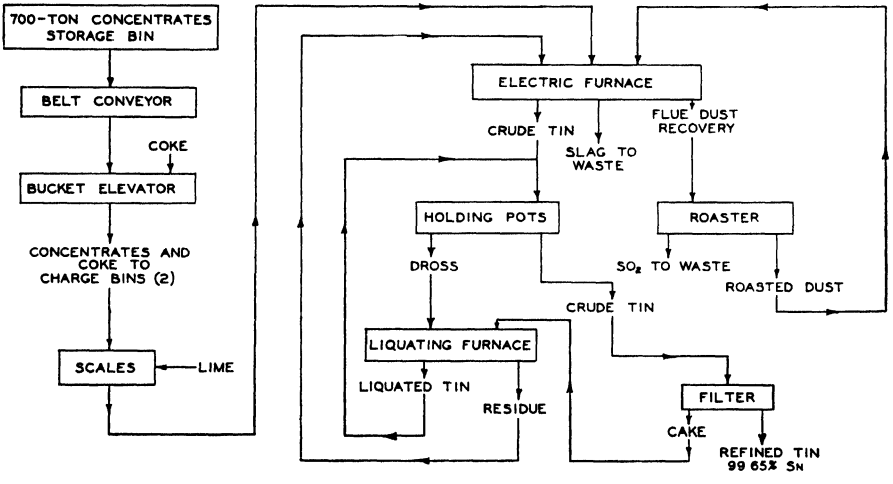


FIGURE 62 Flowsheet of Sullivan tin smelter

changes to a more or less viscous liquid state. During this process a separation of metal and slag occurs The slag, which is continuously discharged, contains only 0 6 to 1 0 per cent tin. The metal is tapped at certain time intervals beneath the sump.

The zinc which is present in the charge is largely volatilized. It is oxidized outside the furnace and is accumulated as zinc oxide which is but little contaminated by other metal oxides. A small part of the zinc is alloyed with the other metals and is of assistance in the subsequent refining of the alloy.

This process has substantial advantages over the use of a reverberatory furnace, inasmuch as it has a greater operating capacity, but chiefly because it immediately produces a tin-poor slag and a better separation of zinc from the other metals.

Canadian Practice. Up to the end of 1947, over five million pounds of metallic tin have been produced by an electric-furnace smelting method at

TABLE 8 OPERATING DETAILS OF SULLIVAN SMELTER

Plant feed	Tailing from zinc rougher circuit of zinc plant
Treatment	Sulfide removal by flotation; gravity concentration of gangue minerals
Heads assay (% Sn)	0 05
Final concentrate (% Sn)	67
Ratio of concentration	2800 to 1
Reduction	(1) Electric furnace smelting, (2) refining crude tin, (3) dross treatment and recovery
Operating data	
Furnace rating	400 kva
Dimensions (outside)	9 ft x 6 ft x 6 ft high
Lining	Alumina-silica bricks
Power	90 volts, 3000 amperes
Electrodes	3 Graphite, 8-in diameter
Charge (lb)	
Concentrate	800
Flue dust (roasted)	175
Liquated residue	100
Coke	130
Limestone	10
Number of charges per complete charge	27 to 31
Capacity per 24 hr (lb)	
Concentrates	15,500
Refined tin	10,000
Operation cycles (hr)	30–33
Refining	Filtration through all steel, single compartment pressure filter
Filter medium	Asbestos cloth on perforated steel plate
Iron in crude tin (%)	0 2 to 0 8
Filter cake	80% Sn, 9 5% Fe
Refined tin analysis (%)	
Iron	0 005
Lead	0 31
Copper	0 003
Zinc	0 005
Bismuth	0 002
Aluminum	0 005
Manganese	0 005
Cobalt	0 004
Antimony	0 01
Tin (by difference)	99 65
Slag analysis (%)	
Tin	3 5
Iron	16
Sulfur	0 4
Alumina	22 1
Lime	9 3
Lead	trace
Silica	22 0
Manganese	6 4
Tungstic oxide	8 0
Magnesium oxide	1 0
Titanium dioxide	11 0
Electrodes per ton of refined tin (lb)	12 6
Power per ton of refined tin (kw -hr)	1,860

the Sullivan concentrator of Consolidated Mining and Smelting Company of Canada, Ltd., at Chapman Camp, B. C. A metal running 99 65 per cent tin is produced, without resorting to electrolytic refining, from concentrate produced in the tin-plant section of the general Sullivan concentrator.[13] Tailings from the zinc rougher circuit of a flotation plant constitute the plant feed for the tin plant The treatment involves the removal of the bulk of the sulfide by flotation. Subsequently gravity concentration of the gangue minerals or tailing is conducted to recover the tin Heads which assay 0 05 per cent tin are concentrated to a 67 per cent material The Sullivan ore contains small crystals of cassiterite of a maximum size of 75 microns, with about 10 per cent occurring as a sulfide

The concentrates for the tin plant are reduced according to the flowsheet in Fig. 62 in three steps. The first involves smelting in an electric furnace. The second refines the crude tin by the usual methods as well as a special

TABLE 9 EFFECT OF TEMPERATURE ON TIN FILTRATION

FILTRATE (Temp , °C)	IRON IN FEED (%)	IRON IN FILTRATE (%)
250	0 488	0 003
276	0 20	0 003
292	0 30	0 004
388	0 215	0 00494
397	0 45	0 00756
478	0 295	0 01208

filtration procedure The third refers to the treatment of drosses and flue dust. The electric-furnace smelting is conducted with a lime-coke mixture which gives a slag low in tin content, and slag treatment or retreatment is omitted. The operating details[14] are given in Table 8

The filtration purification depends upon the solubility of iron in tin at high temperatures and the separation of an iron-tin component $FeSn_2$ on lowering the temperature to a point near the melting point of tin Filtration through asbestos cloth in a special filter lowers the iron content of the crude tin to 0.005 per cent The effect of temperature on the iron removal from tin during filtration is shown in Table 9

Treatment of Slags

Slag produced in the first-run smelting of tin concentrates invariably contains so much tin that it must be retreated before being discarded. Retreatment is done in furnaces of either the blast or the reverberatory type Second-run slag from blast furnaces generally contains higher tin percent-

[13] J B Huttl, *Eng Mining J* , **147**, No 5, 85–7 (1946)
[14] *Ibid.*, **149**, 60–2 (1948)

ages than those from slag-smelting reverberatories. The object in slag smelting is to reduce the tin silicates to metallic tin Higher temperatures are required than are used for concentrates smelting Fairly large amounts of reducing materials are required, being added as culm or anthracite screenings Limestone may be employed as a fluxing material and often metallic iron in the form of scrap is used to replace the tin in the silicates in the slag Tin produced from slag smelting is usually very impure, generally containing considerable amounts of iron-tin alloys. These are known as hardhead. In the best practice, secondary slags should not contain more than 1 per cent of tin, although often slags containing 3 per cent or more are discarded Some of the richer slags at times are added to the concentrates charge in the first smelting

Sixteen to eighteen hours is the time required for reverberatory slag smelting The operation is a batch process Handling of liquid slags and the metallic tin resulting is the same as in blast-furnace practice

Tafel[15] described a method for the detinning of low-tin slags used at the Berzelius-Metallhutten Company, Ltd , plant in Duisburg-Wanheim. The milled slag is formed into briquets with coke dust and powdered limestone and treated in small blast furnaces with water-cooled grates The tin is partly volatilized and partly recovered as a tin-iron alloy.

Refining of Tin

The metallic tin produced from smelting is too impure to be sent to the market as such Refining to eliminate objectionable metallic impurities alloyed with the tin is of two kinds: the *thermal method*, which will be described here, and the *electrolytic method* which, because of its future possible importance, is described separately in Chapter 8.

The thermal refining consists of one or both of the operations of liquating or sweating and boiling, tossing or poling. Liquating is done in a comparatively small sloping-hearth reverberatory furnace with the hearth slope toward an open taphole which discharges into receiving kettles outside the furnace. Liquation has for its object the removal of those metallic impurities, alloys and compounds having a higher melting point than tin. The bars, pigs or slabs of tin are placed on the upper side of the furnace hearth. The furnace temperature is kept just above 232° C , the melting point of tin Long-flame bituminous coal is used for fuel. The melting is slow. The success of the operation depends on careful temperature regulation to avoid melting the metallic impurities The tin runs from the furnace to the outside kettles, leaving the residue on the hearth The dross remaining in the furnace is pushed toward the fire and the temperature is

[15] V. Tafel, "Lehrbuch der Metallhuttenkunde," Bd II, pp 201–2, Leipzig, S Hirzel, 1929

raised until all possible metal is recovered The second sweated portion of tin is caught in another kettle, cast into pigs or slabs and resweated with the next charge The final dross is treated at a higher temperature and roasted, the resultant product going to the tin concentrates smelting furnace.

Some impurities of comparatively low melting points are sweated out with the first-run tin metal. Most of the iron, arsenic, antimony and copper impurities remain with the dross, while most of the lead and bismuth go into the tin.

The first-sweat tin is further refined by boiling or tossing. This is done in kettles holding 6 to 10 tons at temperatures considerably above the melting point. The boiling operation is analogous to copper poling, inasmuch as the molten metal is stirred with a pole of green wood or by immersing in it bundles of green wood sticks The wood undergoes destructive distillation, the resultant steam and gases producing a strong bubbling or boiling action in the bath. Thus different portions of the metal are brought to the surface and exposed to the air Most of the impurities and part of the tin are oxidized The drosses collecting on the surface are skimmed off, to be either resweated or else resmelted with an original tin concentrate charge. In some of the more modern refineries, boiling is done by agitating the metal with compressed air Boiling is continued until the desired grade of refined metal is produced. If the tin contains large amounts of impurities, the operation may be continued for several hours Excessive heating at too high a temperature must be avoided, otherwise large amounts of tin will be oxidized.

Tossing consists in filling hand ladles with the molten tin and pouring it from a height back into the kettle, thus exposing it to the oxidizing action of the air. The result is quite the same as that of boiling.

Iron is almost completely removed by boiling, while the other impurities such as arsenic and antimony are considerably reduced in amount

In the melting of impure Bolivian tin ores, it was therefore possible to obtain a tin of only 99 and 99.5 per cent under the best of circumstances, with the formerly used thermal refining method and a careful wet pretreatment of the ore. Methods have been developed which permit production of tin of the quality of Banka or Straits tin, with a content of 99 75 per cent and more by thermal methods.

Kroll[16] found that the addition of certain metals to impure tin may cause precipitations similar to those which occur at the desilvering of lead by the Parkes process. He determined that the alkali and alkaline-earth metals (including magnesium) form compounds of the light metals with arsenic and antimony with a high melting point when they are introduced in molten tin which contains arsenic and antimony. Those com-

[16] W. Kroll, *Metall u. Erz*, **19**, 317–24 (1922)

pounds aggregate on the surface of the melt owing to their low specific weight. The compounds can be removed by skimming, filtering, separation, or any other suitable method. The Th. Goldschmidt Company[17] developed a method which is based on the same principle. Aluminum and zinc are used as media for the precipitation of arsenic and antimony. According to Savelsberg[18] the process takes place in pots of 4 to 5 tons in such a manner that the proper amount of aluminum (about 0 1 per cent aluminum for 1 per cent of impurities in the form of arsenic, antimony, and copper) is added as a 30 per cent master alloy to the hot tin melt which is rapidly stirred. Air is blown into the melt inasmuch as the compounds formed do not rise to the surface of the melt. In this manner a scum is formed which can be removed after cooling The surplus aluminum which remains in the tin melt is removed by poling with steam at 250° to 260° C. The Zinnwerke Wilhelmsburg Ltd combines the method with reducing and leaching of the tin ores. If the antimony content is above 1 per cent, the amount of dross is quite high and its processing is difficult and expensive. Therefore the method is used only in the case of an antimony and arsenic content of about 1 per cent or less The liquated tin, freed of iron and copper, is brought to a melting point and aluminum is added while stirring. The rising dross can be comminuted by immediate vigorous stirring and thus be transformed into a semi-metallic state, it can then be skimmed off It contains arsenic and antimony corresponding to the added aluminum The aluminum surplus is removed in the usual manner The dross contains a large amount of tin which can be removed by liquation. It is possible to allow the melt to cool down immediately after the aluminum has been mixed into it The dross which has risen to the surface is later removed. This dross, with a substantial tin content, must also be liquated to recover the metal

The aluminum-arsenic compounds may generate poisonous arsenic hydride not only when wetted but even when stored in air. This can best be overcome by liquating the dross immediately after it has been produced at a temperature high enough to cause decomposition of all arsenic-aluminum compounds by oxidation. Under no circumstances should the intermediate products be stored in closed rooms.

The refining methods described up to this point do not succeed in removing the lead from tin This can be accomplished to a certain degree by allowing the tin to remain for a longer period of time at a temperature slightly above the melting point. A bottom layer is formed which is richer in lead than the top layer, and which can be separated by careful ladling. Attempts have been made to improve this process by cooling just below the melting point of tin. This causes the formation of a solid solution of

[17] Th Goldschmidt, *German Patent 411,477.*

[18] W. Savelsberg, *Metallbörse*, **22**, 833–4 (1932).

low lead content on the tin end of the phase diagram, while a melt of higher lead content remains because the eutectic mixture of tin and lead solidifies only at 182° C. Generally one does not proceed as in the pattinsonizing of lead, where the lead crystals are separated from the silver-bearing lead with a ladle. The still-liquid tin of a higher lead content is drained through a tap in the bottom of the melting pot. The separated crystals are remelted by increasing the temperature.

After refining, tin is cast into pigs. The dross is carefully skimmed off in the kettle before casting so that the metal will have a clean, bright surface Tin is cast at temperatures just slightly above its melting point, in cast-iron molds quickly filled and lightly skimmed with wooden paddles just before solidification of the metal.

As an indication of the quality of the product from all the tin mines, reduction works, smelters, and refineries in the world, typical tin analyses are given in Table 6, page 56, which is a composite of data collected from a large number of different sources.

Chapter 7

Gaseous Reduction, Leaching and Metallic Reduction

Carbonaceous Fuel and Gaseous Reduction

Smelting practice is not as simple as might be expected from the chemistry of eliminating oxygen from an oxide of a common metal Nearly all of the difficulties in tin-smelting operations are caused by the rebellious nature of highly heated tin metal The reduction mechanism is not as direct as the generally assumed equation

$$SnO_2 + 2C = Sn + 2CO$$

would lead one to believe

Leplay and Laurent in 1837[1] ingeniously showed that solid carbon reduction is gaseous in its mechanism and that physical contact of reducing agent and reducible oxide is not essential. They placed a piece of solid carbon in a platinum boat in a furnace tube sealed at one end, in another boat alongside of the first they placed metallic oxides. Stannic oxide was used in some of the experiments The tube was heated in a furnace, the open end in contact with the air. The solid carbon oxidized to carbon monoxide and dioxide and the metallic oxides were reduced to metal without contact with the solid reducing agent.

The work of Fink and Mantell[2] on stannic oxide and finely ground tin concentrates has confirmed these results They calcined stannic oxide at 850° for one hour in the presence of air. The tin concentrates were roasted at 850° to 1000° C for four hours. Graphite, ball-mill ground, was calcined at 850° for one-half hour and at 1000° for two hours in closed crucibles in the absence of air. Determinations were also made in which calcined fuel coke and calcined petroleum coke were used.

Stannic oxide was placed in an alundum combustion boat. This boat was placed alongside a similar one filled with ground graphite. Both boats were placed in the center of a vitreosil tube 24 inches long, of 1-inch diameter The tube was heated in an electric furnace Purified air was drawn through the heated tube Determinations were made at 600°, 700°, 800°, and 900° C. each. No reduction was evident at 600° and 700°, reduction at 800° was very slight; but it was easily seen at 900°, with the

[1] Leplay, and Laurent, *Ann chim phys* (2), **65**, 404 (1837).

[2] C. G. Fink, and C. L. Mantell, *Eng. Mining J.*, **124**, 686–91 (1927).

production of small tin globules on the surface of unreduced stannic oxide. Substitution of tin concentrates for the stannic oxide gave similar results. Further runs were made with stannic oxide and fuel coke; concentrates and fuel coke, stannic oxide and petroleum coke; and concentrates and petroleum coke. Practically all of the results were the same. Reduction was determined by testing the charges, after the run was over, by qualitative chemical methods. The furnace charges were cooled in nitrogen (freed of moisture, oxygen, and carbon dioxide) to room temperature before being examined.

Doeltz and Graumann[3] reported that carbon reduction of stannic oxide was not evident after one hour at 800° C., but did show signs of taking place at 830° to 900°. It is interesting to observe that carbon slowly oxidizes at 500°, the oxidation of amorphous carbon is marked at 650°, and the speed of oxidation increases upon further rise of temperature Commercial blast and shaft furnaces used for tin smelting operate over a range of from about 1000° to 1400° C.

Charpy and Bonnerot[4] attempted to determine whether reduction of iron oxide (Fe_2O_3) by carbon may be brought about by direct action between the solids or through mediation of the gas phase only. They studied the rates of reduction under a series of low pressures Ferric oxide and graphite, previously purified, heated to 1000° in vacuum, mixed and strongly compressed, were heated in an electric furnace in a porcelain tube. The pressures were maintained and measured by a mercury pump and MacLeod gage. At 950° C , under pressures of 0 01, 0 1, 1, 2, 4, and 8 mm of mercury, the following rates of evolution of gas were found: 0 10, 0.14, 0.31, 0.56, 0.80, 1.07 cc per hour. The rate thus rapidly decreases with decrease of pressure and the conclusion is drawn that, at least up to 950°, solid carbon does not reduce ferric oxide If solid carbon does not reduce ferric oxide (when the carbon cannot oxidize owing to the absence of oxygen in the surrounding atmosphere) up to 950°, it will not reduce stannic oxide, which it will be shown is harder to reduce than is ferric oxide.

Fink and Mantell[5] confirmed this finding in respect to stannic oxide. Finely ground graphite and stannic oxide were calcined at 850° for one hour. These were intimately mixed and compressed in a small hand press to a more or less compact mass Charges were placed in alundum boats in a tube furnace in a nitrogen atmosphere and subjected to temperatures of 600°, 700°, 750°, 800°, and 850° for four-hour periods. The charges were cooled to room temperature before being removed from the furnace and its nitrogen atmosphere. The nitrogen had been purified of

[3] Doeltz, and Graumann, *Metallurgie*, **4**, 290 (1907)
[4] Charpy, and Bonnerot, *Compt. rend.*, **15**, 644 (1843)
[5] C. G. Fink, and C L Mantell, *Eng Mining J.*, **124**, 686–91 (1927).

oxygen. After cooling, the charges were tested qualitatively by sensitive methods for tin The reduced metal was absent in all cases

These experiments were repeated with finely-ground (ball mill), acid-washed fuel coke and finely-ground petroleum coke treated with concentrated sulfuric acid. These carbonaceous materials were previously calcined to remove volatile matter These materials were intimately mixed with calcined stannic oxide and treated as were the materials used in the experiments previously described In no case was tin found by qualitative tests

Carbonaceous fuels in air atmospheres, out of contact with stannic oxide or tin concentrates, have the power of reducing tin oxides by their own oxidation and passage to the gaseous phase Carbonaceous fuels intimately mixed with stannic oxide, in the absence of oxygen, are without reducing properties, at least up to 900° C. Solid carbon fuel reduction of reducible metallic oxides is gaseous in its mechanism Carbon reduction requires higher temperatures than gaseous reduction, as the carbon must first be gasified at a rapid rate This rate becomes marked above 1000° C

In smelting operations, the coal or coke of a reducing charge is active only as it becomes partly oxidized to carbon monoxide gas Reduction of metallic oxides is not accomplished by reducing fuels in the solid phase If a more efficient, cheaper, and more easily manipulated process would result from the gasification of the reductant, outside of the smelting furnace, the possibility of developing such a process deserves careful consideration The gaseous reduction of tin concentrates has been studied with this end in view.

Tin in metallic form has a low melting point. It is different from most of the other metals occurring in the combined state in nature, in that its ore has a reducing temperature, by gaseous reductants, above the metal melting point.

Reverberatory- and blast-furnace practice in the metallurgy of tin requires temperatures of 1300° to 1400° C Hydrogen reduction may be effected beginning at 250° C., and the most economic point is between 750° and 800° C Hydrogen would be of interest at the location of one of the world's largest tin orebodies, such as those of Bolivia, in regions far from coal but in the midst of sources of water power "Smelting with water" seems to be the obvious answer to the problem Other gaseous agents, such as carbon dioxide, natural gas, manufactured and refinery gases, as well as by-product hydrogen from electrolytic operations, have been studied.

Gaseous reduction was first investigated in 1830 by Despretz,[6] who reported that hydrogen and carbon monoxide each reduces stannic oxide

[6] C. Despretz, *Ann. chim. phys.* (2), **43**, 222 (1830).

to tin metal. W. Muller[7] reported his work on heated oxides in contact with hydrogen in sealed glass vessels. He showed that many metallic oxides give evidence of reduction at temperatures from 200° to 400° C.

Arnold[8] and Hampe[9] proposed hydrogen reduction of tin ores for one or two hours on a 1-gram sample at a red heat as an analytical test. They pointed out the advantage of the ease of separation of the reducible oxides of the metals from those nonreducible (those of silica, nonmetallic minerals, gangue) by acid treatment of the reduced charge and resulting metal solution

Fink and Mantell[10] studied the reduction of stannic oxide by specially purified hydrogen, as well as other gases between the temperatures of 250° and 1000° C. Determination of the rate of change of velocity of the reaction

$$SnO_2 + 2H_2 = Sn + 2H_2O$$

with change of temperature was made They found that stannic oxide could be completely reduced by hydrogen to metallic tin at temperatures as low as 250° C The reaction was caused to proceed as an irreversible one, by inducing an excess of the reactant, molecular hydrogen, to act as a medium of removal of the undesired product of the reaction, water vapor, by causing the gas to sweep across the reacting surface

With stannic oxide in excess of the amount required to oxidize all of the hydrogen present to water vapor, at any particular temperature, further reduction ceases as soon as the water vapor concentration has attained N per cent, where N is a function of the temperature The value of N varies inversely as the temperature The hydrogen gas must be supplied at a sufficiently high rate to maintain an excess of reductant for the stannic oxide, and at a velocity high enough to "sweep out" water vapor as fast as it is formed.

There must be sufficient excess of reductant to prevent the reoxidation of the reduced products of the reaction As the reaction is between a solid material and a gas, the natural inference is that the reduction resulting is a surface phenomenon. Stannic oxide is reduced in two steps or in one step, depending upon whether the temperature employed is below or above the thermal decomposition point of the lower or stannous oxide.

The velocity of the reduction was not the same for all parts of the mass and continued greatest at those points first affected This same phenomenon has been observed by Hilpert[11] in his work on the reduction of iron oxide by hydrogen and carbon monoxide. The curve for the results given

[7] W. Müller, *Pogg. Ann.*, **136**, 51 (1864), **153**, 332 (1875).
[8] A. E. Arnold, *Chem. News*, **36**, 238 (1877).
[9] W. Hampe, *Chem Z.*, **11**, 19 (1887).
[10] C. G. Fink, and C. L. Mantell, *Eng. Mining J.*, **124**, 967–72; 1052–4 (1927).
[11] Hilpert, *Ber.*, **42**, 4574–81 (1909).

in Fig. 63 covers the temperature range of 250° to 850° C The curve for the reduction is logarithmic The general expression was found to be

$$\log T_k + \log M = C$$

where T_k is the absolute temperature, M the time, C a constant Extrapolation of the curve shows that the reaction would be instantaneous at 1000° C , and would require many days at 100° C , assuming reaction possible at that temperature

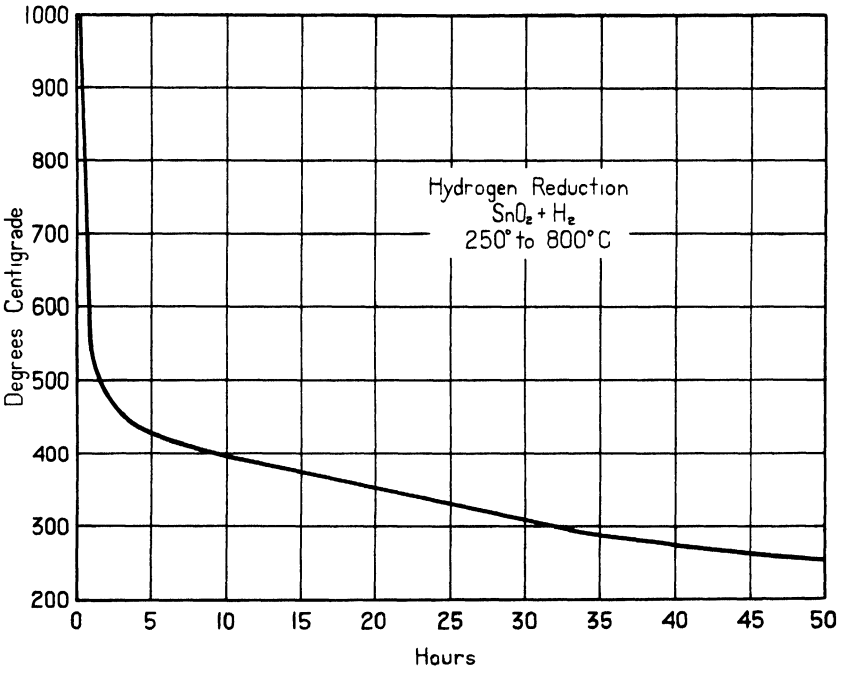


FIGURE 63 Relative reduction rates of stannic oxide at various temperatures

The shape of the curve shows that the most advantageous temperatures at which to operate are those above 750° C., when rapidity of reduction is desired. When the curve for stannic oxide is plotted with a relatively small time interval as ordinate, the curve can be seen to have a distinct inflection at approximately 750° C.

Fink and Mantell[12] determined the rate of reduction of ferric oxide in comparison with stannic oxide, in order to gain an insight into what happens in a complex ore containing iron and tin oxides together, as well as the oxides of the other metals Pure ferric oxide was used.

The time-temperature curve for the reduction of ferric oxide by hydrogen is given in Fig. 64. As was the case with stannic oxide, the ve-

[12] C. G. Fink, and C. L. Mantell, *Op. cit.*, 967–72.

locity of the reduction was not the same for all parts of the mass, being lessened and continuing greatest at those points first affected. For ferric oxide the curve is shifted over closer to the axes than is the stannic oxide curve

Ferric oxide reduction by hydrogen is easier than stannic oxide reduction by hydrogen In a mixture of these oxides the tendency would be: first, for a reduction of the ferric oxide, second, a stage where both were being reduced, the ferric oxide at a faster rate than the stannic oxide, and, third, a stage where all the ferric oxide was reduced with some stannic remaining.

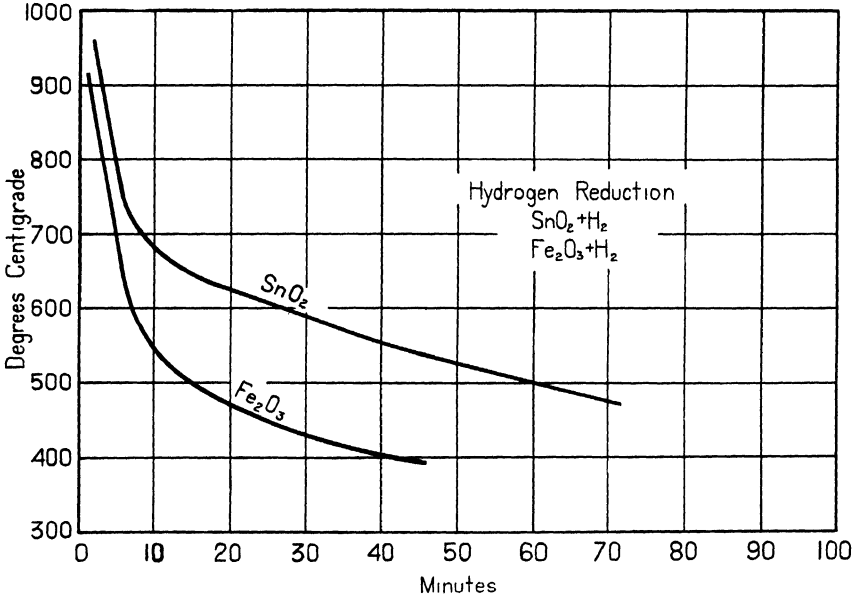


FIGURE 64. Curve showing time necessary for complete reduction of stannic oxide and ferric oxide at various temperatures.

Reduction of tin oxide by hydrogen is rapid at 700° to 800° C. Temperatures necessary are far below those used in tin-smelter reverberatories. Practical commercial operations, as confirmed by pilot plant runs, are at 750° to 900° C. Metallic iron does not appear as such after reduction and cooling of the charge. The oxides of iron are always evident. It was concluded by earlier investigators that the oxide of tin was more readily reduced to metal than were the oxides of iron. This reasoning has been shown to be unsound. Fink and Mantell[13] studied this from the viewpoint of the oxidation of hydrogen-reduced tin and iron. They found no difficulty in producing hydrogen-reduced iron either from any of the iron oxides or from those oxides mixed with the oxides of tin, provided the charges

[13] *Ibid.*, 1052-4.

were cooled to room temperature after reduction in a reducing atmosphere The oxidation points of hydrogen-reduced, gaseous-reduced, and electrolytic iron were studied All three of the varieties of iron mentioned showed rapid oxidation by moist air at 200° C.

The gaseous-reduced iron oxidized more rapidly than did the electrolytic iron after contact with the stream of air for 30 minutes The gaseous-reduced iron was pyrophoric at this temperature Freshly reduced iron was found to be pyrophoric and completely oxidized at 200°, 150°, 100°, 75°, and 50° C.

Gaseous-reduced iron, prepared at temperatures below its melting point, is in the form of a very fine powder. The average particle size will be of the order of 2 to 3μ The surface of these particles in comparison with their volume is enormous Their ready oxidation at low temperatures is understood from the knowledge of surface adsorption phenomena

Metallic tin, when the reduction temperature is 200° or more above its melting point, tends to form small drops or globules, thus reducing the exposed surface Experiments were made with tin particles reduced at low temperatures to determine their temperature of oxidation The tin particles were of the order of 2 to 3μ There was little oxidation of tin at 50°, 75°, 100° and 150° C either by moist or by dry air over a half-hour period At 200° C. there was a slight oxidation, which grew less after passing beyond 230° to 250° C., when there was a tendency toward the formation of globules At no temperature below 250° C nor at 250° C was the tin pyrophoric

We thus have the explanation for the absence of iron in the experiments of other workers in the reduced masses resulting from the reduction of mixed iron-tin oxides or of iron-bearing tin concentrates Since the tin was not oxidized to any appreciable extent below its melting point, the furnaces used were usually discharged after cooling down to or a little below the melting point of tin. The reduced iron, being freshly prepared and very active, is readily reoxidized at these temperatures—so readily oxidized that it is pyrophoric On contact of the reduced masses with air, the reduced tin metal is not affected but the reduced iron changes over entirely to its oxides

Hydrogen reduction of Bolivian tin concentrates on a semi-commercial scale shows time-temperature reduction curves of the same form as the tin-oxide-hydrogen curves At any temperature the time for complete reduction was a function of the hydrogen flow velocity as shown in Fig. 65. Time of reduction varied with the mesh of the ore up to 30 mesh, as shown in Fig. 66. Beyond this screen size further grinding of the ore did not seem to increase the speed of contact between ore particle and gas molecule.

The process of gaseous reduction depends for its success upon the absence of all slagging phenomena until complete reduction is effected.

Even incipient fusion prevents the intimate or rapid contact of ore and gas, slowing down the reduction finally to complete stoppage, when the ore particles become slagged or glazed over In the particular Bolivian concentrates used, no difficulty was encountered owing to the low fusing point of tourmalines, gangue materials, or slagging ore constituents at the temperatures employed After reduction, the furnace charge was

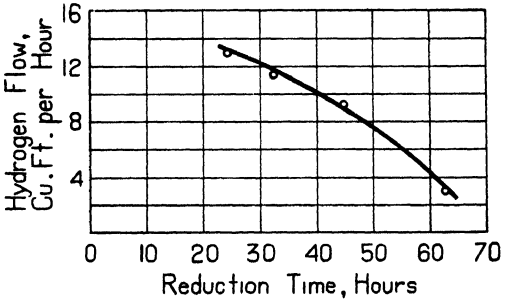


FIGURE 65.
Curve showing flow of hydrogen and time of reduction at constant temperature

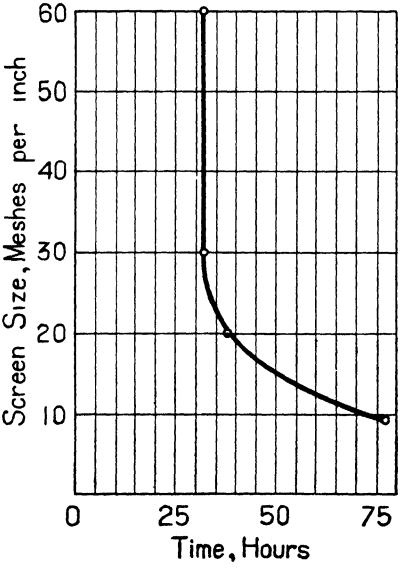


FIGURE 66
Curve showing screen size and time of reduction

cooled in an atmosphere of hydrogen to below the melting point of tin Iron was always found as oxides in the reduced charge, the cause of which has been explained above

In its final solution, the method of tin recovery from the reduced charge was simple The concentrates had the following analysis: SnO_2 86.2 per cent, Sn 67.95 per cent; Fe 4.19 per cent, Fe_2O_3 5.65 per cent; Sb 0.04 per cent, As 0 010 per cent, Cu 0.036 per cent, Bi 0.296 per cent, WO_3 1.42 per cent; SiO_2 1.73 per cent, and S 0.28 per cent. If the ore

charges were stirred or rabbled continuously during reduction, thus exposing fresh surfaces and allowing the molten tin particles to flow together, about 80 per cent of the tin content of the ore was directly liquated from a nonfluid slag

This metal was about 70 per cent of the weight of the concentrates charged into the furnace The remaining 20 per cent of the tin content of the concentrates could be almost completely recovered by fusing the residues at 1000° to 1050° C when the gangue formed a very liquid slag and the metallic tin readily settled out The slag contained only small amounts of tin amounting to 1 to 2 per cent of the total tin content of the original concentrates

The final slags were from 10 to 12 per cent of the original weight of the ore The tin contained all the reducible metals, bismuth, antimony, lead, copper, and silver, but only a small amount of the iron Arsenic was absent in the tin produced, and had apparently been volatilized in the process Tungsten and molybdenum were reduced to their lower oxides only, and did not find their way into the metal

Investigation shows also that there may be possibilities of winning tin from its ores by low-temperature gaseous reduction (300° to 500° C) followed by leaching of the reduced charges, with electrolytic precipitation of the metal in the leaching liquors The leaching solutions, after partial removal of their metal content, can be used again for leaching of fresh reduced ore Almost 100 per cent metal extraction is possible

Using hydrogen for the reduction of tin concentrate, a rough estimate of the power consumption is based on the following factors One pound of metallic tin requires for its reduction from cassiterite (SnO_2), 6 cubic feet of hydrogen gas One kilowatt-hour produces 7 cubic feet of hydrogen gas by the electrolysis of water [14] The theoretical value is about 9 cubic feet Power requirements for the production of hydrogen therefore are 0 86 kilowatt-hour per pound of metallic tin, or 1,030 kilowatt-hours per ton of 60 per cent tin concentrate The reaction is effected economically at 750° C At this temperature the power requirements for heating represent an additional 0 75 kilowatt-hour per pound of tin, or 900 kilowatt-hours per ton of 60 per cent concentrate The total power requirements then appear as 1 6 kilowatt-hours per pound of tin, or 1,930 kilowatt-hours per ton of 60 per cent concentrate)

Leaching of Tin Concentrates and Tin Oxides

This work was undertaken to find some single substance or combination of substances which, in aqueous solution, would dissolve stannic oxide If it is possible to dissolve native stannic oxide with some solvent or combination of solvents, the foundation will then be laid for a leaching process

[14] Allan, *Trans. Am Electrochem. Soc.*, **41**, 239 (1922).

for extraction of tin from its ores or, in other words, the hydrometallurgy of tin. It was also hoped that the work might throw some light on the mechanism of the secondary enrichment of tin ores. Clarke[15] stated that the solubility of cassiterite is indicated by several natural deposits. Cassiterite has been noted in opaline deposits, from hot springs, as pseudomorphs after feldspar, cappings on quartz crystals, and in stalactitic forms Cassiterite is one of the most insoluble compounds known. There seems to be some geologic evidence, however, that there may have been secondary enrichment of veins by solution, transportation, and deposition of cassiterite

An attempt was made to clarify the processes which are involved in the formation of secondary tinstone deposits, and to find a solvent for stannic oxide that could serve as a basis for a hydrometallurgical process for the recovery of tin

The following materials were treated with the same leaching solutions.

(*A*) Unground, unroasted Bolivian concentrates (hereafter termed raw concentrates) of the following analysis

Component	*Per Cent*		*Per Cent*
Sn	67 95	which is equivalent to SnO_2	86 2
Fe	4 19	which is equivalent to Fe_2O_3	5 96
Sb	0 04		
As	0.01		
Cu	0 036		
Bi	0 296	which is equivalent to Bi_2O_3	0 33
WO_3	1.42		
SiO_2	1 73		
S	0 28		

(*B*) Raw concentrates of the above analysis pulverized in a ball mill so that the average maximum particle size was 1 0μ.

(*C*) Unground roasted concentrates—particles retained on a 10-mesh standard Tyler screen. This material is the raw concentrates which had been roasted in Duraloy or ferrochrome crucibles for three-quarters of an hour at temperatures from 900° to 1100° C This roasted material was in part magnetic and black in color in contrast to the red color of the raw concentrates

(*D*) Pure chemical stannic oxide of an average maximum-occurring particle size of 1.8μ.

(*E*) Pure chemical black stannous oxide of an average maximum-occurring particle size of 1.5μ

Many of the solutions remained in contact with the solid materials for as long as six months to a year before analyses of the solutions were made

Dissolution of the stannic oxide, if effected at all, may be presumed

[15] F. W. Clarke, "Data of Geochemistry," *U. S. Geol. Survey Bull.*, Professional Paper 127 (1924).

to take place in several different ways It may, perhaps, get into solution as a salt, such as a stannate, or by reduction to the stannous form in which it is fairly readily soluble, or by chemical reaction, in which the oxygen is replaced by another element, resulting in a soluble compound of tin The substances used for leaching may be divided into various classes:

(1) Strong acids, such as sulfuric or hydrochloric
(2) Weak acids, such as acetic or oxalic
(3) Strong bases, such as sodium hydroxide or barium hydroxide
(4) Weak bases, such as ammonia
(5) Salts, which may be divided into neutral, as sodium chloride, acid, as sodium acid sulfate, or basic, those resulting from a weak acid and a strong base, such as potassium cyanide
(6) Oxidizing agents, such as chlorine or bromine
(7) Salts which are reducing agents
   (*a*) Those whose reducing properties are due to the basic part of the salt, as ferrous sulfate
   (*b*) Those whose reducing properties are due to the acidic part of the salt, such as sodium sulfite
(8) Salts which are oxidizers, divided into those whose oxidizing properties are found in the basic part of the salt, such as ferric chloride, and those whose oxidizing properties are found in the acidic part of the salt, such as sodium nitrate.
(9) Combinations of the above groups in many possible ways, such as neutral salts in saturated sulfur dioxide or saturated chlorine solution, to take merely one of many examples

The soluble salts of tin are limited in number Tin nitrate and tin cyanide do not exist Only the sulfates, halides, the sulfocyanate, and the chlorate are soluble among its inorganic compounds The complex thiostannites and thiostannates are soluble. The organic salts, the acetates, oxalates, tartrates, and malates are soluble

Of the inorganic salts, stannous sulfate very readily changes over in the presence of moisture to oxy and stannic salts. Stannic sulfate is readily hydrolyzed in aqueous solution The fluorides of tin are quickly affected by moisture, with resultant decomposition All the stannous halides readily oxidize to the stannic form, in neutral solutions they readily decompose to form cloudy solutions as a result of the formation of oxy salts. The thiocyanate and chlorate are fairly stable under proper conditions, but they readily hydrolyze in aqueous solution The organic salts of tin are readily decomposed, with the formation of metastannic acid or oxy salts. No tin salts exist which are as stable as copper sulfate, copper nitrate, or copper chloride. Stannic chloride is a fuming liquid at ordinary temperatures, as $SnCl_4 \cdot 5H_2O$ it is a solid readily affected by moisture and easily hydrolyzed in aqueous solution.

Results obtained with the various leaching solutions are tabulated in Table 10 The solubility of the leach constituents is given for reference. Stannous oxide, previously known to be soluble in various reagents, is included in the data for comparison

Since the investigation of the solubility of tin concentrates had as its aim the development of a leaching process, only chemicals available in commercial quantities and at reasonable prices were used

In no case was there marked solubility in a commercial sense. In practically all cases the solubility of the concentrates was the same, irrespective of their previous treatment It did not make any difference in the solubility whether the concentrates were treated as received, or after roasting, or after fine grinding and screening

In some cases, notably those of $M/10$ ferric sulfate, $M/1$ ammonium chloride, and $M/1$ potassium cyanide, roasting the concentrates decreased the tin solubility

In a number of cases the solubility of the chemical stannic oxide is very much higher than the stannic oxide of the tin concentrates Stannic oxide is produced either by furnace oxidation of tin metal or by chemical oxidation (such as through the use of nitric acid) of tin metal or tin salts

The stannic oxide produced by chemical processes is a material with quite different properties from the stannic oxide of cassiterite. The stannic oxide of cassiterite is markedly crystalline, the crystals being of comparatively large size Cassiterite occurs in igneous rocks and was formed at 1132° C, or above the fusion point The chemical stannic oxide is an amorphous material, noncrystalline in its nature. It is produced far below the fusion point. The stannic oxide used in these experiments was roasted but not fused

The results were studied and reassembled in various ways in an attempt to determine whether any particular radicals were more active in causing solution than were others From the results tabulated it can be seen that the sulfate ion causes no great amount of solubility The effect of chlorides and fluorides as well as greater acidity of the leaching solution is shown in the increased solubility. The examples of this are ferric sulfate $M/10$, sulfuric acid 15 per cent, sodium chloride 5 per cent, sulfuric acid 30 per cent, ferrous sulfate 30 per cent, sodium chloride 5 per cent, and the similar series following.

The chlorides cause an increase in the solubility of stannic oxide and of the concentrates In those cases where the ammonium ion was present, the solubility decreased The effect of sulfur dioxide and chlorine may be seen in the case of NaCl $M/2$ saturated with Cl_2 and the same solution with SO_2 substituted for the dissolved chlorine. Solubility of the concentrate decreases markedly. Of all the compounds studied, the chlorides have the greatest solubility effect on the concentrates.

TABLE 10. RESULTS OF TESTS SHOWING SOLUBILITY OF TIN OXIDE AND CONCENTRATES IN VARIOUS SOLVENTS

LEACHING SOLUTION	SOLUBILITY OF LEACHING SALT (grams per 100 cc)	CONCENTRATION OF LEACHING SALT (grams per liter)	CONCENTRATES (grams tin per liter in solution after leaching)				
			SnO	SnO_2	Raw	Roasted	Ground
$FeCl_3$ $6H_2O$ $M/10$	246 0	27 0	1 04	0 05	0 04	0 05	0 05
$FeSO_4$ $7H_2O$ $M/10$	32 8	27 8	2 14	0 04	0 03	0 05	0 03
$Al(NO_3)_3$ $9H_2O$ $M/10$	Very soluble	37 5	—	0 00	0 00	0 00	0 00
$(COOH)_2$ $M/10$	—	12 6	1 16	0 10	0 10	0 19	0.04
NaF $M/2$	4 0	21 0	1 85	0 25	0 13	0 10	0 10
$Fe_2(SO_4)_3$ $M/10$	Very soluble	40 0	62 60	0 17	0 25	0 10	0 30
$MgSO_4$ $M/10$	26 9	24 7	0 41	0 00	0 04	0 02	0 01
Na_2SO_3 $M/10$	14 1	25 0	0 11	0 27	0 02	0 01	0 02
$KHSO_4$ $M/10$	36 3	13 6	2 07	0 22	0 05	0 06	0 01
NH_4Cl $M/1$	29 4	53 5	0 25	0 01	0 14	0 00	0 04
$SnCl_2$ $M/1$	118 7	225 7	—	Loss	Loss	Loss	Loss
$CaCl_2$ $M/1$	49 6	75 5	0 54	0 13	0.14	0 10	0 08
KCN $M/1$	122 0	65 0	0 27	0 05	0 30	0 10	0 15
26% NaCl, sat $PbCl_2$	260 0	260 0	1 10	1 03	0 27	0 29	0.08
HCOOH 20%	—	200 0	29 95	0 02	0 04	0 06	0 04
NaCNS $2M$	177 2	40 5	—	0 07	0 03	0 03	0 03
$HC_2H_3O_2$ $2M$, sat Cl_2	—	120 0	51 04	0 04	0 08	0 07	0 04
H_2SO_4 $2M$, sat Cl_2	—	196 0	139 35	0 48	0 04	0 03	0 04
I_2, sat	0 18	3 0	0 84	0 06	0 08	0 08	0 06
Br_2, sat	4 17	16 0	3 07	0 08	0 10	0 10	0 04
NaCl $M/2$, sat Cl_2	29 3	29 0	0 55	0 20	0 12	0 10	0 11
NH_4Cl $M/1$, sat SO_2	29 4	53 5	0 24	0 07	0 04	0 06	0 05
$(NH_4)_2SO_4$ $M/1$, sat Cl_2	71 0	13 2	8 86	0 03	0 02	0 03	0 05
$FeCl_3$ $M/1$, sat Cl_2	246 0	162 4	24 04	0 18	0 13	0 11	0 11
$MnSO_4$ $M/1$	53 2	151 0	3 40	0 04	0 03	0 02	0 02
Na_2SO_4 $M/3$, sat SO_2	5 02	47 3	—	0 07	0 03	0 02	0 04
$NaHSO_3$ $M/1$	—	104 0	—	0 10	0 07	0 03	0 04
NaCl $M/2$, sat SO_2	35 70	29 25	—	0 10	0 03	0 02	0 03
$NaHSO_3$ $M/1$, sat SO_2	—	104 0	—	0 14	0 07	0 03	0 03
$NaHSO_4$ $M/1$, sat SO_2	50 0	120 1	1 10	0 50	0 09	0 06	0 06
$NaHSO_3$ $M/1$, NaOH $2M$	—	—	5 38	2 05	0 07	0 07	0 07
$(NH_4)_2S$ $M/1$	100 0	68 2	0 31	0 31	0 16	0 09	0 10
$NaHSO_4$ $M/1$, sat Cl_2	50 0	120 1	28 30	0 30	0 09	0 11	0 09
$CuSO_4$ $M/2$	20 0	79 8	1 15	0 50	0 05	0 04	0 04
Na_2S_x, sat.	20 0	160 0	—	162 00	0 80	0 70	0 75
Na_2S, sat	15 4	154 0	—	31 36	0 87	0 74	0 68
Aero Cyanide (50% NaCN) sat.	—	100 0	0 30	1 07	0 06	0 03	0 06
H_2SiF_6 20%	—	200 0	—	0 47	0 42	0 21	0 21
H_2SO_4 15%, NaCl 5%	—	150 0	125 00	5 41	0 89	0 70	0 26
H_2SO_4 30%, $FeSO_4$ 30%, NaCl 5%	—	—	132 50	3 50	0 50	0 60	0 52
H_2SO_4 10%, NaF 4%	—	—	140 00	0 38	0 45	0 47	0 42
H_2SO_4 20%, NaF 4%	—	—	140 20	0 40	0 42	0 38	0 25
$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ $M/2$, sat SO_2	—	196 0	1 56	0 17	0 20	0 20	0 10
HCOOH 10%	—	100 0	20 59	0 09	0 09	0 08	0 07

Iron salts *per se* do not seem to dissolve cassiterite. The combination of relatively strong acidity, an iron salt, and a chloride gave the best solubility of those iron salts tested. Ammonium salts do not have appreciable solvent action on Bolivian concentrates.

Koeberlein[16] described some deposits of cassiterite in which, according to field evidence, it appears that much secondary cassiterite was deposited under conditions resembling those found in the zone of secondary sulfide enrichment. Field observations seem to uphold the conclusion that the solution of cassiterite in the tin veins and redeposition at lower levels is a natural process of the most vital economic importance in Bolivia

Geologically the solubilities of cassiterite observed in this work are appreciable The solubilities observed seem to support the solution theory of enrichment This theory supposes that there is solution of cassiterite in the upper parts of the vein, downward percolation, and redeposition of tin oxide at lower levels That there are objections to this theory is obvious when placer cassiterite deposits are considered This mineral is carried many miles from its source, in the finest state of comminution, subject to attack by waters of various and varying alkalinity and activity Cassiterite is usually considered to be extremely inert and insoluble Chemically this is true, geologically it is appreciably soluble

Koeberlein suggested that the oxidation of associated pyrite has a reducing action on stannic oxide, facilitating its solution in the form of compounds of lower valence It has been shown that in acid solutions sulfur dioxide oxidizes stannous oxide, it would not, therefore, reduce stannic oxide, and the suggested explanation must be modified Elsewhere the presence of copper minerals is cited as having a possible effect, the low solubility of Bolivian concentrates in copper solutions does not seem to support this statement.

On the whole, the values found for the solubility of tin compounds from Bolivian concentrates may bulk large from a strictly geologic viewpoint

Reprecipitation of tin salts may occur easily, as a consideration of the properties of the soluble tin salts will show. The halides of tin are readily hydrolyzed, the decomposition proceeding more rapidly with increase of temperature. These salts in their lower valence forms are readily oxidized The other soluble tin salts easily decompose. None are as stable as the copper salts.

Experiments carried on in attempted leaching of cassiterite by a large number of different reagents at room temperature showed that:

(1) Cassiterite is very insoluble (2) No cheap chemical compound has any appreciable effect on cassiterite. (3) No cheap chemical com-

[16] F. R. Koeberlein, "Geologic Features of Bolivia's Tin Bearing Veins," *Eng. Mining J. Press*, **121**, 636 (1926).

pound was found which, from the results obtained, held out the opportunity or possibility of a leaching process.

Further experimental work was carried on at higher temperatures with aqueous solutions of the mineral acids at various concentrations alone, and with various salt additions The salt additions were made to the concentrates, the acids were then poured on the concentrates, and the mass was well stirred.

Using the above test, no positive results were obtained with the following solutions:

(1a) Concentrated sulfuric acid, specific gravity 1.836. In testing for tin, this solution was diluted to 25 per cent, then tested and calculated back to its original concentration. No hydrolysis of tin salts was observed Tests negative Determinations made at 100°, 120°, 140°, and 180° C.
(2a) 50 per cent sulfuric acid, diluted for testing as (1a).
(2b) (2a) plus 2 per cent NaF.
(2c) (2a) plus 2 per cent NaCl.
(2d) (2a) plus 5 per cent NaCl.
(2e) (2a) plus 2 per cent $NaNO_3$
All tests negative No precipitate with $HgCl_2$
(3a) 25 per cent sulfuric acid.
(3b) (3a) plus 2 per cent NaF.
(3c) (3a) plus 2 per cent NaCl.
(3d) (3a) plus 5 per cent NaCl.
(3e) (3a) plus 2 per cent $NaNO_3$
(3f) (3a) plus 5 per cent $Fe_2(SO_4)_3$
All tests negative
(4a) 50 per cent hydrofluoric acid Copper dish used Time of digestion, one hour Temperature 75° C.
(4b) (4a) plus 5 per cent NaCl. Glass beaker used. Temperature 75° C. Time of digestion, one hour
(4c) (4a) plus 10 per cent Na_2SO_4 Temperature 75° C.
(4d) (4a) plus 2 per cent $NaNO_3$. Temperature 75° C
All tests negative.
(5a) Concentrated hydrochloric acid (38 per cent) Temperature 100° C. Time, four hours
(5b) (5a) plus 2 per cent $NaNO_3$.
(5c) (5a) plus 5 per cent NaF.
(5d) (5a) plus 5 per cent NaCl
(5e) (5a) plus 2 per cent Na_2SO_4.
All tests negative.
(6a) 30 per cent NaOH.
(6b) (6a) plus 2 per cent NaCl.
(6c) (6a) plus 2 per cent NaF.
(6d) (6a) plus 2 per cent $NaNO_3$.
(6e) (6a) plus 5 per cent NaCl.

(6f) (6a) plus 5 per cent Na_2SO_4.
All tests negative as defined above
(7a) 20 per cent solution of ferric sulfate Temperature 100° C Time, four hours
Tests negative

These results do not offer much encouragement for the development of a leaching process

Reduction by Metals

Reduction of Tin Concentrates by Aluminum. Fink and Mantell studied the application of the "thermit" reaction, which is reduction by aluminum, to tin concentrates.[17] The reaction is represented by the equation:

$$3SnO_2 + 4Al = 3Sn + 2Al_2O_3$$

Calculated from the reaction, the proportions are 453 parts of stannic oxide to 108 parts of aluminum, which gives 357 parts of tin. This is approximately $3\frac{1}{4}$ pounds of tin per pound of aluminum. With an ore of 60 per cent tin content, on the basis of tin alone, about one part of aluminum would be required for five parts of ore. Because of the iron and other metals present which are aluminothermically reduced, and to allow excess aluminum for the reaction, a proportion of four parts of ore to one of aluminum was used

There is a decided difference in the specific gravities of molten alumina and liquid tin. There is also a decided difference in specific gravity between the gangue of the tin ore and the liquid tin. The specific gravity of the gangue is very much closer to that of alumina than to the liquid tin As a result, on cooling a good separation was made of the combined alumina and gangue from the heavier liquid tin. A sharp line of demarcation defined the solidified slag and the tin metal. Examination of the slag after crushing showed that it was almost entirely free of tin prills

The tin metal was clean. It liquated easily. In liquation there was considerable amount of dross which could be shown to be caused by an excess of aluminum metal used in the reduction. With careful control, the tin yield from the concentrates could be made almost quantitative. The thermodynamics of the reaction are:

$$Sn + O_2 = SnO_2 + 141{,}300 \text{ calories}$$
$$2Fe + 3/2O_2 = Fe_2O_3 + 195{,}600 \text{ calories}$$
$$3SnO_2 + 4Al = 3Sn + 2Al_2O_3 + 361{,}300 \text{ calories}$$
$$2Fe_2O_3 + 4Al = 4Fe + 2Al_2O_3 + 394{,}000 \text{ calories}$$

[17] C G Fink, and C. L. Mantell, *Eng Mining J*, **125**, 325-8 (1928).

This shows the reaction to be of the same order of magnitude as the Goldschmidt thermit reaction.

Aluminum and iron are stated by Gwyer[18] to be completely miscible in the liquid phase On cooling, mixed crystals are formed having the composition of 40 to 48 per cent iron, and 66 to 100 per cent iron, with an iron-aluminum compound which has a melting point of 1145° C. If this compound be more readily or more easily formed than the iron-tin alloys or hardhead compounds, the aluminum will thus act as a scavenger for iron in the tin metal, producing a tin more free from iron than that produced by any method in which aluminum metal is not used

Metallic reduction of tin concentrate may be of use in localities where tin deposits are too small to warrant a smelter or a reduction furnace Reduction by aluminum or zinc requires practically no equipment

Reduction of Stannic Oxide by Other Metals. Metallic iron does not reduce stannic oxide in the solid phase at temperatures up to 1050° C

It was not to be expected that there would be a reducing reaction between two solid phases, as in the case of the two powders, in an inert gas atmosphere The experimental data show that solid, finely divided iron is without reducing action on solid stannic oxide It follows that it would not be expected that iron in the solid phase would exert any reducing effect on cassiterite

It is known that iron in the liquid phase has reducing action on molten stannic oxide with the formation of the tin-iron alloy, hardhead. This material, one of the banes of the tin-smelter's existence, is formed above 1132° C , the melting point of stannic oxide

If temperatures of furnace operation be such that neither stannic oxide nor metallic iron is in the molten condition, the tendency to form hardhead should be lessened The rate of alloying between tin in the liquid phase and iron in the solid phase is slow in comparison with the reaction when both are in the liquid phase. Gaseous reduction (economical at 750°) operates at temperatures well below the melting points of either stannic oxide or metallic iron. Hardhead troubles should be and are considerably reduced in gaseous reduction

Molten bismuth, at temperatures not much above its melting point, has no reducing effect on stannic oxide. Bismuth compounds are usually constituents of Bolivian tin concentrates. Such compounds, and among these the oxides, are more readily reduced than is stannic oxide by reducing agents.

Similar determinations were made in the case of lead and copper, at temperatures just above their melting points.

[18] Gwyer, *Z. anorg. Chem.*, **57**, 113–53 (1908)

The thermophysics of these reactions are as follows:[19]

$$\begin{aligned}
Sn + O_2 &= SnO_2 + 141{,}300 \text{ calories} \\
Pb + O &= PbO + 50{,}800 \text{ calories} \\
Pb + O_2 &= PbO_2 + 63{,}400 \text{ calories} \\
2Bi + 3O &= Bi_2O_3 + 139{,}200 \text{ calories} \\
2Fe + 3O &= Fe_2O_3 + 195{,}600 \text{ calories} \\
Fe + O &= FeO + 65{,}700 \text{ calories} \\
Cu + O &= CuO + 37{,}700 \text{ calories} \\
SnO_2 + 2Fe &= Sn + 2FeO - 900 \text{ calories} \\
3SnO_2 + 4Fe &= 3Sn + 2Fe_2O_3 - 32{,}700 \text{ calories} \\
SnO_2 + 2Pb &= 2PbO - 39{,}700 \text{ calories} \\
SnO_2 + Pb &= Sn + PbO_2 - 77{,}900 \text{ calories} \\
3SnO_2 + 4Pb &= 3Sn + 2Pb_2O_3 - 175{,}000 \text{ calories} \\
3SnO_2 + 4Bi &= 2Bi_2O_3 - 145{,}500 \text{ calories}
\end{aligned}$$

Molten lead, bismuth, and copper are without marked reducing action on stannic oxide. In the reduction of a concentrate the oxides of these metals will consume the reductant. The reduced metals do not in turn reduce tin oxides with which they are in contact.

Effect of Iron and Bismuth Oxides on Melting Point of Stannic Oxide. Bolivian vein-tin concentrates contain a large number and amount of impurities. Those which are most important are the compounds of iron and bismuth. Ordinarily, concentrates of vein origin fuse at lower temperatures than those of alluvial origin, owing to the greater impurities of the original veins and the difficulty of dressing vein ores.

To determine the effect of iron and bismuth oxides on the melting point of stannic oxide, samples were made containing these materials in the proportions in which they occur in the concentrates.

Melting-point determinations were made following the American Society for Testing Materials[20] procedure for determination of the fusibility of coal ash, using the furnace arrangement as recommended for this work. The furnace was operated with a minimum amount of excess air. The results are given in Table 11. The particle size of maximum occurrence was 3μ.

It is illuminating to see how greatly the small amount of bismuth oxide affects the melting point of stannic oxide. As ferric oxide has a higher melting point than bismuth oxide, the result, though large, is less marked.

These determinations give some insight into the effect that the oxides of iron and bismuth have on the fusion point of tin concentrates. In gaseous reduction, the operation depends upon the absence of slagging until complete reduction is effected. It can be seen that with ores high in

[19] Richards, "Metallurgical Calculations," New York, McGraw-Hill Book Co., Inc., 1918.

[20] *Am. Soc Testing Materials Standards*, 994 (1924); also Fieldner, Hall, and Field, *Bur. Mines*, Bull. No. **129**.

bismuth oxide, means may have to be employed to counteract the lowering of the melting point of the concentrates. Experimental work has shown us that small amounts of lime up to 1 per cent by weight of the charge are very effective in raising the melting point to prevent undesired slagging of the material.

TABLE 11 MELTING-POINT DETERMINATIONS ON STANNIC OXIDE

MATERIAL	SOFTENING TEMPERATURE, (°C)	INITIAL DEFORMATION TEMPERATURE (°C)	FLUID TEMPERATURE OR MELTING POINT (°C)
Fe_2O_3	1,492	1,497	1,503
SnO_2	1,120	1,125	1,130
SnO_2 94 35%	918	925	932
Fe_2O_3 5 65%			
SnO_2 99 01%	841	854	863
Bi_2O_3 0 99%			

Application to Bolivian Concentrates

One of the methods that has been proposed for the winning of tin from Bolivian concentrates consists of the following steps:

(1) Reduce the concentrate by gaseous reduction.

(2) Leach the reduced concentrate with a solution low in tin It is preferable that this solution be a good electrolytic refining agent

(3) Electrolytically precipitate the tin metal under controlled conditions, so that "electrolytic tin" of high purity be obtained.

(4) Reuse the electrolyte now stripped of some of its tin for leaching fresh, reduced concentrate The electrolyte then operates in a closed cycle

Commercial practice prefers a cheap, simple and economical refining electrolyte.

Leaching solutions which have the possibility of being good refining baths are limited in number Additions of sodium sulfate to 15 per cent sulfuric acid do not markedly increase its solvent power for tin, although the sulfate may decrease hydrolysis of tin salts in solution. Good conditions for the tin-refining bath call for a tin concentration of 35 grams per liter Additions of sodium chloride to 15 per cent sulfuric acid increase its solvent power sufficiently to obtain this concentration.

A satisfactory leaching solution for tin metal, and therefore presumably for reduced tin concentrates, contains 15 per cent sulfuric acid and 5 per cent sodium chloride.[21]

Work on a semi-commercial scale on tin concentrates reduced by hydrogen showed that all of the reduced metal was quantitatively soluble in

[21] C G Fink, and C L Mantell, *Eng. Mining J*, **125**, 452–5 (1928).

hydrochloric acid or sulfuric acid plus sodium chloride. Low temperature reduction could be complete and the tin metal produced could be completely recovered

Results from a large number of leachings of gaseous-reduced concentrates show tin recoveries from 95 to 98 per cent With counter-current leaching and continuous electrolytic precipitation of metal and reuse of leach liquor, tin recoveries higher than 96 per cent are possible Iron will build up in the leach liquor with the necessity of constantly bleeding some of the liquor Bismuth, copper, and other metals would also build up in the plant operation

Higher metal recoveries than those obtained from smelting are to be expected, as the operation consists of leaching a loose, sandy mass containing more than 80 per cent of an easily acid-soluble metal.

Reduced tin concentrates were leached in place with simultaneous deposition of the metal electrolytically The results did not seem to hold out hope for a commercial process which would leach reduced ore in place with simultaneous electrodeposition

Leaching with agitation separately from electrolytic precipitation is preferable to leaching and electrolytic precipitation at the same time. The first method gives higher yields, at higher current and energy efficiencies, with the production of better cathode deposits

Gangue from the leaching treatment was clean Under a microscope it showed quartz, garnet, and tourmaline There was no fusion of the tourmaline at the temperatures at which the gaseous reduction took place. The temperature of operation is such as to eliminate entirely the problem of the low-fusing constituents covering over the particles of cassiterite and preventing the reducing gas from coming in contact with the material, thus not allowing its reduction to metallic tin.

Wells[22] proposed zinc and hydrochloric acid as a means of dissolving cassiterite for analytical purposes The zinc when in contact with the particle of cassiterite reduced it as a result of the hydrogen generated This is a common field test

Tin metal has been known not to be readily soluble in sulfuric acid. As a result of studies on the solubility of tin metal and the various constituents of a sulfuric acid tin-refining bath, the important effect of chloride-ion addition on the tin solubility has been shown

In gaseous reduction of tin concentrates, slag troubles are eliminated. Refractory troubles are not in evidence Formation of hardhead is decreased The operation is one of low temperatures (750° C.).

The combination of gaseous reduction, leaching the reduced charge, and electrolytically precipitating the tin metal, offers a cheap method of deal-

[22] Wells, *Columbia School of Mines Quarterly* (1890)

ing with foul Bolivian ore, with the production of tin metal of 99.98 per cent purity. Tin recoveries 95 per cent or better are possible by this combination of steps.

Smelters can handle foul Bolivian ores only with great difficulty. Without electrolytic refining it is difficult even to produce "standard" metal. Hydrogen reduction, leaching, and electrolytic precipitation offers a cheaper method, with greater ease of operation, moreover, it is capable of producing the highest grade of metal from complex and foul ores.

Chapter 8

Electrolytic Refining

Electrolytic versus Thermal Methods

Electrolytic processes for the winning of metals from low-grade ores (too poor in metal content to warrant consideration for smelter charges, but high enough so that by leaching and electrolytic processes large-scale operators are able to produce metal at lower production costs than the smelters of high-grade ores) are well-known in the case of copper, zinc, lead, manganese and the precious metals [1]

The metallurgy of copper has been worked out in great minuteness and detail, in contrast the metallurgy of tin is a virgin field. The tin resulting from thermal methods can be refined to a degree of purity sufficient for most purposes by ordinary dry methods, such as drossing and liquation These are simple processes which are satisfactory for the metal from the reduction of pure ores

The tin metal produced from straight metallurgical processes from impure ores is at best a very impure form containing lead, arsenic, antimony, iron, cadmium and copper as impurities from which it must be refined The usual methods are by (1) liquation, (2) boiling or (3) tossing In liquation, advantage is taken of the low melting point of tin Impure metal is heated on the inclined bed of a furnace to a temperature just above its melting point. Comparatively pure tin trickles down to a basin below, leaving higher-melting-point impurities on the bed of the furnace. Liquation will not remove readily fusible lead and bismuth impurities, these are removed by boiling or tossing. Both of these are oxidizing methods. The first is similar to the "poling" operation of the copper refinery, the second consists of pouring ladlefuls of molten metal from a height back to the bath of metal. The metal is then allowed to stand in the liquid state for several hours to allow gravity separation of the remaining heavier impurities.

From operations such as drossing, boiling, tossing or liquating, a tin metal of a quality equivalent to electrolytic copper or nickel cannot be produced. In 1906 Blount[2] was among those to recognize the great de-

[1] C. L. Mantell, "Industrial Electrochemistry," 2nd Ed., New York, McGraw-Hill Book Co., Inc., 1940.

[2] Blount, "Practical Electro-Chemistry," p. 124, New York, Macmillan Co , 1906.

sirability of producing electrolytically a purer metal than the commercial pure tin containing 0 50 to 1 00 per cent impurities In the manufacture of high-grade nonferrous alloys, particularly bronzes, solders, and gun metal, a pure metal is distinctly preferable to one containing miscellaneous alien substances Nevertheless, in 1906 electrolytic tin had no industrial existence Throughout the literature from that time until 1917, statements were made that there was no field for the electrolytic process for the refining of tin, as metallurgical processes produced tin in a sufficiently pure condition for ordinary uses, and extremely pure metal had no particular sale. Seemingly, electrolytic tin had to overcome the same series of useless prejudices and adverse propaganda that electrolytic nickel and copper met and conquered There is no question that electrolytic refining will produce a purer product than thermal methods, that the purer metal allows the production of higher-grade nonferrous alloys, that many manipulative difficulties in the application of tin metal vanish when the deleterious impurities are no longer present, and that electrolytic processes can be used to obtain pure metal from the impure or "foul" ores, from which straight dry thermal methods of refining produce only a poor grade of metal unless preparatory chemical processes are employed

Electrolytes

In the selection of a salt for any refining process, the following conditions will weigh: The acid radical must be fairly cheap and stable The salt must be soluble If impurities are to be taken out as slime, they should be insoluble in the electrolyte used. The tank lining should not be affected by it. Poisonous fumes should not be given off, and the cathode should not readily redissolve

Plating stands on a little different ground in that it is a quality process Therefore the cost of the salt used is not vital and in small operations poisonous fumes may be controlled.

In the field of tin refining, it is necessary to have an electrolyte in which the tin compounds formed are very soluble The tin concentration of the electrolyte must be great enough for the current density used The electrolyte must be circulated to avoid segregation and polarization The use of a warm electrolyte results in lower voltages and more even anode corrosion. A desirable electrolyte, however, would be one that functioned satisfactorily at room temperature, thus eliminating the necessity of external heating. The presence of suitable addition agents tends to produce smooth, dense, coherent cathode deposits.

Tin electrolytes must be free from metal ions electronegative to tin, otherwise the other metals will plate out with the tin.

Sulfide Baths. One of the oldest electrolytes used for tin refining is the

sodium sulfide bath of Claus and Steiner.[3] This bath was used commercially at Bootle, England, for several years. The electrolyte consisted of a 10 per cent solution of sodium sulfide with dissolved sulfur. Smooth deposits were obtained below 0.2 volt, above which hydrogen was evolved and spongy deposits formed. Peruvian metal of 93 per cent tin content was refined to a 99 9 per cent material. The electrolyte had to be kept uncontaminated from foreign metals either suspended or dissolved. No circulation was possible as the anode mud would foul the solution. The current could not be interrupted during a run, otherwise the polarization current would oxidize the cathode. In his study, Neuman[4] found that in the refining of tin in sodium sulfide solution the metal separates at the cathode as a smooth, dense deposit with a current yield of 98 to 99 per cent (calculated on tetravalent tin), when a current density of 1 ampere per square decimeter (10 amp /sq. ft) is employed. With a current density of 2 amperes per square decimeter (20 amp./sq. ft.) or more, evolution of hydrogen occurs, the deposit of tin on the cathode is spongy, and the current yield falls The sodium sulfide content in the electrolyte must not be allowed to fall below 10 per cent, otherwise a spongy deposit of tin is formed In sodium sulfide solutions containing sodium hydroxide, the current yield is over 100 per cent owing to the discharge of some Sn^{++} ions. Free sulfur in the electrolyte forms polysulfide, which dissolves the tin and hinders its deposition Initially the electrolyte must contain at least 0 6 per cent tin dissolved as stannic sulfide. The temperature of the electrolyte should be maintained above 80°, below 70° evolution of hydrogen sets in and the cathode becomes coated with a gray-black spongy deposit With anodes of alloys of tin with lead, iron, bismuth, silver, copper, and phosphorus, these metals are converted into sulfides which settle as anode slime, the tin deposited on the cathode being completely free from them. Arsenic is not deposited with the tin on the cathode, but antimony is, if the current density be over 0.1 ampere per square decimeter (1 amp /sq. ft.) For commercial usage this bath is difficult to work, hard to control, disagreeable in operation, without compensating advantages over competitive baths.

Alkaline Baths. The alkaline baths[5] studied by many workers consisted of $SnCl_2$ $2H_2O$ dissolved in sodium hydroxide. A typical electrolyte is that of Beneker, which consisted of 125 grams (16.66 oz./gal) of sodium

[3] Claus, and Steiner, *Z. Electrochem* , **15**, 33–6, 63–5 (1909); Steiner, *Electrochem. Met Ind.*, **5**, 309–12 (1907); Fisher, *Z. anorg. Chem.*, **42**, 63 (1904)

[4] Neuman, *Z. Electrochem* , **27**, 256–68 (1921).

[5] *Metal Ind.*, **14**, 200–1 (1916); *Trans Am. Electrochem. Soc.*, **29**, 405 (1916); *Metal Ind* , **18**, 361–2 (1920), Hollard, *Bull soc enc ind nat.* (July, 1912); Mennicke, "Metallurgie des Zinns," Halle, Wm Knapp, 1910; Hughes, *Beama*, **10**, 138–41 (1922); Mathers, and Bell, *Trans. Am. Electrochem. Soc.*, **38**, 135 (1920).

hydroxide, 50 grams (6.66 oz./gal.) of stannous chloride, and 75 grams (10 oz /gal) of sodium thiosulfate per liter. The alkaline baths when used for refining tend to produce spongy and nonadherent cathode deposits. The baths are none too stable, oxidizing by the action of the air to stannates and insoluble stannic acids. The anode corrosion is greater than the cathode deposition. The cathode deposits are difficult to handle and cause large losses in melting down to a compact form. The bath is operated at 80° C. (176° F.), with a current density of 10 amperes per square foot (1 amp./sq. dm.). With current densities as low as 2 amperes per square foot (0.2 amp./sq. dm), a fairly compact cathode deposit may be obtained Straight alkaline baths are not now used for tin refining but find application in electrolytic detinning and tin plating.

Tin anodes in alkaline baths have a tendency to passivate, at which time anode corrosion stops.

Siemens and Halske[6] suggested that, in addition to a colloid, an oxidizer such as ozone, hydrogen peroxide, peroxides of the alkali or alkaline earth metals, be added in order to obtain a pure stannate solution The addition of colloids can be omitted if the electrolyte is free from plumbite and bismuthite.[7]

Acid Baths.[8] A number of patents have been granted in various countries for tin-refining baths using the tin salts of organic acids such as acetic, formic, tartaric, citric, oxalic, and the tin salts of phosphoric and boric acids All of these have the objection that the electrolyte is expensive, easily decomposed, the solutions may be unstable, and the electrolytes must be kept pure These baths have been found useful for electrotinning but not at all for electrorefining

Chloride Baths.[9] Many baths applicable to tin refining have been proposed which make use of the solubility of stannous and stannic chlorides. That of Brand consisted of about 1 per cent by weight of concentrated hydrochloric acid and 9 per cent of stannous chloride. Neutral or acid solutions of stannous or stannic chlorides produce coarse crystalline cathode deposits It has been claimed[10] that "beautiful dense deposits of tin can be obtained without the evolution of hydrogen by electrolyzing a $NaCl \cdot SnCl_2$ solution with low current density at ordinary temperatures." This holds true only for a short while, in continuous operation crystals

[6] Siemens, and Halske, *French Patent 560,579*

[7] *French Patent 37,495*

[8] Mathers, and Cockrum, *Metal Ind.*, **14**, 252–3 (1916); Pasztor, *Electrochem. Z.*, **16**, 281–5 (1910); *German Patent 276,181* (1912); Battle, *U S Patent 1,202,149*, Marino, *British Patent 11,011* (1915), Delahaye, *French Patent, 484,148* (1917).

[9] Schnabel-Louis, "Metallurgy," Vol **II**, p. 549, New York, Macmillan Co., 1907; Quintaine, *British Patent 5,496* (1900); Feith, *German Patent 205,051* (1907); Michaud, and Delasson, *French Patents 16,388* and *435,936* (1912); *U. S Patent 1,124,315.*

[10] *Bull. Soc. enc. ind. nat.*, 28 (July, 1912).

and trees are produced which short-circuit the electrodes The chloride baths have been advocated for use in diaphragm cells, but diaphragms in commercial refining introduce an undesirable cell complication and an increased voltage drop across the cell

Fluosilicate Baths.[11] The successful application of hydrofluosilicic acid as an electrolyte for lead refining caused workers to attempt to apply it to tin It was realized that the addition of small amounts of sulfuric acid in the bath would prevent electrolyte contamination by causing the formation of insoluble lead sulfate which rapidly fell out of the solution and became part of the slimes. Some of the laboratory workers on the problem shortly worked out suitable addition agents without which an entirely satisfactory electrode deposit could not be obtained Kern[12] experimented to find the best current density, addition agent, and electrolyte for use in the electrolytic refining of impure tin bullion so as to obtain tin as an adherent, dense, compact cathode The anodes used were 10 cm (3 937 in) long' 4 4 cm (1 73 in) wide, and 0.94 cm (0 37 in) thick They contained 96 per cent tin, 0 5 per cent iron, 0 1 per cent arsenic, 0 2 per cent antimony, 2 0 per cent lead, 0 6 per cent copper, 0 1 per cent bismuth, and 0 5 per cent silver The cathodes were made of sheet tin 0 4 mm (0 0157 in) thick and were larger than the anodes by 0 6 cm (0 236 in) on each of the two edges and bottom Electrolytes of stannous chloride, sodium stannous chloride, magnesium stannous chloride, sodium stannous fluoride, stannous fluosilicate, and a mixture of acid solutions of stannous fluoride and fluosilicate were tested Each solution contained 100 grams of tin per 100 cc Stannous fluosilicate is the best of the electrolytes which were tried It was found that addition agents were necessary for dense, adherent deposits of tin Alum caused the formation of the best deposits when added to stannous fluosilicate electrolytes in the amount of 1 gram of alum per 500 cc of electrolyte Peptone gave good deposits in many cases, while the others, except in stannous fluosilicate electrolytes, did not improve the deposits With current densities of 12 and 24 amperes per square foot (1 2 and 2 4 amp /sq dm) in many cases similar results were obtained

Kimura[13] made investigations to find a suitable electrolyte for refining the crude tin of the Ikuno Mine in Japan This crude tin contains many impurities, its composition varies between 90 and 96 per cent tin, 2 to 5 per cent copper, 0 3 to 0 7 per cent lead, 0.3 to 0 6 per cent bismuth,

[11] *Eng Mining J* (May 27, 1916); Hollis, *U S Patent 916,155,* Mennicke, *U S Patents 779,091* and *779,092,* Mathers, *U S Patent 1,397,222,* A S and R Co , *French Patent 479,569* (1916); Schulte, *U S. Patent 1,423,686,* Whitehead, *U S Patent 1,157,830, Elec Rev. West Electricity,* **68,** 507 (1916); Vail, *Eng Mining J* , **101,** 927–9 (1916).

[12] E F. Kern, *Trans. Am. Electrochem Soc.*, **33,** 155–68 (1918).

[13] Kimura, *J. Min. Inst. Japan,* **47,** 966–1001 (1931).

0 07 to 0.21 per cent iron, 0 4 to 0 6 per cent arsenic, and 0.5 to 0 6 per cent antimony Kimura based his experiments on electrolytes made from stannous chloride and stannous sulfate to which had been added in the most varied proportions hydrochloric acid, sulfuric acid, sodium sulfate, sodium chloride, ammonium chloride, aluminum sulfate, fluosilicic acid, hydrofluoric acid, sodium fluoride, cresol sulfonic acid, toluene sulfonic acid, and colloids. He determined that in the case of a crude tin greatly contaminated by copper, the best results are obtained with the sulfuric acid electrolyte with an addition of fluosilicic acid Fluosilicic acid is not considered necessary in the case of crude tin whose chief contamination is lead As a suitable electrolyte for the above-mentioned crude tin, Kimura recommended a solution with 5 50 per cent fluosilicic acid, 6 per cent sulfuric acid, 3 per cent bivalent tin, 0 1 per cent glue, 0 01 per cent beta-naphthol, and a very small addition of hydrofluoric acid The anode mud is said to be worked in the following manner· Tin and bismuth are dissolved by treating with hot sulfuric acid, while the copper remains undissolved The bismuth is recovered from the solution by cementation and tin by electrolysis with insoluble anodes

The fluosilicic acid bath works satisfactorily but has disadvantages Its preparation is difficult, the bath is not very stable, and the basic ingredients are expensive.

Sulfate Baths.[14] In the search for baths less expensive than the fluosilicate, workers in the field turned to sulfuric acid as a source of a cheap ion It was shortly found that electrolytes such as sodium sulfate alone produced spongy non-coherent deposits, and that with sulfuric acid crystalline deposits were produced which soon short-circuited the electrodes It is claimed that the cathode deposit can be modified in a satisfactory manner by the use of addition agents such as gelatin, phenol, phloroglucinol, or similar substances Later work by Schlotter showed the necessity of having the straight sulfate bath free from alkalies and ammonium salts. One of Schlotter's baths has the following composition· 120 grams stannous sulfate, 2 grams gelatin per liter Gelatin and cresylic acid soap emulsion as addition agents have temporarily produced satisfactory deposits of tin, but their activity seems to be quickly destroyed.

Kern[15] tested solutions containing 5 per cent tin as (I) $SnCl_2$ 2NaCl with 2 per cent excess sodium chloride, (II) $Sn(BF_4)_2$ with 4 per cent excess HBF_4, (III) $Sn(SO_3 \cdot C_{10}H_7)_2$ with 8 per cent excess of $HSO_3C_{10}H_7$, (IV) $SnSO_4$ with 2, 4 and 6 per cent excess of sulfuric acid. The anodes were 95 per cent tin, 3 per cent bismuth, and 0 5 per cent each of lead, antimony

[14] M. Schlotter, *U. S Patent 1,426,678,* Norrie, *Canadian Patent 211,475,* M Schlotter, *British Patent 148,334* (1920), Michaud, and Delasson, *British Patent 20,557* (1912)

[15] E. F. Kern, *Trans. Am. Electrochem. Soc.*, **38**, 143–62 (1920).

and silver. The current density was 16 amperes per square foot, with electrode spacing 1.75 inches. The tests were made at bath temperatures of 20 and 40° C. It was concluded that (1) no smooth, adherent deposits are formed without addition agents, sulfate baths gave better deposits than the others, (2) a 2 per cent excess of sulfuric acid in sulfate baths was not sufficient to make the solution remain clear, (3) peptone and gelatin, 1 to 2 grams per liter, improved deposits, the effectiveness of addition agents is increased by rise in temperature, (4) current efficiencies are high only when the deposit is smooth, dense and adherent.

The sulfuric acid bath becomes inoperative in the case of anodes containing appreciable amounts of lead, say 2 per cent or thereabouts. This is a disadvantage in using this bath for commercial tin metal produced from Bolivian ores.

Combination Baths. When sulfuric acid and sodium sulfate are used together as an electrolyte, the tendency of the acid to cause crystalline deposits is neutralized by the tendency of the sulfate to form sponge metal. By properly balancing the proportions of one constituent against the other, a coherent, dense cathode deposit, satisfactory for commercial refining, is produced.

Fink[16] proposed the composition 233 grams $Na_2SO_4 \cdot 10H_2O$, 150 grams H_2SO_4, 35 grams Sn, 2 grams aloin per liter, which, in the case of high lead content anodes, is modified to the following: 60 to 120 grams Na_2SO_4, 50 grams H_2SO_4, 35 grams Sn, 2 grams aloin. The Glauber's salts may be replaced by salts such as ferrous sulfate without greatly impairing the cathode deposit, yet improving the anode corrosion.

This bath has the advantage that high lead content anodes can be refined, the electrolyte is inexpensive, thick deposits can be obtained without treeing, the bath is operative satisfactorily at room temperature and no heating is required, no diaphragms are necessary, the impurities in the anode form an easily removed sludge, and circulation with no bad effects but only the desired good ones is possible. The addition agent, aloin, is cheap, easily prepared, and remains active for a relatively long period of time. The bath contains a prepondering concentration of sulfate ions, and small amounts of chloride, fluoride, or fluosilicate ions may be present and not be prejudicial to the final result. In addition, the electrolyte holds a prepondering concentration of ions more electropositive than tin, such as sodium, and as a result of the refining, magnesium, iron, aluminum, chromium, etc., which will not be deposited in preference to tin because of their more electropositive nature.

The commercial current density is 10 amperes per square foot, the voltage being 0.2 or less. With reduced acid concentration the voltage may rise higher.

[16] C. G. Fink, *U. S. Patent 1,466,126.*

Other metal sulfates, such as those of iron, titanium, cobalt, nickel, manganese and chromium, when added to the tin-refining cell have the beneficial effects of loosening the slimes which tend to adhere to the anode, thus rendering anode corrosion easier, and of improving the density, hardness, and blend of crystals deposited on the cathode

Foerster, Klemm and Deckert[17] found that the addition of crude meta-cresol sulfonic acid counteracts the tendency of the tin to form needle-shaped deposits and to promote the formation of smooth and compact deposits. This also eliminates the danger of short circuits

Electrorefining, electroplating and electrolytic tin plate manufacture have many factors of electrolytic composition in common, but refining emphasizes cost, electroplating quality of deposits, and electrolytic tin plate both quality of deposits and stability of electrolyte. All use addition agents as an essential constituent

The alkaline sulfide baths for refining are unstable, will not permit circulation, and have to be externally heated, the same holds true for the alkaline baths which have the additional disadvantage that anode corrosion is greater than cathode deposition The organic acid baths tend to be unstable and expensive, useful only for electroplating, the same holds true for the boric and phosphoric acid baths Tin deposited from neutral or alkaline baths tends to be finely granular or spongy Acid baths tend toward "tree" deposits which may short-circuit the electrodes. Acid baths containing chlorides give rise to very long crystals Organic addition agents in this bath will reduce the size of the cathode crystals, but large quantities of addition agents are required to produce deposits easily handled without mechanical loss. A similar set of conditions holds true for the sulfuric acid bath The fluosilicate bath, while producing satisfactory results, is expensive and needs the addition of sulfuric acid to prevent the deposition of lead along with the tin The sulfate bath (such as sodium sulfate or stannous sulfate) tends to give spongy deposits of the same character as those from alkaline or neutral baths The combination sulfuric acid-alkaline sulfate-tin sulfate bath combined the treeing of the acid bath with the sponge deposit of the alkaline bath by neutralization of one effect by the other.

Perth Amboy Refinery

In the first commercial tin-refining plant in the United States—that of the American Smelting and Refining Company at Perth Amboy, N. J. —the fluosilicate bath was used. Its composition was about 15 per cent hydrofluosilicic acid and 4 per cent tin, with sulfuric acid added as a lead precipitant. The baths produced metal of 99.96 to 99.98 per cent tin

[17] F. Foerster, K. Klemm, and H. Deckert, *Z. Elektrochem.*, **32**, 525-92 (1926); **35**, 409 (1929); **36**, 901-23 (1930).

content At the Perth Amboy plant the company made its own hydrofluosilicic acid in the sulfuric acid plant The cathodes in initial operation were enclosed in porous cells. After the solution had taken up 6 per cent of tin, the porous cells were removed. The voltage across the tanks was then changed from 4 to 5 volts to 0 5 volt Sulfuric acid was added as it was used up The porous cells used in the first part of the process were supported by glass blocks and by clips on rods from which the cathodes were suspended

The tin-refining plant at Perth Amboy in 1917 consisted of 68 tanks similar in size and construction to those used for copper The tanks were wood, lined with an asphalt coating The electrolyte was circulated from tank to tank through hard-rubber fittings Each tank in the refinery contained about 11,000 pounds of anodes The cathode starting sheets were of tin about one-eighth inch thick, made by casting in a manner similar to the making of thin lead cathode sheets The current density was about 12 amperes per square foot (1 2 amp /sq dm), the metal deposition per ampere hour being about twice that of copper (theoretically 2.2188 g /amp hr Sn^{++}) The anode life was about 20 days and the output of the plant about 15 to 20 tons of tin metal per day The product analyzed 99 96 to 99 98 per cent tin, which is purer than the best Straits product. The manufacturers of high grade tin foil, tin plate, and nonferrous alloys reported the absence of manipulative difficulties with this pure metal, these difficulties were always more or less present with metal from Bolivian ores refined by pyrometallurgical methods

Mennicke stated that he obtained excellent deposits by the use of an electrolyte of 10 per cent tin and 10 per cent hydrofluosilicic acid, operated at 20° C. (68° F.), with a current density of 9.3 amperes per square foot (0 9 amp /sq. dm) at 0 4 volt The distance between his electrodes was 2 inches His electrolyte was made by dissolving freshly precipitated stannous hydroxide in hydrofluosilicic acid Free hydrofluosilicic acid was found not to interfere with satisfactory deposition, but the use of lead-containing cathodes caused spongy deposits

While the fluosilicate bath functions in a satisfactory manner, it has the disadvantage that it is difficult to prepare, it is none too stable, and the materials used are expensive

Alexander and Stack[18] described the operation of the Perth Amboy refinery in considerable detail Some of their statements follow.

"Tin is in a most desirable position in the electromotive series of the metals for electrolytic refining The only impurity of frequent occurrence that stands equal or close to tin and would dissolve is lead, all the others being below tin

[18] Alexander, and Stack, "Reduction and Refining of Tin in the United States," Paper read before the *American Institute of Mining and Metallurgical Engineers*, February, 1924.

"Practically, lead is the only impurity that dissolves, consequently the electrolyte must contain a radical that will form an insoluble compound with lead, such as a sulfate, chromate, fluoride, etc The other metals occurring as impurities in tin (arsenic, antimony, bismuth, copper, etc) are not dissolved and remain in the anode slimes.

"The requirements that a tin electrolyte should possess are (1) It must readily dissolve tin from the anode and thus prevent the anode from becoming passive or insoluble, with consequent high voltage and polarization, (2) it must be a good conductor of electricity, (3) the cathode deposit must be adherent.

"Tin is a very crystalline metal and the cathode deposit from most electrolytes consists of long dendritic or needle-like crystals. These crystals are loosely attached and grow rapidly, touching the anode causing short circuits. The tin deposits for satisfactory work should be smooth, dense, and adherent. To obtain such a deposit from most tin electrolytes, an addition agent is necessary The electrolysis of tin had not been considered commercially practical by many metallurgists on account of these difficulties and the venture was undertaken with considerable apprehension."

In the early part of 1915, Whitehead[19] investigated various electrolytes for tin refining, such as hydrochloric acid, sulfuric acid, hydrofluosilicic acid, hydrofluoboric, sodium stannate, sodium sulfostannate, etc. After extensive experiments, hydrofluosilicic acid was selected as being the most satisfactory electrolyte

The electrolytes and addition agents that have been used are protected by a series of patents [20]

[19] Whitehead, *U S. Patent 1,157,830*

[20] J R Stack, *U. S Patent 1,487,124* In refining tin containing lead, contamination of electrolytically deposited tin is prevented by use of an electrolyte comprising a solution of tin in cresolsulfonic acids or other sulfonic acid, together with a protective reagent as glue and cresylic acid, and sulfuric acid which converts the lead in the dissolving anode into an insoluble compound

J R. Stack, *U S. Patent 1,487,125* Specifies a process of refining tin bullion containing various other metals, as gold, silver, lead, copper, arsenic, antimony and bismuth The electrolyte is of dilute hydrochloric acid or other reagent which will hold tin and bismuth in solution while other metals are deposited as slimes or precipitates Bismuth is precipitated, leaving the tin in solution

F C Mathers, *U S. Patent 1,397,222* Electrolytic refining of tin An electrolyte containing hydrofluosilicic acid, cresylic acid and less than 6 per cent tin is employed to produce an even, continuous action without polarizing.

H H Alexander, *U. S Patent 1,487,136* Electric current is passed from impure tin as an anode in an electrolyte of hydrofluosilicic acid, with an excess of sulfuric acid to protect the bath from contamination by lead

R L Whitehead, *U. S Patent 1,157,830* Fluosilicate bath plus sulfuric acid to precipitate lead

A E White, *British Patent 183,507·* An agent such as one of the phenols or their homologs or benzene is added to an electrolyte containing H_2SiF_6 to obtain coherent deposits from a solution containing less than 6 per cent. Electrolyte may be prepared by passing current through an impure Sn anode and a solution containing 5.5 per cent H_2SiF_6, 5 per cent H_2SO_4, 0.3 per cent cresol, the impure commercial form of which is preferred. A little glue may be added.

Alexander and Stack[21] described the electrolytes

The hydrofluosilicic acid bath was used from April, 1915, to October, 1917, and consisted essentially of fluosilicic acid with sufficient sulfuric acid to prevent lead from depositing by precipitating it as lead sulfate The approximate analysis of the electrolyte was

Specific gravity	1 20
Hydrofluosilicic acid	20 0%
Sulfuric acid	0.1%
Stannous tin	6 0%
Total acid in terms of H_2SiF_6	20 15%
Addition agent	glue

The deposit was only fair, not being dense, but sufficiently adherent to run 48-hour cathodes The anode corrosion caused considerable trouble, frequently occasioning high voltage with deposition of silica at the anode

One of the salient features of the process was the glue-cresylic acid addition agent, which was introduced in August, 1917 It was first used successfully in the tin-fluosilicate bath and later adopted in all other electrolytes used The addition agent commonly used is crude cresylic acid, added in the form of an emulsion with the glue Many other coal-tar products analogous to cresylic acid can be used as well The use of these reagents is attributed to Mathers [22]

Z Kimura, *Japanese Patent 42,643* (1922) The electrolyte contains fluosilicic acid 7 per cent, Sn fluosilicate 11 per cent, $SnSO_4$ 0 3–1 per cent, HF 0 02 per cent, glue 0.3 per cent, and beta-naphthol 0 01 per cent Plain and even deposits of Sn above 99 9 per cent purity are easily obtained

American Smelting and Refining Co , *British Patent 220,012* (1923) An electrolyte is used containing an organic sulfonic acid in sufficient amount to prevent the formation of basic Sn salts and to produce a dense, smooth and adherent deposit Electrolyte may comprise Sn 4 per cent, H_2SO_4 5 per cent, hydrofluosilicic acid 2 per cent and cresolsulfonic acid 2 per cent H_2SO_4 must be present in excess of the sulfonic acid to precipitate lead.

J. Neurath, *British Patent 240,147* (1924) In refining Sn alloys containing lead, electrolyte is used which contains an anion such as SO_4 to reduce the concentration of lead ions and prevent cathodic separation of lead Copper and antimony may be deposited with the tin by use of "formers of complexes" such as NH_4 salts, or Sn content of deposit may be raised to 99 5 per cent by introducing S ions into the electrolyte

E. A C. Smith, *British Patent 254,284* (1925): Tin-bearing material is leached with a mixed solvent containing Sn and Fe compounds and acid, and the solution is electrolyzed to deposit a portion of the tin and regenerate the solvent.

L. D Simpkins, *U. S Patent 1,452,573*. An electrolytic bath of a tin salt, *e.g* , stannous sulfate, is formed with an admixture of a peptone or other colloid and beta-naphthol, which serves to facilitate production of dense, coherent deposits.

[21] Alexander, and Stack, "Reduction and Refining of Tin in the United States," Paper read before the *American Institute of Mining and Metallurgical Engineers*, February, 1924.

[22] F. C. Mathers, "Electrolytic Refining of Tin," *U. S. Patent 1,397,222* (1921).

The action of this addition agent produces a dense, smooth, adherent deposit of tin free from growths and frequently shows the vertical striations familiar in copper deposits. Many theories have been advanced as to the action of addition agents, such as (1) They act as a restraining agent to prevent the formation of a crystalline deposit (2) They migrate by the action of the current and form a film or envelope around the cathode, thus insuring even distribution of the current and preventing the formation of points of high current density. (3) They form a compound with the metal from which the metal deposits (simultaneously with the metal from other compounds) in a smooth noncrystalline form or in compact blunt crystals When this form of crystallization has once been established, the metal subsequently deposited tends to follow the same form (4) The addition agent actually deposits at the cathode together with the metal, causing it to deposit in a noncrystalline form of fine blunt crystals

The theory that the addition agent deposits with tin has been found to be a fact in some instances In all tin electrolytes used, the addition agent becomes depleted at a constant given rate, varying from one-third to three pounds of glue and 8 to 16 pounds of cresylic acid per ton of tin refined, depending on the character of the electrolyte used Small fractions of a per cent of hydrochloric acid retard the action of the addition agent

The sulfuric-hydrofluosilicic electrolyte bath was used from October, 1917, to April, 1920, and consisted essentially of sulfuric acid with sufficient hydrofluosilicic acid to prevent the formation of basic salts of tin The approximate analysis of the electrolyte was

Specific gravity.	1.15
Sulfuric acid	8 0%
Hydrofluosilicic acid	5 0%
Stannous tin	3 0%
Total acid in terms of H_2SO_4	11 4%
Addition agent	glue and cresylic acid emulsion

The bath offered many advantages over the straight fluosilicate electrolyte The mastic-lined tanks, hard-rubber solution lines, bronze pumps, etc , were replaced with lead Better anode solubility and less decomposition of hydrofluosilicic acid during electrolysis were obtained

The sulfuric-sulfonic acid electrolyte was used from April, 1920, until the plant ceased operation (1923). A sulfonic acid was substituted for hydrofluosilicic acid to prevent the formation of basic salts of tin, which occurs when sulfuric acid is used alone and renders the anode insoluble

The sulfonic acids can be made from benzol, phenol, cresol, toluene, naphthalene, and other aromatic hydrocarbons, by mixing with strong sulfuric acid and heating according to conventional methods for the manufacture of sulfonic acids If made, for example, from phenol, the new compound called phenol sulfonic acid is produced This is an avid solvent for tin and other metals forming a soluble salt with lead in contradistinction to sulfuric acid If an electrolyte be made up containing 10 to 15 per cent of either cresol or phenol sulfonic acid, 0.5 to 1 per cent of sulfuric acid to prevent the deposition of lead, and 2 to 4 per cent of stannous tin, an excellent cathode deposit of tin can be obtained without the use of an addition agent.

The bath consisted essentially of sulfuric acid with sufficient aromatic sulfonic acids to prevent the formation of basic salts of tin The approximate analysis of the electrolyte was

Specific gravity	1.12
Sulfuric acid	8 0%
Cresol-phenol sulfonic acid	4 0%
Stannous tin	3 0%
Total acid in terms of H_2SO_4	10 2%

The usual addition agent, consisting of glue and cresylic acid emulsion, was added daily in sufficient quantity to produce a dense, smooth, adherent deposit of tin This electrolyte fulfills all the requirements for a satisfactory tin bath in regard to good cathode deposit, conductivity, soft anode slimes, and uniform anode corrosion. The weak liquors, or wash waters containing electrolyte from washing cathodes and slimes, can be evaporated without decomposition

The refinery was similar in arrangement to the usual multiple-tank room The tanks, 340 in number, were constructed of wood, the inside dimensions were 131 by 41 by 42 inches deep. They were lead lined and properly insulated and were served with overhead cranes

Electrically-driven centrifugal pumps of the vertical type were used for circulation of the electrolyte The rate of flow through each tank was about 5 gallons per minute. The overflow from the tanks returned by gravity to the heating tanks, where the solution was maintained at a temperature of 95° F. The circulating pumps were connected to these heating tanks and the electrolyte was kept in continuous circulation throughout the system.

The current was supplied by a steam-driven generator A current load of 3,600 to 4,500 amperes was carried, which corresponds to a current density of 8 to 10 amperes per square foot of cathode surface Under normal working conditions the voltage required per cell was from 0 3 to 0 35 volt, measured across the tank. The current efficiency was about 85 per cent, assuming 1 ampere-day deposits 0.117 pound from a stannous solution.

The anode tin from the smelter contained from 90 to 99 per cent of tin and varying amounts of impurities A representative sample was lead 1 0, copper 0.25, arsenic 0 15, antimony 0.25, bismuth 1 0, and tin 96 0 per cent The anodes were cast with the usual extension lugs and the submerged part was 33 by 36 inches wide; they were about one and one-quarter inches thick and weighed about 350 pounds.

The cathode starting sheets were 34 by 37 inches wide and weighed between 8 and 10 pounds each. These sheets were made by pouring molten electrolytic tin over an inclined steel table of the size and shape of sheet desired, a manner similar to that used for making starting sheets for the electrolytic refining of lead.

Each tank contained 26 anodes and 27 cathodes which were placed alternately and equidistant, the anode spacing being 4½ inches between centers

After seven days of electrolysis, the cathodes weighed about 100 pounds and were removed from the tanks, carefully washed, and melted in a 50-ton capacity cast-iron kettle, then cast into bars of marketable form, weighing 100 pounds and stenciled "Electrolytic Tin." New sheets were placed in the tanks and electrolysis

again started. Three cathodes were obtained from each anode After about 75 per cent by weight of the anodes had been dissolved, they became too thin to conduct the current efficiently and were removed as scrap, remelted and cast again into anodes. Each day the requisite number of tanks of scrap were pulled and replaced with new anodes, so that at the end of 21 days, which is the life of the anode, the circuit of tanks had been completed.

As tin stands above copper, arsenic, antimony and bismuth in the galvanic series of the metals, none of these dissolved from the anode in the presence of the large excess of tin, they therefore remained in the anode slimes. Also, the precious metals went into the slimes The usual reagent for precipitating the lead to prevent its deposition at the cathode was sulfuric acid It has been determined that about half of the lead contained in the anode slimes was present as lead sulfate and the balance as a complex alloy

The tin anode slimes adhered to and closely maintained the form of the anode, so before the scrap anodes were removed the slimes were carefully scraped off, filter-pressed, washed and sent to a department for treatment and recovery of the values Approximately 5 per cent of slimes was produced per ton of tin refined, containing about 30 pounds of tin per ton of metal refined, or 98 5 per cent of the tin was deposited from the anodes

A representative analysis of the anode slimes was lead 20, copper 5, arsenic 3, antimony 5, tin 30, and bismuth 20 per cent

The electrolytic tin was lower in the impurities—lead, copper, arsenic, and antimony—and higher in tin than the foreign high-grade brands of tin.

Electrolytic tin cannot be surpassed for uses that necessitate high-purity tin For some uses, such as tin plating, on account of its high purity it is necessary to add small percentages of impurities in order to produce the same effect as obtained with Straits or Banka tin. It is natural to suppose that certain ingredients would be more desirable than others, hence the high purity of electrolytic tin permits adjusting the composition of the metal to that found best for any particular use.

Chapter 9

Plating

Industrial Applications

The electrodeposition of tin is of considerable importance in industry However, there are a number of misconceptions on this subject. Just as nickel plating is supposed by some to prevent corrosion or rusting when applied to iron and steel, so is tin plating Zinc both protects and improves the appearance of the iron and steel upon which it is applied, but tin mainly serves a decorative purpose. Tin affords protection only when it completely covers the base metal upon which it is deposited. Inasmuch as tin solutions are usually better conductors than nickel-plating baths, with higher throwing powers, the covering of tin over iron and steel is more nearly continuous than that of nickel. Thus there are fewer points or pinholes available for corrosion attack. Tin, like lead and nickel, has no inherent property causing it to protect iron, to which it is electronegative. It will thus protect only where it completely covers. Tin is more resistant to fumes and the atmosphere than is zinc, but it is ordinarily less resistant to gaseous attack than lead or nickel

Tin plating finds application as a covering for copper and steel in cooking kettles for food products, canning machinery, milk-handling pasteurization and dairy equipment, iron and steel containers, refrigerator coils in machines of the electric type, electrolytic tin plate for can and container manufacture, and in a large number of cases where decorative coatings are desired such as builders' hardware.

Electrodeposited coatings are also used on radio and electrical equipment requiring soldering and protection against tarnish and organic acids. While tin is not one of the best bearing metals, it can be used in a large number of cases for this purpose. It is easily applied and may be inexpensive. Tin plating of pistons for internal combustion or gasoline engines is applied in thicknesses of the order of 0.0005 inch to act as a bearing surface during the "breaking in" period of the engine. The tin coating prevents seizing and consequent scoring of the cylinder walls or piston surfaces.[1] Tolerances can be closer and gasoline consumption may be reduced. Electrotinning is used to deposit tin on such classes of goods as lighting fixtures, ornamental hardware, buckles, and a large number

[1] *Mach. Design*, **6**, 9, 20 (1934).

of metal objects. Often it is desired to deposit a coating on the iron, brass or other base metal which is cheaper than silver and yet can be oxidized or colored. Some very beautiful effects can be produced by this method. Close inspection is required to distinguish the finish from that of oxidized silver. Tin has an advantage over silver in this application, if the protective lacquer should wear off, the tin is not so readily tarnished as silver would be. An interesting use of tin plating is the application of exceedingly thin deposits on the white gold jewelry to bring up the "color" and uniformity of appearance

Electrodeposited tin coatings satisfy an industrial demand for methods of coating, with reasonable accuracy and uniformity, fabricated articles made from a variety of base metals such as steel, copper, bronze and others, with a layer as thin as 0 0001 inch (0 0025 mm) and as thick as 0 002 to 0 003 inch (0 05 to 0 075 mm)

Electrolytic Deposition

Electrolytically deposited tin is of a dull- or matte-white color It has so far not been possible to deposit tin so that it might be removed from the bath in a bright condition. Ordinarily it is necessary to scratch-brush the deposit and further polish it if it be desired to produce the same bright surface as is made when the base metal is coated by hot dipping This disadvantage has often prevented the adoption of the electrolytic method for tin coating. Brightening procedures involving the fusion of the coating either by electrical resistance or induction heating, or melting in heated fluids such as oil have found wide application, particularly on electrolytic tin plate. This subject is specifically discussed in Chapter 10 Electrodeposited tin is soft, malleable and very ductile With continued deposition, the deposits tend to become more and more crystalline The deposit is apt to become spongy, slimy or dendritic, with little adherence. The addition of colloids to the bath allows the production of thicker deposits. These retain the ductility and characteristic softness of the metal.

The plating practice may be roughly divided into stages of the art before 1930 and after that date.

Plating Baths. The number of tin-plating baths recommended in textbooks, journal articles and patent specifications has been very large. Few of them have wide application and many are worthless. The alkaline tin baths, modified in a large number of ways, were, up to 1930, practically the only commercially important ones. Ordinarily, the required thickness of a tin deposit does not exceed a fraction of a mill (0 001 inch). These deposits are usually smooth and apparently without definite structure. In their formation they have not had time to appear crystalline to the eye nor develop trees. In a number of cases, comparatively thick deposits

are required. An example is the coating of copper sheets for fabrication into equipment for the dairy and food industries where deposits 0.003 inch thick of an absolutely continuous nature are required. Refrigerator coils also need thick deposits. The acid tin baths proposed before 1930 lacked the necessary throwing power. A common commercial alkaline bath was sodium stannate 28 ounces per gallon (210 grams/liter), hydrated stannic oxide 2 ounces per gallon (15 grams/liter), powdered white starch one-eighth ounce per gallon (0.9 gram/liter). Potassium resinate was used as a colloidal addition agent, being added as required to improve the character of the deposit. The bath was operated at a temperature of 160° to 180° F. (71.11° to 82 22° C.) with a current density of 25 to 40 amperes per square foot (2.5 to 4 amp./sq. dm.) at 4 to 6 volts. Thirty per cent of sheet steel anodes were used and 70 per cent of tin. The anode efficiency was about 60 per cent of that at the cathode. Sodium stannate and hydrated tin oxide were added at intervals to maintain the solution. Small amounts of chlorides are advantageous Hughes[2] gave an English bath composition of ½ pound of caustic soda per gallon (60 grams/liter), and 1 pound of stannous chloride crystals (120 grams/liter), with the addition of 1 ounce of potassium cyanide per gallon (7.5 grams/liter). Blum and Hogaboom[3] gave a bath composition: stannous chloride crystals 4 ounces per gallon (30 grams/liter), sodium hydroxide 10 ounces per gallon (75 grams/liter), glucose 8 ounces per gallon (60 grams/liter), operating at 50° C. (122° F.), at a current density of 9 amperes per square foot (1 amp./sq. dm.). They stated that the dextrin or analogous material is a very essential and efficient addition agent in these baths. Almost every textbook, however, gives its own proportions.[4] Experience shows that considerable variation is allowable. The stannous chloride or the sodium stannite or stannate contains the metal to be deposited. The caustic alkali acts as a conducting salt and helps to dissolve tin from the anodes. The cyanide, if it be added, prevents anode corrosion, keeping the anodes clean and free from slime. Knox[5] stated that with current densities of 10 amperes per square foot (1 amp /sq dm.) of cathode surface, plating efficiencies run 40 to 60 per cent higher in some cases. Mathers and Bell[6] investigated alkaline stannite baths to determine whether they could produce a commercially useful and adherent deposit by the action of addition agents such as gum sandarac, rosin, glue, oleic acid, gum traga-

[2] Hughes, *Beama*, **10**, 138–41 (1922).

[3] W. Blum, and G. B Hogaboom, "Principles of Electroplating and Electroforming," New York, McGraw-Hill Book Co., Inc , 1924

[4] Stockmeier, "Handb. d. Galvanostegie," p 116, Halle, W. Knapp, 1899, Langbein, Brannt, "Electrodeposition of Metals," Philadelphia, H. C. Baird & Co., 1920, Pfanhauser, "Galvanotecknik," p. 601, Berlin, J. Springer, 1910.

[5] Knox, *Metal Ind.*, **18**, 361–2 (1920).

[6] F. C. Mathers, and W H. Bell, *Trans Am. Electrochem Soc* , **38**, 135–42 (1920)

canth, manna, aloin, sodium sulfide and balsam copaiba. Only the last was found suitable and rosin ranked next. The bath contained: crystalline stannous chloride 60 grams per liter (8 oz./gal.), sodium hydroxide 60 grams per liter (8 oz./gal.), and addition agent 1 gram. The current density was 4 7 amperes per square foot (0.47 amp /sq. dm.). Cast iron anodes showed only 76 to 78 per cent corrosion, while amalgamated refined tin gave 100 per cent efficiency. Temperatures of 75° to 90° C. (167 to 194° F.) gave deposits superior to those at 50° C. (122° F.). Continued satisfactory deposits could not be obtained, because of gradual oxidation of the sodium stannite. No method of prevention or regeneration was found.

One of the oldest alkaline baths is that of Beneker, consisting of sodium hydroxide 125 grams per liter (16 6 oz./gal.), stannous chloride 50 grams per liter (6.6 oz./gal), and sodium thiosulfate 75 grams per liter (10 oz /gal.). Mantell developed a bath particularly applicable for plating on copper to produce heavy deposits of a highly protective nature. This bath is decidedly alkaline with all the desirable characteristics of the alkaline baths, none of the bad ones, and all of the desirable characteristics of the fluoborate acid bath. When made from sodium stannite the composition is sodium stannite 10 grams per liter (1.33 oz /gal), borax 1 gram per liter (0 13 oz./gal), sodium fluoride 4 grams per liter (0.53 oz /gal.), sodium hydroxide 2 grams per liter (0.26 oz./gal). When made from sodium stannate (a commercial salt containing 50 to 60 per cent tin, a by-product resulting from the detinning of tin plate scrap by the caustic electrolytic process) the bath is: sodium stannate 12 grams per liter (1.6 oz./gal), borax 1 gram per liter (0.13 oz./gal.), sodium fluoride 4 grams per liter (0.53 oz /gal.), caustic 2 grams per liter (0 26 oz./gal.). The deposit of tin is very white, exceedingly fine-grained, and very readily polishable. The bath has very good throwing powers. In operation it should be practically free from chlorides and sulfates. At current densities of 12 to 20 amperes per square foot (1.2 to 2 amp /sq. dm), at temperatures from 170° F. (76.7° C.) up to the boiling point, and at voltages of 4 to 6 volts, no difficulty is met in obtaining tin deposits as thick as 0 008 to 0.010 of an inch.

Proctor[7] recommended the following bath: sodium stannate 210 grams per liter (28 oz./gal); hydrated tin oxide 15 grams per liter (2 oz /gal), potassium resinate 1.8 grams per liter (0.25 oz./gal), powdered white starch 1 gram per liter (0.13 oz./gal.); temperature 71 to 82° C. (160 to 180°F.). This bath with modifications was used commercially on a large scale. Sometimes spongy deposits were formed and insoluble tin salts precipitated. Throwing power was improved by the addition of stannous chloride. This reduced the caustic content. Steel anodes, at which

[7] C. H. Proctor, *Metal Ind. (N. Y.)*, **27**, 207 (1926)

oxygen was evolved, were employed to correct anode polarization and oxidized stannite to stannate ions

Wernlund and Oplinger[8] found that a stannate solution with a low and controlled sodium hydroxide concentration, with sodium acetate and hydrogen peroxide, eliminated spongy tin deposits Table 12 gives typical compositions and operating conditions.

Smooth white tin deposits of substantial thicknesses could thus be produced in stannate baths varying from about 52 to 150 grams per liter (7 to 20 oz./gal), provided the caustic soda was kept sufficiently low—4 to 15 grams per liter (0 5 to 2 oz /gal)—and the anode current density and temperature were properly controlled

TABLE 12 SOLUTION COMPOSITION

	FOR STILL PLATING		FOR BARREL PLATING	
	(g /l)	(oz /gal)	(g /l)	(oz /gal)
Sodium stannate, Na_2SnO_3 $3H_2O$	90 0	12 0	150 0	20 0
Caustic soda, NaOH	7 5	1 0	18 8	2 5
Sodium acetate	15 0	2 0	22 5	3 0
Hydrogen peroxide (100 vol)	0 5	1/16	0 5	1/16
Anode current density	10–40 amp./sq ft		1–4 3 amp /dm ^{2}	
Cathode current density (optimum)	10–25 amp /sq ft		1 08–2 7 amp /dm ^{2}	
Cathode current density (maximum)	60 amp /sq ft		6 48 amp /dm ^{2}	
Temperature	60–80° C		140–176° F	
Free caustic as NaOH	7 5–15 0 g /l		1–2 oz /gal	
Anode current efficiency	60–90% (on Sn^4)			
Cathode current efficiency	60–90% (on Sn^4)			
Bath voltage	4 volts			
Anodes	pure tin			

The basic problem was to use a high enough anode current density together with a low enough free alkali content so that the anodes filmed over with a greenish yellow film during operation. When this takes place, the anodes remain "clean" and all the tin is dissolved as stannate This occurs at as low as 0.54 ampere per square decimeter (5 amp /sq ft) if the caustic soda is very low, or at 1.1 to 4 3 amperes per square decimeter (10 to 40 amp./sq. ft) when the caustic soda is raised to about 7 5 to 15 grams per liter (1 to 2 oz /gal) in solution containing 75 to 150 grams per liter (10 to 20 oz./gal.) of sodium stannate

The stannate-acetate baths are used commercially almost exclusively, others which may have found small usage are not worth mentioning The stannate-acetate baths are used for depositing tin on many types of small articles, as well as on large-size equipment, with thicknesses of

[8] C. J. Wernlund, and F. F. Oplinger, *U S Patent 1,919,000*, F. F. Oplinger, *Metal Ind. (N. Y.)*, **29**, 529–32 (1931); F. F. Oplinger, *U. S. Patent 1,841,978*.

deposit ranging mainly from 0.0001 inch to 0 003 inch (2.5 to 75μ). The main advantage of these baths is that their application is almost unlimited so far as size and shape of article, and type of base metal are concerned. Another major advantage of these baths is their extreme practicability. Once the basic principles are understood, the bath can easily be operated without difficulty. When specification plate is required, means of control are readily available from a number of sources.

The main disadvantage of these stannate-acetate baths is the slow rate of deposition because of low cathode current efficiency Generally, the cathode efficiency at 1 7 to 3 3 amperes per square decimeter (15 to 30 amp /sq. ft.) does not exceed 60 to 90 per cent, based on stannic tin in still plating Rates of tin deposition in barrel plating are much slower than for deposition of other metals such as copper or cadmium from cyanide solutions.

Another, but minor, difficulty encountered with the stannate-acetate baths is the tendency toward the formation of insoluble tin salts This occurs from absorption of carbon dioxide from the air whenever the alkalinity of the bath is too low. Insoluble tin salts may also form when using hard water. When available, very soft or distilled water should be used to maintain bath levels, and the caustic content should be kept high enough so that carbon dioxide absorption from the air does not cause undue precipitation of insoluble tin salts Bright lustrous tin deposits have not as yet been produced from alkaline baths

Tin may deposit by a voltaic displacement reaction on aluminum automotive pistons in sodium stannate solution, resulting in loosely adherent deposits. To insure against such immersion coating, a satisfactory stannate content from 45 to 60 grams per liter (6 to 8 oz /gal) and a low caustic content are necessary. This procedure makes for good adherence of the tin plate to the aluminum

When steel anodes are used with the tin anodes, the efficiency of the tin anodes markedly decreases As a safeguard against sponging and discoloration of deposits, small amounts of hydrogen peroxide are added simultaneously with each addition of caustic made when the caustic content is too low If the caustic content be too high, small amounts of acetic acid must be added to reduce it Each addition of acetic acid must be followed immediately by the addition of small amounts of hydrogen peroxide.

The simplicity of the alkaline tin bath is more apparent than real. In operation, the composition of the solution will become more complicated, owing to absorption of oxygen and carbon dioxide of the air and the electrode reactions resulting from electrolysis Tin is found to dissolve anodically in the tetravalent form, giving the stannate. This, when coupled with the fact that alkaline stannite solutions decomposed spon-

taneously, giving metallic tin and stannate, led to the belief that the relations between stannic and stannous ions and metallic tin were such that the equilibrium of the equation:

$$2Sn^{2} \rightleftarrows Sn^{4} + Sn^{0}$$

was very much in favor of the right-hand side. In acid solutions, however, tin dissolves anodically as stannous ions. Goldschmidt and Eckardt[9] found that pure tin readily became passive. It dissolves in alkaline solution in the stannous condition. Foerster and Dolch[10] found that tin to stannous ion and not tin to stannic ion is the stable system. They noted that colloidal tin compounds are precipitated on the electrode at certain concentrations. These prevent the diffusion of the stannous or stannite ion away from the anode, with the result that the anode potential is raised to the value necessary for oxygen evolution The tin is thus passivated. The stannite is rapidly oxidized to stannate This film action is catalyzed by insoluble impurities present in the tin The lower the current density and with higher temperatures, the more tin can be dissolved before the formation of stannate occurs If the electrode be scraped, it again becomes active. The chemical precipitation of tin from alkaline stannite solution is preceded by a great diminution of the stannate-ion concentration, owing to a gradual formation of nonionized colloidal metastannic acid

Acid tin-plating baths were developed primarily in connection with electrolytic tin refining.

Hollis[11] proposed a tin fluosilicic acid bath with additions of glue or gelatin.

In 1914 Mathers and Cockrum[12] investigated several acid baths. Of the chloride, fluoride, perchlorate and fluoborate, the fluoborate in conjunction with clove oil gave the best deposits.

Hollard[13] stated that spongy deposits were prevented by the use of an electrolyte of sodium stannite 12 grams per liter (1 6 oz /gal) and sodium sulfate 200 grams per liter (26.6 oz /gal), operated at a current density of 2 amperes per square foot (0.2 amp /sq. dm), at a temperature of 80° C. (176° F). Mathers and Cockrum[14] found that the various baths for tin plating described by Kern[15] did not in any case produce an entirely satisfactory deposit when operated under the conditions recommended. They obtained smooth, firm deposits with the Beneker bath, but considered

[9] Goldschmidt, and Eckardt, *Z physik Chem* , **56,** 385 (1906).

[10] Foerster, and Dolch, *Z Elektrochem* , **16,** 599 (1910)

[11] Hollis, *U S Patent 916,155* (1909)

[12] F. C. Mathers, and B W Cockrum, *Trans Am Electrochem Soc* , **26,** 133 (1914)

[13] Hollard, *Bull. soc enc ind nat* , 28 (July, 1912)

[14] F. C Mathers, and B W Cockrum, *Trans Am Electrochem Soc.*, **29,** 405–10 (1916).

[15] E. F Kern, *Trans. Am. Electrochem. Soc.*, **23,** 199 (1913)

the results far below the quality desired for electroplating. They found that the addition of peptone to a modification of Kern's stannous ammonium oxalate bath containing 2 to 3 per cent stannous chloride, 5.5 to 6.5 per cent ammonium oxalate, and 0.3 to 0.4 per cent of oxalic acid gave a smooth, firm and finely crystalline deposit which was the best obtained from any bath. They[16] recommended a satisfactory bath to be 5 per cent stannous oxalate, 6 per cent ammonium oxalate, 1.5 per cent oxalic acid, and 0 25 per cent peptone. It is run at room temperature at 0.4 ampere per square decimeter (4 amp./sq. ft), with frequent stirring Additional peptone is added when the deposit shows projecting crystals.

Quintaine[17] claimed that he could obtain a good deposit of tin from either stannous or stannic chloride with the addition of a salt such as ammonium chloride Lottermoser and Brehm[18] found that a good deposit of tin can be obtained from a pyrophosphate bath, without further additions, at a temperature of 50° to 60° C (122° to 140° F.). The composition of the bath is as follows: fused stannous chloride 16 grams per liter (2.13 oz /gal), stannous chloride crystals 4 grams per liter (0 53 oz /gal.), sodium pyrophosphate 50 grams per liter (6 7 oz /gal). The best results are obtained if 5 to 6 grams of tartaric acid are added to the above bath This changes the pH from 3 44 to 1.7. The addition of a colloid is unnecessary. The cathodic current density should not exceed 0 02 ampere per square decimeter.

Battle[19] has patented an electrolyte for tin plating containing phosphoric acid, a tin salt such as the chloride or sulfate, and sodium pyrophosphate with the addition of colloids such as gelatin and gums. A phosphate bath first proposed by Roseleur has the following composition: stannous chloride crystals 1 ounce per gallon (7 5 grams/liter), sodium pyrophosphate 8 ounces per gallon (60 grams/liter), dextrin 1 ounce per gallon (7.5 grams/liter), operated at a temperature of about 60° C. (140° F) at 5 amperes per square foot (0 5 amp./sq dm.) Marino[20] has patented a tartrate bath for the deposition of tin, as well as various phosphate baths containing sulfanilic acid In 1918 Mathers[21] patented the use of cresylic acid in a bath containing sulfuric acid. This had the effect of allowing the presence of a higher concentration of sulfuric acid without the detrimental effect of producing tree-like deposits. This also allowed the use of less tin in the solution. A suggested solution composition is tin 2 per cent, sulfuric acid 5 per cent, fluosilicic acid 5.5 per cent, cresylic acid 0.3 per cent

[16] F. C. Mathers, and B W Cockrum, *Op cit.*, 411–4
[17] Quintaine, *British Patent 5,496* (1900).
[18] Lottermoser, and Brehm, *Z Elektrochem* , **27**, 573–9 (1921)
[19] Battle, *U. S Patent 1,202,149* (1917).
[20] Marino, *British Patent 11,011* (1915).
[21] F. C. Mathers, *U. S. Patent 1,397,222* (1921)

Mathers[22] has also patented an electrolyte for tin consisting of stannous sulfate saturated with cresylic acid to improve the smoothness of the tin coating. Schlotter[23] stated that dense adherent deposits are obtained from acid tin salt solutions containing a colloidal substance and free from alkalies and ammonia. A suitable solution contains stannous sulfate 120 grams per liter (16 oz /gal.), and gelatin 2 grams per liter (0 26 oz /gal.). Such solutions are suitable for depositing on copper, brass or the like. For plating iron galvanos prior to backing them with molten lead alloy, it is necessary, however, to employ an addition agent such as phenol or phloroglucinol. The electrolyte may then consist of stannic chloride 150 grams (20 oz.), gelatin 2 grams (0.26 oz), phenol 5 grams (0 66 oz.), hydrochloric acid 5 grams (0 66 oz.) and 1 liter (0 26 gal) of water Schlotter[24] has patented a tin-plating bath containing stannous sulfate with the addition of gelatin, phloroglucinol, or a similar substance to the solution before electrolysis.

Simpkins[25] obtained a patent covering the addition of beta-naphthol and Fink[26] covered several colloidal or near-colloidal substances, such as alum, tannic acid, etc , and the use of sulfates of magnesium, iron, titanium, and aluminum In 1925, Mathers[27] covered a bath containing stannous sulfate, sulfuric acid, cresylic acid and glue

In the 1930's several patents were issued to Schlotter[28] in which addition agents such as sulfonates, phenols, higher alcohols and tin naphthalene tetrasulfonate were used

In 1935, Pine[29] covered addition agents prepared by condensing cresol with glue, alum and aldehydes

Acid baths have found applications in electrolytic tin plating to a large extent commercially.

The acid tin bath depends upon addition agents Pine[30] stated:

"The average bath contains two types of addition agents, namely, a colloid of a low gold number or high protective value and an aromatic compound Of the first class, glue, gelatin and lysalbic acid are the most common Of the second type, cresol is the most common, with mention being made of naphthol and resorcinol The effect of cresol in the tin bath is to prevent loose crystalline deposits

[22] F C. Mathers, *U. S. Patent 1,540,354* (1925)
[23] M Schlotter, *British Patent 148,334* (1920).
[24] M. Schlotter, *U. S Patent 1,424,678* (1922)
[25] Simpkins, *U S. Patent 1,452,573* (1923).
[26] C. G Fink, *U S. Patent 1,466,126* (1923).
[27] F. C Mathers, *U S. Patent 1,540,354* (1925)
[28] M. Schlotter, *British Patents 329,308* (1930) and *443,429* (1936); *French Patent 790,884* (1935).
[29] P. R. Pine, *U. S. Patent 1,987,749* (1935).
[30] P. R. Pine, "Modern Electroplating," pp. 315–28, New York, The Electrochem. Soc., Inc., 1942.

from forming and to give a smooth matte deposit. The effect of the colloid, such as glue, is to give a smoother deposit and also to hold the cresol or other aromatic compounds in solution or colloidal emulsion. The aromatic compound, such as cresol, is sometimes introduced as the sulfonate, although pure sulfonates are ineffective The cresol sulfonate has some effect in preventing air oxidation of the stannous sulfate to stannic sulfate Likewise, sulfonates, being water-soluble and of structure common to the parent compound, produce surprising solvent properties toward the parent compound Water-soluble compounds are thus held in semi-colloidal suspension in such a way that they become active addition agents."

Typical bath compositions and operating characteristics are given in Table 13

The ranges of constituents of the baths are: $SnSO_4$ 30 to 90 grams per liter, H_2SO_4 30 to 150 grams per liter, gelatin or glue 0 5 to 10 grams per

TABLE 13 OPERATING CONDITIONS OF SULFONIC ACID BATHS

	(g /l)	(g /l)
Stannous sulfate	54	45
Sulfuric acid	100	45
Cresol sulfonic acid	100	
Beta-naphthol	1	
Gelatin	2	
Addition agent		45
Cathode current density	10–40 amp /sq ft (1 1 to 4 3 amp /sq dm)	
Temperature	70–80° F (21–27 ° C)	
Voltage of bath	0 6–1 6 volts	

liter, cresol 0.5 to 10 grams per liter, sulfonated cresol 10 to 100 grams per liter, beta-naphthol[31] 0.5 to 1 gram per liter, resorcinol[31] 20 grams per liter; $Na_2SO_4 \cdot 10H_2O$[32] 50 to 350 grams per liter, aloin[32] 1 to 3 grams per liter A bath will ordinarily contain not more than three of the listed addition agents

It will be noted that in practically all of the successful tin-plating baths there is low ionic tin concentration, obtained as a result either of dilute solutions or of the formation of complex ions No tin baths are known which will give bright tin deposits directly from the solution without the necessity of polishing

Deposition of tin alloys, particularly those of lead and tin, from fluoborate solutions has been carried out successfully by the United States Navy Department, particularly for liners in torpedo flasks and similar objects. Blum and Haring[33] found that lead and tin have nearly equal potentials in

[31] *J. Electrodepositors' Tech. Soc* , **12**, 113 (1937).
[32] C. G. Fink, *U. S. Patent 1,466,126* (1923).
[33] Blum and Haring, *Trans. Am. Electrochem. Soc* , **40**, 147 (1921).

fluoborate solutions. They will displace each other depending upon their respective metal ion concentrations Solutions which are of 1 *N* metal and 0 5 *N* free hydrofluoboric acid concentrations, when agitated with tin or lead, reach equilibrium at about 0 81 *N* tin and 0 19 *N* lead, because then the two metals have the same potential. This equilibrium is not affected by glue but is appreciably influenced by the acidity and total metal concentration. Cathode efficiencies under normal conditions are nearly 100 per cent, and the metal deposits obtained depend upon the metal ratio in the solution Current densities of 0 5 to 1.5 amperes per square decimeter (4 7 to 14 amp./sq ft.) are employed with lead-tin anodes containing somewhat less tin than is desired in the deposits

Nonelectrolytic Methods of Plating

Large quantities of small articles such as pins, thimbles, eyelets, dress snap fasteners, chain links, safety pins, buttons and the like, are coated with tin by the contact process This method is an immersion one, and strictly speaking is not electrolytic. The current instead of being furnished from an outside source, arises in the tank itself. This method is applied largely for decorative purposes. The coatings are very thin but very fine-grained and bright. Unlike most deposits produced by immersion, they are decidedly adherent, with considerable resistance to corrosion The ionic concentration of tin in the baths is very low, hence the rate of deposition is slow and treeing is effectively prevented Hydrogen has a relatively high overvoltage on tin; this aids in the production of dense impervious deposits. All of the immersion processes depend upon the electrolytic action of the base metal—(i e , the metal being plated). Deposition thus necessarily stops as soon as the base metal is entirely covered. It is thus possible to secure only very thin deposits.

Where a better deposit is required, immersion tinning in the above or similar baths is done by having the articles in contact with pieces of zinc A quicker action ensues owing to electrochemical effect.

Brass articles to be tinned are rotated for 2 to 4 hours at 80° C. (176° F.) in a barrel containing the solution and small pieces of zinc. One solution is stannous chloride crystals 3 ounces per gallon (25 grams/liter), and potassium acid tartrate ($KHC_4H_4O_6$) 1 3 ounces per gallon (10 grams/liter). When the pieces of brass and zinc come in contact in such a solution, a cell is formed in which the zinc is anode and the brass is cathode and becomes coated with tin. The zinc passes into the solution, displacing the tin. The acid tartrate causes the formation of complex ions to some extent. This produces a small concentration of stannous ions. The complex ions do not readily hydrolyze or precipitate tin hydroxides.

The "cream of tartar" immersion process is somewhat similar to the above, the solution consisting of potassium acid tartrate 0.2 ounce per

gallon (1.5 grams/liter) and sodium chloride 0.4 ounce per gallon (3.0 grams/liter). The brass articles are placed in thin layers on iron wire trays, covered with perforated sheets of pure tin and heated to at least 90° C. (194° F.) by steam coils in a copper tank for 3 to 5 hours. The tin gradually passes into solution. It never reaches a high concentration, for it is speedily plated out on the brass, the potential of which is similar to that of copper, *i.e.*, below that of tin in the electrochemical series Each batch of work requires a freshly made solution. After coating, the work is rapidly rinsed and dried.

Alkaline solutions are also employed for tin coating of brass by immersion. A typical solution contains stannous chloride crystals 4 ounces per gallon (30 grams/liter), and sodium hydroxide 8 ounces per gallon (60 grams/liter). The brass objects are placed in an iron vessel on iron wire trays, covered with perforated sheets of tin The vessel and its contents are heated to 90° C. (194° F.) for 2 to 3 hours. Tin becomes the anode, passes into solution and is deposited on the brass. Solutions more dilute than given in the formula are used for very small articles.

In deposition by immersion, the compositions of a few baths that have already been applied are:

(1) Saturated solution of potassium acid tartrate containing 4 to 30 grams of stannous chloride per liter and at boiling temperature.
(2) Twenty to 30 grams ammonium alum and 1 to 2 grams of anhydrous stannous chloride per liter, at boiling temperature.[34]
(3) Alkaline bath 15 grams of stannous chloride, 18 7 grams of sodium hydroxide, 7.5 grams of sodium cyanide per liter, at boiling temperature.[34]

Copper and many types of brasses and bronzes can be treated by this process [35] However, it cannot be applied to high-nickel copper alloys such as Monel. The concentration of the bath is generally standardized at approximately 2 to 3 grams per liter of tin as sodium stannite; *i.e.*, 3 3 to 5 grams per liter of sodium stannite. For the most satisfactory performance, the concentration of sodium cyanide should surpass 25 grams per liter, and even 50 grams per liter is recommended.

Periodic titrations should be made to effect high enough concentrations. As the stannous tin is reduced, stannous salt—*i.e.*, sodium stannite or stannous chloride—should be added. Sodium stannite is prepared by the process of adding sodium hydroxide slowly and with agitation to an aqueous solution of stannous chloride. After the addition of sodium cyanide, it is necessary to dilute to the required volume. A brass or copper vessel is able to be tinned on the inside if filled with solution and

[34] H. MacFayden, *Monthly Rev. Am. Electroplaters' Soc.*, **22**, No. 11, 13–9 (1935).
[35] J. D. Sullivan, and A. E. Pavlish, *Metals and Alloys*, **11**, 131–4 (1940).

permitted to stand until the necessary coating is deposited. The insides of pipes are successfully tinned if a solution is circulated through them or if they are filled for a certain length of time, drained, and washed. The results from a typical bath are:

PERIOD OF IMMERSION	THICKNESS OF COATING (inch)	WEIGHT OF COATING	
		(g per sq dm)	(oz per sq ft)
5 minutes	0 000004	0 006	0 0020
15 minutes	0 000006	0 012	0 0039
30 minutes	0 000009	0 017	0 0056
1 hour	0 000014	0 026	0 0085
2 hours	0 000021	0 040	0 0131
24 hours	0 00014	0 262	0.0858

Whereas an immersion of $2\frac{1}{2}$ minutes yields a coating with a fine appearance, it is not adequate protection for copper from moist hydrogen sulfide, $6\frac{1}{2}$ minutes yields a coating free from the danger of hydrogen sulfide.

The coating forms an alloy with the copper base if the tin-coated article is heated somewhat higher than the melting point of tin An added immersion treatment is then applied to the surface and the three distinct layers formed are copper, diffused layer copper-tin, and tin.

Iron articles are tinned by placement in thin layers on iron wire screen trays, covered with perforated zinc sheets in a galvanized iron tank. The solution is heated nearly to boiling, the articles immersed and kept there for about three-quarters of an hour. The heating of the solution is stopped when the articles are immersed. A typical solution contains stannous chloride crystals 0.3 ounce per gallon (2 5 grams/liter), ammonium alum ($(NH_4)_2SO_4Al_2(SO_4)_324H_2O$) 0.25 ounce per gallon (2.0 grams/liter), and cream of tartar ($KHC_4H_4O_6$) 0.01 ounce per gallon (0.08 gram/liter). Usually the salts are dissolved in one-third the total quantity of water and then added to the other two-thirds of the water previously placed in the iron tank in which plating is to be done. About one drop of sulfuric acid per gallon of solution is then added. After the tinning process, the solution is discarded and the articles are quickly rinsed and dried.

Articles for simple immersion tinning must be thoroughly and systematically cleaned. Following treatment in the tinning bath, they are generally dried and polished by shaking in sawdust, leather scraps, whiting or other polishing agents in tumbling barrels.

A wartime study of methods for producing a uniformly thin yet continuous metallic layer for decorative purposes—so thin that fine dimensional tolerances would not be disturbed—led to the use of fused baths of metallic salts. A bath of tin chloride, either pure or diluted with small amounts of ammonium or other chlorides or extra metallic tin dissolved therein, was

described by Hoge.[36] He studied the variation of thickness of tin coatings from a molten stannous chloride bath on steel as a function of varying time at constant temperature, and at constant time with varying temperature, as well as stannous chloride, ammonium chloride baths Thicker coatings were produced in baths which had tin dissolved therein

In tin coatings from vapor, which concern the decomposition of volatilized tin compounds at the surface of the metal object, there is a great range of thickness and uniformity of coating This may be similar to cementation in its effect, with the benefit of possessing a moving atmosphere which reaches all parts of the work. In experimental work, cylinder hydrogen which has been dried and purified of oxygen is brought over heated anhydrous tin chloride and passed into a tube furnace holding degreased copper. Because the vapor pressure of the reagent increases with the temperature (19 mm. Hg at 700° F. to 600 mm at 1125° F), the operation is performed more satisfactorily at a temperature where the vapor pressure is high The minimum temperature necessary is generally between 650 and 850° F. At any higher temperature, the amount of coating per unit of time goes slowly up to approximately 1025° F , above which the action augments swiftly. Natural gas, carbon monoxide, nitrogen, and steam present undesirable atmospheres Other metals and alloys are successfully tinned—namely, bronzes and brasses—and steel takes on a light but continuous coat in about 30 minutes at 950 to 1025° F Zinc and other common alloys may be tinned similarly, but no deposit can be made on glass or refractory material [37]

[36] H. R. Hoge, *Metal Progress*, **52**, No 5, 819–23 (1947).

[37] B. W Gonser, and E. E. Slowter, *Metal Progress*, **35**, 155 (1939).

Chapter 10

Electrolytic Tin Plate

With the development of high-speed rolling of continuous strip by the steel industry, plus wartime emphasis on conservation of tin, there was a decided impetus to the development of electrolytic tin plating. The factors involved concern themselves with the electroplating baths, their stability, and for the purpose of speed, their operation at high current densities; and secondly, the mechanical and electrical factors in the handling of long lengths of strip steel at high speeds continuously.

Electrolytic tin-plating lines might be divided into types in which the sodium stannate bath is employed as the electrolyte in one case, and acid baths in the other; into those in which the sheet is handled and caused to pass vertically and over rolls for change of direction with vertical anodes, and another type in which the sheet is processed horizontally, commonly with horizontal anodes. These differences cause markedly different mechanical and electrical arrangements.

Electroplated tin on steel strip does not have the smooth reflecting surface of hot-dipped tin. For many applications, the electroplated surface with scratch brushing or little polishing is sufficient. For general application, "reflow" or melting units which fuse the electroplated coating have become either a portion of the tinning line or the mechanism of a following step.

The "reflow" units have assumed many forms, dependent upon whether the thermal energy for reflowing is furnished by hot oil, hot gases, radiant heat, electrical resistance to currents in the sheet itself, electrical induction, or combinations of these.

As a general statement, although there may be exceptions, it is easier and more economical to put on heavier coatings (from one pound and upwards of tin per base box of tin plate) by hot dipping and lighter coatings (from three quarters of a pound of tin and lower per base box of tin plate) by electrolytic processes.

The physical space of the electroplating part of the line is small in comparison to the electrical, mechanical, physical control and inspection portions, so that the engineering development of equipment plays an important part. If the electrolyte were changed to that of another metal, other plated steels might be made.

Electrolytic Tin Lines

In an electrolytic tin line there are three factors to be considered: (1) the handling of the strip, (2) the proper cleaning of the strip surface, and (3) the plating of the strip. A fourth factor, that of fusion of the tin plating, is important in most lines.

Crown Cork and Seal Co. Cooper[1] has described one of the first lines, that of The Crown Cork and Seal Company at Baltimore, Md.

"Steel is received directly from the temper mills in coils of 6,000 pounds or more and in widths up to 36 inches. These coils are placed on runways that lead to uncoilers, there being two uncoilers, one paying out while the other is being charged This arrangement makes for continuous operation The strip steel is pulled from these uncoilers by a pair of rubber-covered pinch rolls Between this pair of pinch rolls and the uncoiler is a seam-type welder which joins the ending of one coil to the beginning of another

"Following the pinch rolls is a mechanical looping tower which consists of a set of stationary rolls and a set of moving rolls The moving rolls are mounted on a common carriage, free to move vertically This carriage is counterweighted so that the strip is always under tension In operation, this looper serves to store strip (approximately 400 feet) in a vertical serpentine manner. This storage is later utilized when making a weld The counterweight serves two purposes first, to load automatically the looping tower with strip accomplished by overspeeding the pinch rolls, and second, to maintain a uniform back tension throughout the proceeding units This back tension is essential to maintain perfect tracking as there are no side guides used at either end for this purpose.

"The surface of steel strip coming from the temper mills is generally coated with very light oxides These must be removed just as for hot tinning The bond between steel and tin depends upon the surface to be plated, hence the surface must be chemically cleaned to get best results This is accomplished by a continuous-strip pickling unit using either sulfuric acid or muriatic acid with inhibitors

"The continuous-strip pickler used in this process consists of a rubber-lined tank 51 inches wide by 12 feet long by 11 feet 6 inches deep, and has a series of top and bottom rubber-covered rolls mounted in aluminum-bronze bearings The strip travels in a vertical serpentine manner and is acted upon by the acid for 190 feet of its length At 500 ft per min , this would mean a pickling time of approximately 23 seconds. Leaving the pickling tank, the strip passes through a set of wringer rolls to remove the excess pickling solution from the strip. The strip is then subjected to a cold-water rinse to remove any acid adhering to the strip

"Plating takes place in one common cell which is a steel unlined tank 50 feet long by 51 inches wide with a depth of 10 feet, and is equipped with heating coils to control the temperature of the electrolyte. The strip travels as in the pickling tank in a vertical serpentine manner and has a capacity of 524 feet of steel strip. Not all this length is acted upon, as part is external to the bath.

"There are 48 vertical strands of steel and suspended between each strand is a 2,300-pound tin anode. These anodes are grouped eight to a 10,000-ampere,

[1] W. Cooper, *Iron Steel Engr.*, 31–5 (Mar., 1943).

8-volt generator Current is taken off the cathode by 12-inch steel rolls and is connected to the generator through a specially designed current-carrying shoe. These are grouped four to a generator and are capable of carrying approximately 2,500 amperes each Dragout is controlled by a set of wringer rolls and a set of cold-water sprays The cold water is played on the top and bottom of the strip in order to wash away any electrolyte that may be adhering After plating, the strip is rinsed in hot water to remove any particles of electrolyte that may still be on the surface, and is then finally dried by a blast of hot air

"The strip is pulled through the entire line by one master pinch roll, and consists of a 24-inch diameter rubber-covered steel roll with two 12-inch snubber rolls This roll is located immediately after the drying operation and is the only means of pulling the strip and controlling the speed of the line

"Following the master pinch rolls is a delivery looping tower which is a duplicate of that at the entry end and serves to store strip when stripping the finished coil. The coiler is of the collapsible mandrel type and is mounted on a sliding base to permit the coiler to move horizontally, there being no side guides used to control the tracking of the strip. This horizontal motion is the only means of coiling a straight-sided coil. The side movement of the strip is received by a roll free to move horizontally. This lateral movement is transmitted to two switches, one on either side of a given center As the strip moves to one side, the guide roll moves with it, making contact with one of the switches This is transmitted to the sliding base motor and moves the coiler in the same direction as the movement of the strip This method of strip control is very simple and has proven very satisfactory Tension of the strip at the coiler is applied by a drag generator and the counterweights of the looping tower This tension serves to make a tight coil and prevent collapsing after stripping from the mandrel.

"The amount of tin deposited is controlled by the speed of the strip, all other conditions remaining the same, that is, applied current, solution level, and chemical balance of the bath. As an illustration, the speed of 350 ft per min will deposit 0 5 lb. of tin per base box using 60,000 amperes at 8 volts At 500 ft per min, the coating weight of 0 3 lb per base box is to be expected.

"The plating solution (approximately 15,000 gallons) is alkaline and consists of sodium stannate, sodium hydroxide and sodium acetate The control is simple, needing only a chemical check once a day. A continuous-type filter is used to filter out any particles in suspension and to circulate the electrolyte The anode current density is kept at 35 amp per sq ft. and the cathode current density at 26 amp per sq. ft. The efficiency of this process is high—between 95 and 100 per cent.

"Strip as plated from this process has a smooth satin finish and can be produced in various coating weights dependent upon its ultimate use. Bottle caps, screw caps, dry packages, can ends and can bodies are being made from this plate. However, some industries still demand the brightened plate and require a further operation of reflowing."

The general arrangement of the electrolytic tinning unit showing pickling, rinsing, plating, and rinsing is shown in Fig. 67. The general arrangement of the line and its electrical connections are shown in Fig. 68.

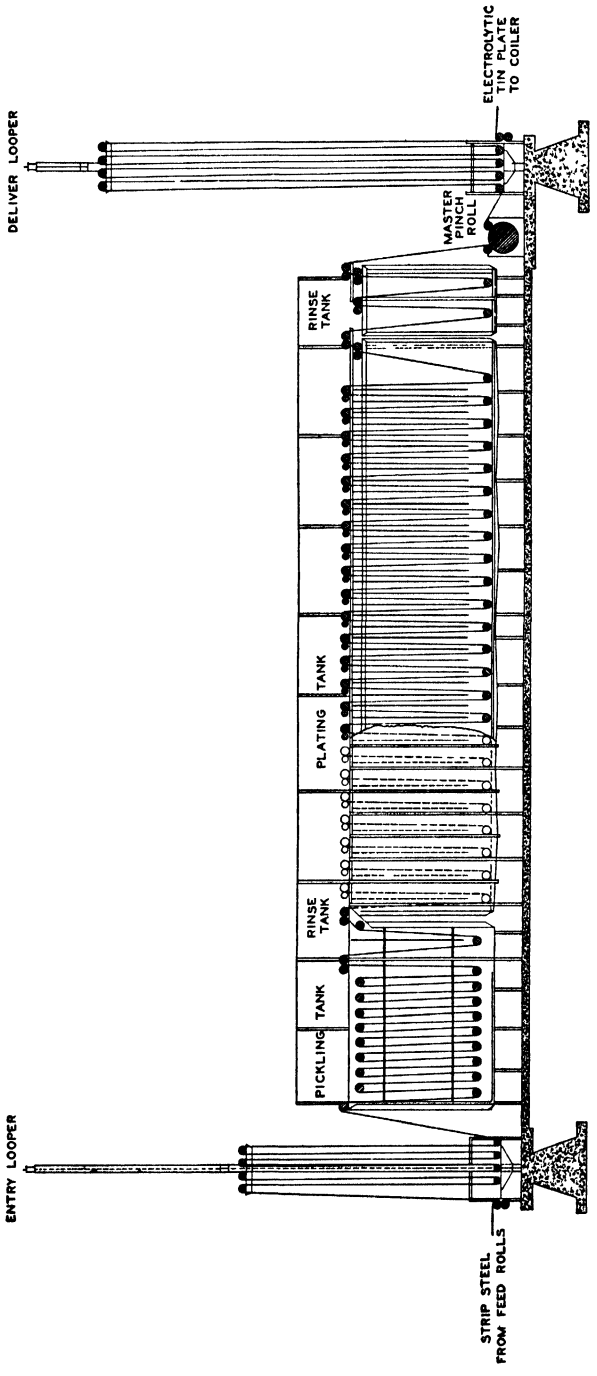


FIGURE 67. General arrangement drawing of electrolytic tinning unit.

Lippert[2] discussed the general subject of electrolytic tin-plate lines and its relation to and effect on the conservation and the canning industry.

Carnegie-Illinois Steel Corp. J. H Hopper[3] described the tinning line developed by the Carnegie-Illinois Steel Corporation as shown in Fig 69

"Figure 69 illustrates diagrammatically a tinning line of the type developed by the Carnegie-Illinois Steel Corporation A number of these are now being installed in the Chicago, Pittsburgh, and Birmingham areas. The original 30-inch

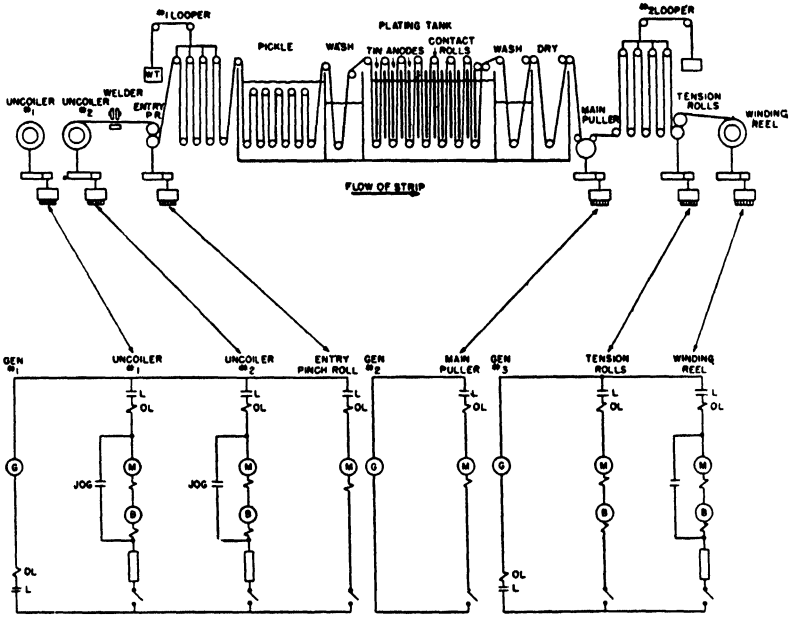


FIGURE 68 General arrangement of electrolytic tinning line developed by Crown Cork and Seal Company, with d c driving motor circuits.

line, which was built mainly for experimental purposes, is still in operation at Gary, Indiana, and is turning out tin plate on a production basis. This original line was slow speed at first, but has been speeded up several times The new lines are expected to do 600 ft per min., and will handle strip up to 36 inches wide.

"Two uncoilers for alternate coils are also used on this line, followed by a small, four-high pinch roll, a shear, a seam welder, and the entry pinch roll which feeds the strip into a deep looping pit, and thus provides strip storage to keep the line running while welding coils together. This loop also provides a convenient place to guide the strip as it enters the main part of the line. Next is the drag bridle for holding back tension on the strip as it passes through the electrolytic pickling tank, a washing operation, electrolytic plating tanks, tin recovery tank, brush burnishing with metallic brushes, and steam dryer to the main puller bridle stand. Following

[2] T. W. Lippert, "Food in Cans," *Iron Age*, **149**, 29 (Apr 30, 1942).

[3] J. H. Hopper, *Iron Steel Engr* , 36–48 (Mar., 1943).

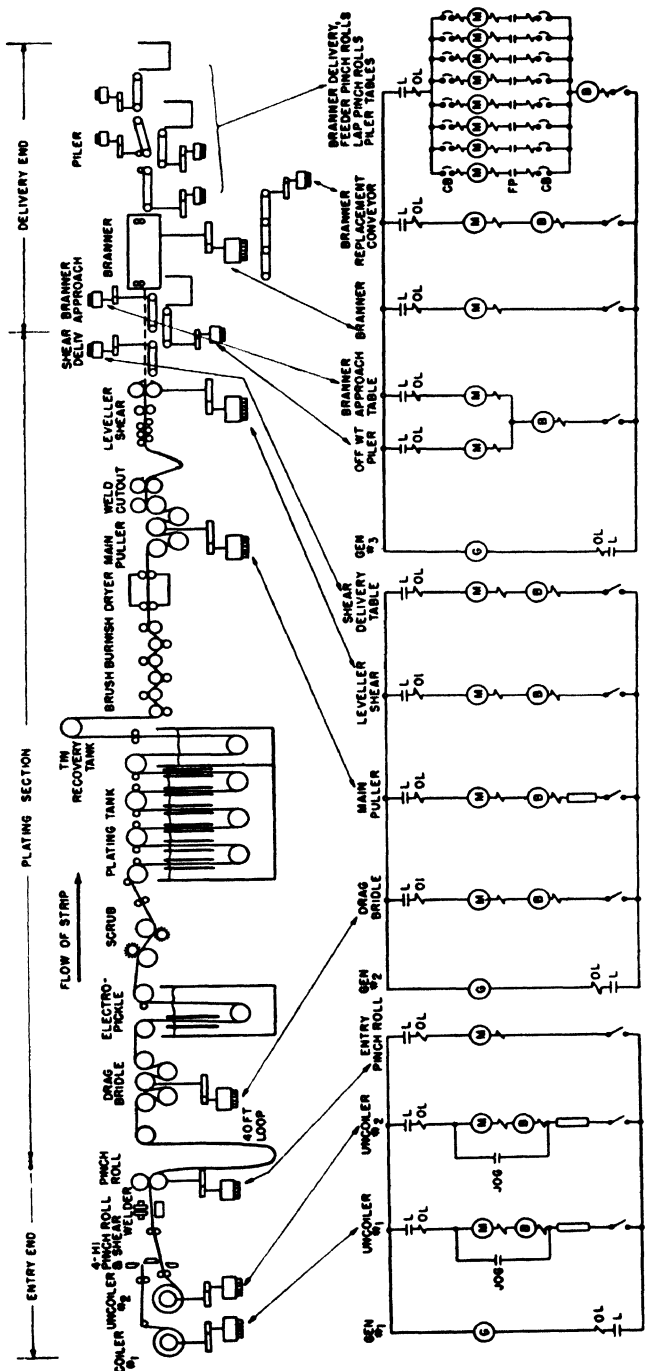
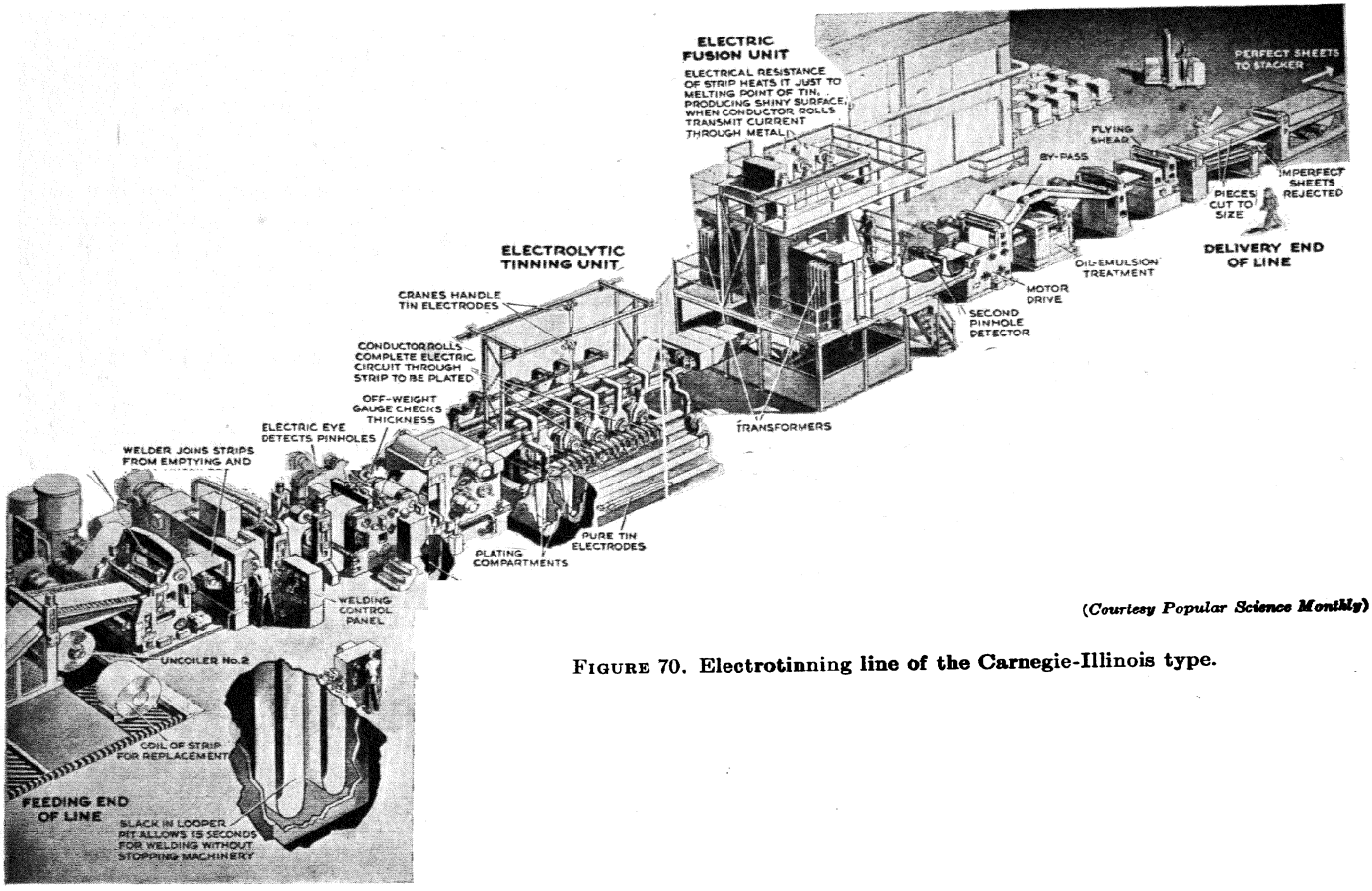


FIGURE 69. Electrolytic tinning line developed by Carnegie-Illinois Steel Corporation, with scheme for d c driving motor circuits.



(*Courtesy Popular Science Monthly*)

FIGURE 70. **Electrotinning line of the Carnegie-Illinois type.**

this is the shear for cutting out the lap weld, followed by a short loop ahead of the more or less conventional leveler shear where the strip is cut into sheets From here the sheets pass by a deflector gate which throws "off-gage" sheets and sheets containing pinholes into the "off-gage piler." The branner is next in line, and is followed by a system of rolls and conveyor belts which convey the prime sheets to either of two piles All this part of the equipment is of somewhat conventional design The branner is arranged so that it can be removed from the line and replaced by a section of conveyor "

An electrotinning line of the Carnegie-Illinois type is shown in Fig 70 The size of the line, by comparison to the workmen, its mechanical and electrical complexity, as well as the small percentage of the total space necessitated by the electroplating tanks, may be appreciated by a study of the sketch.

United Engineering and Foundry Co Hopper[4] also described the horizontal variety of mechanism as the United Engineering type of line illustrated in Fig 71

"Figure 71 illustrates a tinning line of the type developed by the United Engineering and Foundry Company in cooperation with the Hanson-Van Winkle-Munning Company The rated speed of new lines of this type is 600 ft per min , but this speed may be increased to 1,000 ft per min This line also is provided with two cone-type uncoilers In this case, each cone is connected to a drag generator as shown Next in the line is a four-high pinch roll with integral shear followed by the seam welder, shown in Fig 72, the entry pinch roll, and a 40-feet deep looping pit for loop storage while welding coils together Strip steel in the looper pit is shown in Fig 73 Then the strip passes through the No 1 drag unit, which maintains back tension on the entire center section of the line through a short electrolytic cleaning process, a scrubber, acid etch, another scrubber and into the plating unit which consists of 24 sections. The bottom side of the strip is plated in the first 12 sections, then the strip doubles back over itself and the other side (now on the bottom) is plated in the other 12 sections The three-decked plating arrangement is shown in Fig 74 Next comes the solution reclaim, a cold rinse, a long drip pan, a metallic brush-burnishing unit, a hot rinse, a hot-air dryer, and the main puller bridle rolls A slight operational loop is maintained between the main puller and the No 2 drag unit for purposes of strip guiding The No 2 drag unit holds back tension on the strip as it passes through a branner (if used), a pusher pinch roll which engages and pulls the strip while changing reels, and a selector shear, to either of the two winding reels. The winding reels are equipped with belt wrappers and it is said that the equipment is suitable for changing from the full reel to the empty reel at high speed A magnetic pickup which recognizes the approach of the lap weld, initiates starting of the pusher pinch roll and the empty reel, as well as operation of the selector shear and belt wrapper

"The circuit for the entry end section of the line differs from those previously discussed only in that two drag generators are employed on each uncoiler instead

[4] J. H. Hopper, *Iron Steel Engr.*, 36–48 (Mar., 1943).

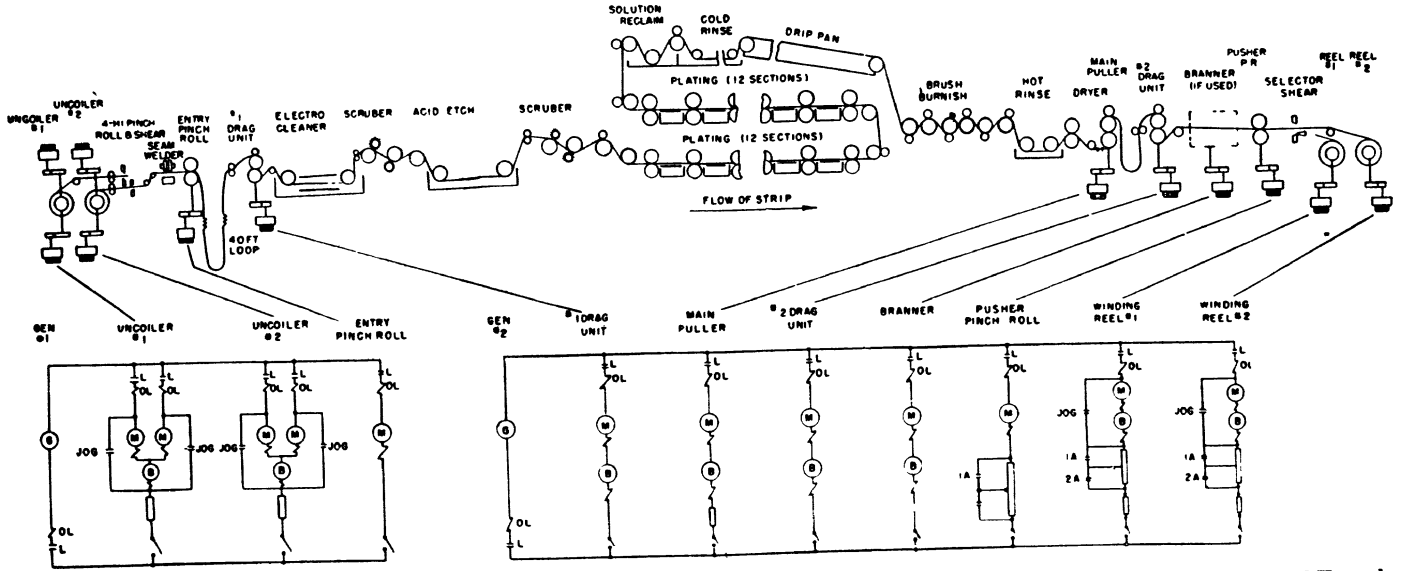
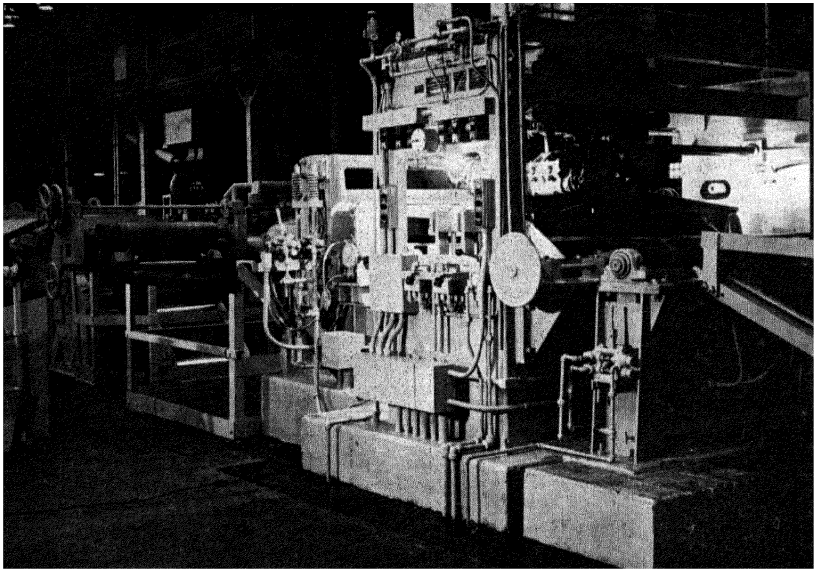


FIGURE 71. Circuit for d c driving motors recommended for electrolytic line developed by United Engineering and Foundry Company.



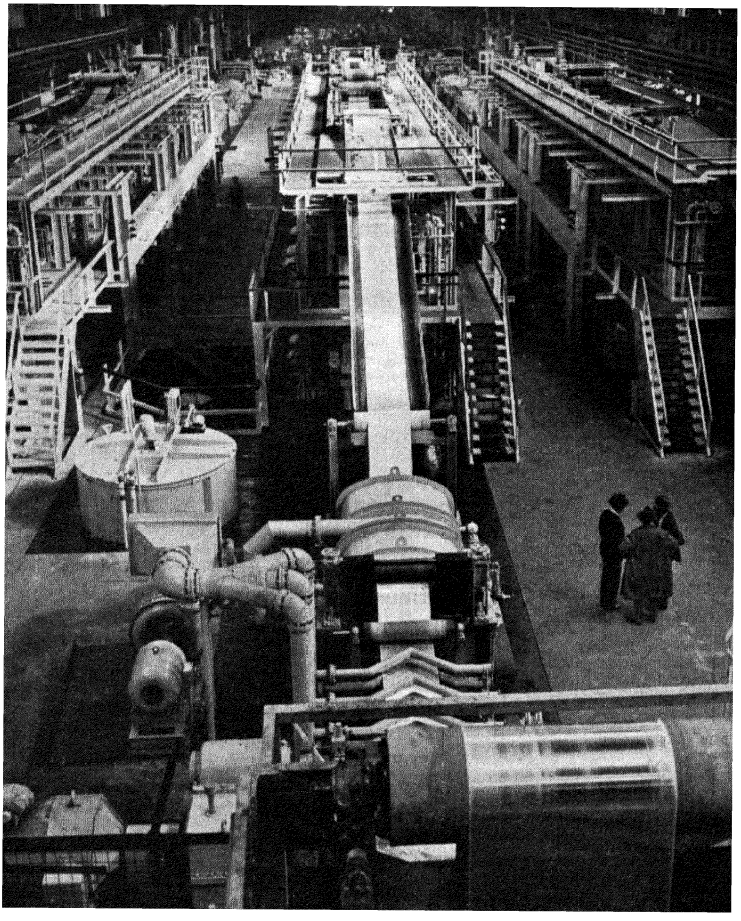
(*Courtesy E. I. du Pont de Nemours & Co., Inc.*)

FIGURE 72. Flow of strip steel continues uninterrupted ahead of high-frequency electrical induction welder, right center above, in the line installed at the Weirton Steel Company, Weirton, West Virginia, which electrotins 1,050 ft. of strip a minute.

(*Courtesy E. I. du Pont de Nemours & Co., Inc.*)

FIGURE 73. This "pay off" loop feeds the line ahead while a fresh coil of steel is being welded to the trailing end of the line of strip to maintain continuous operation.

of one. The use of two machines on each uncoiler has some advantages; however, whether they are important enough to justify the extra cost, is debatable.

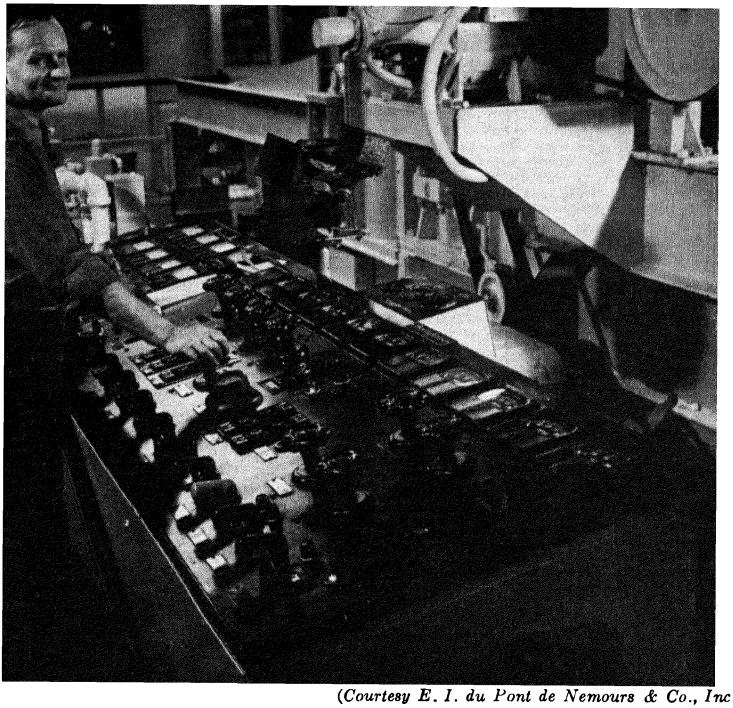


(Courtesy E. I. du Pont de Nemours & Co., Inc.)

FIGURE 74. View showing three-decked units housing the plating cells of three separate continuous electrotinning lines using the Halogen Tin Process developed by the Electroplating Division of the du Pont Co. The central line of this installation at the Weirton Steel Co., Weirton, West Virginia, electrotins 1,050 ft. of strip a minute.

"The plating section and delivery end of the line should both operate from one adjustable voltage generator as shown, because accurate speed matching is required throughout this section. Except for the small loop for guiding ahead of the No. 2 drag unit, the strip is held under controlled tension through this part of the line.

Automatic current regulators control tension ahead of the main puller and also at the winding reel. The pusher pinch roll and the two reels must be equipped with resistor starters to permit stopping and starting of these units while the line is running. Dynamic braking is needed on the reels to assist in stopping the full coil." Electrical control is highly centralized as can be seen in Fig. 75.



(Courtesy E. I. du Pont de Nemours & Co., Inc.)

FIGURE 75. Centralized electrical control characterizes the equipment at the Weirton Steel Company, Weirton, West Virginia, which, controlled by this one-man panel, electrotins 1,050 ft. of strip a minute.

Weirton Steel Co. Operational details of the tin line at the Weirton Steel Company at Weirton, West Virginia,[5] are given below:

"At normal operating speeds it takes, in the largest Weirton line, only 8 seconds to plate both sides of a specific section of strip. This is the time required for its passage through the 24 cells of the plating unit. All of these 24 cells are identical. They are trough-like in form, consisting of watertight boxes, 5½ feet in length along the direction of the production flow, 4 feet in width and 8 inches deep.

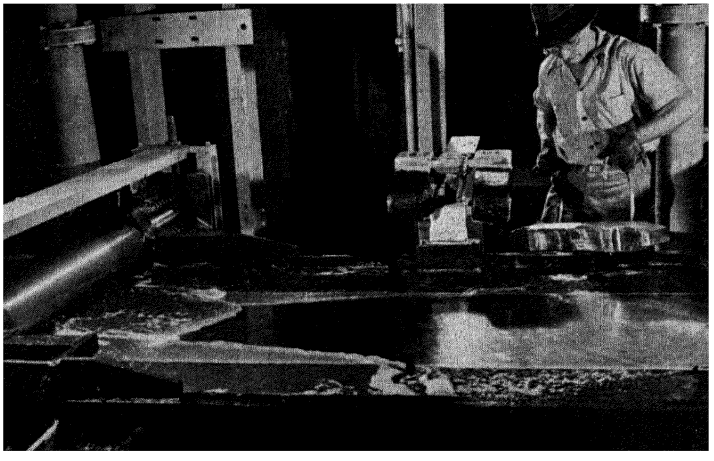
"The tin bath is operated at a pH of about 2.7 and the most effective temperatures have been found to lie between 100° F. and 160° F., with 150° F. regarded as

[5] *Metal Finishing*, **42**, No. 2, 77–9 (1944).

optimum. At the higher temperatures, of course, higher electrical conductivity is obtained. The current used in the process enters the cells by bus bars connected to 16 pure tin anodes, each 96 lb., resting on the floor of each cell."

Figure 76 shows the shape, size, and method of introduction of tin anodes into the cells.

"The strip makes contact with the circuit by means of rollers between which the strip enters and leaves each cell. Cells are kept filled from a reservoir containing 15,000 gallons of tin electrolyte. More than 30,000 pounds of tin anodes are



(Courtesy E. I. du Pont de Nemours & Co., Inc.)

FIGURE 76. Attendant introducing a new anode of pure tin while steel strip continues to travel through plating cell at the Weirton Steel Company, Weirton, West Virginia.

required to keep the cells operating. Anodes are replenished manually without halting the line.

"The low-voltage direct-current equipment is capable of delivering a total of 120,000 amperes to power each plating unit. Voltages of from 2 to 5 normally suffice for the operation.

"The thickness of the tin coat and the speed with which it is deposited depend on the speed of the movement of the strip through the plating bath and the current density.

"Operating at 1,505 ft. per min., one line deposits a half-pound of tin per base box and, by variation of line speed and current density, it has been found entirely possible to deposit as thin a coat as a quarter-pound per base box.

"Depositing a half-pound per base box on a continuous strip 32 inches wide requires a current density of 206 amp. per sq. ft. with the line running at 1,000 ft. per min. To deposit three-quarters of a pound of tin per base box, at a line speed of 1,000 ft. per min., requires a current density of 309 amp. per sq. ft. A current

density of 412 amp. per sq. ft. is required to deposit a pound of tin per base box at the 1,000-ft speed.

"In performing the half-pound operation, the total current required to be developed by the electrical installation serving this line is 72,000 amp. A total of 113,000 amp. is required to accomplish the three-quarter pound operation. To plate a pound of tin per base box at the rate of 800 ft per min. requires a total of 115,200 amp. for the entire battery of 24 plating cells

"In addition to the electroplating proper, equipment to perform other incidental functions is essential to the production of high-quality tin plate These include units for preprocessing strip prior to electroplating, a heater for bright-flowing the tin coating to impart the bright, shining finish familiar on food containers, and the motive units to propel the strip through the line.

"Tinning takes place in two passes of the strip through plating cells. First one side of the strip and then the other are coated The complete process is carried out in a three decked unit

"On the ground level the strip passes through 12 cells in one direction Rising vertically at the end of the first pass to the second level, the flow of the strip is reversed and the upper side of the strip becomes the underside in the second passage through 12 more cells

"The strip again rises vertically at the end of the second pass and, resuming the original direction of flow, travels through a slightly alkaline bath and then through a water bath and scrubbing process before it descends to the ground level again.

"Here the strip passes through a chemical treatment, and is then dried as it flows through a heating device From the heater the line drops into a second "pay-off" pit This provides slack to compensate for possible variations in the speed of the tinning process and the final bright-flowing treatment.

"The strip with its coat of matte tin ascends vertically 30 feet to the top of the high-frequency electric induction heater for this final treatment. Descending through the heater, the tin is heated until the tin flows, which imparts the bright mirror-like finish familiar on the surfaces of tin containers "

Figure 77 shows the tin-coated sheet steel being fed to the induction heater "reflow" unit at the Weirton Steel Company plant

"From the heater, the strip continues its downward course, passing next through a quenching bath and then through dryers where the moisture is removed by intense heat From the dryer the strip proceeds by one of two channels to one of two alternate coilers which receive the finished product. When a roll of strip on a coiler reaches about 5 feet in diameter, the line is cut and the roll is removed."

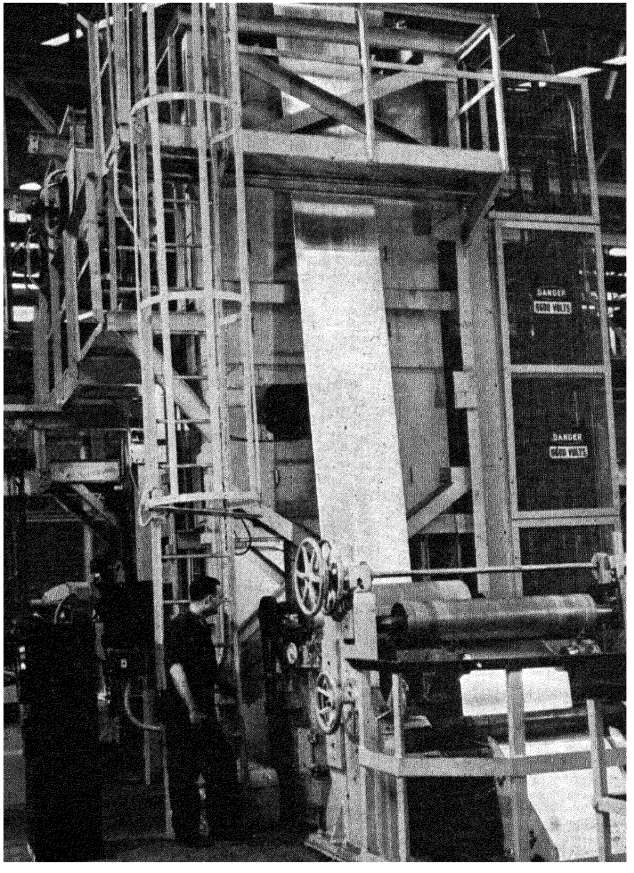
A finished roll of bright finished electroplated strip is shown at the takeup end of the Weirton line in Fig 78.

Electric Fusion

Stoltz, Hutcheson and Baker[6] discussed electric fusion of tin plate as follows:

[6] G. E. Stoltz, J. A. Hutcheson, and R. M. Baker, *Iron Steel Engr.*, 49–57 (Mar. 1943).

"Tin deposited on steel strip electrically is porous and of a crude matte structure. It is refined by heating it to its fusion temperature which also gives it a smooth bright surface. In this form it has improved corrosion-resisting properties.

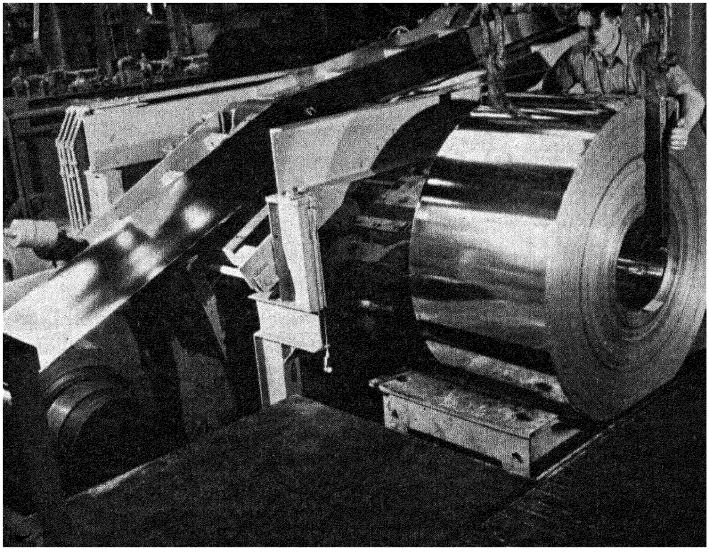


(Courtesy E. I. du Pont de Nemours & Co., Inc.)

FIGURE 77. Steel strip with tin coat in matte finish is shown rising to top of electrical induction heater through which it descends to take on bright, shining surface.

"In the first stages of this development, this process was accomplished by heating the tin plate in an oil bath or in a gas-fired radiant tube furnace. In each case the temperature of the body supplying the heat is materially above the fusion temperature of tin. The strip is passed through the brightening furnace at a constant speed selected to permit it to obtain a temperature slightly above the fusion point of the tin just before it leaves the furnace.

"While the oil and radiant tube furnaces have much to recommend them for early pioneer installations, they do have certain limitations for large high-speed



(Courtesy E. I. du Pont de Nemours & Co., Inc.)

FIGURE 78. Electrotinned steel strip in bright finish is shown being removed at end of the continuous production line at the Weirton Steel Company, Weirton, West Virginia.

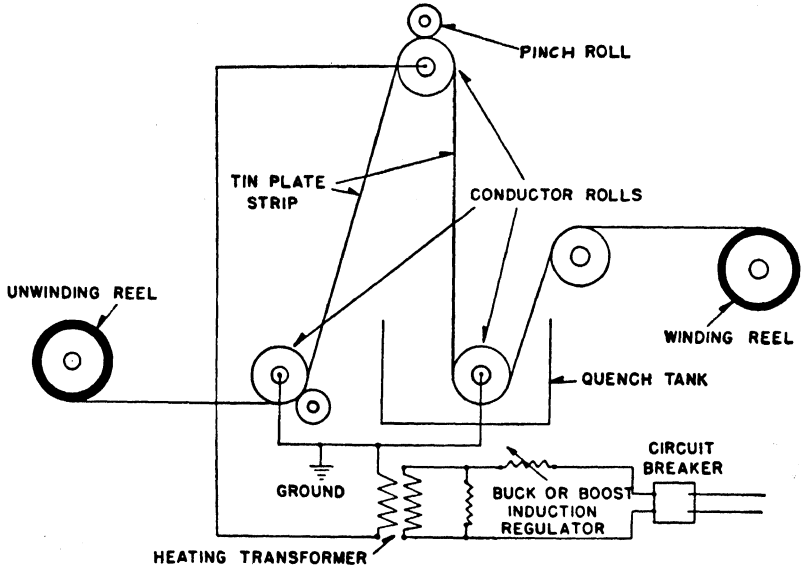


FIGURE 79. Schematic diagram showing one method of heating tin-plate strip by conduction.

lines. This is true where the fusion equipment is to be installed immediately after the electrolytic process, and where it is desired to vary the speed of the strip over a wide range between the normal travel and the slower speed used while one coil end is being welded to another.

"Two electrical methods, one termed conduction and the other induction, may be used as in either case the power input can be quickly and accurately adjusted as the thickness or the speed of the strip is changed

"The conduction method employs metallic rolls over which the strip passes Current is introduced to the strip from these metallic rolls to a value required to heat the tin just above the fusion temperature before the strip enters the quench tank.

"Power from a commercial frequency circuit can be used either three-phase or single-phase Various methods have been used, one of which is shown diagrammatically in Fig. 79. In this instance single-phase power is used having one terminal of the heating transformer connected to a top roll and the other terminal of the transformer connected to the two bottom rolls With this arrangement it is possible to ground a bus to which the two bottom rolls are connected so that ground potential is obtained on the metal as it enters and leaves the flowing equipment "

Application to Canning

Brighton[7] discussed electrolytic tin plate from the can maker's point of view. The application of electrolytic tin plate has required the cooperative efforts of the producers and the can manufacturers

The principal requirements of a material for the manufacture of containers are that it protect the product and that it be readily fabricated at high speeds. Tin plate combines the protective action of a thin film of tin with the mechanical strength of steel, and is a material which ideally meets these requirements. It can be soldered at high speeds and the cans produced are strong, light in weight, and economical The thin film of tin presents an attractive appearance and protects the steel against the corrosive action of the food.

The rust-resistance of tinned steel is adequate for use in cans under average processing and storage conditions Tin is normally cathodic to steel, and if the cans are exposed directly to the atmosphere rusting occurs fairly rapidly, as can be noted on any trash dump. As for internal corrosion, it is singularly fortunate that in the absence of air and in acid solutions a reversal of potential takes place and tin becomes anodic to steel.[8] Upon this reversal is based the satisfactory canning of acid fruits. If the reversal did not take place, and the effect of the tin was merely to cover the steel, rapid perforation could be expected, as hot-dipped tin plate contains pores or pinholes at which the steel base is exposed, particularly after die-forming.

[7] K. W. Brighton, *Trans. Electrochem Soc.*, **84**, 227–47 (1943).

[8] C. L. Mantell, and W. G. King, Jr., *Trans. Am. Electrochem. Soc.*, **52**, 435–44 (1927).

Factors such as enamel adhesion, the effect of chemical treatments, and the lubrication of the tin plate were all important in container performance. Soldering difficulties were met but overcome when silver-lead solders replaced the conventional 40 per cent tin—60 per cent lead material

The resistance of electrolytic plate to rusting is almost directly proportional to the weight of tin coating it bears. As might be expected, the 0 5 lb (0.75μ) electrolytic plate is considerably less rust-resistant than 1.25 lb. (1 9μ) hot-dipped plate. Cans made of electrolytic plate with tin coating weights lighter than 0 5 lb. show considerable rusting in storage, but at about 0 5 lb. the plate possesses enough rust resistance so that it will perform satisfactorily if subjected to favorable handling and storage conditions.

In studies on plain cans comparing melted electrolytic plate with the unmelted plates, either brushed or matte, it was found that without exception the melted plate had better corrosion resistance than the unmelted.

Brighton[9] concluded:

"It might be advisable to outline briefly the can maker's attitude toward the place of electrolytic plate in the post-war period. After the war it is expected that 0.5-lb. electrolytic and cheaper plates will find considerable application in containers for nonprocessed products such as coffee, biscuits, shortenings, etc. Whether or not electrolytic plate is used for processed cans probably depends upon the weight of electrolytic tin coatings which will be required to give a service life equal to that obtained with standard hot-dipped plate, and also whether or not such a coating can be applied more economically by electrodeposition or hot dipping. At present, cans made of 0 5 lb. electrolytic plate must be inside- and outside-enameled to provide performance approximating that obtained with hot-dipped plate, and double-enameled electrolytic plate costs more than plain hot-dipped plate. If the corrosion resistance of electrolytic plate is not improved to the point where enameling is unnecessary, the return to hot-dipped tin plate for processed food cans after the war is indicated."

Hot-dip coatings are specifically discussed in Chapter 14.

[9] K. W. Brighton, *Loc cit*

Chapter 11

Constitutional Thermal Equilibrium Diagrams—Binary Alloys

In this section the constitutional thermal equilibrium diagrams of the binary systems of tin and its alloys are given.

Tin-Aluminum

Tin and aluminum alloy readily Small amounts of either metal have large effects on the properties of the other Tin increases the tensile strength of aluminum when alloyed with it and decreases piping in castings With too much tin, the alloys are brittle and easily oxidizable Heyn and Wetzel[1] found that the length of a sample of tin with 0.5 per cent aluminum decreased for 28 days after quenching, and then increased, but at a slower rate, for the next 150 days

Tin added to aluminum gives sharp castings The high-tin alloys have been studied by Losana and Carozzi [2] Up to 5 per cent tin, the alloys can be cold-rolled, but hot-rolling is not successful above 200° C.

Figure 80, based on the work of Gwyer,[3] gives the thermal diagram of the tin-aluminum system. The curves show simple liquid solubility without compound formation. Electrical conductivity studies do not show the existence of compounds.

Alloys with 15 to 50 per cent aluminum are attacked by water at ordinary temperatures, with the evolution of hydrogen

Tin in amounts below 2 per cent is used by some foundrymen in various casting alloys, such as those with copper, sometimes in an attempt to avoid cracked castings, sometimes to add ductility, or to give a white-looking alloy. Small amounts of tin introduced unintentionally through the use of scrap would ordinarily not be considered a very detrimental impurity

Mortimer[4] stated that in England a 7 per cent copper-aluminum alloy may still contain up to 1 per cent tin The tin content was specified at one time.

[1] E. Heyn, and E Wetzel, *Mitt. Kaiser-Wilhelm Inst Metallforsch.*, **1**, 19 (1922).
[2] Losana, and Carozzi, *Gazz chim ital.*, **53**, 546 (1923)
[3] A. G. C. Gwyer, *Z. anorg. Chem.*, **49**, 311 (1906).
[4] G. Mortimer, *Proc. Am. Soc. Testing Materials* (2), **22**, 335 (1926).

Tin-Antimony

The tin-antimony alloys are of great commercial importance, appearing in type metals, Britannia metal, and Babbitt for lining bearings. Another element, such as lead, is generally added. The tin in such materials is capable of infinite variation. The antimony seems to be confined in commercial alloys to a maximum of about 25 per cent, inasmuch as larger quantities confer increased brittleness.

Molten tin dissolves antimony, and the two elements unite without the evolution of light and heat. The alloys can be made by fusing antimony sulfide with tin, although the usual manner is by mixing the molten metals

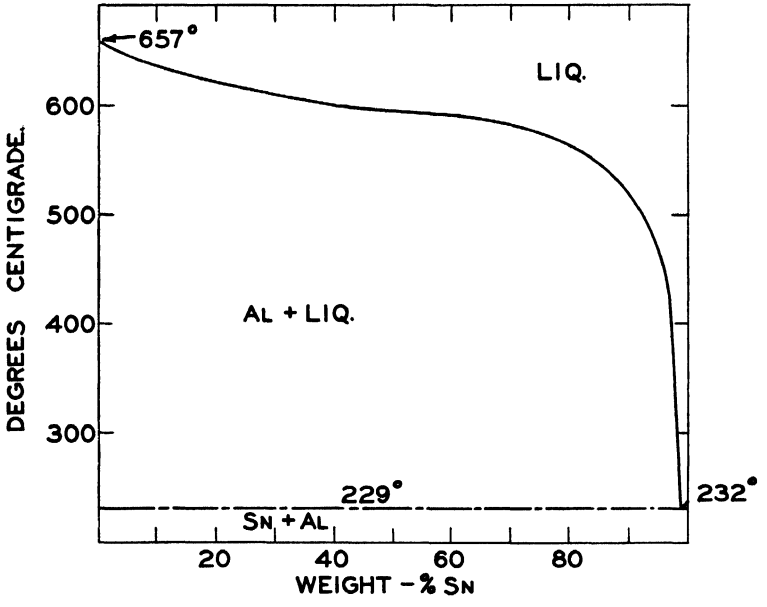


FIGURE 80 Diagram of tin-aluminum system

An alloy of 12 5 per cent antimony is stated to have a fine musical tone. Up to 10 per cent antimony, the alloys are quite ductile, but at 25 per cent antimony the ductility is less than tin, at 50 per cent antimony the alloys are brittle and can be readily powdered If small amounts of lead are present, the brittle alloys are more ductile

Leyman[5] found that the alloys of tin and antimony are hardened by slight or moderate cold-rolling but are softened by further rolling, sometimes be-

[5] R E Leyman, *Intern Tin Research Development Council, Tech Pub* , **A**, No. 53 (1937)

coming softer than in the cast state. The softening on severe working was more pronounced in specimens which contained higher proportions of alloying elements. Annealing after rolling produced further softening, while quenching and aging treatments did not markedly affect the physical properties.

Aoki[6] found that the hardness is not constant for different loads, and that the hardness of alloys rich in gamma and delta phase increased with the load to a maximum and then decreased gradually. Those rich in alpha or beta phase increased until the samples broke. The time of loading, aging at room temperature, and annealing affect the hardness, the effects depending upon the structure of the phase.

Hanson and Pell-Walpole[7] found that the hardness and tensile strength did not improve by using more than 9 per cent in a tin-antimony alloy. At this composition the appearance of primary SnSb is noted. Alloys containing 4.5 or 7 per cent antimony could be permanently hardened by 10 to 30 per cent reduction, but an alloy containing 14 per cent could not, even by small amounts of reduction. Severe cold-working produced a distinct softening, while annealing at 225° C. restored the hardness to the chill-cast value. The investigators suggested that grain size may be an important factor in work-softening and in subsequent recovery by annealing, and may have a marked effect on the tensile strength and strain-hardening properties of these alloys Quenching from 225° C. produced a slight improvement in alloys containing more than 10 per cent antimony, but had no effect on alloys of lower antimony content. Tempering at 100° C. after quenching from 215 to 240° C. caused softening in alloys containing more than 12 per cent antimony, but produced temper-hardening in alloys containing 7 to 10 per cent antimony, the maximum effect being obtained with 9 per cent antimony.

The tin-antimony alloys form the base of Britannia metal, which is mainly tin hardened with antimony in quantities of 6 0 to 9.2 per cent antimony. Algiers metal has 10 to 25 per cent antimony. An antimony content of 33 per cent ordinarily marks the extreme limit when the alloy is very hard. Numerous modifications, alloyed with zinc, bismuth, lead, and copper, appear in commerce.

The tin-antimony system has been constitutionally examined by different experimenters so that the liquidus and solidus curves are fixed with fair accuracy. Little experimental attention has been given to the transformations in the solid state. The system is given in Fig. 81. Most of the solid solubility lines are from the hypotheses of Guertler.[8]

[6] N. Aoki, *Kinzoku no Kenkyuh*, **11**, 1–20 (1934).
[7] D. Hanson, and W. T. Pell-Walpole, *J. Inst. Metals*, **63**, 87–108 (1938).
[8] W. Guertler, "Metallographie," p. 802, Berlin, 1912.

The system has been re-examined by Broniewski and Sliwowski[9] and very closely by Iwasé, Aoki, and Ôsawa.[10]

The liquidus curve, *EDCBA*, irregularly descends from the melting point of pure antimony at 630° C. to the melting point of pure tin at 232° C Four solid solutions form the primary constituents which freeze out The alpha-solid solution exists in equilibrium with liquid between the compositions of 0 and 50 per cent tin (100 and 50 per cent antimony), the beta between 50 and 79 per cent tin (50 and 21 per cent antimony), the gamma only over a small area, and the delta between 91 and 100 per cent tin (9 and 0 per cent antimony).

The solidus curve *ELKJHGFA* is complex, owing to three transformation reactions at *K*, *H*, and *F*. These are responsible for the temperature

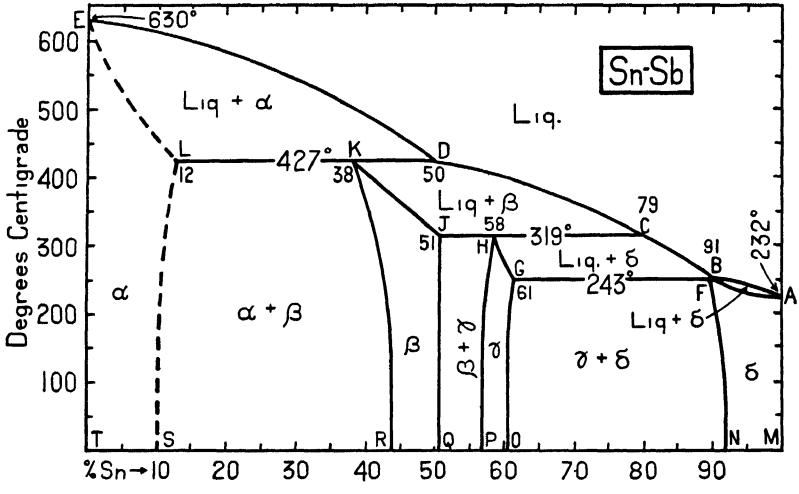


FIGURE 81 Diagram of tin-antimony system

horizontals at 427°, 319°, and 243° C. The completely solid alloys consist of either a single solid solution or a mixture of two solid solutions. The solid solubility curves in each case show that solubilities decrease with decrease in temperature.

An explanation of one of the reactions will serve for all three shown in the diagram. For example, alloys between the compositions of 12 and 38 per cent tin (88 and 62 per cent antimony) form a mixture of solid solutions beta plus alpha on freezing at 427° C. There are three phases in equilibrium at the invariant point *K*. The liquid metal, however, has an excess of tin over that indicated by *K*. The liquidus therefore continues

[9] W. Broniewski, and L. Sliwowski, *Rev. Metallurg.*, **25**, 312 (1931).

[10] K. Iwasé, N. Aoki, and A. Ôsawa, *Science Repts. Tôhoku Imp. Univ.*, **20**, No. 3, 353 (1931).

to slope from *D* to *C*. The alpha-solid solution, previously in equilibrium with the liquid metal, changes to the beta-solid solution This is also in equilibrium with liquid metal in the composition range of 38 to 50 per cent tin (62 to 50 per cent antimony) and at 427° C.

At 51 per cent tin, 49 per cent antimony, it is believed the SnSb compound exists It shows well-formed cubic crystals Stead[11] stated that alloys with 7 5 per cent antimony contain some of these crystals, and that they are particularly well formed in alloys with 25 to 40 per cent antimony Alloys of over 40 per cent antimony contain tabular crystals These crystals of SnSb may be considered responsible for the characteristic cubic structure observed in the gamma-solid solution

Iwasé, Aoki, and Ôsawa[12] investigated the tin-antimony system with reference to the nature of the change occurring in alloys containing 30 to 70 per cent antimony at a temperature of about 320° C. They found that the allotropic transformation of the beta-solid solution, the crystal lattice of which had been determined as simple cubic, is responsible.

Hanson and Pell-Walpole[13] found that the solubility of antimony in tin decreased from 10.5 per cent at 246° C to 3.5 per cent at 100° C. They confirmed the findings of Iwasé, Aoki, and Ôsawa in reference to the liquidus and solidus of the tin-rich phase and the temperature of the peritectic reaction.

Hanson and Sandford[14] found that antimony improved the creep properties of tin, and the alloy containing 8 5 per cent antimony withstands a stress three times that of pure tin for an equal duration. Hanson and Sandford stated that in many cases there is no relationship between resistance to creep and ultimate tensile strength.

Pushin[15] showed that there is an abrupt point on the e m f. composition curve corresponding to SnSb

Gautier[16] and Matthiessen[17] showed that the specific gravity of the tin-antimony alloys is less than that calculated from the specific gravities of the components. They therefore show expansion when alloyed

The thermoelectric powers of the tin-antimony alloys (tin metal and tin-antimony couples) were studied by Rollmann,[18] Naccari and Bellate,[19]

[11] J. E Stead, *J Soc Chem Ind*, **16**, 204, 506 (1897); **16**, 1111 (1898); *J. Inst Metals*, **22**, 127 (1919)

[12] K. Iwasé, N. Aoki, and A Ôsawa, *Loc cit.*

[13] D Hanson, and W T Pell-Walpole, *J Inst Metals*, **58**, 299–310 (1936)

[14] D Hanson, and E. J. Sandford, *J. Inst Metals*, **59**, 159 (1936)

[15] N. A Pushin, *J Russ. Phys Chem Soc*, **39**, 528–656 (1907)

[16] Gautier, *Bull soc enc nat ind* (5), **1**, 1316 (1896)

[17] Matthiessen, *Pogg Ann.* **103**, 412, 428 (1858); **110**, 21, 190 (1860), **130**, 50 (1867); *J. Chem. Soc.*, **20**, 201 (1867); *B. A. Rep.*, 37 (1863).

[18] Rollmann, *Pogg. Ann.*, **83**, 77 (1851), **84**, 275 (1851); **89**, 90 (1853).

[19] Naccari, and Bellate, *Ellectricista*, **1**, 329, 362 (1877).

as well as by Battelli[20] and Hutchins.[21] The curve of the thermoelectric power is given in Fig. 82. A definite break in the curve, corresponding to the compound SnSb on an atomic percentage basis, is found. A similar break is shown in the curve of electrical conductivities (Fig. 83), which had been investigated by Elsasser[22] and Konstantinoff and Smirnoff,[23] from whose results at 25° C the curve has been plotted The values for the magnetic susceptibilities of the tin-antimony alloys, as determined by Leroux,[24] have been used for the curve shown in Fig 84 The alloy of approximately 5 to 9 per cent tin and 90 to 95 per cent antimony shows greater magnetic susceptibility than all the other alloys or pure antimony or tin

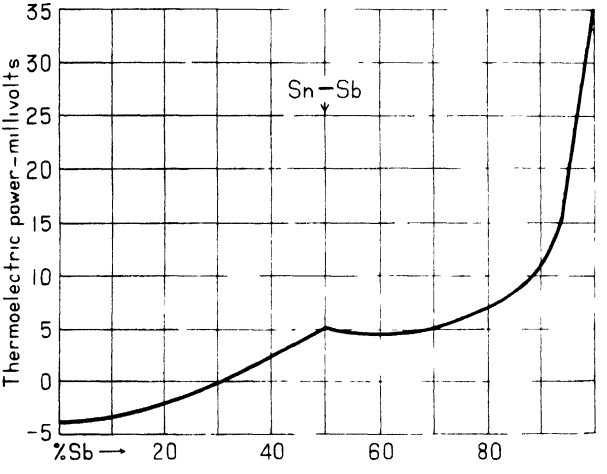


FIGURE 82 Thermoelectric powers of the tin-antimony alloys

X-ray studies on the tin-antimony system were made by Hagg and Hybinette[25] They found that at room temperature the SnSb phase had a homogeneity range between 45 and 55 atoms per cent antimony, and at the tin-rich limit it had a deformed sodium chloride structure with rhombohedral unit cell, where r = 6 117 Å units, α = 89 70° C and the volume was 228.9 cu Å units Hagg and Hybinette found that the deformation increased with an increasing antimony content At the antimony-rich limit, r = 6 183 Å units, α = 89 18° C and the volume was 231 2 cu Å

[20] Battelli, *Mem accad torino* (2), **36**, 487 (1885), *Phil Trans* , **148**, 369, 383 (1858), **150**, 161, 171, 177 (1860), **156**, 861 (1866)

[21] Hutchins, *Am J Sci* (3), **48**, 226 (1894)

[22] Elsasser, *Wied Ann* , **8**, 455 (1879)

[23] Konstantinoff, and Smirnoff, *Internat Z Metallog* , **2**, 154 (1912), *J Russ Phys Chem. Soc* , **43**, 1201 (1911)

[24] M P Leroux, *Compt rend* , **156**, 1764 (1913).

[25] G Hägg and A G Hybinette *Phil Mag*., **20**, 913–29 (1935).

units. They attributed the change to greater proportion of antimony atoms which are larger than tin atoms

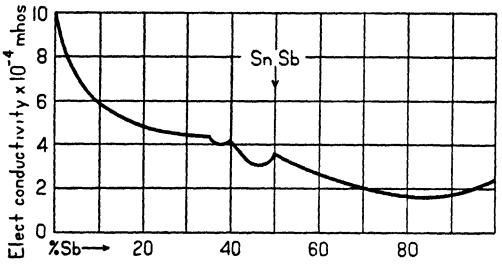


FIGURE 83
Electrical conductivities of the tin-antimony alloys

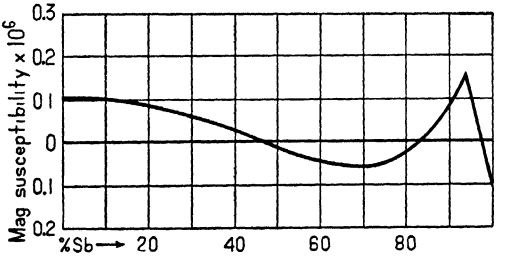


FIGURE 84.
Magnetic susceptibilities of the tin-antimony alloys.

Tin-Arsenic

When powdered arsenic is stirred into molten tin, the union of the two elements is attended by the evolution of heat and light.

Arsenic is appreciably soluble in tin but has little depressing effect on the tin melting point, tin, however, markedly affects the vapor pressure and melting point of arsenic In this system, pressure, usually considered as invariant in metal alloy systems, is a factor and variable.

Hagg and Hybinette[26] found that arsenic is not soluble in tin, at a concentration of 40 atoms per cent arsenic, lines attributed to Sn_3As_2 were found. They reported that the Laue symmetry of this phase is D_{3d}, with a rhombohedral cell containing 7 atoms per cent, where r = 12.23 Å units and α = 19.22°. Tin-antimony has a sodium chloride structure with a lattice constant of 5.716 Å., which does not change with composition. Hägg and Hybinette also stated that arsenic can dissolve 21 atoms per cent of tin, and with increasing tin concentration, the rhombohedral edge of the arsenic phase increases and the rhombohedral angle decreases. These results disagree with those of Bowen and Jones[27] and Willott and Evans.[28]

[26] *Ibid.*
[27] E. G. Bowen, and W. M. Jones, *Phil. Mag.*, **12**, 441–62 (1931).
[28] W. H. Willott, and E. J. Evans, *Phil. Mag.*, **18**, 114–28 (1934).

The fusion equilibrium curves are quite complicated, a condition caused by arsenic vapor being one of the components at higher temperatures owing to the high vapor pressure and subliming of arsenic.

The tin-arsenic alloys are brittle They are of commercial interest in ternary systems The fusion equilibrium diagram is given in Fig. 85.

Mansuri[29] stated that while the two metals alloy in all proportions, they form but two compounds, Sn_3As_2 and SnAs, as indicated by two distinct maxima in the thermal equilibrium curve, by chemical analysis, and by photomicrographs The melting point of arsenic lies between 800° and 850°, but molten arsenic can be supercooled considerably. At

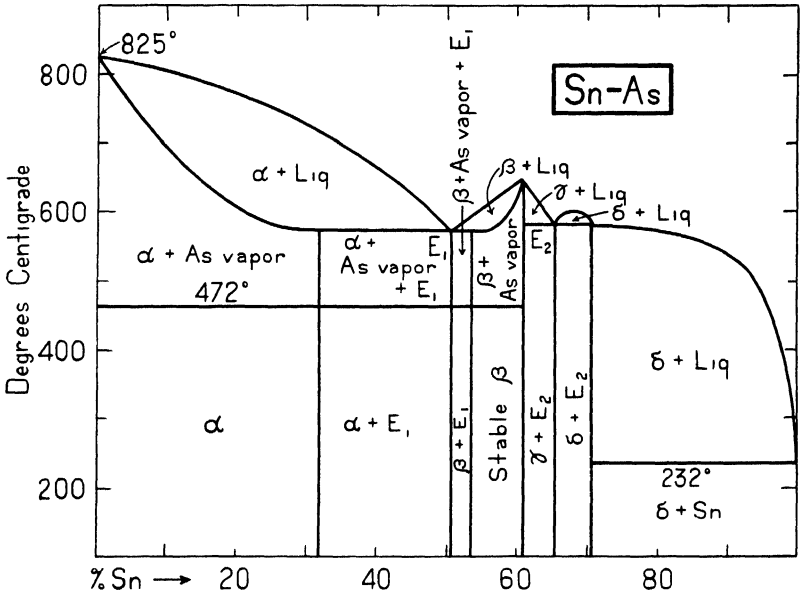


FIGURE 85. Provisional diagram of tin-arsenic system

the concentration of 29.5 per cent arsenic (70 5 per cent tin), the alloy freezes at a single temperature and is the compound delta itself. The rest of the system up to an alloy containing about 39 per cent arsenic (61 per cent tin) is of the usual eutectiferous type. At that composition the compound SnAs is formed This compound yields a partly eutectiferous system with arsenic, forming solid solutions, beta and alpha, at both ends respectively It is these solid solutions that have arsenic vapor present as one of their constituents All alloys containing these solid solutions give a thermal arrest at 472°. Alloys of tin with arsenic are very similar to those of tin with phosphorus in most of their properties and in

[29] Q. A. Mansuri, *J. Chem. Soc*, **123**, 214–23 (1923).

their crystal structure. The thermal curve of the tin-arsenic system is very similar to that of the tin-phosphorus system.

The tin-arsenic alloys are quite hard, arsenic even in small amounts increasing the hardness of tin metal. The alloys are white, sonorous if the arsenic be in not too great an excess They are usually brittle with appreciable arsenic content, as well as being decidedly crystalline, of a lamellar texture. When fused in an open pot or kettle, arsenic is volatilized, the alloy concentrating in tin content When treated with hydrochloric acid, arsine (AsH_3) is evolved, but alloys with an excess of arsenic are not attacked by the acid.

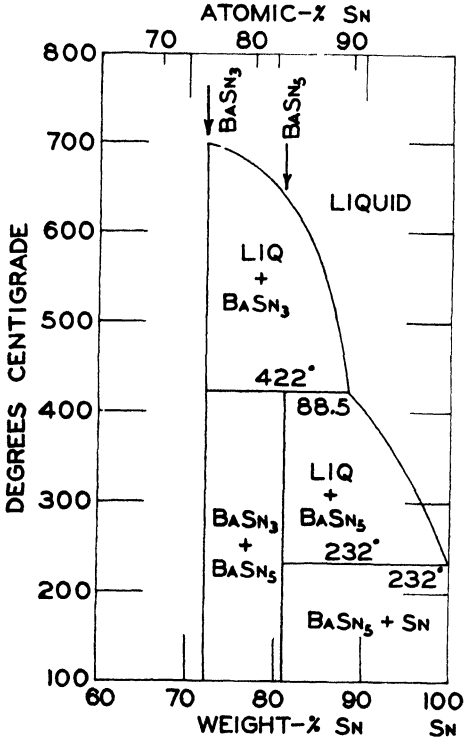


FIGURE 86
Diagram of tin-barium system

Tin-Barium

The alloys of tin and barium are difficult to make, even with protective layers of fluxes, as a result of the rapid oxidation of the barium metal under atmospheric influences. With appreciable percentages of barium they are decomposed by water, leaving a tin skeleton.

The equilibrium diagram for the tin-barium system as shown in Fig. 86 was drawn by Ray and Thompson[30] for alloys containing 70 to 100 per

[30] W. K. Ray, and R. G. Thompson, *Metals and Alloys*, **1**, 314–6 (1930).

cent tin. It indicates the existence of the compounds $BaSn_3$ at 72.16 per cent tin, and $BaSn_5$ at 81.21 per cent tin by the salts at 422° C. and 232° C. and by observation of the structure of the alloys annealed for 12 hours in a closed glass tube at 400° C. The alloys which had not been annealed and which contained 76 to 83.5 per cent tin after quick cooling of the melt consisted of three phases: $BaSn_3$, $BaSn_5$, and Sn. Ray and Thompson attributed this to the incomplete peritectic transformation at 422° C. The compound $BaSn_3$ seems to be formed not only directly from the melt but also by a peritectic reaction of a compound richer in barium with the melt, if observed from the solidification point of the 70 per cent alloy.

Tin-Bismuth

Binary alloys of tin and bismuth are seldom used industrially. They are of considerable importance, however, in connection with fusible alloys, which contain either lead or cadmium or both in addition

The system has often been investigated, and still certain sections have not as yet been definitely established The thermal equilibrium diagram based largely on the work of Kapp,[31] as shown in Fig 87, is essentially of the simple eutectiferous type. Two branches of the liquidus curve, *CB* and *AB*, meet at a eutectic containing 57 per cent tin, melting at 135° C.

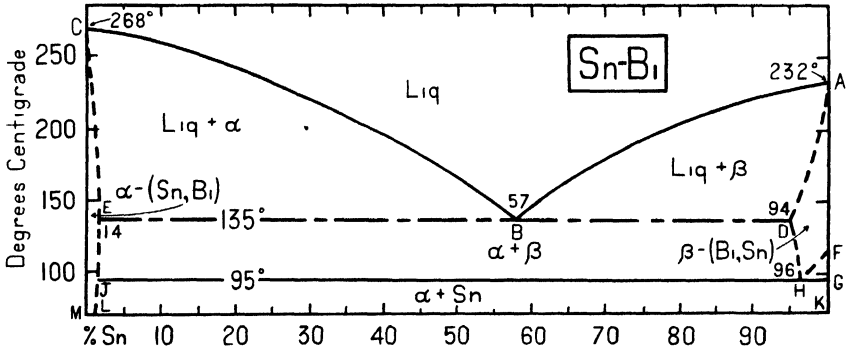


FIGURE 87 Diagram of tin-bismuth system

From 0 to 57 per cent tin, the primary constituent is the alpha-solid solution of tin in bismuth. From 57 to 100 per cent tin, the primary constituent is the beta solution of bismuth in tin. Bismuth-tin compounds are not formed.

The solidus line passes through the points *CEBDA*. Immediately after solidification, alloys between 0 and 1.4 per cent tin, 100 to 98.6

[31] A. W. Kapp, Dissertation, Konigsberg, 1901; *Ann. Physik*, **6** (iv), 754 (1901).

per cent bismuth, consist of the single alpha phase. Those between 1.4 and 94 per cent tin, 98.6 and 6 per cent bismuth, consist of a mixture of alpha- plus beta-solid solutions. Those running 94 to 100 per cent tin, 6 and 0 per cent bismuth, consist, immediately after solidification, of the single beta phase. The exact form of the *CE* and *AD* sections of the solidus curve has not as yet been completely and definitely determined.

Tin is less able to keep bismuth in solution below the eutectic temperature. Eutectoid inversion takes place at 95° C. The dotted lines *FH* and *DH* give the approximate limits of solid solubility. This transformation can be detected by sensitive cooling curve methods (in alloys covering a wide range), as shown by the transformation horizontal *JHG*. Below 95° C., alloys from 2 to 100 per cent tin are duplex in structure. They contain pure tin and alpha- (tin in bismuth) solid solution.

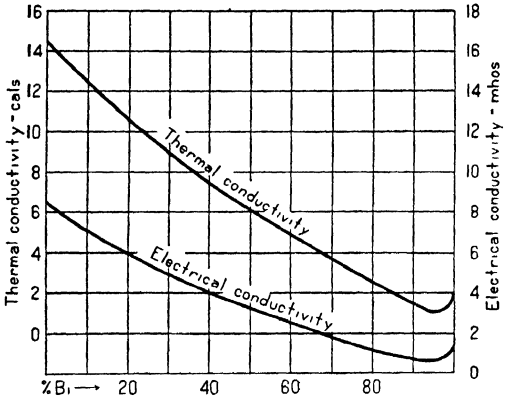


FIGURE 88
Thermal and electrical conductivities of the tin-bismuth alloys

The line *EJL* approximately indicates the solubility limit of the alpha solution. This section of the diagram has been very little investigated

The results of Schultze[32] for the thermal and electrical conductivities of the tin-bismuth alloys are plotted in Fig. 88. The addition of bismuth to tin markedly lowers both the thermal and electrical conductivities of the metal. There are no maximum points in the curve. The addition of small amounts of tin to bismuth lowers its thermal and electrical conductivities, but increasing amounts of tin cause better thermal and electrical conductivity. Caswell[33] stated that there is a remarkable increase in the Thomson effect when very small amounts of tin are added to bismuth; *e.g.*, the value is 58 millivolts per degree C. for pure bismuth, and 676 millivolts for 1 per cent tin alloy. Beyond about 2 per cent, the value of the Thomson effect decreases.

[32] Schultze, *Ann. Physik* (4), **9**, 555 (1902), "Ueber das Verhalten einiger Legierungen zum Gesetz von Wiedemann und Franz," Dissertation, Marburg, 1902.

[33] A. E. Caswell, *Phys. Rev.*, **12**, 231 (1918).

A large number of workers, among them being Ettinghausen and Nernst,[34] studied the thermoelectric properties of tin-bismuth alloys. The results are plotted in Fig. 89. Alloys of approximately 9 per cent tin content show the highest e.m.f values, while those of about 5 per cent tin show the greatest Thomson effect. No compounds seem to be indicated in either the conductivity or thermoelectric curves of the tin-bismuth alloys. The results of Gnesotto and Binghinotto[35] for the magnetic sus-

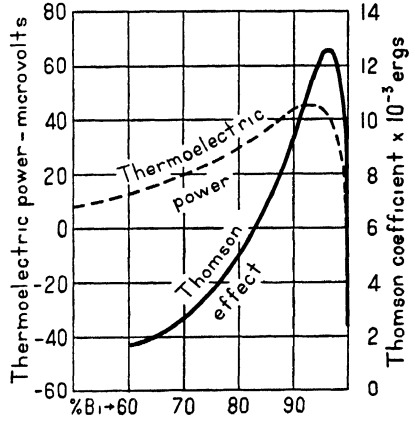


FIGURE 89.
Thermoelectric values for tin-bismuth alloys.

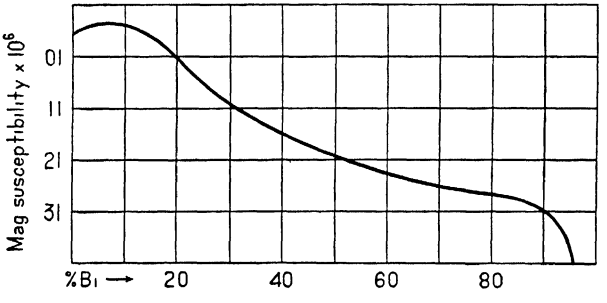


FIGURE 90. Magnetic susceptibilities of the tin-bismuth alloys.

ceptibilities of the alloys are of scientific interest only. The curve, given in Fig. 90, is without sharp maxima or minima.

The solubility of bismuth in tin has been determined by Jette and Foote.[36]

Thompson[37] found that the electrical resistance of single crystals of

[34] Ettinghausen, and Nernst, *Wied. Ann* , **33**, 474 (1888).
[35] Gnesotto, and Binghinotto, *Atti ist. Veneto* (8), **12**, 1382 (1910).
[36] E. R. Jette, and F. Foote, *Phys. Rev.*, **39**, 1018 (1932).
[37] N. Thompson, *Proc. Roy. Soc.* (*London*), **A155**, 111–23 (1936).

bismuth containing small amounts of tin, at temperatures ranging from 14 to 400° K, showed a marked negative temperature coefficient or resistance parallel to the axis and the same effect to a lesser extent perpendicular to the axis

The effect of zinc, indium, antimony, and gallium as impurities is the same as that of lead and tin

Satō and Matuhasi[38] found that the solubility of bismuth in tin was 12 per cent at 120° C, 6 per cent at 80° C, and 4 to 5 per cent at room temperature. Their conclusions, upon x-ray analysis, deny the existence of any intermetallic compound in the tin-bismuth system They stated that the discontinuities appearing at about 95° C. on the curves of electrical resistance and dilatation result from the abrupt change in solubility of bismuth in the tin-solid solution and not to the formation of any compound

Danilov and Radchenko[39] studied the diffraction of x-rays by liquid eutectic alloys of tin-bismuth, tin-lead, tin-zinc, and others, and they reported that the patterns from tin-lead and tin-bismuth resemble those of lead and bismuth respectively. They concluded that in the liquid tin-bismuth eutectic there are regions similar in structure to pure bismuth.

Samson-Himmelstjerna[40] determined the heat contents of tin-bismuth alloys at 500° C. Kawakami[41] made the same determinations at a temperature of 350° C. The maximum heat of alloying calculated from these figures is given below:

HEAT OF FORMATION
(in calories per gram atom)

INVESTIGATORS	TEMPERATURE (° C)	HEAT OF FORMATION
Samson-Himmelstjerna	500	+530
Kawakami	350	+160
Magnus and Mannheimer[42]	Not recorded	+200

Seltz and Dunkerley[43] studied a cell of the type $Sn(l)/SnCl_2(l)/SnBi(l)$ and calculated that the beta-solid solution at the eutectic contained 20 per cent bismuth, whereas the alpha solution contained 2 4 per cent tin. The liquidus points obtained by Seltz and Dunkerley are in good agreement with those obtained by Wurschmidt.[44]

[38] T Satō, and T Matuhasi, *Nippon Kinzoku Gakkai-Si*, **2**, 592–7 (1938)

[39] V Danilov, and I Radchenko, *Physik Z Sowjetunion*, **10**, 261 (1936) (in German)

[40] H O v Samson-Himmelstjerna, *Z. Metallkunde*, **28**, 197–202 (1936)

[41] M Kawakami, *Z. anorg. allgem. Chem.*, **167**, 345–63 (1927)

[42] A Magnus, and M. Mannheimer, *Z. physik. Chem*, **121**, 267–88 (1926)

[43] H Seltz, and F. J. Dunkerley, *J. Am. Chem Soc*, **64**, 1392–5 (1942)

[44] J. Würschmidt, *Z Physik*, **5**, 39–53 (1921)

Bochvar and Zhadaeva[45] studied the tin-bismuth system and observed similar structures on rapid and on slow cooling of the alloy. Slow cooling made the structures more clearly defined and two primary phases were observed simultaneously in both the rapidly and slowly cooling alloys. The minimum total number of primary crystals of both types was observed in the pure eutectic alloy, on both sides of which the number of primary crystals increased sharply at least in one of the phases. Bochvar and Zhadaeva stated that pure eutectic alloys can be regarded as those in which the probability of the formation of primary crystals is the same in both phases In the pre-eutectic alloys, the possibility of the formation of one phase is greater, in the post-eutectic alloys, that of the other The centers of the primary crystallization of both phases are present in both kinds of alloys. The crystallization of one of the primary phases can result in a sharp increase in the possibility of the formation of primary crystals of the second phase. This is connected with the minimum possibility of the formation of primary crystals in pure eutectic alloys. They concluded that pure eutectic alloys possess a minimum capacity for spontaneous crystallization and a maximum tendency for supercooling.

de Haas, van Aubel, and Voogd[46] found that in the eutectic mixture of tin-bismuth the temperature at which superconductivity begins is influenced by the nonsuperconducting admixtures

Hanson and Sandford[47] found that the tin-bismuth alloys are more resistant to flow than pure tin at stresses above 300 lb. per sq. in., but at lower stresses they are inferior to pure tin.

Tin-Cadmium

Cadmium may be alloyed in small quantities with tin as a means of improving the pure metal for certain uses Bucher[48] stated that tin and cadmium are mutually soluble in each other in the solid state to the extent of about 3 per cent.

The thermal diagram is given in Fig. 91. It is of the same type as that of the tin-bismuth alloys. Tin and cadmium form a eutectic at 72 per cent tin, 28 per cent cadmium, with a melting point of 177° C. The primary constituent between 0 and 28 per cent cadmium is the gamma-solid solution of cadmium in tin, and from 28 to 100 per cent cadmium, the first phase to crystallize is the delta-solid solution of tin in cadmium. No definite compounds are formed between the two metals.

[45] A A Bochvar, and O S Zhadaeva, *Bull. acad sci U R.S S Classe sci tech.*, 293–304 (1944).

[46] W. J. de Haas, Edm van Aubel, and J Voogd, *Proc Acad Sci Amsterdam*, **32**, 715–23 (1929).

[47] D Hanson, and E. J. Sandford, *J Inst. Metals*, **59**, 159 (1936)

[48] A. Bucher, *Z. anorg. Chem.*, **98**, 106 (1916).

The solidus line is *ADBEC* All alloys between 9 and 97 per cent cadmium (91 to 3 per cent tin) complete their solidification at 177° C., the eutectic temperature

The solid solution gamma (cadmium in tin) shows a rapidly decreasing power of holding cadmium in solution as the temperature decreases. There is a eutectoid inversion at 127° C which produces beta-solid solution of cadmium in tin. The line *GHJ* is the limit of the structural transformation. This has been observed over a wide range Alloys between 9 and 97 per cent cadmium consist of the gamma- plus delta-solid solutions in the temperature range of 177° to 127° C.

The beta-solid solution shows a gradually diminishing power of holding cadmium in solid solution, becoming practically zero at 18° C. The line *GKM* shows the reduced solubility of the cadmium in the tin. On

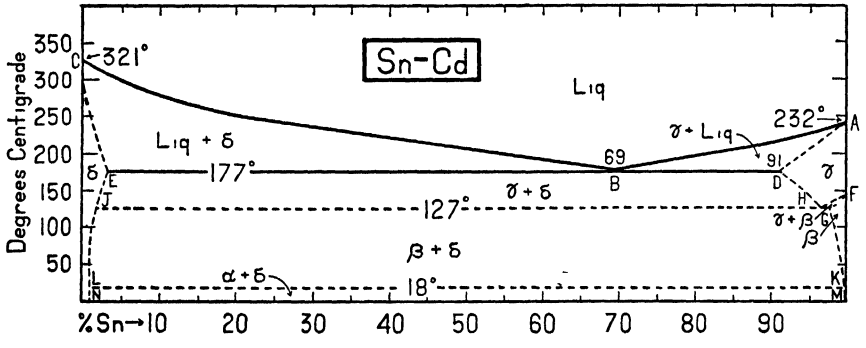


FIGURE 91 Diagram of tin-cadmium system.

the other side of the diagram, correspondingly the line *EJLN* shows the lessening of the solubility of tin in cadmium with fall in temperature

The allotropy of tin which is responsible for the polymorphic modification of gamma- to beta-solid solutions is again responsible for another transformation at 18° C. to the alpha form, which corresponds to the change of white to gray tin.

Stockdale[49] studied the tin-cadmium system and his conclusions based on experimental data are: first, the solute and solvent atoms are present in a simple integral ratio in a saturated solid solution at the temperature of the eutectic or peritectic horizontal, secondly, in a eutectic mixture, the elements are present in a simple integral atomic ratio, and thirdly, in a eutectic mixture the ratio of the number of atoms irrespective of their kind in the phases is simple.

Hanson and Sandford[50] made creep tests of long duration on tin and some

[49] D. Stockdale, *Proc. Roy. Soc.* (*London*), **A152**, 81–104 (1935).
[50] D. Hanson, and E. J. Sandford, *J. Inst. Metals*, **59**, 159 (1936).

of its alloys in the rolled condition. They reported that tin-cadmium alloys are greatly improved by heat-treatment and offer considerable resistance to creep. The system has been studied by Le Blanc, Naumann and Tschesno[51] as well as Matsuyama.[52]

Hanson and Pell-Walpole[53] proposed revisions of the tin-cadmium constitution diagram, as did Homer and Plummer.[54]

It is interesting to note that an alloy of two parts tin, one part cadmium, cut into chips on a milling machine, about 0 05 mm. thick, 12 mm long, 1 to 3 mm wide, and closely packed, without jamming, into a tube 1 cm in diameter, 50 cm. long, was found by Welo[55] to be an effective bar to the passage of mercury vapor from a mercury high-vacuum pump to the vessel to be exhausted. This was shown by means of spectrograms taken after allowing the pump to stand connected to the exhausted vessel through the tube containing the alloy.

Tin-Calcium

There has been considerable study of the tin-calcium alloys. Moissan[56] stated that when tin is heated to temperatures above its boiling point it unites with calcium to form a crystalline alloy. Donsky[57] found that tin dissolved calcium at 650° C

The thermal equilibrium diagram of the system is given in Fig. 92 The addition of calcium to tin produces a sharp rise in the freezing point The liquidus curve rises from the melting point of pure tin (232° C. to a maximum of 627° C , corresponding to the compound $CaSn_3$ corresponding to 10 1 per cent by weight of calcium. From here the liquidus falls slightly to a eutectic point (between $CaSn_3$ and CaSn) at 609° C This corresponds to 31 2 atomic per cent calcium. The horizontal line at 609° C is part of the solidus line of the system. From the eutectic, the liquidus curve rises to 987° C , the melting point of the CaSn compound This corresponds to a slight break in the curve, which, however, is not the maximum The liquidus continues to rise to a maximum at 1122° C. corresponding to the compound Ca_2Sn The remainder of the diagram is of the eutectic type, the constituents being Ca_2Sn and pure calcium From the maximum, the curve drops to a eutectic at 759° C., of 81.4

[51] M LeBlanc, M Naumann, and D Tschesno, *Ber Verhandl. sachs Akad. Wiss Leipzig Math -Phys Klasse*, **79**, 71–106 (1927).

[52] Y. Matsuyama, *Science Repts Tôhoku Imp Univ , First Ser* , **20**, No 5, 649–8 (1931)

[53] D Hanson, and W T Pell-Walpole, *J Inst. Metals*, **56**, 165 (1935); **59**, 28 (1936)

[54] C E. Homer, and H Plummer, *J Inst Metals*, **64**, 189 (1939).

[55] L A Welo, *Phys Rev* (2), **10**, 583 (1917)

[56] Moissan, *Compt. rend* , **127**, 584 (1898)

[57] L Donsky, *Z. anorg. Chem.*, **57**, 185 (1908).

atomic per cent calcium The liquidus then rises to 820° C., the melting point of pure calcium

The effect of small amounts of calcium on the melting point of tin was studied by Heycock-Neville,[58] Donsky,[59] and Hume-Rothery[60] Their work also indicated the compounds $CaSn_3$ and CaSn

No evidence of solid solution has been found in the study of the system As a result, the solidus is simple All of the tin-calcium compounds are readily acted upon by water and atmospheric influences The alloys are

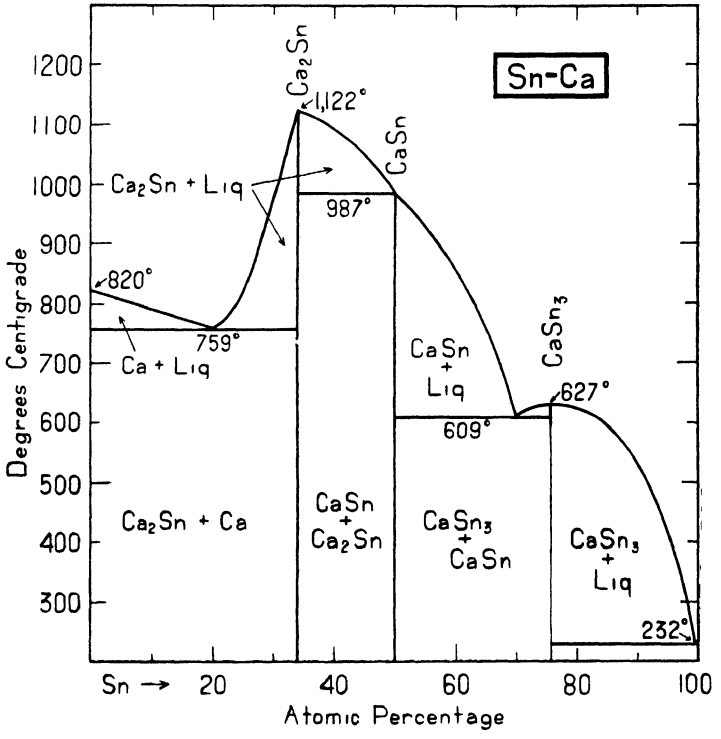


FIGURE 92 Diagram of tin-calcium system

all white. The crystals of the tin-calcium compound cleave into thin plates a little paler in color than mercury The alloys containing up to 4 per cent calcium are harder than tin and fairly tough. With further increase of calcium they become brittle Tin-calcium alloys have been proposed for use as aluminum solders

The tin-calcium alloys in general are rapidly attacked by water, air,

[58] C. T Heycock, and F. H Neville, *J Chem Soc*, **57**, 384 (1890)
[59] L Donsky, *Z anorg. Chem*, **57**, 212 (1908).
[60] W Hume-Rothery, *J. Inst. Metals (London)*, **53**, 319 (1926).

and dilute acids. The alloys have little industrial applications as binary alloys, but are of considerable theoretical interest

Tin-Carbon

Moissan[61] stated that tin does not unite directly with carbon to form carbides. Practically no work has been done at low temperatures on the solubility of carbon in tin. It does not appear that carbon-tin compounds do form at low temperatures, or that carbon has any measurable solubility in the metal.

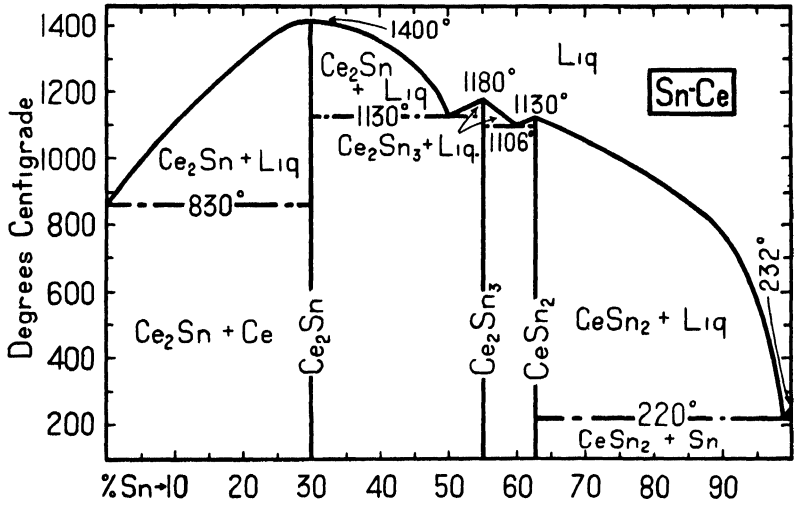


FIGURE 93. Diagram of tin-cerium system

Tin-Cerium

The thermal diagram of the tin-cerium alloys, according to Vogel,[62] is shown in Fig. 93 The freezing point of cerium is raised by the addition of tin to reach a maximum, at 30 per cent tin, of 1400° C This point corresponds to the compound Ce_2Sn Additions of tin lower the melting point of the compound until a eutectic is reached at 1130° C., between Ce_2Sn and Ce_2Sn_3 The latter compound occurs at a second maximum in the curve at 56 per cent tin, at a melting point of 1165° C. A third compound, $CeSn_2$, is formed at 64 per cent tin, melting at 1135° C

Small amounts of cerium depress the freezing point of tin. The alloys of tin and cerium tarnish rapidly, even when polished and covered with oil. They are very unstable against corroding influences All the alloys con-

[61] Moissan, *Bull soc chim* (3), **13**, 959 (1859), *Compt. rend* , **125**, 841 (1897).
[62] R Vogel, *Z anorg Chem* , **72**, 319 (1911).

taining less than 80 per cent tin are pyrophoric. The alloys above 50 per cent cerium produce showers of sparks when merely scratched with a hard object. The Ce_2Sn compound has the maximum hardness, about 6 on the Von Moh scale. It is very unstable in air, and vigorously reacts with water.

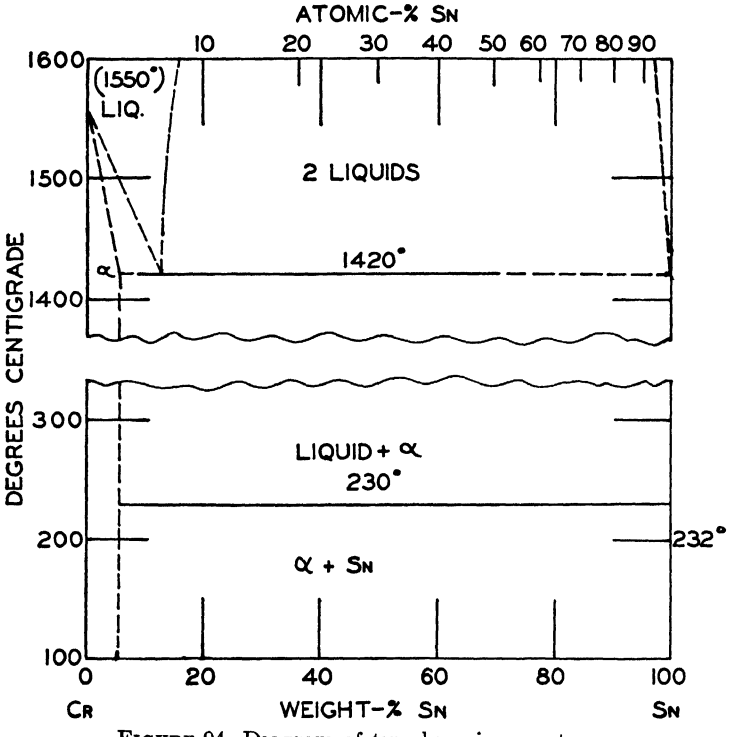


FIGURE 94 Diagram of tin-chromium system

Tin-Chromium

Neither chemical compounds nor solid solutions are stated to be formed, according to the data of Pushin.[63] In the lower chromium ranges, the alloys are very soft and resemble tin. Only those rich in chromium are hard.

Using an impure chromium of the composition 98 7 per cent chromium, 0.32 per cent silicon, and 1.20 per cent iron, Hindrichs[64] made a thermal and microscopic investigation of the tin-chromium system and proposed the solidification diagram of Fig. 94. The concentration of the melt rich in chromium at about 1420° C. is about 13 per cent tin, as derived from the liquidus curve. The composition of the melt rich in tin at 1420° C.

[63] N. A. Pushin, *J. Russ Phys. Chem. Soc.*, **39**, 353–99 (1908).
[64] G. Hindrichs, *Z. anorg. allgem. Chem.*, **59**, 416–20 (1908).

and of the eutectic point at about 230° C. is unknown, but it is likely that both lie very close to pure tin Hindrichs stated that regulı with 5 to 70 per cent chromium show distinct layer formation, even when in several melts no complete separation into two layers has taken place owing to the great speed of cooling, but small chromium crystals or droplets were separated in the tin-rich layer The structure of the alloys with 5 per cent tin was almost homogeneous, in any case not substantially more inhomogeneous than that of chromium made by the alumino-thermic method Chromium is without any influence upon the alpha $\rightleftharpoons$ beta transformation of tin (18° C.).

The diagrams designed by Hindrichs cannot be considered as the phase diagrams of the binary system tin-chromium and need new investigations under better experimental conditions.

Tin-Cobalt

Nial[65] found that the solubility of tin in alpha-cobalt is slight and in beta-cobalt only 2 5 atoms per cent as estimated from the lattice dimensions. With increased proportions of tin, four intermediate phases are encountered. Above 550° C. at around 40 atoms per cent tin, Nial observed a gamma-prime phase of the nickel-arsenic type with lattice dimensions varying from $a = 4.096$, $c = 5\ 161$ Å. to $a = 4\ 116$, $c = 5\ 177$ Å On the basis of density determinations, Nial estimated a composition of 41 or 42 atoms per cent tin Below 550° C. gamma prime undergoes a transition to gamma with $a = 4.089$, $c = 5.198$ Å, still of the nickel-arsenic type, but with a hyperstructure not yet worked out. For tin-rich alloys CoSn is encountered above 500° C , $CoSn_2$ below 500° C The compound CoSn is hexagonal with $a = 5.268$, $c = 4.249$ Å The space group is D^1_{6h}–$C6/mmm$ with 1 tin in 1 (a), 2 tin in 2 (d) and 3 cobalt in 3 (f) The compound $CoSn_2$ is tetragonal with $a = 6\ 348$, $c = 5\ 441$ Å The space group is D^{18}_{4h} – $I4/mcm$ with 4 cobalt in 4 (a), 8 tin in 8 (h), $x = \frac{1}{6}$

Korber[66] found that a noticeable heat of formation results when tin forms compounds with cobalt. The heat of formation of the melts with a high tin content was found to be much smaller than that of the crystallized alloys. The tin-rich melts of the cobalt-tin series showed even a smaller negative heat of formation, while it was positive in the melts rich in cobalt. Korber's explanation of this factor is based on the melting points of the components which differ from 850 to 1260° C.

The constitution diagram of the tin-cobalt system is given in Fig. 95. This diagram is an approximate one in that impure cobalt metal had to be employed and the curves are based on the work of Lewkonja[67] who made

[65] O. Nial, *Z anorg allgem Chem* , **238**, 287–96 (1938).
[66] F. Korber, *Stahl u. Eisen*, **56**, 1401–11 (1936).
[67] K. Lewkonja, *Z. anorg. allgem. Chem* , **59**, 294–304 (1908).

20-gram melts in porcelain crucibles which were attacked by the melts, and the experiments of Zemczuzny and Belynsky[68] who employed magnesia crucibles. Lewkonja's cobalt was 98.04 per cent cobalt, 1.62 per cent nickel, and 0.17 per cent iron, while Zemczuzny and Belynsky used a supposedly pure "Kohlbaum" cobalt but actually of unknown composition.

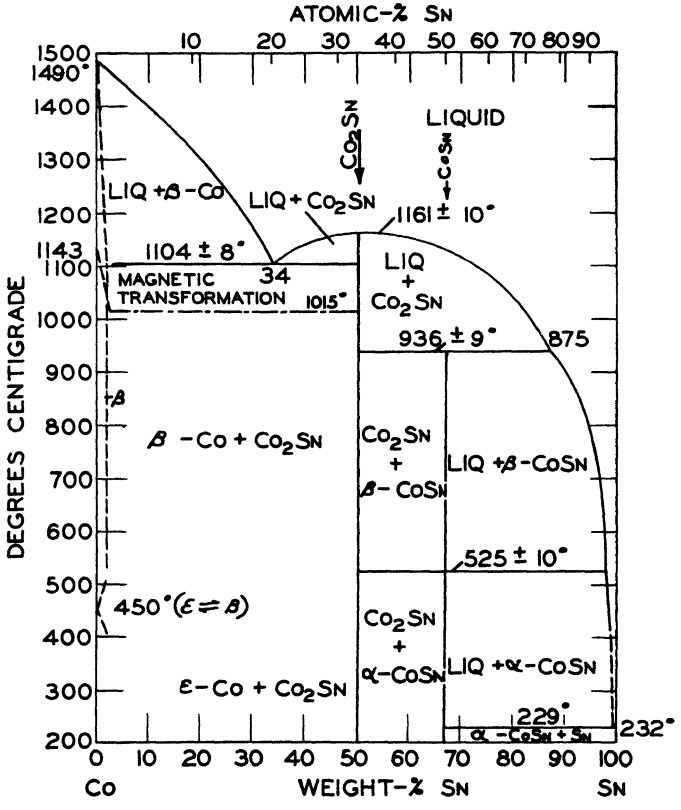


FIGURE 95 Diagram of tin-cobalt system

The compounds SnCo and $SnCo_2$ are believed to form. The microscopic investigation confirmed the results of the thermal analysis with one exception. In the case of quick cooling, the peritectic reaction

$$SnCo_2 + \text{melt} \rightarrow SnCo$$

does not take place completely at 936 ± 9° C., on account of the formation of a covering layer. The alloys in question then consist of three types of crystals. The compound SnCo (66.82 per cent tin) had been found

[68] S. F. Zemczuzny, and S. W. Belynsky, *J. Russ. Phys -Chem. Soc.*, **39**, 1463 (1907); *Z. anorg. allgem. Chem.*, **59**, 364–70 (1908).

earlier by Ducelliez[69] by the residual analysis of alloys of 81 to 92 per cent tin The same type of investigation of alloys with 9 to 57 per cent tin has led to the isolation of crystals of the composition Sn_2Co_3 (57.31 per cent tin) However, no compound of this composition exists according to the diagram. The position of the maximum of the liquidus curve, and the arrest periods at 1104° C. and 936° C from the composition of the alloy indicate the existence of the compound $SnCo_2$ (50 17 per cent tin). The extent of the solubility of tin in cobalt is uncertain. Lewkonja assumed a solubility of 2.5 per cent at 1104° C. on account of the arrest period. His alloy remained in two phases even after annealing for 8 hours at 1000° C.

The concentration of the SnCo-Sn eutectic will probably be found at about 99.5 per cent tin. The curve of the temperatures of magnetic transformation (during heating) which is shown in Fig. 95 was determined by Lewkonja. It appears then that cobalt is capable of forming mixed crystals with tin. The temperatures will be lowered because of the nickel content of the cobalt.

Tin-Copper

The tin-copper alloys are of such great practical importance in the nonferrous industries and are of such a complex nature that it occasions no surprise to find an extensive record of careful investigation in this field. The early work of Heycock and Neville[70] on these alloys has been accepted as one of the classical researches in metallography. It is remarkable how closely their results agree with work performed with apparatus equipped with every modern refinement.

The presence of tin hardens copper. The resulting alloy can take a high polish. Its melting point is comparatively low, and when melted it can be cast very well. The addition of a small amount of tin to copper, however, prevents the product from being easily fabricated by hot rolling If more tin be used, the alloy is not malleable when cold. The term "bronze" is applied to the alloys of copper and tin Bronze is tempered by heating it to the required temperature and rapidly cooling in water Modern bronzes are rarely simple binary alloys They are usually ternary or quaternary, and sometimes even more constituents are added. Among the commercial varieties of bronze are the so-called gun metals which were formerly much employed in the construction of ordnance and artillery weapons The preferred mixtures vary widely among the different countries, usually from 8 to 11 parts of copper to one of tin. The typical

[69] F. Ducelliez, *Compt. rend.*, **144**, 1432–4 (1907), **145**, 431–3, 502–4 (1907)

[70] Heycock, and Neville, *Phil Trans*, **189** (A), 63 (1897), **202**, (A), 1 (1903), *Proc Roy. Soc* (*London*), **71**, 409 (1903).

alloy is 90 copper, 10 tin. The thermal history of the alloy is almost as important as the knowledge of its chemical composition

If tin and copper are simply fused together, bronze is produced. If the mixture is not stirred, two liquid layers containing very different proportions of the two metals are formed. The combination is effected without the production of heat or light. Spring[71] stated that the alloy can be formed by subjecting a mixture of powdered tin and copper to high pressure

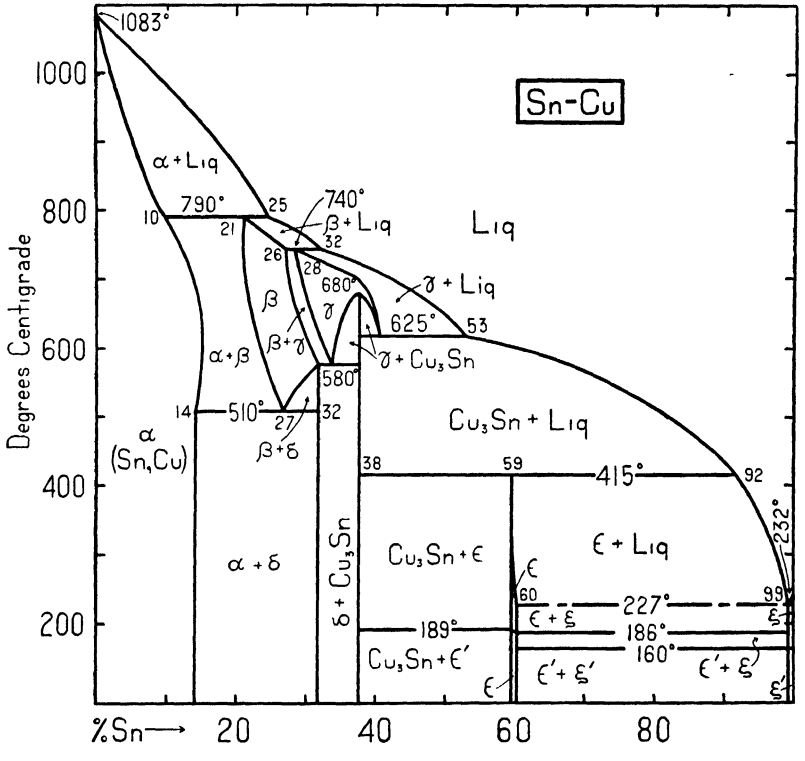


FIGURE 96. Diagram of tin-copper system

The thermal equilibrium diagram for the bronzes is one of the most complicated binary systems known. Figure 96 gives the data, the foundation of which was laid by Heycock and Neville[72] who studied the freezing point curves of the alloys. The alloys containing 0 to 50 per cent copper have been studied by J. L. Haughton,[73] who not only reviewed all previous

[71] Spring, *Z. phys Chem* , **15**, 65 (1894), *Bull Acad Belg.* (3), **28**, 23 (1894); **37**, 790 (1899)

[72] Heycock, and Neville, *Phil. Trans* , **202**, 1 (1903)

[73] J L Haughton, *J Inst. Metals*, **13** (1), 222 (1915), **25** (1), 309 (1921)

investigations, but in his own work made long-period annealings, which are necessary to insure true equilibrium conditions

Referring to the thermal equilibrium diagram, the melting point of copper is markedly affected by the addition of small amounts of tin The area represented by alpha is a solid solution of tin in copper The concentration of the tin in the copper varies with the temperature, being about 10 per cent at 790° and increasing gradually to 14 per cent at 510° The liquidus curve slopes from the melting point of copper at 1083° to a point represented by the junction of the temperature line of 790° and the tin percentage line of 25, where there is a break in the curve The area under this curve consists of the alpha constituent of tin in copper plus liquid. In this area, the alpha crystals are stable in contact with the molten alloy Directly underneath this area, represented by alpha plus beta, are found mixed crystals of alpha- and beta-bronze, and directly alongside is an area in which we find solid beta-bronze Under the liquidus curve, running from the junction point of 790° and 25 per cent tin to 740° and 32 per cent tin, is a small area where the beta-bronze crystals are in stable equilibrium with the molten alloy The liquidus curve then drops from the junction point of 740° and 32 per cent tin to 625° and 53 per cent tin Under this curve we find an area in which gamma-bronze is in stable equilibrium with the liquid alloy Directly adjoining is a small area in which solid gamma-bronze is stable Between the beta- and the gamma-bronze areas there is a thin corridor containing mixed crystals of beta- and gamma-bronze Adjacent and below this there is another small area existing between 510° and 580° and 27 and 32 per cent tin, where mixed crystals of solid beta- and delta-bronze are found. Directly adjoining the area of mixed crystals of beta- and gamma-bronze there is an irregular region in which gamma-bronze and crystals of the compound Cu_3Sn are in stable solid equilibrium In a rectangular region bounded by the temperature line of 580° at one end and 0° at the other, 32 per cent tin on one side and 38 per cent tin on the other, we find a mixed crystal area of delta-bronze and the compound Cu_3Sn Adjoining this on the left, between the temperature lines 510° at one end and 0° at the other and bounded on the left by the line represented by 14 per cent tin and on the right by 32 per cent tin, the diagram shows a rectangular region in which mixed crystals of alpha- and delta-bronze are stable. The liquidus curve drops from the junction point of the temperature line 625° and 53 per cent tin to a point represented by the temperature line of 450° and 92 per cent tin, and then to a eutectic point at 227° and 99 per cent tin, from whence the curve rises to the melting point of pure tin at 232°.

Gurevich and Hromatko[74] who used a delicate cooling curve method, placed the eutectic at 1 per cent copper and 227.1° C. At 625° the pri-

[74] Gurevich, and Hromatko, *Trans. Am. Inst. Mining Met. Engrs.*, **64**, 227 (1920).

mary constituent, gamma-bronze, reacts with the liquid to form the compound Cu_3Sn This is in stable equilibrium with the molten alloy in the area under the liquidus curve from 38 to 92 per cent tin, and between the temperature ranges of 625° and 415°. The compound Cu_3Sn reacts with the liquid along the solidus curve between 92 and 99 per cent tin and below 415° to form the constituent epsilon-bronze, which is in equilibrium with the liquid between 59 and 99 per cent tin and between the temperatures of 415° and 227° At 415°, between 38 and 59 per cent tin and in an area represented at the bottom by 189°, the compound Cu_3Sn plus the liquid reacts to give mixed crystals of Cu_3Sn and epsilon-bronze Below 189° there is an area in which the compound Cu_3Sn plus epsilon-prime-bronze is formed The epsilon-bronze constituent exists alone only in a very small area of thin vertical cross section, as represented at approximately 59 to 60 per cent tin.

Broniewski, Jablonski, and St. Maj[75] annealed alloys containing less than 38 per cent tin for 500 hours at 400° C , and others for 2,000 hours at 200° C Although their figures are generally similar to previous results, there are a considerable number of small differences.

Isaichev[76] studied the transformation in eutectoid alloys of tin and copper and the decomposition of the beta phase at annealing He found that the spacing of the cube-centered beta phase rises from 2.9752 Å. for 25 per cent tin to 2.9851 Å for 28 per cent tin When the specimen is annealed at 100 to 125° C., the spacings diminish and after annealing at 150 to 250° C. the gamma-prime phase appears After annealing at 350 to 400° C., only alpha and gamma phases were found present. Isaichev concluded that the gamma-prime phase contains more than 28 per cent and less than 32 per cent tin.

Ellis[77] found that the tin-copper alloy of the 89:11 type remained molten at temperatures well below the solidus of the alloy. When it was poured into foundry molds it cooled at such a rate that primary crystallization was delayed until the metal in the mold had reached a temperature at least as low as 915° C , a point halfway between the equilibrium liquidus and solidus Ellis pointed out that if crystallization is delayed until a temperature of 915° C has been reached, the crystal nuclei will contain approximately 7 per cent tin, and that upon these nuclei dendrites will form If the nuclei appear in the melt within the body of the casting at 960° F., the tin content would be about 5 per cent. He found that the dendrites that formed around these nuclei on cooling from 960 to 800° C. contained approximately 9 per cent tin, and the melt contained about 30 per cent tin The slower the rate of growth of the dendrites, the richer in

[75] W. Broniewski, J T Jablonski, and St Maj, *Compt rend* , **202**, 305–7 (1936).
[76] I Isaichev, *J. Tech Phys.* (*U.S.S.R*), **9**, 1867–72 (1939).
[77] O. W. Ellis, *Metal Ind* (*London*), **43**, 194–6 (1933)

tin they will be Ellis believed that other factors exert themselves, inverse segregation, which tends to raise the tin content of the outer p of the casting. He concluded that the interdendritic flow theory sugge that cavities are formed around growing crystals because of contracti and that molten alloy richer in tin is forced into contact with the cryst and solidifies

Ellis[78] found that an alloy which when cast under specified conditi gave evidence of inverse segregation subsequent to solidification, m upon the addition of small quantities of phosphorus, manganese, or zi become normal in its behavior under the same conditions of casting. T added element may change the temperature of primary solidification a modify the size of the dendrites, and may alter the vapor pressure of t tin-rich liquid

Ellis[79] also found that castings poured at high temperatures cool m slowly and give larger crystals and form a strong interlocking structu Annealing at 700° C. decreased the porosity of the metal surface oxidati The capillaries formed by the crystallization of the dendrites are fil with tin-rich liquid from the center of the casting.

Although earlier workers assumed that copper was totally insolu in solid tin, Haughton found that the constituent represented by t solution of copper in tin did not appear in alloys annealed for 68 ho at 195° C. until the copper content exceeded 0 23 per cent.

Between 60 and 100 per cent tin and below 227° there are a numb of transformations in the solid state At 227° the epsilon-bronze rea with the liquid to form mixed crystals of epsilon- and xi-solid solutio At 186° there is a hypothetical transformation of the epsilon to epsil prime crystals. This is based largely on the determinations of therm resistance, but microscopic examination shows no difference between t two solid solution structures X-ray analysis should be helpful in furth elucidating this question. At 160° there is another transformation of t xi-bronze to xi-prime.

Hamasumi and Morikawa[80] investigated the high-temperature structu of the phases of tin-copper alloys with a high-temperature x-ray came They found both beta and gamma have the same body-centered cu lattice, and no discontinuous change of lattice parameter occurs with change in temperature as well as concentration. Superstructure aton rearrangement is thought to be the cause of the beta $\rightleftarrows$ gamma transform tion. The same is said of the transformation 175° of the xi phase. T decomposition of the delta phase into alpha + eta at nearly 325°, d covered by another investigator, was confirmed by Hamasumi and Mc

[78] *Ibid.*, 353–4.

[79] *Ibid.*, 223–6

[80] M. Hamasumi, and K. Morikawa, *Nippon Kinzoku Gakkai-Si*, 2, 39–44 (193

kawa The structures of epsilon and eta at high temperatures were ascertained to be the same as those investigated by other workers with the quenched specimens

The solidus curve of the bronzes is quite complicated and can be only approximately indicated (Fig 96) In the ranges of low tin content, it drops from 1083° to a point represented by 790° and 10 per cent tin, proceeding horizontally at this temperature level to 21 per cent tin, and from there dropping to 740° and 26 per cent tin, again traveling horizontally to 28 per cent and dropping in an irregular manner to the temperature level of 625° and about 42 per cent tin It may then be imagined to travel horizontally along the temperature level of 625° to 38 per cent tin, dropping to the temperature level of 415° where it travels at this point horizontally across to 59 per cent tin, dropping again to 60 per cent tin and the temperature level of 227°, horizontally across to 99 per cent tin, from whence it rises to 100 per cent tin at 232°. In the light of the diagram and the numerous changes which occur with different thermal conditions, the great importance of the thermal history of a bronze as affecting its physical characteristics can be readily understood

Gagen-Torn and Hokhshtein[81] studied the influence of heat-treatment on the structure and mechanical properties of the tin-containing brasses They found that alloys with 61 to 63 per cent copper and 1 to 1 66 per cent tin quenched from 600° C. gave good results, and that this treatment prevented the formation of the brittle gamma phase in the structure Further experiments on subsequent annealing at 400° C. produced a change in structure, the beta phase being converted into the alpha phase, with separation of the excess tin and zinc in the form of the gamma phase but with the original grain boundaries being retained. The annealing at 400° C also modified the mechanical properties

Only one compound, Cu_3Sn, is shown on the equilibrium diagram It appears as bluish gray or bluish white lamellae It is rapidly attacked by hot concentrated hydrochloric acid According to Mallet[82] the color of the copper-tin alloys containing 82.81 to 84 29 per cent of copper is reddish yellow, with 78.97 to 81.10 per cent, yellowish red, with 72.80 to 76 29 per cent, pale red, with 68.21 per cent, ash gray, 61.69 per cent, dark grey, with 51.75 per cent, grayish white, 34 92 per cent, white, becoming still whiter with increasing proportions of tin. According to Heyn and Bauer,[83] the fracture of alloys which have been cooled rapidly has a uniform color, but if slowly cooled, there may be gray and yellow

[81] V. O Gagen-Torn, and M B Hokhshtein, *Metallurg* , **13**, No 7-8, 66-70 (1938), *Chem Zentr* , **I**, 1640-1 (1939).

[82] R. Mallet, *Proc. Roy Irish Acad* , **2**, 95 (1842); *Phil Mag* (3), **21**, 66 (1842).

[83] E. Heyn, and O. Bauer, *Mitt Materialprüfungsamt*, **22**, 137 (1904); *Z anorg. Chem.*, **45**, 68 (1905).

flecks. Mallet and Rieffel[84] found that the fracture of alloys with 84.29 to 81.10 per cent copper is fine-grained, with 78 97 per cent, vitreous and conchoidal, with 76.29 per cent, vitreous, with 72 80 to 68.21 per cent, conchoidal, with 61 69 per cent, lamellar and granular, with 51.75 per cent, vitreous and conchoidal, with 34.92 per cent, lamellar and granular; with 21 15 to 15 17 per cent, vitreous and granular, with 11.82 per cent, vitreous and lamellar, and with 9 68 per cent, earthy. Behrens[85] said that the alloy with 15 to 25 per cent of tin is fine-grained; with 25 to 40 per cent tin, conchoidal.

The rates of diffusion in the alpha-solid solution of copper were studied by Rhines and Mehl [86] Diffusion coefficients were determined from concentration-penetration curves by the Matano[87] method for a series of solid solutions in the systems of tin-copper and copper-aluminum. The investigators concluded that the rate of diffusion in these systems increases with increasing concentration of the solute, at first slowly, then with increasing rapidity The increase is more rapid in systems of low solid solubility than in high solid solubility. They found that the rates of diffusion near zero concentration of solute are approximately equal for all the systems, and that this suggests that the value extrapolated to zero concentration of solute is the rate of self-diffusion in copper, and is the controlling rate in dilute solid solutions in the series studied

Kuznetsov[88] studied the equilibrium oxidation of liquid tin-copper alloy with carbon dioxide at 1060 to 1140° C. He stated that the dissociation pressures of SnO_2 decreased with an increase in the molar concentration of tin, the greatest change being observed at small concentrations of the metal All components of the alloy are said to be oxidized simultaneously, the composition of the oxide film being determined by the compositions of the alloy

The alloys for the manufacture of bells contain from 74 to 85 per cent copper and from 15 to 26 per cent tin Other proportions produce different sounds, and other metals, such as zinc, iron, lead, bismuth, silver, antimony, or manganese, may be added either for cheapness or to produce a special tone. The typical alloy is 80:20 The sound from brass bells is of inferior quality. In some of the white table bells tin is the dominating component. Some white alloys, usually approximating $SnCu_4$, admit of

[84] R Mallet, and J Rieffel, *Compt rend* , **37**, 450 (1853)

[85] H Behrens, "Das mikroskopische Gefuge der Metalle und Legierungen," Hamburg, 1894, *Versl Akad Amsterdam*, **2**, 79 (1894).

[86] F. N. Rhines, and R F. Mehl, *Trans Am. Inst Mining Met. Engrs.*, **128**, 185–222 (1938).

[87] C. Matano, *Japan J Physics*, **8**, 109–13 (1933)

[88] M O. Kuznetsov, *Ubileinyi Sbornik Nauch Trudov Inst Tsvetnykh Metal. i Zolota*, No. 9, 556–65 (1940), *Khim. Referat. Zhur* , **4**, No. 5, 25 (1941).

a brilliant polish. These were formerly used for mirrors and hence were called speculum metals. They are sometimes used in the construction of mirrors for optical instruments Their composition ranges from 30 to 34 per cent tin and 62 to 69 per cent copper. In some cases lead, zinc, arsenic, silver, nickel or antimony has been added The typical alloy is 70:30. The term art bronzes is applied to alloys which are employed for statuary, vases, and ornaments of all kinds In a number of statues the proportion of copper ranges from 72 to 91 per cent, tin 0 15 to 10 2 per cent, zinc 0 1 to 26 per cent, lead up to 3 per cent, and small proportions of iron, nickel, and antimony

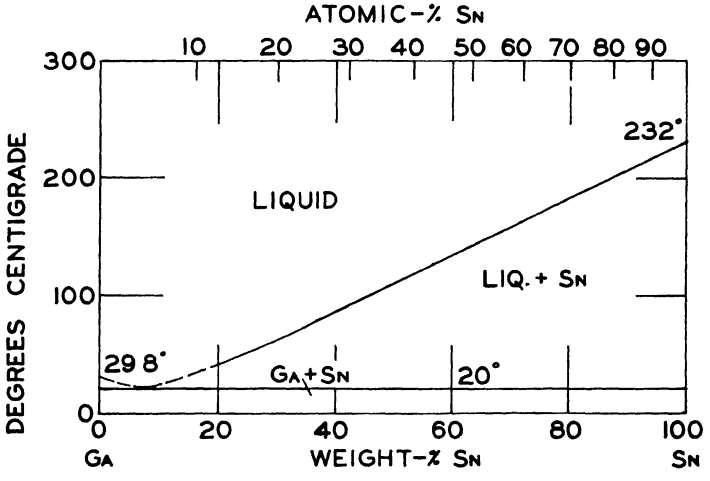


FIGURE 97. Diagram of tin-gallium system

Tin-Gallium

This system has received little study, but Pushin, Stepanovic and Stajic[89] stated that there is a eutectic formed at about 8 per cent by weight of tin, having a melting point of about 20° C Gallium has a melting point of the order of 29 75° C and the addition of tin to gallium lowers this value. Tin and gallium as shown in the constitution diagram in Fig. 97 are miscible in all proportions in the liquid or molten state Little is known of the extent of solid solubility of the metals in each other.

Tin-Germanium

Stohr and Klemm[90] investigated the binary system tin-germanium, and found that tin and germanium form a eutectic with the composition very

[89] N A Pushin, S Stepanovic, and V Stajic, *Z anorg. allgem. Chem*, **209**, 329–34 (1932).

[90] H Stohr, and W. Klemm, *Z. anorg. allgem Chem.*, **241**, 305–23 (1939).

close to 100 per cent tin and a temperature of 232 ± 1°. The solubility of germanium in tin is less than 0.6 atom per cent at 195° C., whereas that of tin in germanium is less than 1 0 atom per cent (Fig. 98)

Tin with 10, 20, 80 and 90 atom per cent germanium was melted in a vacuum and gave x-ray diagrams which showed only the lines of germanium and tetragonal tin. The same results were obtained when the alloys had been annealed for several weeks at 215° C , and then quenched In this case also, the x-ray diagrams showed only the lines of the two original components.

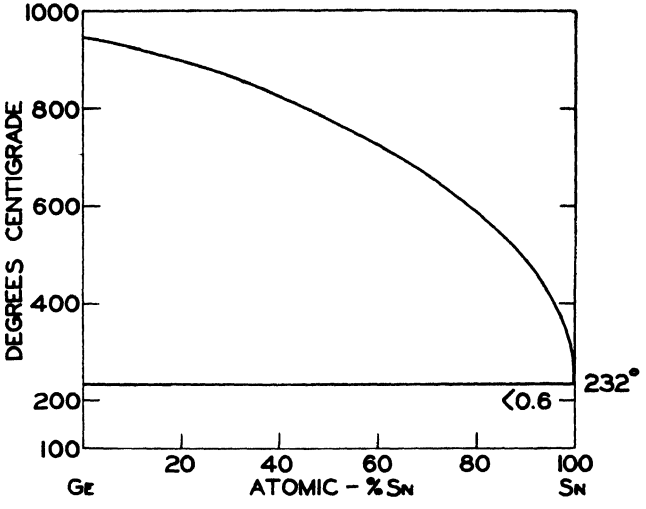


FIGURE 98 Diagram of tin-germanium system.

Tin-Gold

Small quantities of tin have considerable effect on the ductility of gold. They do not, however, make it brittle Tin markedly affects the color of gold In the proportion of 11 parts of gold to 1 of tin, an alloy of a pale yellow color, only slightly malleable and with a fine-grained structure, is produced. Its specific gravity is 17.307, indicating that the volume is less than the sum of the volumes of the constituents.

The thermal equilibrium diagram for the tin-gold alloys, in the main according to Vogel,[91] is given in Fig. 99 The addition of tin to gold lowers the melting point rapidly, causing it to fall from 1066°, the melting point of gold, to a eutectic point at 280° where the tin concentration is 20 per cent. This eutectic has for its constituents gold on one side and the compound AuSn on the other. From the eutectic, the freezing point curve

[91] R. Vogel, *Z. anorg. Chem* , **46**, 60–75 (1905).

rises to a well-defined maximum at 418°, corresponding to 37.63 per cent tin and representing the compound AuSn. This is a silver-gray material more brittle than gold and harder than either gold or tin. Its electrical conductivity is greater than that of all the tin-gold alloys excepting those containing more than 95 per cent gold. The compound AuSn is as resistant as gold ordinarily is to the action of sulfuric, nitric or hydrochloric acid, and is only slowly attacked by aqua regia. The liquidus curve, after passing through the maximum at 418°, falls to a second eutectic at 214°, corresponding to 90 per cent tin, then rises to 232°, the melting point of tin Between the maximum at 418° and the eutectic at 214°, there is a break in the curve at 308° and 60 per cent tin, corresponding to the compound $AuSn_2$. This appears as large crystals in the slowly cooled alloy. It is as resistant to corrosion by the mineral acids as is the AuSn There is a

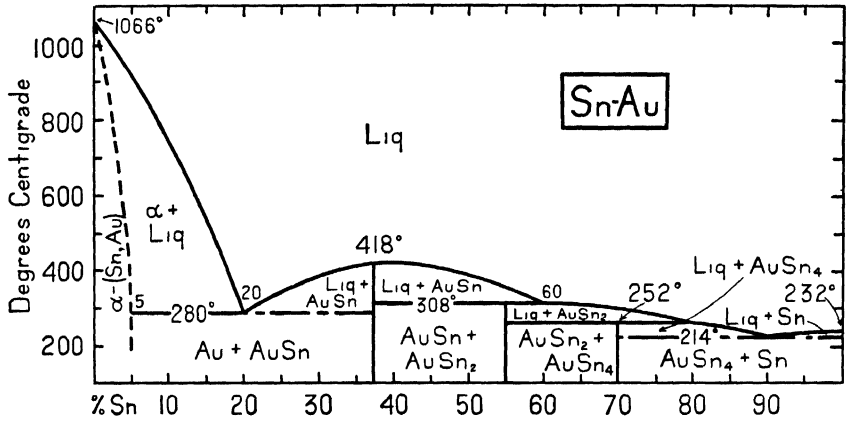


FIGURE 99 Diagram of tin-gold system

second break at 252° and 80 per cent tin, corresponding to the compound $AuSn_4$. This compound is attacked by nitric acid and is colored brown as a result. The same does not hold true for the $AuSn_2$ compound. The solidus curve drops from 1066° and 100 per cent gold along a hypothetical line to a point represented by the junction of the 280° temperature level and 5 per cent tin, the area under the curve representing a solid solution alpha of tin in gold In the area between the solidus and the liquidus curves, the constituent alpha is in equilibrium with the molten metal The alloys containing 5 to 37 63 per cent tin all freeze at the eutectic temperature 280° and show the crystalline structure of gold mixed with the AuSn compound. The solidus curve continues along the temperature level of 280° to 37.63 per cent tin, then rises to 308°, continuing at this temperature level to approximately 55 per cent tin. In the area between

the solidus from 20 to 37.63 per cent tin and the liquidus curves, the compound AuSn is in equilibrium with the molten alloy. The same holds true from 37.63 to 60 per cent. From 37.63 to 55 per cent at 308°, the liquid and the compound AuSn react so that the solid phase consists of a mixture of the compounds AuSn and $AuSn_2$. From 55 per cent tin to 70 per cent tin, the solidus continues at the temperature level of 252° The area between the liquidus and the solidus shows the compound $AuSn_2$ in equilibrium with the molten alloy, and in the solid phases between 55 and 70 per cent tin the alloy consists of a mixture of the compounds $AuSn_2$ and $AuSn_4$ From 70 to 100 per cent tin, the solidus continues along at the temperature level of 214°, the area between the solidus and liquidus curves consisting of the compound $AuSn_4$ in equilibrium with the molten alloy, and the solid phases below 214° consisting of the compound $AuSn_4$ plus tin crystals From 90 to 100 per cent tin, the area between the solidus and the liquidus consists of tin in equilibrium with the molten alloy, and in its solid phases below 214° consists of mixtures of tin and the $AuSn_4$ compound The tin-gold system was reinvestigated by Stenbeck and Westgren[92] who confirmed the existence of the three compounds

McLennan, Allen, and Wilhelm[93] found that in the tin-gold system, the superconductivity metal gold depressed the transition temperature They stated that a binary system composed of one superconductor and one nonsuperconductor may have more than one transition temperature. Superconductivity appears at higher temperatures in eutectic alloys than in compounds of the same metals and this is said to be caused by the large internal forces in eutectics

Kubaschewski[94] determined the heats of fusion by calorimetric observation of the heat content between room temperature and temperatures above and below the melting point for several gold alloys of which tin-gold is one He found that the difference between the observed entropy of fusion and that of the corresponding mixed but uncombined metals agreed with the degree of order of the phase concerned Near the fusion temperature, the tin-gold alloy was found to crystallize in a highly ordered manner, whereas some of the other gold alloys investigated crystallized in complete disorder.

The tin-gold alloys have at times found use as substitutes for the more expensive noble metal applications for resistance to corrosion and chemical attack. Infrequently, tin-gold alloys have been used in jewelry and for decorative work. Their commercial use is limited. Tin is often plated on "white gold" to overcome unevenness in color.

[92] S Stenbeck, and A. Westgren, *Z physik Chem* , **14**, 91–6 (1931).
[93] J C McLennan, J F Allen, and J O. Wilhelm, *Phil Mag* , **13**, 1196–209 (1932)
[94] O. Kubaschewski, *Z. physik Chem* , **192**, 292–308 (1943).

Tin-Indium

Indium dissolves rapidly in molten tin. Heycock and Neville[95] measured the freezing points of the alloys containing small amounts of indium

The binary alloys of tin and indium were studied by Fink, Jette, Katz, and Schnettler.[96] They reported that the dissociation temperatures of the intermetallic compounds beta and gamma were found to be 126.5° and 124 0° C. respectively No arrest points were detected for the peritectic reaction on the indium-rich side of the compound gamma The eutectic reaction occurred at a liquid composition of 48 5 atomic per cent tin and 116 3° C. Both of the intermetallic phases, beta and gamma, are very soft and ductile

Valentiner[97] found a eutectic at 48 atomic per cent tin which melted at 117° C. X-ray measurements point to a eutectic composed of tetragonal crystals of Sn_2In_6 and $Sn_{15}In$. Valentiner also found that the solubility of tin in indium at the freezing point is around 15 atoms per cent tin, and that of indium in tin is close to 7 atoms per cent indium.

Tin-Iron

The tin-iron alloys are not important industrially as a result of their use as alloys, but their study is of decided interest inasmuch as their formation at high concentrations of iron and tin is a source of considerable difficulty in tin metallurgy and the winning of tin from ferruginous ores They cause particular difficulty in the smelting of the complex vein ores such as the Bolivian Their formation at low concentrations of iron in tin is of considerable importance in the manufacture of tin plate.

The early work on the system was done by Isaac and Tammann [98] The complete system is given in Fig. 100 The work of Wever and Reinecken[99] explains to a considerable extent the reactions occurring in the manufacture of tin plate. The right-hand side of the diagram gives data on the alloys of 0 to approximately 20 per cent iron. Wever and Reinecken concluded that tin and iron are completely miscible in the liquid state. Former investigators had stated that the miscibility was only partial Solidification of the tin-rich alloys begins in the area shown in the diagram as Fe_3Sn plus liquid, along the solidus line at 890° by the crystallization of an iron-tin compound out of the melt At 890°, between 81 and 96

[95] Heycock, and Neville, *Chem News*, **59**, 175 (1889), *J Chem Soc* , **55**, 666 (1889)

[96] C G Fink, E R Jette, S Katz, and F J Schnettler, *Trans. Electrochem Soc* , **88**, 229–41 (1945)

[97] S. Valentiner, *Z Metallkunde*, **32**, 31–5 (1940)

[98] Isaac, and Tammann, *Z anorg Chem* , **53**, 281 (1907), Guertler, "Metallographie," Bd 1, Tl 1, p 642, Berlin, Verlag Gebr Borntraeger, 1911.

[99] F. Wever, and W Reinecken, *Mitt. Kaiser-Wilhelm Inst. Eisenforsch Dusseldorf*, **7**, 69 (1925), *Stahl u Eisen*, **46**, 51 (1926), *Z anorg allgem Chem* , **151**, 349 (1926).

per cent tin, a peritectic reaction gives rise to the compound $FeSn_2$ containing 81 per cent tin. For alloys with a tin content greater than 81 per cent, complete solidification does not occur until a temperature slightly below the melting point of tin is reached Wever and Reinecken found thermal changes, which they attributed to polymorphic transformations

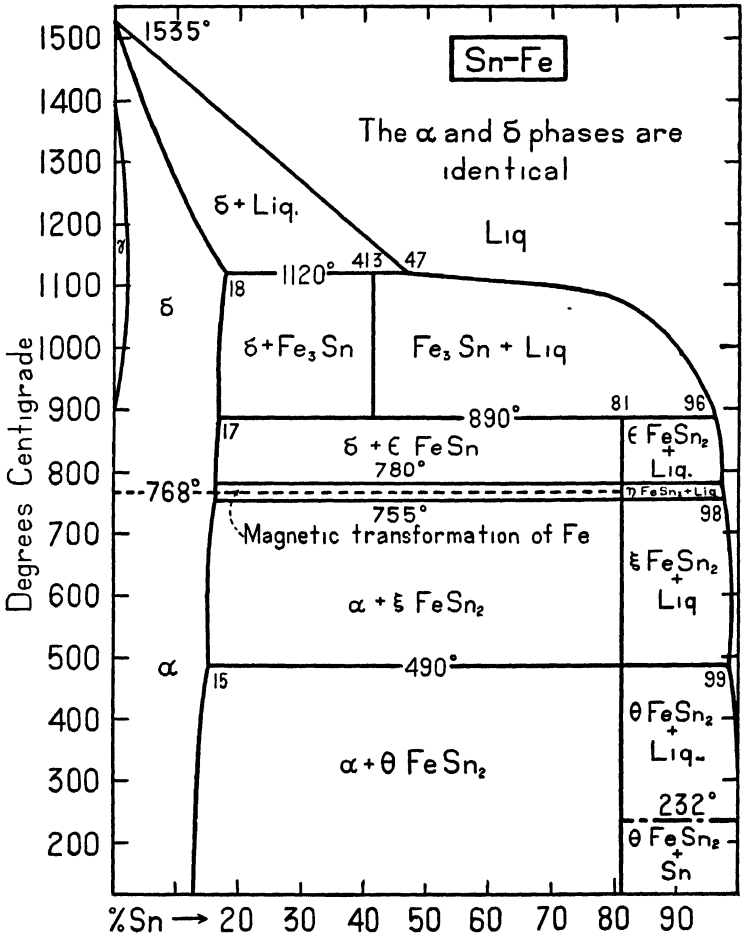


FIGURE 100 Diagram of tin-iron system

in the compound, $FeSn_2$, at 780°, 755°, and 490°. At ordinary temperatures the tin-iron alloys between 81 and 100 per cent tin consist of a matrix of a solid solution of a very small amount of iron in tin Crystals of the compound FeSn are embedded in this matrix At the present date no reliable data are available as to the solubility limit of iron in tin It is believed that at the best it is only a few hundredths of a per cent. Hot-

dipped tin coatings show an alloy layer immediately adjacent to the iron base, with an outer layer of tin covering this alloy. Inasmuch as only relatively low temperatures are used in tinning, and the operation is one of a short time period, the alloy layer in tin plate is exceedingly thin Often no evidence of it can be detected in metallographic sections of the coated sheet Careful polishing and etching of the slightly bent surface of a sheet will usually demonstrate its presence. The alloy layer appears as a bluish film underlining the layer of tin which comprises the body of the coating.

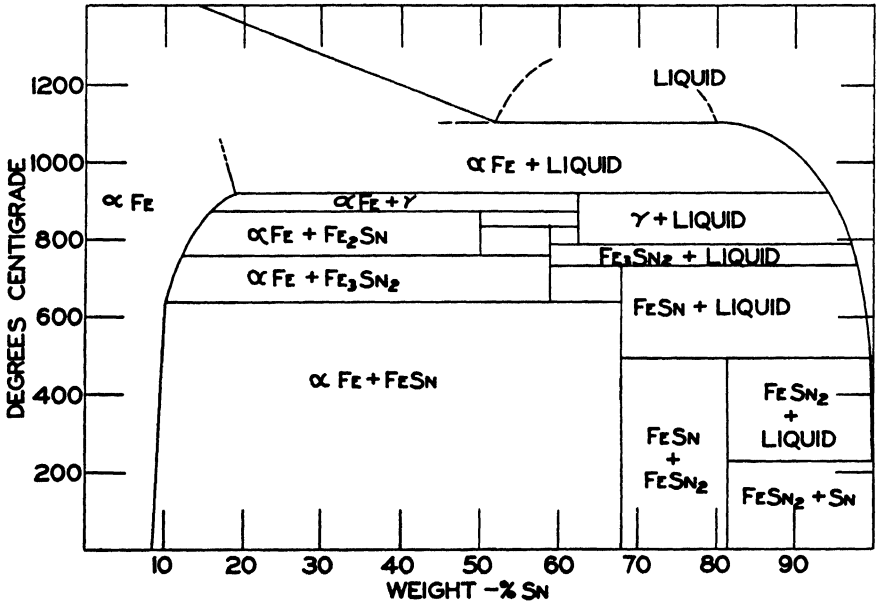


FIGURE 101 Partial phase diagram for tin-iron alloys

A new phase diagram for the system tin-iron (Fig. 101) was proposed by Ehret and Gurinsky.[100] It confirms the diagram sketched earlier by Ehret and Westgren[101] and gives definite temperature intervals of stability for the several intermetallic phases Lattice constants are given for the five intermediate phases, namely, Fe_2Sn, Fe_3Sn_2, gamma (NiAs structure), FeSn and $FeSn_2$ Each of the phases possesses hexagonal symmetry.

Ehret and Westgren examined a number of alloys in the system tin-iron. The following phases were found: alpha phase, a solid solution of tin in alpha iron, beta phase, thought to be a mixture of two or more phases, β'' phase, a hexagonal structure that is probably Fe_2Sn; gamma phase, having

[100] W. F. Ehret, and D. H. Gurinsky, *J. Am. Chem. Soc.*, **65**, 1226–30 (1943).
[101] W. F. Ehret, and A. F. Westgren, *J. Am. Chem. Soc.*, **55**, 1339–51 (1933).

a NiAs structure and assumed to be FeSn, $FeSn_2$ phase, which is probably hexagonal, and a Sn phase. The diffraction pattern of the last does not differ from that of pure tin, hence iron and the other phases are insoluble in tin

Edwards and Preece[102] stated that there exist three compounds between tin and iron of which only $FeSn_2$ is stable below about 500° C. Between 760 and 900° C the compound Fe_2Sn occurs which, however, is transformed to FeSn by addition of tin at 800° C. Further addition of tin leads to the compound $FeSn_2$ at about 500° C. Edwards and Preece were unable to confirm the existence of the compound Fe_3Sn which had been found by Wever and Reinecken [103]

If the tin coating is made at too high a temperature, a heavier intermediary layer is formed which is hard and brittle and has a tendency to scale off very easily, not only while being bent, but also while flat. This has been investigated by Mayer,[104] Feszczenko-Czopiwski and Strzalko,[105] and Bannister and Jones.[106]

A method for determining the amount of alloyed tin in tin coatings has been devised by Kohman.[107] The unalloyed tin readily dissolves in a hot solution of sodium plumbite, while the iron-tin alloy does not dissolve nearly as readily. The percentage of alloy in a tin coating on ordinary coke tin plate is readily increased by keeping the steel sheet immersed in molten tin and allowing it to come to the temperature of the tin bath prior to passage through the tinning machine. Kohman found that in ordinary commercial charcoal tin plate the alloyed tin constituted about 5 per cent of the weight of the coating, while in commercial coke tin plate the amount of alloyed tin was about 17.5 per cent.

Rawdon[108] stated that the effect of the alloyed tin upon the service behavior of the coated iron with respect to corrosion is of no practical importance, inasmuch as the compounds of tin and iron bear the same general electrochemical relation toward iron that tin does. He also added that the alloy formation does not increase the corrosion resistance, since the alloys, like tin, afford no electrochemical protection to iron against corrosion attack, and that since the alloy layer is always extremely thin, the

[102] C A Edwards, and A Preece, *J Iron and Steel Inst*, (*London*), **124**, 41 (1931)

[103] F. Wever, and W Reinecken, *Mitt Kaiser-Wilhelm Inst Eisenforsch Dusseldorf*, **7**, 69 (1925), *Stahl u Eisen*, **46**, 51 (1926)

[104] Mayer, *Stahl u Eisen*, **38**, 960–2 (1918)

[105] Feszczenko-Czopiwski, and Strzalko, *Z d oberschlesischen Berg- und Huttenmännischen Vereins*, **70**, 16 (1931)

[106] C O Bannister, and W D Jones, *J Iron and Steel Inst* (*London*), **124**, 71 (1931).

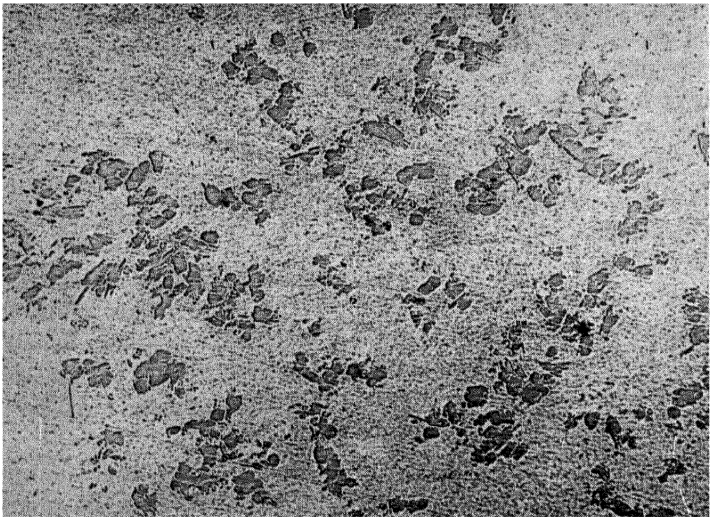
[107] E. F. Kohman, and N H Sanborn, *Ind Eng Chem*, **19**, 514–8 (1927)

[108] Rawdon, "Protective Metallic Coatings," New York, Reinhold Publishing Corp., 1928.

possibility of the mechanical properties of the coating being adversely affected is a very remote one.

The photomicrograph in Fig. 102 is of tin scruff with an iron content of 2.95 per cent and shows the compound $FeSn_2$ occurring as nodules embedded in a soft matrix which is nearly pure tin. The photomicrograph is illustrative of the appearance of the tin-iron alloys from 81 to 100 per cent tin at ordinary temperatures.

The solubility of tin in iron occurs only in a very limited area, as represented by gamma in the thermal equilibrium diagram. The area is restricted by both temperature levels and percentages of tin. At ordinary



(Courtesy H. S. Rawdon)

FIGURE 102. Photomicrograph of tin scruff.

temperatures there does not seem to be evidence of solid solutions of iron in tin. The addition of tin to molten iron markedly lowers the freezing point. The area in which the mixed crystals of iron and tin form as a result of the cooling of the molten alloy is modified by temperature changes. At 1120°, up to 18 per cent tin there is no compound formation. At 890° the limit is lowered to 17 per cent tin, and at 490° to 15 per cent tin. Below the melting point of tin, this percentage becomes still less. In the diagram two phases are given, termed delta and alpha, one existing below 768°, at which point a magnetic transformation of iron occurs, and the delta constituent existing above this temperature. In the area represented by delta plus liquid, the delta constituent is in equilibrium with the

liquid, reacting at 1120° between 18 and 41 3 per cent tin to form the compound Fe_3Sn.

The liquidus curve of the alloy diagram is relatively simple, starting from the melting point of iron, 1535°, dropping with increasing content of tin along a straight line to 1120° and a tin concentration of 47 per cent From this point the curve assumes an irregular shape to the temperature level of 890° and 96 per cent tin, then continues downward to the melting point of tin, with breaks occasioned by the thermal changes of the $FeSn_2$ compound The solidus curve is quite irregular, dropping from 1535° along a curved line to 1120° and 18 per cent tin, continuing at this temperature level to 41 3 per cent tin, then dropping in a straight line to the temperature level at 890° It continues at this temperature level to 81 per cent tin, at which point the compound $FeSn_2$ is formed, dropping then in a straight line to a temperature level just below the melting point of tin, continuing at this level to 100 per cent tin.

The tin-iron alloys between approximately 17 and 81 per cent tin suffer a number of constitutional changes during cooling At 890° the compound Fe_3Sn either suffers a constitutional change or reacts with the liquid to form the solid-phase delta plus the compound FeSn These mixed crystals pass through thermal changes at 780° and 755° C. The delta constituent, as a result of a magnetic transformation of the iron crystals, changes at 768° to the alpha form At 755° the delta form plus the compound FeSn react, with formation of the compound $FeSn_2$, which at 490°, as a result of thermal changes, suffers a constitutional deformation Below 490° alloys containing 15 to 81 per cent tin consist of the alpha phase, which is composed of mixed crystals of iron and tin plus crystals of the compound $FeSn_2$ in its so-called theta form, as a result of thermal changes

In tin smelting, the tin-iron alloys are known as hardheads They are obtained in a more or less pure condition in smelting operations, in the crucibles or the forehearths, or on the beds of furnaces The alloy is also formed in the tinning pots in tin-plate manufacture They form a pale to dark gray, irregularly granular or crystalline, brittle, more or less completely fused mass Hardhead generally consists of more or less metallic tin mechanically intermingled with the alloys of definite composition which appear to be chemical compounds From the thermal equilibrium diagram it can be seen that there is only one compound which is stable at ordinary temperatures This compound, $FeSn_2$, was carefully studied by Oudemans,[109] who isolated it in crystals from Banka tin, and found its specific gravity to be 7.743

[109] Oudemans, "Over verontreiniging van Banka Tin," *Jaarboek van het Mijnwezen in Nederlandsch Oost-Indie*, I, 24 (1890)

The tin-iron alloys in many cases can be liquated. In those containing more than two-thirds tin, tin liquates away leaving the alloy $FeSn_2$ behind

Hardhead, as produced in smelting operations, nearly always contains arsenic. Levey and Ewen[110] gave the following representative analysis:

	Per Cent
Sn	17 92
As	21 92
Fe	52 90
S	1 90
Insoluble	2 03
	96 67

For the occurrence of hardhead in smelting and its reworking, the reader is referred to Chapter 6.

Small amounts of iron in tin markedly affect its working properties, increase its hardness, and decrease its ductility The tin-iron alloys have practically no industrial applications

Korber[111] observed a small but distinct heat of formation for the tin-iron alloys. He stated that it is probable that tin and iron do not form an uninterrupted series of mixtures because they show a strong tendency to separate

Tin as an element is not found in any of the iron ores, but the use of detinned scrap may result in its introduction into steel during the process of manufacture. The steel maker is of the opinion that the presence of tin in steel is not to be overlooked. The tin-iron alloys have the property of making steel very hard at rolling temperatures At one plant it was impossible to roll a heat of steel into which 0.75 per cent tin had accidentally been introduced. Tin in steel increases the yield point and the ultimate tensile strength of the metal, but to a lesser degree than carbon or phosphorus Investigations indicate that 0 05 per cent tin in steel would have little influence on its mechanical or physical properties, but that larger quantities must be religiously avoided

Tin influences iron in the same manner as does arsenic, it causes the iron to become cold-short and red-short and makes rolling difficult. Burgess and Aston[112] stated that soft iron remains malleable and suitable for rolling up to a tin content of 2 per cent, but that Martin steel gets red-short at a tin content of 1 5 per cent.

Bolsover and Barraclough[113] studied the influence of tin on alloy steels

[110] Levey, and Ewen, *Trans Am Inst Mining Met Engrs* , **18,** 466 (1908)

[111] F Korber, *Stahl u Eisen*, **56,** 1401–11 (1936)

[112] Oberhoffer, "Das technische Eisen," p 246, 1925

[113] G R Bolsover, and S Barraclough, *J Iron Steel Inst. (London)*, **144,** 141–55 (1942).

and found that even 0.1 per cent tin lowers the notched-bar impact test of all the hardened and tempered steels This effect was not so marked in the basis carbon steel in oil-quenched conditions after tempering as it was in the normalized condition The effect of tin appeared to be counteracted by the addition of molybdenum Bolsover and Barraclough stated that tin does not have any greater effect on high (0.045 per cent) phosphorus than on low (0.020 per cent) phosphorus steel, the lower impact value being attributed to the higher phosphorus content. The 4¼ nickel-chromium case-hardening steel suffered only a slight decrease of impact

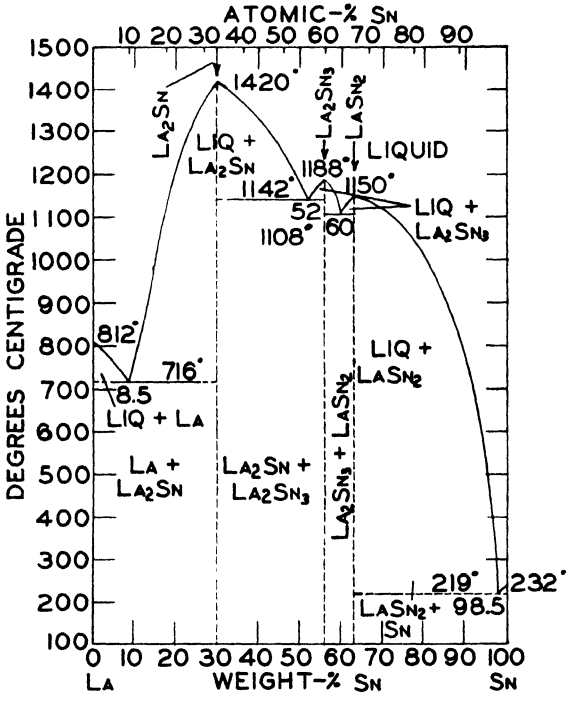


FIGURE 103. Diagram of tin-lanthanum system

value up to 0.15 per cent tin, but with higher tin content the values fell seriously

Tin-Lanthanum

Canneri[114] and Rossi[115] studied the system tin-lanthanum and found evidence for three intermetallic compounds La_2Sn, La_2Sn_3, and $LaSn_2$

[114] G Canneri, *Metallurg ital.*, **23**, 806–9 (1931).

[115] A Rossi, *Rend. Accad Lincei, Roma*, **17**, 839–46 (1933); *Chem. Zentr.*, II, 2499 (1933), *Gazz. chim. ital.*, **64**, 832 (1934).

at 29.94 per cent, 56 18 per cent, and 63.09 per cent tin respectively The constitution diagram in Fig 103 shows that the addition of lanthanum to tin lowers its melting point to an apparent eutectic at 98 5 per cent tin with a melting point of 219° C The addition of tin to lanthanum lowers the melting point of lanthanum with the maximum effect at about 8 5 per cent tin, with a melting point at this composition of 716° C

Little is known of solid solubility conditions in this system The dotted lines making the areas in the diagram are uncertain

Tin-Lead

Tin and lead can be alloyed in all proportions The alloys were made and used by the Romans They were made by Spring[116] by strongly compressing an intimate mixture of the powdered elements, the two solids form an alloy in a few hours at 150° to 200° C

The relation between linear shrinkage and composition of alloys of the tin-lead system, with tin varying from 0 to 100 per cent, was investigated by Bochvar and Dobatkin [117] They reported that as the tin increases, the contraction decreases at a diminishing rate until a composition is reached slightly beyond the point of maximum solubility of tin at the eutectic temperature, which is about 30 per cent tin. With further increases in the two-phase region, the contraction drops slightly along a straight line to about 90 per cent tin line, then increases again along a curve Bochvar and Dobatkin concluded that the fact that the limits of straight-line relationship of contraction to composition do not coincide with the solubility limits is in accord with the theory previously proposed

Stockdale[118] studied the system tin-lead, holding that the eutectic in the system was at 61 86 per cent tin with a melting point of 183 3° C

The thermal equilibrium diagram is still incompletely understood, as the result of varied interpretation of the empirical results For this reason the dotted lines represent changes which the majority of investigators hold to be true, although the experimental data may be meager or capable of mixed interpretation

The liquidus curve *ABC* indicates a system with no compound and with the eutectic at 63 per cent tin at a temperature of 181° C

The line *AD* represents the final solidification of the lead-rich end for alloys from 0 to 19.6 per cent tin Mazzotto[119] first placed *D* at 16 per cent Guertler[120] embodied such a curve in his theoretical conception of

[116] Spring, *J chim Phys* , **1,** 593 (1903), *Bull Acad Belg* (2), **39,** 548 (1875), (3), **11,** 355 (1886), (3), **28,** 23 (1894).

[117] A A Bochvar, and V. I Dobatkin, *Tsvetnye Metal* , No 7, 86–8 (1940)

[118] D Stockdale, *Proc Roy Soc (London)*, **A152,** 81–104 (1935)

[119] D Mazzotto, *Intern J Metallography*, **4,** 273 (1913)

[120] W. Guertler, "Metallographie," p 736, 1911

the tin-lead diagram. In the binary system of lead-antimony, which behaves analogously to the one under consideration, the corresponding solidus of the antimony in lead solid solution has been experimentally determined with great care, and this curve is similar to the solidus AD plotted in Fig 104 The line AD is drawn from the results of Stockdale.[121]

The line DBE is the eutectic horizontal occurring at 183° C All alloys from approximately 19 5 to approximately 97 5 per cent tin become totally solid at this temperature. The point E is possibly questionable, as Goebel[122] observed a solubility of 0.37 per cent lead in tin at the eutectic temperature The line CE represents the solidus for alloys from zero to 2.6 per cent lead as determined by Jeffery.[123]

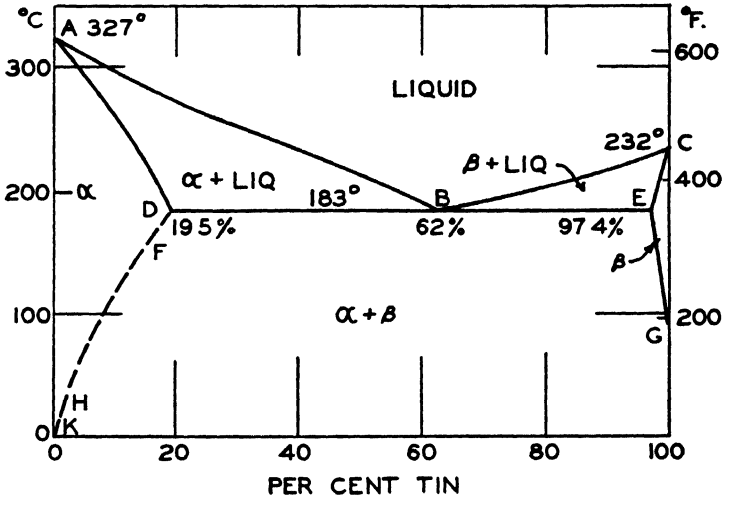


FIGURE 104. Diagram of tin-lead system.

Alloys at the temperatures and concentrations shown in the ADB area consist of a solid solution (α) of tin in lead, and liquid Those in the area CEB are solid solution β and liquid.

The curve $DFHK$ shows the limit of solid solubility of tin in lead, and has been defined by the work of Parravano and Scortecci,[124] and Stockdale.[125] They showed that solubility of tin in lead changes rapidly from 100 to 183° C. and drops to 13 per cent at 155° C. (F). At 183° C. the

[121] D Stockdale, *J Inst. Metals*, **49**, 267 (1932)
[122] J Goebel, *Z Metallkunde*, **14**, 362 (1922)
[123] F H Jeffery, *Trans Faraday Soc* , **24**, 209 (1928)
[124] N Parravano, and A Scortecci, *Gazz chim ital* , **50**, 83 (1920)
[125] D Stockdale, *J. Inst. Metals*, **49**, 267 (1932).

maximum solubility of tin is 19.5 per cent At 155° C. the solubility is 13 per cent. This curve has been studied by Morgen and coauthors.[126]

The area *ADFHK* defined by the solidus *AD* and solid solubility curve *DFHK* represents alloys which consist entirely of solid-solution tin in lead when in equilibrium. Any alloy of temperature and concentration within this area would exhibit a one-phase polygonal structure under the microscope In practice, long annealings are necessary before complete equilibrium is established.

Rosenhain and Tucker,[127] by dilatometric measurements, claimed that "gamma" tin transformed to beta at 161° C Others dispute entirely the existence of gamma tin.

The lead constituent of the eutectic has a diminishing power of holding tin in solution. This solubility decreases from 19 5 to 13 per cent and from 183° to 155° C A line parallel to the base of the diagram through *F* may be the limit of supersaturation of tin in the cooling lead-rich solid solution, and at this temperature there may be a precipitation of the excess tin, which accounts for the slight exothermic reaction or recalescence observed on cooling.

Phebus and Blake[128] studied alloys of lead and tin of variable concentration by x-ray methods. They show a solid solution from 0 to 3 6 per cent tin in lead, which corresponds to the face-centered cubic lattice and varies in size from 4.942 to 4.931 Å. units. Alloys of 10 to 95 per cent tin exhibit mixtures of the lead and tin lattice types.

Alloys between 95 and 100 per cent tin show the lattice of pure tin both in structure and size, which obviously indicates a concentration of maximum solid solubility of 5 per cent lead in tin. This is contrary to the metallographic researches which contributed to the drafting of the equilibrium diagram. Further x-ray data and also more evidence of adequate annealing are desirable.

The facility with which the plumber can "wipe a joint" with high-lead solders depends upon the two freezing points of the alloy, or rather the cooling through the range of solid solution of tin in lead plus liquid in the *ABDA* area of the diagram, when the pasty condition occurs

Binary tin-lead alloys shrink on freezing.

Samson-Himmelstjerna[129] determined the heat contents of tin-lead alloys at 500° C. Kawakami[130] made the same determinations, only at a temperature of 350° C. The maximum heat of alloying in calories per gram atom calculated from these figures is listed below:

[126] R A Morgen, L G Swenson, F C Nix, and E. H Roberts, *Am Inst Mining Met. Engrs.*, Tech. Pub. 43 (1927).

[127] W. Rosenhain, and P. A Tucker, *Trans Roy Soc (London)*, (A) **209**, 89 (1908).

[128] W C Phebus, and F C Blake, *Phys. Rev* , **25**, 107 (1925)

[129] H O. v Samson-Himmelstjerna, *Z Metallkunde*, **28**, 197–202 (1936)

[130] M. Kawakami, *Z. anorg allgem. Chem.*, **167**, 345–63 (1927).

MAXIMUM CALORIES OF HEAT OF FORMATION
(in calories per gram atom)

INVESTIGATORS	TEMPERATURE (° C)	HEAT OF FORMATION
Samson-Himmelstjerna	500	−250
Kawakami	350	−320
Magnus and	Not recorded	−310
Mannheimer[131]	Not recorded	−120

Aoki[132] made hardness measurements on the tin-lead alloys and found that the hardness is not constant for different loads, and that the hardness of alloys rich in the gamma and delta phases increased with the load to a maximum and then decreased gradually Those rich in the alpha or beta phase increased until the samples broke. He stated that the times of loading, aging at room temperature, and annealing, affect the hardness, the effects depending upon the structure of the phase

Aoyama and Hukuroi[133] determined the rigidity moduli for the binary alloys of tin and lead and antimony at temperatures of −195° and 18° C. The moduli for the tin-lead alloys showed steady increase with increasing amounts of lead. The tin-antimony alloys showed a maximum at about 40 per cent antimony The moduli all increased with a decrease in temperature The amount of increase from room temperature to −195° C. was 22 per cent for tin

Moissan and O'Farrelly[134] found that lead could be almost completely distilled from alloys in the electric furnace.

Solders consist of tin and lead in various proportions, and bismuth is added when a more fusible alloy is required. The commercial applications of solders are discussed in greater detail elsewhere in this volume. The same holds true for pewter and bearing metals.

An interesting application of tin-lead alloys is in Fahlun brilliants, used for stage jewelry This is a 40 tin–60 lead alloy, which when molten is cast into molds, facetted like cut diamonds. The finished brilliants showily reflect the light from their bright white surfaces

The hardening of ternary alloys, such as type metal, increases with the tin content, temperature of casting, and rate of cooling. Hardening can also take place starting from the solid metal at a temperature of 180° or over. These alloys can undergo tempering even at atmospheric temperature. At the end of seven months an alloy which had been cast in a chill mold had undergone approximately 67 per cent of the contraction which

[131] A. Magnus, and M Mannheimer, *Z physik Chem*, **121**, 267–88 (1926)

[132] N Aoki, *Kinzoku no Kenkyuh*, **11**, 1–20 (1934).

[133] S. Aoyama, and T Hukuroi, *Science Repts Tôhoku Imp. Univ*, *First Ser*, **29**, 728–36 (1941).

[134] Moissan, and O'Farrelly, *Compt. rend.*, **138**, 1659 (1904).

occurred after complete annealing. Dilatometric study of lead-tin alloys showed that, with 0 to 1 per cent tin, lead which had been cast in chill molds showed signs of hardening; but after annealing at about 200°, it could not be hardened from the solid state On the contrary, tin containing a few tenths per cent lead can be hardened from the solid state. The degree of hardening of lead–tin alloys increases with the tin content to a maximum at 16 per cent. The dilatometric curves obtained on cooling pure lead showed one or two breaks indicating allotropic modifications. In studying the transformation, rhombohedral Sn $\rightleftarrows$ quadratic Sn, the calorimetric curves exhibited a discontinuity (break or flattening) at about 171–2°, when the molten tin had been overheated several hours at or above 500°.

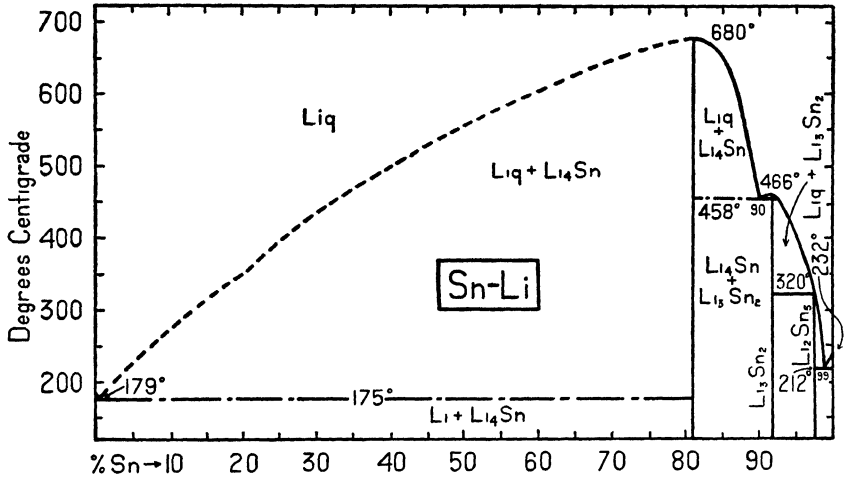


FIGURE 105 Diagram of tin-lithium system

Tin-Lithium

The tin-lithium compounds are of scientific interest only, finding no uses at present in industry. Masing and Tammann[135] showed that three compounds are formed, Li_4Sn, $Li_{13}Sn_2$, and an unstable material, Li_2Sn_5, which reacts with the melt.

The thermal equilibrium diagram is shown in Fig 105. Tin lowers the melting point of lithium four degrees to a eutectic at 175° C. The liquidus curve is assumed to rise to the maximum at 680° C., the melting point of the Li_4Sn compound The liquidus then drops to the eutectic at 458° C. at 90 per cent tin. The eutectic constituents are the compounds Li_4Sn and $Li_{13}Sn_2$. From the eutectic the liquidus rises to 466° C., the

[135] Masing, and Tammann, *Z. anorg. Chem.*, **67**, 183 (1910).

melting point of Li_3Sn_2, to drop rapidly to 212° C. at 99 per cent tin, the eutectic between Li_3Sn_2 and tin The liquidus curve is broken slightly at 320° C. owing to the formation of the unstable compound Li_2Sn_5

The tin-lithium alloys are readily corroded They react with water, the lithium being attacked to leave a tin skeleton. They are all white and silvery in color They oxidize readily and are attacked by most chemical reagents

Tin-Magnesium

The thermal equilibrium diagram is given in Fig. 106 This diagram is based on the work of Grube,[136] Hume-Rothery,[137] Grube and Vosskuhler,[138] and modified by the work of Raynor [139] It is a simple eutectoid type, The liquidus curve, starting at 651° C , the melting point of magnesium

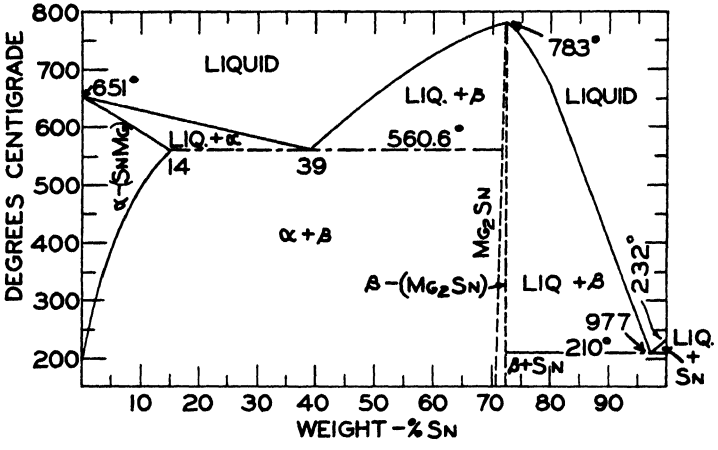


FIGURE 106 Diagram of tin-magnesium system

gradually falls to the eutectic at 560 6° C , containing 39 per cent magnesium The constituents of the eutectic are magnesium and the compound $SnMg_2$ The freezing-point curve rises from the eutectic to 783° C , the melting point of the compound $SnMg_2$ (71 per cent tin, 29 per cent magnesium). From here the curve drops rapidly to a eutectic at 210° C , a point corresponding to 2 3 per cent magnesium and 97 7 per cent tin. The constituents of this eutectic are the compound $SnMg_2$ and pure tin From the eutectic, the freezing-point curve rises to the melting point of pure tin. The compound $SnMg_2$ crystallizes well, is brittle, and readily tarnishes in air

[136] G Grube, *Z. anorg. Chem* , **46**, 76 (1905)
[137] W Hume-Rothery, *J. Inst Metals*, **35**, 336 (1926)
[138] G Grube, and H. Vosskuhler, *Z. Elektrochem* , **40**, 566 (1934).
[139] G. V. Raynor, *J. Inst. Metals*, **66**, 403–26 (1940).

Raynor[139] determined the liquidus lines of the magnesium-rich end of the tin-magnesium system by cooling curves and the solidus and solid-solubility lines by microscopic examination and x-ray experiments. The liquidus curve for tin-magnesium falls smoothly from the melting point of magnesium to a eutectic at 560 6° C. and 10 7 atomic per cent tin The solid solubility of tin is 3.35 atomic per cent at 560.6° C. and decreases to 0 6 atomic per cent at 350° C and less than 0 2 atomic per cent at 250° C , as shown in Fig. 107.

The solidus curve drops from 651° C. to a point located by the solidus line at 560 6° C. and 14 per cent tin All alloys between 14 and 71 per

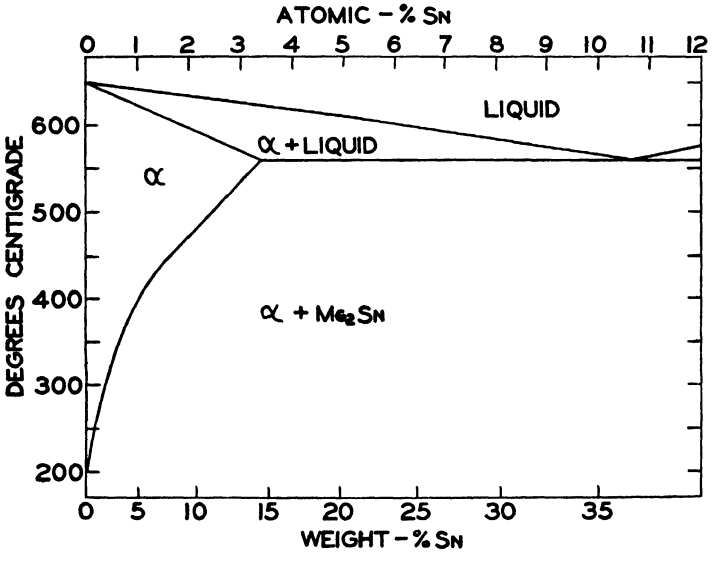


FIGURE 107 Partial diagram of tin-magnesium system showing concentrations in both weight and atomic percentages

cent tin finally become entirely solid at 560 6° C. and consist of mixtures of alpha (solid solution of tin in magnesium) and beta (compound $SnMg_2$) Between 71 and 97 7 per cent tin, the solidus line is at 210° C., at which point all the alloys in this range freeze entirely, becoming mixtures of beta (compound $SnMg_2$) and tin The compound beta exists alone without admixture over a very narrow and small area It has a well-marked octahedral cleavage which makes the alloys brittle.

The heats of formation at temperatures from 600 to 650° C. over wide concentration ranges were obtained by Kubaschewski and Walter.[140]

[140] O. Kubaschewski, and A. Walter, *Z. Elektrochem.*, **45**, 732–40 (1939).

The heat of formation for one molecular weight of $SnMg_2$ was found to be 17.2 k. cal, and for one gram atom, 5 7 k. cal.

Phipson[141] claimed that the alloy with 85 per cent tin, 15 per cent magnesium, was lavender blue It decomposed water at ordinary temperatures Beck[142] stated that the molten alloy containing 50 per cent tin absorbs 40 per cent of nitrogen Borchers and Beck[143] recommended it for obtaining nitrogen from the air

The tin-magnesium alloys in some ways have properties similar to those of tin and aluminum

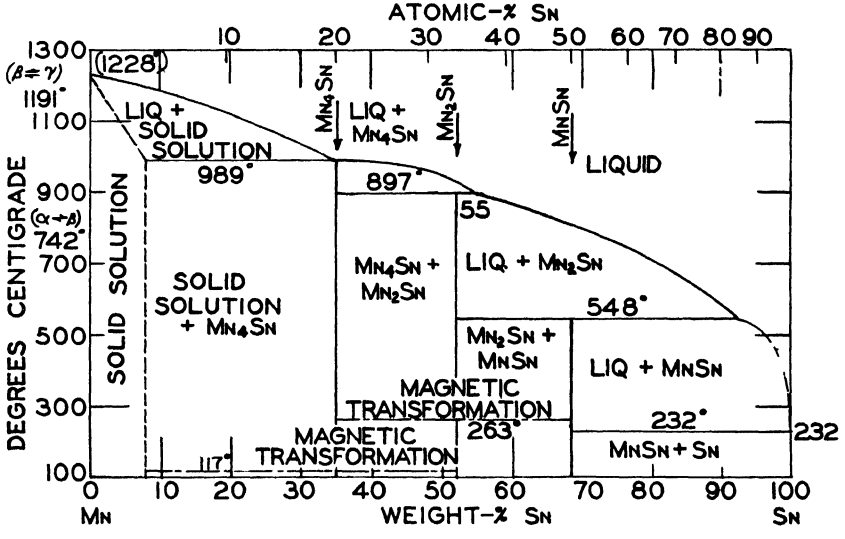


FIGURE 108 Diagram of tin-manganese system

Tin-Manganese

According to the constitution diagram Fig. 108 developed by Williams[144] there are three compounds formed by peritectic reactions: Mn_4Sn (35.07 per cent tin), Mn_2Sn (51.93 per cent tin), and probably MnSn (68.36 per cent tin). The manganese used contained 98.71 per cent manganese, 0.64 per cent iron, 0.32 per cent silicon dioxide, and traces of sulfur and ferric oxide The formulae were determined from the time of the peritectic transformation. In reference to the compounds Mn_4Sn and Mn_2Sn, the microscopic findings were in agreement with the results of the thermal analysis. The alloy which corresponded with the composition Mn_4Sn was homogeneous after the quick cooling of the melt. The alloy which

[141] Phipson, *Proc. Roy Soc (London)*, **13**, 217 (1864).

[142] Beck, *Metallurgie*, **5**, 504 (1908).

[143] Borchers, and Beck, *German Patent 193,323* (1906).

[144] R. S Williams, *Z anorg. allgem Chem.*, **55**, 24–31 (1907)

corresponded with the composition Mn_2Sn was consolidated to one phase after annealing for 24 hours at 850° C. The alloy of the composition MnSn after annealing for 80 hours at 530° C. contained three types of crystals (Mn_2Sn, MnSn(?), and Sn). Williams, therefore, does not think that the formula MnSn is clearly proved, although the maximum of the arrest periods at 548° C is near the corresponding composition of the alloy. It cannot be said whether the horizontal line which corresponds to the solidification of the alloys with more than 68 4 per cent tin is a eutectic or a peritectic line because Williams determined the solidification point at 230° C. (instead of 232° C.) and the temperature of the horizontal line at 230 to 231° C. The solid solubility of manganese in tin is at all temperatures very low.

There is complete miscibility in the liquid condition. In the solid condition, solutions are formed from 96 to 100 atomic percentage manganese. Pushin[145] stated that the alloys of 0 to 30 to 40 atomic percentage manganese are white and soft. At 50 atomic percentage manganese they are harder and porous. With further increases of manganese they become brittle, reaching a maximum at 66 atomic percentage. The alloys of tin and manganese containing 75 atomic percentage of the latter metal are granular in structure, very hard and brittle

Qualitative investigations of Williams showed that the compound Mn_4Sn, and to a smaller extent Mn_2Sn, can be magnetized, the loss of magnetizability occurs at 115 to 119° C and 260° to 265° C. respectively The results of the quantitative magnetic measurements of Honda[146] agree with the phase diagram of Williams, as far as they permit conclusions about the constitution. The alloys which contain the crystal type Mn_4Sn show (except for induced magnetism) a comparatively strong remaining magnetism. The curve of the remaining magnetization has a very steep maximum and passes through zero at about 8 to 10 per cent (saturated solid solution) and 52 per cent tin (Mn_2Sn). The curve of the induced magnetization passes between 52 and 100 per cent tin quite irregularly (no equilibrium); between 8 to 10 per cent tin and 52 per cent tin, the magnetization changes to two straight lines which cross each other at maximum at Mn_4Sn.

The tin-manganese system has not as yet been thoroughly confirmed Potter[147] investigated the magnetic properties of tin-manganese alloys

Tin-Mercury

Tin and mercury unite quickly at ordinary temperatures and still more rapidly if the mercury is poured into molten tin. Tin readily dissolves in

[145] N Pushin, *J. Russ Phys Chem Soc*, **39**, 353–99 (1907)
[146] K. Honda, *Ann physik.*, **32**, 1023–5 (1910)
[147] H. H. Potter, *Rept. Brit. Assoc.*, **98**, 297 (1930).

mercury even in the cold, and mercury dissolves in tin. Liquid tin and mercury are miscible in all proportions.

The freezing-point equilibrium curves are given in Fig. 109. This is based on the work of Heycock and Neville,[148] Pushin,[149] van Heteren,[150] Tammann,[151] and Joyner[152] as coordinated by Hansen.[153] The addition of mercury to tin lowers its freezing point but only at a relatively slow rate The curve is smooth With appreciable amounts of mercury, the alloys are liquid. The curve is almost a straight line from the melting point of tin to about 120°, when it gradually bends until it reaches 40°, at which point it falls almost vertically with the temperature axis At low temperatures, the amount of tin in the saturated liquid amalgam is very small. Liquid amalgams, as represented by the equilibrium curve, deposit either pure tin or tin associated with very little mercury. The solid phase at 25° contains 94 per cent tin On cooling the amalgams containing 0.18 to 85 per cent tin to −34 5°, a change takes place which is accompanied by

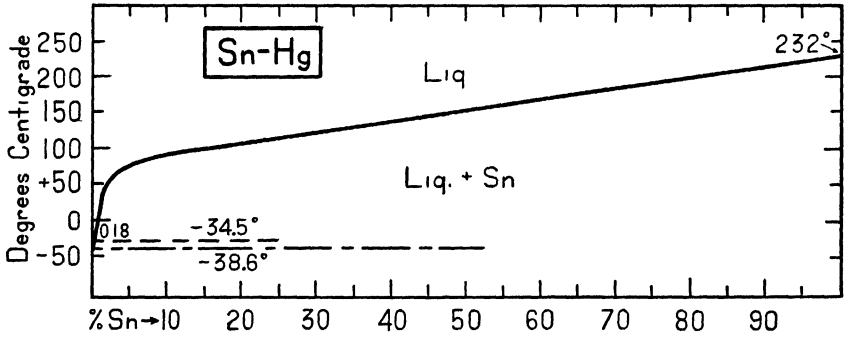


FIGURE 109 Diagram of tin-mercury system

the development of heat and a diminution in volume. The maximum change occurs when the amalgam contains about 50 per cent tin. All amalgams containing up to 60 per cent of tin finally solidify at −38.6°. Between −34 5° and −38 5°, mixed crystals separate and expansion takes place. It has not been found possible to determine what modification of tin is then deposited, but its specific volume must be smaller than that of gray tin and larger than that of the ordinary variety. From the study of the microstructure, there has been no evidence of the formation of chemical compounds. When atomic proportions exceed $SnHg_4$, the alloys are

[148] C T. Heycock, and F. H Neville, *J. Chem. Soc.*, **57**, 383 (1890).

[149] N A. Pushin, *Z anorg Chem.*, **36**, 201–54 (1903)

[150] W. J. van Heteren, *Z anorg Chem* , **42**, 129–73 (1904).

[151] G Tammann, *Z physik. Chem* , **3**, 445 (1889).

[152] R A. Joyner, *J. Chem Soc* , **99**, 204 (1911).

[153] M. Hansen, "Der Aufbau der Zweistofflegierungen," Berlin, Verlag von Julius Springer, 1936.

liquid at ordinary temperatures. Those with more tin than $SnHg_2$ are solid. The amalgam $SnHg_2$ is very soft and is quite fluid at 100°. If the mercury is not in excess, the color of the amalgams is that of tin Behrens[154] stated that an amalgam with 10 per cent of mercury is harder than tin and can be filed. When broken, the fractured structure shows six-sided prisms under the microscope. Under similar conditions, a 20 per cent mercury amalgam shows octahedral crystals.

The tin-mercury alloys have been used for silvering mirrors. When alloyed with a third metal in ternary systems, they have been and are employed in dentistry (see Tin-Silver)

Tin-Nickel

Mikulas, Thomassen and Upthegrove[155] reviewed the work of Heycock and Neville,[156] Gautier,[157] Vigouroux,[158] Guillet,[159] Voss,[160] Oftedal,[161] Hanson, Sandford, and Stevens,[162] and Fetz and Jette[163] and the previously proposed constitution diagrams. The constitution diagram is given in Fig. 110. They reported that two eutectics occur, at low nickel content and 232° C., and at 68.5 per cent nickel and 1124° C. They found two areas of liquid immiscibility, at 5 to 18 per cent nickel, and at 24 to 46 per cent nickel Ni_3Sn_4 forms peritectically at 793° C Ni_3Sn_2 solidifies at 1253° C. with a tetragonal structure having parameters of $a = 5\ 111$ Å. and $c = 4.881$ Å. At 941° C , $Ni_{14}Sn$ decomposes into Ni_3Sn and solid solution of tin in nickel. They found that a small amount of tin dissolved in nickel at 400° C., increasing up to 18 per cent at 1100° C

Heumann[164] stated that the Mikulas diagram was revised by chemical, thermal, microscopic and x-ray analysis Heumann reported that Ni_3Sn_2 (gamma) melts at 1264° C and Ni_3Sn melts at 1160° C. and that there is an unstable peritectic point in the gamma phase at 90 per cent nickel and a transformation at 600° C. Alpha nickel contains a maximum of 19 per cent tin at 1130° to 1010° C., and a minimum of 1.5 per cent tin at 300° C. The beta phase has a maximum of 1174° C. and transforms at approxi-

[154] Behrens, "Das mikroskopische Gefuge der Metalle und Legierungen," p. 53, Hamburg, L. Voss, 1894

[155] W Mikulas, L Thomassen, and C Upthegrove, *Trans Am Inst Mining Met Engrs , Inst. Metals Div* , **124**, 111-33 (1937)

[156] C T Heycock, and F H. Neville, *J. Chem. Soc* , **57**, 378 (1880).

[157] H Gautier, *Bull soc encour ind. nat* , (5), **1**, 1316 (1896), *Contributions a l'étude des alliages (Paris)*, 112-3 (1901).

[158] E. Vigouroux, *Compt rend* , **144**, 639–41, 712–4, 1351–3, **145**, 246–8, 429–31 (1907)

[159] L Guillet, *Rev met* , **4**, 535–51 (1907), *Compt rend* , **144**, 752–5 (1907)

[160] G. Voss, *Z. anorg. allgem. Chem.*, **57**, 35–45 (1908).

[161] I Oftedal, *Z. phys Chem* , **132**, 208–16 (1928)

[162] D Hanson, E J Sandford, and H Stevens, *J. Inst Metals*, **55**, 117–9 (1934).

[163] E. Fetz, and E. R Jette, *Metallwirtshaft*, **14**, 165 (1935)

[164] T. Heumann, *Z. Metallkunde*, **35**, 206–11 (1943).

mately 900° C. from the disordered to the ordered phase with a closely packed hexagonal structure. Heumann did not find Ni_4Sn present.

Fetz and Jette[165] studied the phase relationships in the tin-nickel system They extended the x-ray investigation of the system beyond the solubility limit of tin in nickel The next phase to the nickel solid solution phase occurred at Ni_3Sn, and this phase was in equilibrium with a phase having a typical nickel-arsenic structure up to Ni_5Sn_3 The nickel-arsenic structure first appears alone at Ni_5Sn_3, and extends as a homogeneous phase up to 45 atomic per cent tin, which requires an excess of nickel atoms to stabilize the lattice At Ni_3Sn_2 a new phase forms from the nickel-arsenic-like phase at temperatures below 500° C. It was the opinion of Fetz and Jette

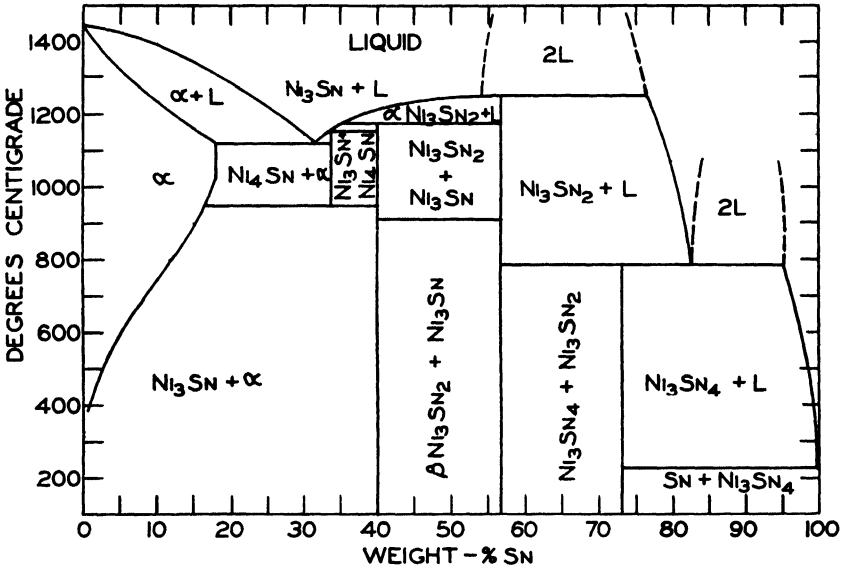


FIGURE 110 Diagram of tin-nickel system

that it may be a deformed modification of the previous phase and does not occur at 38.0 or 42.5 atomic per cent tin. The homogeneity range of the nickel-arsenic structure is said to be independent of temperature on the high-tin side, but increases slightly at higher temperatures on the high-nickel side. They reported that three new phases, eta, theta, and zeta occur at 51, 54, and 56 to 62 atomic per cent tin. The phase forms by a peritectoid reaction between the nickel-arsenic structure and the theta phase The zeta phase coexists with the tin phase from 62 per cent to practically 100 per cent tin. The solubility of nickel in tin is very low.

Hanson, Sandford, and Stevens[166] tried to determine the solidification

[165] E. Fetz, and E R. Jette, *J. Chem Phys* , **4**, 537 (1936)

[166] D. Hanson, E J. Sandford, and H. Stevens, *J. Inst. Metals*, **55**, 117-9 (1934)

points of the tin-rich alloys with up to 2 per cent nickel With a chemical-analytical method they found the melting points of the alloys with 0 18, 0 19, 0 23, 0 31, and 1 29 per cent nickel at 240, 280, 320, 425, and 550° C The end point of solidification was practically at the melting point of tin, the solubility of tin was less than 0 005 per cent at 228° C

The solidus temperature of the high-tin alloys was found to be very close to the melting point of tin Solidus-temperature determinations gave variations from 231 to 232° C The same variations were obtained in calibrating the thermocouple used against Chempur tin The results obtained by Mikulas, Thomassen and Upthegrove[167] confirmed the conclusions of Hanson, Sandford and Stevens that the addition of nickel does not lower the melting point of tin

Tin-Phosphorus

The alloys of tin and phosphorus, particularly with low percentages of the second element, are quite important in commerce as the phosphor tins They find employment, along with the phosphor coppers, in the manufacture of phosphor bronzes

The system, as shown in Fig 111, is largely due to Vivian,[168] adapted from Haughton [169] The system has been only partially investigated, and only that portion from 0 to 50 per cent phosphorus has been studied Vivian prepared the alloys in sealed glass tubes embedded in sand in an enclosing steel case A thermocouple for temperature measurement was cemented into contact with the glass tube Up to 8 per cent phosphorus, the alloys were obtained by carefully fusing a high-percentage product at atmospheric pressure The work was attended by great experimental difficulty in the higher ranges of phosphorus, as it was found that for the formation of alloys above 2 5 per cent phosphorus the vapor phase was necessary. Pressures above atmospheric were required for alloys containing more than 8 5 per cent phosphorus The tin-phosphorus system is noteworthy, therefore, inasmuch as pressure is usually considered as an invariant in thermal concentration diagrams of the metallurgical type

Vivian stated that from 6 5 to 20 per cent phosphorus, conjugate solutions occur, but between 16 and 30 per cent phosphorus there is little sign of conjugate solutions remaining in the cooled ingot Above 30 per cent, elementary phosphorus appears, but conjugate solutions are roughly indicated at high temperatures Up to about 12 per cent phosphorus the ground mass contains 14 7 per cent phosphorus, which repre-

[167] W Mikulas, L Thomassen, and C Upthegrove, *Trans Am Inst Mining Met Engrs , Inst Metals Div* , **124**, 111-33 (1937)

[168] A C Vivian, *J Inst Metals*, **23**, 325 (1920).

[169] Haughton, *J. Inst Metals*, **23**, 361 (1920).

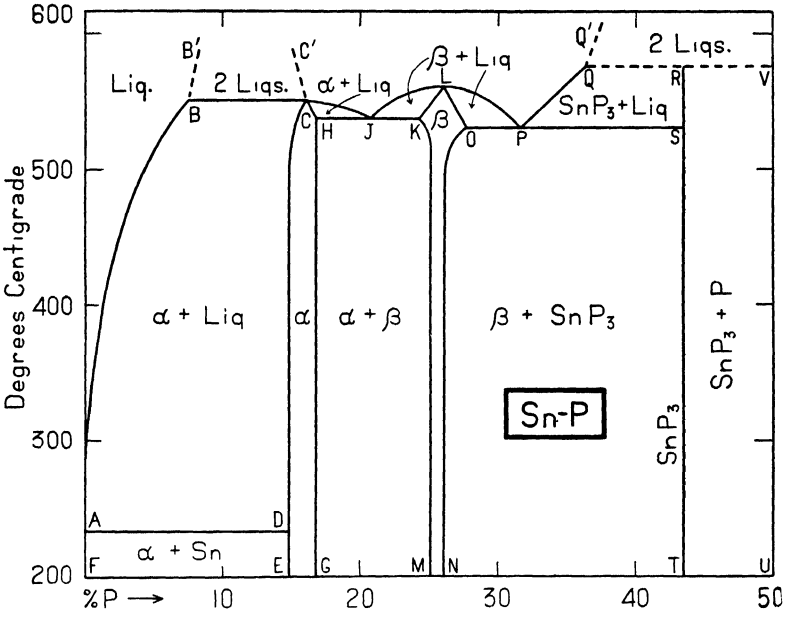


FIGURE 111 Diagram of tin-phosphorus system

sents the maximum solid solution (alpha$_1$) of tin in Sn_4P_3 (alpha$_2$). The alpha-beta eutectic contains 20 5 per cent phosphorus, and freezes at 540° The beta-phosphide contains 25 8 per cent phosphorus, corresponding to Sn_3P_4 Above 26 per cent phosphorus, the gamma-phosphide (about 44 per cent phosphorus) occurs as black strings The beta-gamma eutectic contains about 31 3 per cent phosphorus and freezes at 530°. Above 44 per cent phosphorus, the alloys contain red phosphorus The vapor phase is necessary for the formation of alloys above 2 5 per cent phosphorus The tin arrest decreases with the phosphorus content to nil at 14 5 per cent From the data obtained, a temperature concentration diagram up to 50 per cent phosphorus is indicated

It has been suggested that the diagram shown may be regarded as a sloping section cut through a three-dimensional model having three variables: concentration, temperature, and pressure However, as the pressures used were not measured and necessarily varied in the different experiments, no definite section or plane can be considered. The investigator felt it advisable to reject the view of a three-dimensional model, since the pressure functioned solely in determining the phosphorus concentration.

With this explanation and also the mode of experimentation, the diagram to be described must not in any way be regarded as final. Haughton's nomenclature has been adopted in discussing this work, as his dia-

gram attempts a provisional representation of equilibrium conditions which is in keeping with phase rule requirements.

Alloys from the tin end of the diagram begin to solidify along the liquidus AB which mounts almost vertically up to 400° C, then slopes to 550° for a phosphorus content of 8.5 per cent, shown at the point B From theoretical considerations, Haughton shows the eutectic containing a minute quantity of phosphorus, but as this quantity is unknown and so small, it is difficult to show on a diagram of the size plotted. Further work may establish the existence of the eutectic, but the cooling curves of Vivian certainly did not show it, and for practical purposes its consideration can be rejected.

Alloys between B and C, from 8.5 to about 15 5 per cent phosphorus, form two immiscible liquids at about 550° C Dotted lines BB' and CC' illustrate in a limited way the concentrations and temperatures at which the conjugate solutions may exist Somewhere just above 600° it is probable that the lines BB' and CC' join, and the liquids of these compositions are mutually soluble, one liquid phase only being present The line BC is the liquidus for alloys of the above concentrations Therefore the area bounded by the liquidus curve ABC and the solidus AD, which is the horizontal at 232° C. and the almost vertical solidus DC, contains the alpha-solid solution plus liquid. Below the solidus AD the alloy consists of pure tin and alpha-solid solution.

The area $EDCHG$ denotes the limits of the alpha-solid solution; E indicates 14.7 and G 16.3 per cent phosphorus. The nomenclature adopted in this area is Haughton's interpretation of the experimental results obtained by Vivian, and the line HG shows the maximum solubility of tin in the compound Sn_4P_3. Vivian's notation in this area is confusing and does not fulfill phase-rule conditions

The area CHJ represents two phases, alpha-solid solution and liquid metal The liquidus line CJ meets the solidus CHJ at the first definite eutectic point J at 20 per cent phosphorus. Alloys of increasing phosphorus content begin to freeze along an ascending liquidus JL to the maximum temperature at L, the point of total freezing for a single concentration of the beta-solid solution. The point L may justifiably be regarded as the compound Sn_3P_4 from its mode of freezing, but more experimental data will prove or disprove such a hypothesis. The solidus of alloys of concentrations between C and L is shown by the line CH, eutectic horizontal HJK, and line KL. The area JKL represents the existence of two phases: beta-solid solution, which is a probable solid solution of tin in Sn_3P_4, and liquid metal.

The beta-solid solution is bounded on the one side by the solidus KL and the line of solid solubility KM, and on the other side by the solidus LO and line of solid solubility ON. Vivian's results show a possible

junction of solid solubility lines *KM* and *ON* at about 440°, but for theoretical requirements it is necessary to show a solid solution as an area and not as a line of invariant concentration.

Alloys in the area *GHJKM* consist of the alpha-solid solution plus beta-solid solution.

The area *LOP* denotes mixtures of beta-solid solution plus liquid The liquidus *LP* intersects the solidus *LOP* at the second eutectic *P*.

Proceeding to higher compositions of phosphorus, the liquidus rises to the point *Q* at 580° C and then supposedly proceeds along the horizontal *QRV*.

Alloys of composition *Q* and of increasing phosphorus content are believed to form conjugate solutions above 580° C The line of liquid miscibility *QQ'* is drawn dotted to indicate this probability.

At about 43 per cent phosphorus and at 580° C , a compound which would have a formula SnP_3 appears, and the line *RST* denotes its concentration Alloys in the area *ONTSP* consist of two phases: the beta-solid solution plus the compound SnP_3

Concentrations of phosphorus greater than 43 per cent indicate the existence in the solid state of the compound SnP_3 and elemental red phosphorus, but such mixtures have received little study

Commercially the tin-phosphorus alloys of low concentration are ordinarily formed by causing stick phosphorus, held in a graphite phosphorizer, to dissolve in molten tin.

Tin-Platinum

Upon the addition of platinum to tin, according to Podkopaev[170] the fusion point of tin is gradually lowered, reaching a minimum at the eutectic point of 224° C , corresponding to 2 per cent platinum. Podkopajew and Doerinckel[171] gave the temperature as 228° Further additions of platinum cause a quick rise in the melting-point curve which reaches a maximum at 1324° C. (Podkopajew and Doerinckel 1300°) This corresponds to 50 atomic per cent of platinum The curve then drops to a eutectic point of 1065° C. (Podkopajew and Doerinckel 1072°), corresponding to 59 atomic percentage platinum, then again quickly rises to 75 atomic per cent platinum, corresponding to the compound $SnPt_3$ at 1400° C (Podkopajew and Doerinckel 1365°). The melting-point curve then continues upward to the melting point of pure platinum Tin lowers the freezing point of platinum

Alloys rich in tin—that is, up to about 5 atomic per cent of platinum—are very soft With increase of platinum up to about 50 per cent they become microcrystalline and brittle. The compound SnPt is extremely

[170] Podkopaev, *J Russ. Chem. Soc.*, **40**, 249–60 (1908)

[171] N. Podkopajew, and F. Doerinckel, *Z anorg. allgem Chem.*, **54**, 349–58 (1907)

brittle When fractured it shows shiny shell-like or conchoidal faces. With further increases of platinum up to 60 to 75 atomic per cent, the brittleness decreases Still further additions of platinum cause the alloys to become tougher and more tenacious

A constitutional diagram based on the work of Podkopajew and Doerinckel[172] is shown in Fig. 112 They determined that the compounds Pt_3Sn (16 85 per cent tin), PtSn (37 81 per cent tin), Pt_2Sn_3 (47 65 per cent tin in two polymorphous modifications) exist with another tin-rich intermediary phase

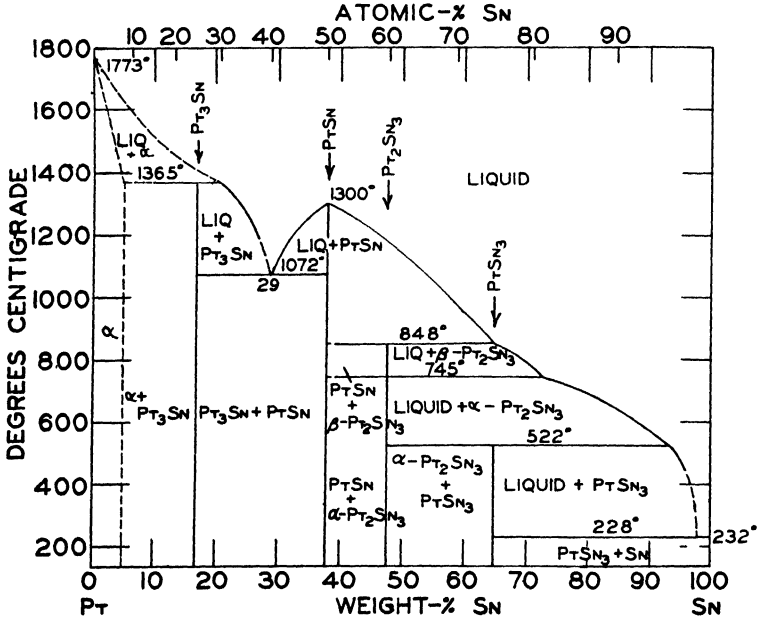


FIGURE 112 Diagram of tin-platinum system

The Pt_3Sn—PtSn eutectic point according to Doerinckel is at about 27 5 per cent tin, and according to Podkopajew about 30 per cent tin. The compound richest in tin is, according to Doerinckel (but not quite certain), Pt_3Sn_8 (61 58 per cent tin) Podkopajew gave the formula $PtSn_3$ (64.59 per cent tin) The simpler formula $PtSn_3$, which requires only 3 per cent more tin, is the more likely one According to Doerinckel, the solidification of the tin-rich melts is terminated by the crystallization of practically pure tin Podkopajew determined a lowering of the melting point of tin by 8° C by platinum The concentration of the eutectic is unknown.

[172] *Ibid.*

The curve of solubility of tin in platinum has not been completely investigated According to the arrest period, which was determined by Doerinckel at 1365° C , about 5 per cent tin is soluble in platinum at this temperature Barus[173] determined the temperature coefficient of the electric resistance of alloys with about 1 4, 2 3, and 6 per cent tin and found progressive lowering of the resistance, indicating the formation of mixed crystals

The compound PtSn has a hexagonal lattice structure of the type of NiAs

Doerinckel[174] also stated that there are only two compounds in the system completely defined by formulae, Pt_3Sn and PtSn He assigns probable formulae to others, Pt_2Sn and Pt_3Sn_8, but finds that most of these so-called compounds decompose during melting Only the PtSn compound melts unchanged.

Tin is ordinarily a deleterious constituent of platinum in its commercial applications

Tin-Potassium

Gay Lussac and Thenard[175] found that a mixture of 7 volumes of tin filings to 2 volumes of potassium united with slight incandescence A fusible brittle alloy was formed The material had a fine-grained structure, oxidized quickly in air, and decomposed water When larger proportions of potassium were employed, the alloy took fire when heated in air The tin-potassium alloys are pyrophoric and liberate hydrogen from water Tin and potassium are stated to be miscible in all proportions in the fused state Most of the alloys melt at temperatures higher than the melting points of the original constituents

The thermal equilibrium diagram according to Smith[176] is given in Fig 113, but inasmuch as a considerable portion of the system is as yet unconfirmed in an authoritative manner, the liquidus curve is represented by dotted lines. The alloys rapidly attack glass and even steel The results of the thermal analysis, therefore, are not very conclusive The addition of tin to potassium or of potassium to tin raises the melting point of the solvent metal Starting from the potassium side, the addition of tin to potassium, melting at 63° C , causes a rise of the liquidus curve at a rapid rate to a break at a point indicated by the cross section of the thermal-level line of 535° and 44 per cent tin The liquidus curve rises to another break at the cross section of the thermal-level line at 670° and 62 per cent tin, owing to the formation supposedly of the compound K_2Sn

[173] J Barus, *Am J Sci* (3), **36**, 434 (1888)
[174] F Doerinckel, *Z anorg Chem* , **54**, 333–66 (1907)
[175] Gay Lussac, and Thenard, *Metall u. Erz* (2), **1**, 40 (1816)
[176] D P Smith, *Z. anorg Chem* , **56**, 129 (1907)

The liquidus curve rises further to an undetermined break at approximately 75 per cent tin, owing to the formation of the compound KSn, and then to an undetermined maximum at approximately 85 per cent tin, owing to the formation of the compound KSn_2. From the maximum, it drops to a break at 96 per cent tin and the temperature level of 600°, where the compound KSn_4 is formed. From this break the liquidus drops directly, with a minor break at 98.5 per cent tin, to 232°, the melting point of pure tin Knowledge of the potassium-tin alloys is unsatisfactory Kremann and Pressfreund[177] found evidence of the compounds

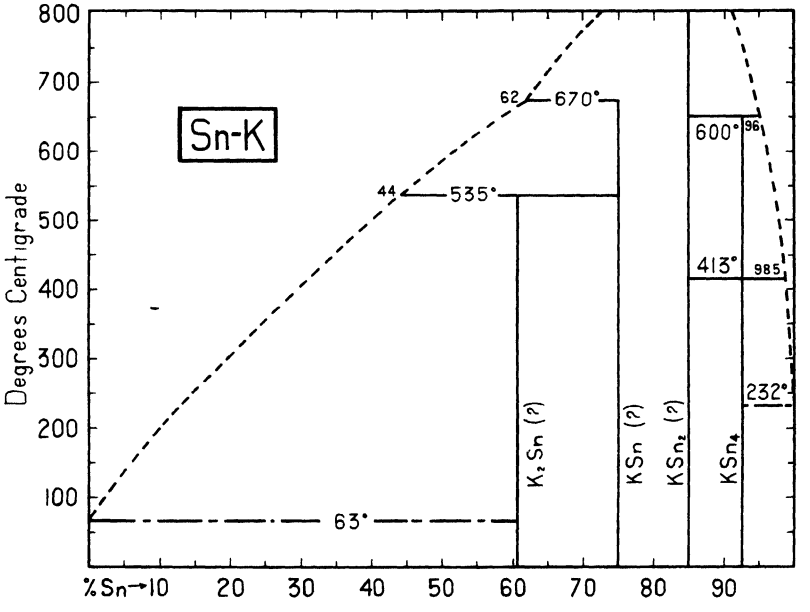


FIGURE 113. Diagram of tin-potassium system

K_2Sn, KSn_2 KSn_4, and possibly KSn in their measurements of the electromotive behavior of the tin-potassium alloys.

The corrosive action of tin-potassium alloys on ordinary materials of construction is quite marked.

Tin-Selenium

The compounds SnSe (59.98 per cent tin) and $SnSe_2$ (42 84 per cent tin) have been described in the chemical and mineralogical literature as products of chemical reaction.

The constitutional diagram is given in Fig. 114 as an approximation

[177] R Kremann, and E. Pressfreund, *Z. Metallkunde*, **13**, 19 (1921).

from the work of Pelabon[178] and Biltz and Mecklenburg[179] who gave an almost complete diagram. They considered a compound Sn_2Se_3 possible from their data as the result of a peritectic reaction of the melt at 650° C. The diagram was drawn from the standpoint that SnSe and $SnSe_2$ are the major compounds formed

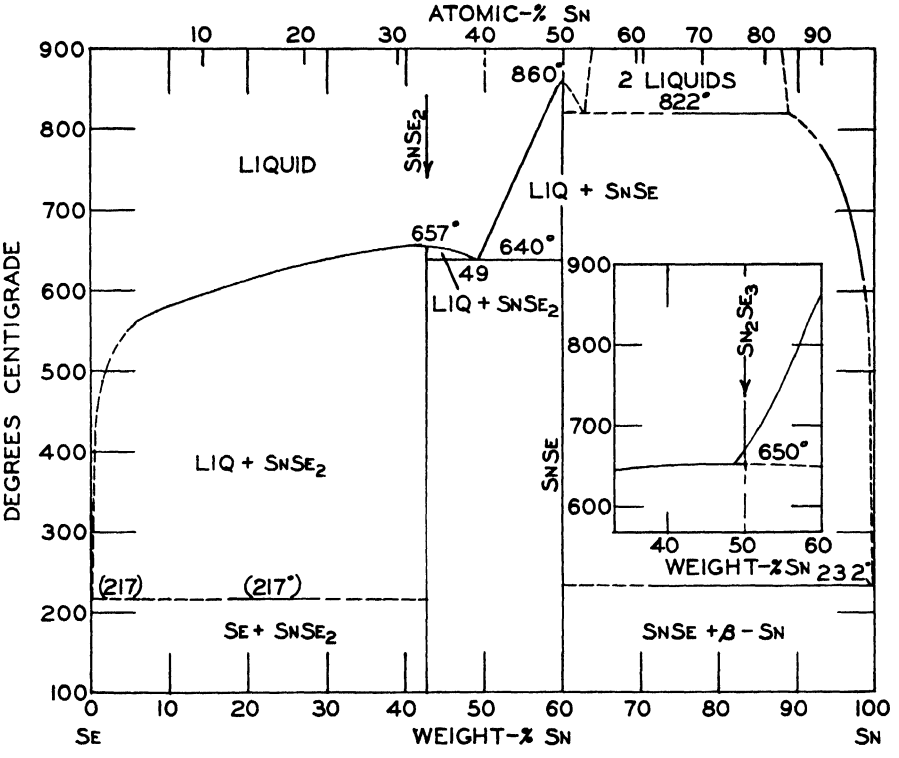


FIGURE 114. Diagram of tin-selenium system

Tin-Silicon

Vigouroux[180] found that the tin-silicon alloys are mixtures of the components This fact was confirmed by Tamaru[181] by thermal analysis and the findings are shown in Fig 115 Melts which were made with quite pure silicon (0 4 per cent iron, 0.4 per cent aluminum) showed a considerably higher temperature of solidification than those which were made with less pure silicon (6.1 per cent iron, 1.74 per cent aluminum). The

[178] H Pelabon, *Compt rend Acad. Sci. (Paris)*, **142**, 1147-9 (1906), **154**, 1414-6 (1912); *Ann. chim. phys* , No. 8, **17**, 526 (1909).

[179] W. Biltz, and H Mecklenburg, *Z. anorg allgem. Chem.*, **64**, 226-35 (1909).

[180] E. Vigouroux, *Compt rend. Acad. Sci. (Paris)*, **123**, 116 (1896).

microscopic investigation showed that all alloys contain primary crystallized silicon which is surrounded by practically pure tin.

Jette and Gebert[182] concluded from measurements of the lattice constants that there are no solid solutions of the two components in each other.

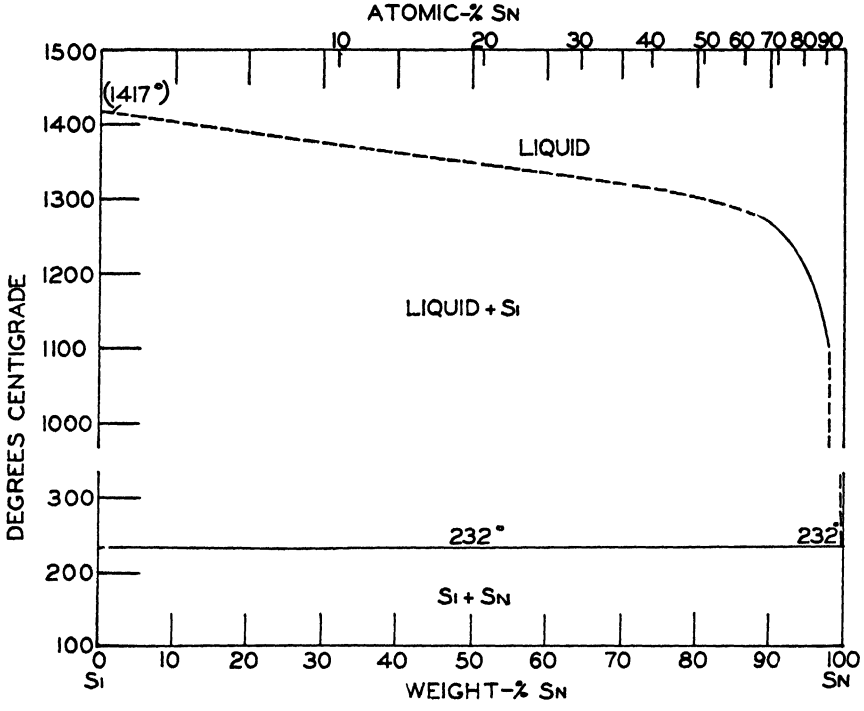


FIGURE 115. Diagram of tin-silicon system

Tin-Silver

The tin-silver alloys are employed in making dental amalgams. The binary alloy appears to undergo profound changes through the lapse of time. Black[183] showed that fresh filings of tin-silver alloys require 50 per cent more mercury for amalgamation than do similar filings which have been aged for several months or heated to 100° for a half hour. The aging does not occur in a bar of alloy during several weeks' heating under the same conditions where filings are aged in an hour. Exclusion of air does not affect the results. Black did not study the effect on bars and

[182] E R Jette, and E B Gebert, *J Chem Phys*, **1**, 753 (1933)

[183] Black, "A Work on Operative Dentistry," Vol. 2, p 309, Chicago, Medico Dental Pub. Co, 1914; *Dental Cosmos*, **37**, 353, 469, 553, 571, 637, 737 (1895), **38**, 43, 965, 982 (1896).

blocks of the alloy Studies by Loebich and Nowack[184] have proven that the mechanical properties of tin-silver amalgams depend not only on their silver content, but also on the manner of preparation as well as other additional material present The specific gravity of the alloys is greater than the mean between the specific gravities of the constituents Alloys with silver and tin in the proportion of 2 to 1 are hard, while those in the proportion of 1 to 2 are malleable. A number of workers[185] have shown that if the tin-silver alloys be well annealed, the presence of only one compound, $SnAg_3$, is shown With alloys containing over 50 per cent tin, there is a solid solution of silver in $SnAg_3$ The $SnAg_3$ compound becomes stable below 460° In the case of solid solutions, a frequent formation of

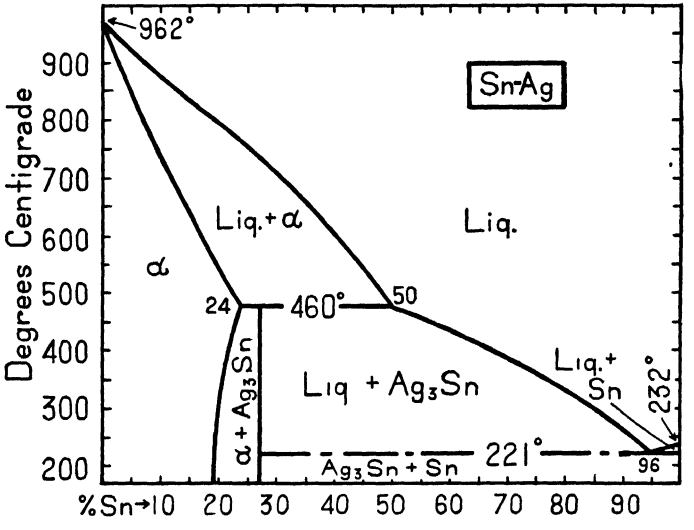


FIGURE 116 Diagram of tin-silver system

twin crystals can be noticed. After annealing for a longer period, the compound $SnAg_3$ consists of polygonal crystals covered by a fine criss-cross pattern Hansen and Sachs[186] studied the electric conductivity of silver-rich tin-silver alloys

The thermal equilibrium diagram for the system, based on the work of Petrenko,[187] is given in Fig 116 Hanson, Sandford, and Stevens,[188] and Homer and Plummer[189] suggested various changes and interpretations.

[184] Loebich and Nowack, *Deut zahnarztl Wochenschr*, **34**, 139–45 (1931).

[185] A. J. Murphy, *J Inst Metals (London)*, **35**, 107 (1926), O. Nial, A. Almin, and A Westgren, *Z physik Chem*, **14**, 81–90 (1931)

[186] M Hansen, and G Sachs, *Z Metallkunde*, **20**, 151 (1928).

[187] G I Petrenko, *Z anorg Chem*, **53**, 204 (1907).

[188] D Hanson, E J Sandford, and H. Stevens, *J Inst Metals*, **55**, 115 (1934)

[189] C E Homer, and H. Plummer, *J Inst Metals*, **64**, 191 (1939).

The liquidus curve starts at the melting point of silver, 962°, and, with increasing percentages of tin, drops to a break at 50 per cent tin and the temperature level of 460°, continuing then to the eutectic at 96 per cent tin and 221°, and rising from there to 232°, the melting point of tin. The solubility of tin in silver varies with the temperature. The area alpha is a solid solution of tin in silver. The solidus curve drops from 962° to the junction point of the temperature level of 460° and 24 per cent tin. In the area between the solidus and the liquidus at this point, the solid solution of tin in silver is in equilibrium with the molten metal. From approximately 19 to 27 per cent tin and between the temperatures of 460° and room temperature, the solid alloy consists of a mixture of a solid solution of tin in silver and the compound $SnAg_3$ Between 27 and 96 per cent tin and 460° and room temperature, the area represented between the temperature levels of 460° and 221° shows the compound $SnAg_3$ in equilibrium with the molten alloy. As a result of the reaction between the compound and the liquid, there are formed below 221° mixed crystals of the compound $SnAg_3$ plus tin metal From 96 to 100 per cent tin, the area between the solidus line at 221° and the liquidus curve shows tin in equilibrium with the molten alloy, reacting at 221° to form mixed crystals of the compound $SnAg_3$ plus tin

The alpha-solid solution is characterized by prolific twinning of the crystals, accompanied by the development of finer marking following the course of cleavage planes in the crystals The compound $SnAg_3$, after prolonged annealing, consists of polygonal crystals with fine crosshatch markings.

There has been considerable diversity of opinion as to the compounds formed between silver and tin. None of these, with the exception of $SnAg_3$, has been confirmed.

McLennan, Allen, and Wilhelm[190] found that in the alloy, silver-tin, the superconductivity metal silver depressed the transition temperature. They stated that a binary alloy system composed of one superconductor and one nonsuperconductor may have more than one transition temperature. Superconductivity appears at higher temperatures in eutectic alloys than in compounds of the same metals, and this is said to be caused by the large internal forces in eutectics.

Silver up to 3.5 per cent greatly improves the creep resistance of tin Hanson and Sandford[191] described the results of creep tests of long duration on tin and some of its alloys. Table 14 gives the results of creep tests on pure tin and silver-tin alloys as reported by these workers, and Fig. 117 shows the duration plotted against the initial stress. It can be seen that an increase in life can be effected by small additions of silver to tin; thus

[190] J. C. McLennan, J F. Allen, and J. O. Wilhelm, *Phil Mag*, **13**, 1196–209 (1932).
[191] D. Hanson, and E J. Sandford, *J. Inst. Metals*, **59**, 159 (1936).

TABLE 14 RESULTS OF CREEP TESTS ON PURE TIN AND TIN-SILVER ALLOYS*

TIN			0 01% SILVER			0 02% SILVER		
Stress (lb /in ²)	Duration (days)	Final Extension (%)	Stress (lb /in ²)	Duration (days)	Final Extension (%)	Stres (lb /in ²)	Duration (days)	Final Extension (%)
1,025	0 5	78	1,027	0 6	102	1,002	1	81
611	4 6	105	603	7	95	604	10	97
468	21	119	460	27	117	472	37	110
402	79	132	407	92	147	404	143	64
327	173	101	323	199	95	324	307	98
196	(551)	(7)	—	—	—	—	—	—
157	(551)	(3 5)	—	—	—	—	—	—
0 04% SILVER			0 1% SILVER			3 5% SILVER		
1,006	1 6	73	1,011	3	49	1,996	10	62
602	24	67	603	44	59	1,845	15	60
475	71	72	462	236	59	1,614	34	52
405	250	68	406	369	74	1,407	74	76
347	602	62	339	644	66	1,193	157	66
—	—	—	200	(541)	(3 5)	1,100	211	50
—	—	—	160	(541)	(1 5)	1,002	449	57
—	—	—	—	—	—	800	(220)	(1 74)
—	—	—	—	—	—	700	(220)	(0 84)

* D. Hanson, and E J Sandford, *J. Inst Metals*, **59**, 162 (1936)
The figures in parentheses are for specimens which did not fracture

0 1 per cent causes a fourfold increase at stresses of about 300 lb per sq in. The strength of the same alloy for any particular duration is about 1.5 times that of pure tin The alloy containing 3 5 per cent silver has a considerably greater resistance to creep than pure tin, under a stress of 1000 lb. per sq. in this alloy fails only after 449 days, whereas pure tin fails in less than one day, for the same duration this alloy is nearly three times as strong as pure tin

Umanskii[192] reported that the alpha phase in a tin-silver alloy shows a limited but increasing solubility of 9 5 to 11 1 per cent tin and the beta phase of 11 7 to 12 4 per cent silver

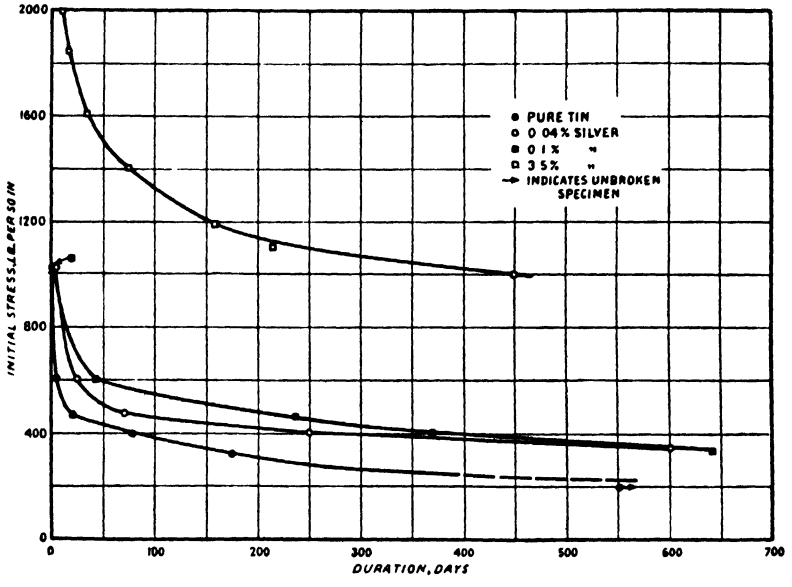


FIGURE 117 Stress duration curves for tin-silver alloys

The commercial application of tin-silver alloys is largest in dental work, in the manufacture of instruments, and similar usages

Tin-Sodium

Studies of the tin-sodium alloys show that they have properties similar to the tin-potassium series Heycock and Neville[193] found that the freezing point of tin was raised 11 61° by the addition of 4 57 atomic per cent of sodium

The thermal equilibrium diagram according to Mathewson[194] is given

[192] M M. Umanskii, *J Phys Chem* , (*U S S R*), **14**, 846–9 (1940)
[193] C T. Heycock, and F. H. Neville, *J Chem Soc* , **55**, 666 (1889), **57**, 380 (1890).
[194] C. H. Mathewson, *Z. anorg. Chem.*, **46**, 94 (1905).

in Fig. 118 It is of the same general nature as the tin-potassium alloys The addition of sodium to tin markedly affects the freezing point The liquidus curve rises from 97 5°, the melting point of sodium, to a break at approximately 58 per cent tin and 405°, which is the eutectic between sodium and the compound Na_2Sn and corresponds to the compound Na_4Sn The liquidus rises from this eutectic to a first maximum at 470° and 72 1 per cent tin The curve then drops to a eutectic at 440°, rises to a break at 478° and 80 per cent tin, corresponding to the compound Na_4Sn_3,

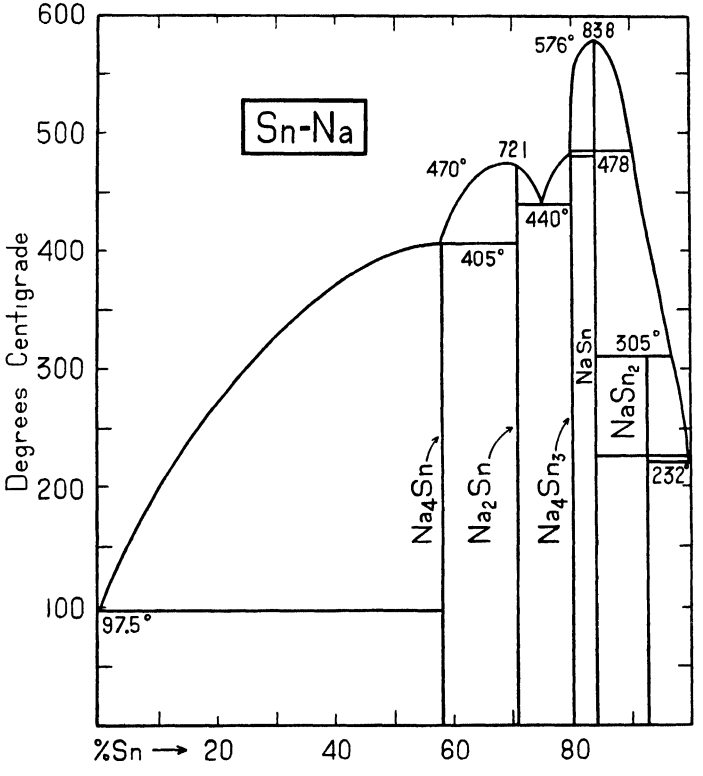


FIGURE 118 Diagram of tin-sodium system

and continues to a maximum at 576°, 83 8 per cent tin, corresponding to the compound NaSn. From maximum the liquidus drops directly to the melting point of tin, 232°, with breaks at 478° and 305°. The compound Na_4Sn above 405°, being in equilibrium with the molten alloy, undergoes transformation at 405° with the formation of the compound Na_2Sn and fused alloy. The compound Na_4Sn_3 is the hardest and most brittle of the five formed At 478° it melts with a transformation into NaSn plus fused alloy. The compound NaSn, with a melting point of 576°, under-

goes a polymorphic transformation at 483°, according to the data of Mathewson.[195] The compound $NaSn_2$ is the softest and toughest of all. This material, as well as NaSn, looks the same as tin metal. Mathewson stated that a freshly cut surface of the Na_4Sn or the Na_2Sn alloy soon becomes covered in the air with a bronze film. When protected by oil, the surface of the Na_2Sn compound resembles that of tin, while the color of the Na_4Sn material is steel blue. The Na_4Sn_3 compound shows a pale blue color on a freshly cut surface. Kremann and Gmachl-Pammer[196] found that the electrical conductivity curve showed singular points corresponding with Na_4Sn, Na_2Sn, NaSn, and $NaSn_2$

Because of their lack of commercial application, as well as the extreme difficulty in studying this system, many of the compounds in the curves are in doubt

Tin-Strontium

The alloys of tin and strontium have been little studied They are difficult to prepare as a result of the rapid oxidation of the strontium metal under ordinary atmospheric influences Even with protective layers of fluxes, considerable metal is lost With appreciable percentages of strontium, they are decomposed by water, leaving a tin skeleton

The tin-strontium system has not been thoroughly investigated. It is stated that the alloys are similar to those of tin and calcium

Ray[197] concluded from thermal and microscopic investigations (especially after annealing for several hours at 240° C) of tin-rich tin-strontium alloys, that there are two compounds, Sn_5Sr (12 87 per cent strontium) and Sn_3Sr (19.75 per cent strontium) Figure 119 shows the corresponding phase diagram.

Tin-Tellurium

Tin and tellurium unite to form the compound SnTe which, according to Fay,[198] melts undecomposed at 769°. This compound forms a eutectic with tellurium, as shown in the thermal equilibrium diagram in Fig. 120, which contains 85 per cent tellurium melting at 399° C The compound SnTe also forms a eutectic with tin of exceedingly low tellurium concentration

The tin-tellurium system has been little studied, partly because of the experimental difficulty in making alloys of high tellurium content Tin and tellurium unite with the evolution of considerable heat.

The solubility of SnTe in tin is exceedingly low and is as yet undetermined. The tin-tellurium alloys are not of industrial importance.

[195] *Ibid.*

[196] Kremann, and Gmachl-Pammer, *Z. Metallkunde*, **12**, 257 (1920).

[197] W. K. Ray, *Ind. Eng. Chem.*, **22**, 519–22 (1930).

inasmuch as they find practically no commercial applications. They are, however, of some scientific interest.

Tin-Thallium

The effect of thallium on the melting point of tin has been studied by a number of workers Thallium can absorb up to 20 per cent tin in solid solution The crystal structure of these alloys has been determined by Sekito [199] In its essentials the thermal diagram according to Fuchs,[200]

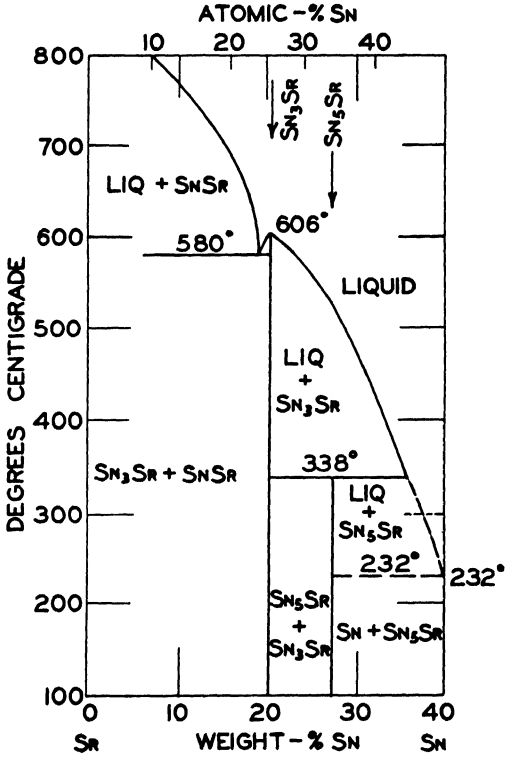


FIGURE 119.
Diagram of tin-strontium system

as shown in Fig. 121, is one of simple solution of the metals in each other, with but one eutectic and no compound formation The diagram is made more complex by the transition of thallium metal

The tin-thallium alloys are fusible and ductile The eutectic occurs at 42.5 per cent thallium, at a melting point of 167° C. Thallium markedly lowers the freezing point of tin. The eutectic line extends from 0 to 80

[198] Fay, *J. Am. Chem. Soc.*, **29**, 1265 (1907).
[199] S. Sekito, *Z. Krist.*, **74**, 189 (1930).
[200] P. Fuchs, *Z. anorg. Chem.*, **107**, 308 (1919).

per cent thallium Tin-thallium alloys with less than 80 per cent of thallium show a second arrest on cooling, in addition to the arrest point at the eutectic temperature, at 143° C This arrest represents the transition point of thallium, lowered through the influence of tin, from about

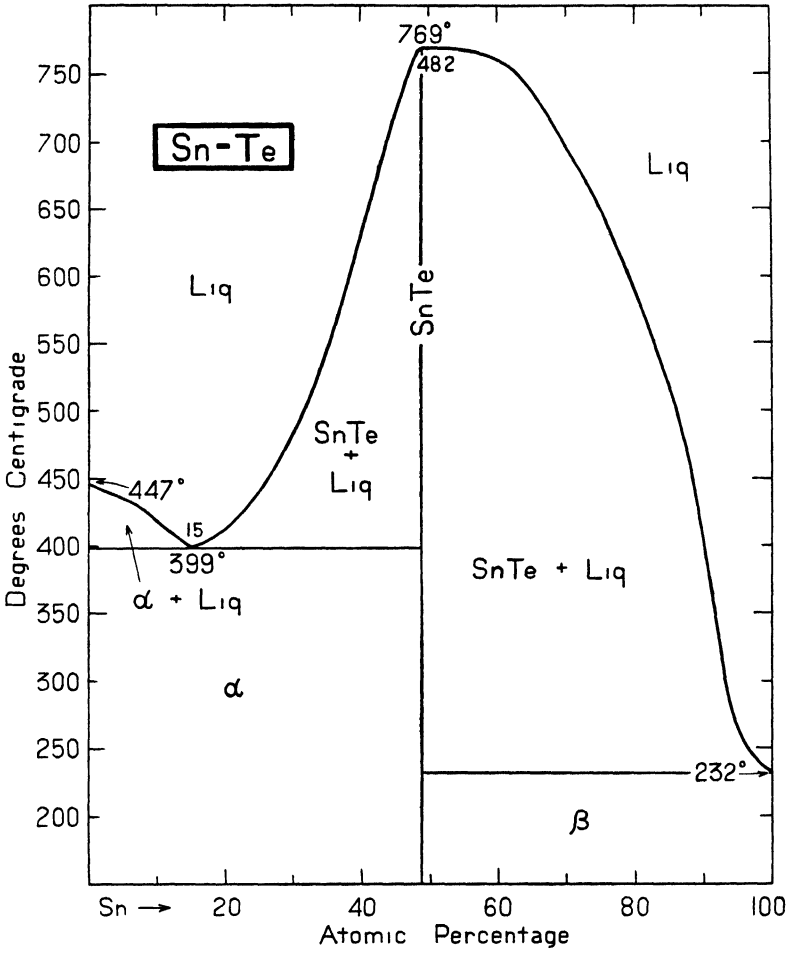


FIGURE 120 Diagram of tin-tellurium system

227° C In the solid solution region, from 80 to 100 per cent thallium, the transition point is lowered according to the amount of tin present.

Electromotive force measurements of the alloys show no signs of compound formation. Omodei[201] gives the melting point of a 30 per cent thallium alloy as 186° C., a specific gravity of 7.786 when molten, and

[201] Omodei, *Atti, accad. Fisico critici siena* (4), **2**, 515 (1890).

8.054 when solid It has a high coefficient of thermal expansion, being 0 0001184

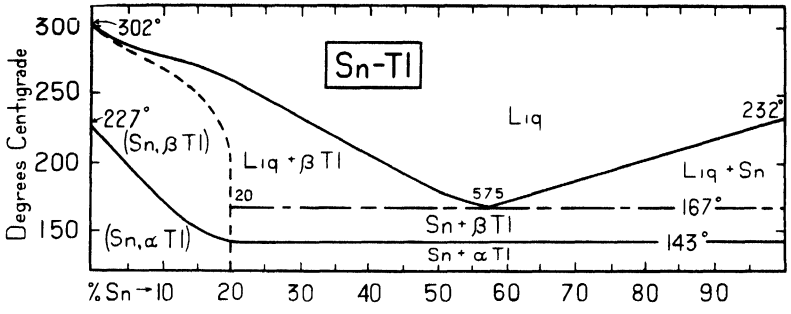


FIGURE 121 Diagram of tin thallium system

Tin-Zinc

The tin-zinc alloys are readily formed by melting together mixtures of the metals A large number of workers in the field have shown that the two metals are mutually soluble in all proportions in the fluid state The system, as shown in Fig 122, is of the simple eutectic type There is no evidence of solid solubility on the zinc side There is definite evidence

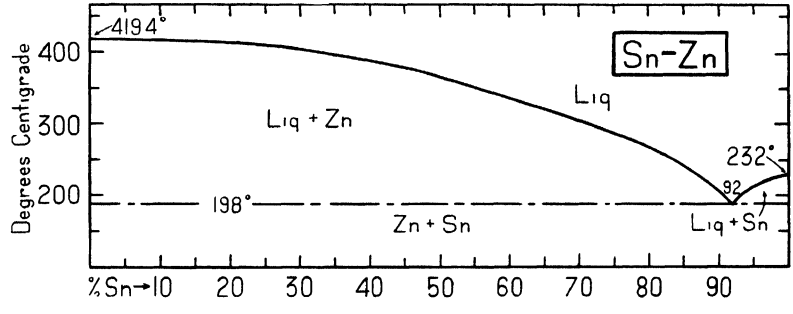


FIGURE 122 Diagram of tin-zinc system

that if zinc holds any tin in solid solution, the limit is less than 0 05 per cent The data of Fuchs[202] and Endo[203] indicate that the limit of solid solubility of zinc in tin is not over 0 03 or 0.05 per cent zinc by weight The eutectic temperature is 198° C The eutectic itself has a tin concentration of 92 1 per cent, with 7.9 per cent zinc Alloys up to 92 1 per cent tin, therefore, contain primary zinc crystals and the eutectic. The surface tension between the eutectic and the zinc crystals is low. The eutectic, therefore, even when present in very small amounts (less than 0.05 per

[202] P. Fuchs, *Z anorg Chem*, **109**, 80–8 (1920).

[203] H Endo, *Science Repts Tôhoku Imp Univ, First Ser* **14**, 479–512 (1925).

cent tin), forms extensive, thin, intercrystalline films These are exceedingly brittle and are ordinarily considered to be a cause of hot shortness, because of their low melting point.

Kurzyniec[204] investigated a series of tin-zinc alloys ranging from 0 to 100 per cent zinc, which were tempered a long time at 190° C , and the R_t/R_o values were determined after four days' standing for 20.3° K (−252.3° C.) and 77.3° K (−195.7° C.) and after standing 50 days for 20.3° K (−252 3° C). Kurzyniec found that above 80 atoms per cent zinc, the time of standing had no effect on the R_t/R_o value, but for alloys containing smaller proportions of zinc, the value decreased considerably during the standing. The maximum value for R_t/R_o lies between 1 and 2 atomic per cent zinc

De Haas, Van Aubel, and Voogd[205] found that in eutectic mixtures of tin-zinc, the temperature at which superconductivity begins is influenced by the nonsuperconducting admixtures Merz and Brennecke[206] studied the speed of diffusion of zinc in liquid tin.

J. W. Richards[207] suggested that the alloy in the proportions of Sn_4Zn_3 would be useful as a solder for aluminum Habermann[208] recommended the alloy with 83 per cent zinc for the production of hydrogen from acids. Lambert[209] used an alloy of tin, zinc, and antimony as an aluminum solder

Bauer and Zunker[210] recommended the addition of small amounts of tin to cast zinc because of the heavy reduction in shrinkage

Vicentini[211] found that the microstructure of the alloys of tin and zinc is difficult to interpret owing to the tendency of the alloys to liquate.

Tin-Zirconium

Marden and Rich[212] were unable to make a zirconium-tin alloy directly Cooper[213] made pyrophoric alloys of zirconium and 20 to 40 per cent tin

The tin-zirconium system has been little investigated. The commercial applications and possible uses of the alloys are only minor and on an exceedingly small basis.

[204] E. Kurzyniec, *Bull. intern. acad. polon. sci., Classe sci. math nat , Series A* (in German) 489–97 (1938).

[205] W J. De Haas, E Van Aubel, and J. Voogd, *Proc Acad Sci. (Amsterdam)*, **32**, 715–23 (1929).

[206] A Merz, and E. Brennecke, *Z. Metallkunde*, **22**, 189, 234 (1930)

[207] J W Richards, *J Franklin Inst.*, **140**, 351 (1895).

[208] Habermann, *Z anal Chem* , **28**, 88 (1889).

[209] Lambert, *U S Patent 906,637* (1908).

[210] O Bauer, and P Zunker, *Z Metallkunde*, **23**, 39 (1931)

[211] Vicentini, *Atti accad lincei* (5), **1**, 383 (1892).

[212] J. W. Marden, and M. N. Rich, "Investigations of Zirconium with Especial Reference to the Metal and the Oxide," *Bur. Mines Bull.*, 186 (1921); *J Ind. Eng. Chem.*, **12**, 651 (1920).

[213] H. S. Cooper, *Trans. Am. Electrochem. Soc.*, **43**, 209 (1923).

Chapter 12

Ternary and Quaternary Alloys

Ternary Systems

A large number of ternary alloys containing tin and lead have been investigated Those upon which a large amount of work has been done have the following as the third constituent: aluminum, antimony, arsenic, barium, bismuth, cadmium, calcium, copper, magnesium, mercury, potassium, silver, sodium, thallium, and zinc

Amalgams. Gayler[1] studied the constitution of the alloys of silver, mercury, and tin with particular reference to their dental applications as amalgams Except for a range of composition extending from the tin corner to a composition of 6 per cent mercury, the liquidus of silver-mercury-tin alloys was determined From the experimental data obtained, isothermal sections were plotted for temperatures of 70, 84, and 100° C. Five invariant reactions occurred, while two others were deduced from experimental and theoretical evidence

The composition of the dental filling itself can be correlated with its dimensional changes on setting. The investigation into the ternary silver-mercury-tin alloys has, however, thrown light on this complex problem.

The compositions of dental fillings made from alloys of various components have been inserted in the diagram representing the constitution at 70° C. of silver-mercury-tin alloys, which, however, will differ only very slightly, if at all, from that at mouth temperature, *i e.*, 37° C. The numbers against the dots in Fig 123 are the numbers of the dental alloys used for making the amalgams; their composition can be read off from Fig. 124

The amalgams may be divided into the following three groups, according to their behavior on setting:

(1) Marked expansion	1, 13, 14, 20
(2) Slight expansion	2, 7, 15, 22, 27, 28
(3) Contraction	5, 6, 8, 9, 11, 12, 19, 26

The dental alloys from which these groups of amalgams are made contain respectively: (1) less than 25 per cent tin, (2) between 25 and 27 per cent tin; and (3) more than 27 per cent tin

[1] M. L. V. Gayler, *J. Inst. Metals*, **60**, 379–406 (1937).

Schulze[2] investigated the silver alloys in reference to their suitability as resistance materials He found that a silver alloy with a composition of 80 per cent silver, 17 per cent manganese, and 3 per cent tin underwent con-

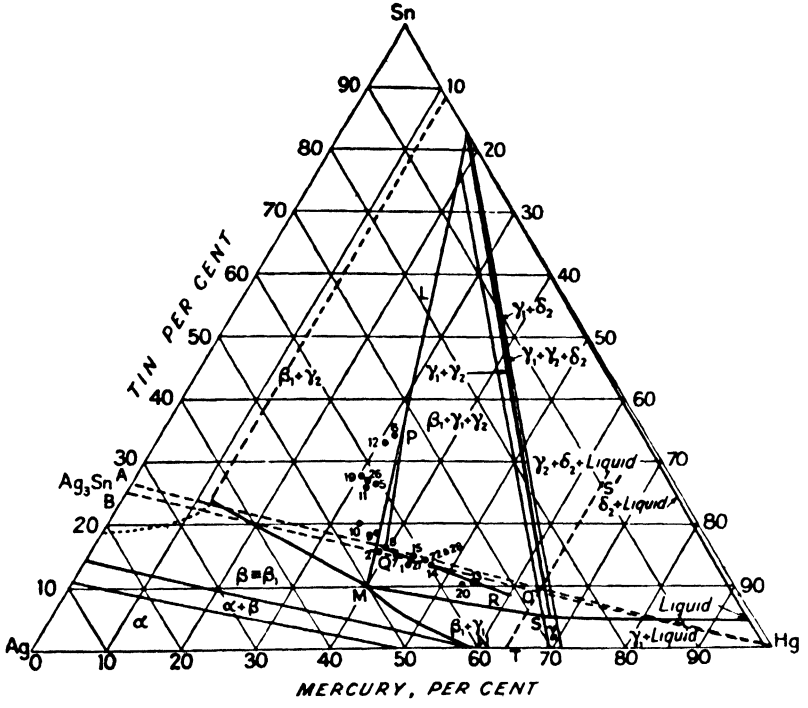


FIGURE 123 70°C Isotherm

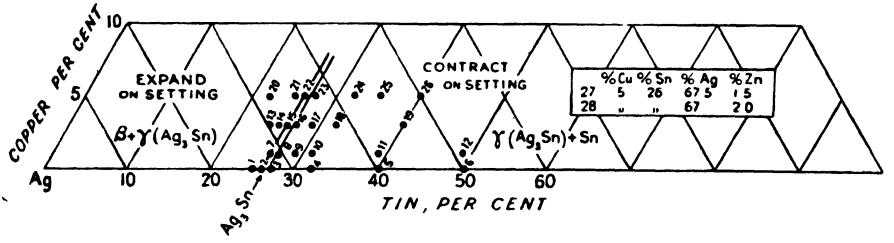


FIGURE 124 Constitution of dental alloys "as cast" Silver-tin-copper alloys. Amalgams made from alloys of composition indicated

siderable changes in electrical and mechanical properties when aged at temperatures up to 300° C It is conditionally suited for standard resistances Another silver alloy with a composition of 85 per cent silver,

[2] A Schulze, *Arch tech Messen Lfg*, **136**, 110 (1940), *Chem Zentr*, **II**, 1568 (1943)

8 per cent manganese, and 7 per cent tin showed quite a different behavior. Aging had practically no effect on the electrical properties This alloy has, however, no advantage over manganin

Duczko[3] investigated and prepared amalgams of silver, tin, and zinc. The two amalgams with the highest silver content were prepared by mixing mercury with electrolytic silver, and the others were prepared by the electrolytic method. This consists of depositing each metal from its anode through a solution of its salt and to the mercury cathode Duczko measured the single potentials against the hydrogen electrode After preparation, the amalgams were pressed under a pressure of 2,500 kg He stated

TABLE 15 PROPERTIES OF AMALGAMS OF SILVER, TIN, AND ZINC*

METAL IN AMALGAM	%	BRINELL HARDNESS	DENSITY	RESISTIVITY (ohm cm 36°)	E_a^1 18°	E_a^2 23°
Ag	47 02	103 00	13 09	0 042 × 10^{-4}	0 4381	0 8290
Ag	32 67	112 00	14 25	0 045 × 10^{-4}	0 3493	0 8396
Ag	32 52	18 50	12 34	0 187 × 10^{-4}	0 7085	0 8336
Ag	27 47	20 00	13 26	0 093 × 10^{-4}	0 6512	0 8410
Ag	21 25	8 7	13 40	0 103 × 10^{-4}	0 6374	0 8357
Sn	79 69	8 00	7 95	0 088 × 10^{-4}	0 2350	0 2119
Sn	79 43	7 40	8 04	0 081 × 10^{-4}	0 2325	0 2119
Sn	72 09	6 42	8 36	0 076 × 10^{-4}	0 2290	0 2119
Zn	42 55	15 20	10 54	0 069 × 10^{-4}	0 7538	0 7355
Zn	32 23	13 40	11 34	0 128 × 10^{-4}	0 7696	0 7295
Zn	31 65	13 30	11 49	0 119 × 10^{-4}	0 7519	0 7332

* K Duczko, *Przemysl Chem* , **19**, 10–13 (1935)

that amalgams of silver and tin form chemical compounds, while those of zinc form only an ordinary mixture This is in agreement with the results of Preston[4] and Stenbeck[5] Results of the investigations are shown in Table 15

Aluminum-Containing Alloys. The constitution, microstructure, and physical properties of the aluminum-rich Al-Mn-Sn alloys in the composition range of 0 to 20 per cent tin and 0 to 6 per cent manganese were studied by Schuck[6] He found that the manganese concentration of the binary aluminum-manganese (Al-Mn) eutectic is lowered by tin additions from 3 per cent manganese at 0 per cent tin to about 2 per cent manganese at 20 per cent tin In this range the eutectic temperature falls from 649° C at 0 per cent tin to 621° C at 20 per cent tin A ternary eutectic (Al-Sn-Al_7Mn) occurred at 228° C, the composition of the pure eutectic lying

[3] K Duczko, *Przemysl Chem* , **19**, 10–3 (1935)
[4] G D Preston, *J Inst Metals*, **46**, 522–7 (1931)
[5] S Stenbeck, *Z anorg allgem Chem* , **214**, 16–26 (1933).
[6] A Schück, *Z Metallkunde*, **27**, 11–8 (1935)

somewhere near 100 per cent tin. The compound Al_7Mn appeared as a primary constituent as well as a constituent of the binary and ternary eutectics and is a very hard material, appearing blue-gray under the microscope. Schuck observed a linear increase in the density of the binary aluminum-tin alloys from 2.74 at 0 per cent tin to 3 74 at 20 per cent tin Additions of manganese decreased the density slightly The Brinell hardness of the ternary alloys was increased linearly by manganese additions up to 3 per cent, beyond which no further increase was found

Tin decreased the hardness of all alloys, but most markedly of those containing the greatest quantities of manganese Both tin and manganese additions lowered the impact values progressively The corrosion resistance of the binary aluminum-tin alloys in dry and moist air and in water was improved noticeably by manganese additions up to 2 per cent. The ternary alloys machine well and take an excellent polish but present some difficulty in hot and cold working.

Nishimura and Tanaka[7] investigated the Al-Mg-Sn alloys containing up to 6 per cent tin and 12 per cent aluminum They annealed the specimens at 400° C. for 24 hours in a molten chromate bath before quenching in water and aging at room temperature The Brinell hardness measurements taken during aging did not show any noticeable increase in hardness at room temperature. Alloys containing 4 to 6 per cent tin and 10 to 12 per cent aluminum, however, hardened appreciably on tempering at 150 to 200° C.

Beryllium-Containing Alloys. Masing and Dahl[8] found that the addition of beryllium to alpha-solid solution of alloys of copper and tin caused them to undergo age-hardening after quenching from 700 to 800° C The presence of a third metal reduces the solid solubility of beryllium in copper so that smaller quantities of beryllium were necessary to produce the maximum hardening than was required in the case of copper With alpha-brasses with a high zinc content a small addition of beryllium increased the hardness of the quenched alloys considerably, and subsequent aging caused only a relatively small increase. The addition of less than 1 per cent aluminum to the 2 to $2\frac{1}{2}$ per cent beryllium-copper alloys accelerated the age-hardening without intensifying the action.

Bismuth-Containing Alloys. Bochvar and Gorev[9] studied the ternary alloys of Bi-Cd-Sn and found that a eutectic formed at 103° C.

Spring[10] also studied the Bi-Cd-Sn system.

[7] H. Nishimura, and K. Tanaka, *Suiyokai-Si*, **10**, 343–50 (1940)

[8] G. Masing, and O Dahl, *Wiss. Veröffentlich Siemens-Konzern*, **8**, No 1, 202–10 (1929).

[9] A. A. Bochvar, and K V. Gorev, *Z. anorg. allgem. Chem.*, **210**, 171–2 (1933)

[10] Spring, *Ber.*, **15**, 595 (1882).

Bochvar and Gorev[11] also studied the structure of the ternary eutectic Bi-Cd-Sn alloy, which had been previously melted, slowly cooled, and etched with a 1 per cent nitric acid solution. They found that the incipient crystallization of all of the three phases takes place not simultaneously, but successively. The metals can be arranged in the following order of their separation: cadmium, lead, tin, and bismuth.

Shishokin[12] stated that the deviation of experimental data plotted as log S *vs.* $1/T$ from the theoretical straight line in binary, and from the rectilinear isotherm in ternary systems, gives an idea of the character of the physicochemical processes which embrace association, disassociation, and combination of the molecular components taking place in the mutual alloying or solution of substances The thermodynamic properties of a ternary system are determined from those of the binary systems which limit it. It has been shown thermodynamically that the Bi-Cd-Sn system is not an ideal system, since the data do not lie on a straight line but gradually deviate from it with a decrease of the bismuth compound. In the same manner it was shown that the solid solution on the side of tin in the Cd-Sn system represents a solution of monatomic cadmium in monatomic tin.

Portevin and Bastien[13] found the castability of a pure metal to be a linear function of the difference between the pouring temperature and the melting point. The slopes of castability were found to vary with the viscosity of the metal, and inversely as the interval of primary crystallization. The castability of a Bi-Pb-Sn alloy is said to vary inversely with the primary solidification range, and in the cases where this is nil, along the binary eutectic lines in the ternary system, it varies with the secondary solidification range, reaching a minimum at compositions corresponding with the transition from the two-phase to three-phase

Bismuth-Lead-Tin Solders

The use of bismuth in low-melting alloys is not a new development. In 1898 Charpy[14] published a ternary diagram of the tin-bismuth-lead system which forms a eutectic at 204.8° F.

A low-melting solder is essential where a soldering operation involves a tempered steel part that can be easily overdrawn and low working temperatures must be maintained. Bismuth solders have long been recommended for this application.[15]

[11] A A Bochvar, and K V. Gorev, *Ann secteur anal. phys -chim , Inst chim gén (U.S S R)*, **8**, 283–90 (1936)

[12] V. P. Shishokin, *Trans Leningrad Ind Inst* No. 7, *Sect. Phys. Math* No. 4, 29–41 (in English, 41) (1937).

[13] A Portevin, and P. Bastien, *J. Inst. Metals*, **54**, 45–58 (1934).

[14] Charpy, *Compt. rend.*, **126**, 1569 (1898).

[15] **U. S. Army Specification No. 57–58.**

According to Rhines and Anderson,[16] the principal disadvantage of bismuth used as a major constituent of soft solders lies in the resulting low melting points which give rise to low strength above room temperature However, where this feature is not objectionable, the tin-bismuth-lead alloys are capable of producing acceptable joints The saving of tin effected by bismuth substitution is not directly proportional to the bismuth added, since lower lead contents must be used with bismuth

Bismuth has been added to solders in quantities sufficient to effect almost any desired lowering of liquidus temperatures An alloy containing 16 per cent bismuth and 14 per cent tin will have a liquidus temperature approximately the same as a 40–60 tin-lead solder.[17]

The transition temperatures of alloys containing bismuth were obtained by McLennan, Allen, and Wilhelm[18] and are shown in Table 16 They stated that the presence of bismuth in an alloy tends to raise the super-

TABLE 16 TRANSITION TEMPERATURES OF ALLOYS CONTAINING BISMUTH*

NAME	COMPOSITION	TRANSITION TEMPERATURE (°K)
Rose's metal	Bi_2PbSn	8 5
Newton's metal	Bi 50, Pb 31, Sn 19%	8 8

* J C McLennan, J F Allen, and J O Wilhelm, *Trans Roy Soc Can* (3) **24**, Sect 3, 25–35 (1930)

conducting temperature, while the presence of antimony sometimes raises and sometimes lowers the superconducting point

Shishokin and Zaporozhets[19] investigated a series of eutectic alloys containing tin, among which was the Bi-Pb-Sn eutectic They found that in all cases the temperature coefficient of hardness was greater for the alloys than for any of their components

Abbott[20] recommended using a fusible alloy of bismuth-lead-tin in vapor-diffusion pumps He boiled the alloy in a metal pump by a tungsten-to-alloy arc. The pump was warmed up in two minutes to approximately 1800° C , and gave a rough to fine vacuum of 40μ to 0.5μ

Hardness determinations were made on ternary and quaternary alloys containing tin by Shishokin and Zaporozhets [21] They found that the tem-

[16] F N Rhines, and W A Anderson, *Metals and Alloys*, **14**, 704 (1941)

[17] A J Phillips, *Metal Ind (London)*, **62**, 150–1 (1943)

[18] J C McLennan, J F Allen, and J O Wilhelm, *Trans Roy Soc Can* (3), **24**, Sect 3, 25–35 (1930)

[19] V P Shishokin, and I D Zaporozhets, *Tsvetnye Metal* , No 5–6, 88–98 (1937)

[20] F R Abbott, *Rev. Sci. Instruments*, **13**, 187 (1942)

[21] V P Shishokin, and I. D. Zaporozhets, *Ann secteur anal phys -chim , Inst chim gén. (U S S R.)*, **10**, 161–86 (1938).

perature coefficient of hardness, alpha, of the ternary and quaternary alloys in the region of the eutectic was greater than alpha of the pure metals It was three to four times greater for the ternary and four to five times greater for the quaternary alloys as compared with the two to three times greater alpha for the binary alloys previously investigated. The hardness coefficient (alpha) of the heat-treated eutectic alloy Bi-Pb-Sn is lower than those of the untreated alloys For the alloys containing both tin and cadmium, the hardness and the temperature coefficient (alpha) values of heat-treated alloys were found to be greater The displacement of the maximum in these systems is said to be explained by the presence of a eutectoid point As with the binary alloy tin-cadmium, the greatest increase of the temperature coefficient of hardness (alpha) was observed not with the eutectic alloys, but with those with the relatively greater cadmium content

Cadmium-Containing Alloys. The ternary system Cd-Ag-Sn was investigated by Moeller[22] by x-rays and microscopically at the sections Ag_5Sn-$AgCd_3$ and Ag_5Sn-AgCd Moeller stated that there is a fairly extensive though not quite gapless miscibility existing between Ag_5Sn and $AgCd_2$, both showing hexagonal densest spherical packing Between the phases Ag_5Sn and AgCd which show hexagonal densest spherical packing, and ordered, however, there is no gap, and the miscibility is assumed Moeller also pointed out that the latter case is an example of a transition of the valency electron ratio from 7/4 to 3/2 within a hexagonal series of solid solutions of densest spherical packing

Cadmium-Lead-Tin Solders

During the first World War, cadmium was advocated as a partial substitute for tin in tin-lead solders in order to produce a cheaper solder at a time when tin was scarce and high priced. This was not because cadmium was cheaper than tin, but because it allowed the use of a higher percentage of lead Although cadmium was successfully used for this purpose, little information of value appeared in the literature at that time regarding the new properties resulting from a change from a binary tin-lead alloy to a ternary cadmium-lead-tin alloy. A phase diagram of cadmium-lead-tin alloys had been prepared by Stoffel in 1907. Figure 125 is a freezing-point diagram based on Stoffel's[23] data, as given by Swartz [24]

During the last decade a considerable amount of research work has been done in the replacement of some or all of the tin in solders by cadmium. An investigation by Swartz[25] showed that solders containing cadmium

[22] K Moeller, *Z. Metallkunde*, **34**, 171-2 (1942), *Chem Zentr* , I, 2179-80 (1943)
[23] Stoffel, *Z. anorg. Chem.*, **53**, 137 (1907)
[24] C Swartz, *Proc. Inst. Metals Div , Am Inst Mining Met. Engrs* , 352 (1928).
[25] *Ibid*

would make joints equal in strength to joints made with lead-tin solders, and that the cadmium alloys were suitable in other respects for use as solders. Similar tests made with the same alloys to which 1.5 to 2 0 per cent zinc had been added showed that the addition of zinc in this proportion improved the properties of the alloys for this use The addition of amounts of zinc of this order was found to lengthen the solidification range and lower the final solidification temperature slightly, decrease the tendency

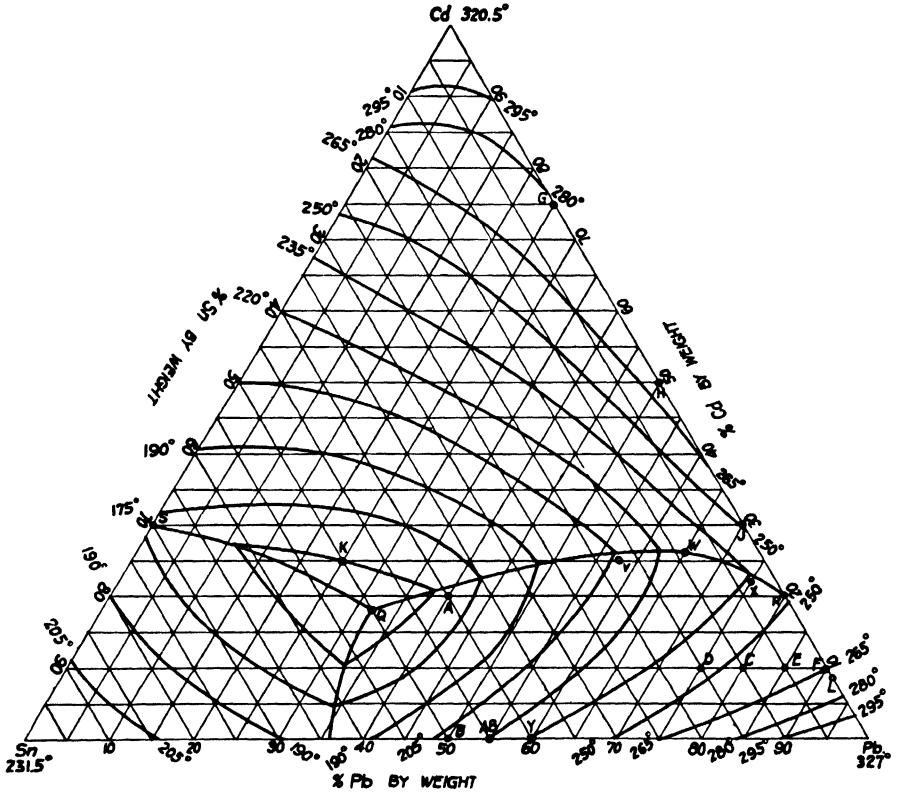


FIGURE 125 Freezing-point diagram of cadmium-lead-tin alloys

to oxidation, and tend to give soldered joints of greater strength and reliability. In general, the observations made in the course of the investigation indicated that the solders in the region of the ternary eutectic composition were the most satisfactory in so far as "wetting" properties and tendency to oxidation are concerned. Larger percentages of cadmium than in the eutectic are likely to increase the tendency of the alloys to oxidize to an undesirable degree while molten. While the solders having compositions in the neighborhood of the cadmium-lead-tin eutectic were considered the

best of the ternary alloys for most soldering work, compositions varying rather widely from this may be more desirable for certain purposes.

Schumacher and Basch[26] presented data which showed that certain cadmium-lead-tin alloys may be advantageously substituted as wiping solders for tin-lead alloys A solder containing 68 per cent lead, 23 per cent tin, and 9 per cent cadmium was indicated as a satisfactory substitute for standard 62 per cent lead, 38 per cent tin solder.

In a study of cadmium as a tin substitute, Burgess and Woodward[27] stated that a solder composed of 80 per cent lead, 10 per cent tin, and 10 per cent cadmium appears to be practical for many of the purposes for which solder is required. The tensile strength of the cadmium solder is about the same as that of 40–60 tin-lead solder, but the ductility is approximately twice that of the ordinary solders The point of complete liquidation is only slightly higher than that of ordinary solders, while the range of solidification is considerably greater

The comparison of soft solders conducted by Rhines and Anderson[28] showed cadmium to be the most promising alloying element that has been used as a partial substitute for tin. When 10 to 26 per cent cadmium is used with 65 to 80 per cent lead, cadmium can be substituted directly for tin with no serious loss except in the tensile strength, which is often unimportant Since the ternary lead-tin-cadmium solders generally show a desirable rise in the capillary test, they are well suited for soldering where a capillary action is employed. Low temperatures are to be recommended for handling the cadmium solders to minimize oxidation which may become rather severe upon overheating, particularly when the tin content is below about 10 per cent Cadmium oxide which is poisonous presents, to some extent, an industrial hazard. Moreover, there is a tendency for the oxide to become trapped in the joint with a resulting increase in porosity effecting a decrease in mechanical properties.

The hazard of cadmium-containing solder has been pointed out by Richnow[29] who stated that cadmium vapor is a strong heart poison.

In a report submitted to the War Production Board by the Advisory Division of the War Metallurgy Committee of the National Academy of Sciences,[30] it was stated that low melting-point solders having a tin content much below that of ordinary solder could be made by the use of cadmium or bismuth. Cadmium solders, however, were barred for food use, not only because cadmium is toxic (and it would take a great deal of work to

[26] E E Schumacher, and E J Basch, *Ind Eng Chem* , **21**, 16 (1929)

[27] G K Burgess, and R W Woodward, *Technologic Paper No. 103*, Bur Standards (March, 1919)

[28] F N Rhines, and W. A Anderson, *Metals and Alloys*, **14**, 704 (1941).

[29] M Richnow, *Tech Blatter*, **30**, 281 (1940)

[30] *Metal Progress*, **44**, 420–1, 454 (1943).

emonstrate what, if any, amount of cadmium in food could be tolerated), ıt even more so because the supply of cadmium would be inadequate The eutectic alloy Cd-Pb-Sn was one of a series of alloys investigated by ıishokin and Zaporozhets [31] They found that in every case the temerature coefficients of hardness were greater for the alloys than for any their components.

Bochvar and Gorev[32] studied the ternary alloy Cd-Pb-Sn and found that eutectic was formed at 145° C In this eutectic system, the cadmium ystals are said to be surrounded by lead, and again surrounded by tin ochvar and Gorev assumed that at first the cadmium centers of crystalzation are formed in the liquid eutectic which grows into needles and then ıe crystallization centers of lead form on the surfaces of the needles fter the remainder of the melt has become almost pure tin, it crystallizes ; the last component They stated that from this it could not be decided hether the crystallization centers of tin form on the surface of the lead ystals or within the liquid melt Bochvar and Gorev[33] also studied the ructure of the ternary eutectic alloy Cd-Pb-Sn, which had been previously elted, slowly cooled, and etched with 1 per cent nitric acid solution. hey found that the incipient crystallization of all the three phases takes ace not simultaneously but successively The metals can be arranged the following order of their separation· cadmium, lead, tin, and bismuth

Other Cadmium Alloys

The ternary system Cd-Sb-Sn was studied by W Campbell [34] Investigations by Hanson and Sandford[35] on the Cd-Sb-Sn alloy revealed at after cold-rolling and self-annealing, the best alloy of tin is that coning 7 per cent cadmium and 9 per cent antimony, which withstood a ress of 1,200 to 1,400 lb per sq in. for many years After annealing at 0° C the best alloy was one containing 2 per cent cadmium and 7 per nt antimony, which they stated may safely be stressed at 3,500 lb per . in. After annealing at 200° C. the alloy containing 3 per cent cadmium ıd 7 per cent antimony withstood a stress of 3,700 lb. per sq in. Hanson ıd Sandford showed that grain size is an important factor in determining eep resistance. In the annealed alloys investigated by them, no relationip was found between the grain size and tensile strength

Pell-Walpole[36] compared the hardness of tin-rich Cd-Sb-Sn alloys exsed to the effect of quenching from the highest practicable temperature

[31] V P Shishokin, and I D Zaporozhets, *Tsvetnye Metal*, No 5–6, 88–98 (1937).
[32] A A Bochvar, and K V Gorev, *Z anorg allgem Chem* , **210**, 171–2 (1933).
[33] A A Bochvar, and K V Gorev, *Ann secteur anal phys -chim , Inst chim gén S S R*), **8**, 283–90 (1936)
[34] W. Campbell, *J Am Chem Soc* , **26**, 1313 (1904)
[35] D Hanson, and E J Sandford, *J Inst Metals*, **62**, 215–33 (1938)
[36] W T. Pell-Walpole, *J. Inst Metals*, **68**, 329–45 (1942)

and prolonged tempering at 100 to 140° C , with the hardness values of the alloys in a state of stable equilibrium He found that the alloys fall into three groups according to the composition First, alloys containing cadmium 0 to 2 and antimony 4 to 7 per cent undergo no appreciable changes either on quenching or subsequent tempering, secondly, alloys containing cadmium 0 to 2 per cent and antimony 7 to 14 per cent undergo appreciable temper-hardening, and thirdly, the remaining alloys harden severely on quenching, but resoften on prolonged tempering Some of the temper-hardening alloys maintain a useful degree of improvement for at least 1,000 hours at 100 or 140° C., the optimum composition range being cadmium 1 to 1.5 per cent and antimony 9 to 10 per cent Pell-Walpole found that these alloys gave Vickers diamond-pyramid hardness values of 30 to 34 after tempering 1,000 hours

Pell-Walpole[37] further investigated alloys of antimony and tin and ternary alloys with 0 5 to 2 per cent cadmium. These were strengthened by quenching and tempering Alloys containing 3 per cent cadmium showed a maximum improvement in the as-quenched condition. Subsequent aging at 140° C caused resoftening in alloys with 2 or 3 per cent cadmium, and with lower cadmium content softening was not obtained during 1,000 hours at 140° C The alloy containing 9 per cent antimony and 1 5 per cent cadmium had a tensile strength of 13,440 lb per sq in and was stable at 140° C. Pell-Walpole recommended air cooling for the quenching in the binary alloys, but not in the ternary alloys because the temper-hardening would be affected.

The mechanical properties associated with the nonequilibrium structures of chill-cast Cd-Sb-Sn alloys were studied by Pell-Walpole [38] He found that alloys containing metastable beta have high mechanical properties as-cast, but aging at temperatures up to 100° C lowered the values to those of the same alloys in stable equilibrium Alloys containing cadmium 1.5 to 10 per cent and antimony 9 to 14 per cent have much higher mechanical properties as chill-cast, when they contain metastable SbSn, than in stable equilibrium when SbSn was replaced by CdSb Chill-cast alloys containing cadmium 0 5 to 2 per cent and antimony 7 to 10 per cent temper-hardened at 140° C , and no grain-boundary embrittlement occurred as when the same alloys were temper-hardened after a preliminary homogenization treatment, owing to the cored condition of the alpha-solid solution. Rolling inhibited temper-hardening

The Cd-Zn-Sn system was studied by Rader [39]

In the series of eutectic alloys containing tin, including the Cd-Zn-Sn

[37] *Ibid* , **69**, 259–68 (1943)
[38] *Ibid* , **71**, 441–54 (1945)
[39] Rader, *German Patent 72,683* (1891)

eutectic investigated by Shishokin and Zaporozhets,[40] they found that in all cases the temperature coefficients of hardness were greater for the alloys than for any of their components.

Janecke[41] made a series of tests on the Cd-Tl-Sn system The metal was molten under a special wax which melts at about 100° C and can be heated to 350° C. without much volatilization and without agitation. The temperatures were measured by thermometers. All the alloys showed distinct critical points in the ternary eutectic; the temperature was between 129.5 and 130° C. The composition is said to be cadmium 19, thallium 39, and tin 42 per cent. The alloys in which cadmium solidifies after tin or tin after cadmium had critical points at 111 to 114° C. The alloys which had cadmium and thallium first and tin later in the ternary eutectic did not show this critical range Janecke explains this by the wide change in composition of the tin solid solution at temperatures near the eutectic and by the transformation of metastable solid solutions. Computed on the basis of atomic weights, the eutectic has the composition of cadmium 22, thallium 27, and tin 51 per cent. Janecke stated that the three basic materials are really solid solutions which contain very little admixed metal

Copper-Containing Alloys. Asato[42] found after studying the Cu-Fe-Sn alloys, that grain refinement is closely related to peritectic reaction between copper and iron, and that iron may be replaced by cobalt. He found that in each case grain size decreased to 1/1000 to 1/10,000 when iron was added over the peritectic point. Asato also investigated the effects of cooling velocity and casting temperature upon grain size, but found no marked effects.

Zakharova[43] stated that alloys of copper with 7.2 per cent tin and 2 5 per cent iron, and alloys with 5 5 per cent tin and 3 8 per cent cobalt can be made to attain the hardness of 255 to 265 kg. per sq. mm. by cold-working followed by aging at 300 to 350° C. The degree of hardening of alloys quenched from the same temperature increased with the degree of deformation by cold-rolling.

The constitutional diagram within the range of 0 to 15 per cent manganese and the quasibinary section of the Cu-Mn-Sn alloy were studied by Vero.[44] He found that tin has a stronger affinity for copper than for manganese. The melting point of bronzes is generally decreased by manganese. To a manganese content of about 4 per cent the constituents were the same, and above 5 per cent manganese the beta-constituents began to disappear and a new, evidently manganese-rich constituent was found.

[40] V. P. Shishokin, and I D Zaporozhets, *Tsvetnye Metal.*, No. 5–6, 88–98 (1937).
[41] E. Janecke, *Z Metallkunde*, **31**, 170–1 (1939).
[42] J. Asato, *Kinzoku-no-Kenkyu*, **9**, 392–411 (1932).
[43] M. I. Zakharova, *Tsvetnye Metal.*, No 2, 69–78 (1938)
[44] J. Vero, *Mitt. berg- huttenmänn, Abt. ungar. Hochschule Berg-Forstw. Sopron*, **5**, 128–55 (1933).

Fetz[45] has proposed a new alpha-phase boundary for the system Cu-Ni-Sn, comprising a wide scope of improvable alloys. He found that all alloys within the limits of 10 per cent tin and 40 per cent nickel could be rendered mechanically workable and homogenized. The progress of hardening during tempering periods of 100 hours at various temperatures was investigated on typical alloys of this group A maximum improvement effect was observed with about equal parts of tin and nickel. The maximum hardening values, contrary to the rate of hardening, were found to be proportional to the degree of supersaturation

Eash and Upthegrove[46] studied the Cu-Ni-Sn system and redetermined the alpha-phase boundary for alloys containing 0 to 20 per cent nickel together with the liquidus and solidus temperatures above that field. They found that the addition of nickel to copper-tin alloys decreased the solubility of the tin in the alpha phase. The tin solubility diminished also as the temperature was lowered. The alpha plus delta eutectoid which occurs in copper-tin alloys is replaced by either the theta phase or the delta-prime phase when nickel is added in amounts above 1 per cent The theta phase is said to be always homogeneous, and the second new phase may be homogeneous or it may be in the form of alpha plus delta-prime eutectoid depending upon the rate of cooling of the alloy. The gamma inversion to alpha plus delta prime or to alpha plus delta prime when nickel is present is raised to higher tin contents as the amount of nickel is increased

Hidnert and Dickson[47] determined the linear expansion coefficient of various copper-base alloys containing tin in the temperature range of 20 to 900° C These are shown in Table 17. Hidnert and Dickson stated that the coefficients given in the table were smaller than those of copper at temperatures of 20 to 600° C For the ranges of 20 to 900° C., the coefficient of expansion of the Cu-Ni-Sn alloy containing 20 per cent nickel is about 16 per cent higher than the coefficient of expansion of copper.

Vero[48] investigated the copper corner of the Cu-P-Sn system and found that the eutectic crystallizes only for the tin-poor alloys In the tin-rich alloys, the peritectic reaction, alpha plus melt equals beta plus Cu_3P, occurred at 637° C The solid solutions of tin in copper passed through the same transformations as the pure tin bronzes. The saturation limits of tin in copper were decreased by phosphorus additions until the Cu_3P point was reached.

Winterton[49] studied the phosphorus-tin bronzes, high in copper, con-

[45] E Fetz, *Korrosion u. Metallschutz*, **11**, 217–29 (1935)

[46] J. T Eash, and C Upthegrove, *Trans Am Inst Mining Met Engrs , Inst. Metals Div* , **104**, 221–53 (1933)

[47] P. Hidnert, and G Dickson, *J Research Natl. Bur Standards*, **31**, 77–82 (1943) (Research Paper No 1550).

[48] J. Vero, *Z. anorg allgem Chem* , **213**, 257–72 (1933).

[49] K. Winterton, *J. Inst. Metals*, **71**, 581–8 (1945).

taining tin 10 to 20 per cent and phosphorus 0 to 0.7 per cent, and tin 5 to 10 per cent and phosphorus 0 to 2.5 per cent. He reported that $SnCu_4$ is visible above approximately 5 per cent tin, and continued to increase the hardness and strength as long as it was in the form of fine, disconnected particles. Above 10 per cent tin the phase formed intercrystalline envelopes and caused brittleness. Cu_3P is said to be distributed similarly. These factors produce a zone of maximum tensile strength

Frolich[50] stated that for the ternary Cu-Pb-Sn alloys the best results are obtained with not over 30 per cent lead and not less than 5 per cent tin The addition of 2 to 3 per cent nickel resulted in improvement in mechanical properties and homogeneity of the casting

Richard[51] studied the Cu-Pb-Sn antifriction alloys and he reported that the tensile strength and resistance to repeated shocks decrease with increasing lead content from 0 25 to 25 per cent and decreasing tin content from 10 to 0 per cent Copper-lead alloys with less than 2 5 per cent tin

TABLE 17*

COMPOSITION ALLOY			AVERAGE COEFFICIENTS OF EXPANSION PER °C ($\times 10^{-6}$)					
Cu	Ni	Sn	20–100°	20–200°	20–300°	20–400°	20–600°	20–900°
70	29	1	15 2	15 4	16 3	—	—	—
68	20	12	—	16 2	—	16 9	18 1	22 9

* P Hidnert, and G Dickson, *J Research Natl Bur Standards*, **31**, 77–82 (1943)

are unsuited for bearing bushings, but are used for oil rings, packing rings for pistons, and air pumps Richard found that a 2 5 per cent lead content seemed sufficient so as not to change the friction properties of copper-tin alloys, and good machinability resulted At least 10 per cent lead is necessary to obtain the plasticity desirable for cold-working and polishing

Tin-rich bronzes with 5 to 8 per cent tin are less sensitive to high temperatures and therefore are said to be suitable for bushings under a heavy load. Richard reported that the wear-resistance is little modified with 12 to 25 per cent lead, but the mechanical properties deteriorate beginning with 15 per cent lead The lead alloys can be machined at high rates of speed, broaching is a particularly suitable process

Investigations on the filtration of metallic systems were made by Slavinskii and Kleiman [52] They fused an alloy containing copper 5 5 per cent, antimony 11.5 per cent, and tin 83 per cent, cooled it at 0 3 to 0 4° C per minute and filtered it in a carbon dioxide atmosphere with a quartz sand

[50] W Frolich, *Chem -Ztg* , **57**, 741–2 (1933)
[51] A Richard, *Usine*, **45**, No 1, 37 (1936)
[52] M. P. Slavinskii, and N L Kleiman, *Metallurg* , **13**, No 12, 68–80 (1938)

filter at 280 and 240° C. CuSn was separated at 280° C. and Sn_2Sb at 240° C. The filtrate contained copper 1 12 per cent, antimony 7.38 per cent, and the balance tin. An alloy containing copper 2 08, antimony 11.60, tin 11.37, cadmium 1.45, arsenic 1.34 per cent and the balance lead yielded SnSb, Sn_2Sb and three phases identified as eutectics

In the ternary systems, the Sn-Cu-Al alloys have been investigated by Wahlert,[53] Stockdale,[54] Read and Greaves.[55]

Burghoff and Blank[56] ran rotating arc fatigue tests on hard-drawn wire of several different compositions such as Sn-Cu, Sn-Cu-Zn, and Si bronzes. They found that the endurance limit of several of these alloys was between 30,000 and 40,000 lb per sq in. at 10^8 cycles. Tin, nickel, and silicon increased the endurance limit in varying degrees. A relationship between the ratio of the endurance limit to the tensile strength and the ratio of yield strength to tensile strength appeared to exist for these materials

Kuznetsov[57] studied the equilibrium oxidation of Cu-Sn-Zn alloys with carbon dioxide at 1060 to 1140° C. He stated that the dissociation pressures of ZnO decreased with an increase in the molar concentration of zinc in the alloy, the greatest changes being observed at small concentrations of the metal. All components of the alloy are said to oxidize simultaneously, the composition of the oxide film being determined by the compositions of the alloys

Iron-Containing Alloys. The diagram of the Fe-Ni-Sn system was investigated by Schafmeister and Ergang[58] in the range Fe-Ni-Ni_3Sn_2-Fe_2Sn thermally and metallographically. The congruently melting compound Sn_2Ni_3, and the incongruently melting compound $SnFe_2$, formed a complete series of solid solutions. Two four-phase transformations and four primary precipitation areas (alpha gamma epsilon and beta) occurred Schafmeister and Ergang stated that the alloys behave differently with respect to precipitation hardening from Fe-Co-W and Fe-Co-Mo precipitation-hardening alloys The purely ferritic alloys reached the highest magnetic hardness by precipitation hardening, while the martensitic alloys attained their highest mechanical hardness by it They concluded that both, however, are lower than those of the molybdenum and tungsten alloys mentioned so that they are of no practical importance

Lead-Containing Alloys. The ternary system Sn-Pb-Tl was studied

[53] Wahlert, *Metall u Erz*, **18**, 298 (1921)

[54] D Stockdale, *J Inst Metals*, **35**, 181 (1926)

[55] Read, and Greaves, *J Inst Metals*, **15**, 264 (1916)

[56] H L Burghoff, and A I Blank, *Proc Am Soc Testing Materials*, **43**, 774–84 (1943).

[57] M. O Kuznetsov, *Yubileĭnyĭ Sbornik Nauch Trudov Inst Tsvetnykh Metal i Zolota*, No 9, 556–65 (1940), *Khim Referat Zhur* , **4**, No 5, 25 (1941)

[58] P Schafmeister, and R Ergang, *Arch. Eisenhüttenw* , **13**, 95–103 (1939)

thermally by Kurnakov and Korenev.[59] It was found that the addition of cadmium or tin to the binary system Pb-Tl disturbed the equilibrium of the latter and changed the ratio of Pb:Tl = 1:(1.67–1.83), corresponding to the maximum fusion temperature. This was similar to the liquid-vapor type of binary system where equilibrium disturbance owing to changes of temperature and pressure resulted in a change of vapor pressure. They stated that eutectic lines in the above ternary system deviate considerably from a straight line connecting eutectic points of the corresponding binary system. Additions of 1 per cent cadmium or 5 per cent tin to the system Pb-Tl slightly changes the electrical conductivity of the system.

The limits of miscibility in the ternary system Sn-Pb-Zn were determined at 520° C. by Mondain-Monval and Gabriel.[60] Equilibrium was established by vigorous stirring for 20 minutes. The critical point was found at a composition of lead 30.5, tin 29, and zinc 40 5 per cent. They stated that in certain cases the separation of the two layers, particularly for the overall composition lead 40.5, tin 19, and zinc 40 5 per cent, took place rapidly It was their opinion that this may have been caused by the presence in the liquid state of $SnPb_3$ which increases the fluidity of the layers and facilitates their separation. The results obtained differ from those of Wright[61] although he also assumed the presence of $SnPb_3$ in the liquid state The equilibrium diagram is shown in Fig 126

The complete ternary diagram of the Sn-Pb-Sb system has been investigated by Loebe,[62] Campbell and Elder,[63] Campbell,[64] Heyn and Bauer,[65] and more recently by Iwasé and Aoki.[66] In the first four investigations the liquidus and solidus surfaces were established by means of thermal analysis and are in approximate agreement, but no true ternary eutectic was found Iwasé and Aoki re-examined the entire ternary diagram by means of thermal and microscopical investigations They found that the ternary peritectic point of earlier investigators is a true ternary eutectic having a composition of 11.5 per cent antimony, 3 5 per cent tin, and 85 0 per cent lead and solidifying at 240° C.

Weaver[67] later confirmed the existence of a true ternary eutectic, as put forward by Iwasé and Aoki, but the temperature of solidification was found to be 239° C. and the composition antimony 12, tin 4, and lead 84 per cent.

[59] N S Kurnakov, and N I Korenev, *Ann inst anal phys -chim (Leningrad)*, **6**, 47–68 (1933)

[60] P Mondain-Monval, and G Gabriel, *Bull soc chim* , **7**, 113–21 (1940)

[61] Wright, *Proc Roy Soc* , **50**, 372 (1892)

[62] R Loebe, *Metallurgie*, **8**, 7, 33 (1911)

[63] W Campbell, and F C Elder, *School Mines Quarterly*, **32**, 244 (1911)

[64] W Campbell, *Metallurgie*, **9**, 422 (1912)

[65] E Heyn, and O Bauer, *Mitt Material*, **29**, 29 (1911)

[66] K Iwasé, and N Aoki, *Kinzoku no Kenkyu*, **8**, 253 (1931)

[67] F. D. Weaver, *J. Inst. Metals*, **56**, 209 (1935).

The ternary peritectic point of Loebe[68] and contemporary workers, at the composition of antimony 10, tin 10, and lead 80 per cent, was shown by Weaver[69] to be the eutectic point of a pseudobinary system of lead and the compound SnSb.

Antimony-Containing Alloys. Leyman[70] also studied the alloys of the Sb-Cu-Sn system and found that they hardened by slight or moderate cold-rolling, and that they softened by further rolling, sometimes becoming softer than in the cast state The softening on severe working is more pro-

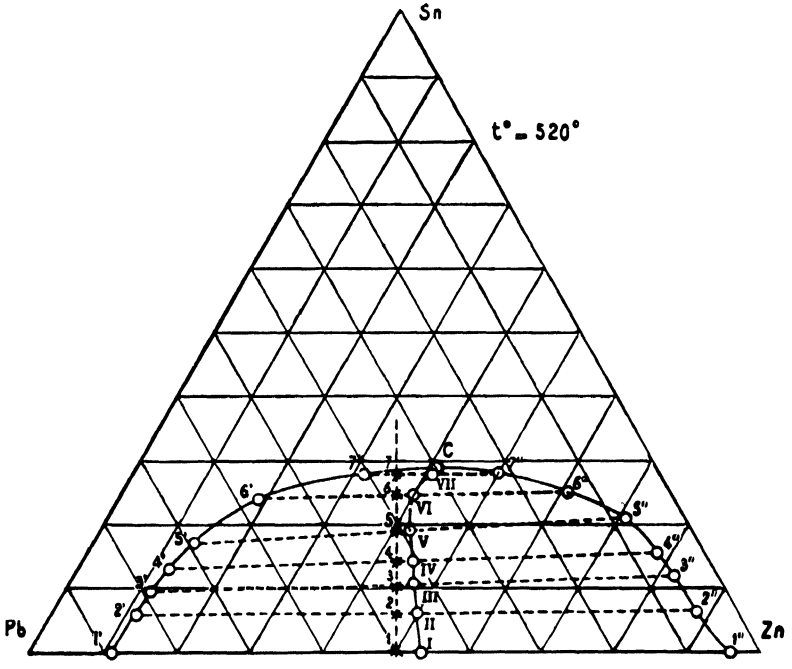


FIGURE 126. Equilibrium diagram of tin-lead-zinc system.

nounced with alloys containing higher amounts of the alloying element. Most of the elements are further softened by annealing after rolling, but those containing 3 per cent copper recover some of their lost hardness on annealing after severe working Quenching and aging treatments do not markedly affect the physical properties

Leyman[71] found that the alloys of the Sn-Ag-Sb system hardened by

[68] R. Loebe, *Metallurgie*, **8**, 7, 33 (1911)

[69] F. D Weaver, *J. Inst Metals*, **56**, 209 (1935)

[70] R E Leyman, *Intern Tin Research Development Council, Tech Pub* , **A**, No 53 (1937).

[71] R E Leyman, *Intern Tin Research Development Council, Tech Pub* , **A**, No 53, (1937).

slight or moderate cold-rolling, and they softened by further rolling, at times becoming softer than in the cast state. Leyman found that the softening on severe working is more pronounced with alloys containing higher proportions of the alloying element. Most of the alloys are further softened if they are annealed after rolling, but those containing 0.5 to 3 per cent silver recover some of their lost hardness on annealing after severe working. Quenching and aging treatment did not markedly affect the physical properties of the alloys An appreciable increase in hardness on quenching was noted by Leyman but he stated that it was rapidly lost at 100° C. and disappeared in 100 days at room temperature.

Blondel and Laffitte[72] studied the ternary alloys of the Sb-Zn-Sn system and found that there are three ternary peritectic points. p (Sb 0 5, Zn 8 0, Sn 91.5), p_2 (Sb 8, Zn 1, Sn 91), and p_3 (Sb 53, Zn 7, Sn 40) These give rise to the transformations liquid p_1 + crystalline ZnSb $\rightleftharpoons$ crystalline Zn + crystalline c at 197 5° C , liquid p_2 + crystalline $b \rightleftharpoons$ crystalline c + crystalline ZnSb at 235° C., and liquid p_3 + crystalline $a \rightleftharpoons$ crystalline b + crystalline c at 395° C ZnSb appears to be the only compound of zinc and antimony stable in the presence of tin.

Blondel[73] made plane equilibrium diagrams and a space model of the ternary liquidus system of Sb-Zn-Sn and found three invariant points at 395, 235, and 197 5° C. corresponding to three ternary peritectic transformations. Differential thermal analysis of annealed specimens showed that while the $b_1 \rightleftharpoons b_2$ transformation occurred at the invariant temperature of 325° C , the peritectic arrest disappeared at 235° C in the zone of two constituents (ZnSb + b) Metallographic study by Blondel of annealed specimens showed the constituents present in the state of equilibrium, particularly in the zones of two constituents (ZnSb + a, ZnSb + b, ZnSn + c) where thermal analysis gave erroneous results because of false equilibrium, and metallographic study revealed a ternary solid solution rich in tin

Density determinations by hydrostatic methods showed that the lines of equal density and the lines of equal electrical conductivity indicated the preponderant role of ZnSb

Hardness tests indicated that ternary alloys containing over 40 per cent antimony are very brittle and practically useless, whereas ternary alloys with less than 30 per cent antimony can be used as antifriction alloys in machines operating at 1,500 to 2,000 r.p.m. and under loads up to 20 kg per sq. cm. The ternary Sb-Zn-Sn revealed a hard constituent, ZnSb, with better bearing properties than those of Sb_2Zn_3 and antimony and less brittle than the latter two

[72] R Blondel, and P Laffitte, *Compt rend* , **200**, 1472–4 (1935)
[73] R Blondel, *Pub sci tech ministere air (France)*, No 89, (1936)

Miscellaneous Alloys. In the ternary system, the Sn-Al-Au alloys were studied by Shepherd,[74] the Sn-Al-Bi and the Sn-Al-Cd by Wright [75]

Campbell[76] investigated the alloys of the Sn-Al-Sb system, and those of the Sn-Al-Zn system were studied by Crepaz,[77] and Losana and Carozzi [78]

Carstanjen[79] studied the system of the Sn-Bi-Tl alloys

Alloys in the Sn-Bi-Zn system were investigated by Wright[80] and Campbell[81] as well as Muzaffar [82]

Alloys of the ternary system Sn-Cu-Zn were studied by Hoyt,[83] Hudson and Jones,[84] Reason,[85] Guillet,[86] and Tammann and Hansen [87]

Campbell[88] studied the system Sn-Sb-Zn

Peredelskiĭ[89] investigated the pseudobinary magnesium alloys containing 0 to 20 per cent SbSn or 0 to 20 per cent Pb_4Sn_3 He found that the maximum tensile strength of Mg-SbSn alloys was 21 5 kg per sq mm., obtained with 0 5 per cent SbSn, with an elongation of 10 7 per cent The maximum tensile strength of Mg-Pb_4Sn_3 alloys was 17 5 kg per sq mm , obtained with 2 per cent Pb_4Sn_3, the elongation being 9 per cent He stated that the SbSn is not soluble in magnesium, and that Pb_4Sn_3 is soluble up to about 3 per cent at room temperature

Quaternary Systems

Shishokin and Vikhoreva[90] investigated the influence of the height of fall and of temperature on the impact hardness of the alloys of Bi-Cd-Pb-Sn

Benson and Coyle[91] studied the expansion of a Bi-Pb-Sn-Cd alloy on cooling after solidification They found that an expansion occurred in the

[74] Shepherd, *J. Phys Chem* , **8,** 114 (1904)

[75] C R A Wright, *J Soc Chem Ind* , **13,** 1017 (1894)

[76] W Campbell, *J Am Chem Soc* , **26,** 1311 (1904)

[77] Crepaz, *Giron chim ind appl* , **5,** 115, 285 (1923)

[78] Losana and Carozzi, *Gazz chim ital* (2), **53,** 546 (1923)

[79] Carstanjen, *J prakt Chem* (1), **102,** 83 (1867)

[80] C R A Wright, *Proc Roy Soc (London)*, **48,** 25 (1890), **50,** 372 (1891), **52,** 11 (1892), *J Soc Chem Ind* , **13,** 1016 (1894)

[81] W Campbell, *J Franklin Inst* , **154,** 1, 131, 201 (1902), *J Am Chem Soc* , **26,** 1312 (1904)

[82] Muzaffar, *J Chem Soc* , **123,** 2341 (1923)

[83] Hoyt, *J Inst Metals*, **10,** 235 (1913), **14,** 178 (1915)

[84] Hudson, and Jones, *J Inst Metals*, **14,** 98 (1915)

[85] Reason, *Metal Ind* , **12,** 325 (1918)

[86] Guillet, *Rev Met* , **18,** 445 (1921)

[87] G Tammann, and M. Hansen, *Z anorg Chem* , **138,** 137 (1924)

[88] W Campbell, *J Franklin Inst* , **154,** 1, 131, 201 (1902)

[89] K V Peredelskiĭ, *Legkie Metal* , **6,** No 3, 27–9 (1937)

[90] V P Shishokin, and N A Vikhoreva, *J Tech Phys (U S S R)*, **10,** 500–4 (1940)

[91] L. E Benson, and M B Coyle, *J Inst Metals*, **69,** 249–57 (1934).

solid state on cooling after casting which overshadowed normal thermal contraction in an alloy containing bismuth 49.75, lead 26.0, tin 14.76, and cadmium 9 35 per cent and melting at 70° C. The expansion was accompanied by a slight evolution of heat The magnitude and rate of expansion was said to vary considerably with the temperature at which the change occurred and was greater and occurred more rapidly as the temperature to which the alloy was cooled was lowered Control was necessary when the alloy was used for tube-bending purposes to prevent bursting of the tubes

McLennan, Allen and Wilhelm[92] studied the quaternary system Bi-Sn-Pb-Cd and obtained a transition temperature of 8 5° K. for an alloy known as Wood's metal which had a composition of bismuth 50, tin 12.5, lead 25, and cadmium 12.5 per cent. They stated that the presence of bismuth in an alloy tends to raise the superconducting temperature while the presence of antimony sometimes raises and sometimes lowers the superconducting point

Cerkesov[93] prepared an alloy suitable for castings for high pressure and superheated steam composed of copper 47, nickel 37, tin 9, and iron 7 per cent. He stated that the alloy is hard, resistant to corrosion, and has a low friction coefficient even when water is used as a lubricant in place of oil.

French[94] prepared a low-melting quintary alloy containing 81.9 per cent Lipowitz metal (50 bismuth, 27 lead, 13 tin, 10 per cent cadmium), and 18.1 per cent indium, and reports its freezing point to be 46.5° C.

Elin and Gol'denberg[95] found that alloy "BM," containing tin 10 to 11, lead 74 to 75, antimony 10 to 12, copper 1 6 to 1 8, cadmium 0.9 to 1.2, arsenic 1.2 to 1.4, and nickel up to 0 4 per cent, and "Termit," containing tin 3 to 4, lead 75 to 78, antimony 15 to 17, copper 0.3 to 0.4, cadmium 0 6 to 1 5, arsenic 0 5 to 0.55, nickel 2.0 and phosphorus 0.3 per cent, were satisfactory in bearings under heavy loads and functioned well with low-grade lubricating oil.

Kern[96] prepared an alloy containing 85 to 93 per cent silver and 3 to 14 per cent tin, the total amount in the range of 96 to 99 per cent, and containing also in solid solution, for workability control, metals such as cadmium, zinc, antimony, nickel-chromium alloy, copper, manganese, lithium, or calcium to give the resulting alloy a Brinell hardness of not less than

[92] J C McLennan, J F Allen, and J O Wilhelm, *Trans Roy Soc Can* (3), **24**, Sect 3, 25-35 (1930)

[93] I Cerkesov, *Chem Obzor* , **9**, 9–12 (in English 13), (1934)

[94] S J French, *Ind Eng Chem* , **27**, 1464–5 (1935)

[95] L V Elin, and A B Gol'denberg, *Vestnik Metalloprom* , **20**, No 11–2, 12–4 (1940).

[96] E. F. Kern (assignor to American Metal Co Ltd.), *U S. Patent 1,970,818* (Aug. 14, 1934).

36, the aggregate amount of calcium and lithium not exceeding 1.0 per cent. Another patent relates to generally similar alloys containing silver and tin together with a small proportion of cadmium, zinc, antimony, copper, manganese or nickel-chromium alloy.

The solidification points of several ternary and quaternary eutectic alloys were determined by Janecke[97] and are shown in Table 18.

The ternary eutectics comprising three of the metals bismuth, cadmium, lead, and tin melt at 103° C (54 bismuth, 20 cadmium, 26 tin), 144 1° C. (18.5 cadmium, 20 lead, 40 tin), 95.5° C. (40 bismuth, 24 lead, 12 tin). The addition of zinc to these alloys gives quaternary eutectics melting at

TABLE 18 SOLIDIFICATION POINTS OF VARIOUS ALLOYS

ALLOY	POINT	COMPOSITION					SOLIDIFICATION POINT °C
		Bi	Cd	Pb	Sn	Tl	
Bi-Cd-Sn	4	54	20	—	26	—	103 0
Bi-Cd-Sn-Tl	L	54	20	—	26	10	94 6
	M	36	20	—	24	50	134 8
Bi-Pb-Sn	2	40	—	24	12	—	95 5
Bi-Pb-Sn-Tl	C	40	—	24	12	10	93 0
	D	17	—	8	25	19	161 6
	E	17	—	4	25	19	166 5
	O	17	—	5	25	19	165 9
Bi-Sn-Tl	o	35	—	—	25	10	124 0
	p	35	—	—	25	20	167 6
	r	35	—	—	25	18	161 8
Cd-Pb-Sn	A	—	18 5	20	40	10	144 6
	1	—	18 5	20	40	—	144 1
Pb-Sn-Tl	a	—	—	13 5	46	23	181 8
	c	—	—	11 5	46	23	181 8
Sn-Cd-Tl	g	—	18	—	25	15	128 3

100 2°, 137°, and 93.5° respectively, but the addition of zinc to the quaternary eutectic alloy (Wood's metal) produces no depression of the freezing point The equilibria in systems containing thallium and three of the metals lead, tin, bismuth, and cadmium are complicated by the existence of the stable compounds $PbTl_2$, Bi_2Tl, and $BiTl_8$

No eutectic with five components is formed by adding thallium to the components of Wood's metal. The melting point of Wood's metal is reduced to 67° C. by the addition of 6 per cent thallium, all of which enters into solid solution in the lead, with more thallium, Bi_2Tl is formed. Aluminum is insoluble in Wood's metal, magnesium forms intermetallic compounds with all the components, and antimony is completely miscible with the alloy in the liquid state, but no five-component eutectic is formed.

[97] E. Janecke, *Z. Metallkunde*, **29**, 367–73 (1937).

Chapter 13

Alloys in Industry

The history of tin and its use in industry, its application to the arts, shows that it has been notable for its profound effect on the physical properties of other metals. It is likely that one of the earliest observations was that tin would harden copper The modifying influence of tin on copper and lead has constituted one of the most useful properties of the metal.

Before World War I, workers in metal were generally content to add one metal to the other Alloy making was largely based on their own experience and the practices of others Scientific work of the type which has resulted in phase diagrams has greatly increased the knowledge of metallic alloys

The commercial alloys of tin may, in general, be divided into two large classes first, the alloys with copper, commonly termed the bronzes, of which there are many variations, especially in the ternary and quaternary systems, and secondly, the "white metals," which are the alloys with antimony, lead, sometimes bismuth, and often with small proportions of copper. The white metals are generally subdivided into the antifriction or bearing metals, printers' alloys, the pewters, and Britannia metal, the solders, and those special alloys applicable for special castings in the chemical industries, battery plates, bullets, collapsible tubes, and foil In addition to these, the alloys for die-casting and those for toys and molds are important.

Bronzes

It is probable that at first it was not metallic tin which was added to copper in the empirical work done for fitting copper for continual use in the edges of knives, axes, swords, and other tools of the same type. It is more likely that the oxidized tin ores together with some reducing agent constituted the material added to the molten copper. It was early found that tin had the power of hardening copper in a remarkable manner. Both the red-colored copper and the white tin are themselves soft. The resulting bronze, when the two metals are alloyed in the proportion of 2 copper 1 tin, is a purer white than the white tin and as brittle as glass. The ancients attributed the influence of tin to the devil. Tin was called

diabolus metallorum, which can be interpreted as either the "devil of the metals" or else the "metal of the devil."

On the other hand, the properties of copper are not always favorably influenced by an addition of tin The electrical conductivity, one of the most important properties of this metal, decreases strongly even with very small additions of tin Figure 127[1] compares the decrease of conductivity as caused by small amounts of a large number of metals It is to be noted that the effect of tin on the conductivity is greater than that of most of the common metals with the exception of silver, cadmium, and zinc Aside from the effect of tin on copper, the effect of lead is important for tin alloys, in that it causes an increase in hardness

Bronzes, estimated to belong to the period of about 3500 B C., have been found upon analysis to have approximately the same proportion of copper and tin as the gun metal which was used for ordnance in all the European countries up to the time of the appearance of the modern steel artillery rifle Some of the bronzes of the Roman period also contained lead Bronzes of considerable antiquity have been found in the relics of some of the most ancient civilizations

One of the best known bronzes is gun metal, consisting of copper with 8 to 14 per cent tin, although the usual proportion in the alloys employed in ordnance is 90:10 A close relative is Admiralty gun metal, containing 88 per cent copper, 10 per cent tin, and 2 per cent zinc The Admiralty alloy is accepted throughout the world as being a metal of widely varying application.

Another bronze of historical importance and application in the arts is bell metal, containing 15 to 25 per cent tin

The colors of bronzes are deeper and more attractive than brass (alloys of copper and zinc) in the polished condition, and they are markedly more resistant to corrosion In general, the addition of tin to alloys or to other metals increases their corrosion resistance

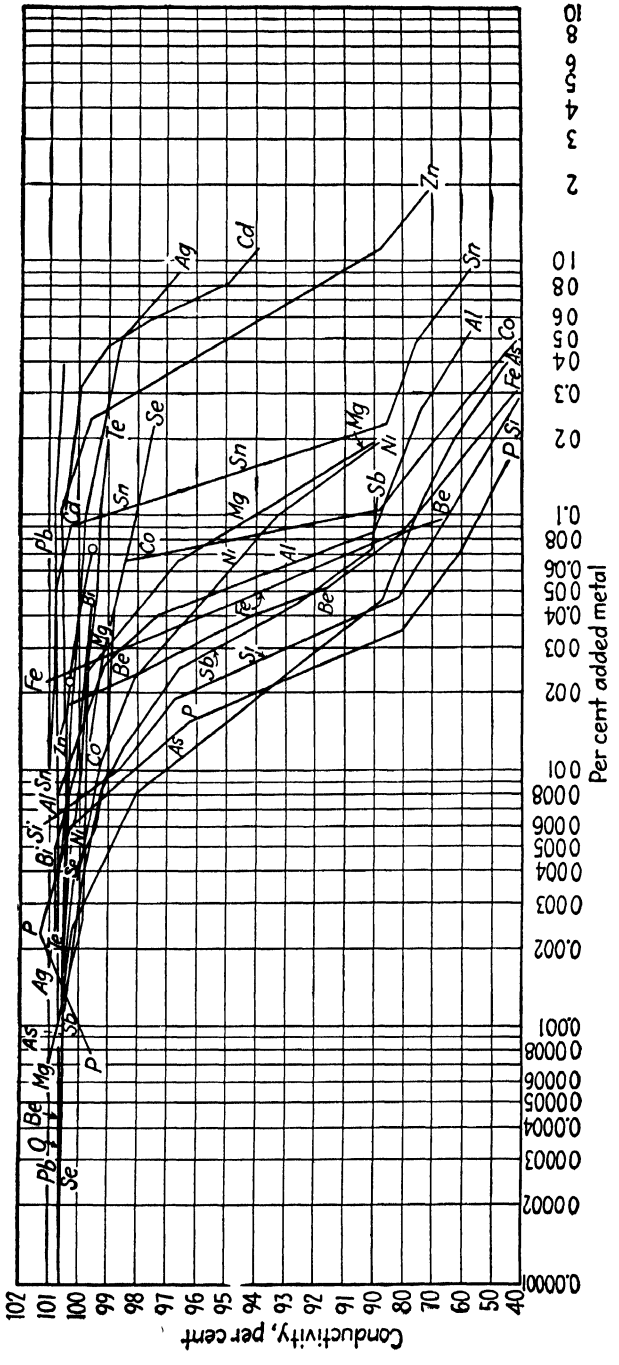
Statuary bronzes have been much discussed in the literature, and the patinas on surface corrosion crusts have been the subject of much study Surface finishes, impossible of attainment with other alloys, add considerable beauty to works of art in enduring bronze

The scientific side of the bronze alloys is discussed in connection with the tin-copper system in Chapter 11

Zinc is often added to bronzes because it is thought that the addition makes the molten alloy more fluid. The addition of zinc decreases the corrosion resistance, particularly when the metal is exposed to the atmospheres of industrial centers.

One of the most characteristic properties of the bronzes is their resistance

[1] S Skowronski, Private communication See also L L Wyman, *Gen Elec Rev*, **37**, 120 (1934)



(Courtesy McGraw-Hill Book Co., N Y.)

FIGURE 127. Effect of impurities on the conductivity of copper

to corrosion. It generally improves with an increase in the tin content and when the least foreign admixtures are present. Zinc is of a particularly detrimental influence. A bronze containing 20 per cent tin is not corroded by sea water. For this reason various parts of ships are made of high-quality bronzes. A distinction is made between casting and rolling bronzes. In the latter, the tin content must not increase above approximately 8.5 per cent and the phosphorus content above 0.35 per cent. Other metals, particularly lead, must not be present. For rolled sheets, usually an alloy with 4 5 per cent tin and 0 2 per cent phosphorus is used. For hard-drawn wires for springs, the tin and phosphorus content is somewhat increased, usually to 6.5 per cent tin and 0.3 per cent phosphorus The tin content of casting bronzes varies over a wide range.

Many of the coveted honors in life are perpetuated in bronze An example is the Victoria Cross, the highest military decoration of the British Empire. These were struck from gun metal taken from the trophies of the previous wars.

Coinage metal of many countries, notable among which are England and France, is a bronze containing 95 per cent copper, 4 per cent tin, and 1 per cent zinc.

The bronze alloys used in bell metal ordinarily contain metals other than tin and copper only in small traces, if at all Bell metal is a hard and somewhat brittle alloy. The purity of tone of a bell is dependent upon the design and the accuracy of founding rather than composition, although the tone is modified by the proportion of copper and tin Bell metal is susceptible to heat-treatment. When heated to redness and chilled, it is more malleable and of a more yellow color than is obtained when it is slowly cooled.

Special bronzes adapted to severe strains, high pressures, and unusual engineering applications have been developed. A number of these are listed elsewhere in this chapter under their special names, and their compositions given. The heat-treatment of bronzes has been the subject of much study.

Phosphor bronze was a development of the tin-copper alloys It is thought that the alloy had its origin as the result of an attempt to deoxidize the molten metal by the addition of phosphorus. Phosphor bronze may be considered as a greatly improved gun metal. It is stronger and harder and has superior corrosion resistance The increased hardness is thought to result from the microscopic crystals of copper-phosphorus and tin-phosphorus compounds embedded in the softer matrix of the alloy. The material is used for tubes, wire ropes, springs, screws, pinions, valves, steam fittings, pumps, axle bearings, cog wheels, parts of machinery exposed to great friction and stresses, as well as ornamental castings. The proportion of phosphorus rarely exceeds 1 per cent, and above 4 per cent the

alloy is considered useless. The addition of lead, causing the alloy to become slightly plastic, is beneficial when the metal is used for bearings. Increases of temperature have little effect upon the mechanical properties of phosphor bronze. In contrast, the physical properties of the brasses are greatly impaired by rise in temperature.

Aside from zinc, lead, and phosphorus, various elements have been suggested as additions to the tin bronzes. These elements are: aluminum, antimony, arsenic, bismuth, cadmium, chromium, cobalt, magnesium, manganese, molybdenum, nickel, silicon, silver, titanium, tungsten, and vanadium. So far, only the nickel-containing bronzes have acquired importance, they are used frequently in this country in the manufacture of gears. Table 19 shows the influence of the nickel content on bronzes.

TABLE 19. INFLUENCE OF THE NICKEL CONTENT UPON BRONZE

Sn (%)	Ni (%)	Cu (%)	YIELD POINT (kg /mm²)	TENSILE STRENGTH (kg /mm²)	ELONGATION (%)	REDUCTION OF DIAMETER (%)
11	—	88.5	17 5	26 5	5 7	5 2
11	1	87 5	23.0	27 5	3 2	2 2
10	1	88 5	21 8	31 2	7 0	8 3
10	2	87 5	21 8	33 2	7 2	8 0
10	3	86 5	22 5	33.8	7.7	8 3

Note Each alloy contains 0 25% lead and 0 25% phosphorus

The casting of the bronzes, especially the phosphor bronzes, has to be carried out with particular care because strong liquation effects occur during solidification. The excess metal at the top of the mold, or "dead head," frequently has a composition quite different from that of the cast Sometimes the dead head itself sweats out metal. This separated material is much richer in tin, lead, and phosphorus than the cast itself. From the point of view of its composition, it consists of that component of the bronze which solidifies last, which in the case of phosphor bronze is the delta-phosphide eutectic. According to Dews[2] a cast object consisted of 87.88 per cent copper, 12.23 per cent tin, 0.87 per cent lead, 0.41 per cent zinc, and 0.44 per cent phosphorus; the separation consisted of 78.82 per cent copper, 19.20 per cent tin, 1.40 per cent lead, 0.29 per cent zinc, and 0 92 per cent phosphorus. Attempts are being made to eliminate such liquation effects as far as possible by means of changes in the casting temperature and other changes in the casting procedure. The casting temperature is again of great influence upon the hardness. Bailey and Rowe[3] investigated this problem extensively; their results are shown in Table 20.

[2] H. C. Dews, "The Metallurgy of Bronze," p. 136, London, 1930.

[3] Bailey, and Rowe, *J. Inst. Metals (London)*, **30**, 401 (1923); **31**, 217 (1924), **32**, 73 1924).

TABLE 20 INFLUENCE OF THE CASTING TEMPERATURE OF VARIOUS BRONZES UPON THEIR HARDNESS*

TYPE OF BRONZE	ADMIRALTY BRONZE (%)		PHOSPHOR BRONZE (%)		PHOSPHOR BRONZE (%)		GUN METAL (%)		GUN METAL (%)		TIN BRONZE (%)	
Copper	87.6		89 2		89 2		88 0		87 6		84	
Tin	10 1		10 6		10 6		6 1		7 5		16	
Zinc	1 9		—		—		5.3		1.3		—	
Lead	0.5		—		—		0 5		4 1		—	
Phosphorus	—		0 15		0.15		—		Nickel 0 4		—	
Cast in	*Green sand molds*		*Dry sand molds*		*Chill molds*		*Green sand molds*		*Oiled sand molds*		*Green sand molds*	
	CASTING TEMP (°C)	BRINELL HARDNESS	CASTING TEMP (°C)	BRINELL HARDNESS	CASTING TEMP (°C)	BRINELL HARDNESS	CASTING TEMP (°C.)	BRINELL HARDNESS	CASTING TEMP (°C)	BRINELL HARDNESS	CASTING TEMP (°C)	BRINELL HARDNESS
	1250	59	1200	67	1225	83	1210	51	1190	60	1240	82
	1200	65	1175	68	1150	81	1170	55	1120	70	1175	88
	1140	65	1150	65	1075	83	1130	58	1050	80	1140	99
	1060	80	1125	64	1000	86	1090	60	—	—	1090	111
	—	—	1100	60	—	—	1050	61	—	—	1060	114
	—	—	1075	65	—	—	1020	63	—	—	1025	118
	—	—	1040	58	—	—	—	—	—	—	—	—
	—	—	1000	71	—	—	—	—	—	—	—	—

* Bailey and Rowe, *J Inst Metals (London)*, **30**, 401 (1923), **31**, 217 (1924), **32**, 73 (1924)

White Metals

Bearing Metals. The attention which the white metals have received from investigators has been small as compared to the bronzes. Often the manufacture of the white alloys has been regarded as a trade secret. Certain it is that the skill and experience of those engaged in preparing the metals are quite important. Gun metals and phosphor bronzes have been displaced as bearing metals by the high-grade white antifriction metals, which have tin as a major constituent. Because of the high price of the tin metal, these alloys are expensive

It is generally held that a homogeneous alloy is not suitable for a bearing. Thus neither a single metal nor a solid solution alloy can be employed with success. The necessary surface for a bearing is obtained by a metal consisting of a soft matrix with hard crystals embedded in it, or of a hard metal interspersed with veins of a softer constituent. The mottled surface in which the harder portions are in slight relief, provides a number of pools and canals to retain the oil film and to promote the spreading of the oil over the surface of the bearing. An alloy of approximately 93 per cent tin, 3.5 per cent antimony, 3.5 per cent copper is representative of the type favored for the big end bearings of aircraft engines It is one of the best bearing metals produced for strenuous and critical service. Tin is capable of dissolving a considerable amount of antimony in the molten state, and retaining about 7 per cent in solution on solidification. In this particular alloy, the cubical crystals ordinarily seen in tin-antimony alloys containing considerable antimony are not in evidence. The copper forms hard compounds with tin, partially separates on cooling, and develops a network of fine needle-shaped crystals. These are hard and remain embedded in the tough and hardened tin-base matrix. This matrix gives the alloy the power to resist shock and bending stresses, as well as the destructive forces of constant and rapid vibration.

As an example of a cheaper alloy of lower tin content, a representative analysis would show approximately 86 per cent tin, 10.5 per cent antimony, 3.5 per cent copper. The antifriction properties are not quite equal to the alloys of higher tin content In the process of cooling, this alloy first deposits rich tin-copper crystals, and at a lower temperature cubical crystals of the tin-antimony compounds settle out or precipitate. These become enmeshed in the already formed but still soft copper-tin compound. Finally the matrix solidifies. Examination shows the two relatively hard materials embedded in the softer matrix. The size and distribution of the crystals are affected by the rate of cooling, which is carefully controlled in the manufacture of bearings using these alloys.

The original patented Babbitt metal was a high tin-content alloy. It was prepared in a special manner. The somewhat mysterious method of metal mixing was the basis of the patent, inasmuch as simple alloys are

TABLE 21 HIGH-TIN-CONTENT BEARING METALS

Sn	Sb	Cu	Ni	TENSILE STRENGTH (KG /MM²)	YIELD POINT (KG /MM²)	ELONGATION (%)	BRINELL HARDNESS			
							(20° C)	(40° C)	(65° C)	(90° C)
93 0	3 5	3 5	—	8.1	5 6	11 6	24 9	24 2	23 6	22.8
92 9	3 5	3 5	0 1	7 25	4 5	18 0	19 3	18 6	18 1	17.4
92 8	3 5	3 5	0 2	7 25	4 5	12 2	21 5	20 8	20 2	19.4
92 7	3 5	3 5	0 3	7 0	4 0	6 1	22 3	21 6	21 0	20.2
92 6	3 5	3 5	0 4	7 25	4 8	11 0	21 5	20 8	20 2	19.4
92 5	3 5	3 5	0 5	5 8	4 85	5.7	21 5	20 8	20 2	19.4
91 5	3 5	4 0	1 0	6 5	4 0	15 4	20 3	19 4	19 0	18.2

difficult to protect. The number of Babbitt metals are legion, many of which are given in the table of alloys.

The bearing metals rich in tin and poor in lead generally have the best properties. Complete absence of lead is, however, no longer necessary according to English experiments.[4] Operating experience has shown that bearing metals with up to 1 per cent lead showed better properties in continuous operation than those which were practically free from lead.

Opinions are divided concerning the influence of an addition of nickel to bearing alloys rich in tin. According to the experiments of Mundey and Bissett,[5] no substantial improvement is imparted to an alloy of 93 per cent tin, 3.5 per cent antimony, and 3.5 per cent copper, as can be seen in Table 21.

TABLE 22 PREPARATION OF LOW-TIN-CONTENT BEARING METALS*

NAME	Pb (%)	Sn (%)	Sb (%)	OTHER METALS
"Normal" White metal	71 0	5 0	24 0	—
American railroad bearing metal	73.5	8 0	18.5	—
"Glievor" bearing metal	76 5	8 0	14 0	1 5 Fe
"Colsesco" bearing metal	77 0	8 0	14.0	1 5 Cu
"Tandem" bearing metal	77 7	5 9	16 8	—
English Magnolia	80 0	5 0	15 0	—
Standard Magnolia	80 0	6 0	14 0	—
Campbells bearing metal I	82 0	2 0	16 0	—
Campbells bearing metal II	83 3	8 3	8 3	—
Lakes metal for heavy loads	87 0	6 0	7 0	—

* Richards, *Metal Ind* (*London*), **45**, 533 (1934).

During World War I, a number of bearing metals of low tin and high lead content were developed owing to the scarcity and high cost of tin. A number of those bearing metals maintained their position after the war. According to Richards,[6] the bearing metals most widely used are given in Table 22.

Attempts to eliminate tin completely from bearing metals has brought about the development of lead-bearing alloys which are hardened with alkali or alkaline earth metals. The German railroad bearing alloy "Bahnmetall" contains 0.7 per cent calcium, 0.6 per cent sodium, 0.04 per cent lithium, and the balance lead.

In the case of most tin alloys, fractional solidification is always present. This phenomenon is recognized by metallurgists, but not as often as it

[4] *Metal Ind.* (*London*), **23**, 148 (1923).
[5] A. H. Mundey, and C. C. Bissett, *Metal Ind.* (*London*), **23**, 270 (1923)
[6] Richards, *Metal Ind.* (*London*), **45**, 533 (1934).

should be by workmen engaged in preparing the metals For this reason the chief benefits and the correct use of the alloys are often lost. In many shops when the metal is cooled in the ladle, little regard is paid to temperature conditions. The alloy is sometimes poured too hot and then allowed to cool. Often, near the end of the operation, pouring is continued when a partial solidification has taken place in the ladle. The still fluid metal is then allowed to run off from the semi-solid residue. A study of the thermal equilibrium diagrams will show that the two portions are not of the same composition, the semi-solid residue being much richer in copper and antimony. Thus a series of bearings may be found to be of varying condition, even when poured from the same ladle, as the result of careless control of temperature conditions.

Printers' Alloys. The printing craft is dependent upon a series of white metal alloys, ordinarily of the ternary type. The alloy generally used for cast type which the printer sets by hand is 5 to 20 per cent tin, 25 to 30 per cent antimony, and the balance lead. In the earlier days of printing, larger amounts of tin were used, but cost considerations have caused a general effort to keep the tin content as low as possible. The printers' alloys have played an important part in the history of publishing.

Alloys for linotype and similar machines are softer than those for cast type, running 2.5 to 3 per cent tin, 10 per cent antimony, 87 to 87.5 per cent lead. Often slightly harder alloys are required. These are obtained by increases in the antimony content and sometimes in the tin content. These alloys have no prolonged period of solidification. They pass almost instantly from the fluid to the solid state Purity of the constituent metals is important. Traces of copper cause the formation of hard copper-tin and copper-antimony constituents which solidify at higher temperatures and tend to clog up machines. Zinc is also deleterious, inasmuch as it is not soluble in the alloy but forms spongy semi-solid masses which destroy the fluidity of the metal. Nickel, iron, sulfides, and oxides are always sources of trouble.

In the monotype machines where single letters are cast in contradistinction to the linotype which casts a line of type at once, a good average alloy contains 8 per cent tin, 15 per cent antimony, and 77 per cent lead. Tin reduces the melting point of the alloy and makes it flow more freely. It toughens the final type, refining the structure and causing the formation of a compact, crystalline growth and a cast surface which is necessary for the production of type faces giving smooth and sharp definition

The constitution of alloys employed in the typograph, stereotyping, and plate casting is given in the table of alloys.

Solders. Conservation measures put into effect during World War II markedly affected solders and brought about many developments of alloys low in tin.

As an indication of the importance of the tin-lead solders, mention of the principal applications of solder should be made. Solder is needed for dip-soldering of automobile radiators; automobile bodies; soldering cans for food and other products; and plumbing and electrical industries. However, its field of usefulness extends well beyond these principal uses to a vast list of miscellaneous applications where metal joints are required, taking small amounts per industry, but a large tonnage in the aggregate.

The soft solders are essentially alloys of tin and lead that came into usefulness by reason of their low melting points and their ready adherence to the surfaces of other metals These alloys are distinguished from the less fusible hard solders (brazing solders and silver solders) which contain practically no lead or tin. The soft solders are fusible at temperatures below 700° F., whereas the hard solders are fusible at or above 1300° F.

Although the soft solders comprise a whole series of alloys the properties of which vary considerably with the composition, two compositions in particular have been found to possess distinctive and valuable properties. The alloy containing 2 parts of tin to 1 of lead has been widely used by tinsmiths and is called tinman's or fine solder. This has the lowest melting point of the series, a high degree of fluidity, and solidifies sharply in the same manner as a pure metal The other, an alloy of 1 part of tin to 2 parts of lead, has been found particularly useful for making wiped joints in lead pipe by reason of its gradual solidification, causing it to pass through a pasty condition. This has come to be known as plumber's solder. For many years, tin-lead alloys with or without various relatively small percentages of impurities or additions have been the standard solders, and alloys other than these have been used only for very special purposes.

The Romans are generally accredited with the introduction of soldering as a method of joining metals. The Roman solders were alloys of tin and lead not unlike those employed at the present time Pliny (23–79 A D) described two compositions in common use· "tertiarium," consisting of tin and lead in the proportion of 1 to 2; and "argentarium," consisting of equal proportions of tin and lead. It is interesting to note that modern plumber's solder has essentially the same composition as the alloy "tertiarium " The Romans, however, were not familiar with the important hand-soldering operation used to produce the wiped joint in lead piping. The actual date of the first use of wiped joints is not known, but it was probably not much before 1432, when they were employed in England on the Bayswater lead conduit

The approximate values for the chief properties of several important tin-lead alloys are given in Table 23.[7]

The A.S T.M. Tentative Specifications for Soft Solder Metal, B-32-40T, issued August, 1940, cover two grades of tin-lead and tin-lead-antimony

[7] *Intern Tin Research Development Council*, Bull. No. 2, (Sept., 1935).

TABLE 23. PROPERTIES OF TIN-LEAD SOFT SOLDERS

PROPERTIES	Sn (%)—BALANCE Pb					
	100	63	50	40	30	0
Temperature of complete liquefaction	232° C (450° F)	183° C (359° F)	212° C (414° F)	238° C (460° F)	257° C (496° F)	327° C. (620° F)
Temperature of complete solidification	232° C (450° F)	183° C (359° F)	183° C (359° F)	183° C (359° F)	183° C (359° F)	327° C (620° F)
Freezing range	0° C (32° F)	0° C (32° F)	29° C (84° F)	55° C (131° F)	74° C (165° F)	0° C (32° F.)
Specific gravity	7 31	8 42	8 91	9 34	9 48	11 34
Tensile strength* (tons/sq in)	0 94	3 35	2 75	2 75	2 66	0 89
Elongation (% on 4 in)	55	32	43	35	26	39
Shear strength* (tons/sq in)	1 28	2 78	2 56	2 22	2 06	0 90
Izod impact strength (ft -lb)	14 2	14 8	15 5	14 1	11 5	5 6
Brinell hardness*	4 6	13 9	12 0	11 3	8 7	4 1
Electrical conductivity (% of conductivity of copper)	13 9	11 9	11 0	10 2	9 5	7 91
Viscosity (poises) at						
280° C	0 0112	0 0133	0 0142	0 0150	0 0160	Solid
300° C	0 0109	0 0109	0 0136	0 0145	0 0151	Solid
350° C	0 0098	0 0120	0 0127	0 0134	0 0140	0 0183
Surface tension (dynes/cm) at						
280° C	546	490	476	471	469	Solid
300° C	544	489	475	458	462	Solid
350° C.	540	484	472	465	458	441

* These tests at fairly rapid rates of loading may be markedly different at slower rates

TABLE 24. PROPERTIES OF SOFT SOLDER METAL*

NOMINAL COMPOSITION (%)			DENSITY	MELTING RANGES				USES
				Solidus		Liquidus		
Sn	Pb	Sb		(°C)	(°F)	(°C)	(°F)	
100			7 30	232	450	232	450	For coating metals.
80	20		7.90	183	361	203	397	For coating metals.
70	30		8 32	183	361	192	378	For coatng metals
60	40		8 65	183	361	189	372	"Fine solder." General purposes but particularly where critical temperature required
50	50		8 85	183	361	216	421	For general purposes. Most popular.
45	55		8 97	183	361	225	437	Automobile radiator cores, heating units.
40	60		9 30	183	361	234	453	Wiping solder Automobile radiator cores
30	70		9 70	183	361	252	486	Low-grade Automobile bodies· dents or seams.
25	75		10 00	183	361	265	509	Low-grade Automobile bodies dents or seams.
20	80		10 20	183	361	273	523	Coating and joining metals Automobile bodies.
15	85		10 50	225	437	284	543	Coating and joining metals
10	90		10 80	275	527	297	567	Coating and joining metals
5	95		11 10	302	576	311	592	Coating and joining metals
49	50	1	8 92	186	367	210	410	General purpose Not recommended for Zn
47 5	50	2 5	8 94	189	372	208	406	General purpose Not recommended for Zn.
44	55	1	9 00	187	369	224	435	General purpose Not recommended for Zn
43	55	2	9 04	188	370	223	433	General purpose Not recommended for Zn.
39	60	1	9 33	187	367	230	446	Wiping solder Not recommended for Zn.
38	60	2	9 38	186	367	226	439	Wiping solder Not recommended for Zn
29	70	1	9 76	186	367	252	486	Low-grade solder Not recommended for Zn.
28 5	70	1.5	9 80	186	367	252	486	Low-grade solder Not recommended for Zn.
19	80	1	10 30	185	365	273	523	Low-grade solder Not recommended for Zn.

* A S T M. Tentative Specifications B-32-40 T, issued August, 1940

alloys. Compositions and melting ranges of these solders with examples of use are given in Table 24.

Table 25 gives the properties of soft solder metals, emergency alternate provisions issued in 1943 by the A S.T.M. in the interest of expediting procurement or conservation of materials In addition to the tin-lead alloys the table lists alloys suggested as substitute solders.

TABLE 25 PROPERTIES OF SOFT SOLDER METAL*

ALLOY	NOMINAL COMPOSITION (%)					MELTING RANGE			
						Solidus		Liquidus	
	Sn	Sb	Pb	Bi	Ag	(°F)	(°C)	(°F)	(°C)
	30	0 –0 4	Remainder			361	183	494	257
	28	1 5 –2 0	Remainder			361	183	484	251
	25	0 –0 4	Remainder			361	183	511	266
	25	1 25–1 75	Remainder			361	183	502	261
	20	0 –0 4	Remainder			361	183	525	274
	20	1 25–1 75	Remainder			361	183	518	270
	15	0 –0 4	Remainder			361	183	543	284
	15 ·	0 4 –2 75	Remainder			361	183	532–541	278–283
11	20	0 –0 5	Remainder	0–0 75	1 25	356	180	518	270
12	20	0 –0 5	Remainder	5	1 25	333	167	486	252
13	15	0 –0 5	Remainder	0–0 75	1 25	358	181	532	278
14	15	0 –0 5	Remainder	5	1 25	333	167	503	262
15	10	0 –0 5	Remainder	0–0 75	1 50	352	178	554	290
16	—	0 –0 5	Remainder	—	2.50	579	304	579	304
17	0 65–0 85	0 –0 5	Remainder	—	0 25	579	304	608	320

Applications These are hand and dipping solders and cannot be used for wiping.

Alloy 11—General commercial work

Alloy 12—Designed for work where a low melting point is a necessity Has a tendency to crack if there is a strain on the joint when cooling

Alloy 13—All-around solder for commercial work

Alloy 15—Designed for use where a high melting point is not detrimental and where high strength and good spread are not important, as in the coating of wire and dipping motor terminals

Lead-Silver Solders—For use where high melting point and moderate spreading are not objectionable

* A S T M Emergency Alternate Provisions, EA-B32a, January 5, 1943

The recognized grades of soft solder as drawn up in the 1932 Specifications of the British Standards Institution are shown in Table 26.

The working properties of all grades of solder are liable to be seriously impaired by small amounts of other metals present in the solders as impurities Standard specifications consequently state the maximum permissible amounts of the common impurities. For example, Federal Specification QQ-S-571a, Amend. 1 (September 15, 1942) limits the total quantity of impurity in Class A solder to 0.40 per cent (see Table 27). In

TABLE 26. ANALYSES OF BRITISH STANDARD SOFT SOLDERS*

B S GRADE	INTENDED USE OF SOLDER	Sn (%)		Sb (%)		Pb
		(min)	(max)	(min)	(max)	
A	Work requiring low melting point steel tube joints	64 0	66 0	—	1 0	Remainder
B	Tinsmith's, coppersmith's fine work, hand soldering	49 0	51 0	2 50	3 00	Remainder
C	General work, hand soldering	39 0	41 0	2 0	2 40	Remainder
D	Plumbers' wiped joints	29 0	31 0	1 0	1 70	Remainder
E	Special electrical purposes	94 5	95 5	—	0 50	Remainder
F	General electrical purposes Zn and galvanized ironwork, machine soldering	49 0	51 0	—	0 50	Remainder
G	Dipping baths Zn and galvanized ironwork, tinned electrical joints	41 0	43 0	—	0 40	Remainder
H	Lead cable wiped joints	34 0	36 0	—	0 30	Remainder
J	Dipping baths	29 0	31 0	—	0 30	Remainder
K	Special machine soldering	59 0	61 0	—	0 50	Remainder
L	Lead cable wiped joints	31 0	33 0	1 6	1 9	Remainder
M	Tinsmith's, general work, hand soldering	44 0	46 0	2 3	2 7	Remainder

* British Standards Institution, Spec No 219, 1932 and Addendum 1940

TABLE 27 CHEMICAL REQUIREMENTS FOR TIN-LEAD SOLDERS*

CLASS	Sn + Pb (%-min)	Sn (%)	Sb (%-max)	Cu (%-max)	Fe (%-max)	Al (%-max)	Zn (%-max)	TOTAL OTHER ELEMENTS† (%-max)	Bi (%-max)
A	99 2	49–51	0 40	0 08	0 02	0 005	0 005	0 08	0 25
B	99 2	38–42	40	08	02	005	005	08	25
D	97 6	34–36	75–1 50	08	02	005	005	50	25
E	98 3	28–32	75	15	02	005	005	50	25
F	99 2	69–71	40	08	02	005	005	08	25
G	98 3	18–22	75	15	02	005	005	50	25
H	99 2	59–61	40	08	02	005	005	08	25

* Federal Specification QQ-S-571a, Amendment 1, Sept 15, 1942

† Analysis shall ordinarily be made only for lead, tin, and the other elements specifically mentioned in this table. If the presence of an excess of other elements is indicated in the course of routine analysis, further analysis shall be made to determine the total of these other elements.

general, the various impurities cause solder to become gritty and sluggish when fluid, to form a film of dross very rapidly when melted, and to become brittle, hard and porous when solid. In wiping solder, they may

cause the metal to set too soon and be liable to crumble in the last stages of wiping, the coarseness of the crystals formed may result in a porous wipe.

Zinc, even when present in very small quantities, has an injurious effect on tin-lead alloys, interfering with the working properties and dulling the surface.[8] Aluminum is similar to zinc and nearly as harmful in its effects. Both aluminum and zinc must be limited to a maximum of 0.005 per cent in solders conforming to federal specifications [9]

Iron in small amounts causes brittleness and grittiness, federal specifications[10] limit this amount to 0 02 per cent. Copper gives rise to grittiness and therefore is limited to 0 08 to 0.15 per cent. The bismuth content of these solders is restricted to 0 25 per cent. Arsenic dulls the surface of the solidified solder and often gives rise to characteristic small white spots on the surface. The British Standards Institution specifications require arsenic to be less than 0.05 per cent

Traces of zinc, aluminum, or cadmium are known to produce "frostiness" on a bar of solder [11] These impurities cause the growth of large crystals in the solder, making it difficult to wipe and liable to be brittle during solidification On the other hand, a frosty surface may be equally well caused by slow cooling because the metal or mold is too hot. In this case the wiping qualities are not affected. Rivett[12] has shown that appearance is not a reliable indication of the working qualities of a solder, a frosty solder being equal or even superior to one with a bright surface.

Latin[13] has determined the interfacial tensions of tin and eutectic solders, respectively, when coated with some of the fluxes used in industrial soldering operations, and has found values markedly lower than the surface tensions of the molten metals themselves.

The seriousness of the tin scarcity created during World War II stimulated large consumers of this metal to develop drastic conservation measures in order to extend the available supply to cover the emergency period. New alloys and soldering methods were devised as part of the tin conservation effort

Early in 1943 the War Production Board issued a new General Preference Order M-43, designed to cut tin use in 1943 to about one-half the 1941 consumption. A large portion of the saving was to be effected by limiting the tin content of general-purpose solders to 20 per cent, and restricting the uses to which tin-containing solders may be applied. Automobile pro-

[8] A J T Eyles, *Sheet Metal Ind* , **15**, 50 (1941).

[9] Federal Specification QQ-S-571a, Amend. 1 (Sept 15, 1942).

[10] *Ibid.*

[11] C L Barber, *Ind Eng. Chem* , **26**, 685 (1934)

[12] F. A Rivett, *Intern Tin Research Development Council, Tech. Pub.*, **A**, No. 73 (1938).

[13] A. Latin, *Trans. Faraday Soc.*, **34**, 1384 (1938).

duction for civilian use had been stopped and the use of tin-containing body solder for repair work had been banned. This left the can-making industry as the largest remaining user of solder.

To effect economy in tin, the British Standards Institution in 1942 restricted soft solders to five grades which were considered adequate to meet

TABLE 28 ANALYSES OF BRITISH STANDARD SOFT SOLDERS*

B S GRADE	INTENDED USE OF SOLDER	Sn (%)		Sb (%)		Pb	Al or Zn (%)	Fe (%) (max)	As (%) (max)	TOTAL (max)
		(min)	(max)	(min.)	(max)					
C	Tinsmith's; coppersmith's; fine work; general work	39 0	40 0	—	1 0	Remainder	0†	0 02	0.05	0.25
D	Lead cable; wiped joints plumber's wiped joints	29 0	30 0	1 0	1.70	Remainder	0	0.02	0.05	0.25
G	General electrical purposes; tinned electrical joints; zinc and galvanized ironwork	41.0	43 0	—	0.40	Remainder	0	0 02	0.05	0.25
M	Special tinsmith's fine work and hand soldering	44.0	45 0	2.3	2 7	Remainder	0	0.02	0.05	0.25
N	Dipping solder. radiator manufacture, etc	18 0	18 5	0 75	1.0	Remainder	0	0.02	0.05	0.25

* British Standards Institution, War Emergency Standard 219 (1942).

† The figure 0 implies that the amount of the element present must be so small as not to be determinable in ordinary routine chemical analysis.

the great majority of needs. Analyses of these solders are given in Table 28.

Much work had been done in Europe and some in the United States during World War I in an attempt to reduce the tin content of solders. Tin-poor solders were developed to the point where the German government was able to limit the percentage of tin in any solder to 15 per cent, but no generally applicable tin-free soft solder was developed. Few of the sub-

stitute solders survived through the peace years because of inferior quality and little advance was made in this field after the war. Rhines and Anderson[14] have made a study of the work done during the former emergency and have presented a tabulation of the 75 principal solder combinations that have been proposed, together with a comparison of the properties of these solders made upon a uniform basis Table 29 (page 334) is taken from the paper of Rhines and Anderson.

The jointing of lead-sheathed cables consumes a large amount of solder. Some fourteen or more wiped joints occur in every mile of lead-sheathed telephone cable, and in making these joints from one to two million pounds of solder are used a year. Common practice of wiping such joints has been found to afford opportunity for economy by restricting the total amount of solder used.[15, 16]

Tin-Antimony-Lead Solders

To a limited extent antimony can be considered a substitute for tin in solders. Although in no case can antimony substitute for a really substantial proportion of the tin used in soft solders, it does displace twice its own weight of the more expensive strategic metal. In 1850 it was known that the use of antimony in tin-lead solders resulted in an economic advantage as well as certain mechanical benefits. It was also recognized at that time that additions of antimony must be strictly limited. The research of Gueterbock[17] in 1909–1910 showed that the amount of antimony permissible in a solder is determined entirely by the tin content of the alloy. Since antimony is only slightly soluble in lead at ordinary temperatures, additions of antimony to tin-lead solders are restricted by the solubility of antimony in tin

Nightingale[18] stated that when the amount of antimony is not more than 6 per cent of the tin content in the solder it can be completely carried in solution by the tin. For every 1 per cent of antimony added, the tin content can be reduced by 2 per cent. If the amount of antimony is more than the tin can carry in solution, tin-antimony cubical crystals of high melting point form in the solder, making it gritty, brittle, sluggish to work, and quite useless as solder.

According to Nightingale,[19] the addition of antimony within the solu-

[14] F. N. Rhines, and W. A Anderson, *Metals and Alloys*, **14**, 704 (1941)

[15] E. E Schumacher, G. M. Bouton, and G S Phipps, *Trans. Am Inst Mining Met. Engrs , Inst. Metals Div* , **152**, 291–7 (1943).

[16] "Tin and its Uses," No 13, 3 (July, 1942).

[17] P. G. J. Gueterbock, Messrs. Capper Pass and Son, Ltd , Bristol, Private communication to Brit. Non-Ferrous Metals Research Assoc.

[18] S. J. Nightingale, and O F. Hudson, "Tin Solders," 2nd Ed , Brit. Non-Ferrous Metals Research Assoc. (London), 1942.

[19] *Ibid.*

bility limit in no way interferes with the main characteristics of the solder alloys. The tin-antimony-lead eutectic solder has a single freezing point 3 degrees higher than that of the tin-lead eutectic and while the presence of antimony has slightly increased the liquidus in the case of plumbers' alloy, the plastic range is relatively unchanged since the solidus is increased proportionately. In the case of ordinary solder compositions, the freezing point is not affected sufficiently to influence the working of the solder.

Table 30 compares the physical properties of tin-antimony-lead solder alloys as determined by Nightingale. In regard to tensile strength and elongation, investigation of alloys *A*, *B*, *C*, *D*, and *E*, which are tin-antimony alloys having an antimony content varying from zero in *A* to 6.2 per cent in *E*, shows that the effect of adding 6 per cent of antimony to tin is to triple the tensile strength and reduce its elongation by about one-third. The tensile strength is also enhanced, but to a somewhat lesser degree, in the alloys containing lead, the improvement being proportional to the respective tin contents The effect of the addition of 6 per cent antimony to tin is to raise the shear strength from 1 28 to 3 01 tons per square inch. This improvement is effected in all grades to an extent progressively less as the tin content decreases. Although antimony increases the impact strength of tin, the antimony in alloys containing lead causes a definite decrease in impact strength.

On the basis of Baker's[20] work on the creep properties of solder alloys, it has been concluded that the antimonial solders were all superior to their nonantimonial equivalents at both room temperature and at 80°C Chill-cast soft solders with antimony contents equal to 6 per cent of their tin contents were 2 to 4 times as resistant to creep as the corresponding non-antimonial alloys. The improvement due to antimony was even greater in creep tests than that evidenced in tensile tests.

Nightingale[21] reported that solders containing antimony in suitable amounts have a slower alloying effect on copper and brass than the non-antimonial solders. Since less intermediate alloy is formed, copper and brass joints made with antimonial solders are, in general, stronger.

Tests by Nightingale showed that in the case of mild steel joints made with antimonial solders the joints were less strong than those made with solder containing no antimony. Where the lead content of the solder was 55 per cent or more, the presence of antimony was considered detrimental. On the other hand, the highest strength of any steel joint made was produced by a solder consisting of pure tin plus 6 per cent antimony, and entirely free from lead.

Solely from the point of view of strength, Nightingale contended that the maximum advantage occurs when antimony is equal to 1.5 per cent of the tin content.

[20] W. A Baker, *J. Inst. Metals*, **65**, 277–97 (1939).
[21] S. J. Nightingale and O. F. Hudson, *Loc. cit.*

After a study of the effects of impurities on the appearance of solder, Barber[22] concluded that antimony up to 2 per cent has no effect on the

TABLE 30 PHYSICAL PROPERTIES OF THE TIN-ANTIMONY-LEAD SOLDER ALLOYS*

SPECIMEN NO	TENSILE STRENGTH (TONS PER SQ IN)	ELONGATION (% ON 4-IN)	SHEAR STRENGTH (TONS PER SQ IN)	IMPACT STRENGTH (IZOD) (FT-LB)	ELECTRICAL CONDUCTIVITY (%) (Cu)	ANTIMONY (%) (OR Sn CONTENT)	ASSSAYED COMPOSITIONS†			DESCRIPTION
							Sn	Sb	Pb	
A	0 94	55	1 28	14 2	13 9	0	100	0 0007	—	Pure Sn
B	2 04	40	2 04	17 8	12 1	3 0	97 1	2 975	—	Sn-Sb
C	2 65	38	2 68	20 4	10 9	5 5	95 0	5 17	—	
D	2 81	42	2 86	21 2	10 7	6 0	94 5	5 59	—	
E	2 9	32	3 01	21 5	10 4	6 5	93 7	6 2	—	
F	3 43	31	2 77	14 7	12 2	0	66 1	—	33 9	Grade "A" Alloys (Sn-rich)
G	3 89	20	2 86	15 0	11 4	1 56	63 9	0 985	35 1	
H	4 5	17 5	3 07	11 5	10 3	5 5	59 9	3 4	36 7	
I	4 42	17 5	3 07	10 7	10 3	6 0	59 35	3 55	37 1	
J	4 55	12 5	3 08	9 9	10 2	6 5	58 85	3 85	37 36	
K	2 95	38 7	2 79	15 7	11 2	0	56 1	—	43 9	Grade "B" Alloys (Sn-rich)
L	3 36	31 2	2 92	15 7	10 2	5 0	52 82	1 62	45 56	
M	3 68	30	2 99	12 2	9 8	5 5	50 67	2 75	46 58	
N	3 75	29	3 06	11 1	9 6	6 0	50 15	3 00	46 85	
O	3 76	27 5	3 01	10 2	9 7	6 5	49 65	3 13	47 22	
P	2 65	45	2 33	15 1	10 5	0	44 8	—	55 2	Grade "C" Alloy (Pb-rich)
Q	3 19	36 2	2 55	14 8	9 6	3 0	42 4	1 22	56 38	
R	3 39	33 8	2 55	11 7	9 2	5 5	40 4	2 24	57 36	
S	3 55	33 8	2 64	10 4	9 1	6 0	40 0	2 45	57 55	
T	3 51	32 5	2 65	11 3	9 2	6 5	39 72	2 61	57 65	
U	2 87	25	2 13	12 2	9 6	0	33 7	—	66 3	Grade "D" Alloy (Pb-rich)
V	3 06	20	2 25	11 8	8 9	3 0	31 8	0 94	67 26	
W	3 23	21	2 26	10 1	8 6	5 5	30 2	1 65	68 15	
X	3 29	21	2 19	11 3	8 6	6 0	30 1	1 75	68 15	
Y	3 3	18 8	2 22	9 2	8 6	6 5	29 8	1 92	68 28	
Z	0 89	39	0 896	5 6	7 91	0	—	—	100	Pure Pb

Each result is the average of values for 5 specimens

* S J Nightingale, "Tin Solders," 1st Ed , Brit Non-Ferrous Metals Research Assoc (London), 1932

† Per cent by weight

appearance of 50-50 lead-tin bar solder. Only at higher concentrations, 3 per cent or more, are there obtained the curious raised, round spots or

[22] C. L. Barber, *Ind. Eng. Chem.*, **26**, 685 (1934)

"cooling spots," usually attributed to antimony impurities, which form as the alloy cools.

In regard to the use of antimony as a partial substitute for tin in solders, Rhines and Anderson[23] concluded that alloys containing up to 7 per cent antimony, as indicated in Table 29, are entirely satisfactory for general use and for some purposes are superior to the binary alloys because of greater strength at elevated temperatures and a slower creep rate.

Other Modified Solders

Eyles[24] carried out various tests and experiments with a view to using zinc as a tin substitute for solder, but found its employment entirely unsuitable for soft-soldering sheet metals The resulting joints were both weak and brittle. It was concluded that zinc, even when present in very small quantities, has an injurious effect on tin-lead alloys, interfering with the working properties and dulling the surface A zinc-containing solder of the composition 90 5 per cent lead, 8 per cent cadmium, and 1.5 per cent zinc has been found, however, to give good results for many purposes.

Rhines and Anderson[25] stated that the addition of zinc to tin-lead solder has generally proved unsuccessful and no substantial saving of tin is likely to be effected. Their comparison of various zinc-containing soft solders is given in Table 29.

Turkus and Smith[26] have described low-tin solders containing bismuth, or bismuth and silver, that appear to constitute acceptable substitutes for high-tin solders in a great many cases Alloys containing 15 per cent tin, 5 per cent bismuth, 1.5 per cent silver, 1 per cent antimony, balance lead or 20 tin, 3 bismuth, 1.5 silver, 0.5 antimony, balance lead, have liquidus temperatures slightly higher than that of the 40–60 tin-lead solders, markedly higher tensile strength, and a bond strength of approximately 80 per cent. The spreading properties are less than for 40–60 solder but much greater than those of the binary lead-silver solders (See Table 31).

Pewter. Pewter is a subject on which little has been written. It is generally considered to be an alloy of 80 per cent tin and 20 per cent lead. French pewter used for drinking vessels is restricted to a maximum of 18 per cent lead.

For centuries the work of the pewterer in England was controlled by the Worshipful Company of Pewterers. This organization supervised individual workshops to the point of confiscating materials not up to the standard requirements. Nevertheless, it appears that pewter specifications varied widely even under these conditions. "Fine" pewter consisted of

[23] F. N. Rhines, and W. A. Anderson, *Metals and Alloys*, **14**, 704 (1941).
[24] A. J. T. Eyles, *Sheet Metal Ind* , **15**, 50 (1941)
[25] F. N. Rhines, and W. A. Anderson, *Metals and Alloys*, **14**, 704 (1941).
[26] S. Turkus, and A. A. Smith, Jr., *Metals and Alloys*, **15**, 412 (1942).

about 81 per cent tin and 19 per cent copper, with brass sometimes replacing the copper. "Common" pewter was composed of about 82 per cent tin and 18 per cent antimony. These alloys are white, relatively hard, and durable. They will take reasonably good polishing and retain the finished surface under careful handling.

Lead has always been a constituent of pewter, its proportion varying up to 30 per cent, but commonly fixed at about 20 per cent. Bismuth and antimony are often added to reduce the melting point of the alloy. Very little antimony entered the pewters on the Continent. Fioravanti

TABLE 31 PROPERTIES OF LOW-TIN SOLDERS CONTAINING SILVER AND BISMUTH*

COMPOSITION (%)					(LIQUIDUS (° C)	SOLIDUS (° C)	TENSILE STRENGTH (psi)	BOND STRENGTH OF LAPPED JOINTS (psi)	SPREAD TESTS (of 1/2 g in sq in)	CREEP RATE PER CENT PER YEAR AT 30 °C			
Pb	Sn	Ag	Bi	Sb						(200 psi)	(400 psi)	(600 psi)	(800 psi)
60	40	—	—	—	238	183	5,660	6,270	1 30	10 9	92 0	300	—
97 5	—	2 5	—	—	304	304	4,980	3,740	0 19	0 10	0 15	—	0 50
95	—	5 0	—	—	375	304	4,915	4,340	0 20	0 18	0 22	—	0.45
90	10	—	—	—	298	183	4,850	4,960	0 27	2 5	12 0	—	—
87 75	10	2 25	—	—	290†	—	4,950	5,000	0 41	—	2 3	8 0	—
80	20	—	—	—	275	183	4,940	5,680	0 37	6 7	18 7	—	—
78	20	2 0	—	—	267†	—	5,620	5,550	0 57	—	—	—	—
70	30	—	—	—	257	183	5,390	5,770	0 83	10.0	50 0	—	—
69	30	1 0	—	—	251†	—	8,810	5,620	0 86	—	4 0	20 0	—
78 5	15	1.5	5	—	264†	—	4,960	5,310	0 47	—	—	—	—
77 5	15	1.5	5	1 0	258†	—	8,000	5,090	0 29	—	—	—	—
74.85	20	1 5	3	0 5	258†	—	8,120	5,380	0 39	—	—	—	—

Note: Bond and spread tests were made on copper sheets

Tensile and creep tests were made on chill-cast strips of the alloys.

* S Turkus and A. A. Smith, Jr., *Metals and Alloys*, **15**, 412 (1942).

† Determined in this investigation from cooling curves; other temperatures from literature.

used 88 per cent tin and 12 per cent lead for dishes. French compositions curtail the amount of lead to avoid the possibility of lead poisoning due to the formation of lead acetate by the beverages, such as acid wines, held in the vessels. Zinc, in small amounts, has sometimes entered among the constituents of pewter.

Specifications for the alloy in England have been supervised and controlled by a government board, which maintains a high standard. The lead content is restricted to approximately 10 per cent, a qualification which is responsible for the return of a high-grade pewter. Britannia metal is a modern form of pewter, being principally a tin-antimony alloy, containing no lead, but often copper and occasionally small amounts of zinc. Some representative compositions are given in the table of alloys on page 377.

A good Britannia metal contains 90 to 94 per cent tin, 5 to 8 per cent antimony, and 1 to 3 per cent copper. The copper increases the hardness of Britannia metal and causes a decrease in elongation. The effects of copper on Britannia metal are shown in Table 32. Frequently Britannia metal contains zinc, bismuth, nickel, iron, as well as aluminum.

The color of true Britannia metal is silver-white with a bluish tint. In the case of a higher copper content the tint changes from the bluish to brownish. The metal is hard and malleable and can be nickel- or silver-plated without difficulties and defects. The "cry" of Britannia metal is no indication of its quality but depends upon composition of the alloy and the mode of its cooling. It is stronger with quenched than with cooled metal.

TABLE 32 EFFECT OF COPPER ON BRITANNIA METAL

COPPER	BRINELL HARDNESS	ELONGATION (%)	NECKING (%)
—	14 3	55	89
0 8	18 3	53	75
1.5	21 5	39	53

Some precautions have to be taken during the working of Britannia metal In order to prevent losses of tin by oxidation in the manufacture of the alloy, antimony and copper are added to the liquid tin in the usual manner as key alloys. Before casting in iron, or preferably brass or bronze molds, the metal is poled. This is done in the simplest manner with potatoes, steam, or green wood. At the present time it is usually done with ammonium chloride which is introduced into the melt by means of a perforated ladle. The casting temperature should be about 80° C above the melting point of the alloy, varying therefore between 315 and 350° C. In order to avoid a chilling of the casting, the molds are preheated. The molds are painted either with lampblack or red lead. The rolling and (in case of not too hard an alloy) spinning do not offer any difficulties. The hardness of the alloy can be considerably increased by annealing and quenching. Britannia metal is polished with a mixture of whiting and glycerin with buckskin.

American pewter[27] usually consists of 91 per cent tin, 7.5 per cent antimony, and 1.5 per cent copper. After poling with steam and ammonium chloride, it is cast at a temperature of 340 to 375° C. into plates of 8 in. by 12 in. by 1 in. size and cold-rolled. Cold-rolling causes separations which soften the metal. Subsequent tempering dissolves the separations in the metal, which in turn causes hardening.

[27] *Monthly Rev. Amer. Electroplater's Soc.*, **18**, 34 (1931).

The distinctive "cry" of tin is considered by collectors to be of value in judging the purity and quality of pewters. It is supposed to be altered by the presence of zinc and to a lesser extent by lead. However, a good solder containing more than 30 per cent lead will give quite a pronounced tin cry

An example of the variation in purity is shown in the following comparison A pewter plate used for printing music showed a perfect engraving. Analysis showed 27 3 per cent tin, 3 4 per cent antimony, 0.6 per cent copper, 68.7 per cent lead. Contrasting sharply, examination of a very common-looking tavern tankard proved it to be 97 per cent tin, the balance antimony with traces of copper and lead

In the manufacture of pewter, the widely varying melting points of the constituent metals need to be taken into account Tin melts at 232° C., lead at 327° C , copper at 1083° C and antimony at 630° C. It is clear that there is a great possibility of overheating the tin in the melting. Pewter is therefore made from tin-copper, tin-lead, and tin-antimony alloys, whose melting points are lower than the mean of their constituents. The molten alloys are poured into the tin The result is not a simple mixture or solution of the individual metals, but of several constituent alloys which have different melting points and which solidify in successive stages, the whole finally being cemented together by the eutectic. The reader is referred to the phase rule diagrams of the tin-copper, tin-lead, tin-antimony and the ternary system of these metals

The alloy is cast into ingots, then remelted and cast into molds. These may be dies of iron or bronze, or may be of a less durable nature, as plaster and the like Permanent or "chill" molds are composed of several sections These are so joined together that they may be separated to release the casting Care in the fitting of the sectors overcomes to a great extent the tendency to form ridges on the casting at such points. Heating the mold prevents a sudden cooling of the alloy The entrance of dross into the casting is to be carefully avoided The inner surface of the die is lined with a finely powdered material, as oxide of iron, mixed with a gum The pewter articles are next cold-worked, a process which is usually finished, if not completely done, by hammering They may be polished to a bright finish Among the ancient craftsmen, "touch marks" to identify the workman were stamped on the completed article.

Pewter is a comparatively durable alloy if properly handled. It tarnishes on exposure to air, but this tarnish or patina does not detract from the value of the specimen. Corrosion does not readily attack pewter, nor is the alloy subject to "season cracking," a disintegration brought about through hardening. It may be cleaned with a composition of soap and kieselguhr, applied by means of a polishing bob The ancient methods employed sand and often elm leaves or plants. These contained siliceous

matter. Unless cleaning materials are completely removed from the joints of pewter objects, they may tend to loosen these connections

Die-Casting Alloys. Tin is quite widely used in connection with zinc-base die-casting alloys, in which the tin content may vary from 2 to 10 per cent. Lead-base alloys containing appreciable amounts of tin, up to as high as 20 per cent, are finding greater use, while the true tin-base alloys, because of the high cost, are generally superseded by other metals having cheaper constituents Of the tin-base metals which are employed, those carrying high tin content are used more often than the low-tin-base white metals. Sometimes a tin-antimony alloy, containing 60 to 90 per cent tin and the rest antimony, is die-cast for valves

Composition of Commercial Alloys Containing Tin

Toy metals from which small toys are die-cast in large numbers are often lead-base alloys containing an appreciable amount of tin

Table 33 gives the compositions of commercial alloys containing tin. These are subdivided into the bronzes which are basically copper-tin alloys; the tin-containing brasses which are basically copper-zinc alloys, the tin-containing nickel silvers which are basically copper-nickel-zinc alloys, the tin-containing aluminum bronzes which are basically copper-aluminum alloys, the tin-containing manganese bronzes which are basically copper and manganese, the tin-aluminum alloys, the tin-base alloys with additions of antimony-copper primarily and small amounts of lead, often classified as white metal, the lead-base alloys primarily tin and lead with additions of antimony and copper, the tin-containing zinc-base alloys in which copper is an important constituent, the fusible metals, being basically bismuth, tin, lead, and cadmium, the silver alloys, the non-corrosive alloys; the platinum-tin materials, the high-copper alloys with small tin additions, and the tin-containing magnesium alloys Solders have been specifically treated in detail and composition earlier in this chapter.

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TABLE 29. Comparison of the Properties of Soft Solder*

Alloy No.	Composition in weight per cent							Liquidus temperature, (°C)	Solidus temperature, (°C)	Soldering temperatures used in tests (°C)	Tensile strength copper joint (0 005 in thick in lbs per sq in)	Shear strength copper joint (0 005 in thick in lbs per sq in)	Capillary rise (in inches between ¼ in copper rods 0 007 in apart)
	Sn	Pb	Sb	Cd	Bi	Zn	Others						
1	100	—	—	—	—	—	—	231 9	231 9	292	22,706	6,880	1 25
2	—	100	—	—	—	—	—	327 35	327 35	387	0	0	0 56
3	25	75	—	—	—	—	—	266	183	326	13,500	5,795	0 62
4	15	85	—	—	—	—	—	285	225	345	13,300	5,640	0 50
5	5	95	—	—	—	—	—	313	291	373	10,700	6,380	0 44
6	63	37	—	—	—	—	—	183	183	243	29,000	8,000	1 19
7	50	50	—	—	—	—	—	216	183	276	23,900	7,580	0 94
8	45	55	—	—	—	—	—	225	183	285	28,800	8,060	1 12
9	40	60	—	—	—	—	—	238	183	298	14,100	8,280	0 94
10	37 5	62 5	—	—	—	—	—	239	183	299	23,700	8,460	1 06
11	33	67	—	—	—	—	—	252	183	312	17,100	6,450	1 00
12	49 25	50	0 75	—	—	—	—	208	185	268	16,300	8,760	1 00
13	43 5	55	1 5	—	—	—	—	220	188	280	17,550	7,720	1 00
14	38	60	2	—	—	—	—	228	188	288	20,100	7,714	0 56
15	35 5	62 5	2	—	—	—	—	231	188	291	15,100	7,600	0 94
16	31	67	2	—	—	—	—	235	188	295	15,300	7,260	0 94
17	37 5	60	2 5	—	—	—	—	224	186	284	17,350	8,250	1 00
18	4	90	6	—	—	—	—	276	239	336	8,500	6,640	0.06
19	66	27 5	—	6 5	—	—	—	172*	137*	242	17,240	9,940	1 12
20	65	13 5	—	21 5	—	—	—	160*	137*	220	13,000	10,020	0 81
21	50	25	—	25	—	—	—	160	145	220	14,600	9,520	0 75
22	50	32	—	18	—	—	—	145 5	145 5	205	14,900	9,600	0 69
23	32 5	39 5	—	19	—	2	—	165	136	225	18,600	9,950	1 06
24	23	68	—	9	—	—	—	235	145	295	16,600	7,900	0 75
25	15	75	—	10	—	—	—	245	145	305	13,710	4,760	0 56
26	10	80	—	10	—	—	—	253	145	313	13,660	6,440	0 62

27	10	85	—	5	—	—		—	260	145	320	11,720	4,770	0 62
28	10	88	—	2	—	—		—	275	145	335	16,780	5,150	0 75
29	9	65	—	26	—	—		—	225	145	285	14,630	6,980	0 69
30	5	85	—	10	—	—		—	257	145	317	11,870	4,770	0 81
31	3	75	—	22	—	—		—	237	145	297	12,910	6,050	0 81
32	2	86	—	12	—	—		—	262*	239*	322	13,880	6,100	0 44
33	50	25	—	—	25	—		—	130*	110*	190	9,140	6,140	0 62
34	45	27 5	—	—	27 5	—		—	94	—	154	10,760	4,880	0 38
35	22	28	—	—	50	—		—	100	—	160	11,150	7,360	0 38
36	20	40	—	—	40	—		—	113	—	173	12,700	6,520	0 75
37	19	31	—	—	50	—		—	94	—	154	5,790	6,510	0 69
38	13	27	—	10	50	—		—	70	—	130	12,120	6,580	0 38
39	37 5	—	—	12 5	50	—		—	66	—	126	9,000	7,040	0.44
40	33 3	—	—	16 7	50	—		—	66	—	126	10,930	9,440	0 62
41	25	—	—	25	50	—		—	66	—	126	8,520	8,250	0 50
42	—	53 8	—	15 4	30 8	—		—	80	—	140	9,820	5,840	0 31
43	—	42 7	—	7 1	50	—		—	88	—	148	11,940	5,540	0 18
44	—	42	—	15 7	42 3	—		—	89 5	—	150	10,300	5,600	0 18
45	30	—	—	50	—	20		—	277*	157*	337	12,370	8,920	1 00
46	15	—	—	20	—	65		—	346*	157*	406	11,300	10,480	2 00
47	5	—	—	65	—	30		—	294*	229*	354	15,850	9,870	1 25
48	—	91 5	—	8 5	—	—		—	276	249	336	13,150	6,980	0 62
49	—	90	—	10	—	—		—	274	249	334	13,940	7,100	0 56
50	—	80	—	20	—	—		—	259	249	319	13,400	8,140	0 69
51	—	70	—	30	—	—		—	260	249	320	14,000	6,510	0 50
52	—	90	10	—	—	—		—	266	247	326	3,490	3,140	0 06
53	—	87	13	—	—	—		—	247	247	307	2,365	5,770	0 06
54	—	—	—	82 6	—	17 4		—	264 4	264 4	324	13,340	11,250	0 88
55	—	—	—	50	—	50		—	326	264 4	386	12,600	10,410	1 69
56	—	—	—	40	—	60		—	335	264 4	395	6,680	12,050	1.94
57	—	—	—	25	—	75		—	364	264 4	424	9,130	8,580	1.56
58	—	90 8	—	7 8	—	1 4		—	267	237	327	16,400	7,410	0.62
59	—	87 5	—	7 5	—	5		—	368	235	428	10,920	5,820	0 94
60	6	86	—	—	—	—	8 Hg		282*	247*	342	13,450	5,770	0 62
61	3	93	—	—	—	—	4 Hg		384*	270*	364	11,160	5,330	0 31

TABLE 29. COMPARISON OF THE PROPERTIES OF SOFT SOLDER (*continued*)

ALLOY NO	COMPOSITION IN WEIGHT PER CENT							LIQUIDUS TEMPERATURE, (°C)	SOLIDUS TEMPERATURE, (°C)	SOLDERING TEMPERATURES USED IN TESTS, (°C)	TENSILE STRENGTH COPPER JOINT (0 005 IN THICK IN LBS PER SQ IN)	SHEAR STRENGTH COPPER JOINT (0 005 IN THICK IN LBS PER SQ IN)	CAPILLARY RISE (IN INCHES BETWEEN ¼ IN. COPPER RODS 0 007 IN. APART)
	Sn	Pb	Sb	Cd	Bi	Zn	Others						
62	50	—	25	25	—	—	—	311*	214*	371	5,110	9,030	0.94
63	50	25	—	—	—	25	—	336*	155*	396	15,960	10,030	1.31
64	37 3	62 7	—	—	—	—	1 As	240	183	300	16,550	7,910	1.12
65	95	—	5	—	—	—	—	240	232	300	14,200	11,080	0.88
66	41 5	56 5	2	—	—	—	02 P	220	—	280	10,300	10,000	1.00
67	—	79 7	2 6	17 7	—	—	—	239*	—	299	14,600	7,130	0 06
68	—	95	—	—	—	5	—	418	318	478	9,460	4,770	0.94
69	—	97	—	—	—	—	0 25 Cu, 2 5 Ag	350	300	410	11,500	4,770	0.75
70	—	—	—	95	—	—	5 Ag	390	337	450	9,510	10,650	0.75
71	—	—	—	—	—	98	2 Ni	550	419	500	9,450	—	0.88
72	—	98	—	—	—	—	2 Ag	308	304	364	9,560	4,420	0 50
73	—	95	—	—	—	—	5 Ag	365	304	425	9,100	4,100	0.62
74	—	98	—	—	—	—	2 Tl	310	308	390	8,600	5,890	0 69
75	95	—	—	—	—	—	5 Ag	295	221	305	14,100	10,610	1.00

* F. N. Rhines, and W. A Anderson, *Metals and Alloys*, **14**, 704 (1941).

ALLOY NO.	SPREAD OF A DROP 0 1 CC IN VOLUME ON COPPER, (EXPRESSED IN SQ IN COVERED)	SPREAD OF A DROP 0 1 CC IN VOLUME ON COPPER (EXPRESSED IN MAXIMUM THICKNESS OF FILM IN INCHES)	APPEARANCE OF CAST SURFACE	"TINNING" QUALITIES WITH REFERENCE TO COPPER	CORROSION IN 3% NaCl SPRAY (% LOSS IN WEIGHT AFTER 98 DAYS)	CORROSION IN 3% NaCl SPRAY (% LOSS IN WEIGHT AFTER 203 DAYS)	RECOMMENDED USES	REFERENCES TO BIBLIOGRAPHY
1	0 35	0 0279	Bright, furrowed	Very good	0 220	0 442	Electrical equipment	(17)
2	0 26	0 0376	Dull	Very poor	0 120	0 247	None	(21)

3	0.81	0.0139	Frosty	Good	0.156	0 326	General low grade, filler	(12)
4	1.17	0.0102	Dull, very frosty, traces of a furrow	Fair	0.190	0 389	General low grade, coating, jointing, high temp uses	(22), (31), (41)
5	0 34	0 0275	Bright, slight frostiness, slight furrow	Fair	0.097	0.260	"	(12), (27)
6	0.97	0 0164	Bright, slightly discolored	Good	0 325	0 708	Fine solder, General purpose	(13), (15), (26), (36), (45)
7	1.5	0 0060	Bright, traces of a furrow	Good	0 292	0 618	General purpose	(9), (13), (15), (16), (26), (36), (45), (46)
8	2 79	0 0055	Bright, slightly frosty in places	Good	0 288	0 678	Radiators, roofing	(13), (15), (26)
9	1 76	0 0070	Frosty, slightly discolored	Good	0 248	0 515	Wiping, radiators	(13), (15), (46)
10	1 69	0 0076	Very frosty	Good	0 260	0 525	Wiping, radiators	(13), (14), (15)
11	1 61	0 0119	Very frosty	Good	0 342	0 697	Wiping	(13), (15), (26), (45)
12	1.49	0 0096	Bright, slightly discolored	Good	0 455	0 765	General, tin plate	(10), (13), (15)
13	1 77	0.0075	Frosty, furrowed, slightly drossy	Good	0 429	0 930	General purpose	(10), (13), (15)
14	1 24	0 0093	Very frosty, slightly discolored	Good	0 457	0 709	Wiping	(10), (13), (15)
15	0 93	0 0155	Very frosty, slightly discolored	Good	0 292	0 756	Wiping	(10), (13), (15)
16	0 99	0 0135	Frosty, spotted, slightly drossy	Fair	0 314	0 629	Wiping	(10), (13), (15)
17	2 03	0 0055	Frosty and bright, spotted	Fair	0 272	0 688	Wiping	(10), (12), (15)
18	0 19	0 0534	Very frosty, furrowed	Poor	0 230	0 406	High temperature service	(15), (41)
19	1.00	0 0145	Dull, frosty, slightly furrowed	Fair	0 097	0 410	Wiping	(19), (39)
20	0 88	0 0162	White, frosty	Fair	0 162	0 950	Wiping	(19), (39)
21	1.18	0 0180	Bright, roughened trace of shallow furrow	Fair	0 153	1 175	General purpose	(19), (46)
22	1.14	0 0187	Bright, smooth	Good	0.040	0 594	Fusible safety devices	(6), (39), (46)
23	0.93	0 0170	Dull, frosty, spotted	Good	0 192	1 172	General purpose	(9)
24	1.24	0 0103	Dull, frosty, grainy	Good	0 017	0.443	Wiping	(14), (39)
25	1.09	0.0094	Slightly frosty	Fair	0 046	0.380	Coating and jointing	(20), (39)
26	0.91	0.0135	Dull, frosty	Fair	0.019	0.405	Gen , elect ; cans; roofing	(2), (5), (9), (19), (20), (25)
27	0.73	0.0120	Dull, rough	Fair	0 214	0.494	General purpose	(41)

TABLE 29 COMPARISON OF THE PROPERTIES OF SOFT SOLDER (*continued*)

ALLOY NO	SPREAD OF A DROP 0 1 CC IN VOLUME ON COPPER (EXPRESSED IN SQ IN COVERED)	SPREAD OF A DROP 0 1 CC IN VOLUME ON COPPER (EXPRESSED IN MAXIMUM THICKNESS OF FILM IN INCHES)	APPEARANCE OF CAST SURFACE	"TINNING" QUALITIES WITH REFERENCE TO COPPER	CORROSION IN 3% NaCl SPRAY (% LOSS IN WEIGHT AFTER 98 DAYS)	CORROSION IN 3% NaCl SPRAY (% LOSS IN WEIGHT AFTER 203 DAYS)	RECOMMENDED USES	REFERENCES TO BIBLIOGRAPHY
28	0 65	0 0200	Dull, frosty, furrowed	Fair	0 143	0 451	General purpose	(41)
29	0 86	0 0121	Bright, frosty, furrowed	Fair	0 150	0 684	General purpose	(39)
30	0 74	0 0141	Dull, frosty, trace of furrow	Fair	0 083	0 551	General purpose	(19), (20)
31	0 94	0 0114	Bright, rough furrow	Fair	0 236	0 743	General purpose	(39)
32	0 69	0 0197	Very dull and frosty, shallow furrow	Fair	0 250	0 787	General purpose	(18)
33	0 71	0 0170	Dull discolored, appears "etched"	Fair	0 151	0 289	Joining pewter	(23), (26)
34	0 66	0 0190	Bright, frosty, appears "etched"	Fair	0 223	0 473	Pewter, lead, tin, Britannia	(23), (32)
35	0 61	0 0290	Bright, slightly frosty, furrowed	Fair	0 216	0 340	Lead, tin, Britannia	(23)
36	0 60	0 0176	Very dull deep frost, trace of furrow	Fair	0 206	0 431	Lead, tin, Britannia	(23), (32)
37	0 41	0 0250	Bright, slightly frosty, "etched," slight furrow	Fair	0 207	0 331	Britannia	(12), (23)
38	0 32	0 0315	Dull, frosty, slight furrow	Fair	0 334	1 048	Fusibility, glass-metal	(12), (23), (44)
39	0 30	0 0265	Dull, frosty, furrowed, appears "etched"	Fair	0 198	0 620	Fusible alloy	(19)
40	0 42	0 0230	Frosty, slight furrow, appears "etched"	Fair	0 342	1 371	Fusible alloy	(19)
41	0 47	0 0221	Frosty with bright facets	Fair	0 196	1 580	Fusible alloy	(19)
42	0 22	0 0459	Frosty with bright facets	Fair	0 405	1 347	Fusible alloy	(19)
43	0 13	0 0785	Dull deep frost	Fair	0 441	0 314	Fusible alloy	(19)
44	0 17	0 0520	Slightly frosty, showing facets	Fair	0 343	1 367	Fusible alloy	(19)
45	0 36	0 0095	Dull, frosty, showing facets	Fair to poor	1 685	3 990	—	(19)
46	0 84	0 0195	Dull white, frosty, appears "etched"	Fair to poor	2 190	4 810	—	(29)

47	0 75	0 0155	Frosty, acicular ridges	Fair to poor	1 130	3 740	—	(19)
48	0 25	0.0140	Dull brown oxide over all	Fair	—	0 198	Carbon copper, zinc, iron	(11), (19), (28)
49	0 32	0 0350	Deep brown oxide over all	Fair	0 0215	0.509	Copper, zinc, iron	(4), (17), (19), (25)
50	0.60	0 0180	Bright, frosty, rough irregular surface	Fair	0 134	0 845	—	(17), (19)
51	0 36	0 0322	Dark blue-brown oxide over all	Fair	—	0 340	—	(19)
52	0 14	0 0770	Bright, frosty	Very poor	0 128	0 368	Lead cable	(38)
53	0 11	0 0945	Bright, frosty	Very poor	0 244	0 425	Lead cable	(38)
54	0 53	0.0195	Bright, shiny	Poor	0 279	1 022	High temp , galvanized	(8), (12), (33), (37)
55	—	—	Bright, frosty, rough	Poor	1 870	3 820	High temp service	(12)
56	1 03	0 0155	White, frosty	Poor	2 230	4 470	Bronze, Al to Cu	(19), (34)
57	0 66	0 0201	Dull white, frosty	Poor	1 480	6 040	High temp service	(18)
58	0 35	0 0279	Dull, frosty, spotted	Fair	0 0541	0 460	Copper, iron, tin, galv	(5), (19), (25), (46)
59	0 41	0 0261	Bright, shiny, rough	Fair	0 519	1 028	Copper, iron, tin, galv.	(3), (19), (46)
60	0 32	0 0327	Bright, frosty	Fair	0 314	0 589	Galvanized, sheet iron	(38)
61	0 36	0 0275	Dull, appears "etched," coarse furrow	Fair	0 195	0 379	Galvanized, sheet iron	(7), (38)
62	—	—	Bright, discolored, acicular ridges	Fair	0 106	0 476	Pewter, Britannia, Sb-lead	(19)
63	0.39	0.0370	Dull, frosty, coarse	Fair to poor	1 280	2 740	Aluminum	(1)
64	1 79	0 0065	White, frosty, spotted	Good	0 478	0 903	Wiping	(40)
65	0 29	0 0340	Bright, shiny, appears "etched," trace of furrow	Good	0 275	0 415	Electrical equipment	(12), (17)
66	0 79	0.0173	Bright, shiny, spotted	Good	—	—	General purpose	(24)
67	0 13	0 0680	Very dull, frosty, rough	Fair	0 087	0 590	—	—
68	—	—	Bright, frosty, coarse	Poor	0 131	0 848	High temp service	(3)
69	0 41	0 0361	Bright, spotted	Poor	0 138	0 513	Electrical equipment	(42), (43)
70	1 91	0 0400	Dull brown oxide over all	Fair	0 893	3 840	High temp service	(12)
71	0 31	0 0440	Bright, frosty, rough, furrowed	Poor	2 240	10 210	Carbon; high temp.	(3), (11)
72	0 35	0 0280	Dull, rough, coarse furrow	Fair	—	—	Electrical, high temp.	(17), (27), (43)
73	0 41	0 0269	Dull, discolored, rough	Fair	0 098	0 379	Electrical, high temp.	(17)
74	0 20	0 0485	Bright, shiny, trace of furrow	Poor	—	—	Electrical, high temp.	(27)
75	0 91	0.0140	Bright, shiny	Good	—	—	Electrical, high temp.	(17)

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TABLE 33 ALLOYS CONTAINING TIN

Aluminum Bronzes

	Cu	Al	Fe	Zn	Sn	OTHER ELEMENTS
Cast Aluminum Bronze	89 5–90 5	9 5–10 5	1 0 max	—	0 2 max	Impurities 0 5
Cast Aluminum Bronze S A E 68	85 0–87 0	7 0– 9 0	2 5–4 0 max	—	0 5 max	Impurities 0 3
Castings	88 0–91 0	9 5–10 5	0 2 max	—	0 5 max	Si and Mn 1 0
Gears, Steel Mill Stupper Nuts	86 0 max	8 0– 9 5	2 5–4 0	—	0 5 max	
Mill Stupper Nuts	88 3–90 5	9 5–10 5	1 3 max	—	0 2 max	
Rods, Bars, Shapes	78 0–93 0	6 5–11 0	4 0 max	—	0 6 max	Mn 2 0 max, Ni 5 5 max *, Si 2 3 max.
Sand Castings	78 0–86 0	10 3–11 2	3 0–3 8	—	0 2 max	Mn 3 5 max, Ni 5 0 max
Tensilite	64 0	3 1	1 2	29 0	0 2	Mn 2 5
Tin Aluminum Bronze	85 5	2 5	—	2 0	10 0	

* When both Si and Ni are present, only one shall be in excess of 0 25%.

Aluminum-Tin Alloys

	Al	Cu	Zn	Sn	Mg	Ni	Fe	Si	OTHER ELEMENTS
Bourbonnes	48 8	0 3	—	50 5	—	—	0 3	—	
Fletcher and Emperer Bearing	92 2	7.5	—	0.3	—	—	—	—	
Fletcher's Alloy	95.5	3.0	—	1.0	—	—	—	—	Sb 0.1, PSn 5.0
Huron· Castings A-5	89 9	6 6	—	0 5	0.5	1.3	—	—	Co 0 3 and (Mn, Cd 0.5)
Ingots Casting 22	83 7	6.3	5.0	5.0	—	—	—	—	
Krupp (Grosmann) Bearing	87 0	8 0	—	5 0	—	—	—	—	
Liberty Piston	76.6	1.1	21.3	0.1	—	—	0 5	—	Pb 0.3
Magnalite	92.9	2.6	—	0 2	1.4	1.7	0 9	0.4	
Magnalium: Cast y	96 0	1.8	—	—	1 5	—	—	—	Sn and Pb
Cast z	94.4	0 2	—	3 2	1 6	—	—	—	Pb 0.7
Manhardts	83 3	6.2	—	10 0	0.1	—	—	—	P 0.1

	Al	Cu	Zn	Sn	Mn	Ni	Fe	Si	OTHER ELEMENTS
Al-Cu-Zn Strong: Ingot	82 7	3 2	12.8	0 1	0 4	—	0.5	0 2	Pb 0.2
Ingot	82 8	5 5	9.9	0 3	0 2	—	0 8	—	Pb 0.3
McAdams, W A.	80.0	—	—	8 0	—	—	—	—	Cd 8 0, Ag 4.0
McLure	85 4	8.2	—	5.0	0 2	—	0.9	0.3	
Mock Silver	84 2	5 5	—	10 2	—	—	—	—	P 0.1
Partinium	96 0	0 6	—	0.2	—	—	—	—	Sb 2.4; W 0.8
Romanium	97.4	0 3	—	0.2	—	1.8	—	—	Sb 0.3; W 0 2
Rosein	30 0	—	—	20 0	—	40.0	—	—	Ag 10.0
Wolframium	97.2	0 4	—	1.0	—	—	—	—	Sb 1.4; W 0.04
Zeppelin Alloys. Angles	90.3	0.7	7.8	0.1	0.3	—	0 5	0 4	
Channels	88.7	0.7	9.1	0 2	0.5	—	0.4	0.5	
Zisium	83.0	1.0	15 0	1.0	—	—	—	—	

Brasses

	Cu	Zn	Sn	Pb	Fe	OTHER ELEMENTS
Admiralty	71 0	28 0	1 0	—	—	
Admiralty A	70 0	29 0	1 0	—	—	
Bell Brass	64 3	35 0	0 8	—	—	
Bismuth Brass	47 0	21 0	1 0	—	—	Ni 30 9, Bi 0 1
Bow Wire	93 0	2 0	5 0	—	—	
Brush Wire	64 3	35 0	0 8	—	—	
Button Brass	89 5	10.0	0 5	—	—	
Buttons (Thurston)						
"Bidery"	48 5	33 3	6 1	12 2	—	
Bristol Alloy	57 9	36 8	5 3	—	—	
Bristol Alloy	61 1	36 1	2 8	—	—	
"Gold"	58 7	33 0	5 5	2 8	—	
Jackson's Alloy	63 9	30 6	5 6	—	—	
Jackson's Alloy	63 0	35 6	1 4	—	—	
Commercial Castings	62 0	30 0	6 0	2 0	—	
Diaphragm Brass	95 0	2 0	3 0	—	—	
Doctor Metal	88 0	9 5	2 5	—	—	
Durana	65 0	30.0	2 0	—	—	Al 1 5
Electric Brass Castings, B E	84 0	13 0	3 0	—	—	
English	70 3	29 3	0 2	0 3	—	
Fob Metal	87 5	12 0	0 5	—	—	
Forging Rods, Bars and Shapes	78–93	—	0 1 max	—	4 0	Si 2 3 max * Ni 5 5, Al 6 5–11; Mn 2 0 max
Forging Rods, Bars and Shapes	57–61	Rem	0 5–1 5	1 0 max	0 8–2 3 max.	Al 0 8 max
Forging Rods, Bars and Shapes	59–61	Rem.	0 5–1 0	0 2 max	0 1 max.	
Fourdrinier Wire	84.6	15.0	0.4	—	—	

* When both Si and Ni are present, only one shall be in excess of 0.25%.

Brasses—continued

	Cu	Zn	Sn	Pb	Fe	OTHER ELEMENTS
Gold Leaf Aix	64 8	32 8	2 0	0 4	—	
Gold Leaf Jem-mapes	64 6	33 7	1 4	0 2	—	
Guettier's Button	61 5	32 0	6 5	—	—	
Guettier's Button	61 4	28 9	9 7	—	—	
Hardware Bronze	88 0	9 5	1 5	1 0	—	
Harlington Bronze	55 7	42 7	1 0	—	0 6	
Harmonia Bronze	55 7	41 2	0 5	0 5	1 3	Al 0 9
Ingot for Sand Casting	84–85 5	4 5–5 5	4 5–5 5	4 5–5 5	0 3 max	Ni 0 5 max , P 0 01 max
Iserlohn, Cast	63 7	33 5	2 5	0 3	—	
Jewelers Metal	91 5	6 5	2 0	—	—	
Jewelers Metal	88 0	11 3	0 8	—	—	
Jewelers Metal	87 5	12 0	0 5	—	—	
Jewelers Metal	91 0	7 5	1 5	—	—	
Machinery Brass	83 0	16 0	1 0	—	—	
Manganese Brass	60 2	34 8	0 9	0 4	1 2	Mn 2 3, Al 0 2
Manganese Bronze						
(1) Propeller Hubs and Blades, Gas Engine	55–62	Rem	0–1 5	0 4 max	0 6–2 0	Al 0 5–1 5, Mn 0 2–3 5
(2) Bases	56–65	Rem	0–1 0	0–0 2	2 0–5 0	Ni 0–3 0, Al 2–7, Mn 2–6
Manganese Bronze, Rolled	64 8	33 7	1 1	—	—	Mn 0 3
Manganese-Nickel Brass	53 5	39 0	0 1	—	2.8	Mn 1 5, Ni 2 4

Brasses—continued

	Cu	Zn	Sn	Pb	Fe	OTHER ELEMENTS
Manganese-Nickel Brass	63.5	28 3	1.2	0 2	1.4	Mn 3.2, Ni 2.1
Manganin	53.4	39.0	2.0–7.0	—	—	Ni 2.5, Mn 1.7, Al 0.2
Manheim Gold	89.4	9.9	0 6	—	—	
Manheim Gold	83 7	9.3	7.0	—	—	PSn 5
Muntz Metal Brass Pipe	59–63	Rem.	0.2 max.	0.5 max.	0.1 max.	
Condenser Tubes, Plates	58–61	Rem.	0.3 max.	0.4–0 9 max	0 2 max.	
Condenser Tubes, Plates	59–61	Rem.	0 5–1.0	0 2 max	0 1 max.	
Naval Brass	61.0	38 0	1 0	—	—	
Naval Brass 45	60.0	39.3	0 8	—	—	
Naval Brass Rods	59–62	Rem.	0.5–1 0	6 2 max.	0.1 max.	
Naval Brass Rods	59–62	Rem.	0.5–1.0	0.4–1 0 max.	0 1 max.	
Naval Brass Tubing	59–61	Rem.	0 5–1.0	0.3 max.	0.1 max.	
Cast and Worked	63.6	34.3	0.2	2 0	—	
Cast and Worked	61.6	35.3	0.6	2.5	—	
Nickel Brasses:						
Condenser Tubes and Ferrule Stock	Rem.	1.0 max.	1.0 max.	0.1 max.	0.5	Ni 19–23, Mn 1.0
Condenser Tubes, Ferrule Stock, and Sheet and Strip	Rem.	3–6	1.0 max.	0.1 max.	0.5	Ni 19–23, Mn 1.0
Fittings, Marine Hardware	55.0	20.0	2.0	10.0	1.0	P 0 1 max., Sb 13.0

Brasses—continued

	Cu	Zn	Sn	Pb	Fe	OTHER ELEMENTS
High-Temperature Corrosion-Resistant Work	33.0	—	13.0	—	—	Ni 54.0
Marine Service	Rem.	1.0 max.	1.0 max.	0.1 max.	1.0–1 3	Si 0.3–0.8, Ni 28.5–31.5, S 0 2 max., Al 0.1 max., Mn 0.6–1.2
Ornamental	55.0	18.0	4.0	8 0	1.0 max	P 0.1 max., Ni 15 0, Mn 1.5 max.
Used for Plumbing	62–65	6–10	2.5–4.0	5.0–6.0	1.0 max.	P 19–20, Ni 19–20, Mn 1.0 max.
Work, Textile Laundry, Dairy Equipment, Chemical Pumps, etc.	56.0	15.0	4 0	1.0	—	P 0.1 max., Ni 20.0
Oker Brass (Harz)	62.8	36.5	0.6	0.1	—	
Optical Bronze	89.0	6.5	4.5	—	—	
Oreide	87.3	11.5	1.3	—	—	
Oreide	80.5	14.5	4 9	0.1	—	
Oreide, Brunswick	68.1	31.5	0 5	—	—	
Parson's Manganese Bronze	60.2	34.8	0.9	0.4	1.2	Mn 2.3, Al 0.2
Pen Metal	85.0	13.0	2.0	—	—	
Pewter (Thurston) Berthier's Alloy	71.9	24.9	1.2	2.0	—	
Cast Gilt	63.7	33.5	2.5	0.3	—	
Cast Gilt	64.5	32.4	0.2	2.9	—	
For Clock Work	60.7	36.9	1.4	0.7	—	
For Clock	64.0	33.5	1.5	0.9	—	

Brasses—continued

	Cu	Zn	Sn	Pb	Fe	OTHER ELEMENTS
Cast Gilt	63 7	33 5	2 5	0 3	—	
Cast Gilt	64 5	32 4	0 2	2 9	—	
For Clock Work	60 7	36 9	1 4	0 7	—	
For Clock Work	64 0	33 5	1 5	0 9	—	
Potinjaune	71 9	24 9	1 2	2 0	—	
Red Brass	69 0	30 0	1 0	—	—	
Red Brass Pipe	83–86	Rem	1 2 max	0 1 max	0 1 max	
Refrigeration Metal	76–78	5 5–6 5	4 0–6 0	9 0–11 0	0 3 max	Si 0 01 max , P 0 1 max , Sb 0 2 max , Ni 1 5–2 5, S 0 1 max
Russian, Cast	78 0	21 0	1 0	—	—	
Sand Castings	84–86	4 0–6 0	4 3–4 8	4 5–6 0	0 3 max	Ni 1 0 max , P 0 03 max
Sand Castings						
Commercial Red Brass	82 0–83 5	6 0–7 5	3 5–4 3	5 8–6 8	0 3 max	Ni 0 5 max , P 0 01 max
Commercial Red Brass	82 0–83 8	5 5–8 0	3 3–4 3	5 5–8 0	0 3 max	Ni 1 0 max , P 0 03 max
Copper Base Alloys	70 0–71 8	Rem	0 8–1 5	2 5–3 5 max	0 5 max	
Free-Cutting Brass Rod	58 0–61 0	Rem	0 8–1 3	0 8–1 3 max	0 5 max	Al 0 1–0 2
Free-Cutting Brass Rod	58 0–62 0	Rem	0 5–1 3	0 8–1 5 max	0 8 max	
High-Strength Yellow Brass	61 0–63 5	Rem	0 3 max	0 1 max	2 5–3 5 max	Ni 1 0 max , Al 4 5–6 0, Mn 3.0–4 5
High-Strength Yellow Brass	58 0–64 0	Rem	1 5 max	0 5–1 5	3 0 max	Al 3 0 max , Mn 3 5 max
High-Strength Yellow Brass	**55 0–60 0**	**Rem**	**1 5 max**	**0 5–1 5**	**2 0 max**	**Al 1 5 max., Mn 1.5 max**

Brasses—continued

	Cu	Zn	Sn	Pb	Fe	OTHER ELEMENTS
High-Strength Yellow Brass	55 0–60 0	38 0–42 0	1 5 max	0 4 max	2 0 max	Al 1 5 max, Mn 3.5 max
High-Strength Yellow Brass	57 0–60 0	Rem	0 5–1 5	0 2 max	0 8–2 0 max	Al 0 3 max, Mn 0 5 max
High-Strength Yellow Brass	56 0–62 0	Rem	1 5 max	0 5–1 5	2 0 max	Al 1 5 max, Mn 1 5 max
High-Strength Yellow Brass	56 0–59 0	Rem	0 5 max	0 4 max	0 8–1 5 max	Ni 0 5 max, Al 0 8–1 5
High-Strength Yellow Brass	56 0–62 0	Rem	0 5–1 0	0 5–1 0	0 8–1 5 max	Ni 0 5 max Al 0 3–1 0, Mn 0 1–0 5
High-Strength Yellow Brass	56 0–59 0	Rem	0 5 max	0 3 max	0 8–1 5 max	Ni 0 5 max, Al 0 8–1 5, Mn 0 1–0 5
High-Strength Yellow Brass	61 0–63 5	Rem	0 3 max	0 1 max	2 5–3 5 max	Ni 1 0 max, Al 4 5–6 0, Mn 3 0–4 5
High-Strength Yellow Brass	66–74	Rem	0–1 5*	2–4	0 6 max	Ni 1 0 max *
High-Strength Yellow Brass	66–74	Rem	0–1 5*	2–4	0 6 max	Ni 1 0 max,* Al 0 2–0 5
Leaded High Brass	65–67 5	Rem	0 8–1 3	2 8–3 5	0 5 max	1 0 max
Leaded High Brass	64–69	Rem	0 5–1 3	2 5–3 5 max	0 8 max	

* Sn and Ni shall not be added intentionally

Brasses—continued

	Cu	Zn	Sn	Pb	Fe	OTHER ELEMENTS
Leaded Nickel Brass	58–61	Rem.	2.5–3.5	4 5–5.5	1.0 max.	Ni 15 5–17, Mn 0.5 max
Leaded Nickel Brass	57–62	Rem.	2.3–3.8	4.3–5.8	1.5 max.	Ni 15.–17.5, Mn 0.5 max.
Leaded Nickel Brass	53–58	Rem.	1.5–3.0	8–11	1.5 max.	Ni 11–14, Mn 0 5 max.
Leaded Nickel Brass	Rem.	1.0–2.0	5.0–5.5	Nil	—	Ni 5.–5.5, P 0.03–0 05
Leaded Semi-Red Brass	78–82	7–10	2 8–3 3	6–8	0 4 max	Ni 0.5 max., P 0 01 max.
Leaded Semi-Red Brass	78–82	7–10	2 5–3 3	6–8	0.4 max	Ni 1.0 max , P 0 02 max
Leaded Semi-Red Brass	75–76.8	14–16	2 8–3 3	5 5–6 5	0 4 max.	Ni 0.5, P 0 01
Leaded Semi-Red Brass	75–76 8	13–17	2 5–3 3	5 3–6 3	0 4 max.	Ni 1.0, P 0 02
Leaded Yellow Brass	70.0–73 8	Rem	0 8–1 5	2 5–3 5	0 6 max	
Red Brass Ounce Metal	84.0–86.0	4 0–6 0	4 0–6 0	4 0–6 0	0 3 max	Ni 0 8 max., P 0 1 max
Screen Plates	58 0	41.0	0 8	0 3		
Screw Brass	78.0	16 0	4 5	1.5		
Screw Bronze	93 5	5 0	1 0	0.5		
Semi-Red Brasses:						
Low Pressure Steam Fittings	83.0	5.0–7.0	3 3–4.8	5 0–7 0	0.3 max.	Si 0 1 max , P 0.1 max., Sb 0.3 max., Ni 1.0 max., S 0.1 max.

Brasses—continued

	Cu	Zn	Sn	Pb	Fe	OTHER ELEMENTS
Plumbing Fixtures	78 0	12 0–14 0	1 5–2 5	6 0–8 0	0 3 max	Si 0 01 max., P 0 03 max., Sb 0 3 max., Ni 1.0 max , S 0 1 max.
Plumbing Fixtures	77 0	9 0–10.0	2 5–3 5	9 0–11 0	0.3 max.	Si 0 005 max , P 0.01 max., Sb 0 3 max., Ni 1.0 max., S 0 1 max.
Radiator Valves	80 0	7 5– 9 5	2 5–3 5	6 3– 7.8	0 3 max.	Si 0 01 max , P 0 1 max , Sb 0.3 max., Ni 1 0 max., S 0.1 max.
Sheet:						
China	56 6	38 2	3 3	1 0	1.4	
Hegermuhl	71 7	27 3	0 2	0 8	—	
Hegermuhl	72 0	27.0	1 0	—	—	
Hegermuhl	62 0	37.0	0 5	0 5	—	
Hegermuhl	62 0	37.0	1 0	—	—	
Jamappes	64 6	33 7	0 2	1 4	—	
Oker	55 0	44 5	0.5	—	—	
Romilly	70 1	29 3	0 2	0 3	—	
Stollberg	64 8	32 8	0 4	2 0	—	
Similor	89 4	9.9	0 6	—	—	
Similor	83 7	9 3	7 0	—	—	
Solder, (Thurston):						
Nearly White, Soft	44.7	50.7	3 4	1.2	—	
White, Very Soft	57.4	28 0	14.6	—	—	
Yellow, Hard	54.4	44 0	1 3	0 3	—	
Sterro Metal	55 0	42.4	0.8	—	1.8	
Talmi Gold	86 4	12 2	1.1	—	0 3	
Thurston's	55 0	44 5	0 5	—	—	
Tissier's	97.0	2 0	0 5	—	—	
Tobin Bronze	60.0	38.0	2 0	—	—	
Tobin Bronze	59.0	39 0	2.0	—	—	

Brasses—continued

	Cu	Zn	Sn	Pb	Fe	OTHER ELEMENTS
Tombac.						
French	80 0	17.0	3 0	—	—	
Golden	82 0	17 5	0 5	—	—	
Trumpet Metal	81 0	17 9	1 1	—	—	
Tubes, Etc ,						
Admiralty	70 0	29 0	1 0	—	—	
Russian	59 7	38 6	0 2	0 3	1 1	
Tungsten Brass (Ni, 0 8)	59 8	33 9	0 2	—	—	Al 2 8, W 2 0 Mn 0 7
Wire	70 3	29 3	0 2	0 3	—	
Wire, English	70 3	29 4	0 3	0 2	—	
Yellow Brass						
Castings	62 0–67 0	Rem	1 0 max	1 5–3.5 max.	0 8 max	
Industry	60 0–62 0	30 0–35 0	1 0 max	1 0–3 0	0.3 max	Si 0 1 max , P 0 01 max , Sb 0 1 max , Ni 0 5 max , S 0 1 max , Al 0 5 max , Impurities 1 0 max
Plumbing	70 0–71 0	20 0–24 5	1 0–2 0	2 0–4.0	0.3 max.	Si 0 1 max , P 0 01 max , Sb 0 1 max , Ni 0 5 max , S 0 1 max , Impurities 0 1 max

Bronzes

	Cu	Sn	Zn	Pb	P	OTHER ELEMENTS
Acid Bronze	82 0	8 0	2 0	8 0	—	
Argozoil	54 0	2 0	28 0	2 0	—	Ni 14 0
Bearing Bronze.						
Automobile	78 0	8 0	1 0	12 0	—	PSn 1
E B D, Breslau	88 0	10.0	2 0	—	—	PSn 5
French	82 0	10 0	8 0	—	—	
Locomotive	74 0	10 0	9 0	7 0	—	
Prussian	84 0	15 0	1 0	—	—	
Railroad Cars	75 0	20 0	5 0	—	—	
Rheinland	86 0	12 0	2 0	—	—	
Russian	77 0	10 2	5 1	7 7	—	
Various	83 0	14 0	2 0	1 0	—	
	83 7	14 2	2 1	—	—	
	85 5	12 8	1 7	—	—	
	83 0	12 0	5 0	—	—	
	85 0	11 0	4 0	—	—	
	74 5	9 5	8 9	7 1	—	
	77 0	9 0	14 0	—	—	
	83 7	8 8	7 5	—	—	
	81 0	7 0	3 0	9 0	—	
	87 5	8 1	2 5	1 9	—	
	86 0	6 0	5 0	—	—	Mn 2 7
	75 0	4 0	21 0	—	—	
	86–70	10–14	0–1	0–0 5	0–0 3	0–0 5 Impurities
	78–84	16–22	0–0 3	---	0–0 1	0–0 5 Impurities
	83–86	4 5–6	2 0 max	8–10	—	0 3
Bearings of Engines	79 0	8 0	5 0	8 0	—	
Bell Metal						
Herbohn	60 0	35 0	5 0	—	—	
Herbohn	71 4	26 4	2 7	—	—	
Karakane	65 9	17 3	3 5	10 4	—	
Karakane	64 0	24 0	9 0	—	—	Fe 3 0
Karakane	62 5	25 0	9 4	—	—	Fe 3 1
Karakane	61 0	18 0	6 0	12 0	—	Fe 3 0
Old Bell at Rouen	71 0	26 0	1 8	1 2	—	
Bismuth Bronze	53 0	15 0	20 0	—	—	Ni 10, Al 1, Bi 1
Brasses	74 4	9 5	8 9	7 1	—	

	Cu	Sn	Zn	Pb	P	OTHER ELEMENTS
Brasses	70.0	10.0	10.0	10.0	—	
Brasses	74.0	1.0	10.0	15.0	—	
Bridge Bronze	88.0	10.0	2.0	—	0.3	
Bushings	86.2	10.2	3.6	—	—	
Bushings	85.0	11.0	4.0	—	—	
Camelia	70.4	4.2	10 2	14.7	—	Fe 0.5
Carbon	75 4	9 7	—	14.5	—	
Carriage Wheel Bearing	84 0	16.0	—	—	—	
Castings:						
Bronze Bearing Casting	81–85	6 5– 7.5	2–4	6–8	—	Fe 0 2 max.
Copper Base Sand Casting	87–89	9.5–10 5	1 5–2 5 max	0.3 max.	—	Ni 0 8 max
Copper Base Sand Casting	87–89	7 8– 8.5	3.5–4.5 max.	0.3 max.	—	Ni 0 8 max
Copper Base Sand Casting	86.5–88.5	9 3–10 5	1 3–2 5 max.	0.8–1.3 max.	—	Ni 1 0
Copper Base Sand Casting	86–89	7.5–9	3–5 max.	0.9 max.	—	Ni 1.0
Copper Base Sand Casting	86–89	7.5– 9	3–5 max.	1.0 max.	—	Ni 1.0
Copper Base Sand Casting	85–88	7.5– 9	3–5 max.	1–2.5 max.	—	Ni 1.0
Copper Base Sand Casting	87–89	5.8– 6.5	3.5–5	1.3–1.8	—	Ni 1.0 max.
Copper Base Sand Casting	83–85	4.5– 5.5	0.5–1.5	8.5–10	—	Ni 0.5 max.
Hard Bronze Casting	86–89	9–11	1–3 max.	0.2 max.	—	

	Cu	Sn	Zn	Pb	P	OTHER ELEMENTS
High-Leaded Tin Bronze Sand Castings	83–86	4 5–6	0 5–2 0	8–10	—	Ni 0 5 max.
Sand Castings	86.5 min.	5 5– 6 5	2.5–5	1–2	—	Ni 1 0 max.
Sand Castings	86–89	9–11	1.0–3.0 max.	0.8–1.5 max.	—	Ni 1.0
Sand Castings	64–66	4 5– 5 5	1–3	1–2	—	Ni 24–26, Mn 1 0 max., Fe 0 5 max.
Sand Castings	64–67	4–5 5	1–3	1–2 5	—	Ni 24–27, Mn 1.0 max., Fe 1.0 max.
Sand Castings	85–88	7 5–9	3–5	1–2 3	—	Ni 1 0 max.
Sand Castings	63–65	3 5–4 5	7–10	3–5	—	Ni 19 5–21, Mn 1 0 max., Fe 1.0 max.
Sand Castings	62 0 min.	2 5 min	10 0 max	6 0 max	—	Ni 19.0 min , Mn 1 0 max
Sand Castings	63–67	3 5–4 5	6–10	3–5	—	Ni 19 5–21 5, Mn 1 0 max , Fe 1 0 max
Tin Bronze Casting	86–89	9–11	1–3 max	0 03 max.	—	Ni 1 0 max.
Tin Bronze Sand Castings	86–89	7 5–9	3–5 max.	0 03 max.	—	Ni 1 0 max.
Tin Bronze Sand Castings	86–89	7.5–9	3–5 max	1.0 max.	—	Ni 1.0 max.
Tin Bronze Sand Castings	86–89	7.5–11	1–5 max	0.6 max.	—	Ni 1.0 max.
Chinese	74.0	1 0	10 0	15 0	—	
Cocks	88 0	10–8	2–4	—	—	
Cogs and Worms	85.0	11.0	4.0	—	—	
Coinage	95 0	4.0	1.0	—	—	
Cooper's Speculum	57.8	27.3	3 6	—	—	As 1 2, Pt 10
Daimler Bearing	76.0	3.0	20.0	1.0	—	
Damar	76.4	10.6	—	12.5	—	

	Cu	Sn	Zn	Pb	P	OTHER ELEMENTS
Damascus	77.0	10 5	—	12.5	—	
Dudley's B	77 0	8 0	—	15 0	—	
Dudley's K	77 0	10 5	—	12 5	—	
Dudley's Phosphor	79 7	10 0	—	9 6	0 8	
Durena	65 0	2 0	30 0	—	—	Al 1 5, Fe 1.5
Dysoid	62 0	10 0	10 0	18 0	—	
Eccentric Ring	84 0	14 0	2 0	—	—	
Edward's Speculum	63 3	32 2	—	—	—	As 1 6
Edward's Speculum	69 8	25 1	2 6	—	—	As 2 4
Eisen-Bronze	82 5	8 6	4 5	—	—	Fe 4 0
Eislers	94 1	5 9	—	—	—	
Expansion Plates, Bearings	Rem	3 8 min.	—	—	0 5 max.	
File Bronze	64 4	18 0	10 0	7 6	—	
File Metal	60 9	30 7	—	8 4	—	
File Metal	54 5	30 5	7 5	7 5	—	
File Metal (Genfer)	64 4	18 0	10 0	7 6	—	
File Metal (Genfer)	62 0	20 0	10 0	8 0	—	
Flange Metal (French)	94 4	5 6	—	0 1	—	
Flange Metal (German)	92 4	2 5	5 1	—	—	
Gear Bronze	88 0	10 0	—	—	2 0	
Gear Bronze	85 0	13 0	2 0	—	—	
Gearing	91 3	8 7	—	—	—	
Gears	85 0	10 0	3 0	2 0	—	
Graney Bronze	75 8	9 2	15 0	—	—	
Gun Metal	90 0	10 0	—	—	—	
Chinese, 1901	93 2	5 1	—	—	—	Fe 1 7
Cochin China	77 2	3 4	5 0	13 2	—	Fe 1 2
Cochin China	93 2	5 4	—	—	—	Fe 1 4
English, Modern	89 3	10 7	—	—	—	
English, Modern	91 7	8 3	—	—	—	
French, Modern	90 1	9 9	—	—	—	
French, Old	89 4	8 9	1 4	0 2	—	

Bronzes—continued

	Cu	Sn	Zn	Pb	P	OTHER ELEMENTS
Leaded Castings	86–89	9–11	0 5 max	1–2 5	0 3	
Prussian, Modern	90 9	9 1	—	—	—	
Russian, 1813	88 6	10 7	—	—	—	Fe 0 7
Russian, Modern	90 8	9 2	—	—	—	
Swiss (Lucern)	88 9	10 4	0 4	—	—	
Turkish, 1464	95 2	4 3	—	—	—	
Turkish, 1907	90 9	8 8	—	—	—	Fe 0 2
Gun Mount	80 0	3 0	17 0	—	—	
Gurney's	75 8	9 2	15 0	—	—	
Hercules	85 5	10 0	2 0	—	—	Al 2 5
High-Lead Tin Bronze						
Heavy Pressure Bearings	80–83	7–10	0–3	7–10	0 1 max	Fe 0 3 max, Si 0 03 max, Sb, 0 5 max, Ni 0 3 max, S 0 1 max
Lower-Load Bearings	73–78	5–10	0 5 max	15–20	0 1 max	Fe 0 3 max, Si 0 03 max, Sb 1 0 max
Railroad Bearings and Liners	63–75	0–5 0	0 5 max	25–35	—	Ni 0 5 max, S 0 1 max
High Temperature	89 8	2 7	6 2	1 3	—	
Hydraulic	83 0	10 8	6 0	0 1	—	
Instrument	82 0	13 0	5 0	—	—	
Instrument	82 1	12 8	5 1	—	—	
Johnson Locomotive Bearing	87 5	7 9	5 1	—	—	
Kern's Hydraulic	78 0	12 0	10 0	—	—	
Kochlin's Bearing	90 0	10 0	—	—	—	
Kuhne Phosphor Bronze	78 0	10 6	—	10 5	0 6	Ni 0 3

Bronzes—continued

	Cu	Sn	Zn	Pb	P	OTHER ELEMENTS
Laderig's Speculum	69.0	28 7	—	—	—	
Lafond's Axle Bearing	80.0	18 0	2 0	—	—	
Lafond's Bronze	83 0	15 0	1 5	0 5	—	
Lafond's Heavy Bearing	83 0	15 0	1.5	0 5	—	
Lafond's Malleable	98 0	2.0	—	—	—	
Lafond's Pumps	88.0	10.0	2.0	—	—	
Lafond's Straps	84.0	14 0	2 0	—	—	
Leaded Tin Bronze	88 0	6 0	4.5	1.5	—	
Lowroff Phosphor Bronze	70.0	13 0	—	16 0	1.0	
Lowroff Phosphor Bronze	90 0	4.0	—	5.5	0 5	
Manganese Bronze	82 0	8 0	5.0	3 0	—	Mn 2.0
Manganese Bronze	83 5	8 0	5 0	3.0	—	Mn 0 5
Manganese Bronze	58.5	1.0	39 0	—	—	Fe 1.4, Mn 0.1
Manheim Gold	83.7	7 0	9.3	—	—	PSn 5.0
McKechnie's	56.7	40.8	1 0	0 5	—	Fe 1.0
Medal	92 0	8.0	—	—	—	
Medal	97 0	1 0	2 0	—	—	
Mudge's Speculum	68 8	31 2	—	—	—	
Naval Gun Metal G	88 0	10 0	2 0	—	—	
Naval Journal, H	83 0	13.5	3.5	—	—	
Naval Journal, HX	83 0	13.5	—	3.5	—	
Naval Phosphor, Cast	88 9	8.1	2.5	—	0 5	

Bronzes—continued

	Cu	Sn	Zn	Pb	P	OTHER ELEMENTS
Naval Phosphor, Rolled	95 0	4.5	—	—	0.5	
Naval Valve, M	87 0	7.0	6 0	—	—	
Needle	84.5	8 0	5 5	2.0	—	
Neogen	58 0	2.0	27 0	—	—	Ni 12 0, Al 0 5, Bi 0 5
Nongran	87 0	11 0	2 0	—	—	
Oil Cups	87 6	5 2	7 2	—	—	
Oil Pump	84 7	3.1	9 2	—	3 1	
Ormulu	59 2	17 0	23 8	—	—	
Ormulu, large	90 5	6 5	3 0	—	—	
Ormulu, small	94 1	5.9	—	—	—	
Ounce Metal	85 0	5 0	5.0	5 0	—	
Perking Brass	76 2	23 8	—	—	—	
Perking Brass	80.0	19 8	0.1	—	—	
Phosphor Bronze						
1 25%	98 75	1 25	—	—	—	
5%	95	5	—	—	—	
8%	92	8	—	—	—	
10%	90	10	—	—	—	
Bearings	82 2	13 9	2 0	1 0	1 0	
Bridge	79 2	19 8	—	—	1-0 2	
Bridge	84 2	14.9	—	—	1.0	
Bushings	79 0	10 0	—	10 0	0.7	
Charpy	87 2	12 4	—	—	0 4	
Charpy	86 0	13 6	—	—	0 5	
English	79 2	10 2	—	9 6	1 0	
Gears	88 0	10 0	—	2 0	0 1	
Gears	85 0	13 0	2 0	—	0 1	
Gears	79 9	12 3	—	7.7	0 1	
Gears	88-90	10-12	—	—	0 1-0 3	
Grade E 2	98 7	1 3	—	—	0 1	
Hard	92 8	7 0	—	—	0 2	
Law	88 1	10 9	—	—	1 0	
Law	89 7	9 6	—	—	0 7	
Pennsylvania Railroad	79 7	10 0	—	9 5	0 8	
Pennsylvania Railroad "B"	76 8	8.0	—	15.0	0 2	

Bronzes—continued

	Cu	Sn	Zn	Pb	P	OTHER ELEMENTS
Pennsylvania Railroad "B"	85 6	9 9	3 8	0 6	0 1	
Pennsylvania Railroad "B"	80 0	8 0	—	10 0	—	PSn 2
Rolling	95 6	4 5	—	—	0 1	
Russian	93 7	5 8	0 3	—	0 2	
Sheet and Strip	Rem	4–5	0 2 max	2 5–4 max	0 03–0 3	
Wire	98 8	1 2	—	—	0 1	
Wire	Rem	3 5–5 8	0 3 max	0 1 max	0 03–0 4	
Wire	Rem	7–9	0 2 max	0 1 max	0 03–0 4	
Wire	Rem	9–11	0 2 max	0 1 max	0 03–0 3	
Wire	Rem	4–6	0 2 max	0 1 max	0 03–0 4	
Piston	83 0	1 0	16 0	—	—	
Piston Rings	84 0	2 9	8 3	4 3	—	
Railroad (Hughes)						
20-Ton Wagon	70 6	5 9	—	23 5	—	
Axle Box Bearing	80 0	5 0	—	15 0	—	
Injector	84 0	8 5	5 0	2 5	—	
Phosphor Bronze	89 4	10 1	—	—	0 5	
Slide Valves	84 5	10 0	—	5 0	0 5	
Railroad (Thurston)						
Axle Bearings, Common French	78 0	20 0	2 0	—	—	
Axle Bearings, French	82 0	10 0	8 0	—	—	
Axle Bearings, Hard	87 1	7 9	5 1	—	—	
Axle Bearings, Lafond	80 0	18 0	2 0	—	—	
Eccentric Strap, Dutch	85 3	12 8	2 0	—	—	

Bronzes—continued

	Cu	Sn	Zn	Pb	P	OTHER ELEMENTS
Eccentric Strap, Lafond	84 0	14 0	2 0	—	—	
Gearing	88 8	8 5	2 7	—	—	
Locomotive Bearings	89 0	2 4	7 8	—	—	Fe 0 8
Locomotive, Durable	73 1	9 5	9 5	7 5	—	Fe 0.5
Pistons and Rods	74 1	3 7	22 2	—	—	
Richardson's Speculum	65 3	30 0	0 7	—	—	As 2 0, Si 2 0
Rods, Bars, and Shapes	Rem	3 5–5 8	0 3 max	0 1 max	0 03–0 4	
Rods, Bars, and Shapes	Rem	3 5–5 8	0 3 max	0 8–1 3 max	0 03–0 4	
Rods, Bars, and Shapes	Rem	7–9	0 2 max	0 1 max	0 03–0 3	
Rods, Bars, and Shapes	Rem	9–11	0 2 max	0 1 max	0 03–0 3	
Roman Bronze	90 0	9 0	—	—	—	
Ross' Alloy	68 2	31 8	—	—	—	
Sallit's Speculum	64 6	31 3	—	—	—	Ni 4 1
Sash Chain	92 0	8 0	—	—	—	
Sash Chain	95 0	5 0	—	—	—	
Schmidt Locomotive Bearing	86 0	14 0	—	—	—	
Screw-Nut	86 0	11 4	2 3	—	—	
Seraing Bearing	86 0	14 0	—	—	—	
Seraing Piston Rings	89 0	2 0	9 0	—	—	
Sheet Bronze	90 0	10 0	—	—	—	
Sheet Phosphor	95 0	4 0	—	—	—	PSn 1 0

Bronzes—continued

	Cu	Sn	Zn	Pb	P	OTHER ELEMENTS
Sheet Phosphor	94.5	5 0	—	—	—	PSn 0 5
Sheet and Strip	Rem.	3.5–5.8	0.3 max.	0.1 max.	0.03–0 4	
Sheet and Strip	Rem.	7–9	0 2 max.	0 1 max.	0 03–0 3	
Sheet and Strip	Rem.	9–11	0 2 max	0 1 max.	0 03–0.3	
Silicon Bronze	98 6	1 5	—	—	—	Si 0 1
Silicon Bronze	91.0	9 0	—	—	—	Si 0.1
Slide Valve	88 5	2 5	9 0	—	—	
Speculum, Chinese	80.8	10 7	—	—	—	Sb 8 5
Speculum, Cu_4Sn	68 3	31 8	—	—	—	
Speculum, English	66 6	33 4	—	—	—	
Statuary Bronze						
Augsburg	89 4	8 2	—	1 1	0 3	Ni 0 2
Augsburg	91 3	1 6	0 5	6 0	—	Ni 0 7
Bacchus, Potsdam	89 5	7 5	1 6	1 2	0 2	
Bavaria, Munich	91 6	1 8	5 5	1 3	—	
Column of July, Paris	91 4	1 6	5 6	1 4	—	
Column Vendome	89 2	10 2	0 5	0 1	—	
Frederick the Grt , Berlin	88.3	1 4	9 5	0.7	—	
Germanicus, Potsdam, (1820)	89 8	6 2	2 4	1 3	—	Ni 0 3
Grosser Kurfurst, Berlin	89 7	5 9	1.7	2 6	0.1	
Henry IV, Paris	89 6	5.7	4.2	0.5	—	
Louis XIV, Paris (1699)	91.4	1.7	5.5	1.4	—	

Bronzes—continued

	Cu	Sn	Zn	Pb	P	OTHER ELEMENTS
Mars and Venus, Munich	93 8	4.8	0 3	0 7	—	Ni 0 5
Melanchron, Wittenberg	89.6	3 0	7 5	—	—	
Munich	92 9	4.2	0.4	2 3	0 2	
Munich	77.0	0 9	19 1	2 3	0 1	
Napoleon I, Paris	75 0	3 0	20 0	2 0	—	
Shepherd, Potsdam	88 7	9 2	1 3	0 8	—	
Steam Fittings	88 0	8 0	2 0	2 0	—	
Stephenson, Locomotive Bearing	79 5	7 5	5 0	8 0	—	
Stephenson, Piston Rings	84 0	2 9	8 3	4 3	—	Fe 0 4
Stone's English Gear	89 0	11 0	—	—	—	
Telegraph Bronze	80 0	5 0	7 5	7 5	—	
Tin Bronze	89 0	11 0	—	—	—	
Uchatius Bronze	92 0	8 0	—	—	—	
Valve Bronze	89 0	5.0	3 0	3 0	—	
Valve Bronze	83 0	4 0	7 0	6 0	—	
Valve Bronzes						
Pressure castings	86 5 max	5 5– 6 5	2 0–5 0	1 5–2 0	0 1 max	Fe 0 3 max , Si 0 01 max , Ni 1 0 max , S 0 1 max.
Pressure Work at Temperatures not above 400° F.	84–86	4 0– 6 0	4 0–6 0	4 0–6.0	0 1 max	Fe 0 3 max., Si 0 01 max , Sb 0 3 max , Ni 1 0 max , S 0 1 max.
Valve, Steam	88.0	10 0	2.0	—	—	
Valves	85.0	9 0	6 0	—	—	

Bronzes—continued

	Cu	Sn	Zn	Pb	P	OTHER ELEMENTS
Valves, Steam Fittings, Pump, Piston Parts for Steam	87–89	7 5–10.5	1 5–4 5	0–2 0	2–0 1	Fe 0–0 3, Ni 0–1 0, Impurities 0–0 5
Weights	90 0	8 0	2 0	—	—	
Whistles	80 0	18 0	2 0	—	—	
Whistles, Lafond	81 0	16 0	2 0	—	—	
Whistles, Lafond	80 0	18.0	—	—	—	Sb 2 0
Wire	98 8	1 2	—	—	0 1	
Worm Gears	87 5	11 0	—	—	0 1	Ni 1 5

Copper Alloys

	Cu	Sn	Pb	Zn	Ni	OTHER ELEMENTS
Copper-Nickel Alloy	Rem	1 5 max	0 1 max	1 0 max	29 0–33 0	Mn 1 0 max, Fe 0 5 max
Duronze	97 6	1 4	—	—	—	Si 1 0
High-Conductivity Copper Alloy	99 9 max	0 02 max	0 02 max	0 02 max	—	Fe 0 1 max, Si 0 02 max Mg 0 02 max, P 0 01 max, Sb 0 01 max.
Phono Electric Silicon Copper	98 6	1 4	—	—	—	Si 1 0
Grade A	Rem	0 3 max	—	0 3 max	—	Fe 0 8 max, Al, 0 3 max, Si 10 0–12 0
Grade B	Rem	0 3 max	—	0 3 max	—	Fe 0 8 max, Al 0 3 max, Si 17 0–21 0
Grade C	Rem	0 3 max	—	0 3 max	—	Fe 0 8 max, Al 0 3, Si 28 0–32 0
50%	Rem.	—	—	—	—	Si 50 0, Ca 0 2, C 0.04, Fe 0 8 max, Al 0 4 max.

	Cu	Mn	Fe	Zn	Sn	Ni	OTHER ELEMENTS
Manganese Brass	53 5	3.2	1.4	38.3	1.2	2 1	
Manganese Brass	60 2	2 3	1 2	34.9	0.9	—	Al 0.2, Pb 0.4
Manganese Brass	53 4	1 7	—	39 0	2 7	2 5	Al 0 2
Manganese Bronze	32 4	0 6	—	—	17.0	—	
Manganese Bronze	85 8	0 3	—	—	14 0	—	
Manganese Bronze	86 3	2.7	—	5 0	6 0	—	
Manganese Copper	85 5	10 7	2 7	—	0 4	—	Pb 0 5
Manganese Copper	84 3	10 6	2 3	2 1	0 4	—	Pb 0 3
Manganese Nickel-Silver	60 0	20 0	—	—	10 0	10 0	

Fusible Metals

	Bi	Sn	Pb	Cd	OTHER ELEMENTS	TEMPERATURE OF FUSION (°C)
Anatomical Alloy	53 5	19 0	17 0	—	Hg 10 5	60
Bismuth Solder	40 0	20 0	40 0	—		
Bismuth Solder	33 3	33 3	33 3	—		
Bismuth Solder	27 5	45 0	27 5	—		
Bismuth Solder	25 0	50 0	25 0	—		
D'Arcet	50 0	25.0	25 0	—		
Eutectic	—	—	82 5	17 5	—	248
Eutectic	—	96 5	—	—	Ag 3 5	221
Eutectic	—	91 0	—	—	Zn 9 0	199
Eutectic	—	61 9	38 1	—	—	183
Eutectic	—	67 7	—	32 3	—	176
Eutectic	60 0	—	—	40 0	—	144
Eutectic	—	51 2	30 6	18 2	—	143
Eutectic	57 0	43 0	—	—	—	138 5
Eutectic	56 0	40 0	—	—	Zn 4 0	130
Eutectic	55 5	—	44 5	—	—	124
Eutectic	53 9	25 9	—	20 2	—	102.5
Eutectic	52.0	16 0	32 0	—	—	95
Eutectic	51 6	—	40 2	8 2	—	91 5
Eutectic	57 5	17 3	—	—	In 25 2	78 8
Eutectic	50 0	13 3	26 7	10 0	—	70 0
Eutectic	49 4	11.6	18.0	—	In 21 0	58.0
Eutectic	44.7	8.3	22 6	5.3	In 19 1	46.7

Fusible Metals—continued

	Bi	Sn	Pb	Cd	OTHER ELEMENTS	TEMPERATURE OF FUSION (°C.)
Fusible Tea Spoons	44 5	16 5	30.0	—	Hg 5–10	
Guthrie's	47 4	20 0	19 4	13.3		
Lichtenberg	50 0	20 0	30 0	—		
Lipowitz	50 0	13 3	26 7	10 0		
Magnetic Chucks	48 0	14 5	28 5	—	Sb 9 0	
Newton's	50 0	18 8	31 3	—		
Onion's	50 0	20 0	30 0	—		96 5–97
Pewter Solder	50 0	25 0	25 0	—		
Rose Alloy	46 0	34 0	20 0	—		
Rose's	50 0	22 0	28 0	—		
Rose's	35 0	30 0	35 0	—		
Silbet Foil	0 5	15 0	Rem	—	Ag 1 3, Sb 0 5	
Sprinkler System Plugs	52 0	16 0	32 0	—		
Sprinkler System Plugs	50 0	19 0	31 0	—		
Wood Press Dies, Punches and Dies	48 0	14 5	28 5	—	Sb 9 0	
Wood's	50 0	12 5	25 0	12 5		74
Wood's Metal	50 0	13 3	26 7	10 0		70

Fusible Noneutectic Metals and Their Freezing Ranges

	Bi	Sn	Pb	Cd	OTHER ELEMENTS	TEMPERATURE OF FREEZING RANGE (°C.)
Noneutectic	12 6	39.9	47 5	—		176–145
Noneutectic	14 0	43 0	43 0	—		163–143
Noneutectic	20 0	30 0	50 0	—		173–130
Noneutectic	21 0	37 0	42 0	—		152–120
Noneutectic	5 0	45 0	32 0	18 0		139–132
Noneutectic	56 2	40 7	2 0	0 7	In 0 4	130–124
Noneutectic	48 0	14 5	28 5	—	Sb 9 0	227–103
Noneutectic	33 3	33 3	33.4	—		143– 95
Noneutectic	59 4	25 8	14 8	—		114– 95
Noneutectic	56.0	22.0	22 0	—		104– 95
Noneutectic	52 0	15.3	31 7	1.0		92– 83
Noneutectic	42.5	11 3	37.7	8.5		90– 70

Lead-Base Alloys

	Pb	Sn	Sb	Cu	OTHER ELEMENTS
Accumulator Metal (Condenser Foil)	90 0	9.3	0 8	—	
Aluminum Solder, Frismuth	27 8	69 1	—	—	Al 3 1
Antifriction	77.0	10 0	12.5	0 5	
Antifriction	77 0	8 0	14 0	1.0	
A S T M. Bearing Alloys					
No 6	63 7	19 8	14 6	1 5	
No 7	75 0	10 0	14 5	0 1	
No. 8	79 4	5 2	14 9	0 1	
No. 10	82 0	2 1	15 7	0 1	
No 11	84 7	0 1	14 8	0 2	
No. 12	89.4	0 1	9 9	0 1	
No 15	82 5	1 0	15 0	0.5	As 1 0 nominal
No 16	77 0	10 0	12 5	0 5	
No 19	86 0	5 0	9 0	—	
Babbitt	86 0 max	4 5–5 5	9 3–10 8	0 5 max.	
Babbitt	76 0 max	9 3–10.8	14–16	0 5 max	
Babbitt	63 5	20 0	15 0	1 5	
Babbitt	75 0	10 0	15 0	0 5 max	
Babbitt	80 0	5 0	15 0	0 5 max.	
Babbitt	85 0	5 0	10 0	0 5 max	
Babbitt	83 0	2 0	15 0	0 5 max.	
Babbitt	Rem	2 0	15 0	0 2	Ag 5 0
Babbitt	Rem	5 0	15 0	0 2	Ag 4 8
Babbitt	Rem	5 0	15 0	—	Ag 4 8
Babbitt	Rem	3 0	10 0	—	Ag 2 6
Bearing	80 5	11 6	7 4	0 5	
Bearing	73 0	8 5	18 0	0 4	
Bearing	68 0	9 6	20 5	1 6	
Bearing	71 6	7 7	18 6	2 0	
Bearing	62 5	26 2	10 0	1 3	
Bearing	61 0	25 0	13 0	1 0	
Bearing	48 0	40 0	10 0	2 0	
Bearing	40 0	42 0	16 0	2 0	
Bearing	37.0	50 0	12 0	1 0	
Bearing	25 5	61 0	10 5	2 8	
Bearing	11 8	74 0	9 5	4 7	
Bearing	10.0	75 0	12 0	3 0	
Bearing	86 0	1.0	13.0	—	
Bearing	77.2	7.7	7.7	7 4	
Bearing	82.0	2.0	16 0	—	

Lead-Base Alloys—continued

	Pb	Sn	Sb	Cu	OTHER ELEMENTS
Bearing	80 0	10 0	10 0	—	
Bearing	80 0	5 0	15 0	—	
Bearing	76 0	7 0	17 0	—	
Bearing	62 6	27 3	10 0	—	
Bearing	60 0	20 0	20 0	—	
Bearing	10 0	75 0	15 0	—	
Bearing	40 0	45 0	15 0	—	
Bearing (American)	46 0	36 5	16 5	1 0	
Bearing, American Railroad	73 5	8 0	18 5	—	
Bearing, American Railroad	68 0	21 0	11 0	—	
Bearing, Chemin de fer de l'est France	42 0	42 0	16 0	—	
Bearing, Compagnie de l'Est	80 0	12 0	8 0	—	
Bearing, French Railroad	70 0	20 0	10 0	—	
Bearing, Graphite Metal	68 0	15 0	17 0	—	
Bearing, Italian Railroad	37 0	38 0	25 0	—	
Bearing (Katzenstein)	76 0	7 2	16 5	0 4	
Bearing, Paris-Lyon-Mediterranean Railroad	70 0	10 0	20 0	—	

Lead-Base Alloys—continued

	Pb	Sn	Sb	Cu	OTHER ELEMENTS
British Standards, Soft Solders					
Dipping Solder for Radiator Mfg	Rem.	18 0 min 18 5 max	0 8 min 1 0 max	—	Impurities Fe 0 02 max, As 0 03 max, Total 0 3 max
General Electric Purposes	Rem	41 0 min 42 0 max	0 4 max	—	Impurities Fe 0 02 max, As 0 1 max, Total 0 3 max
Lead Cable Wiped Joints	Rem	29 0 min 30 0 max	1 0 min 1 7 max		Impurities Fe 0 02 max, As 0 1 max, Total 0 3 max
Special Tinsmith's Finework	Rem	44 0 min 45 0 max	2 3 min 2 7 max	-	Impurities Fe 0 02 max, As 0 1 max, Total 0 3 max
Tinsmith's Coppersmith's Finework	Rem	39 0 min 40 0 max	2 0 min 2 4 max	—	Impurities Fe 0 02 max, As 0 1 max, Total 0 3 max
Capsule Metal	92 0	8 0	—	—	
Clichier Metal	46 0	33 0	—	—	Cd 21 0
Clichier Metal	50 0	36 0	—	—	Cd 14 0
Clichier Metal	32 5	48 0	10 5	—	Bi 9 0
Clichier Metal	5 0	80 0	—	—	Bi 15 0
Electrotype Metal	93 0	3 0	4 0	—	
English Linotype	83 0	5 0	12 0	—	
English Stereotype	82 5	4 5	13 0	—	
Fahlun Brilliants	40 0	60 0	—	—	

Lead-Base Alloys—continued

	Pb	Sn	Sb	Cu	OTHER ELEMENTS
Foil-Lead (Calin)	86 5	12.5	—	1.0	
French Auto	75.0	10 0	15 0	—	
Glievor Bearing	76 5	8 0	14 0	—	Fe 1 5
"Glyco"	80 5	4 5	14.5	—	As 0 5
Hard Lead	57 8	33 2	8 7	0 4	
Hoyle's Metal	42 0	46 0	12 0	—	
Hoyt Metal	96–90	1 0	3 9	—	
Jacana Metal	70 0	10 0	20 0	—	
Linotype, Cheap	85 0	3 5	11.0	—	
Linotype Metal	85 0	3 0	12.0	—	
Linotype, Standard English	83 0	5 0	11.0	—	
Locomotive Bushing	73.1	9.8	17.2	—	
Mackenzie Metal	70.0	13.0	17.0	—	
"Magnolia"	78 0	6 0	16.0	—	
"Magnolia"	79.8	5 0	15 0	—	Bi 0 3
Marine Babbitt	72 0	21 0	7 0	—	
Metallic Packing	94.5	5 5	—	—	
Metallic Packing, Compagnie d'Orleans	76 0	14.0	10 0	—	
Monotype Standard	74 0	8 0	18.0	—	
Noheet	98 4	0 1	0 1	—	Na 1 4
Non-Pareil	78 4	5.0	16 7	—	
Pewter	10 9	82.2	5.4	1.6	
Pewter	20 0	80 0	—	—	
Piston Packing, Compagnie de Nord	73 0	12.0	15 0	—	
S.A.E. Bearing Alloys					
No. 13	86.0 max.	4.5–5.5	9 2–10.8	0 5 max.	As 0 6 max
No. 14	76.0 max.	9.3–10.8	14.0–16 0	0.5 max.	As 0.6 max.
Small Castings	5.0	75.0	20.0	—	

Lead-Base Alloys—continued

	Pb	Sn	Sb	Cu	OTHER ELEMENTS
Solder	60 0	39.0	1 0	—	
Half and Half	50.0	50 0	—	—	
Lead-Tin-Bismuth-Silver	78 5	15 0	—	—	Bi 5 0 max., Ag 1 5
Lead-Tin-Bismuth-Silver	77.5	15 0	1 0	—	Bi 5 0 max., Ag 1 5
Lead-Tin-Bismuth-Silver	74 9	15 0	0 5	—	Bi 5 0 max., Ag 1 5
Lead-Tin-Cadmium	68 0	23 0	—	—	Cd 9.0
Plumber's	66.6	33 3	—	—	
(Save Tin) ST-10	88 0	10 0	0 5	—	Ag 1.5
(Save Tin) ST-16N	81 8	16 0	1 5	—	Ag 0.8
(Save Tin) ST-20N	77 3	20 0	1 5	—	Ag 1 3
(Save Tin) ST-21	76 8	21 0	1 5	—	Ag 0.8
(Save Tin) ST-30	67 8	30 0	0 5	—	Ag 1.3
(Save Tin) ST-30	66 8	30 0	2 0	—	Ag 1.3
Standard 50–50	50 0	50 0	—	—	
Standard Tin-Lead,					
10–90	89 5	10 0	0 5	—	
20–80	79 5	20 0	0 5	—	
25–75	74.5	25 0	0 5	—	
30–70	69 5	30 0	0 5	—	
35–65	63.0	35 0	2 0	—	
40–60	59 5	40 0	0 5	—	
50–50	49.5	50 0	0 5	—	
Tin-Lead,					
10–90	89.5	10 0	0 5 max.	—	Others 0.1 max.
20–80	—	18–20	0 4 max.	—	Bi 0 3 max., Pb + Sn 99 2 min.
25–75	75 0	24 5–25 5	0 1 max.	—	Others 0 1

Lead-Base Alloys—continued

	Pb	Sn	Sb	Cu	OTHER ELEMENTS
30–70	Rem	30 0	0 5–0 8 max	—	Bi 0 3 max
40–60	60 0	39 6–40 4	0 1	—	Others 0 1
40–60	Rem.	38 0 min	0 4 max	—	Others 0 1
50–50	50 0	49 5–50 5	0 1 max	—	Others 0 1
50–50	50 0	48 8–49 7	0 8 max	—	Others 0 1
50–50	Rem	49 0 min	0 4 max	—	Bi 0 3, Others 0 1
55–45	55 0	44 5–45 5	0 1 max	—	Others 0 1
Tin-Lead-Antimony	75 0	22 5–23 5	2 0 max	—	Others 0 1
Tin-Lead-Antimony	60 0	37 6–38 4	2 0 max	—	Others 0 1
Tin-Lead-Antimony	55 0	43 1–43 0	1 5 max	—	Others 0 1
Tin-Lead-Silver	87 8	10 0	—	—	Ag 2 3
Tin-Lead-Silver	87 8	10 0	0 5 max	—	Bi 0 5 max, Ag 1 5
Tin-Lead-Silver	82 8	15 0	0 5 max	—	Bi 0 5 max, Ag 1 3
Tin-Lead-Silver	81 8	16 0	1 5 max	—	Ag 0 8
Tin-Lead-Silver	78 0	20 0	—	—	Ag 2 0
Tin-Lead-Silver	78 3	21 0	1 5 max.	—	Ag 0 8
Tin-Lead-Silver	69 0	30 0	—	—	Ag 1 0
Tinman's	33 3	66.6	—	—	
Stereotype	82–70	3 2–17	12–23	—	
Stereotype	35 0	60 0	5 0	—	
Stereotype Metal	82 0	6 0	12 0	—	
Stereotype Metal	82 0	3 2	14.8	—	
Stereotype Metal	76 0	4 0	20 0	—	
Stereotype Metal	70 0	7 0	23 0	—	
Stereotype Metal	65.7	16 7	17 7	—	
Stereotype Metal	35 0	60 0	5 0	—	
Stereotype, Standard English	83 0	4.5	13 0	—	
Tandem	77.4	5.9	16 7	—	

	Pb	Sn	Sb	Cu	OTHER ELEMENTS
Tea Lead	98 0	2 0	—	—	
Terne Metal	81 7	16 7	1 6	—	
Type Metal	70 0	10 0	18 0	2 0	
Type Metal	78–55	12–35	5–30	0 1	
Type Metal	70 0	10 0	18 0	2 0	
Best	50 0	25 0	25 0	—	
Common	60 0	10 0	30 0	—	
Common	55 5	40 0	4 5	—	
Common	60–56	10–40	4 5–30	—	
English	63 2	12 0	24 0	0 8	
English	60 5	14 5	24 2	0 8	
English	58 0	15 0	26 0	1 0	
English	77 5	6 5	16 0	—	
English, Old	69 6	9 2	19 6	1 7	
French	55 0	22 0	23 0	—	
French	55 0	15 0	30 0	—	
German	75 0	2 0	23 0	—	
German	60 0	35 0	5 0	—	
German	60 0	34 6	5 4	—	
German	60 0	15 0	25 0	—	
Krupp	59 6	12 0	18 0	4 7	Ni 4 7, Bi 1 0
Standard	58 0	26 0	15 0	1 0	
U S Electrotype Backing	92 5	4 0	3 5	—	
U S Large Monotype	71 0	10 0	19 0	—	
U S Printing Office Linotype	84 0	4 0–4 5	11 5	—	
U S Printing Office Monotype	75 9	4 0–4 5	16 8	—	
U S Stereotype	80 5	6 5–7 0	13 0	—	Bi 1 0–4 0
White	77 5	5 0	15 1	2 3	
White	33 0	53 0	10 6	2 4	Zn 1 0
White	33 9	49 1	13 6	3 3	

Magnesium Alloys

	Mg	Al	Sn	Si	Mn
Magnesium Forging Alloy Am 65S D-1	Rem	3–4	4–6	0 3 max.	0 4 min.

Nickel Silver

	Cu	Zn	Ni	Fe	Sn	Pb	OTHER ELEMENTS
Alpakka	63.9	19 2	14 5	0.4	0 1	0.03	Ag 2 0
American Silver, Cast	49.4	20.7	24 2	1.3	0.5	—	Mn 3.8, Al 0.1
American Silver, Cast	57.7	24 2	15.3	0.6	0 7	1.5	
Arguzoid	55 8	23 2	13 4	—	4 0	3 5	
Bismuth Brass	46 6	20 8	30 6	—	1.0	—	Bi 0 9
Bismuth Bronze	38.8	18 5	28 0	—	13 8	—	Bi 0.8
Bismuth Bronze	53 0	20 0	10 0	—	15.0	—	Bi 1 0, Al, 0.1
Casting	55 8	23.7	23 4	—	4 0	3 5	
Maillechort, Paris	68 5	13 9	13 9	3 3	0 2	0 2	
Neogen	58 0	27 0	12 0	—	2.0	—	Bi 0 5, Al 0 5
Nickel Bearing	50 0	—	25 0	—	25 0	—	
Nickel Bronze	60 0	12.0	20.0	—	8 0	—	
Nickel Bronze	77 1	—	4 9	—	16.4	—	PSn 1.6
Nickel Bronze	47.0	21.0	30 9	—	1 0	—	Bi 0 1
Nickel Bronze	50 0	18 0	12 0	—	2 0	18 0	
Nickel Bronze	61.5	10 9	15.4	—	1 9	10 2	
Nickel Bronze	88 0	2 0	5 0	—	0–0 01	—	P 0.1
Seawater Bronze	45 0	5 5	32.5	—	16 0	—	Bi 1 0
Smitter-Lenian	72 0	9 8	12 8	2.0	2 3	—	Bi 1 0
Toucas	35 8	7.1	28 6	7.1	7 1	7 1	Sb 7.1
Turbine Bushing	61 5	10 9	15.4	—	1.9	10 2	

Non-Corrosive Alloys

	Sn	Co	Ni	Cu	Fe	Zn	OTHER ELEMENTS
Non-Oxidizable, Lemarquand	9 0	8 0	7 0	39 0	—	37 0	
Non-Oxidizable Marties	10 0	—	35 0	17.0	10 0	18 0	Cr 10.0

Platinum-Tin Alloys

	Pt	Zn	Sn	Cu	As
Platinum-Gold Cooper's Mirror	9 5	3 5	27 5	58 0	1 5

Silver Alloys

	Ag	Cu	Zn	Sn	MELTING POINT (°C)
High Temperature, Fusible Silver Solders.	3 5	—	—	96 5	248
Bureau of Standards	40 0	14 0	6 0	40 0	
Quick	62 5	20 9	10 4	6 2	
Quick	56 9	27 7	11 5	3 8	

Tin-Base Alloys

	Sn	Sb	Cu	Pb	OTHER ELEMENTS
Algiers Metal	94 5	0 5	5.0	—	
Algiers Metal	90 0	10 0	—	—	
Algiers Metal	75 0	25 0	—	—	
Aluminum Solder	85–50	—	—	—	Zn 15–50
Burgess	76 0	—	—	—	Zn 21, Al 3.0
Frismuth	69.1	—	—	27.8	Al 3.1
Grimm's	69.1	—	—	28 8	Zn 1 4, Ag 0 7
Grimm's	50 0	—	—	25 0	Zn 25 0
Wegner & Guhr's	80 0	—	—	—	Zn 20 0
Wilmotts	86.0	—	—	—	Bi 14 0
Various	87–73	—	—	—	Zn 8–15, Al 5–12
	33 4	—	—	22 2	Zn 44 4
	47.5	—	—	47.5	Ca 5 0
	49.5	3 4	1 1	26 1	Zn 20 3
	85 0	—	—	—	Al 10; PSn 5 0
Argentin	85 0	14 5	0 5	—	
Ashberry Metal	82.5	14.4	2.1	—	Zn 1.0
Ashberry Metal	79.8	15.2	3 0	—	Zn 2 0
Britannia	77 8	19.4	2.8	—	
Britannia	77 9	19.4	—	—	Zn 2 8
A.S.T.M. Bearing Alloys					
No. 1	91 0	4 5	4 5	0 35 max.	As 0 10 max , Bi 0 08 max.
No 2	89 0	7.5	3 5	0 35 max.	As 0 10 max., Bi 0 08 max.
No 3	83 3	8 3	8 3	0 35 max.	As 0 10 max., Bi 0 08 max.
No. 4	75 0	12 0	3.0	10 0	As 0.15 max
No. 5	65 0	15 0	2 0	18 0	As 0.15 max.
Babbits, Hard	83 3	8.3	8 4	—	
Babbits, Original	89.0	7.3	3.7	—	
Bearing:					
Automobile, American	89.0	7.0	4 0	—	
Automobile, American	89.3	8.9	1.8	—	
Automobile, American	88.9	7.4	3.7	—	

Tin-Base Alloys—continued

	Sn	Sb	Cu	Pb	OTHER ELEMENTS
Automobile, American	87.0	7 0	6.0	—	
English	74.5	17.9	7 6	—	
English Railroad	90.0	7.0	3.0	—	
French Car	83 3	11.1	5.5	—	
French Railroad	82 0	12 0	6 0	—	
French Railroad	67.0	22 0	11 0	—	
German	84.4	7.8	7.8	—	
German	70 8	15 1	4 9	9 2	
German Ludenscheidt	71.8	24 3	3 9	—	
German Railroad	83.0	11.0	6.0	—	
G. W. R. England	67.0	11.0	22 0	—	
Heavy	85 0	7.5	7.5	—	
Kamarsch	70.7	19 7	9.5	—	
Kamarsch	71.4	7.2	21.4	—	
Navy	89.0	7.3	3.7	—	
Navy	91.0	4.5	4.5	—	
Piston	81.0	12.5	6 5	—	
Prussian	91.0	6.0	3.0	—	
Prussian	90.0	6.0	4 0	—	
Prussian	66.7	13.5	9 9	9.5	Zn 0.2, Fe 0.2
Prussian	73.0	18 0	9.0	—	
Prussian	72.0	26 0	2 0	—	
Swiss Railroad	80 0	10 0	10.0	—	
Valve Packing	71.0	24 0	5.0	—	
Valve Rods, etc.	82.0	10.0	8.0	—	
Blatt-Silver	91.1	—	—	0 4	Zn 8 3, Fe 0 2
Britannia:					
Birmingham I	90.6	9.4	0.03	—	
Birmingham II	85.5	10 5	1.0	—	Zn 3.0
Cast	90 6	9 2	0 2	—	
Cast	85.5	10.5	1.0	—	Zn 3.0
Cast Tutania	91.4	—	0.7	7.6	Zn 0.3

Tin-Base Alloys—continued

	Sn	Sb	Cu	Pb	OTHER ELEMENTS
Cast Tutania	92 4	4 7	2.5	0.3	
English	94 0	5 0	1 0	—	
English	95 2	3 4	1.4	—	
English	92 0	6 1	1.8	—	
English	90 0	8 0	2 0	—	
English	90.0	6 0	2 0	—	Bi 2.0
English	90 0	7 0	3 0	—	
English	85 5	9 7	1 8	—	Zn 3 0
German	84 0	9 0	2 0	—	Zn 5 0
German	81 9	16 3	1 8	—	
German	70 8	15 1	4 9	9 2	
German, Queen's Metal	88 5	7 1	3.5	—	
German, Various, Turn	93 7	3 8	2 6	—	
Plate, Birmingham	91 5	7 1	1 4	—	
Plate, Deutsch (Ludenscheidt)	71 9	24 3	3 9	—	
Plate, Hard Spelter	90 6	7.8	1.5	—	
Plate, Tutania	90 0	—	2.7	6.0	Zn 1.3
Sheet	91 5	7.1	1 4	—	
Sheet	90 6	7.8	1.5	—	
Spinning	93.7	3 8	2 6	—	
Spoons	88 4	8 7	2 9	—	
Spoons	85 5	14 4	0 2	—	
Spoons	84 7	5 0	3.7	—	Bi 4 9, Zn, 1 0
Spoons	88 4	8 7	2 8	—	
Spoons	85 4	14 4	0 2	—	
Spoons	84 5	5 6	3 7	—	Zn 1 5, Bi 4.9
Bushing Russian	72 2	—	1 3	—	Zn 26.5
Clichier Metal	48 0	10.5	—	32 5	Bi 9.0
Clichier Metal	80 0	—	—	5 0	Bi 15 0

Tin-Base Alloys—continued

	Sn	Sb	Cu	Pb	OTHER ELEMENTS
Deurance Metal (Locomotive)	33.3	44.5	22 2	—	
Dudley Antifriction	98 1	—	1.6	0 3	
Fahrig Antifriction	90 0	—	10 0	—	
Gilding Foil	97 6	—	2 2	—	Fe 0 1
Hammonia Metal	64 5	—	3 3	—	Zn 32 3
Hard Head	90 0	8 0	2 0	—	
Hoyles Metal	46 0	12 0	—	42 0	
Husmann Metal	73 6	11 0	4 0	10 6	Zn 0 2, Fe 0 2
Jacoby Metal	85 0	10 0	5 0	—	
Kamarsch Bearing	87 9	5 2	3 7	—	Bi 1 7, Zn 1 5
Minofor	66 7	20 2	4 0	—	Zn 9 1
Minofor (Britannia)	68 5	18 2	3 3	—	Zn 10 0
Navy Bearing	89 0	7 3	3 7	—	
Navy Bearing, Hard	80 0	15 0	5 0	—	
Parsons White Brass	60 0	—	5 0	—	Zn 35 0
Parsons White Brass	81.0	11 0	4.5	3 5	
Parsons White Brass	76 0	6 0	5.0	13.0	
Pewter	80 0	—	—	20 0	
Pewter	73 5	5 5	1 0	20 0	
Pewter	88 4	7 2	3 5	—	Zn 0 9
Pewter	88.9	7 6	1 8	1 8	
Pewter	82 3	5 4	1 5	10 9	
Pewter	89 3	7 6	1.8	1 8	
Pewter	84.7	1 7	6 8	—	Bi 6 0
Phosphor Tin	95 0	—	—	—	P 5.0
Phosphor Tin	90.0	—	—	—	P 10 0
Plastic Metal	80 5	8.6	9.5	—	Fe 1.4

Tin-Base Alloys—continued

	Sn	Sb	Cu	Pb	OTHER ELEMENTS
Poterie D'Etain	90 0	9 0	1 0	—	
Prince's Metal	84 8	15 3	—	—	
Queen's Metal	52.6	17.2	—	17.2	Zn 13.0
Queen's Metal	87 0	8.5	3 5	—	Zn 1 0
Queen's Metal	73 4	8 9	—	8.8	Zn 8.9
Queen's Metal	88.5	7 1	3.5	—	Zn 0.9
Queen's Metal	88.5	7 0	3.5	—	Bi 1.0
S.A.E. Bearing Alloys					
No. 10, Bearing	90 0 min	4 0–5 0	4.0–5.0 max.	—	
No. 11, Bearing	86.0 min	6 0–7 5	5.0–6 5 max.	—	
No. 110, Bearing	87.8 min.	7 0–8 5	2 3–3.4 max.	—	
Ships Nail Alloy	50 0	17.0	—	33.0	
Silver Foil	90 0	—	—	—	Zn 10.0
Silver Foil	97 5	—	2 5	—	
Solder	59 0 min.	0 4 max.	—	Rem	Bi 0 3, Others 0 1
Solder	70.0 min	0.4 max	—	Rem.	Bi 0 3, Others 0 1
Sprinkler System Plugs	66.6	—	—	33.3	
Sprinkler System Plugs	63 0	—	—	37 0	
Stanniol	96.2	—	1 0	2.4	Ni 0 3, Fe 0 1
Tinfoil	87.5	0 5	4.0	8.0	
Tin-Lead Eutectic	62.0	—	—	38.0	
Tin-Lead Eutectic	61.9	—	—	38.1	
Tin-Lead Eutectic	63.0	—	—	37.0	
Tinsel	60.4	—	—	39.6	
Tourun Leonard's Metal	90.0	—	10.0	—	

Tin-Base Alloys—continued

	Sn	Sb	Cu	Pb	OTHER ELEMENTS
Trabuk Metal	87.5	5.0	—	—	Ni 5 5, Bi 2 0
Tutania, Cast	91.4	—	0.7	7.6	Zn 0.3
Tutania, Cast	92 4	4.6	2 5	0.3	Fe 0.1
Tutania, English	80 0	16.0	2.7	—	Zn 1.3
Tutania, Plate	90.0	—	2.7	6 0	Zn 1 3
White Casting Metal (Rubber Molds)	91.3	8.4	0 3	—	As 0 04, Bi 0 003
White Metal, Dutch	81.5	8 8	9 6	—	
White Metal, Hanover	86 8	7 6	5 6	—	

Type Metals

	Pb	Sn	Sb	OTHER ELEMENTS
Electrotype.				
Curved Plates	93	4	3	
General	95	2.5	2.5	
General	94	3	3	
Foundry Type	70	10	20	
Foundry Type	62	13	25	
Foundry Type	54	18	28	
Hard	60 5	13	25	Cu 1.5
Hard	58 5	20	20	Cu 1 5
Hard	61	12	25	Cu 2.0
Linotype·				
Eutectic	84	4	12	
Standard	86	3	11	
Standard	84	5	11	
Monotype.				
Case Type	64	12	24	
Case Type (Lanston Standard)	72	9	19	
Display	78	8	17	
Ordinary	78	7	15	
Rules	75	10	15	
Stereotype.				
Curved Plates	77	8	15	
Flat Plate	80	6	14	
General	80.5	6.5	13	

Zinc-Base Alloys

	Zn	Cu	Sn	Sb	Pb	OTHER ELEMENTS
Aluminum Solder	30 0	—	65 0	—	—	Bi 5 0
Aluminum Solder, Cormande and Cruiys	52 0	—	30 0	—	—	Al 17 5, Ni 0 5
Aluminum Solder, Frismuth	47 3	5 5	31 3	—	—	Al 10 4, Ag 5 5
Aluminum Solder, Frismuth	47 4	5 3	36 8	—	—	Al 10 5
Aluminum Solder, Richards	25 0	—	71 5	—	—	Al 3.5
Babbitt Metal	63 9	4 6	24 1	2 8	4 6	
Battery Plates	63 4	3 2	21 3	—	12 0	
Bearing	88 0	8 0	2 0	2 0	—	
Bearing	85 0	5 0	10 0	—	—	
Bearing	77 0	5 5	17 5	—	—	
Bearing	66 5	4 2	29 3	—	—	
Bearing	55 3	0 6	22 8	—	1 3	Al 20 1
Bearing, English	75 2	8 2	16 6	—	—	
Bearing, Hard	90 0	7 0	1 5	1 5	—	
Biddery	90 2	6 3	0 8	—	2 6	
Biddery, Henie's	84 3	11 4	1 4	—	2 9	
Britannia, Cast	47 5	3 0	47.5	1 0	1 0	
Dunnlevic and Jones	52 0	1 6	46 0	0 04	—	
Ehrhardt's Metal	89 0	4 0	4 0	—	3 0	
Ehrhardt's Type	89.0	3 0	6 0	—	2 0	
English White Metal	76 7	5 6	17 6	—	2 0	
Fenton's Alloy	80 0	6.0	14.0	—	—	

Zinc-Base Alloys—continued

	Zn	Cu	Sn	Sb	Pb	OTHER ELEMENTS
Glievor Bearing	73 5	4 4	6 7	9 0	5 0	Cd 1 4
Hammonia Metal	32 3	3 3	64 5	—	—	
Heavy Axle	49 0	1 0	39 6	6 3	4 2	
Iridium	77 3	1 1	21 6	Trace	—	
Iridium	83 0	1 3	15 8	Trace	—	
Kneiss Metal	50 0	—	25 0	—	25 0	
Kneiss Metal	40 0	3 0	15 0	—	42 0	
Ledebur's Bearing	77 0	5 5	17 5	—	—	
Parsons White Brass	30 0	5 0	65 0	—	—	
Pierrot Metal, Beugnot	78 8	7 9	7 2	3 3	2 8	
Propeller Bushing	69 0	5 0	19 0	7 0	—	
Pump Cocks	72 0	7 0	21 0	—	—	
Russian	26 5	1 3	72 2	—	—	
Russian, Packing	98 5	—	1 0	—	0 3	Fe 0 2
Salge Metal	85 1	4 0	9 9	—	1 1	
Schomberg-Bearing	59 4	0 4	39 8	—	0 2	Fe 0 2
Silver Leaf	8 3	—	91 4	—	0 4	
Vaucher's Alloy	75 0	—	18 0	2 5	4 5	

Chapter 14

Hot-Dipped Coatings

Tin Plate

Historical Development of the Industry. Little information is available concerning the early history of tin plate, for secrecy appeared to be the only policy by which early inventors might benefit from their discoveries However, it is certain that the art of coating metal, particularly iron, with tin was known as far back as 25 A.D., in the time of Pliny. The Romans were credited with considerable skill in plating copper and iron vessels by dipping them in baths of molten tin, or by applying tin to the surface of the heated object. The tin-plate industry is nevertheless supposed to have originated late in the thirteenth century in Bohemia, where, carefully guarded, its development was extremely slow. Visiting that country about 1620, an agent for the Duke of Saxony succeeded in ferreting out enough information to establish a like industry in Saxony. By 1665 it was in a flourishing state. England, with a large production of iron and with the resources of active tin mines in Cornwall and the Scilly Islands, likewise turned her attention to the manufacture of tin plate. Through Andrew Yarranton, details of the methods used in Saxony were carried to England, where experiments resulted in opening up the industry about 1670. Tin plating advanced little in the succeeding half century because of many obstacles; and it was not until Major Hanbury entered the field in 1720 by establishing a works at Pontypool that anything approaching success could be marked.

In Hanbury's plant the base metal was of wrought iron, made by treating charcoal pig iron in small rectangular furnaces. To form the base plate, pieces of iron thus prepared were twice heated in a blacksmith's forge and hammered as thin as possible. Then several sheets of this metal, packed together, were reheated to redness and hammered down to the desired thickness. The low temperature and the formation of oxides on each sheet were guards against the possibility of welding the layers together. The small finished pieces, separated from each other, were trimmed to size, ready for cleaning.

Since acid pickling was then unknown, the base plates were cleaned by immersing them in fermented barley water for several days. After washing, they were dipped into hot grease to drive off all moisture, then set into

a bath of molten tin covered with palm oil Upon withdrawal the plates were brushed, redipped into a second and sometimes a third tin bath, and finally returned to the grease pot to remove any excess tin Bran or barley meal was used to absorb the grease Polishing the sheet with sheep fleece completed the process. The coating was evenly distributed over the surface of the plate but was decidedly heavy as compared with the modern product.

Since 1720, marked improvements in manufacturing methods have been adopted, resulting not only in a superior product but in a reduction of costs. Chief among them is the first sheet-rolling mill which appeared in 1728 to replace the hammering operation. It is thought that both Hanbury and John Payne were responsible for its construction. Through its use, base sheets were turned out more pliable, of more uniform thickness, and of a greater size than was possible by the earlier hand methods The sheet mill made Wales the foremost producer of tin plate. The perfection of the steam engine in 1770 further increased the efficiency of the rolling mill, substituting steam for water power in its operation. About the same time the idea of replacing charcoal with coke in making wrought iron resulted in the production of two grades of tin plate, referred to as "cokes" and "charcoals." The terms in present-day practice designate only finishes rather than the composition of the base metals. Other innovations were injected into the industry, such as the use of sulfuric acid as a pickling agent in 1806 instead of barley water, the adoption in 1829 of the practice of box annealing of base plates in preference to fire-bed annealing; the invention by Morewood about 1863 of a device for carrying the sheets out of the tin bath through a set of rolls located in the oil layer, insuring uniform distribution of the tin. During 1874 an attempt was made to manufacture tin plate in the United States. Works were erected at Demmler, Pa., by the United States Iron and Tin Plate Company, and at Wellsville, Ohio, by the American Tin Plate Company. However, competition from the imported tin plate proved too great, and in 1878 both plants were obliged to divert their efforts to the manufacture of light sheets, largely for enameled ware. Attempts made at the Demmler works in 1876 to roll Bessemer steel into sheets resulted in the general substitution of steel for iron in making tin plate in England. Other changes and refinements included the cold-rolling of the black base sheet, giving an improved finish; the use of a flux instead of grease to take out all moisture prior to tinning; the mixing of lead with tin to give a dull finish or terne plate; the invention of power-driven trimming shears. As a result, Wales continued to lead the world, as far as the tin-plate industry was concerned, for more than 175 years. It is reported that in 1890 her output of tin plate exceeded 13,000,000 base boxes, of which about 70 per cent was exported to the United States. In that year, the McKinley tariff bill placed a protective

tariff of 2.2 cents per pound on tin plate. The following year, when the bill went into effect, the Demmler works resumed tin-plate manufacture, and the industry began to grow in various sections of the country. As a result of government protection and the invention of automatic can-making machinery, the annual production of tin plate in the United States has become greater than all the rest of the world combined.

Method of Tinning. The application of the tin coating to steel is only a very small amount of the work involved in the manufacture of tin plate. The rolling of the black plate is similar to the manufacture of light sheets. The original "tin bar" is of soft steel, known as tin-plate quality. The greater portion of the steel is produced by the open-hearth process, although it is also produced by any of the standard steel-making methods. More than two-thirds of the tin plate made require black plate between 30 and 34 gage (U.S.S.G.), that is, between 0.5000 and 0.3437 pound per square foot

The steel plate is prepared for tinning by "black-pickling" mechanically in 4 per cent sulfuric acid at 180° to 190° F. for 8 to 10 minutes The pickling loss, as the result of scale removal, is about 2 per cent by weight. After black-pickling, the sheets are "black-annealed" in closed boxes sealed with sand. This operation is done at 1400° F. (760° C.), the sheets being brought up to temperature slowly, remaining in the furnaces 16 to 18 hours, and then slowly cooling to room temperature in 40 to 48 hours. Annealing removes rolling strains and stresses and adsorbed gases resulting from pickling, it eliminates brittleness and clears up the surfaces of the plates.

After pickling and annealing, the plates are cold-rolled to improve the etch-roughened and porous surface resulting from the previous operations Cold-rolling also flattens the plates. To remove the slight hardening resulting from cold-rolling, the sheets are "white-annealed" at 1020° F. (550° C.), being brought to temperature in 10 to 12 hours, and then allowed to cool slowly to room temperature.

Light films of oxide are formed during the cold-rolling and white-annealing. These are removed by "white-pickling" by machines in 2 per cent sulfuric acid, at lower temperatures than black-annealing, for 3 to 5 minutes. It is distinctly desired to avoid etching of the plate. Overpickling will cause the plate to take up larger amounts of tin and make it more difficult to obtain bright-polished and lustrous surfaces on the final tin plate. The plates are carefully washed in clean cold water and inspected. They are stored in water boshes (to which small amounts of hydrochloric acid are added to prevent surface oxidation of the plate) until needed for tinning.

A tinning stack consists of a tinning pot for holding the molten tin, a furnace for heating the pot, a tinning machine for mechanically carrying the plate through the tin, a cooling table for receiving the tinned plate and

delivering it to the cleaning and polishing machine. A tinning set consists of a pot and its setting, the furnace, and the tinning machine. Most of these are simple in construction, although some, such as the Thomas designed to white-pickle, wash, tin, clean and polish the plates automatically, are quite complicated.

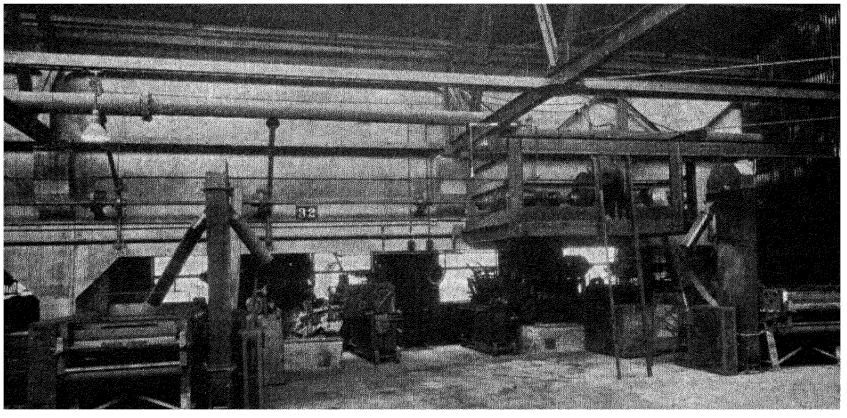
The simplest form of tinning machine consists of four high-carbon steel rolls, held in place in heavy housings, and arranged in two pairs so that the rolls in each pair lie in the same horizontal plane and the gripping faces of the rolls in the two pairs lie in the same vertical plane. At one end the rolls of each pair are geared together. At the other end one roll in each pair carries a larger gear which meshes with an idler mounted between the two pairs. The gear on the top roll is driven by a small motor. The rolls are thus revolved in a manner to draw the plates upward when they are inserted between the rolls of the bottom pair.

The tinning pots vary in size according to the machine. They are made in one piece of close-grained cast iron. They consist essentially of two long narrow chambers separated by a partition extending almost to the bottom and by an elevation in the bottom that rises to within 3 or 4 inches of the bottom edge of the partition. The opening thus made permits a continuous bath of molten tin in the bottom of the pot, and provides a passageway for the plate to pass from one chamber to the other. The first or entering chamber is seldom more than 2 feet deep, while the other or finishing chamber is about 4 feet deep and projects above the first. Both chambers are sloped inward from the vertical. The pot is mounted in a brickwork furnace setting, so that the tin or entering chamber projects about 9 inches into the combustion chamber. Hoods are set over the tinning machine and the pot to take off fumes. A modern tinning unit (two stacks) in a large tin-plate plant is shown in Fig. 128. A typical mechanically operated pot is shown diagrammatically in Fig. 129.

When operation is begun, the pot is filled with molten tin to within about 3 inches from the top of the entering chamber. This brings the surface of the tin about half a foot above the slit or opening in the partition between the chambers, closing the slot except through the tin. Pots usually require from 5,000 to 10,000 pounds of pure tin, of Banka or Straits grade or the equivalent. The upper part of the exit chamber is now filled with palm oil. The tinning machine is immersed in the molten oil and is suspended from the top of the chamber. The tin and oil levels are adjusted so that the lower pair of rolls of the machine are about 2 to 3 inches above the tin level, and the exit rolls at the top of the oil layer are partially exposed for ease of inspection. On the entering side of the pot, the narrow flux box, of the same length as the rolls, is inserted so that its lower edges dip into the molten tin and its upper edge is elevated above the top of the chamber. The flux box holds the fused mixture of zinc and ammonium

chloride used to keep the sheets clean and dry and flux them preparatory to tinning.

Tinning is performed either by hand or mechanically. In both cases the pickled and soaked sheets pass through the flux into the molten tin, through the tin and the slot in the partition between the chambers, then up to the nip of the lower rolls of the tinning machine in the palm oil. The rolls draw the tinned sheet through the palm oil and deliver it to raising rolls and frames which drop it on an incline to a conveyor. Mechanically fed tinning pots, through increases of speed, have more than doubled the output per pot of hand tinning, and permit the production of brighter and more uniformly coated plates.



(*Courtesy American Sheet and Tin Plate Co.*)

FIGURE 128. Commercial tinning plant.

The thickness of the tin coating is a function of the temperature of the tin and the palm oil, within certain limits; the speed of the plate through the tin; and the tightness of the rolls of the tinning machine. Tin in the entering chamber is kept at about 575° F. The temperature of the oil in the exit chamber is about 475° F., being heated from the molten tin underneath. The temperature of the tin in the second chamber must be considerably cooler than the tin in the first section, otherwise the plate will not be as brilliant and lustrous as is desired. The oil protects the tin from oxidizing while it is cooling. The flux is kept molten by heat received from the tin underneath.

The tin plates carry oil on their surfaces. They next pass to a cleaning and polishing machine. These are arranged in two sets. In the first set the sheet is passed through rolls consisting of compressed disks of canton flannel mounted on a long mandrel. As the plate passes through the rolls,

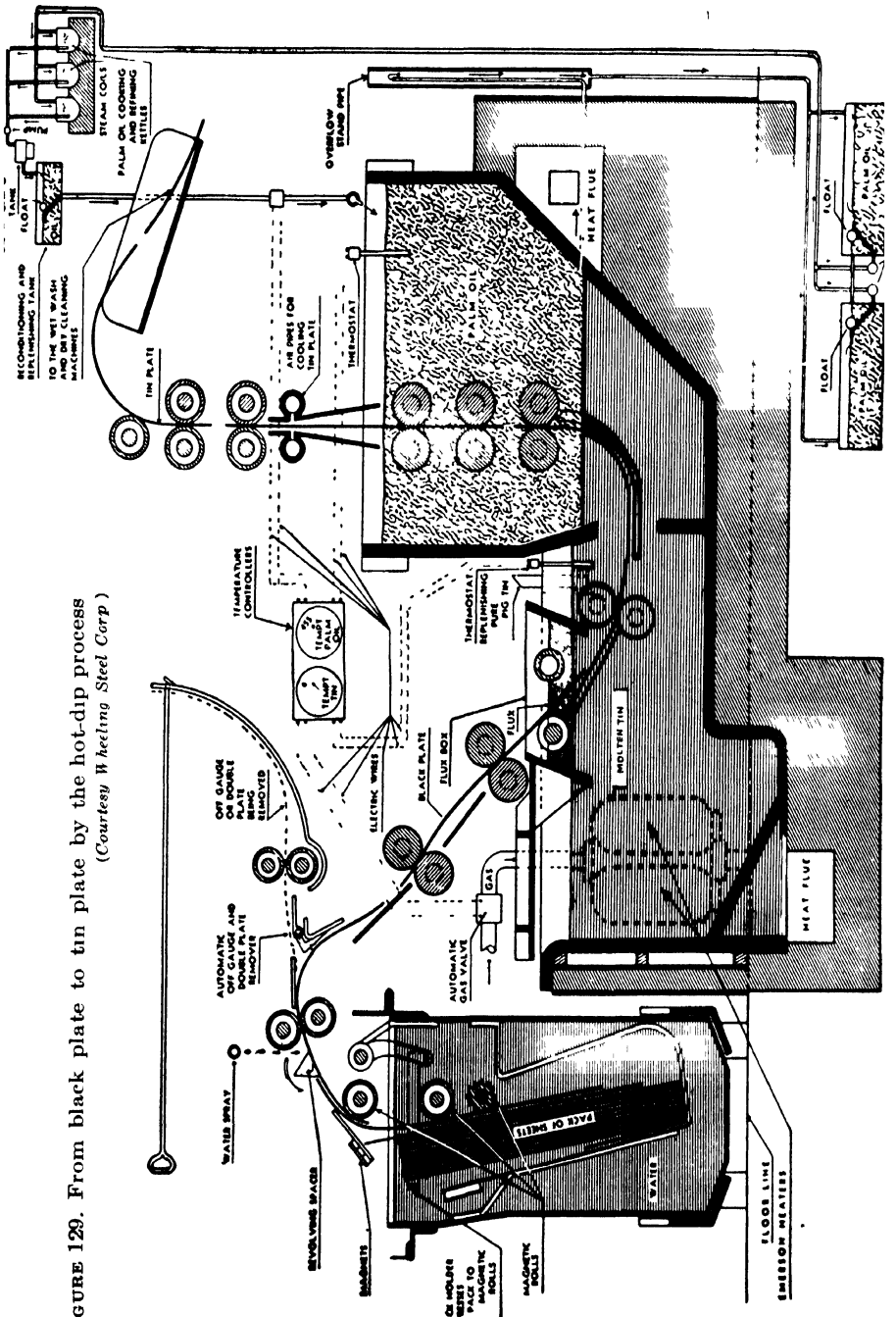


FIGURE 129. From black plate to tin plate by the hot-dip process
(*Courtesy Wheeling Steel Corp.*)

a constant stream of finely ground cleaning mixture capable of adsorbing the oil falls on the plate. The cleaning mixtures consist of about 25 per cent of rye and wheat middlings and about 75 per cent of soft and fine bran, sawdust, ground peanut hulls and finely ground corn cobs. After the cleaning mixture has adsorbed as much oil as is commercially possible, it is sold for cattle feed. The plate cannot be cleaned until it is cooled well below the melting point of the tin. After cleaning, the sheets are polished on polishing rolls and then sorted and inspected.

The tinning method as described is not practicable for the production of some grades of heavily coated charcoal plates nor for all charcoal plates weighing over 135 pounds per base box. These are made by combination dipping in which the sheets are first tinned in the same manner as described under tinning of coke plates, after which they are dipped by hand in a pot of pure tin kept at a low temperature, then into a bath of palm oil and finally passed through a system of rolls by which the excess tin is wiped off and the remainder evenly distributed.

Classification and Marketing. The finished plates are classified into primes, seconds, menders and waste plate. Waste plates are detinned and the base metal sent back to the steel plant as scrap. Primes cannot be considered as perfect plates. They represent the best grade, however. Seconds are plates which will give more or less waste or scrap when applied to the purpose for which they are made. Poorly cut plates, or plates with small uncoated spots or defects confined to a small area, cannot be classified as primes, but this does not prevent their utilization. Menders are plates that contain some defect in the coating that can be corrected by retinning.

The assorted primes and seconds are now counted, collected into packs of 112 plates each and calculated into base boxes of 31,360 square inches each. High-grade charcoal plates are best packed with tissue paper separating the surfaces of the plates. Plates for export are hermetically sealed in tin-plate boxes and then enclosed in wooden boxes.

The commercial sizes, weights, coatings, and designations of tin plate are given in Table 34.

Terne Plate

Manufacture. Terne plate is a sheet-steel product made by coating the steel sheet with an alloy of lead and tin. It is also known as roofing tin, inasmuch as it was first produced for use as a roofing material. For this use it is manufactured in sheets of approximately 20 inches by 28 inches and either IC or 107 pounds per base box, the sheet being 30 gage (U.S.S.G.), or IX or 135 pounds per base box and about 28-gage thickness. Many other uses for terne plate have been developed, so that perhaps now more than 40 per cent is consumed in the manufacture of articles other than roofing materials. It is employed in containers such as auto-

TABLE 34 SIZES AND WEIGHTS OF TIN PLATE

GAGE NO	LB PER SQ FT	LB PER BASE BOX	SYMBOL	GAGE NO	LB PER SQ FT	LB PER BASE BOX	SYMBOL
23	1 1250	—		29	0 5625	—	
	1 079	235	6X		0 542	118	
	1 047	228	6XL		0 514	112	
					0 505	110	
24	1 0000	—					
	0 987	215	5X	30	0 5000	—	
	0 964	210	D2X		0 491	107	IC
	0 955	208	5XL		0 459	100	ICL
	0 895	195	4X				
				31	0 4375	—	
25	0 8750	—			0 436	95	
	0 863	188	4XL		0 413	90	
	0 827	180	DX				
	0 804	175	3X	32	0 4062	—	
	0 771	168	3XL		0 390	85	
				33	0 3750	—	
					0 367	80	
26	0 7500	—		34	0 3437	75	
	0 748	163			0 321	70	
	0 712	155	2X				
				35	0 3125	—	
27	0 6875	—			0 298	65	
	0 680	148	2XL				
	0 657	143		36	0 2812	—	
	0 638	139	DC		0 276	60	
28	0 6250	—		37	0 2656	—	
	0 620	135	IX		0 253	55	
	0 588	128	IXL				
	0 574	125		38	0 2500	—	
	0 565	123					

mobile gasoline tanks, oil cans and other forms of manufactured containers. For some of these purposes it is produced in the form known as long ternes, as large as 40 by 120 inches in area and from 16 to 30 gage thickness. The smaller size sheet, 20 by 28 inches, is commonly known as short or small ternes.

The steel used for the base metal of terne plate must be very ductile and of uniformly good quality to withstand the severe distortion which the material undergoes in its fabricating operations. Open-hearth steel is generally preferred. The preparation of the sheets for dipping is the same as tin-plate mill practice.

Terne coatings vary from 12 per cent tin and 88 per cent lead to 50-50 mixtures, according to the intended use. Roofing tin is generally about 25 per cent tin and 75 per cent lead. Steel can be coated with lead alone The coatings are often porous. An alloying agent is necessary, inasmuch as lead does not alloy with iron. It appears that the tin first alloys with the iron and this iron-tin alloy acts as a binder between the base metal and the lead-tin alloy coat. From this viewpoint, the greater the percentage of tin in the mixture, the better, but from a cost standpoint, the tin content should be kept as low as possible. Experience has shown that the lowest economical proportion of tin that can be efficiently employed is not less than 15 per cent.

Terne-plate coatings are comparatively heavy to insure long life. The thickness of the coat is expressed in pounds per base box of 112 plates, 20 by 28 inches in size, or just twice the area of the tin-plate base box. Coating weights vary from 8 to 40 pounds per base box, the range being 8, 12, 15, 20, 25, 30, 32, 35 and 40 pounds. Even with the heavy coatings, all exposed work should be kept well coated with paint to give full protection against corrosion.

There are three general methods of coating small ternes, known as the palm oil, the flux, and the combination process. In the palm oil process the sheets are first "boiled" for about 20 minutes in palm oil at a somewhat lower temperature than the terne pot. They are then dipped into the molten alloy covered by a layer of oil and allowed to soak in the molten metal for several minutes. They are then lifted out of this pot, drained, and dipped singly into another terne-metal pot of extra fine quality, and immediately transferred to a grease pot containing oil. After removal from the grease pot they are cooled, branned and cleaned. In the flux method, the plates are coated in a tinning machine similar to that used for tin plate, and the original drying of the plate before dipping is done in a neutralized saturated solution of zinc chloride. The combination process provides for redipping of the plates by a combination of the palm oil and flux methods.

Classification and Marketing. After the plates are finished, they are sorted and inspected, and divided into four grades known as primes, men-

ders, strippers, and scrap. The primes are first grade, while the menders are plates whose defects can be remedied by rerunning. Strippers correspond to tin-plate seconds; but inasmuch as all heavily coated terne plates must be primes because their application generally requires full-size sheets, strippers are reclaimed by passing them through a flux tinning pot in which some of the coating is removed, to form primes of a more lightly coated plate. Scrap consists of sheets that cannot be reclaimed. They are detinned by melting off the coating in furnaces. The base metal is returned to the steel mill as scrap.

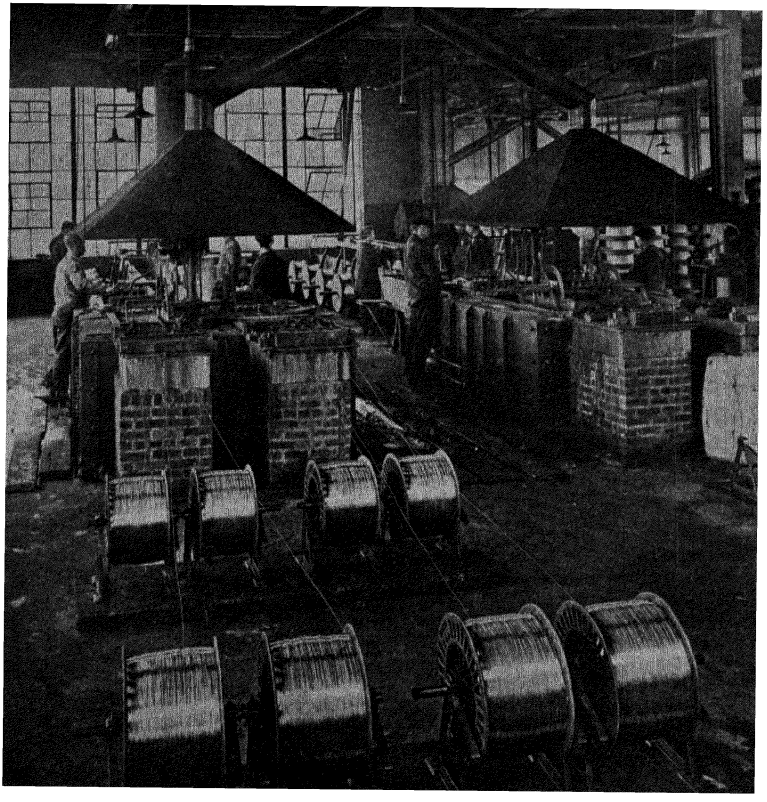
Terne plate is sent to the market in boxes of 112 sheets, stamped with the base weight, the size, the weight of the coat, the finish, and the kind of steel on the ends of the wooden box. From the nature of lead in the alloy, terne plates do not have the bright lustrous appearance of tin plate. As a result of the crystallization of the alloy on cooling, the surface of heavily coated terne plates shows a ramification of more or less fine lines which divide the surface of the plate into small areas almost uniform in size and shape This marking is known as the mottle. It appears on plates carrying 12 pounds of alloy per base box or more The fineness or coarseness of the mottle can be controlled by the rate of cooling It is also affected by the presence of antimony in the terne alloy.

Miscellaneous Hot-Dipped Coatings

Tinning of Wire. Comparatively little steel wire is tinned; first, because of the high cost of the tin metal; second, because of the difficulty of entirely avoiding pinholes in the tin coating, and third, tin is electronegative to iron and the destruction of the steel base is accelerated when corrosion begins. All copper wire which is to receive an insulating covering of rubber compound must first be tinned to protect the copper from the action of the free sulfur in the insulating materials. Were the copper not protected, its electrical properties would be affected. Tinning of wire is shown in Fig. 130. The wire has to be thoroughly cleaned, usually by some sort of pickling, and fluxed in perhaps saturated zinc chloride solution or fused salts such as zinc chloride or mixtures of it with ammonium chloride, before entering the bath of molten tin. As the wire emerges from the tin bath, it passes through a wipe of wicking, such as asbestos. After wiping, it goes to the take-up blocks, either with or without an intermediate water cooling. The temperature of the molten tin during the operation is kept fairly constant at 500° to 550° F. If the tin temperature is too low, the coating will be rough, uneven and more porous; if too high, oxidation will occur with subsequent discoloration owing to the formation of yellowish tin oxides.

Pinholes exist in the tin coating on copper wire. They form a means of gradual ingress of sulfur vapor from the insulating rubber coating.

Lead coating of wire by the same mechanisms but at higher temperatures has replaced tin coatings in many cases for rubber-covered electrical cables. Mantell[1] has shown that adherence of lead is facilitated either by a predip of the cleaned and pickled wire in mercuric chloride, or by the use



(Courtesy Metal Industry, New York)

FIGURE 130. Tinning tanks in a wire-drawing plant.

of a lead alloy containing 1 to 3 per cent of tin. Fluxing of the wire before dipping in the molten metal must be carefully done.

Tinning of Copper Sheets. Copper sheets are often tinned by hand operations. The tin mixture is melted in a cast-iron pot. The copper sheets are cleaned and pickled prior to the tinning process. They are then rubbed with a fluxing solution of zinc chloride and hydrochloric acid. The operators lay them, one by one, on an inclined table adjacent to the pot. A ladle of molten tin is emptied and caused to flow over the sheet,

[1] C. L. Mantell, *Wire and Wire Products*, **15**, No. 7, 353 (July, 1940).

the excess running back by troughs into the pot. Then, beginning at the top, the sheet is wiped off with a brush or bundle of tow to remove the excess tin. In this manner a smooth, even coating is produced.

In another method, the cleaned and pickled sheet is laid on a bench which contains an inset gas grate flush with the top, or else the sheets are heated in a furnace preparatory to tinning In the first method, the sheet is passed over the grate and heated. The operator takes small, flat plates of tin of a calculated and weighed amount, lays them on the heated sheet, allows them to melt, and rubs them into the copper sheet when they have melted. The flux employed is usually dry, powdered ammonium chloride In the second method, weighed quantities of tin are dropped on the heated sheets as they come from the furnace As the tin melts, it is brushed onto the sheet by means of bundles of tow or brushes as rapidly as possible, and spread over the whole surface of the sheet Manufacturers claim that this method gives a more uniform coating than when molten tin is caused to flow over the sheet.

In the so-called powdering method, a mixture of tin powder and flux is spread over the object which has been heated above the melting point of tin The molten tin is spread with a bundle of tow. The purpose of the flux is to remove the thin layer of oxides that has formed by the heating The flux is ammonium chloride or a mixture of ammonium chloride and zinc chloride This method is said to produce a more uniform coating than that of the drip-off method.

Tinning mixtures containing a small amount of lead are often used, as it is claimed that the latter exerts no harmful effect provided the material is not used in containers for foodstuffs or liquids for drinking purposes, but that the lead has the advantage of increasing the fluidity of the mixture

Tinning of Small Articles. A large number of previously stamped or fabricated articles or parts of sheet metal, mostly steel but often of other nonferrous materials, are coated with tin by hot-dipping. This method of tinning seemingly is quite simple, but examination shows that there must be constant attention to the small details incidental to the production of the finished piece. The surfaces of articles to be tinned must be carefully cleaned, usually by chemical methods employing alkali cleaners of various natures to remove grease, followed by pickling with acids such as sulfuric or hydrochloric. Tinning procedures vary largely in different plants. In some plants the pot of molten tin is covered with a flux consisting of either zinc chloride or mixtures of zinc and ammonium chloride, sometimes with small additions of sodium chloride. The article to be tinned is passed through the layer of flux and immersed in the molten tin metal, allowed to coat and then withdrawn, cooled, cleaned, and in some cases polished. The surplus of tin is frequently removed by centrifuging. For this purpose, centrifuges are mounted directly over the tin bath and the tinned

goods are transferred to them immediately after the tinning. In another method, the molten tin is kept free from flux, and the article before dipping is passed into a dehydrating solution consisting of approximately a saturated solution of zinc chloride. From the dehydrating solution, the object is dipped into molten tin, withdrawn, the excess allowed to drain off, cooled, and cleaned usually in bran or sawdust. Tin-pot temperatures vary from about 525° to as high as 600° F., the average practice being about 560° to 575°.

Cleaning practice in some plants is quite complicated, involving, perhaps, grease removal in an alkali cleaner either with or without the aid of electric current, pickling in sulfuric acid, washing, etching in ferric sulfate or similar materials, washing again, and pickling finally in hydrochloric acid before tinning.

The quality of the finished product will vary with the care given to the cleaning, the technique of tinning, and the purity of the tin metal employed.

Hot-dip tinning is employed in the manufacture of milk cans, so-called "tinware," small pieces, the parts of milk separators, pails, and other articles of the same nature.

Tinning pots in small plants are usually gas-fired, and often coal- or oil-fired in larger units The pots are provided with draft hoods to take care of fumes from the decomposition of the flux and from the tin metal The coatings produced in hot dipping by the usual hand methods are considerably thicker than those produced on tin plate.

Large objects, such as milk cans, are tinned either in pieces, the tinned parts later being assembled by soldering, or in one piece.

Tinning is applied in the nitriding of iron or steel objects to cover those parts which are not intended to be nitrided.

Tin Cans

The tin-plate industry found a great outlet early in the nineteenth century in the adoption and development of the tin container. The first of these articles were made and patented by Peter Durand, an Englishman, about 1810. Dry foodstuffs, as beans, coffee, etc., had up to this time been packed in reed baskets, called "canisters," the word being derived from the Greek name for "reed." Durand's invention accordingly became known as the "tin canister." Increased usage in trade among the early canners shortened the name for convenience to its present form of "can."

In the beginning, tin-can manufacture was a hand process, extremely slow and correspondingly expensive. A skilled tinsmith could complete only about 60 cans per day. With hand shears and a soldering iron for equipment, he cut the body blanks from the tin-plate sheet, shaping them by hand. He joined the edges with solder, often an eighth of an inch thick. A circular piece whose edges were hammered up with a mallet was soldered on to form the bottom. The top was a similar disk, in which

a small hole had been cut, fixed in place in the same way after the can had been packed. The hole served as a vent for the escape of air when the can was heated to preserve its contents. A drop of solder closed it while the can was still hot.

Since the tin can was developed primarily to preserve food products, the question of lessening the amount of solder in its manufacture became immediately important. The present-day tin can is the result of a long succession of improvements in material and fabrication over the first hand-made "canister." One modern type is the sanitary can, used more largely in America than on the Continent. This variety has for its distinctive feature the elimination of practically all solder by the use of a gasket of a rubber compound for joining the ends to the body. The top diameter is equal to the diameter of the container itself.

The manufacture of the modern can involves more apparatus and machinery than does canning itself.

Fruit and vegetable cans are familiar examples of packers' or processed food cans This type of can was the industry's first product, and from the standpoint of sales volume is still No. 1. These cans, made at better than 300 cans per minute on a single assembly line, are produced in quantities that defy the imagination. For instance, the Continental Can Company's Clearing Plant No. 5, in Chicago, the world's largest can-manufacturing plant under one roof, turned out over a billion cans in 1945 and has made as many as 10,000,000 cans in a single day.

About 10 per cent of the total annual production of steel in the United States goes into the manufacture of "tin" cans. This steel is rolled to exact specifications, coated with a relatively thin film of tin, cut into sheets, and shipped to the can-making plants in packages of well over 1,000 sheets each. (For some commercial products, the tin coating is replaced by a tin-lead alloy coating or by a phosphate treatment, but lead alloy coating is never used in the manufacture of food containers.)

These coated steel sheets may fall into any one of the following categories:

(1) Hot-dipped tin plate, having a relatively heavy coating of commercially pure tin, applied by dipping the steel in molten tin.

(2) Electrolytic tin plate, having a relatively thin coating of tin, applied by the electrolytic process.

(3) Hot-dipped terne plate, coated as above, but with a low-tin alloy having a lead content of 80 to 90 per cent.

(4) Black plate, having no tin at all. (Sometimes these sheets are also "Bonderized" with a phosphate coating before being coated with a special corrosion-resisting lacquer.)

Manufacture. The first step in can-making may be to enamel one side of the sheet. This may be required to prevent excessive corrosion of the can, or change in the appearance of the product through discoloration or

loss of color. Two kinds of enamel are in common use: "R"-enamel, to prevent excessive corrosion of the can or the bleaching of red fruits and similar acid food products; and "C"-enamel, to prevent discoloration of the cans when packed with high sulfur-content products. When enamel is used, the sheet is coated in the lithographing and enameling department before it is cut into bodies and ends. The enamel is applied in a thin film by coating machines, after which the sheets are carried by an endless chain conveyor through an oven that bakes the enamel on the plate, often at temperatures up to 420° F.

Next, the tin-plate sheets pass through a slitter which cuts them into body blanks of the right size. These blanks are fed into a bodymaker which notches and slits them so that the opposite edges, turned or hooked in opposite directions, will lock together when the blank is bent into a cylinder over the bodymaker horn. Flux for soldering is applied, and the seam is pressed or "bumped" tight. The side seam is soldered to make sure that the can is absolutely air-tight and has the strength to withstand the pressure of food processing. A flanger then flares out both the ends of the cylindrical body, in preparation for the ends to be sealed on. One of these ends is put on by the can manufacturer, the other end, or top, is sealed on by the canner after the can is filled The same method of sealing is used for both top and bottom

Ends are punched from the plain or lacquered tin-plate sheets by a punch press, and are then passed through a machine that curls the outer edges. A thin film of rubber compound is applied in the channel adjacent to the curled edge, and a double-seamer seams the end on the body. In the final operation the cans are air-tested to detect and eliminate possible leaks.

More than 500 sizes and styles of general-line cans have been developed for scores of products ranging from aspirin boxes to five-gallon oil cans

General-line cans often differ from packers' cans in shape, design, opening, and other details. Whereas packers' cans are, with a few exceptions, cylindrical in shape, usually reach the consumers with a paper label, and, again with a few exceptions, are hermetically sealed at top and bottom, general-line cans may in addition be variously shaped, such as round, square, oblong, or oval; they may have a sifter top, hinge cover, slip cover, screw cap, slide cover, pouring spout, nozzle, or other kind of fitting; and they are usually lithographed, meaning that they have a design printed directly on the metal.

Prior to the actual lithography, a sketch is photographed and transferred photographically to a master printing plate. A separate printing plate is made for each color to be used. The tin-plate sheets are then coated with the base color and printed in the flat modern high-speed presses. They pass through an oven to have the color baked on, and usually are varnished to protect the design. They are then ready for fabrication.

Bodymaking operations are about the same as those for packers' cans, except that small neck openings or spouts may also be attached after the can body is made. The closures, covers, or caps are punched out and formed on punch presses, shipped separately and attached in customers' plants.

Designing and building can-making machinery is a highly specialized field. As much as five years may elapse between preliminary sketches and the finished machine, and equipment development engineers must keep abreast of all new developments in tin-plate manufacture and can manufacture as well as operations in customers' plants.

More than 2,500 products, from foods to pharmaceuticals, from motor oil to milk, are normally packed in cans by more than 135 different industries.

An abundant variety of top-grade foods is always available in cans Practically all fruits and vegetables used by canners are grown under exclusive contracts. In most cases the canner not only furnishes the seed in order to insure getting the variety most desirable for canning, but also generally supervises the growing and especially the harvesting to insure deliveries at the cannery when the right stage of maturity is reached Since most canneries are located close to the source of supply, fruits and vegetables are canned soon after they are harvested, and consequently suffer little loss of nutrients or flavor due to long transportation

Cleanliness is the first rule of the modern cannery. The food is washed under high-pressure sprays (some products are first dry-cleaned by air). If blanching is necessary, it is done in hot water or live steam. After the necessary peeling, shelling, dicing, slicing or coring, the cans are then filled with hot products by mechanical feeders and pass through some form of steam or mechanical exhausting device where the air and other gases contained in the food and in the head-space area of the can are expelled. Covers are double-seamed on, hermetically sealing the can, and the contents are cooked directly in the can. Then the cans are cooled.

Cooking the food directly in the container makes each can a miniature pressure cooker, flavors, minerals, and vitamins are sealed in Quality is rigidly controlled in most modern canneries, where trained experts regularly test the texture, flavor and nutritional qualities of foods after they are canned.

Canned foods keep because they have been sterilized by heat in air-tight containers, and it is just as safe to leave food in the open can as it is to transfer it to a dish. Occasionally some acid foods tend to dissolve traces of iron from microscopically small areas where the tin coat has been ruptured, in which case the food may have a harmless but slightly astringent or metallic taste.

The cans themselves can take considerable abuse without damage to the contents.

Chapter 15

Foil and Collapsible Tubes

Tin Foil

Uses. Tin can be rolled into very thin plates or sheets. The metal is then called "tin foil" or at times "silver leaf." It is stated that a pound of tin may be rolled to an area of 11,000 to 14,000 square inches. The usual thickness of foil is from 3½ to 8 mils (0.0035 to 0.0080 in.). It is estimated that 5 to 9 per cent of the total tin consumption of the United States goes into tin foil and collapsible tubes when tin is freely available and not subject to governmental restriction of use.

Foils are used to protect perishables against deteriorating conditions. They are also used for beautifying and adding to the attractiveness of packages. Another use for foil is to be found in the making of electrical condensers. Light gage metals are also employed in the manufacture of novelties, such as bon-bon cups, Christmas tree ornaments, tea balls, etc.

The metallic covering offered by foils gives a most economical and efficient protection against climatic conditions when they are used for foodstuffs, tobacco, soaps, and similar products. An ordinary piece of chocolate, for instance, if exposed to atmospheric conditions without any covering, will become unfit as an edible in a few days. If it is wrapped in a foil, it retains its freshness and blend for a period of many months. When used in wrapping tobaccos, the metallic covering keeps the moisture content unchanged by preventing evaporation losses. Merchandise which has a delicate aroma can well be wrapped in foil, for it prevents the loss of delicate odors such as may be found in the better grades of soap and candies.

Foils can be printed and colored, making attractive wrappers. Beautiful effects can be obtained by combinations of these colors. Since most products today which are sold over the counter are in keen competition with each other, a package which appeals to the eye will unquestionably have a better sale than one which does not. In the case of confections where most of the sale value lies in the appearance of the package, it is extremely difficult for a candy wrapped in paper or unwrapped to compete with a good looking, foil-wrapped bar.

The ease with which foil can be formed makes it an economical material for forming novelties of various sorts.

Tin is soft enough to be cut with a knife, but it files very badly as it chokes up the teeth of a file, except when such a file has been plated with chromium metal. It is softer than gold but harder than lead. The relative hardnesses on the Von Moh scale are: lead 1.5, tin 1.8, and gold 2.5. The variation of the Brinell hardness of tin with temperature is shown in Fig. 131. Tin is slightly work-hardened, as for example by hammering or rolling, but it anneals spontaneously at ordinary temperatures. Tin is most ductile at a temperature in the vicinity of 100° C.; at about 200° C. it becomes so brittle that it breaks to pieces when hammered. At that temperature the metal can be pulverized in a mortar.

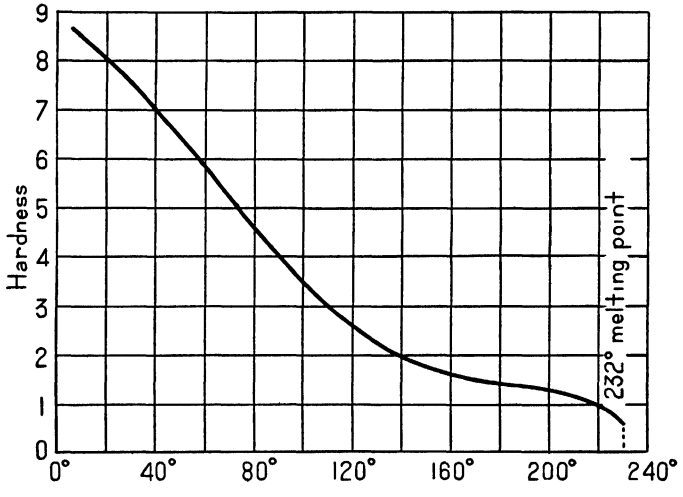


FIGURE 131. Hardness of tin at different temperatures.

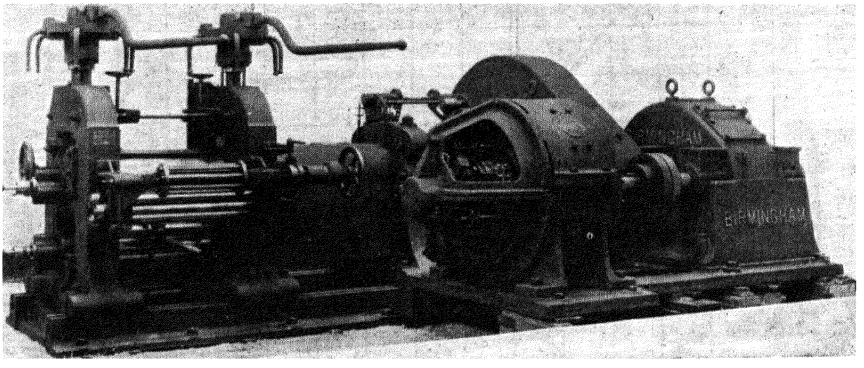
The pressure required to produce plastic flow of tin through an aperture increases regularly with temperature. No discontinuity corresponding with the transformation of tetragonal into rhombic tin is observed. The plastic flow of tin depends on its previous history. Slowly cooled metal flows under a pressure about one-third as great as that required to cause rapidly cooled cast tin to flow. Burton and Marshall[1] found that when the pressure on tin is suddenly increased to 300 atmospheres, the temperature rises 0.277° C. When the pressure is released, the temperature falls 0.264° C.

In stereotyping and electrotyping, tin foil is used in sheets of considerable area in operations in which impressions are made in a manner similar to the way the school boy obtains impressions of coins in tin foil or silver paper. Great care is demanded in this work from the operators.

[1] Burton, and Marshall, *Proc. Roy. Soc.* (*London*), **50**, 130 (1891).

Mundey[2] stated: "An unusual and extraordinary use for tin foil is its introduction into big guns, or ordnance, before firing, a very small quantity being added with the charge." He pointed out that the tin foil does much to prevent or diminish the deposit of copper on the rifled bore of the gun, derived from the copper driving band. The thinness of the tin foil presents the metal in the required state of fine division, and thus facilitates the interaction of the metals with the necessary rapidity.

Manufacture. Tin suitable for use in foil manufacture should be very pure; particularly the arsenic content should be the minimum possible. Antimony in tin is in solid solution. It has been experimentally proved a number of times that the antimony cannot in any way contaminate the foodstuff or sweetmeat for which it constitutes a seal or wrapper.



(Courtesy Birmingham Iron Foundry)

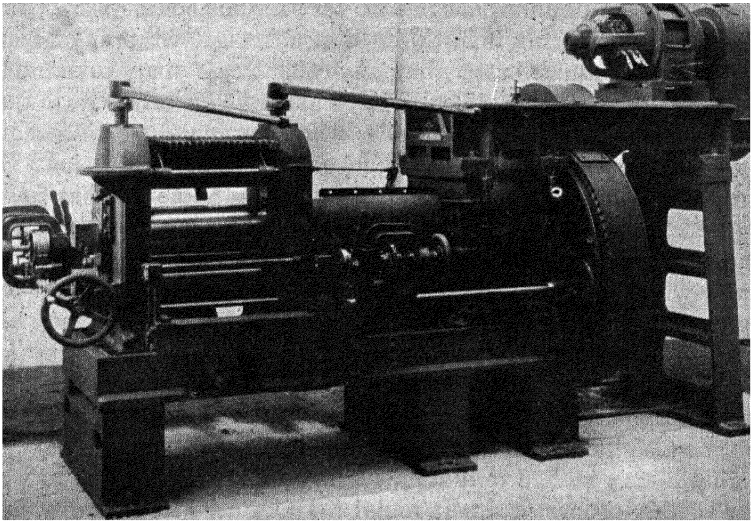
FIGURE 132. A break-down mill.

The manufacture of foil itself may be subdivided into a number of stages. The tin is first cast into rolling ingots with as smooth a surface as possible. The cast slabs are then rolled in a break-down mill. The usual type is shown in Fig. 132. These mills are of very heavy construction with very large reduction gearing, somewhat along the same lines as steel-mill rolls. The metal slabs are rolled in several passes to a given thickness, so that they are thin enough to be sent to the finishing mills. These are of somewhat lighter construction, as the reduction in thickness per pass is considerably smaller. Such a mill is illustrated in Fig. 133. Here the metal slabs are run through a sufficient number of passes to give the required thickness. When thin enough, the foil is wound on reels or spools and from there on handled the same as paper. Polishing may be done in the finishing mill, the steel rolls of which are very hard, having a scleroscope reading of about 100, ground and buffed to a perfect mirror finish. From

[2] A. H. Mundey, "Tin and the Tin Industry," London, Isaac Pitman & Sons, Ltd.

the finishing mills the foil goes to slitting machines of the conventional type and the product is handled the same as paper. These machines cut the material into the required widths and the product goes to the market in wound rolls.

When it is considered that pure tin foils are often made four to sevne ten-thousandths of an inch in thickness, it is easily appreciated, especially by those experienced in the rolling of metals, that satisfactory results can be obtained only by constant attention to metallurgical and other manufacturing details.



(Courtesy Birmingham Iron Foundry)

FIGURE 133. Finishing mill.

There is an increasing demand for all the highly decorative lines of tin foil. Practically any variation of coloring, embossing, stamping, and printing is now possible. The most effective results are obtained with brilliantly colored lacquers. On certain colored backgrounds, bronze printing can be applied to produce most attractive results.

"Gage" in the trade refers not to the thickness of the foil but to its covering power. If one excludes gold leaf, tin foil ranks among the thinnest of metal sheets.

Competitive Foils. There are five principal kinds of foil. These are pure tin foil, foils made from an alloy of lead and tin consisting of about 85 per cent tin, 15 per cent lead, and the two competitors of tin foil—lead foil and pure aluminum foil. In addition a tin-lead foil is sometimes produced

from the rolling of lead and tin sheets together to give a tin surface to a lead sheet. Alloy foils of tin and lead range from comparatively thick tin-coated lead, having about 1 per cent of tin in the core and ½ to ¾ per cent tin on each face, up to a 95 per cent tin-5 per cent lead alloy.

In the preparation of these foils, the chief defect met is minute perforations in the finished sheet. With exceedingly thin material, immunity from pinholes is not easily obtained.

Inasmuch as different thicknesses of each of the above metals may be employed for certain purposes, there is not much to choose from, considered from a competitive standpoint, when the protective properties are considered. Aluminum has been a very serious competitor of tin foil, almost entirely displacing it in the field of chocolate wrapping because it holds chocolate products better than any other grade of approximately the same thickness. Chocolate blends have a tendency to separate out the cocoa-butter when exposed to mildly warm temperature and sunlight. Aluminum foil prevents this occurrence more than any other. When foodstuffs are being considered, however, it is to be noted that foils containing lead are poisonous. While in the United States they may be used for wrapping edibles if backed with paper, many countries have passed food laws which prohibit the use of any wrapping containing lead even when paper-mounted. This cuts down the kinds of foil which may be used for this purpose to pure tin and aluminum.

Tin foil has the disadvantage that it has a tendency to darken under certain atmospheric conditions. It loses some of its luster. Aluminum does not tarnish but keeps its original appearance longer.

Aluminum may be had in different tempers. It hardens when worked. Because of this property, a soft metal may be used and readily formed. It will have a desirable rigidity after fabrication.

Tin foil cannot be readily produced in different hardnesses, as the metal does not work-harden. Aluminum is about one-third as heavy as tin. An equivalent weight of aluminum will have three times the area of tin metal when it is rolled into fine sheet. Fabrication of aluminum foil is more difficult and more costly than that of tin foil.

In making electrical condensers, since the area of surface is the only factor which determines the capacity of such a condenser, there is little choice between the common foils when this factor alone is considered. Aluminum has better electrical conductivity. It has the disadvantage, however, that it cannot be readily soldered. Connections must therefore be mechanical, although spot welding may be employed.

Collapsible Tubes

Analogous to tin foil, there are four principal types of collapsible tubes: those made from pure tin, tin and lead alloys including those made from tin-coated lead, and the competitors made from lead and aluminum.

Pure tin tubes are prepared from the purest metal obtainable, usually Straits, Banka, or Billiton, to which is added a fractional percentage of antimony or other suitable hardening constituent.

Manufacture. The manufacture of tubes is a stamping, deep-drawing, or extrusion operation. The most interesting feature is the fundamental operation of extending the body, shoulder, and nozzle of the tube in one pressing operation from a disk of varying size and shape, depending upon the size of the tube to be made. The length of engagement between the ram and the die is quite small. The tube is squirted out of the space between the two at a rate of flow which the eye can just about follow. Caps are stamped or pressed out of the small portions of metal resulting when the sheet has had circular disks stamped out of it. Threading of the top of the tube and tapping of the disk are screw-machine operations. The caps are of all varieties, from a simple plain type with a sunk milled edge to the regal crown cap. The relatively plastic nature of tin permits its being readily formed into exceedingly complicated and decorative shapes.

The greater share of collapsible tubes are highly decorated, being enameled, printed, lacquered, or embossed by the usual well-known methods. Quite often, fancy designs are printed on a white or colored enameled background. Electric heating for enameling is employed in the most up-to-date plants.

Competitive Tubes. Lead tubes obviously have very limited uses because of the poisonous character of lead and its salts. Practically the same restrictions apply to lead tubes as apply to lead foil.

Aluminum collapsible tubes become an active competitor of tin collapsible tubes in all cases where the product to be packed is nonalkaline or is without chemical reaction when in contact with aluminum. It is estimated that 50 per cent of the products formerly packed in tin can be safely packed in aluminum, and an additional 25 per cent of the total is susceptible to a treatment whereby a slight change in formula will prevent reaction with aluminum.

Aluminum is not as readily fabricated as tin, and a good part of the saving in metal cost is absorbed by increased labor and tool costs. Aluminum-tube extrusion requires better tools and heavier press equipment than tin. The cleaning and annealing operations required for aluminum-tube manufacture are not necessary for tin.

The thickness of metal used in tube manufacture is practically the same for both metals. It ranges from a minimum of 0.0035 to a maximum of 0.008 inch.

"Tin-coated" Tubes. Conservation and restriction measures during World War II brought tin-coated tubes into prominence. Lead tubes are readily made but they have severe limitations as to the kinds of products which may be packed in them. Composite tube blanks were made by two methods, core casting and lamination.

In the first process, a slab of lead, either cast or rolled, is fixed in a mold, and molten tin whose temperature is carefully regulated well below the melting point of lead is cast around the lead core. After cooling, the slab is rolled to the proper thickness for the tube blank. The rolled slab is a sandwich with an upper and lower layer of tin, and a lead layer between. Dimensions of the core, the tin layer, the reduction by rolling are all coordinated to give products having 2 to 7.5 per cent tin coatings, for example.

In the second or lamination method, there is greater flexibility as one side of the final product may be one thickness of tin and the other side the same or a different one, or even none at all if desired. A top lamination is made of pure tin rolled to a definite thickness, and in turn duplex-rolled to a low tin-content solder strip. The bottom lamination is made in a similar fashion. The two laminations are assembled on a rolled lead or lead alloy core strip and the three layers joined together by rolling Joining takes place very readily The top and bottom thicknesses of tin may be readily regulated by coordination of original layer thicknesses to the whole assembly and the total tin content may be controlled. Tube blanks are stamped of the composite slabs or bars in the same manner as out of a tin or lead slab.

The tin-coated lead tubes are satisfactory for a large number of products for which lead can not be employed and in many give service lives almost as good as pure tin. The coated materials tend, in thin tin coatings, to have bare lead spots. For a number of pharmaceutical products only pure tin tubes are satisfactory.

Chapter 16

Compounds

Chemically tin is related to silicon, titanium, zirconium, germanium, and cerium It forms stannous compounds in which the tin has a valence of 2, and stannic compounds with a valence of 4 Probably the most important of these are the oxides, the hydroxides, and, inasmuch as tin is amphoteric, the corresponding acids and their salts, the hydrides, the halides, the sulfides, the thio compounds, the phosphides, phosphates, as well as a number of complex salts Tin does not form nitrates or stable carbonates The organic compounds of tin are also of interest

Stannous Oxide

Stannous oxide is a blue-black, iridescent, crystalline substance It is reduced by some reducing agents On the other hand, even mild oxidizing agents readily oxidize it to stannic oxide or metastannic acid It is easily soluble in nonoxidizing mineral acids and in a number of organic acids to form the corresponding stannous salt

Various experimenters have failed in attempting to get pure stannous oxide, using stannous chloride as a source, treating with soda, forming the hydroxide, heating the same, filtering and washing Sufficient oxidation or hydration took place during these procedures so that a heavy precipitate of stannic oxide was formed

Ditte[1] gave the following rapid method which he claimed was perfectly satisfactory for the preparation of pure stannous oxide Stannous chloride is dissolved in water and treated while hot with the smallest amount of concentrated hydrochloric acid necessary to clear the solution The stannous hydroxide is then precipitated by the addition of a soda solution (*e g* , a carbonate) which is added in small amounts until the mixture is just alkaline to phenolphthalein but not to litmus The milk-white solution is then kept at 110° C for several hours After two to three hours the white material changes to a blue-black substance, stannous oxide, with its characteristic metallic sheen The material is then washed by decantation, dried, and made ready for use.

Fraenkel and Snipischsky[2] repeated Ditte's method successfully. Nu-

[1] Ditte, *Pogg Ann* , **27**, 145 (1882)

[2] Fraenkel, and Snipischsky, *Z anorg Chem* , **125**, 235 (1922)

merous methods are proposed in the literature for SnO preparation, but practically all of them, except Ditte's, produce contaminated products

Following the method of Ditte, stannous oxide was prepared from pure stannous chloride crystals The strict adherence to his directions as to control of alkalinity is the most important factor in the production of pure SnO Solutions too highly alkaline (greater than pH 7) cannot be made to yield stannous oxide even after several hours' boiling Within the range of pH 5 to about pH 6 5, stannous oxide can be readily produced The product, after filtration, careful washing with distilled water to free the precipitates from chlorides, and careful drying at 110° C , is blue-black, lustrous, somewhat iridescent and decidedly crystalline The material corresponded exactly to SnO as shown by chemical analysis for Sn by iodine titration

Stannous oxide, boiled in distilled water for half an hour, did not produce any stannous hydroxide or metastannic acid which could be determined by visual examination It did not change in color, appearance, or crystalline form, in any manner observable under the microscope

It would, therefore, seem that the reaction

$$Sn(OH)_2 = SnO + H_2O$$

is not readily reversible The thermal data

$$Sn(OH)_2 = SnO + H_2O - 1910 \text{ Cal}$$

show it to be endothermic

The physicochemical properties of stannous oxide are important as they are the key to the explanation of the manner in which stannic oxide was reduced by a reducing gas[3] The reduction of stannic oxide may be assumed to take place in either of two ways The stannic oxide may either be reduced directly to tin metal or it may be first reduced to stannous oxide (SnO) which may be further reduced to tin metal

Fink and Mantell[4] have shown that

(1) Stannous oxide is thermally unstable above 385° C , giving Sn and SnO_2

(2) Stannous oxide is readily oxidized by both moist and dry air above 240° C At higher temperatures it is pyrophoric

(3) Stannous oxide is oxidized by sulfur dioxide in acid solutions, and reduced by the same reagent in alkaline solution

(4) The reduction of stannic oxide, reasoning from the data on stannous oxide, is a single-step reaction above 385° C and a two-step reaction below that temperature

Table 35 gives the physical properties of stannous oxide

[3] C G Fink, and C L Mantell, *Trans Am Electrochem Soc* , **51**, 175 (1927)

[4] C G Fink, and C L Mantell, *J Phys Chem* , **32**, 103–12 (1928)

Stannous Hydroxide

Stannous hydroxide is obtained as a white mass by the addition of an excess of an alkali or an alkali carbonate to an aqueous solution of stannous salts The precipitate is gelatinous and slimy It filters badly It may be washed by suction filtration or decantation The amount of contained water depends upon the method and speed of drying Britton[5] stated that stannous hydroxide begins to be precipitated by alkali hydroxide from stannous salts at a pH of 1 9 Freshly prepared stannous hydroxide is white It gradually absorbs oxygen from the air, being converted to hydrated stannic oxide It is only very slightly soluble in water, but readily soluble in acids to form stannous salts Nitric acid oxidizes the material to either an insoluble basic stannic nitrate, metastannic acid or stannic

TABLE 35 PHYSICAL PROPERTIES OF STANNOUS OXIDE

		Authority
Electrical conductivity	150×10^{-6} mho	Friederich (1)
Heat of formation	66 8 Cal	Mixter (2)
Magnetic susceptibility	$-0\ 158 \times 10^{-6}$ units per g , $-0\ 012 \times 10^{-6}$ units per mol	S Meyer (3) " "
Specific gravity	6 9	International Critical Tables

(1) *Z Physik* , **31**, 813 (1925)
(2) *Am J Sci* (4), **27**, 229 (1909)
(3) *Wied Ann* , **69**, 236 (1899)

oxide When stannous hydroxide is treated with solutions of alkali hydroxides, soluble stannites are formed Aqueous ammonia and alkali carbonates do not cause this reaction, however When a little potassium hydroxide is added to a stannous hydroxide suspension in water at ordinary temperatures, crystals of stannous hydroxide are formed These increase in size until all the hydroxide has been transformed The reaction is cyclic in that at first potassium stannite is formed, this being hydrolyzed by water into stannous oxide, which is less soluble in the solution, and potassium hydroxide, which is thus regenerated to begin the reaction anew Sodium hydroxide acts in a similar way, but ammonia does not Proust[6] stated that when stannous hydroxide is mixed with water and cupric carbonate, stannic oxide and crystals of copper are formed, while carbon dioxide is

[5] H T S Britton, *J Chem Soc* , **127**, 2110 (1925)

[6] Proust, *J Phys* , **51**, 173 (1800), **61**, 338 (1804), *Ann chim phys* (1), **28**, 213 (1798), *Nicholson's J* (1), **2**, 515 (1798), (2), **14**, 38 (1806)

given off Reichard[7] stated that stannous hydroxide reduces a solution of arsenic oxide in sodium hydroxide to metallic arsenic. The work of Dhar[8] showed that the oxidation of stannous salts is hindered by the presence of easily oxidized organic substances Stannous hydroxide is amphoteric and can function as either a weak base or a weak acid The stannites react with sodium thiosulfate with the formation of stannous sulfide, sodium stannate, sulfite and sulfostannate On treatment with sulfur, the stannites form stannous sulfide which unites with the excess alkali stannite to form sulfostannites in which the sulfur replaces the oxygen.

The stannites are known only in solution They are readily oxidized and act chemically as reducing agents With Fehling's solution, copper oxide is precipitated Alkaline solutions of antimony oxide are reduced to metallic antimony Lead is precipitated from lead salts, and bismuth and lower oxides of the metal from solutions of bismuth salts Alkali stannites do not reduce nitrites and nitrates The stannites are relatively unstable, decomposing into tin and stannous oxide, or they are oxidized by the oxygen of the air to stannates and metastannic acid

Stannic Oxide

The properties of native stannic oxide have been discussed under tin ores, ore dressing, and smelting and metallurgy It is very decidedly insoluble in practically all known materials (see leaching of tin ores)

When tin is heated nearly to its boiling point in air, it burns with a white luminous flame The stannic oxide so formed is in a very fine state of subdivision It was formerly known as *Flores jovis* (flowers of Jove) or *Flores stannic* (flowers of tin) When the metal is fused in the air, the surface soon becomes covered with an oxide dross known as "tin ash" This is a mixture of finely divided metal and oxide which can be converted by prolonged roasting to white stannic oxide The product obtained by high temperature oxidation is less soluble in fused silicates It is preferred as an opacifying agent in glazes and enamels Stannic oxide is obtained by treating tin with nitric acid, by oxidizing stannous oxide or stannous hydroxide, by roasting sulfides, or by the hydrolysis of stannic salts or the drying and igniting of stannic hydroxide When a solution of a stannic salt is treated with ammonia, a gelatinous precipitate very difficult to wash is obtained, but if the mixture is warmed with a concentrated solution of sodium sulfate, the dense precipitate is easily washed, and it furnishes stannic oxide upon ignition

Chemically prepared stannic oxide is usually white or grayish white It differs markedly in many of its chemical properties from native stannic oxide Both forms are readily reduced at temperatures as low as 250° C. by hydrogen, carbon monoxide, and similar reducing gases. It can be ca-

[7] Reichard, *Ber.*, **30**, 1915 (1897)
[8] N R Dhar, *Z. anorg. Chem.*, **144**, 289 (1925).

thodically reduced by electrolytic means. It is not affected by air, oxygen or water. Gibbs[9] found that fused potassium acid fluoride dissolves stannic oxide. When stannic oxide and sulfur are heated together, stannic sulfide is formed. Rose[10] stated that a molten mixture of sulfur and sodium carbonate transforms stannic oxide into sodium thiostannate. He further said that when a mixture of concentrated sulfuric acid is heated with stannic oxide, a sirupy liquid is formed from which all the stannic oxide precipitates upon dilution Molten potassium acid sulfate dissolves stannic oxide. When the cold mass is treated with water, the oxide is reprecipitated

Below 500° C. the oxide is not affected by nitrous oxide, nitric oxide or nitrogen peroxide[11] Stannic oxide is reduced to metal when heated with carbon (see Smelting) Moissan[12] stated that stannic oxide is reduced to metal when heated with calcium carbide.

Stannic oxide is quickly reduced by molten potassium cyanide This was the method employed in the old Cornish assay Milbauer[13] found that molten potassium thiocyanate, when used with stannic oxide, forms stannous sulfide and then potassium thiostannate Carbon tetrachloride reacts with stannic oxide at red heat to form stannic chloride.

Stannic oxide is insoluble in fused boric oxide, as shown by the work of Burgess and Holt[14] Lomax[15] showed that the solubility of stannic oxide in fused silicates increases with the proportion of contained alkali

The oxide is reduced to metal by potassium and sodium, magnesium and aluminum. The properties of stannic oxide are given in Table 36.

Stannic Acids

Tin and its compounds are amphoteric. When tin is precipitated from its salts by alkalies, the resulting hydroxide is soluble in further quantities of the alkali to form salts such as the stannites or stannates In other words, in its simplest forms stannous hydroxide may act as such with a formula of $Sn(OH)_2$ when acted upon by nonoxidizing acids to form tin salts, but when acted upon by alkalies such as NaOH, it functions as an acid, H_2SnO_2, to form corresponding salts, the stannites, as Na_2SnO_2. In the same way, the following representations of reactions may occur:

$$SnCl_4 + 4NaOH = Sn(OH)_4 + 4NaCl$$

$$Sn(OH)_4 + 4HCl = SnCl_4 + 4H_2O$$

$$H_4SnO_4 + 4NaOH = Na_4SnO_4 + 4H_2O$$

[9] Gibbs, *Am J. Sci.* (2), **37**, 355 (1864).
[10] Rose, *Liebig's Ann.*, **91**, 104 (1853), **112**, 163 (1861).
[11] Sabatier, and Senderens, *Compt rend.*, **120**, 619 (1895).
[12] Moissan, *Compt rend*, **125**, 839 (1898).
[13] Milbauer, *Z. anorg Chem.*, **42**, 337 (1904).
[14] Holt, *Proc. Chem. Soc.*, **19**, 221 (1903); *Trans. Cer. Soc*, **5**, 163 (1906).
[15] Lomax, *Trans. Cer. Soc.*, **11**, 118 (1912).

The reactions are not as simple as represented, inasmuch as hydration and hydrolysis occur with the formation of a number of intermediate hydrated substances of varying hydroxyl and water content

When dilute nitric acid acts on tin, depending upon the concentration of the acid, either stannous or stannic nitrate is formed These salts readily decompose with the separation of stannic acid When concentrated nitric

TABLE 36 PHYSICAL PROPERTIES OF STANNIC OXIDE

		Authority
Compressibility coefficient	$3\ 38 \times 10^{-12}$ dynes per sq cm	Madelung and Fuchs (1)
Dissociation pressure of the oxygen at 927° C	$4\ 47 \times 10^{-15}$	Maeda (2)
Electrical resistance		
On a rising temperature	ohms per cu in	
° C.		
360	3550	Doelter (3)
500	1060	"
700	1050	"
900	29	"
1060	5 0	
1200	1 2	
1430	0 85	"
On a falling temperature		
1270	0 980	"
1200	1.105	"
1080	1.488	"
1010	1.688	"
930	2 677	"
780	55 80	"
Hardness (von Moh)	6–7	
Heat of fusion	1 66	Fränkel and Snipischsky (4)
Heat of formation		
Sn liquid, O_2 at 800° C	130.26 cal	Maeda (2)
From solid tin	135 8 cal	Fränkel and Snipischsky (4)
From molten tin	137.46 cal	Fränkel and Snipischsky (4)
Crystalline oxide	137.8 cal	Mixter (5)
Magnetic susceptibility		
Per gram	$-0\ 082 \times 10^{-6}$	S Meyer (6)
Per mol.	$-0\ 006 \times 10^{-6}$	" "
Melting point	1132° C	
Specific gravity		
Chemically prepared	6.6–6.9	
Natural crystals	6.7–6.85	
	7.0	International Critical Tables
Specific heat		
0° to 100° C. . . .	**0.0931**	Neumann (7)

TABLE 36.—*Continued*

Thermal conductivity		
In direction of chief axis	1	Jannettaz (8)
In vertical direction	0 79	"
Thermal expansion coefficient		
16° to 46° C	a = 0 000004	Kopp (9)
Cubical, 0° to 100° C	0 0000172	Playfair and Joule (10)

References to Table 36

(1) *Ann Physik* (4), **65**, 289 (1921)
(2) *Bull Japan Inst Phys Chem Research*, **2**, 350 (1923)
(3) *Sitzber Akad Wien*, **119**, 70 (1910), *Z anorg Chem*, **67**, 392 (1910)
(4) *Z anorg Chem*, **125**, 235 (1922)
(5) *J Am Sci*, (4), **27**, 231 (1909)
(6) *Wied Ann*, **69**, 236 (1899)
(7) *Pogg Ann*, **23**, 1 (1831)
(8) *Compt rend*, **75**, 1501 (1872), *Bull soc min*, **15**, 138 (1892)
(9) *Liebig's Ann*, *Suppl*, **3**, 1 (1864), *Liebig's Ann*, **81**, 1 (1852), *Pogg Ann* **86**, 156 (1852)
(10) *J Chem Soc*, **1**, 121 (1849)

acid acts on tin, a white insoluble powder, so-called metastannic acid, is formed with the evolution of considerable heat.

Berzelius, in 1811, showed that the compound prepared by the action of nitric acid on tin and the hydroxide precipitated from tin chloride by alkalies, like ammonia, had different properties Both compounds contain the same proportion of oxygen, but possess different characteristics. The hydroxide precipitated from stannic chloride is SnO_2 nH_2O, which saturates three times as much base as the hydroxide obtained by the action of nitric acid on tin He likened the former to ordinary phosphoric and the latter to metaphosphoric acid, Fremy designated the former stannic, and the latter metastannic acid, while Berzelius designated them α- and β-stannic acids, respectively The α-acid is the more basic one It furnishes salts which are readily soluble in water without decomposition The moist material is easily soluble in nitric acid It is also soluble in dilute sulfuric acid to form sulfates, and is easily dissolved in hydrochloric acid to form chlorides. The solutions do not gelatinize when they are boiled The β-, or metastannic, acid furnishes salts which are only sparingly soluble in water and are readily hydrolyzed into insoluble basic salts and acids Metastannic acid is insoluble in nitric and even in concentrated sulfuric acid When treated with hydrochloric acid, it unites to form a substance insoluble in an excess of the acid, but soluble in water When the solution is boiled, it gelatinizes

The causes for these differences have not been clearly shown. The forms readily change from one to the other One explanatory hypothesis assumes that the acids are colloidal, and that the differences in behavior are caused by differences in particle size; another assumes that the acids

are isomeric or polymeric forms. Vignon[16] inferred, from his work on heats of neutralization of the various stannic acids, that a whole series of variously hydrated compounds exists between the completely water-soluble substance and ignited stannic oxide. Lorenz[17] compared the dehydration rates of the α- and β-acids and stated that their composition was identical, both existing in all stages of hydration between H_4SnO_4 and H_2SnO_3. The characteristic properties of the compounds are retained after repeated precipitation, but the salts are different. Kleinschmidt[18] stated that the α- and β-acids are colloidal substances capable of reversible transformation, and that the change of α to β occurs more readily than β to α. Experimental indication of the formation of definite hydrates is seen from the results of a number of workers. When gels are prepared from stannic chloride by the action of ammonia and ammonium chloride, at low hydroxyl-ion concentration in a short time, and the precipitate is dried by acetone at $-35°$ to $-10°$ C, they have the composition $Sn(OH)_4 \cdot H_2O$. Under similar treatments at room temperature, the composition of the precipitate is $Sn(OH)_4$, or orthostannic acid Stannic acid is transformed in aqueous solutions into more feebly basic acids of the α-stannic acid series. The union of several molecules of stannic hydroxide, with loss of water, appears to give a series of polyorthostannic acids with diminishing basic properties.

Mecklenburgh,[19] Zsigmondy[20] and Weiser[21] believed that the differences in behavior of the different stannic acids are caused by differences in the sizes of particles. β-Stannic acid is supposed to consist of the largest primary particles. Franz[22] assumed that the primary particles are less than a micron in size, and that there is a gradual grouping of molecules, through formation of complexes, to larger secondary particles. The particular properties, therefore, of any stannic acid may be considered to be a function of the grain size, which in turn is dependent on temperature, conditions of formation, etc.

α-Stannic acid may be prepared by treating a soluble tin salt with alkalies, or by decomposing stannates with acids, or hydrolyzing dilute solutions of tin salts. The α-acid is a white voluminous or colloidal precipitate, which, when dried, looks like broken bits of glass. When moist, it reddens litmus and is peptized rather than dissolved by water The heat

[16] L. Vignon, *Compt. rend.* **108**, 1049 (1889), **109**, 372 (1889).

[17] R. Lorenz, *Z. anorg Chem*, **9**, 369 (1895), **12**, 436 (1896).

[18] Kleinschmidt, *Monatsh.*, **39**, 149 (1918).

[19] Mecklenburgh, *Z. anorg Chem*, **64**, 368 (1909); **74**, 207 (1912); **84**, 121 (1914).

[20] R Zsigmondy, *Liebig's Ann*, **301**, 368 (1898).

[21] Weiser, *J. Phys. Chem*, **26**, 654 (1922), **28**, 232 (1924); "Colloid Symposium Monograph," p. 38, Wisconsin, Cooperative Publishing Co, 1923.

[22] Franz, "Beitrage zur Chemie der Zinnsauren vom Kolloidchemischen Standpunkt," Dissertation, Göttingen, 1913.

of formation for the compound $SnO_2 \cdot 2H_2O$ is 133.49 Cal as given by Thomsen, the heat of neutralization as a base (with HCl) is 3.11 Cal., and as an acid (with NaOH) is 9.56 Cal.

Colloidal α-stannic acid may be made in the same manner as silicic acid Graham[23] found that when he dialyzed a solution of stannic chloride and an alkali, he obtained a gelatinous mass on the dialyzer. As the salts diffused away, the jelly was again peptized by the small amount of free alkali remaining The liquid α-acid is converted by heating to the β form Both in liquid form are remarkable for the ease with which they are peptized by minute additions of hydrochloric acids as well as salts. Bellucci and Parravano[24] found that when potassium stannate solutions, ice-cooled, are decomposed by small amounts of hydrochloric acid, stannic hydroxide, $Sn(OH)_4$, or orthostannic acid, $H_2SnO_3 \cdot H_2O$, is formed, whose composition remains constant after extended drying

Freshly prepared α-stannic acid is soluble in dilute mineral acids, but nitric acid solutions gelatinize on standing The property of solution in acids is gradually lost with increasing age. Stannic acid is soluble in, or is peptized by, solutions of alkalies, including ammonia. The salts of α-stannic acid behave as if they were dibasic, as $K_2SnO_3 \cdot 3H_2O$, for example Stannic hydroxide diffuses in alkaline solution like stannous hydroxide $Sn(OH)_2$ is a feeble base, but when one OH radical is replaced by an ethyl or similar group, strong bases result.

When stannic acid is precipitated from alkaline solutions, it absorbs basic dyes, precipitated from acid solutions, it absorbs acid dyes Weiser[25] has studied the colloidal action of stannic acid.

α-Stannic acid has a strong tendency to pass into the β form The change is accelerated by heat. β-Stannic acid can be prepared by oxidizing tin with nitric acid. The nature of the product is different, depending upon the acid concentration. Engel[26] stated that with one volume of concentrated nitric acid and two or more volumes of water, stannous nitrate is formed, with equal volumes of water and acid, a thick sirupy solution of stannic nitrate results, and with concentrated acid, stannic nitrate which readily decomposes and is precipitated, as it is not soluble in moderately concentrated nitric acid. The tin nitrates are readily decomposed by hydrolysis, heating, drying, or standing, into metastannic or β-stannic acid Ignition gives stannic oxide. When the products from the action of nitric

[23] T. Graham, *Proc Roy Soc (London)*, **13**, 335 (1864), *J. Chem Soc*, **17**, 318 (1864); *Phil Trans.*, **156**, 399 (1866), *Phil. Mag* (4), **32**, 401, 503 (1866), *Liebig's Ann*, **13**, 146 (1835)

[24] Bellucci, and Parravano, *Atti accad Lincei* (5), **13**, II, 307 (1904); *Z. anorg. Chem*, **45**, 142 (1905)

[25] Weiser, "The Hydrous Oxides," New York, McGraw-Hill Book Co., Inc., 1926.

[26] Engel, *Compt rend.*, **124**, 765 (1897); **125**, 464, 651, 709 (1897).

acid on tin are washed, it is found that very large quantities of water are necessary to wash out the nitric acid which is adsorbed by the precipitate.

Moist β-stannic acid reddens litmus This may be the result of its acidic nature, but it is more likely to be the effect of small amounts of adsorbed nitric or other acids Vignon[27] gave the heat of neutralization against potassium hydroxide as 11 5 Cal for air-dried β-stannic acid, and 5 3 Cal. for material dried at 250° C β-Stannic acid is sparingly soluble in most acids and insoluble in nitric It absorbs small amounts of acids such as hydrochloric and sulfuric. It dissolves in hydrochloric, but further additions of the acid precipitate the stannic acid Treadwell[28] gave the following reactions:

$$(SnO(OH)_2)_5 + 10HCl = 10H_2O + (SnOCl_2)_5$$

for the product insoluble in water, and

$$(SnOCl_2)_5 + 8H_2O \rightleftharpoons 8HCl + Sn_5O_5Cl_2(OH)_8$$

where the product is soluble in water, and

$$Sn_5O_5Cl_2(OH)_8 + 2HCl \rightleftharpoons 2H_2O + Sn_5O_5Cl_4(OH)_6$$

for the insoluble product formed upon further additions of acid When the water-soluble material is boiled, hydrolysis takes place, as

$$Sn_5O_5Cl_2(OH)_8 + 2H_2O = Sn_5O_5(OH)_{10} + 2HCl$$

Berzelius stated that the β-stannic acid is less basic than the α-acid Dilute alkalies dissolve β-stannic acid, forming stannates of the formula $M_2Sn_5O_{11}\ 4H_2O$, which do not crystallize readily An excess of alkali reprecipitates the β-stannic acid Aqueous solutions of alkali carbonates or ammonia do not dissolve the β-stannic acid

Stannic acid is peptized by a number of electrolytes It has considerable power of absorbing ions and electrolytes from solution In the case of hydrochloric acid, after equilibrium has been established, the concentration of the acid in the colloidal β-stannic acid is often greater than that in the aqueous solution In the case of potassium chloride and nitrate, absorption is such as to cause equal concentrations of the electrolyte in the colloid and the solution. In certain proportions a mixture of the hydrated oxides of iron and tin is soluble in dilute ammonia Weiser[29] showed that hydrated stannic oxide is peptized by the hydroxyl ion while hydrated ferric oxide is not Colloidal stannic oxide, or metastannic acid, adsorbs ferric oxide and carries it into colloidal solution as long as the tin compound is in excess Hydrated ferric oxide adsorbs the tin compound and tends to take

[27] L. Vignon, *Compt rend*, **108**, 1049 (1889), **109**, 372 (1889)

[28] Treadwell, "Kurzes Lehrbuch der analytischen Chemie," Vol. **1**, p 215, Leipzig, 1907, Vol **1**, p 220, London, 1903

[29] Weiser, "The Hydrous Oxides", New York, McGraw-Hill Book Co , Inc., 1926.

it out of colloidal solution, so that while the former is present in large excess, none of the latter remains peptized. Stannic oxide does not precipitate in the usual way from a solution of tin in nitric acid containing a suitable amount of iron Stannic oxide, when peptized by nitric acid, coagulates spontaneously since the aged oxide or stannic acid is neither peptized nor dissolved by nitric acid If freshly prepared colloidal stannic oxide be peptized by either ferric nitrate or a suitable mixture of this salt and nitric acid, aging or boiling the solution does not cause coagulation because the strongly adsorbed ferric ion exerts a stabilizing action If the ferric-ion concentration in the solution is too low, complete or partial coagulation of the peptized stannic acid takes place on standing or boiling Chromic oxide and stannic acid gels mutually precipitate each other, the maximum effect occurring when equinormal concentrations of the two solutions are mixed For further discussion of the rates of adsorption of various materials by colloidal stannic acid, the reader is referred to the extensive work given in the colloid chemistries

Spring[30] stated that perstannic acid, $H_2Sn_2O_7$, is formed when a hydrated barium dioxide is added in excess to a hydrochloric acid solution of stannic chloride, the turbid liquid dialyzed until barium chloride no longer passes through the membrane, and the colloidal residue evaporated on a water bath Tanatar[31] stated that permonostannic acid, $HSnO_4$ $3H_2O$, was formed when a solution of stannous chloride was treated with sodium carbonate, the precipitate triturated with an excess of 30 per cent hydrogen peroxide at 70° C , and the product dried in a desiccator When this product was further dried, it slowly lost water and oxygen and underwent partial decomposition in water, giving stannic acid and hydrogen peroxide He also prepared the salt potassium permonostannate, $KSnO_4$ $2H_2O$, by the action of hydrogen peroxide on potassium stannate It has an alkaline reaction in water and decolorizes potassium permanganate when acidified with sulfuric acid When heated it is converted into potassium perdistannate, $K_2Sn_2O_7 \cdot 3H_2O$ Sodium salts are prepared in a similar manner They are all white amorphous powders

When concentrated alkali stannate solutions are electrolyzed at low temperatures and low current densities, small amounts of perstannates are formed as a result of anodic oxidation The addition of alkali fluorides increases the rate of formation, but the final equilibrium of the perstannate formation is not altered The yield is small, inasmuch as considerable of the perstannate formed decomposes. The yield diminishes rapidly as the temperature of electrolysis rises Decomposition of the perstannates yields stannates

[30] Spring, *Bull soc. chim* (3), **1**, 180 (1889)
[31] Tanatar, *Ber.*, **38**, 1184 (1905)

Stannites and Stannates

It has been previously pointed out that tin is amphoteric and can exist either in the hydroxide form in some of its compounds or in the acid form in which the summation formula is the same. A large number of different stannates, the salts of the stannic acids, are referred to in the literature. They have been made either by the fusion of the oxides or the hydrates with alkali hydroxides or carbonates, or by the solution of the hydroxides or the tin acids in alkali solutions Depending on the method of preparation, the trihydrate $K_2Sn(OH)_6$, and the tetrahydrate $K_2Sn(OH)_6\ H_2O$, and the pentahydrate $K_2Sn(OH)_6\ 2H_2O$ have been made The potassium salts are more soluble than the sodium and lithium salts The composition of the trihydrate agrees with the formula $K_2SnO_3 \cdot 3H_2O$ They are colorless, shining, oblique, rhombic prisms often with the acute lateral edges truncated They are isomorphous with potassium hydroxyplatinate $K_2Pt(OH)_6$ They lose only small amounts of water at 100° C , but at 140° C moisture is copiously given off The dehydrated salt is hygroscopic Long-continued drying decomposes the stannates into tin oxides and alkalies. Crystalline stannates are readily soluble in hot and cold water On continued standing, however, they hydrolyze with the production of insoluble stannic acids.

In its acid form, $Sn(OH)_4$ is stronger than as a base. Collins and Wood[32] found the velocity constant of the reaction

$$K_2Sn(OH)_6 + 2H_2O = H_2Sn(OH)_6 + 2KOH$$

to be $k = 0\ 0188$, and the amount of free alkali present in an 0 128 N solution corresponds with a 13 per cent hydrolysis. With a similar solution of stannic chloride, the hydrolysis was 94 per cent. Frémy[33] found that aqueous solutions of stannates are precipitated by soluble salts α-Stannic acid is precipitated by the addition of acids to the stannates, this reaction even being shown to a limited extent by carbonic acid If carbon dioxide is introduced very slowly in contact with stannate crystals, monohydrated stannic oxide, seemingly amorphous, is formed. Lead and copper precipitate tin from stannate solutions Sodium stannate is used in calico printing under the name of "preparing salts "

At low temperatures, concentrated solutions of sodium stannate free from alkali hydroxides furnish long prismatic crystals of the decahydrate $Na_2SnO_3 \cdot 10H_2O$. These are six-sided tablets belonging to the trigonal system Mixter[34] gives the following thermal values:

$$2Na_2O_2 + Sn = Na_2SnO_3 + Na_2O + 138\ \text{Cal.}$$
$$(Na_2O, Sn, O_2) = 172.6\ \text{Cal.}$$

[32] G E. Collins, and J K Wood, *J Chem Soc* , **121**, 441, 1122 (1922).
[33] Frémy, *Ann. chim. phys* (3), **12**, 484 (1844), (3). **23**, 399 (1847).
[34] Mixter, *Am. J. Sci* (4), **27**, 229 (1909).

and with crystalline stannic oxide

$$(Na_2O, SnO_2) = 35\ 4 \text{ Cal}$$

and with amorphous oxide, 37 1 Cal In many respects the sodium salts are similar to the potassium stannates Zocher[35] prepared lithium stannate, $Li_2SnO_3\ 3H_2O$ or $Li_2Sn(OH)_6$, and the pentahydrate $Li_2Sn(OH)_6 \cdot 2H_2O$. Ammonium β-stannate has not been made, inasmuch as the β-stannic acid is insoluble in ammonia Frémy[36] stated that a number of β-stannates were produced with varying proportions of K_2O and SnO_2 but these have been regarded by van Bemmelen[37] as adsorption products since they have not been obtained in the crystalline state The supposed β-stannate, $K_2O\ 5SnO_2 \cdot 4H_2O$, prepared by the action of potassium hydroxide on a solution of β-stannic acid in potassium hydroxide, appears as a horny, translucent colloid when dried It cannot be crystallized, but is apparently soluble or at least dispersable in water, α-stannates are formed when it is heated with concentrated alkalies It is completely soluble in water after dehydration at 130° Similar sodium β-stannates have been prepared There have been reported in the literature a large number of so-called salts containing alkalies, tin oxides, and water in various proportions The existence of a great number of them is doubtful

It is thought that the opacity produced in glass and enamels by stannic oxide is caused by the formation of compounds of potassium and sodium carbonate and stannic oxide in various proportions Zulkowsky[38] regarded $K_2Sn_2O_5$ as potassium mesodistannate Moberg[39] stated that he had prepared ammonium α-mesodistannate, $(NH_4)_2Sn_2O_5\ nH_2O$, as a viscous mass, by evaporating a saturated solution of stannic hydroxide in aqueous ammonia over sulfuric acid.

Copper stannates are formed when copper salts are treated with stannates They are yellowish-green precipitates which become yellow if kept out of contact with air, or, on exposure to the air, form mixtures of copper hydroxide and stannic acid, or mixtures of copper and tin oxides Moberg prepared green cupric α-stannate, $CuSnO_3 \cdot 3H_2O$ Ditte[40] produced small blue crystals by the addition of a solution of potassium stannate to an ammoniacal solution of a cupric salt until the precipitate failed to redissolve. The product dissolved readily in aqueous ammonia and dark blue crystals were obtained which were sparingly soluble in cold water and formed a

[35] Zocher, *Z Kryst.*, **112**, 1 (1920).

[36] Frémy, *Ann. chim. phys* (3), **12**, 484 (1844), (3), **23**, 399 (1849)

[37] Bemmelen, *Z. anorg Chem.*, **23**, 124 (1900).

[38] Zulkowsky, *Chem Ind*, **22**, 280 (1899), **24**, 422 (1901)

[39] Moberg, "Dissertatio de Stannatibus," Helsingfors, 1838, *Liebig's Ann*, **44**, 261 (1842), *J prakt. Chem* (1), **28**, 231 (1843)

[40] Ditte, *Ann chim phys* (5), **27**, 167 (1882), (6), **30**, 282 (1893), *Compt rend*, **94**, 1114 (1882); **96**, 702 (1883), **104**, 172 (1887)

green solution with acids The material was assumed to be ammonium cupric α-stannate.

It is stated that silver α-stannate, $Ag_2SnO_3 \cdot 2H_2O$, and silver β-stannate, $Ag_2Sn_5O_{11}$, exist The β-stannate, dried at 80° C , has a deep blue-black color. When heated it loses water and detonates The anhydrous material is insoluble in dilute acids, but warm concentrated nitric acid dissolves out the silver, leaving metastannic acid The α-stannate is soluble in dilute nitric acid but insoluble in water When heated it loses water and becomes insoluble in dilute acids

Calcium α-stannate has been formed by fusing molten proportions of calcium and stannic oxides It crystallizes in small transparent crystals as plates and cubes of more or less altered octahedra It is stated that calcium stannates are formed by the addition of calcium salts to solutions of stannates Strontium, barium, and magnesium stannates are made in a similar manner References are found in the literature to the stannates of zinc, mercury, lead, and manganese, as well as the rose-red crystals of cobalt α-stannate, pale green cubic crystals of nickel α-stannate, and salts of the precious metals such as platinum and palladium Many of these are true salts, but others are mixtures of oxides of the metals and tin A number of them are adsorption products of metallic salts by stannic acid or tin oxide, or of colloidal metals adsorbed by metastannic acid or stannic hydroxide The literature is exceedingly contradictory on the metal stannates

Chrome-tin pink is developed when a mixture of stannic oxide and a small proportion of chromic oxide is calcined in the air at high temperatures If some calcium carbonate is present, the color develops at a lower temperature It is probably related to the chrome-alumina crimson of the ruby, in that finely divided chromic oxide is deposited on or adsorbed by the stannic oxide

Tin Hydrides

Tin is chemically related to silicon, titanium, zirconium, germanium, and cerium in accordance with its position in the periodic system Though the metal is not corroded by hydrogen, the latter is soluble in liquid tin According to Iwasé,[41] its solubility is low as compared to that of other metals Small amounts of hydride are formed during hydration (a few thousandths of 1 per cent) The hydride SnH_4 has a melting point of $-150°$ C., and a latent heat of 4.55 Cal The gaseous hydride decomposes spontaneously within a few hours if it is stored in glass vessels at room temperature At temperatures above 145° C , the decomposition is instantaneous. Tin hydride is unstable in the presence of drying agents such as calcium chloride and the oxides of phosphorus Paneth and Rabinowitsch[42] reported that

[41] K. Iwasé, *Science Repts. Tôhoku Imp Univ* , **15**, 531 (1926)

[42] F. Paneth, and E. Rabinowitsch, *Ber* , **57B**, 1877 (1924).

the hydride is not influenced by diluted solutions of alkali hydroxide, sulfuric and nitric acid, as well as most metal salts It is, however, absorbed by solid alkali hydroxide, soda lime, and solutions of silver nitrate and silver sulfate

Halides of Tin and Related Compounds

Aqueous hydrofluoric acid has relatively little action on tin even when warmed, but it readily dissolves stannous oxide to form crystals of stannous fluoride, SnF_2 When exposed to the air, the salt is transformed into stannic oxyfluoride, $SnOF_2$ The tin fluorides are easily soluble in water but hydrolyze readily Hydrogen sulfide precipitates stannous sulfide from a solution of stannous fluoride containing some free acid Frémy[43] claimed that an excess of hydrofluoric acid and stannous oxide react to form hydrofluostannous acid, H_2SnF_4 or $2HF \cdot SnF_2$. Wagner[44] stated that corresponding ammonium and potassium fluostannites are formed

Tin is not readily attacked by fluorine at ordinary temperatures, but at 100° C white stannic fluoride is formed with incandescence. The compound may also be formed by the addition of stannic chloride to anhydrous hydrofluoric acid at low temperatures After removal of the excess hydrogen chloride and stannic chloride, the residue has the composition $SnCl_4 \cdot SnF_4$, which later decomposes with the evolution of stannic chloride. Stannic fluoride sublimes at 750° C The salt is very hygroscopic When its solutions are boiled or allowed to stand, hydrated stannic oxide is deposited, although stannic fluoride is more resistant to hydrolysis than stannic chloride Stannic fluoride reacts with a number of substances and has similar effects on organized vegetable matter as the other tin halides

Complex fluostannates, isomorphous with the fluosilicates, exist as salts of the hypothetical hydrofluostannic acid, H_2SnF_6 These salts, however, may also be considered as double fluorides Ammonium, lithium, sodium, potassium, rubidium and cesium salts are known and have been studied Somewhat less is known of the copper, silver, calcium, strontium, barium, magnesium, zinc, cadmium, manganese, nickel, and lead salts, although the crystallographic data for practically all of these as well as their solubilities have been determined

Analogous to the fluorides, two types of chlorides corresponding with the oxides exist—stannous chloride $SnCl_2$, and stannic chloride $SnCl_4$ Each of these forms hydrates and hydrochlorides

Tin dissolves readily in warm hydrochloric acid to form stannous chloride; if a solution of stannous chloride in dilute hydrochloric acid is evaporated and cooled, crystals of dihydrated stannous chloride, $SnCl_2 \cdot 2H_2O$, are formed This material is the so-called "tin salt" of commerce Stan-

[43] Frémy, *Ann. chim phys* (3), **47**, 37 (1856)
[44] Wagner, *Ber.*, **19**, 896 (1886)

nous oxide is readily soluble in hydrochloric acid to form the chloride The physical properties of the stannous chlorides are given in Table 37.

Engel[45] found that the solubility of stannous chloride in water is increased by a large proportion of hydrochloric acid. The anhydrous salt

TABLE 37 PHYSICAL PROPERTIES OF STANNOUS CHLORIDE

		Authority
Boiling point	603–606° C	
Electrical conductivity:		
Solid chloride, 222° to 244° C.	0 002 to 0 014 mho	Klemm and Biltz (1)
Molten chloride,		
263° C.	0 89 mho.	" " "
302° C.	1 12 "	" " "
314° C.	1.18 "	" " "
353° C	1.42 "	" " "
411° C	1 72 "	" " "
Heat of formation		
Sn, $2HCl_{gas}$	36 4 cal	Thomsen (2)
Sn, Cl_2 (with solid stannous chloride)	80 79 cal	"
Sn, Cl_2, $2H_2O$ at 18° C.	5 72 cal	"
Heat of solution		
$SnCl_2$ $2H_2O$ + Aq	53 7 cal	"
($SnCl_2$, Aq)	350 0 cal.	"
In 1% HCl.	0 9 cal	Biltz and Fischer (3)
Heat of vaporization	46 84 cal.	Regnault (4)
Mol. heat of vaporization at 622 8° C. and 371 4° C	21,100 cal	Maier (5)
Magnetic susceptibility		
Per gram	$-0\ 334 \times 10^{-6}$	
Per mol	$-0\ 055 \times 10^{-6}$	
Mass units at 18° C.	$-0\ 29 \times 10^{-6}$	
Mass units	$-0\ 07 \times 10^{-6}$	Quincke (6)
Melting point	246.8° C	Kendall, Crittenden and Miller (7)
Solubility		
In H_2O at 0° C	83.9 parts in 100 of H_2O	Engel (8)
at 15° C.	269 8 g per 100 g H_2O	
In formic acid (95%) at 19° C	4 1 g per 100 g. acid	Aschan (9)
In acetone, saturated, at 18° C.	1 g per 1 8 g acetone	Naumann (10)
$SnCl_2$ $2H_2O$		
In ethyl acetate		
at −2° C	31 2 g. in 100 parts	von Laszczynsky (11)
22° C.	35.5 g. in 100 parts	" "
82° C	73 4 g. in 100 parts	" "
Specific heat, 20° to 99° C	0 10162	Regnault (4)

[45] Engel, *Ann. chim. phys.* (6), **17**, 338 (1889); *Compt rend.*, **106**, 1398 (1888).

TABLE 37 —*Continued*

Specific gravity at 24° C	. 2 634	F W. Clarke (12)
Thermal expansion coefficient	0 000319	Lorenz and Herz (13)
Vapor density at 619–697° C.	12 96	V. and C. Meyer (14)
Vapor pressure		
at 372.7° C	10 2 mm. Hg	Maier (5)
447 8° C.	56 4 " "	"
499 4° C	116 6 " "	"
536 2° C.	205 3 " "	"
563 1° C.	346 9 " "	"
596 6° C	537 5 " "	"
617 5° C	706 3 " "	"
633 9° C.	882 0 " "	"
641 0° C.	972 4 " "	"

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(1) *Z. anorg Chem*, **152**, 225, 267 (1926)
(2) *J. prakt Chem*, (2), **14**, 429 (1876), (2) **18**, 1 (1878).
(3) *Z anorg Chem*, **129**, 1 (1923)
(4) *Ann. chim. Phys.* (3), **1**, 129 (1841), "Relation des expériences entrepris pour déterminer les principales lois physiques et les données numériques qui entrent dans le calcul des machines à vapeur," Paris, 1847
(5) "Vapor Pressures of the Common Metallic Chlorides," *Bur. Mines Tech Paper*, **360**, p 38 (1925).
(6) *Wied Ann.*, **24**, 347 (1885), **34**, 401 (1888)
(7) *J Am Chem Soc*, **45**, 963 (1923).
(8) *Ann chim phys* (6), **17**, 338 (1889), *Compt rend*, **106**, 1398 (1888)
(9) *Chem Ztg*, **37**, 1117 (1913)
(10) *Ber*, **37**, 3601, 4336, 4609 (1905)
(11) *Ber*, **27**, 2285 (1894).
(12) *Am J Sci* (3), **14**, 281 (1877)
(13) *Z anorg Chem*, **145**, 88 (1925), **147**, 135 (1925)
(14) *Z phys. Chem*, **12**, 1195 (1879)

is readily dissolved by alcohol and to a less extent by ether. It is soluble in pyridine, and to the extent of almost 16 per cent in methyl acetate, and almost twice as much in ethyl acetate, in which the solubility increases rapidly with the increase of temperature

Anhydrous stannous chloride is fairly stable in the air, but it shows appreciable oxidation after continued exposure The salt is converted into oxychlorides by oxygen If aqueous solutions are exposed to the air, both hydrolysis and oxidation occur with the formation of complicated materials consisting of mixtures of oxychlorides and metastannic acid. Scheurer-Kestner[46] showed that oxygen is absorbed by a dilute solution of stannous chloride to form stannic chloride and stannic acid, but that with concentrated solutions, oxygen is not absorbed The oxidation of stannous chlo-

[46] Scheurer-Kestner, *Compt. rend.*, **52**, 531 (1861), *Ann. chim. phys.* (3), **58**, 471 (1860).

ride solutions is promoted by the presence of rubber, sulfur, ferrous and cupric sulfates, but is retarded by manganous salts, some of the alkaloids, and potassium cyanides. The oxidation of stannous chloride simultaneously induces the oxidation of sodium arsenite, formate, and oxalate if these are present in the solution Easily oxidizable substances such as hydroquinone, sugars, glycerol, and a number of organic substances retard the oxidation of stannous salts by air.

Aqueous solutions of stannous chloride are hydrolyzed when heated to 200° C in sealed tubes, with the resulting formation of yellow flocculent oxychloride. A large number of investigators have studied the hydrolysis of stannous chloride A number of compounds containing various proportions of SnO, $SnCl_2$, and H_2O are supposed to exist

Chlorine oxidizes stannous chloride to stannic chloride The reaction, according to Berthelot[47] is

$$SnCl_2 + Cl_2 = SnCl_{4liq} + 48\ 8\ Cal$$

and in aqueous solution,

$$SnCl_{2aq} + Cl_2 = SnCl_{4aq} + 72\text{-}78\ 2\ Cal.$$

Bromine causes the formation of stannic salts in aqueous solution, while the dichlorodibromide is formed with the anhydrous stannous chloride. At ordinary temperatures iodine has little oxidizing power, but when it comes in contact with stannous chloride, the salt gradually becomes pale red If a solution of stannous chloride is saturated with hydrochloric acid at 0° C. and cooled to −40° C , crystals of the addition compound $SnCl_2$ HCl are formed. The salt melts at −27° C. Young,[48] from his studies of the electrical conductivity of a solution of stannous chloride in hydrochloric acid, believed that the compound $SnCl_2 \cdot 2HCl$ was also formed Stannous chloride reduces hypochlorous acid and potassium chloride, the latter being catalyzed by vanadic oxide. It also reduces antimony pentachloride

Hydrogen sulfide precipitates stannous sulfide from solutions of stannous salts. Hering[49] found that stannous chloride is oxidized by sulfur dioxide according to the following equation:

$$6SnCl_2 + 2SO_2 + 8HCl = 5SnCl_4 + SnS_2 + 4H_2O$$

This agrees with the work of Fink and Mantell on the oxidation of stannous oxide by sulfur dioxide, discussed elsewhere The compounds resulting from the action of sulfur dioxide and stannous chloride depend upon the proportions of the components entering into the reaction Fedoroff[50]

[47] Berthelot, *Ann chim phys* (5), **15**, 200 (1878), "Thermochimie," Vol. **2**, p 154, Paris, 1897

[48] S. W Young, *J Am. Chem. Soc.*, **23**, 21, 450 (1901)

[49] Hering, *Liebig's Ann.*, **29**, 90 (1839).

[50] Fedoroff, *Z. Chem* (2), **5**, 15 (1869).

showed that the sulfides of arsenic, copper, antimony, bismuth, and platinum are formed when their salts are treated with a hydrochloric acid solution of stannous chloride and sulfur dioxide, while all the tin remains in solution as stannic chloride The action of concentrated sulfuric acid on a cold solution of stannous chloride produces only a little hydrochloric acid, but gives rise to stannic sulfate, stannic chloride, sulfur dioxide, hydrogen sulfide, and a little free sulfur, as a result of the marked reducing action of stannous chloride Ordinarily stannous salts are stronger reducing agents than sulfur dioxide

Ammonia and alkalies precipitate the hydroxides when caused to react with stannous chloride When treated with liquid ammonia, stannous chloride forms a yellow compound of low solubility. Persoz[51] found that warm stannous chloride absorbs gaseous ammonia to form the compound $SnCl_2NH_3$ A number of supposed compounds of stannous salts and hydrazine are said to exist. Stannous chloride reduces nitric acid to form stannic chloride, stannic acid, and the oxides of nitrogen The reaction is accelerated by the presence of vanadic oxide The reduction reactions vary widely according to the concentration of the nitric acid employed. Stannous chloride can be used as a reducing agent for the conversion of colloidal metallic oxides, such as those of antimony and arsenic, as well as for the reduction of bismuth nitrate to the black lower oxides or to the metal It also has marked reducing action on many organic compounds, such as the conversion of the nitro compounds to the amides

Tin is precipitated from stannous salts by the more electropositive metals, such as magnesium, zinc, cadmium, and aluminum Pleischel[52] found that lead precipitates tin quantitatively from stannous solutions, while Reinsch[53] noted that copper precipitates tin as a grayish black powder from solutions strongly acid with hydrochloric acid

In the presence of tartaric acid, solutions of stannous salts do not yield precipitates when treated with hydroxides A number of oxidizing agents, such as the nitrates and chlorates, convert stannous salts to stannic compounds and oxides Chromic acid is reduced to a chromic salt, while tungstic and molybdic acids form the lower blue oxides when treated with stannous salts The analytical reaction of the reduction of mercuric chloride to white calomel is well known With silver salts, metallic silver is precipitated, and in the case of gold salts, the colloidal metallic gold known as "purple of Cassius" is formed

A large number of complex double chlorides are formed by the interaction of stannous chloride and salts of other metals These compounds, as well as their best known properties, are given in the table of salts

[51] Persoz, *Ann chim phys* (2), **44**, 315 (1830)
[52] Pleischel, *Sitzb Akad. Wien*, **43**, 555 (1861)
[53] Reinsch, *J. prakt. Chem.* (1), **24**, 248 (1841).

Stannic chloride is often stated to be the discovery of Libavius in 1605, when he obtained the material by distillation of a mixture of tin or tin amalgam and mercuric chloride The fuming liquid was named *spiritus fumans Libavii*. The material is made commercially by the direct action of chlorine on tin. The reaction is highly exothermic and is discussed in some detail in the section of this book dealing with the detinning of tin-plate scrap.

TABLE 38. PHYSICAL PROPERTIES OF STANNIC CHLORIDE

		Authority
Boiling point at 760 mm	114° C.	Kendall, Crittenden and Miller (1)
Critical density	0 732–0 743	S Young (2)
Critical pressure	28,080 mm.	" "
Critical temperature	318 7° C.	" "
Critical volume	1 347	" "
Cubical expansion coefficient, 0° to 100° C.	0 00129977	Pierre (3)
Dielectric constant at 22° C	3 2	Schlundt (4)
	2 0	Mathews (5)
Ebullioscopic constant	0 515 to 0 65	de Kolossowsky (6)
Electric conductivity	nil	Coldridge (7)
Freezing point	-33° C.	
Heat of formation		
Sn, $2Cl_2$	127.25 cal.	Thomsen (8)
$SnCl_{2aq}$ Cl_2	76 03 cal.	"
Heat of fusion at melting point	8 42 cal per g.	Latimer (9)
Heat of solution in H_2O	29.92 cal.	Thomsen (8)
Heat of vaporization	32 6 cal.	Hammick (10)
Total from 0° C to temp of vaporization	46 838 cal per kg.	Regnault (11)
Internal pressure of liquid	1184 atm	Schuster (12)
Magnetic susceptibility	-0.18×10^{-6} mass units	Quincke (13)
Specific gravity		
0° C (H_2O at 4° C. = 1 00)	2 2788	
Aqueous solution at 15° C		
10% $SnCl_4$	1 082	Gerlach (14)
20% "	1.174	"
30% "	1.279	"
40% "	1 404	"
50% "	1.556	"
60% "	1.743	"
70% "	1.943	"
100% "	2.234	"
Specific heat		
Vapor, for equal weights	0 0939	Regnault (11)
Vapor, for equal volumes	0.8416	"
Liquid 14° to 98° C.	0.1476	"
Aq solution 10° to 15° C.	0.1402	"
Specific volume	131.07	Thorpe (15)

TABLE 38 —*Continued*

Vapor pressure (p) at ° C.		
−10	2 78 mm Hg.	S Young (2)
0	5 53 " "	" "
10	10 33 " "	" "
20	18 58 " "	" "
40	50 82 " "	" "
60	122 2 " "	" "
80	256 7 " "	" "
100	496 0 " "	" "
120	895 4 " "	" "
130	$p \times 10^{-3}$ = 1 171	" "
200	" = 5 145	" "
250	" = 11 514	" "
310	" = 25 079	" "
319 35	" = 28 079	" "

References to Table 38

(1) *J Am Chem Soc*, **45**, 963 (1923)
(2) *J Chem Soc*, **59**, 911 (1891), "Fractional Distillation," p 12, London, Macmillan, 1903, *Proc Dublin Sci Soc* (2), **12**, 428 (1910), *Phil Mag* (5), **34**, 505 (1902)
(3) *Ann chim phys* (3), **19**, 193 (1847); (3), **20**, 1 (1847)
(4) *J. Phys Chem*, **5**, 503 (1901)
(5) *J Phys. Chem*, **9**, 641 (1905)
(6) *J chim phys*, **23**, 353 (1926)
(7) *Phil Mag* (5), **29**, 383 (1890)
(8) "Thermochemische Untersuchungen," Vol **3**, p 327, Leipzig, 1883.
(9) *J Am Chem Soc* **44**, 90 (1922)
(10) *Phil Mag* (6), **44**, 590 (1922)
(11) "Relations des expériences entrepris, pour déterminer les principales lois et les données numériques qui entrent dans le calcul des machines à vapeur," p 203, Paris, 1862, *Mem Acad*, **21**, 1 (1847), *Ann chim phys*, (3), **9**, 322 (1843)
(12) *Z Elektrochem*, **32**, 191 (1926)
(13) *Wied Ann.*, **24**, 347 (1885), **34**, 401 (1888)
(14) *Dingler's J*, **178**, 49 (1865)
(15) *Proc. Roy. Soc. (London)*, **24**, 283 (1876), *J Chem. Soc.*, **37**, 331 (1880).

The commercial operation takes place at low temperatures. The reaction is catalyzed by sulfides and sulfur compounds A large number of methods, mostly of the laboratory type, are given in the extensive literature on the subject of stannic chloride.

Stannic chloride forms hydrates with varying quantities of water, depending upon the amount of water with which it is allowed to come in contact. The phase-rule diagram of the stannic chloride-water system has often been studied, but as a result of the formation of oxy salts there is still considerable disagreement in reference to the system. Difficulty is found in the commercial preparation of solutions of stannic chloride. Dilution can be done only under carefully controlled conditions. The physical properties of stannic chloride are given in Table 38.

The vapor pressure of stannic chloride is quite appreciable at low temperatures. When exposed to the air, the material fumes markedly It has been employed in times of war for the formation of smoke screens to cover military tactics It has been superseded for this use by compounds of silicon, titanium, and phosphorus It finds extensive application in the textile industries, particularly in silk weighting

Stannic chloride forms a number of addition compounds analogous to the complex stannous chlorides Upon hydrolysis, a large number of complicated compounds are formed These have been widely studied, but the results are confusing and show little concordance At low temperatures, stannic chloride absorbs large quantities of chlorine, with considerable increase in volume and lowering of the freezing point The freezing point

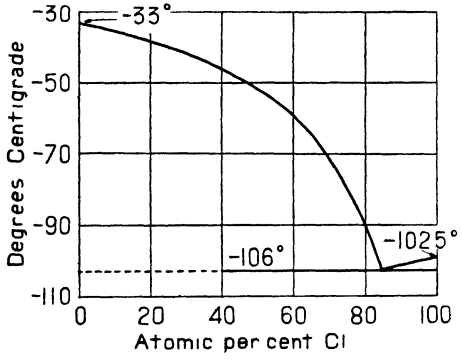

FIGURE 134.
Freezing-point curve of mixtures of chlorine and stannic chloride.

curve of mixtures of chlorine and stannic chloride is shown in Figure 134 There is no evidence of the existence of complex salts Hydrogen sulfide precipitates stannic sulfides from stannic salts only with difficulty after long periods of treatment Stannic chloride forms compounds with materials such as sulfur monochloride, S_2Cl_2 These fume more strongly in air than does stannic chloride In a current of hydrochloric acid, the compound sublimes with very little decomposition at 30° C It dissolves in water without the separation of sulfur to form stannic chloride, hydrochloric and sulfuric acids Rose[54] pointed out that stannic chloride absorbs appreciable amounts of sulfur trioxide without giving off sulfur dioxide. Weber[55] claimed that he formed stannic selenoxychloride, $SnCl_4 \cdot 2SeOCl_2$ Sulfuric acid has practically no effect on stannic chloride Davy[56] found that stannic chloride absorbs dry ammonia at ordinary temperatures, with the development of heat, forming a white solid. When sublimed, the material corresponds to the formula $SnCl_4\ 2NH_3$ On ex-

[54] Rose, *Pogg Ann*, **16**, 339 (1829), **24**, 339 (1832), **42**, 517 (1837), **44**, 320 (1838)
[55] Weber, *Sitzb Akad Berlin*, 154 (1865)
[56] Davy, *Phil Trans*, **102**, 169 (1812)

posure to the air, it gives off white pungent fumes It dissolves completely in water

Nitric acid attacks stannic chloride with the formation of chlorine, nitrogen oxides, and stannic acid A number of compounds are supposed to be formed by the interaction of stannic chloride and the oxides of nitrogen, but many of these are unconfirmed Stannic chloride absorbs phosphine, according to Rose,[57] to form a fuming hygroscopic solid of the formula $3SnCl_4$ $2PH_3$ The material decomposes in carbon dioxide at 100° C Stannic chloride mixes with phosphorus trichloride without chemical combination, but forms an addition compound with phosphorus pentachloride Phosphorus pentachloride reacts with tin to form stannic chloride The reactions of the phosphorus and the stannic compounds have been studied by Casselmann [58]

Stannic chloride reacts with alcohol and organic compounds of the same nature to form the corresponding chlorides and stannous oxychloride In general, it is an oxidizing agent toward organic materials, and a number of complex salts are known Stannic chloride is reduced by potassium metal in toluene solution It reacts with mercury to oxidize the mercury, and is itself reduced to stannous chloride It forms a large number of complex salts with the metal chlorides Biron[59] prepared the addition compounds of stannic chloride with the chlorides of calcium, strontium, beryllium, magnesium, manganese, iron, nickel, cobalt, and zinc, but not of barium, cadmium, silver, copper, lead, and thallium The presence of the chlorides of those elements which form addition compounds retards the speed of hydrolysis of stannic chloride No one metal salt is more effective than the others

The pink salt used by the calico printer is a double chloride of tin in the stannic form and ammonia, having the formula $SnCl_4$ $2NH_4Cl$ The salt crystallizes in octahedra of the cubical system.

Stannous bromide has been prepared by heating tin in an atmosphere of hydrogen bromide. An oily liquid condenses close to the hot zone Upon cooling, it freezes to a gray mass Stannous bromide forms a pale yellow crystalline material consisting of hexagonal columns belonging to the rhombic system The material is oxidized by the same reagents as affect stannous chloride. Its analytical reactions are quite analogous to those of the chlorides. It hydrolyzes readily and forms addition compounds with ammonia and the bromides of other metals

Tin burns in an atmosphere of bromine to form stannic bromide The material is a white crystalline substance which may be sublimed without decomposition. The crystals are rhombic pyramids with a melting point

[57] Rose, *Pogg Ann*, **24**, 159 (1832)

[58] Casselmann, *Liebig's Ann*, **83**, 257 (1852), **91**, 242 (1854), **98**, 213 (1856)

[59] Biron, *J Russ. Phys Chem Soc*, **36**, 489 (1904); **37**, 994, 1036 (1905).

of 31° C. The salt is fairly stable when heated. Its reactions are quite analogous to those of stannic chloride With water it forms hydrates and hydrolyzes fairly readily to form hydroxy compounds of the same nature as those formed by stannic chloride It does not react with liquid hydrogen sulfide at −78 5° C , nor does it form compounds with sulfur dioxide below the melting point of sulfur dioxide, −72° C In the system $SnBr_4 \cdot SO_2$, the critical solution temperature is 48 6° C. and there is a eutectic at 16.3° C. on the stannic bromide side of the percentage solubility in sulfur dioxide curve. Molten stannic bromide dissolves iodine readily as well as sulfur. When dissolved in liquid sulfur dioxide, it is not a good electrical conductor. Balard[60] stated that stannic bromide dissolves readily in sulfuric acid without perceptible decomposition, to form an oily liquid Analogous to stannic chloride, the bromide absorbs ammonia to form an addition compound, $SnBr_4\ 2NH_3$ With nitric acid the vapor of bromine is given off vigorously. Walden[61] found that stannic bromide is soluble in arsenic tribromide

Fine colorless prisms of needle-like crystals are obtained when very concentrated solutions of stannic bromide are saturated with hydrobromic acid. The material is regarded as the addition compound $SnBr_4\ 2HBr \cdot 8H_2O$. The salt is very deliquescent and readily gives off hydrogen bromide. The crystals fume in air

A series of addition compounds with the bromides of other metals is known. Those which have been studied include the ammonium, cesium, rubidium, potassium, sodium, lithium, calcium, strontium, magnesium, manganese, iron, cobalt, and nickel double bromides

A number of stannic bromochlorides, or mixed salts containing both chlorine and bromine, have been reported They are made ordinarily by the addition of bromine to stannous or stannic chlorides, or by the addition of chlorine to stannous or stannic bromides

Analogous to the other halides, tin forms stannous and stannic iodides Mixtures of the two are obtained when tin filings are heated with iodine They can be separated by sublimation, inasmuch as stannic iodide volatilizes at 180° C and stannous iodide remains fixed at red heat Stannous iodide can be prepared by the reducing action of tin on stannic iodide in a sealed tube under prolonged heating at 360° C. Stannous iodide is precipitated by treatment of stannous chloride with iodine, a mixture of stannous iodide and chloride as well as stannic chloride remaining in solution Metallic iodides, when added to solutions of stannous chloride, precipitate yellow reddish crystalline tufts of stannous iodide, if the mixture is warmed, the crystals are yellow-red needles. When crystallized from its aqueous solution, the iodide contains two molecules of water When dried over

[60] Balard, *Ann chim. phys.* (2), **32**, 337 (1826).

[61] Walden, *Z. phys. Chem.*, **43**, 385 (1903); *Z. anorg. Chem.*, **29**, 377 (1902).

sulfuric acid, the monohydrate is formed. Exposure to sunlight changes the yellow iodide to the red form, the reverse change taking place in the darkness The yellow form is considered the stable modification at 100° C

Adsorption compounds with ammonia are formed by the iodides in a manner analogous to those formed by the other halides Similar oxy salts result from hydrolysis Stannous iodide is soluble in a solution of stannous chloride Complex addition compounds are formed with hydrobromic acid and the metallic iodides, as well as complex chloroiodides and bromoiodides, analogous to the complex compounds formed by the other halides Complex double iodides with ammonium, sodium, potassium, rubidium, cesium, barium, and strontium have been studied. Young[62] prepared yellow-red prisms of the addition compound, $SnCl_4 \cdot SnI_2$, by the action of iodine chloride on stannous chloride. A number of replacement compounds, in which chlorine or bromine replaces part of the iodine in the stannous and stannic iodides, are known.

When a warm solution of iodine in carbon bisulfide is allowed to act on tin metal, red, singly refracting crystals are obtained which belong to the rhombic system According to Henry[63] the salt sublimes at 180° C , forming reddish yellow needles The stannic iodides are hydrolyzed in aqueous solution The salt is soluble to the extent of 140 parts per 100 in carbon bisulfide, and readily dissolves in chloroform, alcohol, ether, and benzene, forming compounds with all of these except chloroform. Biltz and Kuenecke[64] observed no reaction with liquid hydrogen sulfide at −78 5° C A number of complex addition compounds are formed Those of importance are given in the table of solubilities of tin compounds on page 440. Analogous to the other halides, the stannic iodides react with ammonia to form addition compounds whose formulas vary with the concentration of the ammonia employed and the quantity used in the reaction. Stannic iodide dissolves in stannic chloride and antimony chloride. Chloro- and bromoiodides, obtained by the reaction of chlorine and bromine on stannous iodide, are formed.

Sulfides of Tin

Tin forms two well-established sulfides, the stannous form, SnS, and the stannic compound, SnS_2. Many statements as to the formation of hydrated forms of these sulfides are found in the literature, but few of them have been confirmed Stannous sulfide is formed when a mixture of sulfur and tin is heated above the melting point of the metal, or when a stannous salt is caused to react with hydrogen sulfide in aqueous solution. At red heat, stannic sulfide decomposes into stannous sulfide and sulfur. Stan-

[62] Young, *J. Am. Chem. Soc* , **19**, 845, 851 (1897).
[63] Henry, *Phil. Mag* (3), **5**, 354 (1845), *Phil. Trans.*, **135**, 363 (1845)
[64] Biltz, and Kuenecke, *Z. anorg. Chem* , **147**, 171 (1925).

nous sulfide melts at 880° C , passes into a viscous liquid at 950° C., and becomes limpid again at nearly 1100° C.

Reinsch[65] found that if a solution of 1 part of stannous chloride in 100 parts of water and 15 parts of hydrochloric acid be treated with hydrogen sulfide, all the tin is precipitated at once, but if 25 parts of acid be used, precipitation occurs only after a considerable time interval, and if 40 parts of acid be used, no tin sulfide is precipitated until the solution is diluted with water The physical properties of stannous sulfide are given in Table 39.

When roasted in air or oxygen, stannous sulfide is converted into stannic oxide Colloidal solutions of stannous sulfide are oxidized in sunlight and air with the formation of colloidal sulfur Stannous sulfide is very sparingly soluble in water to the extent of 0 14 x 10^{-6} gram molecular weight per liter of water at 18° C Steam oxidizes the sulfide to hydrogen sulfide and stannic oxide The material is oxidized by hydrogen peroxide in

TABLE 39 PHYSICAL PROPERTIES OF STANNOUS SULFIDE

		Authority
Boiling point	1230° C	International Critical Tables, Vol 1
Melting point	880° C	Pelabon (1)
Specific gravity	5 080	International Critical Tables, Vol 1

(1) *Compt rend* , **142**, 1147 (1906), *Ann chim. phys* (8), **17**, 526 (1909)

alkaline solution with the formation of a sulfostannate At low temperatures, chlorine reacts on the compound to form stannic chloride and sulfur tetrachloride Hydrochloric acid gas at ordinary temperatures converts the sulfide into the chloride, with the formation of hydrogen sulfide. Stannous sulfide is not affected by sulfurous acid. It is not ordinarily dissolved by metallic sulfides when solutions of these are less than 20 per cent, but more concentrated solutions gradually form metallic tin and sulfostannates Stannous sulfide is readily soluble in solutions of alkali metal or ammonium polysulfide Nitric acid readily oxidizes the amorphous sulfide to stannic oxide, but the crystalline form is but slowly attacked. Phosphine is reduced by warm stannous sulfide, with the formation of hydrogen sulfide and phosphorus. Perkin[66] found that some preparations of precipitated stannous sulfide readily dissolve in alkalies. With concentrated caustic solutions, tin and alkali stannates and sulfostannates are formed. Fusion of stannous sulfides with sulfur, carbon, and sodium carbonate con-

[65] Reinsch, *J prakt Chem.* (1), **13**, 132 (1838).

[66] Perkin, *J. Soc Chem. Ind.*, **20**, 425 (1901)

verts the salt into a soluble alkali sulfostannate Potassium cyanide, especially when fused and in the liquid form, reduces stannous sulfide to tin Schurmann[67] showed that stannous sulfide is completely converted into the sulfate when heated with a solution of either copper or cadmium sulfate, but not by solutions of zinc sulfate Raschig[68] found that a solution of cuprous chloride dissolved in sodium chloride reacts with stannous sulfide to form cuprous sulfide and stannous chloride, and a boiling dilute solution of cupric chloride causes the formation of cuprous sulfide and stannic chloride Mourlot[69] stated that stannous chloride is volatilized as the result of the heating of magnesium chloride and stannous sulfide in an electric furnace Stannous sulfide dissolves in molten glass with scarcely any color effect

Stannic sulfide in the form of mosaic gold was largely used in the eighteenth century as a paint pigment. It was prepared by heating a mixture of tin, sulfur, ammonium chloride, and mercury At the present day, its

TABLE 40 PHYSICAL PROPERTIES OF STANNIC SULFIDE

		Authority
Specific gravity	4 5	International Critical Tables
Specific heat (12° to 95° C)	0 11932	Regnault (1)

(1) *Ann chim phys* (3), **1**, 129 (1841)

application as a bronzing powder for wood, metals, and wallpaper is decreasing, inasmuch as it is being displaced by cheaper "bronze powders" made of metal Stannic sulfide can be made by the fusion of stannous salts with excess sulfur The color of the final product varies considerably as a result of different proportions Amorphous or colloidal stannic sulfide is produced when hydrogen sulfide is passed into an acidic solution of stannic chloride, or into water in which freshly precipitated stannic hydroxide is suspended It is also produced when a strong mineral acid is allowed to act on an aqueous solution of a sulfostannate Schmidt[70] stated that the egg-yellow precipitate obtained by the action of hydrogen sulfide on stannic chloride solutions contains SnS_2 when moist, but that it decomposes during drying, giving off hydrogen sulfide, and becomes dark brown Jorgensen[71] found that the precipitate produced by the action of hydrogen sulfide on a solution of metastannic acid in hydrochloric acid has a sulfur

[67] Schurmann, *Liebig's Ann* , **249**, 341 (1888)
[68] Raschig, *Ber* , **17**, 697 (1884), *Liebig's Ann* , **228**, 19 (1885)
[69] Mourlot, *Compt rend* , **124**, 768 (1897), *Ann chim phys.* (7), **17**, 537 (1899)
[70] Schmidt, *Ber.*, **27**, 2739 (1894), *Kolloid-Z* , **1**, 131 (1907)
[71] Jörgensen, *Z anorg. Chem* , **28**, 140 (1901)

content which varies with the concentration of the acid and the salt, the time, and the temperature of action A large number of workers, notably Weiser[72] and his associates, have studied the colloidal stannic sulfides The physical properties of stannic sulfide are given in Table 40 In its crystalline form, the material consists of golden yellow plates which are soft and feel like graphite. The salt reacts with a number of compounds in manners analogous to the stannous sulfide reactions Chlorine converts it at ordinary temperatures to a brown liquid which solidifies to yellow crystals of $SnCl_4 \cdot 2SCl_4$. It reacts at red heat with phosphorus pentachloride, producing stannic chloride and sulfophosphide and phosphorus sulfide and sulfochloride Sulfuryl chloride converts stannic sulfide into stannic chloride and sulfur Aqueous alkalies dissolve the sulfide with the formation of stannates and sulfostannates Solutions of alkali sulfides, ammonium sulfides and polysulfides dissolve stannic sulfide, forming sulfostannates A number of sulfochlorides are formed by the action of chlorine on stannic sulfide. Analogous sulfohalides are formed by the action of iodine and bromine on the tin sulfides Stannic sulfoiodide is soluble in carbon bisulfide and chloroform Alcohol separates out the sulfur, and the tin and iodine dissolve as stannic iodide

Stannic sulfide unites with the more basic sulfides of the other elements to form a series of sulfostannates or thiostannates These are regarded as the salts of sulfometastannic acid, H_2SnS_3, or of sulforthostannic acid, H_2SnS_4, in which sulfur has replaced the oxygen of the stannic acids By themselves the acids are not known, being definitely hypothetical and existing only in stable form as their salts When mineral acids are caused to act on the thiostannates, tin sulfide is produced but not the thiostannic acids The analytical separation of tin from copper, mercury, and cadmium depends upon the formation of the sulfostannates as a result of the solution of the tin sulfides in alkali polysulfides The sulfostannates may also be considered addition compounds of the sulfides. Many of them are stable only in solution Although a large number have been described in the literature, only a few have been confirmed

The complex mineral sulfides are described elsewhere in this volume under Tin Ores A number of the sulfostannates are given in the table of tin-salt solubilities on page 441.

Other Simple Tin Salts

Tin forms stannous and stannic sulfate as the result of the action of sulfuric acid on tin metal and tin salts Freshly precipitated stannous hydroxide dissolves readily in dilute sulfuric acid, but the action of sulfuric acid on tin is slow. In this connection the preparation of refining solutions for

[72] H B Weiser, "The Colloidal Salts," New York, McGraw-Hill Book Co , Inc , 1928.

tin metallurgy is of interest, as discussed elsewhere The tin sulfates, unless they be kept in contact with metallic tin in solution, show definite tendencies toward hydrolysis, although they are among the most stable of the tin salts A number of oxy salts are known, with widely varying composition Double sulfates, analogous to the alums, have been studied, the best known being those formed with sodium and potassium sulfates

Stannic sulfate may be formed by the solution of stannic hydroxide in dilute sulfuric acid, or by the action of oxidizing agents on stannous salts It forms oxy salts analogous to those of stannous sulfate, and a number of addition compounds (similar to the alums), of which potassium, rubidium, sodium, silver, calcium, strontium, barium, and lead compounds are best known Many double sulfates are formed with the rare metals.

Tin carbonates are mentioned often in the literature, but they are not believed to exist If they do exist, they are exceedingly unstable, breaking down into the corresponding oxides An analogous situation exists in respect to the nitrates, which are not known in their pure forms but only as oxidized compounds which are generally tin oxides with adsorbed nitric acid Berzelius[73] stated that stannic hydroxide dissolves copiously in nitric acid with a complete neutralization of the acid to form a solution which, if concentrated, deposits silky needles of stannic nitrate At 50° C it deposits almost all of its tin content as stannic oxide in the hydrated form This precipitate is soluble in ammonium nitrate. When tin acts on metallic nitrates such as copper, the metal rapidly becomes colored with a mixture of precipitated copper and a basic salt When this salt is dried, it burns and at the same time gives off sparks When it is suddenly heated or struck, it explodes The salt is assumed to be a basic nitrate.

Tin phosphates are produced by the addition of soluble phosphates to soluble tin salts The properties of a number of these are given in the table of solubilities Stannous hydrophosphate, the diphosphate, the meta- and the pyrophosphate are all known, as well as analogous stannic salts

Addition compounds between the tin phosphates and alkaline earth phosphates may be formed by fusion of these materials. They are exceedingly complicated compounds and can be resolved upon analysis into phase rule systems of the oxides

Table 41 gives the properties of the simple tin salts

Complex Tin Salts

Many complex tin salts found in the literature have not been thoroughly investigated, therefore comparatively little is known concerning them For completeness, some of the formulae given by investigators are listed below They include addition compounds, compounds forming as a result of the binary system of metals, and various complex salts.

[73] Berzelius, *Schweigger's J* , **6**, 284 (1812), *Ann. chim. phys.* (2), **5**, 141 (1817)

TABLE 41 PHYSICAL PROPERTIES OF TIN SALTS

	COMPOUNDS	M W	SP G	M P (°C)	B P (°C)	SOLUBILITY—(g PER 100 cc)			CRYSTAL FORM AND COLOR
						Cold Water	Hot Water	Other Solvents	
1	$SnBr_2$	278 5	5 12$^{17°}$	215 5	617	Sol	Sol – decomp	—	Yellow, rhombic
2	$SnCl_2$	189 6	2 63$^{24°}$	246 8	603	83 9$^{0°}$	269 8$^{15°}$	Sol alkalies, tartaric acid, acetic acid, ether and pyridene	—
3	$SnCl_2$ $2H_2O$	225 7	2 71$^{15°}$	37 7	Decomp	118 7$^{0°}$	∞	Same as $SnCl_2$	Colorless, monoclinic
4	$SnCl_2$ $2NH_4Cl$ $2H_2O$	314 6	2 10$^{3\ 9°}$	—	—	27 5$^{1\ 6°}$	—	—	Colorless, rhombic
5	$SnCl_2$ SnO $4H_2O$	396 4	—	—	—	Sl sol	Decomp	Sol in dil min acids	Colorless crystals
6	$SnCl_2$ KCl H_2O	282 2	—	—	—	23 2$^{3\ 2°}$	Sol	Sol in chloride sols	White
7	$SnCl_2$ $2KCl$ $2H_2O$	374 8	2 51	—	—	26 7$^{35°}$	—	Sol in chloride sols	White, rhombic
8	SnF_2	156 7	—	—	—	V sol	V sol	KOH, fluorides	Prisms
9	SnI_2	372 5	5 29	320 0	720 0	0 98$^{20°}$	4 03$^{100°}$	Sol dil HCl, KOH	—
10	SnO	134 7	6 9$^{0°}$	Decomp	Decomp	Insol	Insol	Sol min acids, org acids	Black, regular
11	$Sn(OH)_2$	152 7	—	—	—	0 00018	Decomp	Sol dil acids, alkalies	Yellowish white amorphous
12	SnP	149 7	6 56	Decomp	Decomp	Insol	Insol	Sol HCl, insol HNO_3	—
13	$Sn_3(PO_4)_2$	546 2	3 82$^{17°}$	Stable	—	Insol	Insol	Sol dil min acids, and alk	White, amorphous
14	$SnHPO_4$	214 7	3 48$^{15°}$	Stable	—	Insol	—	Sol dil min acids	Colorless, tabular
15	$Sn(H_2PO_4)_2$	312 8	3 17$^{22°}$	Decomp	Decomp	—	Hydro-lyzes	—	White, rhombic
16	$Sn_2P_2O_7$	411 5	4 00$^{16°}$	Stable	—	Insol	Insol	Sol in conc min acids	Amorphous, white
17	$Sn(PO_3)_2$	276 8	3 38$^{22°}$	Hydroscopic		Insol	—	Sol diff conc min acids	Glassy, amorphous

18	SnS	150 8	5 08$^{15°}$	880	1230	0 000002	Insol	Sol conc HCl, $(NH_4)_2S_x$	Brown or gray needles
19	$SnSO_4$	214 8	—	SO_2, 360°	—	18 9$^{20°}$	18 2$^{100°}$	H_2SO_4	Acicular, colorless
20	SnSe	197 9	6 18°	86	—	Insol	Insol	—	Steel gray prisms
21	$Sn_2Fe(CN)_6$	449 3	—	—	—	Insol	Insol	Sol hot conc HCl	White
22	$Sn_2[Fe(CN)_6]_2$	779 9	—	—	—	Insol	Insol	Sol HCl	White
23	SnC_2O_4	206 7	3 56$^{18°}$	—	—	Sl sol	—	Sol oxalates	White
24	$SnBr_4$	438 4	3 35$^{36°}$	31	206 7	Sol	Decomp	—	Colorless, rhombic
25	$SnCl_4$	260 5	2 28	−33	114 0	V sol	Decomp	Alcohol, org liquids	Liquid, white
26	$SnCl_4$ $2NH_4Cl$	367 5	2 39	—	—	33 3$^{15°}$	Sol	—	Octahedra
27	SnF_4	194 7	4 78	Sublimes	—	V sol	Decomp	—	White
28	SnI_4	628 4	4 70	143 5	340 0	V sol	Decomp	—	Orange-red octahedra
29	SnO_2	150 7	6 90	1132	—	Insol	Insol	—	Amorphous
30	SnO_2, natural	150 7	6 85	—	—	Insol	Insol	—	Tetragonal or rhombic
31	K_2SnO_3 $3H_2O$	298 9	3 20	—	—	110 5$^{10°}$	Sol	—	Rhombic prisms
32	$Sn_2P_2O_9$ $10H_2O$	623 6	3 98	—	—	Insol	Insol	Insol HNO_3	White
33	Na_2SnO_3 $3H_2O$	266 7	—	—	—	61 3$^{20°}$	Sol	—	Rhombic
34	SnS_2	182 9	4 50	Decomp	—	0 00002	Insol	Sol conc HCl, alk sulfides	Yellow hexagonal
35	$Sn(SO_4)_2$ $2H_2O$	346 7	—	—	—	V sol	V sol	Sol dil H_2SO_4, HCl	Rhombic leaflets
36	$SnSe_2$	277 1	4 85	—	—	Insol	Insol	Insol dil acids, sol alkalies	Gray
37	SnTe	246 2	6 48	780	Decomp	Insol	Insol	—	Gray crystals
38	$Sn(C_2H_3O_2)_2$	236 7	—	182	Decomp	Sol	Sol	Sol acids	Rhombic(?)
39	H_2SnO_3	168 7	—	Decomp	Decomp	S sol	S sol	Sol dil acids, alkalies	Amorphous
40	$H_{10}Sn_5O_{15}$ (meta)	843 6	—	Decomp	Decomp	Insol	Insol	Insol acids, sol NaOH, KOH	Amorphous, glass-like

Bromostannites or double bromides are formed by the union of stannous bromides and the bromides of other metals They crystallize out of solutions containing both these salts A number of double bromides found in the literature, with the formulae given to them by the workers who studied them, are as follows:

$SnBr_2$ $2AlBr_3$	melting point 205° C
$SnBr_2$ $AlBr_3$	melting point 183° C
$SnBr_2$ $2NH_4Br$ H_2O	colorless needle-like crystals
$SnBr_2$ $4NH_4Br$ H_2O	crystals
$SnBr_2$ $2NH_4Cl$ H_2O	prismatic crystals, rhombic system
$SnBr_2$ $2KBr$ H_2O	rhombic bipyramids
Sn_3OBr_6 $12H_2O$	colorless prismatic crystals

Various chlorides react with stannous chloride or with tin filings (as in the case of $SnCl_2$ NH_4Cl H_2O) to form chlorostannites A number of such compounds, other than those represented below, are supposed to exist, although little definite information is found in the literature Below are given a number which are known

$SnCl_2$ $AlCl_3$	melting point 158 5° C
$SnCl_2$ $2AlCl_3$	melting point 209 3° C
$SnCl_2$ NH_4Cl H_2O	needle-like crystals, 57 374 grams soluble in 100 cc water between 16° and 81° C
$SnCl_2$ $BaCl_2$ $4H_2O$	prismatic crystals
$SnCl_2$ HCl	melting point −27° C , crystals
$(N_2H_5)SnCl_3$	melting point 105° C , crystals, soluble in water, slightly soluble in alcohol
$SnCl_2$ SnO $6H_2O$	insoluble in hot or cold water, soluble in dilute acids and alkalies
$SnCl_2$ $SrCl_2$ $4H_2O$	needle-like crystals
$SnCl_2 \cdot TlCl$	melting point 244° C
$SnCl_2$ $3TlCl$	melting point 310° C.

Analogous to the bromides, the stannous iodide compounds appear in crystalline forms, most of them easily decomposed by water

NH_4SnI	greenish yellow needles, decomposed by water
$SnIBr$	pale yellow needles
$SnICl$	white needles
$SnClI$	yellow crystals, decomposed by water
SnI_2 $SnCl_4$	yellowish red prisms
$2SnI_2$ $2KI$ $9H_2O$	yellow silky needles, decomposed by water; soluble in hot alcohol
SnI_2 RbI	yellow needles
$2SnI_2$ RbI	orange yellow cubic crystals
$NaSnI$	pale yellow crystals, decomposed by water

Brownish red crystals of $Sn(HS)Cl$, easily decomposed by water, have been reported. Two complex stannous sulfates known to exist are:

$2Sn_3O_2 \cdot SO_4$, a red crystalline powder soluble in hot water, and $4K_2Sn(SO_4)_2 \cdot SnCl_2$ which appears as hexagonal prisms as a result of the action of warm potassium sulfate solution on stannous chloride.

The chlorobromides (in which one or two chlorine atoms are substituted for the corresponding bromine atoms), together with some of the numerous addition salts formed by stannic bromide and the bromides of other metals are given

$SnBr_4$ $2NH_4Br$	specific gravity 3 505, pale yellow or colorless octahedral crystals, soluble in hot and cold water
$SnBr_4$ $CaBr_2$ $6H_2O$	slender needle-like crystals, deliquescent
$SnCl_3Br$	specific gravity 2 51 at 13° C , melting point −31° C ; boiling point 50° C at 30 mm pressure and 45° C. at 20 mm pressure, colorless liquid
$SnBr_2Cl_2$	specific gravity 2 82 at 13° C , melting point −20° C , boiling point 65° C at 30 mm pressure
$SnClBr_3$	specific gravity 3 12 at 13° C., liquid, melting point 1° C , boiling point 73° C
$SnBr_4$ $CoBr_2$ $10H_2O$	yellowish red tabular crystals, deliquescent
$SnBr_4$ $2HBr$ $8H_2O$	colorless prisms, or yellow needle-like crystals, or triclinic plates
$SnBr_4$ $FeBr_2$ $6H_2O$	greenish yellow granular crystals
$SnBr_4$ $2LiBr$ $6H_2O$	yellow plates, hygroscopic
$SnBr_4$ $MgBr_2$ $10H_2O$	pale yellow tabular crystals
$SnBr_4$ $MnBr_2$ $6H_2O$	pale yellow crystals, deliquescent
$SnBr_4$ $NiBr_2$ $8H_2O$	apple green granular crystals, deliquescent
$Sn_3O_2Br_8$ $10H_2O$	colorless needle-like crystals
$SnBr_4$ $2KBr$	specific gravity 3 783, octahedral crystals, stable in air; easily soluble in water
$SnBr_4$ $2NaBr$ $6H_2O$	pale yellow prismatic or acicular crystals, monoclinic system
$SnBr_4$ $SrBr_2$ $6H_2O$	pale yellow crystalline mass, deliquescent

The literature offers formulas for stannic oxychlorides and chlorostannates These, with their crystal forms, are·

$SnCl_4$ $2NH_3$	yellowish white acicular crystals, soluble in cold water
$SnCl_4$ $BeCl_2$ $8H_2O$	white powder
$SnCl_4$ $CaCl_2$ $6H_2O$	rhombohedral crystals
$SnCl_4$ $2CsCl$	specific gravity 3 3308 at 20 5° C , octahedral and cubic crystals, insoluble in hydrochloric acid, decomposed by sulfuric and hydrofluosilicic acids
$Sn(N_2H_4)_2Cl_2$	decomposed by water, insoluble in aqueous ammonia
$SnCl_4$ $CoCl_2$ $6H_2O$	specific gravity 2 699, rhombohedral crystals, trigonal system
$SnCl_4$ $2HCl$ $6H_2O$	melting point 20° C , tabular crystals
$SnCl_4$ $2LiCl$ $8H_2O$	colorless octahedral crystals, soluble in water
$SnCl_4$ $MgCl_2$ $6H_2O$	specific gravity 2 08, rhombohedral crystals, deliquescent, soluble in hot and cold water
$SnCl_4$ $MnCl_2$ $6H_2O$	specific gravity 2 215, pale red rhombohedral crystals, trigonal system, deliquescent

$SnCl_4$ $NiCl_2$ $6H_2O$	specific gravity 2.699, greenish rhombohedral crystals, trigonal system
$SnCl_4$ N_2O_3	lemon yellow crystalline mass
$SnCl_4$ 2RbCl	octahedral crystals
$SnCl_4$ 2NaCl $6H_2O$	crystals
$SnCl_4$ $SrCl_2$ $6H_2O$	prismatic crystals
$SnCl_4$ $ZnCl_2$ $6H_2O$	crystals
$SnCl_4$ 2NOCl	specific gravity 2 60, melting point 180° C , pale yellow octahedral crystals, decomposed by water
$SnOCl_2$	soluble in water
$Sn_5O_3Cl_2$ $4H_2O$	soluble in small amount of water, soluble in alcohol, translucent deliquescent mass
$(SnO)_4Cl_7$ $5H_2O$	yellow plates, soluble in water and alcohol
$SnCl_4$ 2KCl	specific gravity 2 70, octahedral crystals, soluble in hot and cold water
$SnCl_4$ $POCl_3$	crystals, melting point 58° C ; boiling point 180° C
$SnCl_4$ PCl_5	colorless crystals, decomposed by water
$SnCl_4$ $5H_2S$	white crystals
$SnCl_4$ $2SCl_4$	melting point 37° C , yellow crystals, soluble dilute nitric acid, chloroform, carbon bisulfide, phosphoryl chloride, benzene, ether, acetic ether, sulfur chloride

Stannic fluoride unites with other metallic fluorides, forming fluostannates with formulas and crystal shapes as follows.

SnF_4 $2NH_4F$	trigonal crystals
SnF_4 BaF_2	monoclinic crystals, solubility in 100 cc of water is 5 6 grams, at 18° C
SnF_4 CaF_2 $2H_2O$	monoclinic crystals
SnF_4 CdF_2 $6H_2O$	trigonal crystals
SnF_4 2CsF	hexagonal plates
SnF_4 CuF_2 $4H_2O$	blue monoclinic crystals
SnF_4 PbF_2 $3H_2O$	monoclinic prisms
SnF_4 $2LiF$ $2H_2O$	monoclinic prisms
SnF_4 MgF_2 $6H_2O$	trigonal crystals
SnF_4 MnF_2 $6H_2O$	trigonal crystals
SnF_4 NiF_2 $6H_2O$	trigonal crystals
$SnF_4 \cdot 2KF$ H_2O	specific gravity 3 053, white crystals, slightly soluble in water
SnF_4 3KF HF	monoclinic prisms
SnF_4 2RbF	hexagonal plates
SnF_4 2NaF	crystalline crust, solubility in water at 20° C. is 5 5 grams
$SnF_4 \cdot SrF_2$ $2H_2O$	monoclinic crystals, solubility in water at 18° C. is 18.2 grams
SnF_4 ZnF_2 $6H_2O$	specific gravity 2 445, crystals

Replacement compounds of stannic iodide in which chlorine or bromine replaces some of the iodine are:

$SnBr_2I_2$	specific gravity 3 631 at 15° C., orange-red crystals; melting point 50° C ; boiling point 225° C. or 130° C. *in vacuo*, soluble in cold water, solution decomposing at 80° C.

$SnBr_2I$	yellowish red crystals
$SnCl_2I_2$	specific gravity 3 287 at 15° C , red liquid, boiling point 297° C , although it begins to distill at 190° C , soluble in water, benzene, chloroform, carbon bisulfide
SnS_2I_4	red rhombic crystals, decomposed by water, hydrochloric acid, nitric acid, aqua regia

In addition to the stannates previously discussed, those listed below are of interest, but many of their physical and chemical properties are not as yet thoroughly confirmed

$SnO_2\ (NH_4)_2\ CuO\ 2H_2O$	slightly soluble in cold water, soluble in acids
$BaSnO_3 \cdot 7H_2O$	slightly soluble in cold water, soluble in nitric acid
$CaSnO_3$	needle-like crystals
$CaSnO_3\ 3H_2O$	insoluble in water, soluble in nitric acid
$CoSnO_3\ 6H_2O$	rose red crystals
$CuSnO_3\ 4H_2O$	pale blue crystals, soluble in aqueous ammonia
$Hg_2SnO_3\ 5H_2O$	yellow precipitate, turning green
$HgSnO_3\ 6H_2O$	white, turning dark green
$NiSnO_3\ 5H_2O$	pale green cubic crystals
$KSnO_4\ 2H_2O$	white amorphous powder
$K_2Sn_5O_{11}\ 4H_2O$	horny translucent colloid, soluble in water
$Ag_2SnO_3\ 2H_2O$	dark red precipitate, soluble in dilute nitric acid, insoluble in ammonia
$Ag_2Sn_5O_{11}$	grayish powder turning deep red, soluble in dilute nitric acid, insoluble in ammonia
$Na_2SnO_3\ 10H_2O$	long prismatic crystals
$Na_2Sn_5O_{11}\ 8H_2O$	crystalline powder, slightly soluble in water
$Na_2Sn_9O_{19}\ 8H_2O$	insoluble in alcohol and sodium hydroxide
$NaSnO_4\ 2H_2O$	white amorphous powder, slightly soluble in cold water, decomposed by hot water
$SrSnO_3\ 3H_2O$	white crystalline powder
$ZnSnO_3\ 2H_2O$	colorless crystals, soluble in dilute acids

Crystal forms of some of the salts of tin and phosphorus are recorded. They are:

Sn_4P_3	specific gravity 5 18
$Sn_2O(PO_4)_2$	octahedral crystals
SnP_2O_7	cubic crystals
$Na_2Sn(PO_4)_2$	tetragonal prisms
$NaSn_2(PO_4)_3$	rhombohedral crystals

The complex sulfides and sulfates of tin, according to various investigators, formed by the reaction between stannic salts and sulfuric acid or the sulfides or sulfates of other metals are given below Their study is quite complicated.

H_2SnS_3 .	gray prisms; insoluble in hot or cold water
$(NH_4)_2SnS_3 \cdot 3H_2O$	thin yellow plates
$BaSnS_3 \cdot 8H_2O$	lemon yellow crystals; soluble in cold water
$Ca_2SnS_4 \cdot 14H_2O$ . .	lemon yellow crystals, very soluble in water

$PbSnS_3$	specific gravity 6 36, grayish black rhombic crystals, decomposed by hot hydrochloric or nitric acid
Sn_2S_3O $11\frac{1}{2}H_2O$	slightly soluble in water, soluble in ammonium carbonate
K_2SnS_3 $3H_2O$	colorless transparent prisms, sparingly soluble in water
$K_4SnS_4 \cdot 12H_2O$	monoclinic prisms
Na_2SnS_3 $2H_2O$	yellow octahedral crystals, melting point at temperature approaching redness
Na_4SnS_4 $12H_2O$	colorless monoclinic crystals
$SrSnS_3$ $12H_2O$	thick colorless prisms
$Bi(OH)Sn(SO_4)_3$	rhombic leaflets
$CaSn(SO_4)_3$ $3H_2O$	colorless cubes
$CeHSn(SO_4)_4$	colorless microcrystalline powder
$LaHSn(SO_4)_4$	small six-sided plates
$Sn(OH)_2SO_4$.	white needles, soluble in cold water
$K_2Sn(SO_4)_3$	needle-like crystals
$Rb_2Sn(SO_4)_3$	six-sided leaflets
$Ag_2Sn(SO_4)_3$ $3H_2O$	needles
$Y_2Sn(SO_4)_6$	microcrystalline powder

Tin Salts in Commerce

The only tin salts which are of commercial importance or are consumed in large quantities are the dioxide, the stannic and stannous chlorides, the stannous sulfate, stannous tartrate, phosphate, and oxalate.

Stannic oxide is known under the commercial names of tin oxide, tin dioxide, tin peroxide, or flowers of tin. It is made commercially by heating molten tin in the air or in large furnaces through which air is blown over the surface of the molten metal, or into which air is bubbled under pressure through the molten metal. The raw material is usually Straits tin or equivalent quality. The furnaces are often equipped with dust collectors, usually of the bag-house type, for catching the very fine oxide particles After manufacture, the material is screened, in some cases ground, and separated into grades. The commercial containers are usually wooden kegs The grades of the product are the white or pure, and the technical grade gray The oxide finds extensive use in the glass industry for the production of opaque glasses, in ceramic manufacture, the making of porcelain and enamels on metal, particularly cast iron, examples of which are found in our bathtubs and white enameled sinks and sanitary ware. Other uses are in connection with putty making, polishing powders, special abrasives, and electrical uses. It also finds some application in textile manufacture

Because of its relatively high price, stannic oxide is finding increasing competition from antimony oxide which has replaced it in some of its applications, either in part or wholly.

Stannic chloride in its anhydrous form is produced to a greater extent than formerly as a result of the recovery of tin from tin-plate scrap by the

chlorine process This material is the anhydrous product and is a colorless, thin, fuming, caustic liquid which moisture or water converts into a buttery, crystalline substance known as butter of tin The anhydrous stannic chloride must be kept hermetically sealed for stability It is also made commercially by dissolving granulated tin in concentrated hydrochloric acid of 20° Baumé. It is soluble in a large number of organic solvents such as alcohol, ether, carbon bisulfide, oil of turpentine, and to some extent in benzol The grades are water-white and technical It is sold either in the anhydrous liquid form or as crystals, $SnCl_4$ $5H_2O$, or as solutions of various concentrations The containers for the anhydrous form are iron drums or glass bottles, glass containers are used for the other grades The material was formerly used in dyeing and in silk weighting, often as the pentahydrate or as pink salt, which is ammonium stannic chloride, $(NH_4)_2SnCl_6$ Its use as a mordant in dyeing depends on the ready decomposition of the salt and its hydrolysis to stannic hydroxide from weak solutions of the chloride The stannic hydroxide resulting is adsorbed on the fiber With the help of this salt, a permanent red is obtained from cochineal Its use in the weighting of silk consumes the greater part of the production Stannic chloride is also used in the manufacture of fuchsine It is commercially known as tin chloride, butter of tin, tin tetrachloride, often erroneously as tin bichloride, and tin oxymuriate

Stannous chloride, known commercially as tin bichloride or tin salt, is made by treating tin with a calculated quantity of hydrochloric acid The crystalline form, $SnCl_2$ $2H_2O$, is the result of crystallization out of solution In the anhydrous form it is a heavy, colorless, corrosive liquid, giving off fumes on exposure to the air The hydrated form is a white crystalline solid and is not classed as a dangerous article under the Interstate Commerce Commission regulations The salt was used in dyeing, in the manufacture of textiles, and in calico printing as a mordant It also finds some application in glass making, ceramics, ink making, tin plating and tin coatings, to a small extent in sugar bleaching, in fermentology, and in a large variety of applications of tin salts The major use is in textile dyeing and calico printing, as a mordant Its commercial forms are the anhydrous, the crystalline, and solutions of various concentrations

Stannous sulfate is commercially obtained either by the action of sulfuric acid on stannous chloride with the production of a ponderous white or yellowish powder or crystals, or else by the action of sulfuric acid, often in the presence of chlorides, on tin There is only one commercial grade made, and that is the technical variety The containers are wooden kegs The salt is used in the dyeing industry and to a small extent in electroplating Stannous sulfate employed in refining baths in tin electrometallurgy is manufactured by the consumer

Stannous oxalate finds application in the dyeing and textile printing

TABLE 42 PHYSICAL CONSTANTS OF ORGANIC COMPOUNDS OF TIN

NAME	FORMULA	CRYSTALLINE FORM, COLOR AND INDEX OF REFRACTION	DENSITY (g./ml.)	MELTING POINT (°C.)	BOILING POINT (°C.)
Diethyldimethyltin	$(C_2H_5)_2Sn(CH_3)_2$	Colorless liquid	1.2319^{19}	<-13	144–6
Tetraethyltin	$Sn(C_2H_5)_4$	Colorless liquid 1.5143	1.187^{23}	-112	181
Tetraisoamyltin	$[(CH_3)_2CHCH_2CH_2]_4Sn$	Liquid	$1.035^{19.6}$	—	188^{24}
Tetramethyltin	$Sn(CH_3)_4$	Colorless liquid 1.5201	1.314_4^0	—	78
Tetraphenyltin	$(C_6H_5)_4Sn$	Colorless tetragonal from xylene	1.490_4^0	226	>420
Tetrapropyltin	$(CH_3CH_2CH_2)_4Sn$	Colorless liquid	$1.1065^{20.2}$	—	222–5
Tetra-*o*-tolyltin	$(CH_3C_6H_4)_4Sn$	Colorless liquid	—	158–9(215)	—
Tetra-*p*-tolyltin	$(CH_3C_6H_4)_4Sn$	Colorless needles	—	230–3	—
Dibenzyldiethylstannane	$(C_6H_5CH_2)_2Sn(C_2H_5)_2$	Liquid	1+	<20	$223–4^{20}$
Dibenzylethylpropylstannane	$(C_6H_5CH_2)_2(C_2H_5)(C_3H_7)Sn$	Liquid	—	>0	$220–5^{15}$
Diethyldiisoamyltin	$(C_2H_5)_2Sn(C_5H_{11})_2$	—	1.0725^{19}	—	$131^{13.5}$
Diethyldiisobutyltin	$(C_2H_5)_2Sn(C_4H_9)_2$	—	1.1030	—	$108–2^{13}$
Diethyldiphenyltin	$(C_2H_5)_2(C_6H_5)_2Sn$	—	—	—	$154–6^{4}$
Dimethyldiisobutyltin	$(CH_3)_2Sn(C_4H_9)_2$	—	$1.1179^{20.1}$	—	$85^{16.5}$
Dimethylethylpropyltin	$(CH_3)_2C_2H_5C_3H_7Sn$	—	1.2014_{20}^{20}	—	149–51

TABLE 43 PHYSICAL CONSTANTS OF ORGANIC COMPOUNDS OF TIN

NAME	FORMULA	CRYSTALLINE FORM AND COLOR	DENSITY (g /ml)	MELTING POINT (°C)	BOILING POINT (°C)
Tribenzyltin chloride	$(C_6H_5CH_2)_3SnCl$	White needles	—	142–4	Decomposes
Triethyltin chloride	$(C_2H_5)_3SnCl$	Colorless liquid	1 428[8]	10(15 5)	208–10
Triisoamyltin chloride	$[(CH_3)_2CHCH_2CH_2]_3SnCl$	—	1 1290[34 2]	−30 2	114[13]
Triphenyltin chloride	$(C_6H_5)_3SnCl$	Colorless crystals	—	106	240[13 5]
Diethlytin difluoride	$(C_2H_5)_2SnF_2$	Square plates or long rhombic tablets, from methyl alcohol	—	229	—
Methyltin trichloride	CH_3SnCl_3	Colorless crystals	—	43	—
Di-*o*-anisyldichlorostannane	$(CH_3OC_6H_4)_2SnCl_2$	—	—	113	—
Dibenzyltin dichloride	$(C_6H_5CH_2)_2SnCl_2$	Colorless needles, from acetone-HCl	—	163–4	—
Dibutyltin dichloride	$(C_4H_9)_2SnCl_2$	Needles	—	43	—
Dichlorodi-*m*-tolyl stannane	$(CH_3C_6H_4)_2SnCl_2$	—	—	39–40	—
Diethylisoamyltin chloride	$(C_2H_5)_2(C_5H_{11})SnCl$	—	1 2994[19 9]	—	125 5[13]
Diethyl-*n*-propyltin chloride	$(C_2H_5)_2(C_3H_7)SnCl$	—	1 3848[15 7]	—	108[17]
Diisoamyltin dichloride	$(C_5H_{11})_2SnCl_2$	—	—	28	—
Diisopropyltin dichloride	$(C_3H_7)_2SnCl_2$	Colorless, transparent crystals	—	80–4	—
Dimethyltin dichloride	$(CH_3)_2SnCl_2$	—	—	90(107)	188–90
Diphenyltin dichloride	$(C_6H_5)_2SnCl_2$	Colorless crystals	—	42	333–7 Decomposes
Dipropyltin dichloride	$(C_3H_7)_2SnCl_2$	Colorless crystals	—	81	—
Di-*o*-tolyltin dichloride	$(CH_3C_6H_4)_2SnCl_2$	—	—	49–50	—
Di-*p*-tolyltin dichloride	$(CH_3C_6H_4)_2SnCl_2$	—	—	49–50	—
Methyltin trichloride	CH_3SnCl_3	Colorless crystals	—	43	—
Phenylbenzyltin dichloride	$(C_6H_5)(C_6H_5CH_2)SnCl_2$	Colorless needles, from dilute HCl	—	83–4	80–100
Phenyltin trichloride	$C_6H_5SnCl_3$	—	—	—	142–3[25]

TABLE 44 PHYSICAL CONSTANTS OF ORGANIC COMPOUNDS OF TIN

NAME	FORMULA	CRYSTALLINE FORM, COLOR AND INDEX OF REFRACTION	DENSITY (g /ml)	MELTING POINT (°C)	BOILING POINT (°C)
Dibenzyltin dibromide	$(C_6H_5\ CH_2)_2SnBr_2$	Colorless needles from petroleum	—	130	—
Dibenzyltin diiodide	$(C_6H_5\ CH_2)_2SnI_2$	Colorless long silky yellow needles from petroleum ether	—	86–7	—
Dibutyltin dibromide	$(C_4H_9)_2SnBr_2$	Small needles	—	20	—
Diethylisoamyltin bromide	$(C_2H_5)_2(C_5H_{11})SnBr$	—	1 4881[17]	—	137 5[17]
Diethyl-*n*-propyltin fluoride	$(C_2H_5)_2(C_3H_7)SnF$	—	—	271	—
Diethyltin dibromide	$(C_2H_5)_2SnBr_2$	Colorless needles	2 068[74]	63	232–3
Diethyltin difluoride	$(C_2H_5)_2SnF_2$	Square plates or long rhombic tablets from methyl alcohol	—	229	—
Diethyltin diiodide	$(C_2H_5)_2SnI_2$	White needles	—	44 5–5 0	240–5 Decomposes
Diisoamyltin dibromide	$(C_5H_{11})_2SnBr_2$	—	—	−25 to −24	—
Diisoamyltin diiodide	$(C_5H_{11})_2SnI_2$	Oily liquid	—	—	202–5[8]
Diisobutyltin diiodide	$(C_4H_9)SnI_2$	—	—	—	290–5
Dimethyldibromodipyridinetin	$(CH_3)_2SnBr_2(C_5H_5N)_2$	—	—	172	—
Dimethylethyltin iodide	$(CH_3)_2C_2H_5SnI$	1 5705[18]	2 0264$^{20}_{20}$	—	77–8[11]; 185–7[718]
Dimethyltin difluoride	$(CH_3)_2SnF_2$	White, fine plates	—	—	Decomposes <360
Dimethyltin diiodide	$(CH_3)_2SnI_2$	Rhombic, white	2 872	43(30)	228
Diphenyltin dibromide	$(C_6H_5)_2SnBr_2$	Colorless crystals	—	38	230[42]
Diphenyltin difluoride	$(C_6H_5)_2SnF_2$	—	—	360	—
Diphenyltin diiodide	$(C_6H_5)_2SnI_2$	Colorless crystals	—	71–72	176–82[2]

Ethylpropyltin dichloride	$(C_2H_5)(C_3H_7)SnCl_2$	Needles from light petroleum	—	57–8	—
Ethyltin triiodide	$C_2H_5SnI_3$	—	—	—	181–4[19]
Isopropyltin trichloride	$C_3H_7SnCl_3$	—	—	—	75[16]
Methyltin tribromide	CH_3SnBr_3	White needles	—	53–5	210–11[24]
Methyltin triiodide	CH_3SnI_3	Light yellow needles	—	86 5	—
Tribenzyltin iodide	$(C_6H_5CH_2)_3SnI$	Needle-like prisms from glacial acetic acid	—	102–3	—
Tri-*n*-butyltin bromide	$(C_4H_9)_3SnBr$	1 5000	1 3365	—	—

industries. It is a white ponderous crystalline powder obtained by the action of oxalic acid on stannous oxide, or on stannous chloride. It is soluble in acids. The only commercial grade is the technical one, and the containers are wooden kegs.

Stannous tartrate has characteristics quite similar to those of stannous oxalate, and is obtained by the action of tartaric acid on stannous chloride. The technical grade is soluble in water. The containers are wooden kegs, and the material finds application in calico printing and in textile dyeing. A similar situation holds for stannous phosphate produced by the action of phosphates on stannous chloride.

Organic Compounds of Tin

Stannane or tin hydride, SnH_4, is a gas which is produced by the reaction of hydrochloric acid on tin-magnesium alloys. The solid melts at $-150°$ C. The gas is stable for a short time in glass at room temperature. In contact with tin or desiccants, such as calcium chloride or phosphorus pentoxide, it is unstable. At 150° C. or above, it decomposes rapidly. It is absorbed by sulfuric acid, solid alkalies or soda lime, and gives a black precipitate of tin and silver with silver nitrate. It does not react with dilute alkalies or acid or lead acetate or copper sulfate, nor is it oxidized by dilute or concentrated nitric.

A considerable number of organic compounds of tin are known in which alkyl or aryl groups are substituted for the hydrogen in stannane. Typical of these is tetraethyl tin, or $Sn(C_2H_5)_4$, corresponding to the well-known tetraethyl lead and made by the use of sodium-tin alloys and alkyl halides such as ethyl bromide, corresponding to the commercial method for tetraethyl lead manufacture. Some of the trialkyl tin derivatives have appreciable vesicant action and are toxic.

Some of the tetraalkyl and aryl compounds are given in Table 42.

Compounds corresponding to ethane, C_2H_6, with tin replacing the carbon, are represented by triethyltin or hexaethylditin, $(C_2H_5)_3SnSn(C_2H_5)_3$. This is a liquid with a density of 1 4115 which decomposes at its boiling point of 270° C. It is insoluble in water and alcohol, but soluble in ether and benzol.

Organotin compounds related to stannic chloride, in which one or more organic groups replace one or more chlorine atoms, are numerous. Typical compounds are tabulated in Table 43.

Other halogens form similar compounds, typical examples of which are listed in Table 44.

Organic derivatives of the tin oxides or tin substituted ethers are known as diethyltin oxide or $(C_2H_5)_2SnO$, corresponding to the compound R_2SnO where R is an organic radical. In a similar manner, there are organic sulfides $RSnS$, as dimethyltin sulfide, which might be considered as a substituted stannane.

Stannyl groups, RSn—, may substitute for hydrogen in compounds like methane, CH_4, to give compounds like triphenylstannylmethane or $[(C_6H_5)_3Sn]_3CH$, which is a white crystalline solid melting at 128° C.

Organic compounds resulting from the substitution of organic groups in stannic acid, chlorostannic acid, and thiostannic acid and their salts are known, examples of which are ethyl stannic acid, $C_2H_5SnO—OH$, which is a white amorphous gelatinous powder, ethylchlorostannic acid, $H_2SnC_2H_5Cl_5$, a colorless deliquescing material crystallizing in prisms; and phenyltetrathioorthostannate, $Sn(SC_6H_5)_4$, which has a melting point of 67° C.

Derivatives of the hydroxides are analogous to those of the oxides, as tribenzyltin hydroxide $(C_6H_5CH_2)_3SnOH$, a rhombic tabular crystal, melting at 117 to 121° C., or triethyltin hydroxide $(C_2H_5)_3SnOH$, a colorless crystalline material, melting at 43° C. and boiling at 271° C., and showing water solubility.

Substituted sulfides are illustrated by trimethyltin sulfide, $[(CH_3)_3Sn]_2S$, a light yellow oil with a density of 1 649 at 25° C., melting at 6° C , and with a boiling point of 233.5°, insoluble in water but soluble in organic solvents.

Chapter 17

Corrosion

The Effect of Water

Tin is widely used in alloys, in the manufacture of tin foil, and for coating other metals, such as copper and iron, to render them more resistant to corrosion. Tin metal itself is very resistant to corrosion by the atmosphere or the various gases contained therein as a result of manufacturing processes. Water affects tin hardly at all. At ordinary temperatures there is no tendency toward oxidation. Were it not for the fact that tin is electronegative to iron and strongly accelerates its corrosion in the presence of atmospheric electrolytes if the two metals be exposed at the same time—that is, if the coating be noncontinuous—tin would serve admirably as a protection to sheet steel or iron. Naumann[1] confirmed this and stated that heavy coatings free from defects should be applied to the iron or steel surfaces to obtain complete protection. He also pointed out that water does not dissolve objectionable quantities of tin. This statement needs modification, inasmuch as the relative electrode potentials of tin and iron depend upon the corroding agent, and in some cases tin is electropositive to iron. As has been pointed out under tin compounds, the metal dissolves rather slowly in most acids, but reacts readily with nitric acid to form metastannic acid. Tin also reacts with water solutions of the alkalies to form soluble stannites and stannates. The corrosion of tin in the form of tin plate in one of its widest uses, that of tin cans, is discussed in Chapter 18.

Small amounts of tin, when added to other metals or alloys, markedly increase their corrosion resistance. This point has been discussed in connection with bronzes and the copper-tin alloys. Desch and Whyte,[2] in their studies of the microchemistry of corrosion, showed the protective influence of tin on the copper-zinc alloys.

Haehnel[3] reported that an addition of 3 per cent tin to lead cables buried in the soil extends their useful life by 700 to 800 per cent compared with pure lead cables. On the other hand, tin is liable to lose its anticorrosive properties as the result of impurities. Zinc and aluminum are particularly

[1] E. Naumann, *Gas- u. Wasserfach*, **76**, 146–7 (1933).

[2] Desch, and Whyte, *J. Inst. Metals*, **10**, 304 (1913); *Metal Ind. (London)*, **11**, 430–2 (1914); **12**, 115–7 (1914).

[3] O. Haehnel, *Elek. Nachricht. Tech.*, **3**, 229 (1926).

damaging. Heyn and Wetzel[4] reported that tin foil containing 99.1 per cent tin, 0.5 per cent aluminum, 0.25 per cent lead, and the remainder copper, iron, and antimony became, under influence of the atmosphere, so brittle that it could be ground up with the bare fingers. The damaging effects of zinc have been observed particularly on boiler plugs Burgess and Merica[5] stated that safety plugs of tin which contain zinc are transformed completely into tin oxide, which can create boiler explosions.

A peculiar form of destruction of tin which is, however, not exactly corrosion, has been reported by Bauer and Vollenbruck.[6] They noted that certain types of beetles are able to bite through sheets of tin or lead.

Even the purest water has practically no solvent action upon pure tin. Long experience has shown that block-tin pipe, when the tin metal of which it is made is of good quality, is one of the best materials for conveying distilled water to be used for experimental purposes. Carbonated water has practically no solvent effect on tin metal. Collins[7] investigated the effect of steam derived from carbonated water upon steam heating systems. Tin was found to be practically free from corrosion when brought in contact with the condensate, while copper alloys and Bessemer steel showed corrosion.

When the solubility of metals in water is determined by the conductivity method, it is found that twice-distilled water has practically no solvent effect on tin when the resultant effect is tested for by delicate conductivity measurements

Brown, Roetheli and Forrest[8] investigated the influence of oxygenated water on the initial corrosion of tin. They found that the corrosion tendencies of tin calculated from the decrease of the free energy in electrolytic cells agree more with the experimental findings than the corrosion tendencies obtained from the consideration of the molal forces. They also found that the corrosion rates decrease with a lengthening of immersion of the metal into oxygenated water. They attributed this phenomenon to the formation of a surface film which reduces the rate of diffusion between ions and dissolved oxygen.

The extraordinary resistance of tin against humidity is demonstrated in the analysis by Smythe[9] of ancient samples of tin which had corroded in the earth. When analyzing the scales of these samples, 25 to 40 per cent of tin oxide was found. He surmised that a stable oxide is formed of the composition $2SnO \cdot 3SnO_2 \cdot 2H_2O$.

[4] Heyn, and Wetzel, *Mitt. Kais.-Wilh.-Inst Metallforsch*, **1**, 19 (1922)
[5] Burgess, and Merica, *Bur Standards Tech. Paper*, 53 (1915).
[6] O. Bauer, and O Vollenbruck, *Z. Metallkunde*, **22**, 230 (1930).
[7] L F. Collins, *Proc Ann Water Conf, Eng. Soc. Western Penna.*, **4**, 33–51 (1943).
[8] R. H Brown, B E Roetheli, and H O. Forrest, *Ind. Eng Chem.*, **23**, 350–2 (1931).
[9] J. A. Smythe, *J. Inst. Metals*, **66**, Pt 10, 355–60 (1940).

The Effect of Halides

The halides are among the most active substances corroding tin. The effect of a material known under the name of Flammon which consists of a mixture of ammonium fluoride and hydrofluoric acid, on the metals used in the brewing and related industries has been investigated by Will and Landtblom.[10] All percentages of Flammon show no effect on tin metal.

Hale and Foster,[11] in their study of the action of dilute solutions of acids, alkalies, and salts upon metals, found that tin is appreciably attacked by calcium chloride solutions of fifth-normal concentrations, although only aluminum and nickel are attacked less, while zinc, cast and wrought iron, lead, and copper are more readily attacked. Their results are of the weight-loss type, and at the present time, in view of better corrosion technique, are of little value except as indications. The attack on tin was about one and one-half times greater than that on nickel, but only about one-third of that on lead.

Solutions of ferric chloride, as a result of their acidic reaction, markedly affect tin. Together with small amounts of tin chlorides and a little hydrochloric acid, ferric chloride has been patented for the recovery of tin from tin-plated sheets, but it has found no industrial application.

Kutzelnigg[12] pointed out that the purity of tin and the character of the impurity in question is of importance for the corrosion resistance of tin to halides. As little as 0.01 per cent antimony increases the corrosive effect of hydrochloric acid and ferric chloride solutions, while small amounts of bismuth give considerable protection against corrosion. The relatively great resistance of pure tin is ascribed to the formation of a protective layer of oxide.

The attack of tin by magnesium chloride solutions occurs to some extent, but the action is slow, being of the same order as the attack by calcium chloride. The resistance of metals to magnesium chloride, however, as studied by Hale and Foster,[13] showed that only nickel is superior in its resistance to the attack by this salt. Halla[14] studied the susceptibility of tin plate to attack by neutral magnesium chloride solutions. He found that when the partial pressure of oxygen is high, the corrosion of tin plate in gas meters is accelerated. When, however, the partial pressure of oxygen is lowered by the presence of illuminating gas, the salt seems to retard solution of oxygen in the liquid, and at the same time decreases the corrosion rate.

[10] Will, and Landtblom, *Z. ges. Brauw.*, **42**, 81–2 (1919).
[11] Hale, and Foster, *J. Soc. Chem. Ind.*, **34**, 464 (1915).
[12] A. Kutzelnigg, *Z. Metallkunde*, **28**, 5 (1936).
[13] Hale, and Foster, *J. Soc. Chem. Ind.*, **34**, 464 (1915).
[14] Halla, *J. Gasbel.*, **56**, 908 (1913); *Chem. Zentr.*, **II**, 709 (1913).

Miethke and Witt[15] made extensive investigations of the effect of various brines on metals. The tests were made by subjecting the metal samples to the various brines for 30 days at −5° C., after which time the loss of weight of the metal samples was determined. The results are given in Table 45.

Hale and Foster[16] stated that sodium chloride by itself in fifth-normal concentrations does not corrode tin. The results of other workers, however, seem to indicate that this salt has an appreciable corrosion effect on the metal. Jermstad and Gaule[17] reported that when tin test pieces are boiled in a 1 per cent salt solution and are not in rubbing contact, no tin is dissolved. If the test pieces be in rubbing contact, colloidal solution of the tin takes place. Fink and Mantell[18] have shown that the addition of sodium chloride to dilute solutions of sulfuric acid markedly increases the rate of solution of the tin by the acid. Jarvinen[19] studied the attack of tin by sodium chloride solutions.

Krystof[20] exposed tinned steel bars to fatigue tests with artificial sea water. The experiments were executed under high and low loads, running as high as 350 million reversals. In both cases the corrosion was strong.

Pure tin with a tin content of 99.75 per cent was found to lose slightly more weight than commercial tin in a three-year submersion test in sea water in the port of Southampton, England.[21] The commercial tin contained 0.3 per cent antimony, 0.017 per cent arsenic, 0.4 per cent lead and 0 06 per cent copper.

When an outside electromotive force is impressed on a cell in which tin is the anode in a sodium chloride solution, the metal dissolves at a relatively slow rate.

Stannous chloride readily attacks tin metal. It has often been suggested in connection with acids and other salts as a detinning material for the removal of tin from tin-plate scrap. It accelerates corrosion of tin by mineral acids. Stannous chloride attacks the metal most readily at the grain boundaries. It has been used as an etching reagent in the microscopic study of tin and its alloys.

As early as 1850, Wöhler[22] studied the action of sulfur chloride on tin. He found that the action was very marked, inasmuch as tin reacted readily with this compound. His results agree with those of Nicolardot,[23] who found that of all the metals only tin, aluminum, mercury, and iron react

[15] M. Miethke, and G Witt, *Molkerei-Ztg. (Hildesheim)*, **48**, 842–3 (1934).
[16] Hale, and Foster, *Loc cit.*
[17] Jermstad, and Gaule, *Schweiz Apoth Ztg*, **57**, 89–92, 109–13 (1919).
[18] C G Fink, and C. L. Mantell, *Eng Mining J*, **125**, 452–5 (1928).
[19] Järvinen, *Z. Untersuch Nahr. Genuss.*, **50**, 221 (1925).
[20] J. Krystof, *Metallwirtschaft*, **14**, 305–7 (1935).
[21] J. Newton Friend, *J. Inst Metals*, **48**, 109–20 (1932).
[22] Wöhler, *Ann.*, **73**, 375 (1850).
[23] Nicolardot, *Compt. rend.*, **147**, 1304 (1908).

TABLE 45. CORROSION BY CALCIUM AND MAGNESIUM CHLORIDE MIXTURES

BRINE	COMPOSITION	°Bé	ADDITIONAL COMPONENTS	METAL SAMPLES			
				Bronze	Tinned Brass	Tinned Copper	Soldered Tin
1	$CaCl_2$ $6H_2O$—$MgCl_2$ $6H_2O$ 1:3	28	Protective colloids plus buffer	Corrosive	Corrosive	Corrosive	Especially corrosive
2	$CaCl_2$ $6H_2O$—MgCl2 $6H_2O$ 1:3	22	None	Corrosive	Little or no corrosion	Corrosive	Corrosive
3	$CaCl_2$ $6H_2O$—$MgCl_2$ $6H_2O$ 1:3	19	Silicate sediment	Corrosive	Little or no corrosion	Little or no corrosion	Little or no corrosion
4	$CaCl_2$ $6H_2O$—$MgCl_2$ $6H_2O$ 1:37	22	Na_2CrO_4 as anti-corrosive	Corrosive	Corrosive	Corrosive	Little or no corrosion
5	$CaCl_2$ $6H_2O$—$MgCl_2$ $6H_2O$ 1:3	27	Na_2CrO_4 as anti-corrosive	Little or no corrosion	Little or no corrosion	Little or no corrosion	Little or no corrosion
6	$CaCl_2$ (technical)	22	None	Especially corrosive	Especially corrosive	Especially corrosive	Especially corrosive
7	$MgCl_2$ (technical)	22	None	Especially corrosive	Especially corrosive	Especially corrosive	Especially corrosive
8	NaCl (technical)	22	None	Especially corrosive	Especially corrosive	Especially corrosive	Especially corrosive
9	NaCl brine with carbonates and silicates	36	Carbonate and added silicate	Little or no corrosion	Little or no corrosion	Little or no corrosion	Little or no corrosion

with sulfur chloride. In 1916 Domanicki,[24] after reviewing all previous work on this reaction, found that ether accelerates the combination as a result of the formation of a complex between the ether and the sulfur chloride.

Thionyl chloride reacts with most of the common metals and metalloids North and Hageman[25] stated that when tin is heated in a sealed tube with thionyl chloride to 150° to 200° C , reaction takes place with the formation of stannous chloride, sulfur dioxide, and sulfur chloride. In the presence of an excess of thionyl chloride, the stannous salt is oxidized to the stannic form At lower temperatures, thionyl chloride has an appreciable action on tin metal

The halides in their free form unite directly with tin, forming stannic salts. Fluorine does not react readily with tin at low temperatures, but at 100° C. it forms stannic fluoride Dried chlorine and bromine act on tin at ordinary temperatures Liquid chlorine markedly attacks tin. The attack of chlorine on tin at room temperatures was utilized in the chlorine process of detinning described in Chapter 20. Even in low concentrations, when mixed with other gases, the free halogens markedly attack the metal. Tin is readily susceptible to attack by iodine, whether in the form of solution or vapor The rate of solution of tin is abnormally high, as shown by the work of Van Name and Bosworth[26] in their study of the attack of various metals by a solution of iodine in potassium iodide. Iodine vapors, even in low concentrations, rapidly tarnish tin metal and tin coatings. Tammann[27] showed that tin was soon colored yellow when placed in the desiccator in an atmosphere of iodine vapor, and that a fine, dark dust gathered on the surface of the metal.

The Effect of Acids

All of the halogen acids attack tin According to Berthelot, in agreement with the thermal values of the reaction, tin is easily attacked by hydrogen iodide and hydrogen bromide, less readily by hydrogen chloride, and but feebly by hydrogen fluoride It is slowly dissolved by dilute hydrochloric acid; and with hot concentrated hydrochloric acid, hydrogen is evolved and stannous chloride is formed The dissolution of the tin is accelerated by the presence of a little platinic chloride or if the tin be in contact with copper, silver, lead, antimony, platinum, or other of the noble metals. Nöllner[28] stated that the action of hydrochloric acid on tin ceases when the solution contains one mole of stannous chloride for every two

[24] Domanicki, *J Chem Soc* , **II**, 112, 369 (1917)
[25] North, and Hagerman, *J Am. Chem Soc* , **34**, 890 (1912)
[26] Van Name, and Bosworth, *Am J Sci* , **32**, 207 (1912)
[27] Tammann, *Z. anorg allgem Chem* , **111**, 78–89 (1921)
[28] Nollner, *Liebig's Ann.*, **115**, 233 (1860)

moles of hydrochloric acid. Watts and Whipple[29] found that with normal hydrochloric acid 0.0016 and 0.0015 gram per sq. cm were dissolved from hammered and cast tin respectively at 38° C. in 20 hours.

Bryan[30] investigated the corrosion of tin under diversified conditions. He found that in 0.1 *N* acids, hydrochloric acid is more corrosive than sulfuric acid, and that phosphoric acid has but little effect upon tin. He also found that the corrosion of tin by 0.1 *N* mineral acid is about 35 per cent greater if the test arrangements be affected by vibrations caused by motors or other machinery. This advantageous effect is, however, offset by the bubbling of air or oxygen through the test containers. The test period was seven days and the test containers were Pyrex tubes of 3.5 cm diameter.

If potassium permanganate to the extent of about 5 per cent were present in solution, approximately 0.06 gram per sq. cm. was dissolved from cast tin. The rate of corrosion of cast tin in normal hydrochloric acid is fairly low, and that of hammered tin is about 20 per cent greater. Since tin dissolves in hydrochloric acid with the evolution of hydrogen, the addition of potassium permanganate, a strong oxidizing agent, rapidly accelerates the corrosion. Hale and Foster[31] found that fifth-normal hydrochloric acid dissolved tin at the rate of 0.42 gram per sq. dm. per day during seven days at 20° C., and 0.90 gram during 28 days. The resistance of tin among the metals tested is exceeded only by that of nickel and aluminum, but tin was found to be considerably better than zinc, cast and wrought iron, lead, and copper. The superior corrosion resistance of aluminum was attributed to the formation of the protective layer of oxide. Whitman and Russell[32] found that the corrosion of tin by hydrochloric acid is increased by the presence of oxygen. Salkowsky[33] stated that if hydrogen peroxide be present, free chlorine is evolved and the tin is attacked more readily. Prins[34] found that the presence of easily reducible substances like benzaldehyde or nitrobenzene accelerates the attack of acids on tin. Vaubel[35] stated that during the dissolution of polished tin in hydrochloric acid, a black powder is deposited. This dissolves only very slowly even in concentrated acid. He suggested that this may be a peculiar modification of the metal produced by the reduction of stannous chloride by nascent hydrogen.

[29] O. P. Watts, and N. D. Whipple, *Trans. Am. Electrochem. Soc.*, **32**, 257–84 (1917).

[30] J. M. Bryan, *Dept. Sci. Ind. Research (Brit.), Rept Food Invest. Board, 1936*, 185–93 (1937).

[31] Hale, and Foster, *J. Soc. Chem. Ind.*, **34**, 464 (1915).

[32] W G Whitman, and R. P. Russell, *J. Ind. Eng. Chem.*, **17**, 348 (1925); *Münch. med Wochschr.*, **72**, 1161 (1925).

[33] Salkowsky, *Chem. Ztg.*, **40**, 448 (1916).

[34] Prins, *Proc. Acad. Amsterdam*, **23**, 1449 (1922).

[35] W. Vaubel, *Ber.*, **57**, B, 515 (1924).

The effect of cold-working on rates of corrosion of nonferrous metals was investigated by Garre.[36] The rate of attack of 10 per cent hydrochloric acid on pure tin (99 99 per cent) decreases with the extent of cold-working. For tin containing small quantities of impurities (99.90 per cent) cold-working has the opposite effect. The rates of corrosion of lead and copper are also decreased by cold-working. It was found that the rate of corrosion decreases with the degree of cold-rolling. The removal of the surface layer of tin by treating it twelve times with concentrated nitric acid did not influence the behavior of the tin towards the 10 per cent hydrochloric acid. A survey of the test samples showed that the purest tin was much less corroded than that with a slight content of impurities.

The rapid attack of tin by the halogen acids and halide salts is well known. Alloys containing tin, antimony, and lead are readily dissolved by a strong solution of hydrochloric acid containing a little nitric acid.

Hot hydrobromic or hydroiodic acid readily dissolves tin. When mixtures of hydrochloric and nitric acids act on tin, ammonia and hydroxylamine are formed.

Chloric acid readily attacks tin, causing it to pass into solution with the formation of stannic chloride, without the evolution of hydrogen and with the production of only very small amounts of stannic acid.

Hypochlorous acid attacks tin, and the action is accelerated by increasing concentrations of the acid or by the presence of other acids, particularly chloric acid.

Pure liquid hydrocyanic acid has no action on pure tin, and probably none on commercial tin. Gray and Hulbirt[37] stated that the contact of this acid with commercial tin causes the decomposition of the acid, and that the use of tin in connection with hydrocyanic acid should be avoided. Taplay[38] reported that hydrocyanic acid gas plays a part in the corrosion of tinned sheet-iron parts of gas meters employed in connection with the distribution of manufactured gas.

Nitric acid readily reacts with tin and exerts a strong corrosion effect. The oxides of nitrogen in small concentrations tarnish tin metal. Nitric acid oxidizes considerably more tin than it dissolves, and hot nitric acid converts the metal completely to hydrated stannic oxide. The products of the action of nitric acid on tin vary greatly with the concentration of the acid and with the temperature. Hale and Foster[39] found that with fifth-normal nitric acid, the loss of metal per sq. dm. at 20° C. was four grams per day in seven days, and 7.2 grams per day in 28 days.

[36] B. Garre, *Korrosion Metallschutz*, **6**, 200–1 (1930).
[37] Gray, and Hulbirt, *Calif. Agr. Expt. Sta.*, Bull. **308**, 408–28 (1919).
[38] Taplay, *Gas. J.*, **150**, 583–7 (1920); *Gas World*, **72**, 481–5 (1920).
[39] Hale, and Foster, *J. Soc. Chem. Ind.*, **34**, 464 (1915).

Yamamoto[40] studied the corrosion of tin by nitric acid solutions by means of the determination of the degree of attack, measurement of the electrode potential of tin in nitric acid, and observation of anodic behavior of tin.

Aluminum and copper are markedly superior in their corrosion resistance to nitric acid. The presence of nitric acid in hydrochloric acid markedly accelerates the corrosion by hydrochloric acid

Barth[41] has studied the loss of weight of cobalt-tin, copper-tin-cobalt, and copper-tin-molybdenum alloys in various concentrations of nitric acid.

Tin is appreciably attacked by sulfuric acid, even in dilute solutions The corrosion is accelerated by the presence of chlorides In one of the early articles on the corrosion of tin by sulfuric acid, Muir and Robbs[42] studied the effect of the concentration of the acid and the relative proportions of hydrogen, hydrogen sulfide, sulfur dioxide, and sulfur produced. They found that when the molar proportions of sulfuric acid and water are as seven to two at 20° to 25° C., there is but little action. No hydrogen sulfide is produced, but little sulfur, and a trace of sulfur dioxide is formed. At 110° to 120°, small amounts of hydrogen sulfide and appreciable quantities of sulfur and sulfur dioxide are produced. When the acid-water concentrations are equal at 20° to 25° C., traces of hydrogen sulfide and sulfur are found. At 110° to 120° C. a little hydrogen and sulfur, some hydrogen sulfide, and a large quantity of sulfur dioxide are formed When the acid-water proportions are as one to three, there is only a slow action at 20° to 25°; but at 110° to 120° much hydrogen sulfide and a trace of sulfur dioxide are formed. When the acid-water concentrations are as one to five, at 25° C. the action is very slow; at 110° to 120° C. hydrogen and a trace of hydrogen sulfide are given off. Watts and Whipple[43] made a careful study of the corrosion of tin in normal sulfuric acid. They found that 0.0006 gram per sq. cm. of tin was dissolved in 20 hours at 38° C. The addition of sodium chlorate caused an enormous acceleration of the corrosion. With approximately 5 per cent of sodium chlorate, 0.13 gram of tin per sq. cm. was dissolved in 20 hours at 38° C Rather unexpectedly, potassium dichromate was found to reduce the corrosion figure in grams per sq. cm. from 0.0006 to 0.0003. Instead of strongly accelerating the corrosion, it reduced it to less than half. This effect was the result of the formation of a fine white precipitate which acted as a protective coating. Hale and Foster[44] found that with fifth-normal sulfuric acid at 20°, 0.022 gram per

[40] Y. Yamamoto, *Bull Inst Phys Chem Research (Tokyo)*, **19**, 281–366, 437–88, 587–713 (1940).

[41] Barth, *Metallurgie*, **9**, 261 (1912)

[42] Muir, and Robbs, *Chem. News*, **45**, 69 (1882)

[43] O. P. Watts, and N. D. Whipple, *Trans. Am. Electrochem. Soc.*, **32**, 257–84 (1917).

[44] Hale, and Foster, *J. Soc. Chem. Ind.*, **34**, 464 (1915).

sq. dm. per day was lost during seven days, and 0.25 gram per sq. dm. per day during 28 days.

Oxygen accelerates the attack of tin by sulfuric acid. In dissolving tin, when sulfate electrolytic refining baths are made, it is found that the tin dissolves much more rapidly in the electrolyte if baskets containing the metal are exposed alternately to the solution and to the air. Hydrogen dioxide does not affect the rate of dissolution of tin by sulfuric acid. Pyrosulfuric acid dissolves tin with the evolution of heat, forming stannous sulfate and sulfur oxides.

Formaldehyde has little effect in decreasing the corrosion of tin by sulfuric acid. Van Name and Hill[45] and Selvig and Enos[46] studied the rate of solution of tin in sulfuric acid and in mine waters containing sulfuric acid and iron and aluminum sulfates.

Jones[47] stated that tin metal stands oleum very well and is useful for making condensing coils where copper would be attacked. The advisability of the use of tin in this connection is questionable, inasmuch as it can be supplanted by cheaper metals which have sufficient corrosion resistance.

Tin is corroded somewhat by various concentrations of chromic acid, as has been shown by Van Name and Hill.[48] When the acidity is sufficiently high, the determining factor of corrosion is diffusion.

A large number of patents have been taken out for etching agents, employing the numerous salts of boric, acetic, tartaric, and nitric acids which are to be used in dilute acid solutions for commercial etching. The salts are to be used either singly or in combination with each other. Although the salts themselves do not readily corrode tin metal, it is probable that they have some influence on the rate of corrosion. The attack of these etching agents is usually more severe along the grain boundaries of the metal surface than in the interior of the grain.

A number of tests to determine the effect of the attack of acetic acid on block tin are reported by Calcott and Whetzel.[49] Their corrosion figures are given in Table 46.

Block tin was subjected to the attack of 20, 60, and 100 per cent acetic acid at 25° C. and at the boiling point of the solutions. Although the data were obtained by one of the early corrosion methods, they clearly indicate that acetic acid may be safely handled in tin, at least up to 60 per cent concentration. It is very likely possible that at room temperatures somewhat higher concentrations may be stored in tin or tin-lined containers.

[45] Van Name, and Hill, *Am. J. Sci.*, **42**, 301–32 (1916).
[46] Selvig, and Enos, *Bull. Carnegie Inst Tech Cooperative Mining Courses*, 4 (1922)
[47] Jones, *Chem. Age*, **4**, 394–395, 416–417 (1921).
[48] Van Name, and Hill, *Loc. cit.*
[49] Calcott, and Whetzel, *Trans. Am. Inst Chem. Eng.*, **15**, (I), 1–113, 142–153 (1923).

The results also show that boiling acetic acid should not be handled in tin in concentrations much over 20 per cent.

A number of organic fruit acids, such as citric and malic, attack tin quite rapidly in contact with air, but scarcely at all when air is excluded. These findings were corroborated by other investigators,[50] who found that tin and various metals are much more readily corroded in the presence of air than in its absence when attacked by 1 per cent citric acid solution.

This phenomenon was subjected to a closer investigation by Bryan,[51] who removed oxygen from a citric acid-sodium citrate buffer solution by boiling in a vacuum and introducing oxygen-free nitrogen by the method of Kautsky and Thiele.[52] Under these conditions, no appreciable corrosion of tin was observed at any concentration of hydrogen ions.

TABLE 46 CORROSION OF TIN BY VARIOUS ACIDS

ACID	DESCRIPTION OF CONCENTRATION (%)		TEMP (°C)	RATE OF CORROSION (INCHES PENETRATION PER MONTH)
Acetic	20		25	0 000412
			B. P.	0 000896
	60		25	0.000511
			B. P	0.00131
	100		25	0.00160
				0.0140
	ACID	ANHYDRIDE		
Acetic + anhydride	10	90	25	0.00169
			B. P.	0 0103
	60	40	25	0 00140
			B. P.	0 0456
	80	20	25	0.00405
			B. P.	0.0588

When air was present, the corrosion was at a maximum at a pH of about 3 in 10 days and at a pH of about 2.5 in 28 days. During this process more oxygen was absorbed than was necessary to account for the oxidation of the tin in solutions of low acidity. This discrepancy is probably brought about by the oxidation of the citrate ion.

Bryan[53] compared the resistance of tin and aluminum against corrosion

[50] Anon., *Dept. Sci. Ind. Research (Brit.) Rept. Food Invest. Board, 1932*, 173–8 (1933).

[51] J. M. Bryan, *Dept. Sci. Ind. Research (Brit.) Rept. Food Invest. Board*, 107–9 (1930).

[52] H. Kautsky, and H. Thiele, *Z. anorg. allgem. Chem.*, **152**, 342–6 (1926).

[53] J. M. Bryan, *Dept. Sci. Ind. Research (Brit.) Rept. Food Invest. Board, 1934*, 187–95 (1935).

by citric acid of various pH concentrations. At a pH of 4 to 5.5, the corrosion was approximately the same at 75° C. for 3 days. Below a pH of 4, the corrosion of tin was much faster over this limited period, but at a pH of 2.4 it was nearly double that of aluminum. It must be considered, however, that the corrosion of tin of the oxidative type would cease when the oxygen is exhausted, while the corrosion of aluminum of the hydrogen-evolution type would continue until the acid was neutralized completely.

At any rate, the attack is very much lessened at reduced oxygen pressures. A similar condition holds true for lactic acid, which attacks tin in the presence of oxygen but scarcely at all *in vacuo* or in an atmosphere of carbon dioxide. Appreciable concentrations of lactic acid definitely corrode tin.

The purity of tin was shown by Bryan[54] to be an important factor in the corrosion resistance of the metal. Two parts per million of iron in solution had no effect upon the rate of corrosion of tin by a 0.5 per cent solution of citric acid, while a content of 5 parts per million caused a marked increase in the corrosion of tin. Copper has a slighter effect than iron.

The electrochemical processes that are involved in the action of tin-iron couples in dilute acid media, particularly dilute organic acids, have been investigated by Hoar.[55] He explained the reversal of the electromotive force of tin-iron couples with the dissolution of the initially present oxide films on the metals. Tin functions as anode in diluted oxalic and citric acids because the tin ion is removed as a complex. It functions as cathode in dilute sulfuric acid because no complex is formed. Tin and iron corrode both in citric acid and citrate buffer solution, but when the elements are electrically coupled, the tin corrodes more rapidly than the iron because of the superimposed effect of the couple current. This couple current is quantitatively equivalent to the increase in tin corrosion and to the decrease in the iron corrosion.

van Heyningen and Was[56] studied the effect of diluted citric, lactic, benzoic and propionic acids on thin layers of tin by optical methods. They found that an intermediate reaction product is formed which dissolves in the liquid with the formation of complex ions. Calculations of the order of reaction from the reaction rates indicate that two acid ions A^- react per atom of tin to form the intermediate compound SnA_2. The complex ions which are the final reaction products are formed by the addition of one ion of organic acid to the intermediate product, and in the case of lactic acid, two acid ions are required.

Since tin is widely used in coating steel plate for containers for canned

[54] J. M. Bryan, *Dept. Sci. Ind. Research (Brit.) Rept. Food Invest. Board, 1932*, 163–5 (1933).

[55] T. P. Hoar, *Trans. Faraday Soc.*, **30**, 472–82 (1934).

[56] J. A. Ninck Blok-Kits van Heyningen, and D. A. Was, *Proc. Acad. Sci. Amsterdam*, **41**, 717–24 (1938).

foods, a great deal of attention has been given to its corrodability by organic acids. The corrosion of tin plate by food products is discussed separately in Chapter 18. As has been pointed out under malic and lactic acids, the effect of the dilute fruit and vegetable acids on tin is very small in the absence of air, but the attack is accelerated by oxidizing agents, particularly nitrates. These results are equally valid for commercial products which contain one or more fruit acids. Ash[57] investigated the suitability of tin for employment in wineries and found that it is readily dissolved by grape juice and wine.

Oxalic and tartaric acids dissolve tin in the presence of air, but the removal of oxygen definitely retards the action.

The presence of pectin substances, particularly in canned tomatoes, materially retards corrosion of tin coatings.

Kino[58] studied the effect of stearic acid at elevated temperatures on tin He found that stearic acid attacks tin readily at 330 to 340° C.

Phenol tarnishes and corrodes tin. When practically pure phenol is boiled with tin, it becomes opalescent. The phenol vapors are accompanied by benzol, which is a reduction product. This reaction has been studied by Zoller.[59] As a result of the reaction, tin is oxidized. The reaction does not seem to take place to any appreciable extent at room temperatures, but only above 100° C.

Picric acid shows a definite corrosion effect on tin. Similar to other organic reducible compounds, the acid shows a strong accelerating effect upon the corrosion of tin in sodium hydroxide. According to Watts and Whipple,[60] amalgamation does not protect the tin, since no hydrogen is evolved.

The corrosive effect of solutions of organic acids in organic solvents was investigated by Dubrisay[61] who used solutions of acetic, propionic, butyric, lauric, palmitic and stearic acids in benzol. Tin showed little or no corrosion; only aluminum showed greater resistance. Nickel showed about the same resistance to corrosion as tin, but both were slightly corroded by the solution of acetic acid, and not at all by the higher acids. The corrosion was caused by 0.1 *N* acetic acid at room temperature as well as during refluxing Tin did not show any corrosive effects when subjected to treatment with aromatic solutions of stearic and palmitic acids.

The moist vapors of salicylic acid, according to Whittaker,[62] do not seem to affect tin when the metal is used as a condensing surface. When the vapors of salicylic acid are condensed in iron equipment, they are given a

[57] C. S Ash, *Ind. Eng Chem* , **27**, 1243–4 (1935).
[58] K. Kino, *J. Soc. Chem. Ind. (Japan)*, **40**, *Suppl. binding*, 312 (1937).
[59] Zoller, *J. Am. Chem. Soc.*, **43**, 211 (1921).
[60] O. P. Watts, and N. D. Whipple, *Trans. Am. Electrochem. Soc.*, **32**, 257 (1917).
[61] R. Dubrisay, *Chimie industrie*, **44**, 277–84 (1940).
[62] H. F. Whittaker, *Trans. Am. Inst. Chem. Engrs.*, **15**, 129–30 (1923).

violet coloration; but there is no coloration effect when condensed in tin equipment.

The Effect of Alkalies

When present in small amounts in manufactured gas, gaseous ammonia has been considered to cause corrosion of gas mains and the tinned sheet iron parts of gas meters. Taplay[63] has attributed the corrosion to the products resulting from the reactions between carbon bisulfide and ammonia. Henderson and Galletly[64] stated that when tin is heated in ammonia gas, the surface of the metal becomes frosted and blistered. At high temperatures the ammonia is decomposed. The metal seems to "fix" no appreciable amount of nitrogen. If the work of Henderson and Galletly be confirmed, it is probable that the corrosion of gas meters may be the result of contact between the ammonia and the iron at imperfections of the tin coating. Liquid ammonia, according to Kraus,[65] does not dissolve tin, but when metallic sodium has been first dissolved in the ammonia, the liquid has a strong solvent action on tin metal. Kraus stated that solutions of tin in this reagent are red, and readily conduct the electric current.

Libinson, Kukushkin and Morozova[66] claimed that solutions of ammonium nitrate in liquid ammonia caused a slight corrosion of tin. The solutions contained 70 to 80 per cent ammonium nitrate and the partial pressure of the ammonia over the solutions was 220 to 450 mm. at 20 to 26° C. and 739 to 747 mm. barometric pressure

Hale and Foster,[67] in a report of their corrosion tests on tin acted on by ammonium hydroxide, suggested that this reagent is without attack on tin metal.

Tin is readily attacked by sodium and potassium hydroxides. The corrosion in potassium hydroxide has been studied by Nutton and Law[68] with the object of determining the potential of hydrogen liberated from this metal, and the possible application of electrolytic reduction to organic processes Hale and Foster showed that tin is appreciably soluble in caustic soda, giving a weight loss of 0.30 gram per sq. dm. per day for seven days, and 0.50 gram per sq. dm. per day for 28 days, being markedly inferior to all the other metals tested, and being better only than aluminum and lead Tin corrodes slowly in pure sodium hydroxide solution Oxidizing agents, such as potassium permanganate or picric acid, markedly

[63] Taplay, *Gas J.*, **150**, 583 (1920); *Gas World*, **72**, 481 (1920)

[64] Henderson, and Galletly, *J Soc. Chem. Ind.*, **27**, 387 (1908)

[65] Kraus, *J. Am. Chem. Soc.*, **29**, 1556 (1907).

[66] I. M. Libinson, I I. Kukushkin, and A. S. Morozova, *J. Chem Ind (Moscow)*, **12**, 590–7 (1935).

[67] Hale, and Foster, *J. Soc. Chem. Ind.*, **34**, 464 (1915).

[68] Nutton, and Law, *Trans. Faraday Soc.*, **3**, Part I, 50 (1907).

intensify the attack. Sodium arsenate and potassium nitrate do not accelerate the corrosion.

Mohr and Wullhorst[69] tested various cleaning agents upon tinned milk cans and found sodium carbonate and caustic soda in concentrations of 0.25 per cent at 85° C. for a period of 12 seconds has a sufficient corrosive effect so that it could not be recommended for cleaning purposes. The addition of silicate as a preventative of corrosion renders these solutions suitable as cleaning agents for tinned containers.

In practice, tin is found to dissolve anodically in the tetravalent form, giving stannate as follows:

$$Sn + 4\oplus = Sn''''$$

$$Sn'''' + 6OH' = SnO_3'' + 3H_2O$$

This, together with the fact that alkaline stannite solutions decompose spontaneously to give metallic tin and stannate, leads to the belief that the relation between stannic and stannous ions and tin metal was similar to that between cupric and cuprous ions and metallic copper. Opposed to this was the fact that tin dissolves anodically in acid solutions as stannous ions. Goldschmidt and Eckardt[70] found that although pure tin readily became passive, it also readily dissolved in alkaline solutions to form stannous ions. Foerster and Dolch[71] found that tin is not really analogous to copper in this connection, but that tin metal-stannous ion and not tin metal-stannic ion is the stable system. Anodic tin readily passivates in alkaline solution as the result of the formation at definite concentrations of colloidal tin compounds which are precipitated on the electrode. This prevents a diffusion of the stannous ions, and the anode potential is raised to the value necessary for oxygen evolution. The oxygen rapidly oxidizes the stannite ion to stannate. Any insoluble impurities present in the tin favor the occurrence of this film action. The higher the temperature and the lower the current density, the more tin can be dissolved before the formation of stannate occurs. Eventually the surface becomes coated with stannic compounds, and the tin becomes passive.

Shatalov[72] examined the electrode potential of tin in sodium hydroxide solutions and found that it is almost constant with regard to time. The tests were extended up to 100 hours' duration and were made in solutions whose concentrations varied from 0.001 *N* to 4.0 *N*.

Derge[73] employed potentiometric measurements to determine the effect of sodium carbonate on pure tin which had been annealed by various meth-

[69] W. Mohr, and Wullhorst, *Molkerei-Ztg.* (*Hildesheim*), **50**, 2490–2, 2525–8 (1936).
[70] Goldschmidt, and Eckardt, *Z. phys. Chem.*, **56**, 385 (1906).
[71] Foerster, and Dolch, *Z. Elektrochem.*, **16**, 599 (1910).
[72] A. Ya. Shatalov, *J. Phys. Chem.* (*U.S.S.R.*), **15**, 401–9 (1941).
[73] G. Derge, *Am. Inst. Mining Met. Engrs., Inst. Metals Div.*, **128**, 391–7 (1938).

ods. He found that the tendency to corrode increases with increasin alkalinity and that oxide films produced by annealing in air cause the ti to become passive. Moreover, when the annealing in air was replaced b anodic oxidation in an electrolyte which contained disodium phosphate an phosphoric acid, the test samples turned electrochemically active withi 24 hours. The test solutions were 0.1 *N* sodium carbonate and sodiur bicarbonate or mixtures of these solutions. The addition of sodium chlorid until the solution had reached a concentration of 0.001 *M* did not influenc the behavior of tin sheet towards carbonate and bicarbonate solutions The pH range was 8.4 to 11.2.

Derge,[74] with the cooperation of Markus, further investigated the influ ence of other anions upon the corrosive effect of carbonate and bicarbonat solutions on tin. They found that carbonate solutions with a pH of 9. showed exceptional passivity in the presence of 0.01 mole of sodium chlo ride per liter. Fluoride, bromide and iodide had the same effect, but thei passivating effect became apparent at a halide concentration of 0.00] Similarly, 0.001 molar chromate solution has a passivating effect upo carbonate solutions at a pH of 11.2. Perborate and phosphate solution with a 0.01 molar concentration also have a marked passivating effect upo tin in a carbonate solution with a pH of 11.2.

The protective effect of the perborate was apparently caused by a filr of oxygen on the surface of the sample tested, and the protection cease with the consumption of the excess oxygen of the perborate. Of all th ions investigated, only chromate and phosphate reduce the tin potentia permanently in such strong alkaline solutions.

Concerning the mechanism of the carbonate corrosion of tin, Derge stated that the grain boundaries inhibit the corrosion of tin by carbonat solutions.

Tin metal is thus seen to be readily corroded by alkalies, but the cor rosion may be slowed down as the result of the formation of oxide coating by the chemical action of the hydroxides on the tin metal.

The Effect of Salts of the Inorganic Acids

Salt solutions act more rapidly on tin metal than does water. In certai cases, as for example the chlorides which have been previously discussed the corrosion is quite marked. Salts which are decidedly alkaline, such a the carbonates and bicarbonates, corrode tin in a manner quite similar t the action of hydroxides.

The formation of black spots on tinned containers is generally assume

[74] G. Derge, and H. Markus, *Trans. Am. Inst. Mining Met. Engrs., Inst. Metal Div.*, **133**, 294–301 (1939).

[75] G. Derge, *Trans. Electrochem. Soc.*, **75**, 449–62 (1939).

to be caused by neutral or almost neutral salt solutions. Brennert[76] found that no black spots are formed on a free tin surface until a certain potential against the solution, the "dissolution potential," is reached, the value of which depends on the composition of the solution. The black spots continue to grow, however, at potentials less noble than the dissolution potential, particularly in very dilute solutions. In neutral or nearly neutral solutions, the potential of a polished tin surface or a newly tinned surface is usually less noble than the dissolution potential, but through the growth of air-formed films on the surface of the tin, the potential can rise above the dissolution potential. At weak points of the surface film, such as scratches for instance, the tin will corrode and black spots will form. Copper-containing tin is more subject to the formation of black spots than pure tin. The black spots were found to consist mainly of stannous oxide. Brennert suggested the reduction of the surface potential below the dissolution potential by means of cathodic polarization, that is, by contact with a less noble metal such as zinc or aluminum or the reinforcement of the protective film by anodic oxidation, as a means to prevent the formation of black spots.

Mohr and Schulz[77] investigated the origin of the "black spots" on articles used by the dairy industry. They determined that the main cause of this phenomenon is to be found in the dissolution of tin and its subsequent oxidation of the tin salts which may be caused by anodic oxidation, acid spots, disinfectants, etc. The spots can be removed by scrubbing. As remedies, Mohr and Schulz recommended careful hot-dipping with pure tin or immediate retinning of used articles whose tin layer was defective.

Hoar[78] believed that black spots are caused only by a limited number of salts. Those salts whose solutions do not form a precipitate with stannous ions form black spots; some of these are the chlorides, bromides, chlorates, perchlorates, sulfates and nitrates. The salts which do form stable precipitates with the stannous ion but do not cause black spots are iodate, borate, monohydrogen phosphate, chromate, thiocyanate, iodide, nitrite, bicarbonate, permanganate, ferricyanide, ferrocyanide and sulfite. Chlorides were found to cause the greatest attack, and solutions of ammonium chloride, magnesium chloride, calcium chloride and zinc chloride cause a more rapid spread of black spots than sodium chloride or potassium chloride. The rate of oxidation of freshly abraded tin was found to be very great in the first few minutes, but becomes relatively slow after six hours.

[76] S. Brennert, *Tech. Pub. Intern. Tin Research Development Council, Series D*, No. 2, 27 pp. (Aug., 1935).

[77] W. Mohr, and M. E. Schulz, *Milchw Ztg. Stendal*, 1037–47, 1057–60, 1081–4, 1101–4, 1121–4 (1930).

[78] T. P. Hoar, *Trans. Faraday Soc.*, **33**, 1152–67 (1937).

Salt solutions, such as warm aqueous solutions of ammonium chloride, sodium chloride, potassium hydrosulfate, potassium-aluminum sulfate, and many other soluble sulfates and chlorides, dissolve tin.

Darrin[79] stated that sodium chromate at concentrations of 0.1 to 0.3 per cent serves to prevent completely or to retard greatly the corrosion of tinned iron. He added that under some conditions dichromate is not as efficient as chromate as a corrosion retardant.

Ritter and Nussbaumer[80] examined a number of salts and their effect on tinned copper and iron. They found that trisodium phosphate does not cause any corrosion of tinned iron and copper. Sodium silicate is a suitable inhibitor of the corrosion by alkalies, if it is present in sufficient quantities A 1 per cent solution of potassium bitartrate is strongly corrosive towards tinned iron and copper. This effect increases when the tinned metal is in

TABLE 47 TIME-CORROSION RATES OF WATER ON TIN
(g. per 24 hr per sq meter)

TIME INTERVAL	18° C	75° C
10 sec	45 2	82 3
30 sec	31 8	66 4
1 min 10 sec	24 0	58 4
2 min 30 sec	17 2	53 0
5 min 10 sec	14 6	42 4
10 min 30 sec	10 2	31 8
21 min 10 sec	8 1	26 5
42 min 30 sec.	6 4	18 7
1 hr 25 sec	5 9	10 6
2 hr 50 sec.	5 3	8 1
5 hr 10 sec	5 3	7 0
8 hr. 40 sec	4 3	5 3
22 hr 40 sec.	3 2	—

contact with a metal which acts as a noble metal towards tin, such as copper or stainless steel which will not be corroded even if it were subject to corrosion by itself, such as copper in potassium bitartrate.

The effect which even small quantities of salts found in hard well-water can exert is illustrated by the corrosion experiments which Bleyer and Schwaibold[81] carried out with Munich drinking water at 18 and 75° C. over a period of 24 hours. The samples were tested in time intervals of increasing length and the loss of weight was computed in grams for 24 hours and 1 square meter surface. The results are shown in Table 47. As can be seen, the corrosion is most intense in the beginning and slows down rapidly.

[79] M. Darrin, *Ind. Eng. Chem., Anal. Ed*, **13**, 755–9 (1941)

[80] W. Ritter, and T. Nussbaumer, *Schweiz. Milchztg*, **63**, 301–2, 311, 323–4, 330, 337–8 (1937).

The action of 10 per cent ammonium persulfate in sulfuric acid solution causes marked corrosion. Ammonium sulfate, ammonium sulfocyanide, and ammonium thiosulfate all corrode tin. The action of calcium hypochlorite on tin is somewhat analogous to the action of hypochlorous acid. White[82] stated that when calcium hypochlorite is in contact with tin, oxygen is liberated, and that the hypochlorite slowly oxidizes tin to stannic oxide with the evolution of chlorine. There are a number of references in the literature concerning the action of alkali hypochlorites on tin. They all agree that there is appreciable destruction of the metal surface. Weston[83] investigated the effect of small amounts of calcium hypochlorite in water upon tin and other metals. In dilute solutions, the action is relatively slow.

Quam[84] stated that a 0.0225 per cent aqueous solution of sodium hypochlorite dissolved 1.1 mg. of tin in 3 hours from 3 sq. in. of surface. The addition of trisodium phosphate in amounts of 0.1 to 0.5 per cent, 0.5 per cent of a mixture of sodium hydroxide and sodium carbonate, or 0.1 per cent calcium hydroxide causes a marked lowering in the corrosive action of hypochlorite. The addition of 0.1 to 0.5 per cent of various detergents reduced the amount of dissolved tin to 0.1 to 0.4 per cent.

Quam[85] later contradicted some of his findings and stated that the addition of alkalies to sodium hypochlorite as a stabilizer caused an increase of the corrosive action.

Taplay,[86] as a result of his investigation of the corrosion effect of ferric sulfocyanide on tinned sheet iron parts of gas meters, came to the conclusion that this salt has little corrosive effect.

Potassium chlorate and sodium chlorate markedly accelerate the solution of tin and tin alloys when they are subjected to attack by mineral acids. Watts and Whipple[87] have shown that their accelerating effect is several hundredfold in normal sulfuric acid solution. Eckelmann[88] employed sodium chlorate in a rapid analytical method for the solution of alloys of tin in concentrated hydrochloric acid with the addition of a small amount of concentrated nitric acid.

Halla[89] found that potassium cyanide hinders the corrosion of tin plate.

It might be expected that potassium dichromate or sodium dichromate, being strong oxidizing agents, would greatly accelerate the corrosion of tin in nonoxidizing mineral acids. As the result of the formation of an in-

[81] B. Bleyer, and J. Schwaibold, *Biochem. Z.*, **230**, 136–45 (1931).
[82] White, *J. Soc. Chem. Ind.*, **22**, 132 (1903).
[83] Weston, *J. New England Water Works Assoc.*, **24**, 559–68 (1910).
[84] G. N. Quam, *Food Ind.*, **2**, 121–2 (1930).
[85] *Ibid.*, 366–7.
[86] Taplay, *Gas World*, **69**, 230 (1918); *Gas J.*, **144**, 359 (1918).
[87] O. P. Watts, and N. D. Whipple, *Trans. Am. Electrochem. Soc.*, **32**, 257 (1917).
[88] Eckelmann, *Chem. Analyst*, **25**, 22 (1918).
[89] Halla, *J. Gasbel.*, **56**, 907 (1913).

soluble coating on the metal, the tin is protected from further destruction, and potassium and sodium dichromate are thus found to have passivating action instead of accelerating corrosion.

Van Name and Hill[90] found as a result of their study of the solution of tin in potassium ferric sulfate and sulfuric acid that when the acidity of the solution was sufficiently high, diffusion became the most important factor in the velocity of the corrosion.

Potassium ferricyanide is generally believed to be without corrosive attack on tin. It has been used in the conventional Walker or ferroxyl test[91] for the detection of pinholes in tin coatings, especially tin plate. The reagent consists of a mixture of 50 parts of gelatin, 450 parts of water, 1 part of potassium ferricyanide, and 1 part of sulfuric acid. When spread over a tin-coated surface and allowed to set, blue spots appear at the pinholes. This reagent allows us to detect pinholes so small as to be not readily observable by the naked eye.

Burns[92] stated that a simple and convenient method for finding pinholes in tin coatings on steel consists in immersing the plated part for about four hours in a dilute salt solution containing a trace of hydrogen peroxide The solution is made by adding 5 8 grams of sodium chloride and 3 cc of 3 6 per cent hydrogen peroxide to a liter of water. The pinholes are revealed by the development of spots of red iron rust. The larger pinholes appear within thirty minutes, and the smaller ones after one or two hours. Thus it is possible to get an idea of the size of the pinholes by observing the rate of appearance of the rust spots.

Pitschner[93] pointed out that the American Chain Company at Bridgeport, Conn., has developed a very satisfactory modification of the Walker test which consists in the application of the ferricyanide reagent to paper with the ingredients in different concentrations. The paper is wetted and applied to the clean surface, taken off in about two minutes, and examined for blue spots which are indicative of the porosity of the coating.

Potassium and sodium nitrates, in spite of the fact that they are strong oxidizing agents, do not accelerate the solution of tin in alkalies Potassium nitrate itself exerts only a slow corrosion effect.

A number of workers agree that acid solutions of potassium permanganate are reduced by tin and cause solution of the metal with roughening of the tin surface. The tin is oxidized and the permanganate reduced. In their study of the influence of oxidizing agents on the corrosion of metals, Watts and Whipple[94] showed that the presence of a small amount of potassium permanganate in a normal hydrochloric acid solution accelerates the cor-

[90] Van Name, and Hill, *Am. J. Sci.*, **42**, 301 (1916).
[91] *J. Ind. Eng. Chem.*, **1**, 295 (1909).
[92] R. M. Burns, *Trans. Am. Electrochem. Soc.*, **52**, 284 (1927).
[93] K. Pitschner, *Trans. Am. Electrochem. Soc.*, **52**, 283 (1927).

rosion rate almost forty times, while in normal sodium hydroxide the corrosion is only twenty times greater.

Sodium acetate affects tin only at a slow rate.

Jermstad and Gaule[95] have reported that a 0.35 per cent solution of sodium acid arsenate affects tin with the production of a noncolloidal solution of the metal The normal sodium arsenate, despite the fact that it is an oxidizing agent, shows no accelerating effect upon the corrosion of tin in sodium hydroxide, although its own solutions cause appreciable tarnish on tin plate.

Whittaker[96] found tin is a satisfactory material of construction to resist solutions of sodium hydrosulfite. The best materials of construction to insure cleanliness of the product are tin, nickel, and Monel metal. They not only withstand corrosion by solutions and suspensions of the salt itself, but also other reagents that are met in the process of manufacture. This does not include the first step of the process—that is, digestion.

Tichauer[97] maintained that tin is made resistant to corrosion by dipping it in a solution of salts of heavy metals containing a small amount of a soluble molybdate. As an example, a bath is given which contains 25 parts of copper sulfate, 15 parts of nickel sulfate, 3 parts of ammonium molybdate and 1,000 parts of water.

The Effect of Organic Compounds

The resistance of tin metal to attack by organic compounds is quite varied. The effect on the metal of various organic acids has been discussed The reactions of tin with the hydrocarbons, both saturated and unsaturated, have been little studied except in the case of acetylene. This gas, when either pure and dry or impure and moist, does not perceptibly attack tin metal Acetylene gas in a pure dry state was passed over tin by Reckleben and Scheiber[98] for twenty minutes without any deleterious effect The recommendation has been made that tin be applied as a protective coating to apparatus or metal surfaces which come in continuous contact with acetylene gas Hodgkinson[99] found that tin was unaffected by acetylene at high temperatures.

Bespolov[100] stated that the hot vapors of cracked gasoline have little effect upon tin, only iron and steel show higher resistance.

[94] O. P. Watts, and N D Whipple, *Trans Am. Electrochem Soc*, **32**, 257 (1917).

[95] Jermstad, and Gaule, *Schweiz. Apoth. Ztg*, **57**, 89–92, 109–13 (1919)

[96] Whittaker, *Trans Am Inst Chem Engrs*, **15**, (I), 114–141, 153–169 (1923).

[97] H Tichauer, *French Patent 777,314* (Feb. 16, 1935). **15**, (I), 114–141, 153–169 (1923)

[98] Reckleben, and Scheiber, *Chem Ztg*, **39**, 42 (1915).

[99] Hodgkinson, *J. Soc Chem. Ind.*, **37**, 86T (1918).

[100] I. E Bespolov, *Repts. Conf. on Cracking Hydrogenation, Grozny*, **1**, 358–77 (1931).

Wood and Parrish[101] reported that the combustion products of illuminating gas have little effect on tubes made from commercial tin sheets If the gas contains sulfur the tin tubes show increased corrosion, but not in proportion to the sulfur content.

Haringhuizen and Was[102] investigated the effect of lubricating oils on tin and found that the reaction products of tin and oil form a durable protective film. The viscosity, surface tension and acidity of the lubricants are not influenced by tin. The same investigators[103] stated that transformer oils initially cause a rapid corrosion of tin, which subsequently slows down Haringhuizen and Was recommend the use of a protecting layer of tin for copper parts which are subject to corrosion by insulating oils They reported that the acidity of the oils is not a determining factor in the corrosion and that tin has a reducing effect upon lubricating oils

Sklyarenko and Pakshver[104] stated that solutions of nitrocellulose in mixtures of ether and ethyl alcohol or ether and methyl alcohol corrode tin slightly or not at all. They attributed the corrosion to traces of sulfuric and nitric acids in the nitrocellulose and said that nitrocellulose itself has a protective effect upon tin.

Schonfeld[105] and Hirt[106] attributed the turbidity resulting in beer which has been in contact with tin to the presence of acids contained in the beer or originally in the wort. The turbidity is said to be approximately proportional to the acidity, which may be removed by treatment with neutralizing agents such as limestone or calcium carbonate Neutralized beer is without attack on tin and is immune to tin turbidity

Kutter[107] stated that tin is corroded by fermenting worts. For this reason he did not include it among the metals which he recommends for the brewery industry.

Drugs, such as caffeine even up to 20 per cent solution, or caffeine containing small amounts of sodium salicylate, have no solvent action on tin either at ordinary or elevated temperatures up to the boiling point.

There is no unanimity concerning the behavior of tin in tinned vessels during the preparation of coffee. Rohrig[108] stated that coffee of 40°C

[101] J W Wood, and E Parrish, *Inst. Gas Engrs Communication* No 100, (1934) *Gas World*, **101**, 456–7, 499–502, 643–5 (1934), *Gas J* , **208**, 356–7, 527–30, 742–4 (1934),

[102] P. J Haringhuizen, and D A Was, *Proc. Acad Sci Amsterdam*, **39**, 201–14 (1936)

[103] *Chem Weekblad*, **33**, 351–2 (1936)

[104] S I. Sklyarenko, and A B Pakshver, *J Chem Ind (Moscow)*, No 7, 47–50 (1934)

[105] Schönfeld, *Chem Ztg* , **34**, 1144 (1910)

[106] Hirt, *Wochschr. Brau.*, **27**, 633–5 (1910)

[107] F. Kutter, *Bull. Inform Refrigeration*, **11**, 637 (1930), *J Inst Metals*, **47**, 84–5 (1930).

[108] Röhrig, *Ber. chem. Untersuchungsanstalt Leipzig*, 41–2 (1908)

temperature dissolves 7 to 8 milligrams per liter when standing for 2 to 3 hours. This dissolving has been observed even when the coffee was made from caffeine-free coffee beans. Lendrich[109] reported that the tannic acid which is contained in the coffee reacts with tin and destroys the aroma. Strunk,[110] however, asserted that coffee has no corroding effect when poured over tinned sheet iron, even when the tin contains 10 per cent lead.

Bleyer and Schwaibold[111] tested the effect of teas and coffee on tin. They made their tests at 75° C. The intensity of the corrosion was measured at increasing time intervals and calculated for the loss in weight in

TABLE 48*

TIME	TEA	COFFEE
10 sec	37.1	44.6
30 sec	31.4	36.7
1 min. 10 sec	28 2	25 0
2 min. 30 sec	24 4	18 7
5 min 10 sec	18 0	12 7
10 min. 30 sec	15 5	8.5
21 min. 10 sec	13.3	5 9
42 min. 30 sec	10.2	4.3
1 hr. 25 min.	9 6	3.8
2 hr. 50 min.	8.1	4.3
5 hr. 10 min	7 0	3.8
8 hr 40 min.	5.9	—
22 hr. 40 min.	7.4	4.3

75° C	pH
Drinking water	7.54
Tea	6.52
Coffee	5.89

* B Bleyer, and J Schwaibold, *Biochem Z*, **230**, 136–45 (1931).

grams for 1 square meter of tin surface and for 24 hours. They also determined the pH for tea and coffee as shown in Table 48.

When in contact with tin metal, carbon bisulfide, particularly when impure, readily tarnishes polished tin surfaces. Beyond a tarnishing effect, the attack is relatively little.

Many of the nonferrous metals react with chlorinated hydrocarbons. Berger[112] described reactions between tin and carbon tetrachloride, hexa-

[109] Lendrich, *Gesundh.-Ing.*, **39**, 389–95 (1916).

[110] Strunk, *Veröff. Gebiet Militärsanitätswesens, Arbeiten Untersuchungsstellen*, **5**, 1 (1912).

[111] B. Bleyer, and J. Schwaibold, *Biochem. Z.*, **230**, 136–45 (1931).

[112] Berger, *Compt. rend.*, **171**, 29–32 (1920).

chloroethane, hexachlorobenzol, chloroform, tetrachloroethane, and hexachlorocyclohexane. These, as well as other chlorinated and halogenated hydrocarbons, corrode tin metal. In many cases the action is accelerated by free acid they may contain, free chlorine, or decomposition products formed by their exposure to sunlight and heat. Formanek[113] stated that the corrosive effect of carbon tetrachloride on tin over a period of eight months was so small that a coating of the tin in tanks of fire extinguishers seemed unnecessary. The corrosive effect of trichloroethylene and tetrachloroacetylene is greater but comparatively small.

It appears, however, that carbon tetrachloride has some corrosive effect on tin since Ohlmann[114] recommended the use of 0.1 to 1.0 per cent by weight of finely divided and oxidized rosin and 0.001 to 0.1 per cent by weight of a primary monoamine as an inhibitor of corrosion by carbon tetrachloride.

Popov and Lebedeva[115] stated that the maximum permissible vapor concentration for fumigation of metal containers is 300 grams for 1 cu. m. for dichloroethane and 700 grams for 1 cu. m. for carbon tetrachloride at 18 to 22°. Tin was darkened slightly by dichloroethane while carbon tetrachloride did not effect discoloration.

Tin is readily dissolved and attacked by alkaline pastes which are employed as cosmetics; but it is corroded hardly at all by those materials, such as shaving creams, which are very slightly acid in reaction owing to excess of the fatty acids, such as stearic. The use of tin in collapsible tubes for various creams, toothpastes, and shaving soaps is well known. The average shaving soap is as nearly neutral as possible, and often is found to be slightly acid, because of the fatty acids. Lead was found by Beythien[116] to be less susceptible than tin to loss in weight.

Haringhuizen and Was[117] compared the corrosion of tin in olive and peanut oils with that of iron and cadmium and found that while cadmium is heavily corroded, tin and iron show a better resistance.

Rosenberger[118] examined the reaction between tin and essential oils in alcoholic solutions. He found that 18 months of contact did not cause any reaction between tin and oils. These findings were confirmed by Devey[119] who stated that tin in air-tight vessels was not affected by essential oils during 142 to 147 days of exposure.

Formaldehyde, when in contact with tin metal, causes no noticeable

[113] J. Formanek, *Chem. Obzor*, **5**, 57–9 (1930).

[114] E. O. Ohlmann (*assignor to Dow Chemical Co.*), *U. S. Patent 2,387,284* (Oct. 23, 1945).

[115] P. V. Popov, and N. I. Lebedeva, *Trans. Sci. Inst. Fertilizer Insectofungicides (U.S.S.R.)*, No. 135, 102–4 (1939); *Khim. Referat. Zhur.*, No. 9, 125–6 (1939).

[116] Beythien, *Z. Nahr. Genussm.*, **43**, 47–55 (1922).

[117] P. J. Haringhuizen, and D. A. Was, *Proc. Acad. Sci. (Amsterdam)*, **41**, 62–7 (1938).

[118] G. A. Rosenberger, *Seifensieder-Ztg.*, **64**, 976–8 (1937).

[119] J. D. Devey, *Soap, Perfumery and Cosmetics*, **15**, 329 (1942).

effect, but when it is oxidized to formic acid it corrodes tin. It is known that when as little as 1 per cent of formaldehyde is present in solutions of the common mineral acids, their attack on steel is markedly lessened, but the same effect does not hold true in respect to tin metal.

A 1 per cent solution of formic acid in methyl alcohol is reported to be without corrosive effect upon tin after a test period of four months at room temperature and in the dark.[120] Anhydrous methyl alcohol shows corrosion under the same conditions, while methyl alcohol with an admixture of 20 per cent water forms a protective layer of oxide on the tin surface.

Jermstad and Gaule[121] found that tin metal was colloidally dissolved when heated for ten hours in distilled water or 0.5 per cent phenol with the tubes in rubbing contact. The same concentration of phenol has no effect on tin when pieces of the metal are not in contact They found that the following solutions with or without the addition of phenol had no destructive effect on tin metal: 1 per cent morphine hydrochloride, 0.01 per cent atropine sulfate, 0.1 per cent cocaine hydrochloride, 5 per cent sodium cacodyl, 0.1 per cent strychnine nitrate, 25 per cent caffeine with sodium salicylate, digalen, 1 per cent novocaine.

The widespread use of tinned apparatus in the production, transportation, and preparation of milk leads one to the belief that the metal has been found by experience to be exceedingly satisfactory for this work. Milk has practically no corrosive effect on tin metal, irrespective of the length of time during which it is exposed, or the temperature. Sour milk readily corrodes tin in tin plate, owing to the lactic acid formed. Much of the corrosion found in cream separator parts which are made of stamped sheet steel coated with tin, has been found to be caused by lactic acid formed by the souring of the milk left in the separator as the result of careless or insufficient cleaning.

Brennert[122] studied the reaction between milk and tin and found that the reaction which leads to the formation of black spots on dairy machinery is substantially the same as that which has been described under the reactions between tin and salts. The main difference is the longer time interval which is required for the formation of black spots in dairy equipment: 4 to 5 months, as compared with 2 hours for a 5 per cent solution of sodium chloride. Originally, a protective film is formed on the tinned surfaces, but when this film is damaged corrosion sets in.

Gebhardt and Sommer[123] studied the corrosive effect of milk on tinned iron, copper, and soldered copper.

[120] A Guillemin, *Ann. chim* , **19**, 145–201 (1944)
[121] Jermstad, and Gaule, *Schweiz Apoth Ztg* , **57**, 89–92 (1919).
[122] S Brennert, *Tek. Tid Uppl C , Bergsvetenskap*, **62**, 57–9, 69–72 (1932).
[123] H T Gebhardt, and H. H. Sommer, *J. Dairy Sci.*, **15**, 42–61 (1932).

Stas[124] stated that lead is etched out of tin-plated lead and solder by fresh milk at a decreasing intensity.

Pyridine and pyridine bases have been stated at various times to be partially responsible for the corrosion of tinned parts in gas meters and gas lines, although this statement is disputed by some investigators. The same holds true for cyanogen and cyanogen compounds.

Sugar solutions, particularly in canned foods, serve to protect tin from corrosion by vegetable acids, according to Lehmann[125] and Carles.[126] More recent work by the National Canners Association does not confirm this in all respects. The results of earlier investigations appear, however, to be confirmed by Bryan[127] who found that the addition of sucrose to a solution of citric acid reduced corrosion to one-third at a pH of 2.4, and to one-half at a pH of 5 5. The effect of the sucrose consists in the reduction of the solubility of air in the solution, since the corrosion by citric acid is largely of the oxidation type. At 75° C. the corrosion is inhibited by concentrations of less than 15 per cent sucrose, but stimulated by larger amounts.

Tin is little affected by leather according to Innes.[128] Tin was kept in contact with various leathers which had been tanned with either organic or inorganic tanning materials for 36 weeks at various humidities and room temperatures. Tin showed the best resistance to corrosion of all metals tested.

The slight effect of fats and fat-like substances on tin is illustrated by the recommendation of beef suet and glycerol esters of oleic, linoleic and palmitic acid as antioxidation coatings for tin. The coated tin article is to be heated for 5 minutes above the melting point of the ester used.[129]

The action of photographic solutions on tin has been studied by Crabtree, Hartt, and Matthews.[130] They found that tin and alloys containing tin tend to produce high initial fog when the metal is used as a container for photographic developers. This fog later decreases to a normal value when the solution acquires better developing powers. There is a definite indication of the possibility of the use of tin alloy or metallic couple which will gradually discharge tin into the developer and act as a preservative of the solution. If the tin be in contact with another metal, the fog it creates in the developed plates is materially increased. Tin as a metal is one of the least suitable for use as a material of construction for photographic apparatus such as trays, tanks, clamps and pipes for conveying photo-

[124] M E. Stas, *Pharm. Weekblad*, **78**, 25–35 (1941), *Chem. Zentr.*, **I**, 2192 (1941).

[125] Lehmann, *Arch Hyg.*, **63**, 67–122 (1907).

[126] Carles, *Bull. Agr. Intelligence*, **10**, 621 (1919).

[127] J. M. Bryan, *Dept. Sci. Ind. Research (Brit) Rept. Food Invest. Board, 1934*, 177–9 (1935).

[128] R. F. Innes, *J. Intern. Soc. Leather Trades Chem.*, **19**, 548–63 (1935).

[129] M. R. Gilbert, *U. S Patent 2,341,513* (Feb. 15, 1944).

[130] J. I. Crabtree, H. A. Hartt, and G. E. Matthews, *Ind. Eng. Chem.*, **16**, 13 (1924).

graphic developers and fixing solutions. Practically all the other nonferrous metals are more suitable. In the case of developer tanks, tinned or tin-lined brass faucets should be carefully avoided. Tin, solder, or any alloy containing tin should be eliminated from all developing apparatus.

The Effect of Sulfur

The affinity of tin for sulfur is not very great, although the two elements unite when heated. The reaction is vigorous and usually accompanied by incandescence. Schutz[131] listed the affinity for sulfur of seven metals in the following order: manganese, copper, nickel, iron, tin, zinc, and lead. Hydrogen sulfide even in dilute concentrations tarnishes tin metal. The discoloration in tin cans has been shown by Mantell and Lincoln[132] to be caused by sulfides of tin. When moist, sulfur dioxide is markedly destructive of the surface of tin metal, forming some stannous sulfide but also oxidizing the tin to metastannic acid.

Cooke[133] reported that liquid and gaseous anhydrous sulfur dioxide corrodes tin to stannous hyposulfite, a straw-colored transparent compound which resembles a thiosulfate in its reactions.

Nachtigall and Schroder[134] stated that the corrosion product of tinned copper wire in an atmosphere with a trace of hydrogen sulfide is mostly copper sulfide and small amounts of tin sulfide.

Tin metal is slightly soluble in its fused salts, particularly when these are subjected to electrolysis. If the temperature of the melt be allowed to drop rapidly, the fused salt fogs as a result of the metal precipitating out of the solution in the form of minute drops, which give the melt a dark color.

The Effect of Oxygen

It has been well established that oxygen accelerates the corrosion of tin by acids. Jordis and Rosenhaupt[135] have shown that no oxidation of tin occurs at ordinary temperatures, but that the oxidation does begin at 100° C., taking place only at a slow rate. Below 200° C. tin is oxidized more slowly in moist than in dry oxygen, as a result of the formation of the partially protective coating. These findings are confirmed by Schmidt-Nielsen and Bjørgum,[136] who found that under otherwise identical conditions tin is more heavily corroded in a solution which contains free oxygen.

[131] Schutz, *Metallurgie*, **4**, 659–67 (1907).

[132] C. L. Mantell, and E. S. Lincoln, *Canadian Chem. Met.*, **11**, (2), 29–31 (1927).

[133] W. T. Cooke, *Australian Chem. Inst. J. & Proc.*, **6**, 58–60 (1939).

[134] G. Nachtigall, and H. Schroder, *Vom Wasser*, **10**, 197–200 (1935).

[135] Jordis, and Rosenhaupt, *Z. angew. Chem.*, **21**, 50–66 (1908); *Chem. Ztg.*, **32**, 19 (1908).

[136] S. Schmidt-Nielsen, and T. Bjørgum, *Kgl. Norske. Videnskab. Selskabs Forh.*, **13**, 99–102 (1940); *Chem. Zentr.*, **I**, 2194 (1942).

Whitman and Russell[137] have shown that the corrosion of tin by weak nonoxidizing acids is determined primarily by the oxygen which is dissolved in the liquid. They also showed that the presence of hydrogen exerts a retarding influence. The following data are taken from their paper:

METAL	ACID	CONCENTRATION (% BY WEIGHT)	AVERAGE PENETRATION PER YEAR			
			Under O_2		Under H_2	
			(cm)	(in)	(cm)	(in)
Tin	H_2SO_4	6	2.20	0.865	0.018	0 007
	HCl	6	5 69	2 24	0 030	0 012
	HNO_3	3	0 325	0.128	0 320	0.126
	$HC_2H_3O_2$	6	1.18	0.465	0 008	0.003

These figures indicate over a hundredfold increase with sulfuric, hydrochloric, and acetic acids in low concentrations when saturated with oxygen. In the case of nitric acid, the effect of dissolved oxygen is not important because its oxidizing action is overshadowed by that of the acid itself.

Derge and Markus[138] reported that oxygen induces passivity of tin in solutions of sodium carbonate and sodium bicarbonate.

It is interesting to note that one investigator ascribed the corrosive effect of aqueous solutions of sodium hydroxide and sodium carbonate largely to the oxygen dissolved in those solutions,[139] and asserted that concentrations of alkali and the temperature are of little importance. He proved his assertion by adding sodium sulfite, a reducing agent which decreases the corrosion of tin from 6.6 mg. per sq. dm. to 0.8 mg. per sq. dm. The same inhibitor is equally satisfactory for alcoholic solutions.

Corrosion of Bronzes and Their Restoration

Many bronzes have resisted the corrosion of ages, having been recovered from graves, bogs, beds of lakes and rivers, buried cities, and from the earth. The corrosion crusts of these are generally termed patina, of which there are several kinds: malachite, $CuCO_3 \cdot Cu(OH)_2$; atacamite, $CuCl_2 \cdot 3Cu(OH)_2$; and azurite, $2CuCO_3 \cdot Cu(OH)_2$, admixed with silver, stannic oxide, iron oxide, and cupric and lead chlorides. These patina are the result of surface attacks by waters which contain oxygen, carbon dioxide, and a greater or lesser percentage of salts. The soluble salts that are formed are removed by solution, while the bronzes become covered according to circumstances with an insoluble layer of either the carbonate or the oxide, whereby the form of the objects is preserved.

[137] W. G. Whitman, and R. P. Russell, *Ind. Eng. Chem.*, **17**, 348 (1925).

[138] G. Derge, and H. Markus, *Trans Am. Inst. Mining Met. Engrs., Inst. Metals Div.*, **143**, 198–208 (1941).

[139] G. Genin, *Lait*, **16**, 612–5 (1936).

Fink and Eldridge[140] have devoted considerable study to the restoration of antique bronzes. Metal corrosion is very strongly evidenced in the ancient bronzes found in public or private museums. Scientists have constantly endeavored, with questionable success, to restore articles so attacked to their original condition. Variation in the composition of bronzes is undoubtedly responsible for the lack of a scientific method for cleaning. A method which may be successful in restoring one bronze may have no satisfactory effect on another of like composition.

There are two classes of bronze corrosion: the green crust which coats bronze and other copper alloys that have lain buried in the ground, and the bronze disease, akin to the familiar tin pest. The red, green, or brown layers on ancient bronzes are composed chiefly of copper, lead, and tin minerals in the article which have been attacked by the nitrates and nitrides of the soil in which they have lain, forming a crust of copper oxychlorides and oxycarbonates, and tin oxide. A layer of copper oxide lies beneath this crust, often covering a core of metal. Sometimes the entire mass of bronze is converted to these compounds, leaving none of the original metal in the specimen. Moisture of the ground, whether clear water or water containing dissolved salts, is another important corroding agent. There are some evidences that former methods of removing corrosion crusts were drastic. Some samples show without doubt that strong chemicals such as mineral acids had been applied. Others carry the marks of a chisel, denoting the use of crude mechanical means Fink and Eldridge,[141] in their work along these lines, found that the details of design in the original bronze were exactly reproduced in the layer of copper oxide which lies beneath the outer crust. Their fundamental idea was to replace cathodically the metal that had gone into the crust, since corrosion is generally conceded to be an electrolytic reaction. Experiments determined that the use of a 2 per cent solution of caustic soda as the electrolyte is the safest for this purpose. The corroded object, without any preliminary cleaning, is hung in this bath as cathode, totally immersed. If the specimen is particularly soft as a result of attack, it is often necessary to wind it in several coils of fine annealed copper wire, or pack it in white sand. Anodes of iron, duriron, or platinum are hung on either side of the article. The container is generally a glass jar, although large tanks of heavy sheet iron or stoneware may be used, depending on the size of the bronze. Low current densities are preferred. The evolution of hydrogen at the cathode will alter the crust to a powdered or spongy copper. When the gas is freely given off, the object is removed from the bath and washed by soaking several times in warm water. The

[140] C. G. Fink, and C H Eldridge, "First Report on the Restoration of Ancient Bronzes and Other Alloys", New York, Metropolitan Museum of Art, 1925.

[141] *Ibid.*

film of reduced copper is brushed from the specimen, provided the latter were of hard metal under the corrosion crust, or is taken off by means of an acid dip if no core of metal is present. The exposed oxide surface, smooth and metallic, preserves all details of design.

Some gun metals have shown remarkable corrosion resistance, as is exemplified by the Swedish guns with the inscriptions 1535 and 1632 which were salvaged from the sea. The bronze had suffered very little corrosion action, although it had been submerged nearly 300 years.

Litvinovich[142] pointed out that the good resistance of bronzes towards sea water should not induce one to use bronze articles soldered with tin solder in contact with sea water, as tin in tin-bronze couples shows strong local corrosion after immersion in sea water.

The bronzes are attacked by the free halides. Alloys with at least 50 atomic percentage of tin are most resistant to the action of hydrochloric acid mixed with ferric chloride, while the alloys corresponding to 80 per cent atomic weight of copper have the greatest resistance to hydrochloric acid alone. Sulfuric acid attacks bronze much less vigorously than either copper or tin.

Claus and Goederitz[143] determined the corrosive effect of various chemicals upon German standard brasses. The tests consisted in shaking the alloy in the presence of air with the solutions at 20° C The loss of weight is given in grams per square meter per day in Table 49.

Eder and Kendol[144] noted that the resistance of a bronze towards sulfuric acid is determined by the copper content of the alloy and that the addition of tin reduces the resistance against corrosion. The addition of small quantities of zinc or lead is of little importance to the resistance against sulfuric acid.

It was reported by Gopius[145] that tin bronzes, phosphorus bronzes and bronzes containing 8.77 per cent aluminum and 3.91 per cent iron were resistant to 1 per cent sulfuric acid, but were corroded by a solution of 2 per cent sulfuric acid, 1 per cent copper sulfate, and 2 per cent ferrous and ferric sulfate Ammonia dissolves copper from bronzes containing 1 to 12 per cent tin, but is almost without action on bronze with 25 per cent tin. Nitric acid acts less vigorously on bronze than on copper. Certain of the bronzes become passive and resistant to corrosion as the result

[142] S. V. Litvinovich, *Proizvodstvenno-Tekh. Byull. Zaboda im. Ordzhonikidze*, 31-3 (Aug , 1939), *Khim. Referat Zhur* , No 10–11, 132-3 (1940).

[143] W. Claus, and A. H. F. Goederitz, "Gegossene Metalle und Legierungen," p. 204, 1933.

[144] T. Eder, and F. Kendol, *Korrosion u. Metallschutz*, **15**, 85–6 (1939).

[145] A. E. Gopius, *Trudy Tsentral Gosudarst. Nauch -Issledovatel. Inst., Sbornik Rabot Metalloobrabotke i Splavam, 1930–1934*, 270–88 (1937); *Chem. Zentr.*, **I**, 411–45 (1939).

of the formation of a film of stannic oxide. Oxygen causes an intensification of the corrosion of bronze, just as it does with pure tin.[146]

Chapman and Cuthbertson[147] examined the resistance of bronzes with 12 to 14 per cent tin against sea water under various conditions. They reported that the bronzes are most resistant to stagnant sea water, sea water through which air is bubbling and through which nitrogen is bubbling

TABLE 49 EFFECT OF VARIOUS CHEMICALS ON BRONZES*

MATERIAL		CONDITION	AMMONIA			HYDROCHLORIC ACID			SULFURIC ACID	
Copper (%)	Tin (%)		(3%)	(6%)	(10%)	(3%)	(5%)	(15%)	(5%)	(10%)
100	—	annealed	241	206	441	73	116	117	35	27
94	6	annealed	209	157	339	204	217	138	35	33
90	10	annealed	198	157	242	176	336	110	35	46
86	14	annealed	198	144	167	130	166	131	47	42
80	20	annealed	125	120	152	156	167	136	52	38
94	6	unannealed	228	165	246	173	163	95	29	33
90	10	unannealed	216	143	222	195	195	103	45	39
86	14	unannealed	199	143	194	155	171	96	42	34
80	20	unannealed	144	116	176	155	166	94	48	40

MATERIAL		POTASSIUM HYDROXIDE (3%)	SEA WATER	SODIUM SULFATE		SODIUM BISULFATE		CHLORINATED LIME	SODIUM CARBONATE (5%)
Copper (%)	Tin (%)			(2%)	(4%)	(2%)	(4%)		
100	—	After slight corrosion for the first two days a protective layer is formed	—	—	—	—	—	Behaves similar to Potassium Hydroxide	—
94	6		0 8	0 2	—	1 9	1 7		0.15
90	10		0 35	0 45	—	1 6	4 5		0 05
86	14		0 15	0 03	—	1 2	8 8		0.15
80	20		0 00	0 12	—	1 8	4 4		0 09
94	6		1.06	1 20	0 002	2 16	5 4		0 15
90	10		1 00	1 00	0 015	7 7	8.8		0 26
86	14		0 32	0 50	0 007	7 3	6 0		0 00
80	20		0 10	0 08	0 012	1.5	5 8		0 008

* W. Claus, and A H F. Goederitz, "Gegossene Metalle und Legierungen," p 204, 1933

In sea water which is stirred by oxygen, cupro-nickel proved to be more resistant than the bronzes.

Henderson and Roadhouse[148] reported that the corrosion of copper-nickel alloys used in the equipment of the dairy industry is reduced by the addition

[146] T. Eder, and F. Kendol, *Loc. cit.*

[147] J. Chapman, and J. W. Cuthbertson, *J. Soc Chem Ind*, **58**, 330–4 (1939)

[148] J. L. Henderson, and C. L. Roadhouse, *J. Dairy Sci.*, **23**, 215–20 (1940),

of tin to those alloys The reduction of corrosion also favorably influences the flavor of milk because less copper goes into solution.

Admiralty brass is an important alloy of tin despite its low content of tin [149] The function of the tin is to inhibit dezincification of the alloy. An addition of aluminum is useful in increasing the corrosion resistance of the alloy, as is annealing at 250 to 300° C. Sodium carbonate solutions of 1 to 5 per cent concentration cause corrosion even at 20° C. Five per cent solutions of hydrochloric acid and sulfuric acid did not cause any important corrosion of the alloy at 50 and 75° C over a period of 10 hours.

Bassett[150] described a copper alloy with 0.5 to 6.0 per cent tin with varying additions of silicon, zinc, and lead in which the tin components are said to impart corrosion resistance and to increase the structural strength of the alloy.

Bassett[151] also determined the loss of weight of a copper-tin alloy in various corroding liquids. The alloy contained 85.92 per cent copper, 4.98 per cent tin, and 4 18 per cent zinc. The loss in weight was determined in grams per square inch over a period of 96 hours

			grams
90%	H_2SO_4	Room temperature	0 152
50%	H_2SO_4	60° C	1 064
10%	Brine	Room temperature	0 008
10%	Brine	60° C	0 010
10%	Brine + 1% HCl	Room temperature	0 136
10%	Brine + 1% HCl	60° C	0 622
10%	Na_2SO_4	Room temperature	0 000
10%	Na_2SO_4 + 1% HCl	Room temperature	0 488

The American Society for Testing Materials conducted tests[152] over a long period of time on the atmospheric corrosion of various alloys under different conditions. Alloys of 92 per cent copper and 8 per cent tin, and 70 per cent copper, 29 per cent nickel and 1 per cent tin showed but slight corrosion over a 6-year period in industrial as well as in marine atmospheres.

Price[153] claimed that an alloy of 91 to 94 per cent copper, 2 to 3 per cent tin, and equal amounts of nickel and aluminum is resistant against acid and oxidation.

[149] I. S Katsen, *Korroziya i Bor'ba s Nei.*, **7**, No. 3, 14–22 (1941)

[150] W H Bassett (assignor to American Brass Co), *U S Patent 2,075,004* (Mar 30, 1937)

[151] W. H. Bassett, *Nat'l Elec Light Assoc. Bull* , **17**, 275-8 (1930)

[152] C. W. Borgmann, *Proc Am Soc Testing Materials*, **39**, 674–84 (1939)

[153] W. P. Price (assignor to Scoville Mfg Co.), *U S Patent 2,085,544* (June 29, 1937).

Corrosion of Alloys Other Than Bronze

Alloys of lead and tin are in some cases resistant to corrosion where tin alone is not satisfactory. As reported by Ivanova and Fedorchenko,[154] tin-coated copper apparatus for the production of liquid nitrogen and hydrogen is not suitable, inasmuch as during the repeated heating and cooling of the apparatus the tin is converted into gray tin and the surface may be destroyed. This difficulty is eliminated by replacing tin with an alloy of 50 per cent tin and 50 per cent lead.

In lead alloy coatings used for fire extinguishers, tin content is of great importance. Hewlett[155] stated that lead-tin alloys show increasing corrosion with a decrease in tin content. Drits[156] found that lead-tin alloys are more corrosion-resistant than pure tin for locomotive safety plugs.

The corrosion resistance of tin-alloy bearings is of great importance for various purposes.[157] Tin-base Babbitt metal contains 89 per cent tin, 7.5 per cent antimony, and 3.5 per cent copper, and is of eminent importance for bearings used in motor vehicles. This alloy has been found to be completely resistant to severely deteriorated and decomposed lubricants. Lead-base Babbitt metals with 5 to 10 per cent tin are somewhat less resistant to deteriorated lubricants, but are still quite satisfactory.

According to Walde,[158] a noncorrosive lead alloy is said to contain 4.75 to 6 per cent tin, 4.5 to 5.75 per cent antimony and small amounts of copper and arsenic.

Hoar[159] investigated the corrosion of pewter alloys. He found that soft water tarnishes the alloy and that hard water forms a protective film. If, however, a chalky deposit is formed, corrosion may occur at the water line.

Bryan[160] stated that an addition of 0.5 per cent antimony or 0.4 per cent bismuth to tin gave the best resistance to corrosion by citric acid of 0.5 per cent concentration.

An excess of tin content has been found[161] to be of deleterious effect when alloyed with zinc which is to be used for the hot galvanization of livestock watering tanks.

Certain ternary alloys of magnesium and tin[162] showed high corrosion resistance towards sodium chloride solutions such as:

[154] A. Ivanova, and A. Fedorchenko, *J. Chem Ind.* (*U S S.R*), **18**, No. 15–16, 40–3 (1941).

[155] W. L. Hewlett, *Chemistry & Industry*, **54**, 1094–5 (1935).

[156] M Drits, *Novosti Tekhniki*, No. 4, 36–7 (1937).

[157] H. H. Zuidema, *Oil Gas J.*, **44**, No. 41, 100–8, No. 42, 151–8, No. 43, 66–72 (1946).

[158] A. H. Walde, *U. S Patent 2,252,104* (Aug. 12, 1941)

[159] T. P. Hoar, *J. Inst Metals*, **55**, 135–147 (1934).

[160] J. M. Bryan, *Dept. Sci. Ind. Research* (*Brit.*) *Food Invest. Board, 1935*, 163–4 (1936).

[161] G. C. Bartells, *J. Am. Zinc Inst.*, **21**, 99–118 (1940).

[162] S. Morioka, *Kinzoku-no-Kenkyu*, **12**, 322–56 (1935).

Mg-Zn (1-3%)—Sn (2-8%)
Mg-Sn (more than 3%)—Cd (1-3%)
Mg-Sn (more than 4%)—Pb (1-6%)
Mg-Sn (2-3%)—Sb (less than 0 8%)

Good corrosion resistance is claimed for magnesium alloys[163] with 1 to 15 per cent tin and varying quantities of aluminum, cadmium, and bismuth. Alloys of tin, silver, and mercury are corroded by 0.1 *N* citric acid, 0.1 *N* sodium hydroxide, and 0.1 *N* sodium chloride solutions.[164]

Assmann[165] described an alloy which is resistant to corrosion using 70 to 99.4 per cent silver, 20 per cent tin, and various other metals in amounts ranging from 0.3 to 29.7 per cent.

Schulz and Carius[166] claimed that an alloy of ferrous metal with 0 05 to 5.0 per cent tin, 0.05 to 5.0 per cent arsenic or antimony, and varying small amounts of copper, titanium, and vanadium, is corrosion-resistant to sea water.

Atmospheric Corrosion of Tin

Atmospheric corrosion is the composite effect of various influences, largely that of humidity of the air and of the components of air—oxygen, nitrogen and carbon dioxide. To this is added, from specific localities, sulfur gases and other by-products of industrial activity.

The American Society for Testing Materials conducted a number of tests on tin and other metals under conditions which were considered representative of the most important atmospheric conditions to which the metals may be subjected.[167] The samples of tin which were exposed to the wet oceanic air, fog, precipitation, and some salt spray for about a year showed a considerable loss of tensile strength and an even greater loss in elongation. Industrial atmospheres cause the formation of light-gray corrosion products. The tests were continued for 10 years, and all through this period tin and tin bronzes showed a slight but steady increase of weight, indicating a continuous corrosion. The behavior of the samples was uniform throughout this period. The loss of weight of the sample is no valid criterion for this type of test because there is no possibility of the removal of the corrosion product by the liquids, which in most other tests remove these products from the samples. It is therefore necessary to remove the corrosion prod-

[163] A. Burkhardt, and R. Knabe, (assignors to Georg von Giesche's Erben) *U. S. Patent 2,226,549* (Dec. 31, 1941).

[164] N. Brecht-Bergen, *Z. Elektrochem.*, **39**, 927–35 (1933).

[165] P. Assmann, *German Patent* **496,348** (July 30, 1926).

[166] H. Schulz, and C Carius, (assignors to Vereinigte Stahlwerke A.-G.,) *U. S. Patent 2,053,846* (Sept 8, 1936).

[167] W. H. Finkeldey, *et. al.*, *Proc. Am. Soc. Testing Materials*, **33**, Pt. 1, 234 (1933); **35**, Pt. 1, 142 (1935); **38**, Pt. 1, 194 (1938), **44**, 224–32 (1944); L. J. Gorman, *et. al.*, *Proc. Am. Soc. Testing Materials*, **39**, 247–55 (1939).

ucts by chemical means which may cause a certain amount of additional corrosion.[168]

Kenworthy[169] investigated the corrosion of tin and tin alloys having a high tin content. The experiments were conducted indoors, outdoors with the samples shielded from rain, and out of doors with the samples unshielded from rain He found that in an indoor atmosphere, tin and its alloys were superior to copper, zinc, and cadmium, and that the weight increase of the sample was uniform with the exception of the first 3 to 4 days. In sheltered outdoor exposure, the samples showed superiority to nickel, but were inferior to copper. In complete outdoor exposure, tin was superior to all comparison metals in corrosion resistance and its mechanical properties were less affected than were those of cadmium, but slightly more than those of copper

Tin and Its Alloys as Materials of Construction

A summary of the applications of tin in industry as a material to resist corrosion shows its marked utility in connection with the preparation of distilled water where the metal is the preferred material of construction; in apparatus in which food products are made, stored, or preserved, such as tinned kettles and tin cans; in the collection, transportation, and distribution of milk, and in the manufacture and use particularly of the tin-copper alloys, such as the sea-water bronzes, the gun metals, and phosphor bronze. Phosphor bronze resists the corrosion of sea water better than copper, and mine waters better than iron and steel. Many of the so-called hydraulic or high-pressure bronzes are markedly resistant to the corrosive action of steam and condenser water. The use of Admiralty metal and condenser tubing of tin-copper alloys to resist severe corrosion is too well-known to require comment.

[168] C. W Borgmann, *Proc Am Soc Testing Materials*, **39**, 674–84 (1939)
[169] L Kenworthy, *Trans Faraday Soc* , **31**, 1331–45 (1935)

Chapter 18

Corrosion of Tin Plate by Food Products

The problem of corrosion of tin cans by food products which are packed, stored or canned in these containers is complicated by the large number of factors entering into the situation Tin cans are made of tin plate It is understood that it is an exceedingly difficult matter to form a perfectly continuous coating of tin over the iron base metal Hoare[1] stated that tin plate with a coating of 1 lb of tin per base box has a porosity of 8,000 pores per 100 sq cm., 300 pores at 3 lb of tin per base box, and 2 pores at 15 lb. of tin per base box.

Chalmers' rule stipulates that no normal pore can be formed unless the site of the potential pore has a diameter which is greater than 0 7 times the thickness of the coating This porosity can be reduced by the electrodeposition of a thin layer of tin on top of the layer of hot-dipped tin [2]

It is commonly conceded that when tin plate is exposed to atmospheric influence, corrosion takes place most rapidly at those points where iron is exposed. Small electrolytic cells are set up, and the corrosion of the iron plate is actually accelerated by the presence of the tin When in contact with an electrolyte, iron and tin will function as a battery, iron being the anode and tin the cathode The tendency will, therefore, be for the iron either to oxidize or to disintegrate and for corrosion to be accelerated Corrosion can proceed so far as to form holes in the tin plate at those points at which iron has been uncovered

Corrosion of tin-plate containers used for food products is of three different types· first, "discoloration" which results in tarnishing, darkening or blackening the bright metal surface of the inside of the container, second, "perforation," which results in the formation of holes in the cans to the detriment and spoilage of the enclosed food products (it will be shown that perforation is the result of electrolytic action), and third, "solution," the result of chemical action of the food product constituents on the metal of the container. The action does not usually produce discoloration but makes itself evident in other ways One of the most usual is termed "etching," which is descriptive of the effect. It is not meant by this classification that these factors are entirely separate and do not occur to-

[1] W E Hoare, *J Iron Steel Inst (London)*, **136**, No 2, 99–130 (1937)
[2] T. W. Jones, *Soc Chem Ind , Chem Eng Group, Proc ,* **22**, 46–64 (1940)

gether, but they may occur separately without relation to each other, if conditions are favorable; or they may supplement each other or occur progressively.

McKay and Worthington[3] stated that, from the distinctly chemical solution viewpoint, work by a large number of experimenters indicated corrosion rates of from 0.01 to 1.0 mg. per sq. dm. per day. In this case an evenly distributed tin coating 0.0001 in. thick (1.7 lb. per base box) would, if the attack were evenly distributed, disappear in one-half year at the rate of 1 mg per sq. dm. per day or in 100 years at 0.01 mg. per sq. dm. per day.

The coating of tin on tin plate is very thin. For a coating in tin-plate trade terms of 1 lb. of tin per base box (112 sheets each 14 in. x 20 in. or 31,360 sq. in. x 2 sides equals 62,720 sq. in.), the thickness is 0.000059 in., and for 2 lb. per base box of the order of 0 00012 in. Electrolytic tin plate of $\frac{1}{2}$ lb. per base box might have tin coatings of the order of 0 00003 in. thick. An average tin coating before World War II was 1.5 lb. per base box or of the order of 0 000085 in. thick.

The rate of disappearance is greatly increased by electrochemical action.

Tin-can corrosion may be considered the effect of the relative noncorrosion of tin in the absence of, and corrosion in the presence of oxidizers, while iron is corroded under both conditions, and as the effect of the electrochemical action resulting from the cathodic relation of iron to tin under the conditions of the inside of a packaged can. The problem, however, is far more complex. Factors such as oxidizers, which are constituents of foods, methods of packing either in salt or sugar solutions, constituents of the foods, electrochemical effects, acidity, temperature, and inhibitors, as well as accelerators all play a part.

Discoloration

Discoloration is largely the result of chemical action of the food-product constituents, or resulting products of these, on the metals of the container. If any electrolytic action does occur, it is of secondary importance.

It is well known that many food products such as the legumes (corn, peas, beans, etc.) contain sulfoproteins. These materials, as a result of the processing of the foods in canning, may break down and produce hydrogen sulfide or related compounds. Iron is affected by hydrogen sulfide, with the formation of black iron sulfide. Tin also reacts with hydrogen sulfide, with the formation of black or brownish-black stannous sulfide. With a small amount of sulfides, the attack on tin may be evident only as a tarnish whose color may vary from blue to brownish black. The iron sulfide would be more readily formed, the iron being attacked more readily than the tin.

Adam and Dickinson[4] remarked that *rutabaga* "swedes" (a yellow species

[3] R. J. McKay, and R. Worthington, "Corrosion Resistance of Metals and Alloys," *A.C.S. Monograph No. 71*, New York, Reinhold Publishing Corp., 1936.

of turnips) cause the formation of a layer of tin sulfide which acts as a protective film for the tin, but increases the corrosion of the iron base.

In the case of food products, it is easy to observe the formation of "can black" on the covers of tin-can containers Where iron has been exposed, the black iron sulfide forms readily. The attack on tin is less rapid Chemical analysis confirms the statement that can black is iron sulfide. The tarnish on tin where iron has not been exposed is stannous sulfide. This has been confirmed both by microscopic examination, duplication of similar tarnishes on pure tin by the action of dilute hydrogen sulfide solution, and by chemical analysis. Duplication was done on both electrolytic tin and commercial tin sheet. The samples were matched microscopically. There is no doubt that to a large extent discoloration is the result of sulfide formation.

It is possible to prevent sulfide stains on tin cans by passivation. Kerr[5] recommended the immersion of the tin plate in a hot solution of chromic acid or in a hot alkaline solution of sodium chromate and phosphate. Satisfactory results were obtained by dipping the plate for 15 min. at 90° C. in a solution containing 100 grams of trisodium phosphate and 20 grams of potassium chromate per liter. This film not only prevented sulfide stains, but it also acted to some degree as a protective agent for artificial coloring and protected the tin plate from rust at the discontinuities of the tin coating. Kefford and Lynch[6] suggested that this coating is particularly suitable for the canning of corned beef, sausages, crayfish, salmon, peas, asparagus, and corn. It did not give protection against tuna fish or onions.

Kefford and Lynch also studied a wide range of methods for the prevention of black staining of tin plate. They experimented with a lacquer containing zinc oxide, an anodic oxide film of alkali phosphates, and an electrodeposited lacquer from an emulsion of various soluble alkali salts in a sodium aluminate solution.

In some of the large number of cans examined in discoloration studies by Mantell and Lincoln,[7] there was a tarnish which was not stannous sulfide but looked like stannous oxide. Other sections of the can showed some iron sulfide tarnish in an adherent layer, usually along the intercrystalline boundary. In this connection, the work of Chapman[8] on the action of organic acids on tin is of interest. In the absence of air, tin is not oxidized by such acids as tartaric, but in the presence of air oxidation of the metal takes place at the surface of the solution, the oxides of tin and stannous tartrate being formed. With a restricted amount of oxygen the corrosion

[4] W. B. Adam, and D. Dickinson, *J. Iron Steel Inst. (London)*, **152**, 195–205 (1945).
[5] R. Kerr, *J. Soc Chem Ind.*, **59**, 259–65 (1940).
[6] J F. Kefford, and L. J. Lynch, *J. Council Sci. Ind. Research*, **14**, 16–24 (1941).
[7] C. L. Mantell, and E. S. Lincoln, *Can. Chem. Met.*, **11**, 30 (1927)
[8] Chapman, *J. Chem. Soc.*, **103**, 775 (1913).

product first formed is stannous oxide. The stannous oxide may be gradually oxidized further with the production of a brown colloidal material. This substance on heating may be converted to the bluish-white hydrated stannic oxide. DeFoud[9] reported that dilute oxalic, tartaric, citric, malic, acetic, and lactic acids all attack the tin coatings of cans rapidly in the air; at a slower rate in the presence of restricted amounts of air; but scarcely at all in vacuum or in an atmosphere of carbon dioxide. All of the acids oxidize more than their equivalent of tin, the main product being stannous oxide or stannous hydroxide It is fairly adherent to the surface of the metal Oxygen has an accelerating action upon the corrosive effect of most reagents on tin

Perforation

Many foods are preserved in saline solutions Sodium chloride by itself does not corrode tin [10] It would not be expected that the saline solutions or strong electrolytes would cause perforation troubles in cans, but that they might have discoloration effects

If a pair of electrodes, one of iron and the other of tin metal, is immersed in the contents of a tin can containing food products preserved in saline solutions, an e.m.f. will be generated. The potential is very small and is only indicated on a sensitive millivoltmeter. The remarkable happening is that the voltage will rise to a peak value, fade off, drop to zero and then build up to a peak value in the reverse direction. Mantell and Lincoln[11] observed that the phenomenon of reversal of potential occurs only with those foods preserved in strong electrolytes. The term "strong electrolytes" is used from the viewpoint of the theory of electrolytic dissociation. The fact that potentials are reversed is indicative that the iron has been passivated, and instead of being as usual, less noble than tin, becomes more noble than tin. Instead of functioning in an electrolyte as anode, its position is changed to that of cathode. The manner of passivation of the iron is relatively unimportant; it might be caused by a gaseous film, or a thin oxide layer, formed as a result of electrolytic action, or even as a result of chemical action. Examples of foods which show the phenomenon of reversed potentials are corn, peas and beans. These do not have perforation effects but all cause discoloration when canned. Morris and Bryan[12] stated that the phenomenon of reversal of potential occurs also with comparatively weak electrolytes such as an 0.5 per cent aqueous solution of citric acid. The iron was at first anodic and later turned cathodic.

In contradistinction to those food products which are put up in strong electrolytes, most fruits, berries, etc., are put in sugar solutions. These

[9] DeFoud, *Pharm Weekblad*, **55**, 498 *et al* (1918)
[10] Hale, and Foster, *J Soc Chem Ind* , **34**, 464 (1915)
[11] C L Mantell, and E. S Lincoln, *Can Chem Met* , **11**, 30 (1927)
[12] T. N. Morris, and J. M. Bryan, *Food Manuf.*, **6**, No. 4, 100–2 (1931)

weak electrolytes are of low conductivity and high resistance, while the saline solutions are of high conductivity and low resistance. The effect of sugars on tin plate has been extensively studied.[13] Sucrose is a good inhibitor of corrosion and its effect increases with increasing concentration. This probably results from the decrease in the solubility of air as solutions become more concentrated. Raw beet sugar has the greatest anticorrosive effect of all the materials mentioned The effect of sugar, however, is not uniform. While it inhibits the corrosion of tin satisfactorily, it reduces the corrosion of iron slightly and even causes a decrease of the anticorrosive action of tin salts toward iron. The presence of 15 parts of sulfur dioxide in a million neutralizes the anticorrosive effect of sugars. Sugars cause an

TABLE 50 TIN PICK-UP IN THE CAN*

	PPM			
	1½ to 5 Months		10½ to 13 Months	
	(max)	(min)	(max)	(min)
String beans	97	75	220	154
Corn	13	3	—	—
Peas	32	9	26	12
Pumpkin	82	31	476	44
Tomatoes	175	42	148	58
Apples	166	34	203	27

* T N Morris, and J M Bryan, "The Corrosion of the Tin-Plate Container by Food Products," *Dept Sci Ind Research (Brit) Food Invest , Special Rept* , No **40,** (1931)

increased hydrogen swell of the canned goods They have proved to be satisfactory inhibitors of corrosion in canned greengages, cherries, loganberries, and grapefruit. They have but little effect on canned dried prunes There is no reversal as shown on a millivoltmeter with iron and tin electrodes. As a general rule, those foods which do not show a reversal of potential do not give discoloration troubles, but do give perforation difficulties. If there is no reversal of potential, the iron has not been passivated, and at exposed spots the iron will be the anode, tin the cathode, and both will be in contact with the electrolyte. Galvanic action will be set up, the anodic iron will disintegrate, and, if carried far enough, will cause perforation of the can.

Kohman and Sanborn[14] conducted experiments to determine the mechanism of the corrosion of tin and iron, both when in contact and when not in

[13] T N Morris, *Dept Sci Ind Research (Brit) Rept Food Invest Board, 932,1* 170–1 (1933), *Ibid., 1935*, 165–9 (1936), T N Morris, and J M Bryan, *Dept Sci. Ind Research (Brit.) Food Invest , Special Rept* , No. 44 (1936)

[14] E. F. Kohman, and N. H. Sanborn, *Ind. Eng Chem.*, **20,** 76–9 (1928).

contact, in fruits, and the relation of the results to the electrochemical theory of corrosion. They found that in a number of fruits tin is anodic to iron. Although not all fruits were studied, the data indicate that this

TABLE 51. ATTACK ON TIN AND IRON IN ABSENCE OF AIR

	(MG. PER SQ. DM. PER DAY)	
	Iron	Tin
Fruit Acids:		
Citric ...	5.1	0.06
Tartaric.	3.3	0.04
Malic .	4.0	0.06
Oxalic	6.1	0.17
Fruits:		
Grapefruit	1.8	0.08
Pineapple	1 5	0.11
Strawberries	2.4	0.23
Blackberries	3.4	0 6
Rhubarb	1.3	0.32
Black sweet cherries	3 4	0.26
Red sour cherries	4 5	0.11
Foods:		
Apple		
Delicious	1.06	0.019
Paragon	1 7	0.14
Crab	0 87	0.36
Winesap	1 9	0 048
Sweet Non-such	1 4	0 071
Beet		
Detroit dark red	4 0	1 08
Blackberry		
Oregon evergreen	6.2	0.22
Cherry		
Bauman May	1.1	0.071
St. Medard	3 3	0.074
Napoleon	2 5	0.11
Montmorency	3.7	0 095
Blackheart	1 4	0 12
Sand	2 0	0.103
Cranberry	3 9	0 32
Dewberry	3 3	0.30
Elderberry	1 4	0 32
Grape		
Empire State ...	1.08	0.16
Monito	0.86	0.24
Groff ...	1.4	0 15
Peach		
Hiley.	0.96	0.017
Elberta.....	2.0	0.035

TABLE 51—*Continued*

	(MG. PER SQ. DM PER DAY)	
	Iron	Tin
Foods—Continued:		
Raspberry		
Ranere . . .	2.8	0.096
Rhubarb ..	3.0	2.1
Strawberry		
Howard 17 . .	2.1	0 22
Tomato		
Marglobe .	2 1	0.061

is a rather general condition in canned fruits. Many of the facts which did not conform to the older idea that tin is cathodic to iron are explained in accordance with these findings. They likewise made electrical measurements which bear out the results of the corrosion tests that tin is anodic to iron. The nature of corrosion in fruits differs from that in solutions of the fruit acids. This is in harmony with commercial experience.

For the sake of clarity at this point it is assumed that none of the constituents of the food products in the can can chemically dissolve tin. This condition may not exist as such in any actual specific food product. In order to avoid electrolytic action and resultant perforation, it would be necessary to have only one metal exposed to the action of the contents of the can. If there are two dissimilar metals there will be electrolytic corrosion. In the case of tin cans, the only manner by which we can obtain the condition that only one metal is exposed to the action of the electrolyte is to have the steel surface of the base metal completely covered by tin metal.

Tin which might be contained in foods as the result of solution of the tin by the food in the can, is physiologically inactive.

Some indications of the quantity of tin in parts per million for various foods and periods of storage in the can are given in Table 50.[15]

Block tin, and therefore a tin surface on a tin can, from the viewpoint of chemical solution is resistant to corrosion in neutral and mildly acid solutions in the absence of air. This is often explained as the result of hydrogen polarization, there being no oxygen or oxidizer in the absence of air to remove the hydrogen and cause the reaction of tin solution to continue.

Culpepper and Moon[16] studied the corrosion of tin and iron in the absence of air and their results in milligrams per square decimeter per day are given in Table 51. Kohman and Sanborn's results[17] for 34-day tests on acid

[15] T. N. Morris, and J. M. Bryan, *Dept. Sci. Research (Brit.) Food Invest., Special Rept.*, No. 40 (1931).

[16] C. W. Culpepper, and H. H. Moon, *Canner*, **68**, No. 9, 13 (1929).

[17] E. F. Kohman, and N. H. Sanborn, *Ind. Eng. Chem.*, **20**, 76–9 (1928).

foods treated by boiling to exhaust the air are given in the same table. Culpepper and Moon[18] also studied the relative attack of foods in air-free conditions on tin and iron for 12 months. These results are also tabulated with those mentioned above.

The work of Kohman in his studies on perforation in the case of Bing cherries, strawberries, and loganberries, showed that oxygen accelerates corrosion, but with the removal of the oxygen perforation is not prevented. Excessive extension of the exhaust with resultant air removal does not prevent perforation Even from Kohman's work the basic explanation for perforation can be seen to be electrolytic. Kohman offered the explanation for the lack of hydrogen production in cans of those fruits which develop holes, on the basis of depolarizers or oxidizing agents which convert the hydrogen to water.

It has been stated that the greening of vegetables with copper sulfate prior to canning is a reason for perforation of tin plate.[19] The copper attacks the tin plate, causing exposed pin-point areas of iron which are subject to the usual electrolytic corrosion. This process is initiated at as low a concentration of copper sulfate as 0.02 per cent.

In the case of threatening perforation, it is important to use a steel base for the tin plate which shows as much resistance as possible to corrosion.[20] It was found that a steel base with a maximum of 0.015 per cent phosphorus, 0.06 per cent copper, and a trace of silicon was not suitable. The content of manganese, carbon, and sulfur was of no importance. McLeod[21] reported on the other hand that a copper content up to 0.2 per cent is usually beneficial, and that a minor content of phosphorus has an anticorrosive effect Jones[22] stated that the steel plate should have a low sulfur content and that the copper content should be at least twice the sulfur content.

The substitution of nickel-tin alloys for tin in cans was recommended by Copson and Wesley[23] on account of the galvanic behavior of the product It is possible to use platings of considerably less weight than a customary tin plating. The alloy coatings were anodic to steel in dried prunes in sirup, sauerkraut, tomatoes, and peas and slightly cathodic in the case of spinach. The tin content of the alloy helps to overcome the noble potential of pure nickel and permits taking advantage of the anticorrosive effect of tin compounds in the corrosion of the steel at pin-point pores, bends, and other defects of the coating

[18] C W Culpepper, and H H Moon, *Op cit*, 17–21

[19] P. Nehring, and E Nehring, *Konserven-Ind*, **18**, 199–201, 214–5 (1931)

[20] R R Hartwell, *Am Soc Metals*, "Symposium on Surface Treatment of Metals," pp 69–102, Am Soc Metals, 1941

[21] A McLeod, *Canning Age*, **21**, 501–3, 557–8 (1940)

[22] T W Jones, *Soc Chem. Ind., Chem. Eng. Group, Proc*, **22**, 46–64 (1940).

[23] H R. Copson, and W A. Wesley, *Trans Electrochem. Soc*, **84**, 211–26 (1943)

Solution

Absence of chemical action on the tin of the tin plate by the contents of a can is unusual It is quite usual to have chemical action on the tin by organic acids along with or preceding electrolytic action. The corrosion of tin by organic acids has been extensively studied by workers who were experimenting without reference to the canning industry. Citric acid, a common fruit acid, definitely etches tin, the attack being most pronounced along the intercrystalline boundaries. Malic acid, occurring in apples, readily attacks tin in the presence of air. With lessened amounts of air the attack will not proceed as rapidly. Acetic acid attacks tin and its alloys While particularly evident in sour milk, lactic acid is also found in other foods.

Morris[24] stated that the hydroxy acids such as malic, tartaric, and lactic acid corrode tin plate at a uniform rate between 25 and 75° C., whereas nonhydroxy acids such as acetic or succinic acid do not corrode. In 0.5 per cent citric acid with sodium citrate as a buffer, the corrosion of tin plate is greatest at a pH of about 3. At this pH a maximum development of hydrogen also occurs. The effect of the citric acid is not uniform, however Under certain conditions it may act as an inhibitor of the corrosion of tin plate Morris[25] also reported that, on the whole, those canned fruits which cause a high corrosion of tin cause low corrosion of iron and vice versa. There also seems to be a correlation between discoloration of canned fruit and corrosion

Shalaikin[26] noted that potassium nitrite causes depolarization of the corrosion of tin plate in organic acid, and that the velocity of the corrosion depends upon the concentration of potassium nitrite.

Several authors[27] directed attention to the fact that tin cans corrode to the greatest extent and have the strongest hydrogen swell at low acidities.

With the exception of canned clams, all canned foods show pH values lower than 7, that is, they are acid in reaction. While the effects of the different foods show slight variations, the general results are the same. The etching by peaches is somewhat small, but the detinning action of spinach is quite severe. The chemical attacks of the acids in spinach on the tin of tin cans has been reported a number of times in the German and American literature The action of pumpkin and squash is quite the same as that of spinach. The constituents of rhubarb, grapefruit, and apples markedly attack tin plate It would be expected from what is known of

[24] T. N Morris, *Dept Sci Ind Research (Brit) Rept , Food Invest Board, 1929*, 86–94 (1930)

[25] T N. Morris, *Ibid , 1934*, 180–3 (1935)

[26] F P Shalaikin, *J Applied Chem (U.S.S R)*, **13**, 1578–81 (1940).

[27] T N Morris, *Canning Trade*, **56**, No 35, 13–6 (1934); E G Lipsett, *Can. Chem. Met* , **17**, 171–2, 174 (1933)

the effects of vegetable acids that the detinning action of cider and berries would be severe in a relative sense. This is found to be the case.

The strong corrosive effect of rhubarb and eggplant on tin plate is explained by the presence of nitrate which causes the oxidation of tin to stannous oxide which is then dissolved in the organic acids.[28] Long sterilization at high temperature is said to increase the corrosion.

Canned beets[29] have a sufficiently strong corrosive effect to cause a hydrogen swell after two years of storage. Canned stringless and runner beans show the same effect in three to four years. Beans in tomato sauce and carrots cause severe corrosion of tin cans which may progress to the point of stripping under the influence of oxidizing agents.

The anthocyanins and tanning substances[30] have a corrosive effect upon tin plate. Tests with anthocyanin of red beets in 0.1 *N* sulfuric acid showed that the anthocyanin increases the corrosion. Tannin solution corrodes tin, but to a lesser degree than iron or lead. Its corrosive effect cannot be inhibited by gelatin or agar-agar.

Florentin[31] reported that the tin which was dissolved in cans of fish preserved in vinegar is largely fixed by the fish rather than the liquid. This condition causes digestive disturbances. However, other authors[32] pointed out that the amounts of tin which are brought into solution by the corrosion of tin cans generally have no harmful effect upon the consumer.

Perforation troubles are usually associated with those food products containing constituents which chemically attack tin. With a completely tinned sheet free from pinholes and exposed iron in contact with those foods, no electrolytic action would be expected at first, but chemical attack would be anticipated If the chemical action continues long enough, sufficient tin will eventually dissolve to expose the iron of the base metal. When this happens, two metals will again be in contact with the electrolyte, with the iron as anode and the tin the cathode. If there are no neutralizing factors (that is, if the attacking constituent is neither consumed nor brought to equilibrium), no matter how heavy a coating of tin is put on tin cans, perforation will eventually occur.

Prucha[33] determined the effect of sterilizing and washing agents on tin plate, tin, and tinned copper.

[28] K. S. Grzhivo, and K I. Novikova, *Konservnaya Prom.*, No. 5, 10–5 (1936).

[29] Univ. Bristol, *Fruit Vegetable Preservation Research Sta , Campden, Ann. Rept ,* 37–45 (1944)

[30] A. R. Vetchinkin, *Zapiski Saratov. Planovogo Inst , Voprosy Ispol'zovaniya Mestnykh Resursov*, No 7, 136–68 (1940); *Khim. Referat. Zhur.*, **4**, No. 2, 116 (1941).

[31] D. Florentin, *Ann fals ,* **26**, 594–7 (1933)

[32] C Dawson, *Australian Chem. Inst. J. & Proc ,* **5**, 427–34 (1938); T. W. Jones, *Soc Chem Ind , Chem. Eng. Group, Proc.* **22**, 46–64 (1940).

[33] M. J. Prucha, *Milk Dealer*, **19**, No. 5, 104–10 (1930); *J. Inst. Metals*, **44**, 545 (1930).

Corrosion Prevention

To return to the subject of discoloration. This has been shown to be largely caused by the action of sulfides and sulfo-compounds. Iron and tin sulfides are both black—this is an objectionable color in food products. Many metals form white sulfides, an example of which is zinc. It is understood that before the advent of the so-called "sanitary" can, the use of zinc chloride flux for soldering the cans effectively prevented discoloration. Paper liners in the cans of food products which discolor badly have been effectively used, the paper containing zinc salts.

Enameled or lacquered cans have been used, the additional coating being made on tin plate. It is no less difficult to make a perfectly continuous coating of enamel or lacquer on a commercial scale on tin plate than it is to make a perfectly continuous coating of tin on the base steel plate. Chemical attack on the tin is usual in the case of those foods which perforate. If the enameled or lacquered coating on the tin plate is not perfectly continuous, chemical action of the constituents of the food product, instead of being spread over the whole area of the can, will be localized at those points where the coating is not continuous and the tin plate is exposed. With localized action, corrosion will be accelerated and perforation will result more rapidly than in an unenameled can. Commercial experience has shown that enameled cans perforate more readily than those which are not enameled.

According to Morris,[34] these difficulties are eliminated when the tin plate is lacquered with three coats of lacquer, of which the last one applied is a quick-stoving lacquer. Corrosion can also be prevented by the addition of gelatin or other colloid materials to the canned food, but the anticorrosive effect of gelatin is lowered by a decrease in the acidity of the canned material.[35]

Lueck and Brighton[36] reported that enameled electrolytic tin cans with salmon, shrimp, and tuna fish give an even longer shelf life than hot-dipped plate cans with 1.25 lb. of tin per base box. The application of an additional stripe of enamel over the vertical seam of inside enameled cans for red fruits and berries seems to increase the shelf life of the can.

Wartime conditions caused a decrease in tin supplies. An investigation was therefore made for the use of tin cans with less than 1.5 lb. of tin per base box.[37] Electrolytic tin-plated cans showed localized corrosion and pitting and proved to be unsuitable for many purposes such as packing of

[34] T. N. Morris, *Dept. Sci Ind. Research (Brit.) Food Invest. Board, 1935*, 169–70 (1936).

[35] T. N. Morris and J. M. Bryan, *Dept Sci. Ind. Research (Brit.) Food Invest., Special Rept.*, No 44 (1936).

[36] R. H. Lueck, and K. W. Brighton, *Can. Food Packer*, **15**, No. 6, 17–23; No. 7, 18–21, 23, 25, 29 (1944).

[37] *Ibid.*

pears, peaches, apricots, apples, and fruit cocktail, inasmuch as the fruit discolored. The combination of plain bodies with electrolytic enameled ends has possibilities because the tin which is dissolved from the plain body of the can has a corrosion-inhibiting effect

Whether the electroplating is done in an acid or alkaline medium is important. Throughout the tests it was observed that cans made from alkaline plate gave better results than cans made in an acid-plating bath This difference in behavior, however, does not show up after the enameling of the plate. It can only be observed on plain cans

Enameled cans of 0 5 per cent electrolytic tin plate were found suitable for canned food containing more than 20 per cent moisture [38] It is considered possible that an electrolytic tin plate with 0 75 to 1.00 per cent tin will be developed which can be used without an enamel coating.

Electrolytic tin plate on a copper base showed the highest resistance of all electrolytic copper platings in an atmospheric exposure test of a year's duration in the vicinity of a mineral oil refinery on the coast of Texas.[39]

There seems to be a definite field for containers in which tin is absent, that is, a container made of sheet iron with an enameled surface. If the enameled coating on the steel plate were not continuous, the exposed iron would be chemically attacked and rusted. The commercial feasibility of making such a container with a minimum of uncovered iron spots is an open question. How much rusting would occur in cans made of enameled sheet steel or how objectionable this rusting would be is not known. A large number of tinless cans have been used for fish products. The cans stood up very well. The food products were preserved in better condition than in ordinary cans.

Bonderized (phosphate-coated) steel plate performs very satisfactorily as a substitute for tin plate[40] in the canning of noncorrosive vegetables with a pH above 5.5, for example, peas, corn, and lima beans It may also be used for ends in cans with a tin-plate body for canning semi-acid vegetables like asparagus, spinach, and green beans of a pH of 5.0 to 5 5. The use of the tin bodies serves the purpose of preventing discoloration, or at least an undesirable color by the canned foods which exert a strong detinning action. Bonderized steel also is a satisfactory material for ends of electroplated tin plate cans in the meat-packing industry Electroplate with as little as 0.5 pound of tin per base box may be used for such composite cans

With an adequate lacquer it was possible to replace the tin-plate ends of cans of canned vegetables with black plate [41] The can bodies could not be replaced because the lacquer fractured during the seaming

[38] K W Brighton, *Food in Canada*, **4**, No 9, 36, 38, 40 (1944)

[39] W L Maucher, and B W Jones, *Trans Am Soc Mech Engrs*, **66**, 624–32 (1944)

[40] R H Lueck, and K W Brighton, *Can Food Packer*, **15**, No 6, 17–23; No 7, 18–21, 23, 25, 29 (1944)

[41] W B Adam, and D Dickinson, *J Iron Steel Inst (London)*, **152**, 195–205 (1945).

Aluminum plate is another prospective substitute for tin plate provided its surface remains unscratched [42] It was found to be much less corroded by 0.5 per cent citric acid in the presence of air than tin plate in the absence of air. There is little difference in the corrosive effect.

Lacquering is of little use in preventing the corrosion of nontinned iron. The hydrogen development is stronger with the lacquered than with the unlacquered surfaces, inasmuch as the lacquer prevents the subsequent combination of hydrogen and oxygen at the metal surface

Tin cans are exposed not only to the corrosive action of their contents, but also to the corrosion by external influences such as the galvanic effect of steam and the iron of the tanks used for the sterilization of the food, inclement weather, and wet storage facilities where the cans are in contact with hard water.[43] Those effects can be counteracted by the treatment of the tin plate with sodium chromate, but it is often necessary to line the iron processing tanks with wooden slats in order to prevent contact between the iron and the tin can. Careful rinsing of alkaline washes for fatty foods is also helpful in preventing corrosion. The rusting of the cans during thermal treatment can also be prevented by employing an aluminum liner on the crate bottom with holes to aid the circulation of the steam.

McLeod[44] reported that an aqueous dispersion of raw drying oils with a suitable drier serves as a good protection against corrosion. When this coating is washed and dried, the metal surface is unaffected by water at usual sterilizing temperatures.

Vaurio, Clark, and Lueck[45] devised a method to test the resistance of tin plate. The test consists of measuring the hydrogen which is developed by the contact between normal hydrochloric acid and a standard sample of die-formed tin plate. Correlation between hydrogen evolution values and can-service values with several fruits shows that the test is reasonably accurate. It is, however, important to note that in several cases alloying of metals of the steel base affects the service value of certain foods, but does not affect the hydrogen evolution value

The following steps are considered necessary to obtain full information on the causes of corrosion of tin cans:[46] visual inspections of the can, measuring of the thickness of the tin coating, testing of corrodibility of the steel base, analysis of the steel base, determination of the original vacuum, gas

[42] T N Morris, and J M Bryan, *Dept. Sci Ind Research (Brit) Rept Food Invest Board, 1933*, 145–55 (1934)

[43] C L Smith, and J W Barnet, *Proc 1st Food Conf , Inst Food Tech* , **1**, 199–204 (1940)

[44] A McLeod, *Canning Age*, **21**, 501–3, 557–8 (1940)

[45] V. W Vaurio, B S Clark, and R H Lueck, *Ind Eng Chem , Anal Ed* , **10**, 368–74 (1938)

[46] W B Adam, and D Dickinson, *Chemistry & Industry*, **22**, 426–8 (1944).

TABLE 52. RELATIVE VALUE OF TIN CANS IN THE CANNING INDUSTRY

PRODUCT	RELATIVE VALUE OF TIN CAN AS CONTAINER
Vegetables:	
Peas	Practically a perfect container.
Tomatoes..	No trouble when the article is properly prepared, closed, and cooked.
Tomato pulp and paste	Tin cans are very satisfactory as containers.
Corn	Very considerable difficulty was formerly experienced from discoloration by the formation of iron sulfide by the action of sulfur from the corn on the iron of the steel base. There is no longer any necessity for the iron sulfide discoloration in canned corn, as it has been found during a period of years that it can be completely prevented by the use of C-Enamel cans Practically all of the higher grades of corn are packed in C-Enamel cans, and a very large proportion of the standard corn is also packed in the C-Enamel can Apparently it is only a question of time when no corn will be packed in any other kind of container
Baked beans and red beans	Ideal.
Asparagus	Very satisfactory.
String beans	Eminently satisfactory.
Hominy	Discoloration trouble, not a defect inherent in the tin.
Sauerkraut	Ideal
Tomato and other soups	No ground for complaint on any score
Sweet potatoes	Discoloration, resulting from improper preparation, not attributable to the tin container
Spinach	Hard to keep in a tin can, special preparation of product is necessary; detinning action is rather severe
Lima beans	Very suitable.
Succotash	Very little trouble experienced
Okra	A great deal of trouble with discoloration unless special methods are used.
Spaghetti	Eminently satisfactory.
Pumpkin and squash.	Severe dissolving action on the tin coating and the contents of the can are affected An enameled can is highly satisfactory.
Beets	Difficulty in preserving color, an enameled can necessary.
Fruits:	
Pears, peaches and apricots	Almost ideal.
Pineapple	Eminently satisfactory.
Prunes, grapes, raisins, figs	Eminently satisfactory.
Ripe olives	No difficulties experienced.

TABLE 52—*Continued*

PRODUCT	RELATIVE VALUE OF TIN CAN AS CONTAINER
Rhubarb	Unsatisfactory except for a short period of time.
Grapefruit	Special precautions in preparation are necessary; not satisfactory for long periods.
Apples..	Trouble was formerly experienced in perforations of the can. Some of this trouble is attributable to method of preparation of the product. Soaking and steaming methods have been developed to the point where perforations no longer seem to be commercially significant
Cherries	
White	Very little trouble experienced
Black ..	"Probably the most severely perforating article ever packed in a tin can "
Red, sour	Much trouble from perforations, some of which is attributable to improper preparation. Charcoal tin plate should be used, an enamel coating is necessary to preserve the color.
Apple butter	At the best, only a temporary container. Heavy tin coatings should be used
Jams and preserves	Very little difficulty experienced
Plums	Same as red cherries.
Berries	
Strawberries	Not a satisfactory container. The chance of perforation is very high Enameled cans of charcoal tin plate should be used
Blueberries	Much the same as strawberries. Enameled cans are not necessary to preserve the color
Huckleberries	An enameled can must be used to preserve the color, but the chance of perforation is very great
Cranberries	Should be regarded at best as a semi-perishable article
Black raspberries	Fairly good results, if not kept too long.
Red raspberries, loganberries	Reasonably safe to can Enameled cans must be used to preserve the color and charcoal plate will give assurance of added safety
Other Foods:	
Canned sirup	Considerable trouble experienced, on account of improper preparation; the tin plate itself gives no trouble
Cider.	The cans are readily perforated. Unsatisfactory.
Salmon. . .	Excellently adapted for this product. At the present time a very large proportion of the pack is sealed in vacuum The preheating by exhaust boxes has been largely discontinued
Oysters	Satisfactory.
Clams	Formerly gave trouble on account of discoloration. Tin plate and can not at fault. Use of C-Enamel cans prevents iron sulfide discoloration (see Corn).

TABLE 52—*Concluded*

PRODUCT	RELATIVE VALUE OF TIN CAN AS CONTAINER
Sardines	No trouble attributable to the use of tin cans At the present time practically all sardine cans are sealed with lining compounds in the curl of the covers, so that hermetic sealing is possible and seepage of oil is prevented Formerly no sealing medium was used in the curl of sardine can covers
Tuna fish	Satisfactory, with improved canning methods now used
Lobster	Some trouble from discoloration caused by iron sulfide The C-Enamel can will practically prevent the trouble, although with the dry product the results cannot be described as absolutely perfect
Shrimp	Satisfactory for the "wet pack" The C-Enamel can prevents all formation of iron sulfide in wet pack, and in the "dry pack" iron sulfide formation is also practically controlled, although with this dry product there may be at times slight signs of iron sulfide formation, as the enamel is not so efficient when liquid is not present The C-Enamel can will not prevent the formation of a certain amount of rust with dry-pack shrimp, but this can be prevented by sealing the can in vacuum
Canned meat	Much of the trouble which has been experienced can not be attributed to the tin plate Heavy grades of tin coating should be used
Canned milk	Such trouble as has been experienced is not attributable to the tinplate

analysis, and the determination of the pH and acidity, tin and iron content, as well as corrosivity of the canned material.

C-Enamel Lined Cans. There has been one major improvement in containers, namely, the development of what is known in the industry as the "C-Enamel Lined Can" This C-Enamel was developed primarily to prevent iron sulfide discoloration in canned corn, and for this purpose it has been eminently successful. It has also been found that C-Enamel will prevent iron sulfide discoloration with clams, lobster, shrimp, and crabmeat

C-Enamel is made by baking a plate, under very accurate heat control, that has been coated with a lacquer composed of oil and gums which have been specially treated and mixed with an exceedingly small amount of zinc oxide The small amount of zinc oxide present is completely imbedded and protected in the enamel, so that practically none of it comes out into the canned food The total amount in the enamel is so small that even if it all came out in the food, the Bureau of Chemistry's tolerance for zinc in foods would never be reached. This C-Enamel is designated only for nonacid foods and cannot be used with acid foods, as acid will disintegrate the enamel. The regular enamel used with acid foods is of entirely different character.

Dr Bohart, a chemist with the National Canners Association, Washington, D. C , discovered and proved the efficacy of a minute amount of zinc oxide in a coating medium. A patent was taken out in his name and made available to the industry. Commercial can makers have developed C-Enamel on the basis of his discovery

Value of Tin as Food Container

Although much of the foregoing would seem to justify the conclusion that the tin can leaves much to be desired as a perfect container for preserving foods, it is well to remember that there is not available at the present time as good a substitute which has all the commercial features of the tin can. Glass containers would eliminate corrosion, but they are not suitable or adaptable for cheap shipping and transportation. Paper containers will not ordinarily stand processing of foods Metal containers other than those made of tin plate bring along their own corrosion problems. They are also more costly Tin cans are relatively cheap because of the quantities in which they are made and consumed

Commercially, it is to be observed that even with its defects the tin can is adapted to a great many different food products Food product losses owing to can failures bulk very large in actual money, although the percentage of cans failing is low. An estimate of the size of the industry can be gained from the fact that approximately 8,000,000,000 cans per year are used in the United States.

A factor to be considered in tin cans and their use is the thought that in many cases the use of tin in cans is decorative At other times it is, or should be, protective.

Baker[47] summarized the earlier situation with respect to the use of tin cans in the canning industry in Table 52.

Stewart and Pilcher[48] tabulated all data pertaining to the corrosion resistance of plain, enameled hot-dipped, and electrolytic tin plate and bonderized steel plate to apricots, cherries, fruit cocktail, loganberries, peaches, tomato juice, beans, beets, spinach, asparagus, chicken-noodle soup, sausage, and tuna fish at 70 and 100° F. for periods of 100 to 300 days

Containers Ordinarily Used for Food Products

Table 53, prepared by the Research Department of the American Can Company, lists the containers ordinarily used with different foodstuffs The table carries as well the approximate pH value of each product.

"Two types of enamel are in common use, both a golden yellow. One type (sanitary enamel) is used to prevent the bleaching of red fruits and also to protect the tin coating. The other (C-Enamel) is used to prevent discoloration of the con-

[47] Baker, "Status of the Tin Can in the Canned Food Industry," New York, American Can Company, 1923

[48] J. A Stewart, and R W Pilcher, *Chem. Eng News*, **22**, 422–34 (1944).

TABLE 53. CONTAINERS FOR FOOD PRODUCTS

PRODUCT	APPROX pH	CONTAINERS ORDINARILY USED
Acid Fruits and Vegetables (Sanitary Enamel)		
Apple Butter	3 9	Plain
Apples	3 3	Plain
Applesauce	3 4	Plain
Apricots	3.2	Plain
Beets	5 3	Sanitary enamel
Blackberries	3.3	Sanitary enamel
Blueberries	3 7	Plain
Cherries (except Royal Anne)	3 4–3.8	Sanitary enamel
Cherries (Royal Anne)	3.8	Plain and san enamel
Cranberries	2 6	Sanitary enamel
Cranberry Sauce	2 6	Sanitary enamel
Gooseberries	3 0	Plain
Grapefruit	3 5	Plain
Grapefruit Juice	3 4	Plain
Orange Juice	3 6	Plain
Peaches	3 5	Plain
Pears	3 9	Plain
Pickles (Dill)	3 9	Plain and san enamel
Pickles (Sour)	3 5	Plain and san. enamel
Pimientos	4 7–5 1	Plain
Prunes (Pureed)	4 0	Sanitary enamel
Pumpkin	5 0	Sanitary and C-enamel
Raspberries	3.6	Sanitary enamel
Rhubarb	3 2	Sanitary enamel
Sauerkraut	3 6–4 1	Plain and san enamel
Strawberries	3 4	Sanitary enamel
Tomato Juice	4 2–4 5	Plain and san enamel
Tomato Pulp	4 2–4 5	Plain
Tomato Soup	4 7–5 3	Plain
Tomatoes	4 2–4 5	Plain and san enamel
Nonacid and/or Sulfur-Bearing Products (C-Enamel)		
Artichokes	varies	Plain
Asparagus (Green)	5.6	Plain
Asparagus (White)	5 6	Plain and C-enamel
Beans (Green)	5.3	Plain
Beans (Kidney)	5 8	Plain and C-enamel
Beans (Lima)	5 9	Plain and C-enamel
Beans (Pork and Beans)	4.6–5.2	Plain
Beans (Wax)	5 3	Plain
Carrots	5 0	Plain san and C-enamel
Corn	6.3	C-enamel

TABLE 53—*Continued*

PRODUCT	APPROX pH	CONTAINERS ORDINARILY USED
Nonacid and/or Sulfur-Bearing Products (C-Enamel)—Continued		
Figs	4 9	Plain and C-enamel
Hominy Lye	7 0	Plain and C-enamel
Okra	4 9	Plain
Onions	5 3	C-enamel
Peas	6 2	Plain and C-enamel
Potatoes (Sweet)	5 4	Plain and C-enamel
Potatoes (White)	5.9–6 2	Plain
Spaghetti	4 8–5.4	Plain
Spinach	6 2	Plain
Succotash	6 0	C-enamel
Turnip Greens	6 2	Plain
Marine Products		
Clam Cakes	6 4	C-enamel
Clam Chowder	6 2–6 5	C-enamel
Clam Juice	6.6–6 8	C-enamel
Clams	6 6–6 8	C-enamel
Clams (Minced)	6.6–6 8	C-enamel
Crabs (Plain)	6 9–7.7	C-enamel
Lobster	6 6–6 8	Plain and C-enamel
Oysters	6 6	Plain and C-enamel
Salmon	6 1–6 6	Plain
Shrimp	6 8–7.0	C-enamel
Tuna	6 0	Plain
Meat Products		
Beef (Corned)	6 2–6.3	Plain
Chicken (Deviled)	6 3	Plain and enamel
Chicken (Half, Sliced, Whole)	6 0–6 3	Plain and enamel
Chili Con Carne	4 7–6 0	Plain and enamel
Frankfurters	6 3	Plain
Ham (Deviled)	6 3	Plain
Ham (Spiced)	6 3	Plain
Ham (Whole).	6 3	Plain
Sausage (Vienna)	5 9–6 3	Plain
Tamales	varies	Plain
Tongue (Lunch)	5 8–6 0	Plain and enamel
Tripe	6 2	Plain

tents and the staining of the inside of the can such as occurs with some vegetable and meat products when packed in plain cans. Some foods contain sulfur and under heat this sulfur discolors the tin plate for the same reason that it discolors a spoon left in contact with a cooked egg. The stain is harmless but unattractive."

Chapter 19

Secondary Tin

Sources

The tin-containing waste products can be divided into two basically different classes There are, however, limiting cases

(1) Materials of predominantly oxidic character such as tin ash, liquation residues, and slags

(2) Materials of a predominantly metallic character

(a) Tin plate waste of the plate and canning industry.

(b) Tin alloys and alloys containing tin such as bearing alloys and filings, type metal, die-cast alloys, impure alloys of the hot-tin dipping industry, and others.

(c) Old red brass, bronzes, and other tin-containing alloys with a predominant copper content

The recovery of tin from tin plate will not be discussed in this chapter This branch of the industry has developed to such an extent that a separate chapter has been devoted to it (Chapter 20).

Tin drosses, ashes, and at times slags, result from many commercial operations such as wire coating, tin-plate manufacture, hot-tin dipping, or copper-sheet coating The discussion of the metallurgical treatment of the drosses cannot be limited to tin alone, since residues of this sort are ordinarily not available in sufficiently large quantities to permit continued and efficient tin production from them as a raw material Tin ashes are quite generally treated with solder drosses and other lead residues containing considerable amounts of tin. In the majority of smelters, the final products of smelting are lead-tin alloys of widely varying proportions These are worked up into alloys of commercial application

Processing of Oxidic Waste Materials

If the oxidic materials still contain substantial amounts of tin metal, this is first separated by liquation in melting pots or liquating furnaces and processed by itself The wastes of the tinning industry are processed in the same manner. They originate as drosses in the dipping tanks and are strongly contaminated with flux such as zinc chloride. For the recovery of the metal from these drosses, a melting pot with a vertical separation wall

is used On the bottom of the vessel there is a connection for the two sections through the separation wall. The dross is introduced into one of the sections and melted there, and the oxide and zinc chloride collect on the surface of the melt The metal is ladled out from the other section The residue is freed from zinc chloride by leaching with water and then remelted. If it contains sulfur and arsenic, it is roasted before the melting

The residues are smelted in either blast or reverberatory furnaces, in a manner analogous to the methods employed for tin ores The reverberatory has generally proved to be the more advantageous type, although the blast furnace is very definitely applicable to handling lead-tin alloys containing 40 to 50 per cent tin Small-grained powdered materials, such as most drosses are, must be either briquetted, slagged or sintered before being charged into a blast furnace, otherwise the dust losses will be very high The volatilization and mechanical losses are high in blast furnaces. Blast furnaces are often preferred for treating reverberatory residues rich in tin and tin alloys by alloying through the use of iron or lead

Blast-Furnace Smelting. The structures employed for tin-residue smelting are much lighter than the blast furnaces used for ore smelting Figure 135 shows a commercial type, with the small forehearth to receive the product of the furnace Usually the structure is only a fireclay-lined steel shell The forehearth usually is divided into two sections by a partition, with a slot near the bottom connecting the two sections. The bottom slot is kept covered with metal to prevent slag from closing it The forehearth serves as a settling device when slag and molten metal are discharged from the furnace The slag remains in the forehearth, the metal rises in the hearth itself until high enough to be ladled out or removed to be cast into commercial forms. Care must be taken so that the slot is continually filled with liquid metal during this operation or it may become clogged by the slags

Smelting of residues in blast furnaces follows the ore-smelting methods In the first treatment the main object is to recover as large quantities of metal as possible, irrespective of the tin content of the slags, which are retreated.

The raw materials such as slags, drosses, scums, liquation residues, sweepings and other products, are mixed with about 5 to 10 per cent of coke and slag-forming materials such as lime, iron oxide, at times fluorspar, and small quantities of thin iron scrap to remove arsenic and sulfur present in the drosses Fuel in too great quantities will cause tin losses, too small amounts will allow the reducing zone to be carried higher in the furnace, with perhaps cooling of the tuyere section, and freezing of the furnace by slag cooled by the blast.

The slags for best practice are stated to be: 10 to 15 per cent CaO, 40 to 45 per cent FeO, and 30 to 35 per cent SiO_2. The slags produced run 5

ɜr cent tin, sometimes as high as 15 to 18 per cent tin. These must ɜated at least once, and often a number of times. The slags are ʋith small amounts of coke, lımestone and ıron scrap and resmelted ʻer the tın In slag-cleanıng smelting, the oxıdes of tın are reduced l The tın silicates present are decomposed by replacement of the

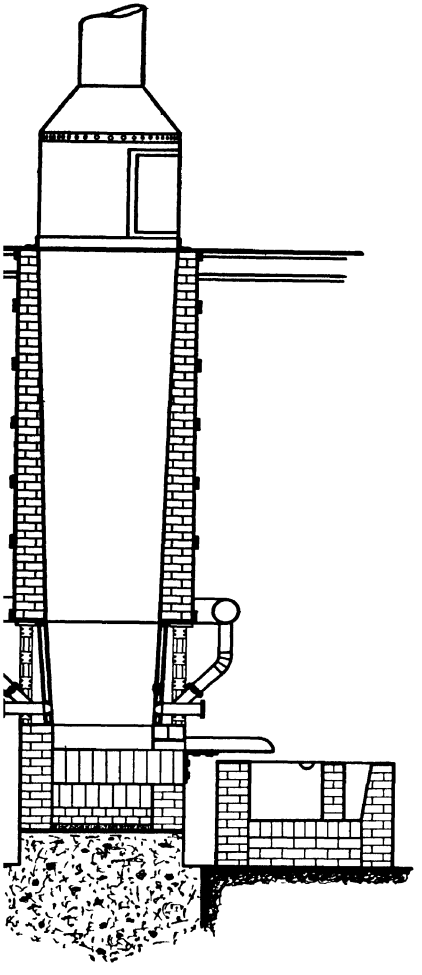

FIGURE 135.
Tın blast furnace with open shaft

ıme or ıron to form calcium or iron sılıcates. If slag-cleanıng smelt- been properly performed, the resultıng slag wıll not run more than ɜnt tın, and the tın wıll be obtaıned as a tın-ıron alloy running 30 ɜr cent tın and 55 to 60 per cent iron. Thıs ıs resmelted wıth tin- ɔsses.

lternative method is the use of lead-antimony drosses as extracting

agents for tin from residues All lead or lead-antimony ashes or slags running at least 30 to 35 per cent metallic constituents, excepting strongly oxidizing materials such as accumulator plates or red lead, may be used. Sometimes roasted lead ores are employed.

In order to eliminate excess iron, sulfur or arsenic is added to form matte or speiss Arsenic compounds are far more difficult to handle If considerable amounts of speiss are present in smelting the products, these may form serious obstructions, owing to the fact that all the arsenic-iron compounds are viscous and, consequently, easily chilled As a rule, the arsenic is added as arsenical iron speiss containing 25 to 30 per cent of arsenic. Many smelters prefer to add sulfurizing agents instead of arsenic, thus producing matte, which is much more easily worked than speiss.

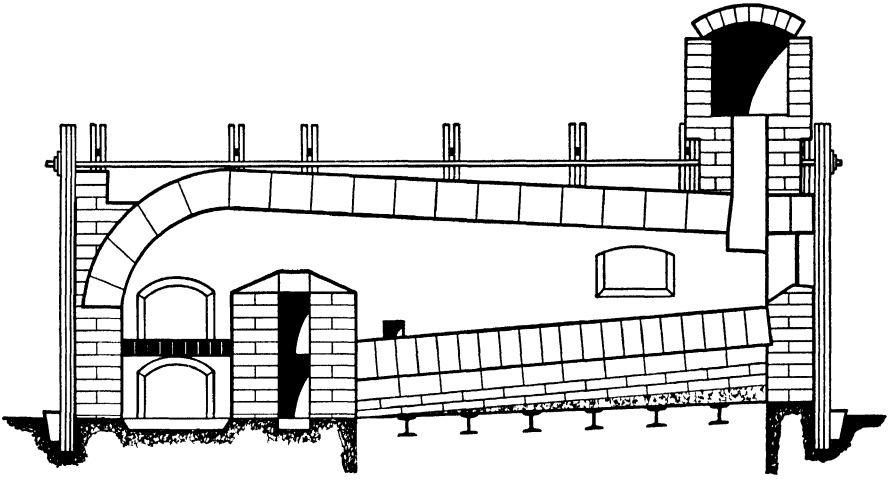

FIGURE 136. Tin-smelting reverberatory furnace.

Thews[1] stated that the best method consists in melting the tin slag with tin-lead ashes of low content such as ashes of type metal in order to obtain tin-lead alloys. The raw materials are best sorted in a manner so that a tin-lead alloy with 15 to 25 per cent tin is obtained.

Reverberatory-Furnace Smelting. When tin ashes and residues are smelted in reverberatory furnaces, many of the disadvantages of the blast furnace are eliminated. The usual furnaces are small, having hearths 7 to 10 feet long and 5 to 6 feet wide, with a hearth slope about one-half inch per foot The concavity of the hearth is about 5 to 7 inches total A typical furnace is illustrated in cross section in Fig 136.

Tin has a much stronger penetrative action on the brickwork of the fur-

[1] E. R. Thews, *Metallbörse*, **21**, 3–4 (1931).

naces than lead The hearth is usually composed of four layers of bricks, the top layer of which is made up of high-quality fireclay bricks standing on end The second layer of bricks, laid sideways, is also of high-grade material, while the two lower layers are of ordinary fireclay bricks laid flat

The hearth is laid upon heavy cast iron plates extending about 2 inches beyond the brickwork of the furnace on three sides

The bottom plate rests upon heavy girders stretched across a cellar or vault cooled by outside air. Cooling of the bottom plate will prevent too copious a flow of tin through the hearth, or even freeze up the tin penetrated to the bottom plate

In treating tin ashes and residues containing metallic oxides almost exclusively, reverberatory practice does not necessitate slag-forming materials Metallic iron is usually removed in advance by magnetic separation. Residues containing considerable percentages of metal, such as skimmings, sweepings and dross, should first be treated in melting pots or liquating furnaces to remove as much metal as possible

If the residues for treatment contain considerable quantities of sulfur, arsenic, iron, copper or antimony, they are given a combined roasting and liquation treatment in a reverberatory furnace. They are changed into a hard, powdery material, which is added to tin ores or other tin materials smelted in blast furnaces.

The liquating treatment has been replaced by a segregation process Charges of 4 or 5 tons are treated in a reverberatory furnace in small lots of about 500 pounds each until the furnace is half-filled with metal. The ashes collected on top of the metallic bath are then drawn off. Fresh drosses are charged until the furnace is almost filled with metal. After removing all of the ashes, the metal is heated to a temperature of about 1450° F Arsenic is removed by washing the metal with thin iron scrap. The temperature is gradually raised to 1550° to 1600° F. The metal is puddled for about ten minutes in order to remove any zinc and sulfur present.

The metallic bath is now cooled down as rapidly as possible, firing being stopped. All working doors are opened When a hard crust about 1-inch thick has been formed, the white metal below is tapped and cast into molds

The process is concluded by again heating up the furnace until all of the white metal adhering to the dark crust has been liquated. The residues are removed and treated in blast furnaces.

Tin and tin-alloy ashes, immediately prior to charging, are mixed with about 12 to 15 per cent of powdered magnesite and moistened in order to prevent excessive dusting. After charging, the furnace is closed and luted tightly and the temperature slowly raised to 1850° F. About one hour after reaching this temperature, the material is rabbled thoroughly, 2 or 3 shovelfuls of ground anthracite added, the charge again spread out, and heated for

another half hour Treatment is continued until the hearth has filled with a bath of metal. In rabbling, care must be taken not to stir up the molten tin more than absolutely necessary A reducing atmosphere must be maintained in the furnace. The metal should be tapped at the end of the treatment of each charge

In contrast to the smelting of tin ore, the reverberatory furnace method of smelting tin residues is comparatively simple if the high temperatures necessary are maintained If the slag produced is too viscous for satisfactory treatment, a little fluorspar may be added.

The semi-melted residue remaining on top of the metal at the end of the process is mixed with a small amount of lime, the mixture rabbled for a few minutes and exposed to the full heat of the furnace about 30 minutes The greater part of the mechanically suspended metal in the residues in the form of prills is liberated Too much lime will destroy the slaggy nature of the residues, which then become dry, powdery and unsuitable for blast-furnace treatment.

Tin ashes produced in the Harriss lead refining process contain about 5 to 15 per cent of tin, the exact amounts of tin depending upon the percentages of tin contained in the lead and upon the speed of oxidation If this material is treated with the object of extracting both tin and lead, comparatively high temperatures and strongly reducing conditions must be maintained However, if the smelting is carried out below 1500° F. and in a neutral or even slightly oxidizing furnace atmosphere, 5 per cent of ground anthracite is the only reducing agent needed for satisfactory results.

In dip-tinning plants, the excess tin on the tinned objects is whirled off mechanically or shaken off on the floor immediately after the object comes out of the tinning pot These are swept up and treated, with the drosses and skimmings from the pots, in cast-iron melting pots Considerable flux (zinc chloride) is contained in the skimmings and sweepings The pot is of two sections, divided by a partition with a slot connecting the two sections. On the higher side the skimmings and sweepings are charged, the metal melted from them and ladled out on the lower side The residues remaining are leached with water to recover the flux, centrifuged to clarify the flux solution, and the separated slimes smelted for tin metal recovery

Treatment of Alloys Containing Tin

White Metal Alloys. The old white metal is rarely pure enough to permit simple remelting into a commercial alloy These alloys are usually contaminated by other materials, in particular iron, sulfur, or zinc, similar to the products obtained from oxidic waste materials Such noxious materials must be removed Iron is removed in the same manner as crude tin by liquation in the usual furnaces Sulfur is usually removed with thin scrap iron, *e g* , sheet iron scrap, which is stirred in the melt, brought

to a suitable temperature, and then removed again. Zinc is separated, as with crude tin, by poling with steam. The purified alloys are then alloyed with other alloys or new metal in the proper proportions to form commercial alloys. This method is rarely suitable for solder because most alloys contain more copper and antimony than is permissible for solder alloys, and only the solder is of great commercial value. Therefore, a number of methods have been developed which pertain to the removal of copper and antimony from such alloys in order to obtain master alloys suitable for the production of soldering tin. Those methods are dependent upon the formation of the eutectic alloy with 54.5 per cent tin, 41.9 per cent lead, and 3.6 per cent antimony. This is done by liquation under increasing or decreasing temperature. The method with decrease of temperature is usually effected in such a manner that the molten metal is cooled cautiously in a reverberatory furnace with a hearth that is as deep as possible, and to a temperature near the eutectic point. The liquid eutectic alloy is then drained off.

Not all the white metal alloys are suitable for the eutectic alloy method. Only those are suitable whose composition approaches that of the eutectic alloy with copper and antimony calculated as antimony. This can be done because copper acts similar to antimony in liquation. In the phase diagram of Heyn and Bauer[2] the range of alloys which are suitable, according to Moldenhauer, is shown shaded in Fig. 137.

In industrial operation, the eutectic alloy method is usually effected in stages. In this case, other alloys are obtained aside from the eutectic alloy. These alloys are suitable either as master alloys for the manufacture of standard bearing alloys, particularly for railroad bearings, or as intermediate alloys which are returned to the process The alloy with the highest melting point which is produced in this process is the so-called "speculum" metal, a tin-antimony alloy of a high copper and a low lead content. It requires a costly working-up process. The bulk of the copper is frequently separated by a preliminary liquation. Vogel[3] determined the amount of the various final products of a liquation of mixed tin with preliminary liquation as shown in Table 54.

Moldenhauer[4] determined the phase separation on liquation in an electric furnace. He used a master alloy with 41 per cent tin, 40 per cent lead, 14 per cent antimony, and 4 per cent copper and obtained about 23 kg. of eutectic *A*, 15 kg. of eutectic *B*, 46 kg. of white metals of varying composition *C*, *D*, *E*, and 16 kg. of speculum metal *F*. (See Fig. 138.)

White metals poor in tin and rich in lead can also be decomposed in the

[2] Heyn, and Bauer, "Untersuchungen über Lagermetalle Antimon-Blei-Zinn-Legierungen," Berlin, 1914.

[3] F. Vogel, "Neuere Wege in der Metallurgie der Lager- und Weissmetalle," pp. 28–9, Halle, Wilhelm Knapp, 1933.

[4] M. Moldenhauer, *Metall u. Erz*, **30**, 81–4, 103–12 (1933).

manner described A large amount of the second eutectic alloy is thus obtained which is suitable as master alloy for the manufacture of type metal. The alloy contains 10 per cent tin, 80 per cent lead, and 10 per cent antimony Intermediate alloys and speculum metal are also obtained. From an original alloy with 15 per cent tin, 63 per cent lead, 12 per cent antimony, and 9 per cent copper there were obtained about 65 kg. of type metal A, 10 kg. of type metal of the second grade B, 10 kg. of intermediate alloys C, and 15 kg. of speculum metal D Moldenhauer[5] determined the phase relationships for this liquation as shown in Fig. 139

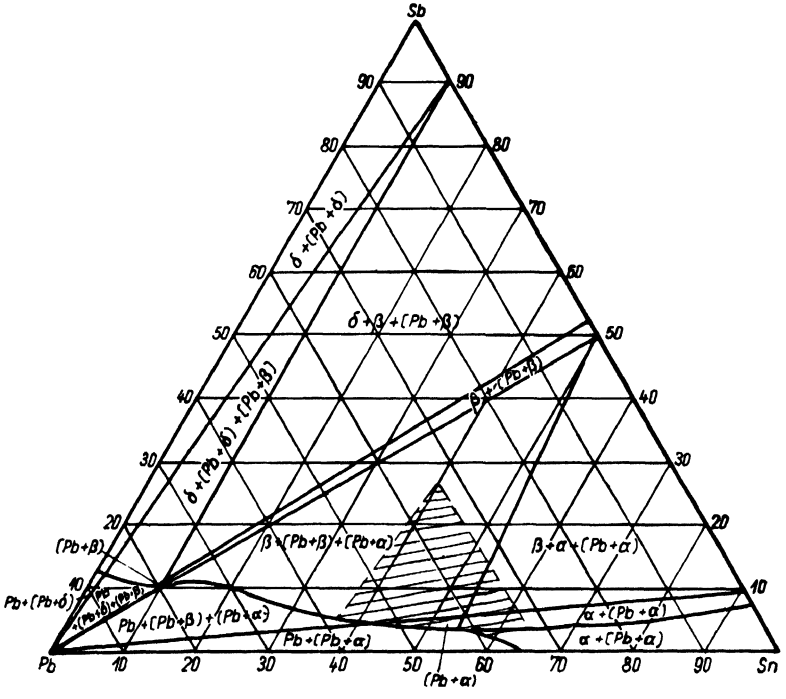

FIGURE 137. Phase diagram of the tin-antimony-lead system, according to Heyn and Bauer.

Many suggestions have been made for the treatment of the liquation residue, especially the speculum metal. Two of these have found industrial application. One process consists of adding the metal to copper alloys which contain tin and which are to be blown in a converter. Copper is taken out as converted copper and refined electrolytically or by heat-treatment. Tin, lead, and antimony are recovered as flue dust which is made into tin or tin-lead alloys by the wet process or heat-treatment.

The second method utilizes the fact that sulfur is more closely related to

TABLE 54. YIELD OF THE LIQUATION OF EUTECTIC TIN*

ORIGINAL ALLOY AT PRELIMINARY LIQUATION (30,000 KG.)	TAP TEMPERATURE	FRACTION 1 (19,500 KG —65%)	FRACTION 2 (2,700 KG —9%)	FRACTION 3 (3,600 KG —12%)	ASH (3,000 KG —10%)
Sn 46 05%	350° C.	Sn 51 26%	Sn 47 30%	Sn 39 90%	Sn 32 10%
Pb 31 02%		Pb 35 86%	Pb 33 29%	Pb 2 87%	Pb 23 16%
Sb 11 70%		Sb 10 70%	Sb 14 40%	Sb 12 82%	Sb 24 14%
Cu 11 23%		Cu 2 18%	Cu 5 01%	Cu 43 80%	Cu 18.86%
		To liquation of eutectic alloy	*Back to same treatment*	*To speculum metal treatment*	*To blast furnace*

FRACTION 1 OF PRELIMINARY LIQUATION USED AS ORIGINAL ALLOY (20,000 KG)	TAP TEMPERATURE	FRACTION 1 (4,200 KG —21%)	FRACTION 2 (7,100 KG —36%)	FRACTION 3 (1,500 KG —7 5%)	FRACTION 4 (3,000 KG —15%)	FRACTION 5 (1,800 KG —9%)	FRACTION 6 (1,200 KG —6%)	ASH (1,200 KG.—6%)
Sn 51 26%	190° C.	Sn 54 29%	Sn 55 07%	Sn 51 17%	Sn 53 05%	Sn 50 19%	—	—
Pb 35 86%		Pb 41 99%	Pb 41 10%	Pb 39 46%	Pb 30 41%	Pb 24 76%	—	—
Sb 10 70%		Sb 3 58%	Sb 3 67%	Sb 8 70%	Sb 14 60%	Sb 21.70%	—	—
Cu 2 18%		Cu 0 14%	Cu 0 16%	Cu 0 67%	Cu 1 94%	Cu 3 35%	—	—
		After decopperizing treatment, used as commercial eutectic alloy		*Back to same treatment*		*Back to preliminary liquation*	*To antimony treatment*	*To blast furnace*

* F. Vogel, "Neuere Wege in der Metallurgie der Lager- und Weissmetalle," Halle, Wilhelm Knapp, 1933.

copper and tin than it is to lead and antimony. The alloy is melted with the appropriate amount of sulfur and a tin-copper matte is obtained together with antimony which is more or less contaminated by lead. The tin-copper matte is roasted and leached with acid. The residue is tin oxide which is reduced by the usual methods.

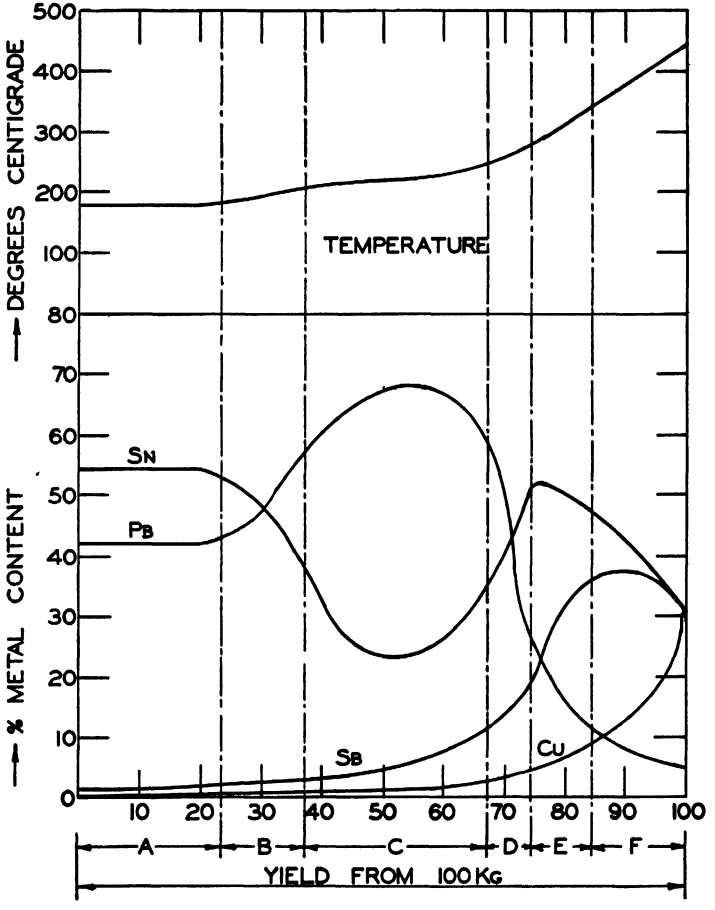

FIGURE 138. Phase separation on liquation in stages of eutectic tin. (Alloy contains 41 per cent Sn, 40 per cent Pb, 14 per cent Sb, and 4 per cent Cu.)

Kroll[6] made another suggestion for the separation of antimony, arsenic, and bismuth from white metals. Antimony and arsenic form antimonides and arsenides with a high melting point when alkali or alkaline earth metals, zinc, or aluminum are added to the liquid white metal. These antimonides

[6] W. Kroll, *Metall u. Erz*, **19**, 317-24 (1922).

and arsenides rise to the surface of the melt and can be separated by liquation The process has been described in the chapter on the refining of tin.

The electrochemical method has also been suggested for the processing of old white metal It has been pointed out that this method would permit the elimination of the complicated and costly treatment of the liquation residue. This problem has been studied by Vogel.[7]

Copper Alloys. The purpose of the working up of old red brass and old bronze primarily is to obtain an alloy of commercial value by simple remelting in reverberatory crucible type furnaces Troublesome impurities

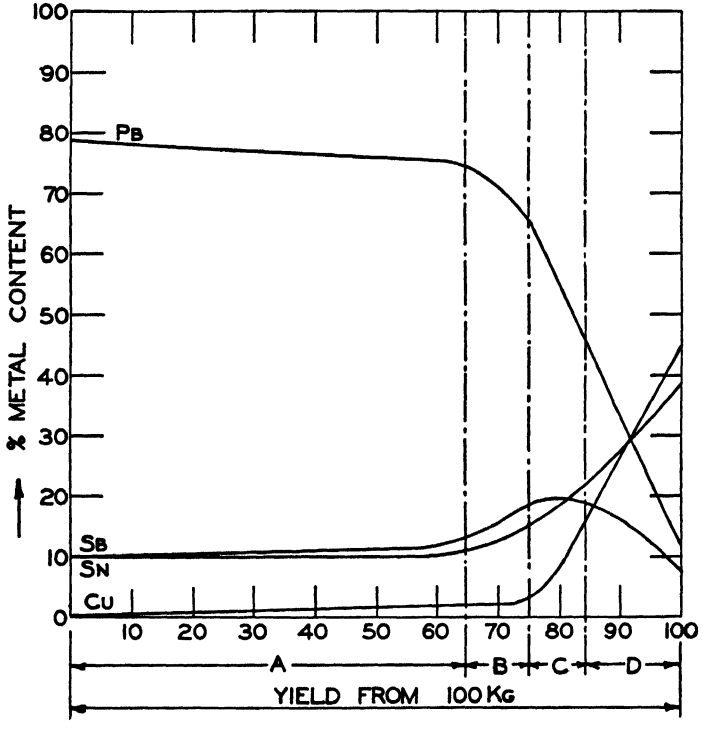

FIGURE 139 Phase separation on liquation of an alloy poor in tin and rich in lead (Alloy contains 15 per cent Sn, 63 per cent Pb, 12 per cent Sb, and 9 per cent Cu)

are best removed by poling with green wood and by treatment with sodium carbonate Prior to casting, deoxidizing agents are added to obtain castings free of occlusions of oxide Generally copper or tin phosphide is used for this purpose Cupola furnaces are sometimes employed for the remelting of scrap red brass and bronze.[8] In this case the sulfur content of

[7] F. Vogel, "Neuere Wege in der Metallurgie der Lager- und Weissmetalle," pp. 28, 129, Halle, Wilhelm Knapp, 1933

[8] *Metallbörse*, **21**, 678 (1931).

the coke has to be low, otherwise it is absorbed by the metal Muratsch[9] described the separation of zinc from old tin-rich bronzes.

The scrap, consisting of broken church bells, was melted in a 25-ton furnace with magnesite lining After melting it had the following composition: 18.27 per cent tin, 1 09 per cent zinc, 79.19 per cent copper, 0.03 per cent iron, 0 92 per cent lead, and 0 10 per cent nickel. After air had been blown through the melt for about 6½ hours, it was permitted to stand for 2 hours Then 500 kg of copper scale and 200 kg of sodium chloride were added, and finally the melt was poled The cast metal contained 12 78 per cent tin, 0 08 per cent zinc, 85 70 per cent copper, 0.04 per cent iron 0 92 per cent lead, and 0 15 per cent nickel. (See Fig. 140.)

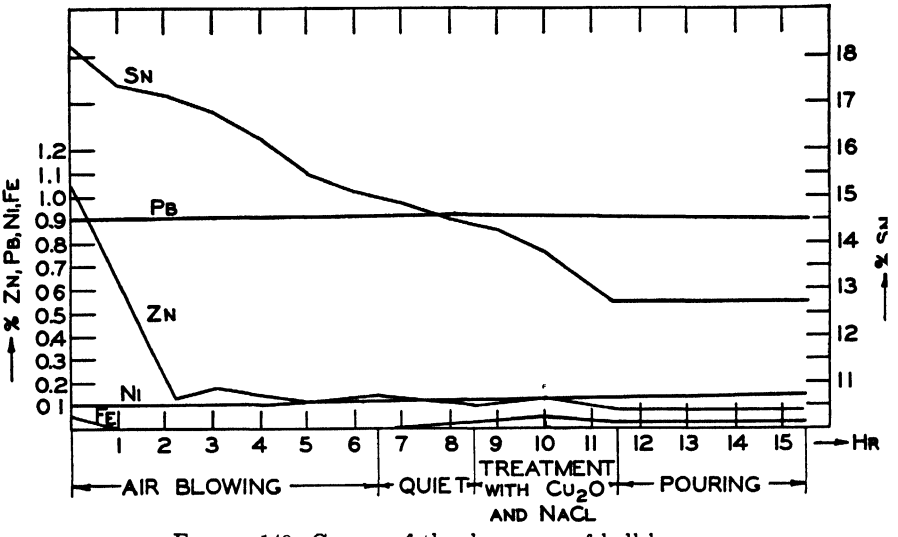

FIGURE 140. Course of the dezincing of bell bronze

Frequently, however, scrap alloys are so greatly contaminated that they must be separated into their components Various methods have been suggested but only two have found application: (1) blowing in converters, and (2) electrochemical separation. The electrochemical method was used in Austria and Germany during World War I in the years 1914 to 1918 for the working up of church bells. Engelhardt[10] described a plant in which bronze anodes were directly electrolyzed. The blowing is done in converters which are usually horizontal and of the Pierce-Smith type. These are smaller than are customary for copper matte. They are usually 6½ to 10 feet long with a diameter of 6½ feet, corresponding to a capacity of 4 to 6 tons of scrap metal.

[9] Muratsch, *Zwetnyje Metally*, **9**, 69 (1934), *Metall u. Erz*, **31**, 456–7 (1934).

[10] V. Engelhardt, "Handbuch der tech. Elektrochemie," Vol. **1**, Sec. 1, pp. 525–8, Leipzig, Akademische Verlagsgesellschaft M.b.h., 1931.

In general, bronze, red brass, speculum metal, and other alloys containing tin are blown in converters in addition to brass scrap. The process is as follows:

Lump coke to the extent of 10 to 15 per cent of the charge is fed into the converter which is still at red heat, and is brought to a glow by slight blowing. Then the scrap is thrown into the converter at a speed commensurate with the progress of the melting process. Simultaneously the air pressure is slowly increased. The reaction starts immediately with the melting. Zinc, tin, and lead, which are more readily volatilized, are expelled through the mouth of the converter. They immediately form white oxidic fumes which are precipitated in condensing chambers Cessation of these white fumes marks the end of the process. The converter is then tilted, the slag is skimmed off, and the copper is cast into blocks Samples were removed after melting and at short intervals during the blowing in the converter. The results of the process are shown in Table 55.

TABLE 55. COURSE OF VOLATILIZATION OF TIN, ZINC, AND LEAD DURING BLOWING IN A CONVERTER OF TIN-CONTAINING COPPER ALLOYS

	Cu (%)	Sn (%)	Zn (%)	Pb (%)
Charge	80 00	6 45	8 80	4 70
Metal sample No. 1	94 00	1 75	0 25	2 40
Metal sample No 2	95 80	1 03	0 08	1 40
Metal sample No 3	97 60	0 20	0 02	0 40
Slag sample No. 1	8 50	16 80	12 20	4 20
Slag sample No 2	16 30	16 10	8 00	6 20
Slag sample No 3	31 60	12 60	4 00	7 80

If the brass does not contain sufficient iron or other slag-forming material, iron is added to form a liquid slag which can be readily separated from the liquid crude copper. The addition of iron is also advantageous in reducing the oxides which have passed into the slag, and thus aids in freeing them for volatilization Further, it thermally assists the reaction by its heat of combustion. The addition of iron, however, is comparatively expensive, and attempts have been made to replace it with an increase in the coke charge. This has been successful up to a certain point. Sand should be avoided, inasmuch as it adds considerably to the slagging of tin and lead.

In industrial conditions the blowing process is expected to yield 80 to 85 per cent of the copper as metal, 40 to 70 per cent of the tin, 60 to 80 per cent of the zinc, and 60 to 75 per cent of the lead with the flue dust The remainder of the metals pass into the slags with the exception of 3 to 5 per cent of the tin and lead which remain in the crude copper in solid solution as oxides. The composition of the slags varies for the blowing of red brass, within the following limits:

Copper	25–35%
Tin	10–20
Zinc	10–15
Lead	2– 5
Iron oxide	8–20
Silicon dioxide	3– 6
Aluminum oxide	4– 8

The slag is subjected to melting in a reduction atmosphere in a blast furnace, in such a manner as to cause the volatilization of the major share of tin, zinc, and lead These metals are recovered from the flue dust as mixed oxides. In order to prevent an extensive slagging of the tin, only small amounts of sand are added. The black copper with a widely varying tin content is returned to the converter.

TABLE 56 METAL DISTRIBUTION BY BLOWING OF TIN-CONTAINING COPPER ALLOYS

FROM THE METAL CHARGE INTO	Cu (%)	Sn (%)	Zn (%)	Pb (%)
Crude copper	98 5	4 0	—	4 5
Converter oxide	—	65 0	62 5	72 5
Blast furnace slag	1 5	18 5	16.5	5 0
Blast furnace flue dust	—	12 5	21 0	18 0

The composition of the mixed oxides which are obtained by the blowing of tin-containing copper alloys, varies widely, the following limits can be assumed:

Zinc oxide	18 –55%
Tin oxide	15 –50
Lead oxide	10 –20
Antimony trioxide	0 2– 0.5
Cuprous oxide	0 5– 1.0
Sulfur	1 – 2

The oxides are treated in the same manner as the tin-containing flue dust, either by wet or thermal processing. In the first case, the mixed oxides are treated with sulfuric or hydrochloric acid, and sometimes with ammonium carbonate and ammonia. Zinc is dissolved by this treatment, while tin oxide remains almost completely undissolved. The dissolved tin and lead are precipitated from the zinc solution by cementation with zinc scrap. The residue from the leaching process is melted together with the metals precipitated by cementation to form a eutectic alloy. The thermal process is the same as described for the smelting of tin ores.

The working of a scrap charge with 75 per cent copper, 5 per cent tin,

10 per cent zinc, and 5 per cent lead, effected the distribution of the metals in various products as shown in Table 56.

Characteristics and Uses of Secondary Tin

The tin alloys produced in the reverberatory- and blast-furnace processes are chiefly tin-lead alloys containing 20 to 75 per cent tin. Those containing up to about 35 per cent tin are used for the manufacture of ordinary tin-lead or lead-tin-antimony alloys. Products with more than 35 per cent tin are employed for the production of "tin alloy" and alloys rich in tin used as base alloys for the manufacture of tin solders and high-grade bearing metals.

The liquation process may be used in concentrating the tin contents of alloys containing more than 60 per cent of tin. The melting point of the tin-lead eutectic containing from 55 to 62 per cent of tin (depending upon the amount of antimony and other impurities present) is 360° to 365° F. If, therefore, a material containing, say, 70 per cent of tin is deposited on the inclined hearth of a reverberatory furnace and carefully heated to a temperature of about 370° F , the eutectic alloy will be "sweated out "

Chapter 20

Detinning of Tin-Plate Scrap

Early Detinning Processes

As the tin-plate industry grew to large proportions, the problem arose as to the disposal of clippings and other scrap, which accumulate in large quantities Tin-plate scrap, made as a result of working up of tin plate into cans, boxes, containers, etc , has been the subject of much study. In its plated state the scrap cannot be puddled or charged into the open-hearth furnace The tin coating prevents a satisfactory iron or steel product being made Hundreds of patents in all the different industrial countries have been granted for the removal of this coating The tin coating has a considerable value, either as metallic tin or as tin compounds, used in various industries

The problem at first did not appear to be difficult. The can factories were glad to give their scrap tin-plate away simply to get rid of it Decades of study and experimentation were required before a feasible method was developed which yielded sufficiently valuable commercial results.

Many of the chemical and electrochemical processes were failures, as were most of the mechanical processes, either because the acids used attacked the iron as well as the tin, or because they would not dissolve the tin sufficiently and left a considerable part adhering to the iron It was found in many cases that the chemicals used were too expensive to make the process an economical one. Three processes, however, have operated successfully and have been more or less in competition with one another. These three processes are the electrolytic alkali process, the alkali chemical process, and the chlorine process.

As far back as 1876, Keith[1] recommended the electrolysis of tin scrap in an alkali solution, while in 1882 Thomas Goldschmidt, in Germany, conducted experiments with a warm solution of caustic soda, using the tin-plate scrap as the anode and an iron plate as the cathode. This simple idea has been the basis for the further development of the industry. The operation on a plant scale offers difficulties, both electrochemical and mechanical, which have been solved in commercial operation.

The tin is recovered at the cathode in the form of a spongy or finely granulated precipitate, which can be removed and melted. The process

[1] Keith, *U. S. Patent 176,658.*

yields a serviceable iron in a single operation, which may be compressed into solid billets, and for which a market can be readily found The apparent simplicity of the method caused it to come into quite general use.

Alkaline Electrolytic Detinning

This method consists essentially of electrolyzing the tin-plate scrap at the anode in a bath of caustic soda and depositing spongy metallic tin at the cathode.

The tin-plate scrap serves as the anode in the cell, the cathodes are either steel plates or the sides of the steel tanks. Iron is the cheapest and the most generally used electrode material The tanks are connected to the negative conductor, while the positive part of the cell is connected to copper bars or tubes which are placed on insulated supports lying along the edges of the tanks. The baskets are charged with tin-plate scrap and are of suitable size and dimensions so that they may be handled with ease The baskets are made of heavy iron wire gauze of wide mesh, bound with strong heavy angle-iron bands The bands extend up from the basket and are bent into hooks above, which rest on and make contact with the positive bus bars. The basket design is usually on the basis of about 3 to $3\frac{1}{2}$ pounds of scrap per cubic foot of basket volume. Baskets fit the tanks rather closely, with enough clearance between the sides of the baskets and the inner walls of the tanks or the cathodes to prevent electrical short circuits. The capacity of baskets bears about a 3:5 relation to the volume of the bath The electrical resistance of the electrolyte is thus kept as low as possible The baskets are suspended side by side. If an increased cathode area is needed, iron plates are hung between each pair of baskets. More careful control of the bath is then required. The nature of the tin-plate scrap and the impossibility of charging the anode baskets uniformly on a large scale, although equal weights may be electrolyzed, make it impossible to provide a constant anode area per bath. The current conditions are constantly changing. Control, at best, is always difficult.

The pipes carrying the electrolyte from and to the tanks are insulated from the electrical conductors. Circulation of the electrolyte is essential. The discharge pipe is provided with a screening arrangement and an overflow for the purpose of holding back suspended particles of spongy tin. Diaphragms are not used.

The scrap is sometimes moved and loosened during electrolysis. Thus the electrical contacts are well made and no permanent resistance is offered to the current. It is important that the tin-plate scrap be open, so that the electrolyte may reach the middle of the basket readily. The scrap must be as far as possible immersed in the solution.

Speedier stripping is obtained with baths at 60° to 70° C. At this temperature there is about 5 per cent evaporation of liquid per 24 hours. The

water lost by evaporation is replaced by the addition of hot water to the electrolyte

With the solutions as hot as possible, they should be as high in free soda and as low in stannates and carbonates as operation will allow. Periodic regeneration of the electrolytes is necessary, as the stannate and carbonate content builds up, also to reduce the iron and lead compounds as well as soaps formed from the resins, lacquer and fatty materials introduced with the scrap. The electrolytes take up but little iron and lead unless they contain chlorides.

The whole of the caustic does not remain in the free condition during electrolysis. Even without the aid of the current, especially in the presence of atmospheric oxygen, it would dissolve the tin with formation of stannites and stannates As open tanks are used, carbon dioxide will be taken up. The higher the free caustic concentration in the solution, the more rapid will be the absorption of the gas, with resulting formation of carbonates.

Work is begun with a solution containing at most 9 per cent sodium hydroxide (7 per cent sodium oxide). This quantity is maintained throughout the process The caustic is on the average distributed as follows among the compounds formed during electrolysis:

3 –3 5% sodium oxide, free as hydroxide
1 –1 5% sodium oxide, combined with 3% stannous oxide (2 34% stannate) as stannate
1 7–2 8% sodium oxide combined with carbon dioxide as carbonate

When a larger proportion of carbon dioxide than the above is taken up, stannic acid is precipitated in the baths, so that regeneration of the solution becomes necessary.

The time necessary for the complete detinning of the scrap is dependent not only on the current employed but also on the tin content of the scrap, the temperature of the electrolyte, the strength of the electrolyte, the number of baskets per cell and the quantity of scrap per basket. These factors differ so much in different works that it is usually stated that the detinning takes anywhere from 2 to 7 hours for completion

With any chosen density, knowing the weight of scrap in the bath and its tin content, the time of detinning can be calculated, as one ampere hour dissolves about 1.1 grams of tin. More tin is dissolved off the anode than is deposited on the cathode, so that the concentration of stannite and stannate in the solution increases during its use.

The dissolved tin may be precipitated as oxide by bubbling carbon dioxide through it (carbon dioxide from waste furnace gases, motor exhausts, etc.) and the stannic oxide is recovered by filtration, washed, and dried either to be sold as such for use in ceramic work or smelted to metallic tin. The electrolyte, now free from tin and saturated with carbonate, is causticized by the use of lime. Iron in the electrolyte is precipitated along with

the calcium carbonate formed. The regenerated solution, after being restored to the proper concentration, is returned to the system for reuse. The following operating conditions hold good in one modern plant:

Current	1,500 amperes
Tank size	13 ft. long by 3½ ft. wide by 5 ft. deep
Baskets	12 ft long by 2¾ ft. wide by 4 ft. deep
Total tanks	42
Voltage per tank	1 5
Scrap	1 2 to 1 5% tin
Operating time	22 hours per day
Current density	10 to 12 amp per sq ft
Detinning time	4 to 6 hours
Detinned scrap	0 1 per cent tin

Of the 1,500 amperes in the system, about 80 per cent of the current was useful in detinning, the rest being consumed in side reactions and polarization counter effects

The insertion and removal of the scrap baskets in the electrolyte take place in a regular and systematic manner The completion of the detinning can be checked by the change in color of the scrap from its original appearance to colors varying from blue-black to red-brown

The detinned scrap is allowed to drain from the electrolyte and is washed with water. The material is then dumped out of the baskets, dried, either compressed or baled for shipment, or sold as it is.

At intervals the tin sponge is removed from the cathode plates by iron scrapers, the cathodes being lifted out of the cells at the time. The sponge tin is washed free from alkali by more or less violent agitation with water It is then a granular material. It is dried by centrifuging and melted to massive tin. In some works the washed and dried tin is compressed before melting.

Tin-bearing slimes are produced at the bottom of the electrolytic baths, from particles falling off the cathode or anode and material dropping into the bath when the cathodes are scraped. This material contains tin, sand, iron and alkali and various organic substances introduced into the bath through dirt on the scrap. The slimes are recovered by draining them off at intervals, adding them to slimes resulting from the detinned scrap washing tanks and the tin oxide produced by regenerating the electrolyte. The whole mass is smelted for tin.

Often in handling dirty scrap the bath will become contaminated through lacquer, grease, oils and soaps formed as a result of the action of the caustic on organic matters. At the time of regeneration of the electrolyte it is usual to remove these materials by cooling the electrolyte down to a low enough temperature so that they separate out.

The detinned scrap, containing under good operation less than 0.1 per cent tin, is quite suitable for the manufacture of open-hearth steel.

Many methods have been suggested for the recovery of tin from tin-plate scrap in alkaline baths with the aid of the electric current. Many of them have had only small development and quite a number after being in operation for some time have been abandoned in favor of the straight caustic bath. Mantell[2] has reviewed the old processes of historic interest.

Some plants operate on disassembly of large canners' cans. These used cans are cut down to recover the sides, the resulting scrap serving as raw material for a detinning plant Figure 141 gives the flowsheet of such a unit. Inasmuch as solder seam material constitutes a share of the plant raw material, the tin is recovered as solder

During the period before World War II, the silk textile industry consumed large quantities of tin chloride for "weighting" or restoration of weight to the fiber or textile to compensate for the loss during the boiling off, scouring, and degumming of the silk Electrolytic detinning produced sodium stannate for use in electroplating of tin, but the market for tin chloride caused the chlorine detinning method to be favored When silk to a very large extent was not available during World War II, the chlorine process could not market its product so that chemical and electrochemical detinning again came to the front. Up to 1940 the chlorine method was of greater importance It was easier to operate, cleaner, more efficient, and produced more valuable materials which found a very ready market.

Alkali Chemical Process

A process of considerable commercial importance is that of detinning with alkalies, with or without the aid of oxidizers This method was practiced at an early stage of the industry, but did not always remove a sufficient amount of tin, with the result that a considerable part was left on the iron.

During World War II, chemical process plants using caustic solutions were built to recover tin from waste tin cans. The collection of used containers has always been an economic problem. Cans were discharged at the plant from railroad cars to a bin from which they were fed to picking tables. Here nontin materials, nonmetals and waste were removed. The picking table discharged to a shredder which perforated the cans to expose more surface for chemical attack. Shredded material, containing paper labels, food particles, lacquers, and other organic matter, passed to an incinerator where they were subjected to oxidation at temperatures of about 425° F. This temperature was not hot enough to alloy the iron and tin. After incineration, the shredded fragments were washed in a rotary screen to remove charred fragments of organic matter. In order to avoid tin loss, the wash water was recirculated after settling in a sludge pit.

The washed cans were then detinned in an alkaline caustic solution in

[2] C. L. Mantell, "Tin, its Mining, Production, Technology and Applications," 1st Ed., pp. 335–40, New York, Reinhold Publishing Corp., 1929.

huge cast-steel rotary drums. Provision is made for heating the solutions. The tin dissolves in the solution to form sodium stannate. The solution

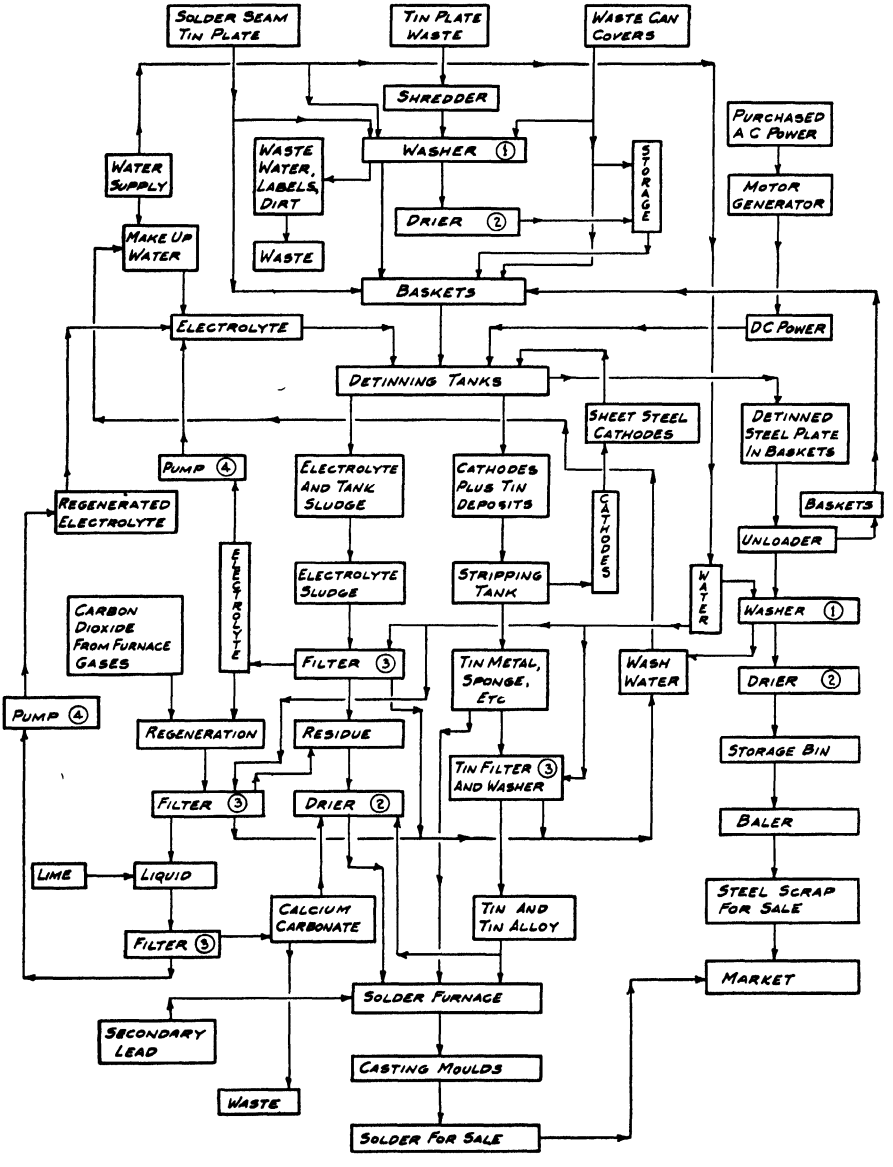

FIGURE 141. Detinning plant flowsheet for recovery from disassembled large cans.

falls to the bottom of the drum and drains through pipes for further treatment; the detinned steel passes to a washing drum. Here the steel meets a series of washers to remove adhering detinning solution and tin values.

Wash water is recycled and used for makeup for the detinning solution. The washed steel scrap then is dried and sent to the hydraulic baler to become compressed steel-plate scrap.

The detinning solutions in their cycle are settled, or the tin values may be precipitated and the filtered solutions sent back to do detinning on further amounts of shredded cans. The tin chalk, oxide or black mud is separated after washing, and dried to become tin oxide which may be sold as such or smelted to tin metal and alloys Photographs showing such a plant have been published.[3]

In a further modification of the chemical process, the scrap is cleaned carefully and is then placed in a well-heated solution containing a considerable excess of free alkali and saltpeter or other oxidizer. The mass is then kept at a boiling temperature for several hours, during which the tin reacts to form sodium stannate which accumulates as crystals. These crystals are drawn off and subjected to centrifugal action while the remaining mother liquor is diluted with the necessary caustic and saltpeter to enable it to be used again in the same way as the original solution.

The stannate is subjected to further treatment by dissolving in water and precipitating tin oxide by means of sodium bicarbonate. It should be borne in mind that the alkali used in this process is always recovered and used over and over, so that only a small loss results. The saltpeter is also recovered at the end of the operation, with the exception of the amount required for the oxidation of the tin.

The tin oxide obtained in this process is used extensively as a coloring matter in the enamel industry or is smelted in reverberatory furnaces to form pig tin. The Goldschmidt Detinning Company uses this process in addition to the chlorine process in its various plants.

Various oxides have been suggested as a replacement for the saltpeter. Donath suggested the treating of scrap with concentrated sodium hydroxide and manganese dioxide. Kardos[4] utilized a circulating process which employs nitrous gases. It is said that this process offers special advantages in a low consumption of concentrated sodium hydroxide solution, and the stannate solution obtained is suitable for the electrolytic precipitation of tin, and contains 5 to 6 per cent tin.

A solution of lead oxide in sodium hydroxide has also been recommended. The solution of the tin is explained by the equation:

$$2\,NaOH + 2\,PbO + Sn = Na_2SnO_3 + 2\,Pb + H_2O$$

Miscellaneous Chemical Processes

Scott and Davis[5] suggested a method based on the solubility of tin in tartaric acid in the presence of oxygen. The detinning is done using a 5

[3] *Chem. Eng News*, **22**, 618–9 (1944).

[4] Kardos, *German Patent 531,112.*

[5] W. W. Scott, and N. E. Davis, *Ind. Eng. Chem.*, **22**, 910–1 (1930).

per cent solution of tartaric acid in a container in which a perforated cylinder filled with scrap is moved around.

Among the acid electrolytes for detinning, use has been made of sulfuric acid, hydrochloric acid, acid sulfates and chlorides. Gutensohn[6] patented the use of sulfuric acid The acid electrolytes are only of historical interest.

The old Siemens and Halske process, using a sulfuric acid solvent for the detinning of scrap by electrolysis, is no longer in operation This was practically the only one ever used commercially By the treatment of six tons of scrap per week, there would be obtained about 28 tons of crystallized ferrous sulfate in addition to the metallic tin recovered. It is doubtful whether the ferrous sulfate yield would even repay the outlay on the sulfuric acid used, as green vitriol is produced as a by-product in many other metallurgical industries and is thrown on the market in large quantities at a very cheap rate It is evident that if it were intended to strip the tin completely from the scrap by electrolytic means in a sulfuric acid bath, an enormous quantity of iron would be dissolved and pass into the solution.

Other than the old Siemens and Halske process, there has been little commercial use made of acid electrolytes, largely because of the quantity of iron of the scrap that is unavoidably dissolved in the electrolyte. After some time the electrolyte becomes unfit for use and must be renewed, with or without recovery of the iron compounds it contains, the compounds are recovered as commercial iron salts In this process the tin is deposited as a sponge on the cathode as long as the solution is acid, but as the bath becomes more and more neutral the deposit becomes pulverulent and in some cases crystalline

Chlorine Process

The chlorine process was first taken up by Higgins in 1854, in England,[7] and later by Parmalee,[8] Seeley,[9] and Panton[10] in the United States

In 1883 there was a plant operating successfully, using the chlorine process, at Metikon, on Lake Zurich, Switzerland. A fixed iron cylinder, thirteen feet (3.96 m) high, of 39-inch (99-cm) diameter, was used. The cylinder had a perforated false bottom on which the cuttings were placed, and through the openings of which the chlorine gas passed and came in contact with the clippings The stannic chloride which formed collected as a liquid in a receiver under the cylinder.

Further progress was made in chlorine detinning in 1885, when Lambotte, in Brussels, started to operate on a large scale with a shaft furnace filled with tin scrap from the top, while chlorine gas, strongly diluted with air,

[6] Gutensohn, *German Patent 12,883.*
[7] Higgins, *British Patent 766* (1854)
[8] Parmalee, *U S Patent 102,148.*
[9] Seeley, *U. S. Patent 127,375*
[10] Panton, *U. S. Patent 135,678.*

was introduced at the bottom. The air carried away the stannic chloride to the condensers, where it was condensed as a watery solution of the stannic chloride. The detinned clippings were then removed from the bottom of the furnace and compressed into billets.

A chlorine detinning plant was established in New York in 1873, operating according to the Seeley patent, but the venture failed when the financial panic of that year brought ruin to many concerns

It was not until 1907 that the chlorine detinning process gained importance. In that year Goldschmidt abandoned the electrolytic process in favor of the chlorine process which he had developed. Since then the chlorine process grew rapidly up to World War II and immense quantities of tin scrap and old tin cans were detinned by this method.

Some of the basic conditions of chlorine detinning had been correctly observed by the early experimenters, the most important of which is that all moisture must be excluded in order to avoid any corrosive action of the chlorine on iron. It has also been found that the material must be free from all organic substances, such as paper, straw, varnish, etc.

Chlorine gas will combine with tin, under the development of considerable heat, to form anhydrous tin tetrachloride This is a heavy liquid which fumes strongly in air It has been known to chemists for about 300 years In fact, as early as 1605 Libavius described this product, and ever since that time it has been known under the name of *liquid fumans Libavii*. By cautious addition of water to this fuming liquid, solid stannic chloride crystals were precipitated and sold in that form for use in dyeing.

The thermal datum of the reaction is:

$$Sn + 2Cl_2 = SnCl_4 + 127{,}250 \text{ Cal}$$

The heat of formation of stannic chloride is given by various authorities at 127,250 calories to 129,600 calories The heat of a solution of stannic chloride is 29,920 calories It has a density of approximately 2.29, a melting point of −33° C., and a boiling point of about 114° C. It dissolves readily in water, forming a solution from which the hydrated stannic oxide separates on boiling or standing.

Perfectly dry chlorine gas or mixtures of chlorine and other gases only can be used. Moisture even in small quantities is detrimental to the process. Only dry clippings can be detinned. The clippings must be clean Chlorine will only slightly detin dirty, greasy, or oily clippings. The process cannot be used for unclean tin plate scrap

Provision must be made for keeping the temperature of the reaction chamber below 38° C. or 100° F., otherwise the iron of the chamber or detinning vessel will be affected by the chlorine to form ferric chloride. Chlorine also acts on the iron in the presence of water, the ferric chloride formed accelerating the attack of the chlorine on the iron.

The chief difficulty of this process was that the iron scrap was exceedingly

liable to rust, as was the case with all former processes of detinning with chlorine. Even if all moisture were carefully avoided and the resulting steel gray iron were stored in a very dry place, it would rust and the resulting corrosion would quickly spread. It was found that chlorine is not absolutely without an attack on the iron, but forms a thin invisible film of anhydrous ferric chloride, which will attract water from the air, forming oxychloride, this is again reduced by the iron, forming more rust The corrosion of the iron was prevented by removing the ferric chloride film by a washing process.

The important modifications of the chlorine process are those of Goldschmidt, Sperry, Acker and Von Schutz. There have been manifold and multitudinous methods and apparatus proposed and used, for practically all of which patents have been granted. The same result can be obtained in many different ways.

In the Goldschmidt process, chlorine is introduced into the detinning chamber under pressure The dry tin scrap is put into large cylindrical containers, either in more or less loose form or compressed into baskets. These containers, after being filled, are closed tightly. Dry chlorine is then introduced. The heat of reaction of the chlorine on the tin is dissipated by outside cooling of the reaction chamber. After detinning has been completed, the remaining gases are drawn off by suction, along with any volatilized stannic chloride, and the detinned bales of scrap washed and dried. The detinned scrap is then ready for sale.

Pressure is used in the Goldschmidt process to cause the reaction gas to penetrate all parts of the scrap material in the reaction cylinder. When the gaseous chlorine forms liquid tin chloride, the pressure is reduced owing to the decrease in volume of the gases. As long as the pressure continues to drop, detinning is taking place. When the pressure remains constant for some time, it is evident that the chlorine does not have any more tin with which to combine. This is a sure indication that the detinning is completed.

It is stated that the pressures employed in the Goldschmidt process are about 3.7 atmospheres (54 lb. per sq. in.) at 0° C., and 7.6 atmospheres (112 lb. per sq. in.) at 25° C.

In the method of Von Schutz a dry mixture of chlorine, diluted with other gases (as dry air), is drawn through the scrap by suction. Any inflowing gases which are too cold can be preheated by being passed through pipes around which exit gases of the process are drawn off, these exit gases being heated by the heat of the detinning reaction. The vacuum is produced in part by the cooling and contraction in volume of the exit gases. Little trouble is experienced with clogging of the pipes, owing to the deposit of stannic chloride.

The detinned scrap is washed in the same cylinder in which the detinning

was done; and drying is done in place, after washing, by blowing hot furnace gases through the tin scrap bales in the detinning chamber. The finished material is removed from the chamber and sold.

Murray and Fernberger[11] proposed employing chlorine in a solvent such as carbon tetrachloride. The tin salts produced and the solvent are recovered by the addition of water or steam. If desired, the solution of the tin salts in carbon tetrachloride may be electrolyzed after the addition of water.

In the Acker process liquid chlorine, which continuously sets free chlorine gas, is used as a detinning agent.

Sperry used mixtures of stannic chloride and chlorine, usually in a closed system. The vapors given off are cooled and condensed in chambers in the system outside of the reaction chamber.

Von Kugelen and Seward, in patents assigned to the Tin Products Company of New York, suggested a process which depends on arranging the amount of scrap to be treated so that the heat generated by the detinning can be dissipated rapidly enough to maintain the temperature below the point at which chlorine attacks iron. The stannic chloride is removed by volatilizing it in a current of chlorine. In other patents Von Kugelen and Seward condensed the stannic chloride in the detinning chamber. They also have patented the idea of keeping that part of the detinning chamber adjacent to the walls at approximately 38° C.

Goldschmidt and Weber have a number of patents on the chlorine process under pressure, the gas acting on laminated bundles of tin scrap. In some patents, the gas passes from the bottom to the top, in others from the top to the bottom.

The chlorine process possesses advantages over the electrolytic method, as it can be carried on in larger units, and the labor charges are therefore materially reduced The detinning is somewhat more thorough. Less tin is lost than in the competing processes. The tin is recovered in the form of tin tetrachloride, which is a valuable chemical product, formerly used in the silk-dyeing industry.

Practically all the corrosion problems in handling of commercial dry chlorine gas have been successfully solved. Transporting and handling gaseous chlorine, while less easy than other commercial gases, is not relatively difficult.

Economics of Detinning

Plants for recovery of tin from tin-plate scrap are fairly simple, but need to be designed with due regard to details. The plant cost per ton of scrap will vary considerably with the size of the plant.

[11] Murray, and Fernberger, *U. S. Patent 913,275*, filed Jan. 17, 1906; granted Feb. 23, 1909. This patent antedates that of Dubois and Kaufman, *German Patent 228,958*, filed May 16, 1907; granted Jan. 11, 1911.

Tin-plate scrap has no market as such; on the other hand, detinned scrap has a ready sale. Stannic chloride crystals were in constant demand until World War II, and salable at an attractive price. Tin metal can be recovered from the stannic chloride, but this involves additional processing so that such processing is not economic if the stannic chloride crystals can be disposed of as such on a price basis equivalent to their tin content.

The cost of handling a ton of tin scrap in process, including all labor, interest, taxes, depreciation, materials (as chlorine), repair and maintenance is just about equal to the amount obtained per ton of detinned scrap when it is sold as baled scrap on the open market. This cost of handling does not include the nominal cost of the original tin-plate scrap The values obtained then for the stannic chloride produced (or the tin recovered from such) are on the profit side of the ledger.

There will be consumed approximately 80 to 100 pounds of chlorine per ton of tin plate, of the quality and weight of tin coating on tin plate commonly used for tin cans. The amount of scrap resulting from the fabrication of these containers is tremendous. Recovery of tin is of great and pressing importance.

Chapter 21

Analytical Methods

Properties and Reactions of Tin

When stannous salts are treated with hydrochloric acid, no precipitation occurs. Concentrated solutions of stannic salts become turbid in aqueous solution, owing to oxidation and hydrolysis The formation of basic salts in this manner can be prevented by hydrochloric acid, and the oxidation may be eliminated by keeping the solution in contact with granulated tin Stannic salts such as the chloride are hydrolyzed by water according to the reaction

$$SnCl_4 + 4H_2O = 4HCl + Sn(OH)_4$$

In very dilute solutions, sulfuric acid may precipitate a basic sulfate from stannic chloride

The stannous salts are all colorless The soluble ones yield solutions in water which have an acid reaction. All of the salts readily absorb oxygen, with the formation of stannic compounds Alkalies, such as sodium, potassium, or ammonium hydroxide, or sodium carbonate give white precipitates of stannous hydroxide which are readily soluble in excess sodium hydroxide with the formation of sodium stannite The precipitate also dissolves in mineral acids such as hydrochloric acid. From solutions containing not more than 2 5 per cent of concentrated hydrochloric acid, hydrogen sulfide throws down a precipitate of brown stannous sulfide This material is soluble in strong hydrochloric acid, which distinguishes it from the sulfides of arsenic It is nearly insoluble in colorless ammonium sulfide, which distinguishes it from the sulfides of antimony, arsenic, and stannic tin. It is soluble, however, in hot ammonium polysulfide, with the formation of ammonium thiostannate, from which hydrochloric acid precipitates yellow stannic sulfide, SnS_2. The reaction, according to Curtman,[1] is:

$$SnS + (NH_4)_2S_x = (NH_4)_2SnS_3 + (x - 2)S$$
$$(NH_4)_2SnS_3 + 2HCl = SnS_2 + 2NH_4Cl + H_2S$$

When mercuric chloride is added in excess to a solution of stannous chloride, it is reduced to white insoluble calomel, HgCl, the stannous

[1] Baskerville, and Curtman, "Qualitative Analysis," New York, Macmillan Co., 1918

chloride at the same time being oxidized to the stannic salt. If the stannous chloride is present in excess, the calomel first formed is further reduced to gray or black metallic mercury. Stannic salts do not give this reaction. Bismuth salts in solution are reduced by alkali stannites Metallic zinc, or other metals higher in the electrochemical scale than tin, precipitates the metal as a gray, spongy mass when introduced into a hydrochloric acid solution of either stannous or stannic chloride

Alkalies give a white precipitate of stannic hydroxide, $Sn(OH)_4$, which on drying becomes H_2SnO_3, as a result of their action on stannic salts in solution. From moderately acid solutions of stannic salts containing not more than 2.5 per cent of concentrated hydrochloric acid, hydrogen sulfide precipitates yellow SnS_2, or stannic sulfide. The sulfide is readily soluble in hydrochloric acid of one part acid to one part water. Stannic sulfide readily dissolves in colorless ammonium sulfide, which distinguishes it from stannous sulfide, with formation of ammonium thiostannate, from which solution hydrochloric acid reprecipitates the sulfide. When strongly ignited in air, stannic sulfide is quantitatively converted to stannic oxide

Mercuric chloride gives no precipitate with stannic salts, nor do hydrochloric and sulfuric acids when they are moderately concentrated. If solutions of stannic salts are boiled, a more rapid hydrolysis occurs, with the formation of a precipitate of stannic hydroxide, $Sn(OH)_4$. In the cold, potassium or sodium sulfate does not yield precipitates with stannic salts, but upon boiling, insoluble stannic hydroxide is formed.

Stannic compounds occur in two forms, the normal and the metastannic variety The first may be considered as derived from stannic hydroxide formed by the action of alkalies on stannic chloride It is readily soluble in acids The metastannic compounds are derived from the white substance obtained by the action of hot dilute nitric acid on metallic tin and termed metastannic acid. Its empirical formula is the same as the partially dehydrated stannic hydroxide, that is, H_2SnO_3, with the distinction, however, that it is insoluble in acids. When metastannic acid is boiled for a short time with concentrated hydrochloric acid, a compound of the formula $Sn_5O_5Cl_2(OH)_8$ forms, which is readily soluble in water although quite insoluble in hydrochloric acid. From these reactions and the fact that similar compounds may be formed from metastannic acid, the formula $Sn_5O_5(OH)_{10}$, or $5(H_2SnO_3)$, has been assigned to it. Metastannic acid is thus seen to be a polymer of stannic hydroxide. The reactions of metastannic chloride, $Sn_5O_5Cl_2(OH)_8$, are of considerable analytical interest. The substance is precipitated out of aqueous solution by hydrochloric acid, and prolonged boiling of the aqueous solution causes the precipitation of all the tin as metastannic acid, which is insoluble in dilute acids. Sulfuric acid, or sulfates, precipitates a white substance which changes on washing with water to metastannic acid, which reaction is distinctly different from the analogous

one occurring with stannic chloride. Sodium or potassium hydroxide precipitates metastannic acid which is soluble in excess of the reagent, but ammonium hydroxide precipitates metastannic acid which is not soluble in excess ammonia. Hydrogen sulfide forms stannic sulfides. Solutions of stannic compounds are converted into the metastannic form by diluting and boiling; and conversely, metastannic compounds are converted into the stannic form by boiling with concentrated hydrochloric acid or concentrated alkalies.

A solution of a stannous salt added to a solution of auric chloride gives a separation which is brown by transmitted light and bluish-green by reflected light, as the result of the formation of colloidal gold, also known as "purple of Cassius." Stannous salts give white precipitates when treated with either ferro- or ferricyanides in aqueous solutions, while stannic salts give a white turbidity with soluble ferrocyanides, the turbidity changes to a yellow gelatinous precipitate insoluble in hydrochloric acid The stannic salts form no precipitate with ferricyanides Lowenthal[2] found that small amounts of stannous chloride give a very sensitive reaction when added to a mixture of ferric chloride and potassium ferricyanide, with the resulting formation of a precipitate of Berlin blue Longstaff[3] found that stannous salts can be detected to the extent of one part in a million and a half parts by the blue coloration formed with solutions of ammonium molybdate. Stannous chloride gives a yellowish-white precipitate with potassium iodide, and with excess of the reagent, orange, needle-like crystals of the double salt are formed, while stannic chloride gives a yellow precipitate. Stannous salts give a white precipitate with oxalic acid or oxalates, but stannic salts do not. Pfaff[4] found that succinic acid and alkali benzoates give white precipitates with stannous salts, which are visible in dilutions as low as one in ten thousand Berzelius[5] found that stannic salts are completely precipitated by ammonium succinate

There has been a large amount of work on tin analysis employing organic reagents.

Quantitative Analysis of Tin Ore

There are three general methods in use for determining the amount of tin in ores and other products: fire assay, fusion method, and volumetric wet analysis.

Fire Assay.[6] The fire assay for tin is usually conducted in the following manner: Grind slightly more than 5 grams of the sample until it will pass

[2] Lowenthal, *J. prakt. Chem.* (1), **60**, 267 (1853), (1), **77**, 321 (1859).

[3] Longstaff, *Chem News*, **80**, 282 (1899).

[4] Pfaff, "Handbuch der analytischen Chemie," Vol. **2**, p. 337, Altona, 1822

[5] Berzelius, *Ann. chim. Phys.* (1), **94**, 187 (1815)

[6] Hallett, Chapter on tin in Liddell's "Handbook of Non-Ferrous Metallurgy," pp. 1389–92. New York. McGraw-Hill Book Co., Inc., 1926.

through a 100-mesh screen. Dry at 100° C., cool, and weigh out exactly 5 grams into an 8-oz. wide-mouth flask Add 100 cc. hydrochloric acid (concentrated) and digest at a low heat until the volume is reduced to about 15 cc Add 50 cc. nitric acid (concentrated) and continue the evaporation to a volume of 10 to 15 cc. Add about 200 cc. of water, boil, and allow to stand. Filter on double filter papers containing paper pulp, washing with warm water just acid with nitric acid. If tungsten is present, treat with ammonia (concentrated) and again filter and wash with water. Transfer the precipitate to a porcelain crucible and ignite. Brush the contents of the crucible onto a clean sheet of glazed paper, break up lumps with a spatula, mix thoroughly with 20 grams of sodium cyanide (free from chlorides), and transfer to a 20-gram clay crucible in which has been placed 4 or 5 grams of sodium cyanide Cover with sodium cyanide, fuse in a muffle furnace at a red heat for 20 to 25 minutes, cool, wash with water, break crucible to obtain the button, clean the button, and soak in hot water to remove adhering cyanide. Dry and weigh Run in duplicate Duplicates should agree within 0 15 per cent

Fusion Method. The routine determination of tin by fusion with alkalies and peroxides is carried out as follows: Weigh 1 gram of low-grade tin or 0.5 gram of medium or high-grade tin concentrate into a 50-ml high-form iron or nickel crucible, add 4 grams of sodium carbonate, mix thoroughly, and cover with 8 grams of sodium peroxide Heat the crucible and contents over a small Bunsen flame to expel any water in the flux and until the charge starts melting, then carefully finish fusion by holding and revolving the crucible around the edge of the flame until the mixture melts down quietly When the contents are in quiet fusion, continue heating with the full flame of the Bunsen burner, while rotating the crucible, for about 2 minutes

Let the melt solidify and cool, then place the crucible in a 400-ml. beaker, add 60 ml of cold water, and allow the melt to disintegrate Remove the crucible from the beaker with a glass rod, rinsing it thoroughly with warm water Add 50 ml of concentrated hydrochloric acid to the beaker, agitating the solution until all has dissolved, as indicated by the clear green color of nickel chloride or the brown color of ferric chloride. Clean the crucible with 50 ml of hydrochloric acid and add to main solution.

Transfer the solution to a 500-ml. Erlenmeyer flask and dilute to 250 ml. Introduce a nickel strip of foil weighing about 5 grams and boil the solution gently for about 25 minutes until all ferric chloride has been reduced (if fusion of the sample was carried out in an iron crucible). Introduce a second nickel strip and close the flask with a rubber stopper containing a glass outlet tube so bent that it terminates at the level of the bottom of the flask Boil the solution gently for 20 minutes more, then seal the end of the glass tube with a hot solution of sodium bicarbonate in a

250-ml. beaker. Remove the flask from the hot plate, cool to below 15° C, and titrate with a 0 125 *N* iodine solution, using starch as indicator.

Potassium Iodate Method Weigh 2-gram portions of tin concentrate, and 2 grams of a standard sample containing approximately the same amount of tin, into nickel crucibles and fuse with 5 grams of sodium carbonate and 10 grams of sodium peroxide Acidify, reduce, and cool along the lines indicated in the regular iodine method, using a 750-ml. Erlenmeyer flask.

Weigh in a beaker 0 8800-gram portions of potassium iodate if the sample contains 75 to 78 per cent of tin, or 0 8500-gram portions of potassium iodate if the sample contains 73 per cent of tin, add about 0 5 gram of sodium bicarbonate and about 1 gram of potassium iodide, and dissolve in 75 ml of cold water As 0 9 gram of potassium iodate oxidizes approximately 1.50 grams of tin, the amount of potassium iodate weighed in as directed above is sufficient to oxidize approximately 96 to 97 per cent of the stannous chloride present.

$$0\ 6010 \text{ gram of } KIO_3 \simeq 1\ 0000 \text{ gram of tin}$$

Remove the stopper with glass tube from the Erlenmeyer flask containing the reduced tin solution and add at once quantitatively the potassium iodate solution prepared by the above method, washing the beaker with cold water. Add starch solution and titrate immediately with standard potassium iodate solution

Reagent

Standard Potassium Iodate Solution· Dissolve 3.000 grams of potassium iodate and about 3 grams of sodium bicarbonate in cold water Transfer to a 1,000-ml volumetric flask, fill up to mark, and shake [7] 1 ml of solution contains 0 0030 gram of potassium iodate.

Volumetric Wet Analysis.[8] The volumetric determination of tin is applicable to nearly all kinds of ores, metallurgical products, and other materials containing tin. A number of volumetric methods have been proposed, the best of which depends on the titration of stannous chloride with standard iodine in cold hydrochloric acid solution This is called the Pearce-Lowe method,[9] and is one of the simplest, shortest and most accurate for the volumetric estimation of tin It depends on the oxidation of stannous to stannic chloride by iodine in cold hydrochloric acid solution according to the equation:

$$SnCl_2 + 2HCl + I_2 = SnCl_4 + 2HI$$

[7] S. Kallmann, *Ind Eng Chem, Anal Ed*, **15**, 166–74 (1943)

[8] Hallett, *Loc cit*

[9] *J. Soc Chem. Ind*, **35**, 1088 (1916), also Mellor, "Treatise on Quantitative Inorganic Analysis," p 311, London, Chas. Griffin & Co, Ltd, 1913

Starch solution is used as indicator. A small amount of sulfuric acid is not objectionable, but nitric acid and nitrates must not be present.

The method requires that the tin shall be brought into solution in hydrochloric acid. When possible, the finely ground sample is dissolved directly in hydrochloric acid; in some cases the addition of a small quantity of potassium chlorate, antimony chloride, or platinic chloride, or the presence of a piece of platinum foil, accelerates solution. In the analysis of materials containing sulfides or certain alloys, a mixture of hydrochloric and nitric acids may be used, followed by treatment with sulfuric acid and then with hydrochloric acid. Siliceous products frequently respond to treatment with hydrofluoric acid

For the decomposition of insoluble silicates, fusion with alkali carbonates is effective Practically all silicates are decomposed by this process, but it is not suitable for use with samples containing insoluble tin oxide, and if sulfides or salts of tin soluble in acids are present they should be removed before the fusion process is applied The addition of 10 per cent of borax to the alkali carbonate accelerates the decomposition in some instances

Acid-insoluble residues may be decomposed by fusion with sodium or potassium hydroxide, the melt being subsequently dissolved in hydrochloric acid This method is perhaps the most useful of the fusion processes, since it is applicable to almost all products and generally requires only a very simple preliminary acid treatment. An iron crucible is the most suitable for use with this process.

Sodium peroxide may also be used for the fusion process, but it corrodes the crucibles very rapidly, and generally its disadvantages more than offset the extra speed gained by its use. The addition of organic matter to the peroxide, to furnish the necessary heat for the reaction, has been suggested as a means of preventing the corrosion Quieter fusion results if zinc sulfide, iron sulfide, or potassium persulfate is added to the peroxide.

In the final hydrochloric acid solution, the tin will usually be found in the stannic condition and must be reduced to the stannous condition before titration. This reduction is usually accomplished in one of four ways: by the use of iron in the form of rods; nickel or aluminum in the form of sheets or strips; or finely powdered antimony. Only pure soft iron may be used. If carbon is present in the iron, it will generally cause high results

The use of aluminum renders this part of the method somewhat uncertain and makes it difficult to control the operation. The principal objection to the use of antimony is that the presence of so much finely powdered material in the solution obscures the end point. The only objection to nickel is the light green color given the solution, but this does not affect the sensitiveness of the end point if the concentration of nickel salts is only that derived from the metal used for the reduction.

The reduction and the titration are best performed in an atmosphere of carbon dioxide and in a solution containing not less than 25 per cent nor more than 40 per cent by volume of free concentrated hydrochloric acid The temperature of the solution to be titrated should not exceed 22° C

One-half to 2 grams of the sample (depending on the percentage of tin) is first brought into hydrochloric acid solution. The solution is transferred to a 12-ounce wide-mouth conical flask, enough concentrated hydrochloric acid is added to make a total of 50 cc of free concentrated hydrochloric acid present, and the solution is diluted to 200 cc with water. A nickel coil is prepared by rolling 6 sq. in. of heavy sheet nickel (4 in long and $1\frac{1}{2}$ in wide) into a loose roll of such size that it may be easily inserted into the flask. A narrow strip of nickel is left attached to one side of the coil, long enough to reach above the top of the flask. This coil is placed in the flask containing the tin solution; the nickel strip is bent over the edge, and the flask is covered with a small watch glass The solution is heated to boiling and gentle ebullition is maintained for 30 minutes after all the iron, which is present, is reduced. The reduction of the iron is indicated by the yellow color of the solution changing to a pale green. Thirty minutes is more time than is necessary for the complete reduction of the stannic chloride from 0.5 gram of tin oxide, and if complete reduction does not result in that length of time, either the nickel coil is too small or the nickel is inactive owing to impurities and should be discarded and replaced by pure nickel.

It has been stated as an objection to this method, that it is impossible to tell when the reduction of the tin is complete and that the operator may titrate the solution before the tin is all in the lower form. It has been found that larger amounts of tin than would ever be taken as a sample are entirely reduced long before the expiration of the time allowed for the reduction, and no trouble need be anticipated from this cause

The solution in the flask is cooled in an atmosphere of carbon dioxide generated by adding two $\frac{1}{2}$-inch cubes of crystalline marble to the solution. The nickel coil is then removed and is washed with cold hydrochloric acid solution (1 part of concentrated acid to 3 parts of water) as it is withdrawn from the flask. A small amount of starch solution is then added and the solution titrated at once with standard iodine.

Reagent

Standard Iodine Solution: Dissolve 10.7 grams of iodine in 50 cc. of water containing 20 grams of potassium iodide in solution and making up to 1 liter with water. When a half-gram sample is taken for analysis, 1 cc. of this solution will equal 1 per cent of tin. It may be standardized against tin or arsenious oxide

Few of the elements which are ordinarily found in materials to be analyzed for tin interfere with this method. Nickel, cobalt, manganese,

molybdenum, uranium, chromium, aluminum, zinc, lead, calcium, magnesium, sulfates, phosphates, bromides, iodides, and fluorides have no effect unless present in such large amount that their color masks that of the indicator Arsenious and antimonious compounds in weak acid solution consume iodine, but in a hydrochloric acid solution of the strength used in this method they have no effect.

If about 0.1 gram or more of antimony is present in the solution, the nickel coil will precipitate metallic antimony in a very slimy condition which does not settle and obscures the end point. This may be prevented by using a solution containing more hydrochloric acid If, therefore, the sample taken contains 0 1 gram or more of antimony, the solution is made up to contain 75 cc. of free concentrated hydrochloric acid instead of 50 in 200 cc of volume, before reduction. If this is done, the precipitation of slimy antimony will be prevented and no trouble will be experienced. If the antimony content is not known and the slimy antimony begins to precipitate during the reduction, an additional 25 cc. of concentrated hydrochloric acid may be added, which will generally cause the antimony to dissolve and prevent further precipitation. If the precipitated antimony does not dissolve, another sample can be treated, adding more hydrochloric acid before reduction

Copper in small amounts has no effect on the method, but if 0.05 gram or more are present in the solution it will be incompletely precipitated during the reduction, the titration will consume more iodine than is required by the tin, cuprous iodide will be precipitated, and the results will be erratic and high.

If copper is present in the sample in large enough amount to interfere, it must first be removed by treatment with nitric acid.

Bismuth is precipitated in the metallic form during the reduction with nickel. In this form it is said to consume iodine slowly, but the action is slight, and, unless present in large amount, its effect is negligible If it is desired to remove it, the metallic precipitate may be filtered and the filtrate again reduced and finished as usual.

Tungsten is reduced by the nickel coil to a lower state of oxidation, with the formation of a blue precipitate, said to be W_2O_5. This is said to be slowly oxidized by iodine, thus giving high results, but the oxidation is not proportional to the amount of tungsten present. Tungsten in amounts usually met with does not interfere to any extent, and its effect is only noticeable when it is present in large quantity. In case it should be desirable to separate the tungsten, the blue oxide may be filtered off with the precipitated bismuth, the solution afterwards being again reduced and titrated.

Titanic chloride is reduced to titanous chloride by the nickel coil. In

the Pearce-Lowe method titanium alone or with iron is said to consume no iodine, but in the presence of tin large amounts of titanium will consume iodine, giving high results. The error caused by titanium seems to be approximately a constant one and is independent of the amount of titanium present. Titanium may best be removed by converting the tin to insoluble oxide by evaporation with nitric acid and then fusing for 5 minutes with potassium bisulfate The melt is dissolved in water and sulfuric acid and filtered.

If titanium and tungsten are both present, the tungsten will remain with the tin after filtering the extracted melt of the bisulfate fusion. The tungsten may be removed from this residue by heating with ammonium carbonate solution, in which the tin is insoluble.

Neither bismuth, tungsten, nor titanium, in any reasonable amount, such as is usually met with, interferes with the method, and they may, in general, be neglected, especially if the titration is performed rapidly, which to a large extent will eliminate secondary reactions. The interference of all of these metals is greatly increased by very slow and careful titration, which seems to accelerate their action and give them time seriously to affect the results This is especially true of titanium, for bismuth and tungsten are not so active and, as a rule, need not be considered.

Ferrous chloride is oxidized only by excess of iodine, and no action takes place unless a very large amount of iodine is run in and allowed to stand. Its action is very slow even then, and the presence of iron does not affect the accuracy of this method.

A tin determination may be run through and results obtained by this method in about 1½ hours, and the method is accurate to about 0.1 per cent

Hydrogen Reduction Method. At the Penpoll tin smelter the standard method for the determination of the tin content of ores is based on the reduction by hydrogen. The following is taken from an article by W H. Allen, general manager of the Penpoll Tin Smelting Company, Limited:[10]

For clean ores: Weigh 0.5 gram of agated ore into a porcelain crucible (platinum shape 30-mm diameter) containing 0.6 gram pure CaO. Mix intimately with a brass wire rod and brush the rod with a camel's-hair brush. Reduce in hydrogen for 20 minutes at a red heat over a Meker or other suitable burner. The hydrogen is passed into the crucible through a Rose crucible leading tube with cover, and sufficient gas should be used to allow of a small flame of burning hydrogen to be visible round the lid. Cool while the hydrogen is still passing and if the hydrogen flame persists, blow it out. After cooling place the crucible in a conical beaker (400 cc.), add a few drops of water to slake the lime and then 30 cc. of concentrated

[10] *Mining Mag.*, **40**, 25 (1929).

hydrochloric acid. Heat the beaker gently until all metal has dissolved. Remove the crucible with a bent glass rod and wash with 5 per cent hydrochloric acid. Wash the contents of the beaker into a 1,000 cc. flask. The solution should now have a bulk of about 100 cc.

Now add 2.5 grams of pure aluminum ribbon and lay the flask on its side in water until action has almost ceased (about half an hour). The sponge of reduced tin and remaining aluminum are then redissolved by adding 40 cc. concentrated hydrochloric acid and boiling on a hot plate

During boiling, the neck of the flask is closed by a rubber bung carrying a short tube with a bulb blown in it above the bung, and the lower end cut off obliquely. The upper end of the tube is slightly drawn out. On completion of solution the flask is connected to a carbon dioxide apparatus, by slipping the delivery tube from the latter over the drawn-out tube in the bung of the flask, at the same instant removing the flask from the hot plate. This ensures the flask being filled with carbon dioxide. Cool in a water trough and titrate with standard iodine solution, using a few cc. of the starch solution as indicator.

Reagents

Standard Iodine Solution: 700 grams iodine, 28 lb. potassium iodide, and 40 liters water. Standardize the iodine solution with 0 5 gram of pure tin dissolved and treated with aluminum ribbon as above. About 61 5 cc of solution is equivalent to 0.5 gram of tin. (This concentration of iodide inhibits the effect of titanium which interferes when less iodide is used.)

Starch Indicator: Mix 5 grams of potato starch with a little cold water. Add 70 cc. boiling water, boil for a minute, and pour into a solution of zinc chloride in 20 cc. water and 40 cc. hydrochloric acid.

Treatment of ores containing tungsten and/or antimony, bismuth, copper, and arsenic: These elements interfere with the assay and must be removed before titration. The ore is treated as before up to the stage where the metal is dissolved after the hydrogen reduction.

The crucible is removed as before, but is washed with 50 per cent hydrochloric acid instead of 5 per cent. A little potassium chlorate is added to the solution to oxidize and dissolve the antimony. The solution is cooled, and 30 cc. of cold water added. This gives an acid strength of 50 per cent. One gram of reduced iron is added and the solution allowed to stand 20 to 30 minutes. This removes tungsten, antimony, bismuth, arsenic, and copper from solution.

The iron must be free from sulfur, and the ordinary ferrum reductum is not satisfactory. Merck's iron reduced by hydrogen is guaranteed free from sulfur and is the only satisfactory brand for this purpose.

The solution is then filtered into the flask through a 9 cm. (C. S. and S. No. 597) paper. The beaker is washed twice and the paper three times

with 5 per cent hydrochloric acid. In cases where much antimony is present, the precipitate is washed only once on the paper, and is then washed back into the beaker, dissolved in hydrochloric acid and a little potassium chlorate, and reprecipitated. The solution is then treated with aluminum as before.

Analysis of Pig Tin and Tin Alloys

Cowan[11] reported on the composite work of analysts in the laboratories of the major tin consumers, giving accepted methods for the analysis of pig tin and tin-bearing metals for small amounts of impurities.

Tin in Lead-Base Bearing Materials.[12] Place a 2-gram finely divided sample in a 300-ml. Erlenmeyer flask, add 5 grams of potassium sulfate and 15 ml. of concentrated sulfuric acid; heat mixture on hot plate until lead sulfate turns white. Cool, first in air and then tap water, dilute with 10 ml. water followed by 150 ml. of 2:1 hydrochloric acid. Add 10 grams of Stanreduce (Harshaw Scientific Company, Cleveland, Ohio) and place 1-hole rubber stopper through which passes short capillary tube lightly on mouth of flask. Place on hot plate at 150° C. and bring to a boil. Boil gently, maintaining a height of foam of 0.925 to 1 25 cm. Stopper flask tightly, cover capillary tube with rubber policeman, quickly remove flask from hot plate Let stand about 2 minutes until hydrogen formed replaces condensing steam. Place flask in water bath and cool to 30° C. or lower.

Into a 500-ml. Erlenmeyer flask, pour 10 ml. of 1:2 hydrochloric acid and 5 ml. of starch solution. Add one 2.1-gram compressed sodium bicarbonate tablet While carbon dioxide is forming, fill a 100-ml. burette with standard potassium iodate solution, add second bicarbonate tablet to 500-ml. flask, withdraw 300-ml. flask from water bath and remove rubber policeman and rubber stopper. Add 135 ml. of cold water to a 500-ml. flask and into it quickly decant solution from the 300-ml. flask. Immediately wash 300-ml. flask and Stanreduce with 1:2 hydrochloric acid and decant, washing into 500-ml. flask. Add another bicarbonate tablet as needed. A total of 3 to 4 tablets will suffice. Titrate at once to a blue end point. Without delay, wash Stanreduce with 10 ml. of 1:2 hydrochloric acid, decant into a 500-ml. flask and again titrate. Repeat latter procedure until permanent end point is obtained.

To standardize results, weigh out 0.200-gram portions of pure tin or use 2-gram portions of National Bureau of Standards sample and treat by appropriate method.

The solution of sample is best obtained at 440° C. If lead-base Babbitt contains sufficient copper to interfere, determine as for tin-base Babbitt.

[11] W. A. Cowan, *J. Am. Inst Metals*, **8**, 196–229 (1914).

[12] E. T. Saxer, and R. E. Minto, *Ind. Eng. Chem., Anal. Ed.*, **15**, 261–2 (1943).

Stanreduce may be recovered for reuse by washing and drying. Sift and discard portion finer than 65 mesh.

Tin in Tin-Base Bearing Materials. Place 0.5 gram of finely divided sample in a 300-ml. Erlenmeyer flask; add 10 ml. of 1:1 nitric acid. When dissolved, evaporate solution to dryness on hot plate at 125 to 140° C. Bake it for 15 minutes, digest residue with 20 ml. of 1:1 nitric acid for 5 minutes and decant onto a 9-cm. No. 42 Whatman paper. By decantation, wash metastannic acid in flask three times with hot 2 per cent nitric acid, wash contents of filter paper three times with hot 2 per cent nitric acid, discard filtrate and return filter paper to flask with 15 ml. of sulfuric-perchloric acid mixture (666 ml. of concentrated sulfuric acid, sp. gr. 1.84, and 333 ml. of 72 per cent perchloric acid) and 2 grams of potassium sulfate. Heat mixture on a hot plate at 150° C until all the carbon is oxidized, and gradually increase temperature to 400° C to drive off perchloric acid. Cool the solution, first in air and then tap water, and dilute with 10 ml of cold water, followed by 180 ml of 1:2 hydrochloric acid Starting with the addition of Stanreduce, and increasing the time of reduction to 15 minutes, the complete determination is the same as in the case of lead-base metal, but the addition of 135 ml. of cold water is omitted.

Tin in Copper-Base Material or Bronze. Place a 1-gram sample in a 300-ml. Erlenmeyer flask and add 15 ml of 1:1 nitric acid. Dissolve sample on hot plate at 150° C., add one-half of a 9-cm soft filter paper and continue to heat and swirl until paper is macerated Dilute to 50 ml. with water and heat to boiling. Filter through a 9-cm. No. 42 Whatman paper containing small amount of pulp, wash flask once with hot 2 per cent nitric acid, and pour washings into filter paper.

Wash filter paper five times with hot 2 per cent nitric acid, discard filtrate. Return filter paper with contents to flask, add 15 ml of sulfuric-perchloric acid mixture and 2 grams of potassium sulfate. Heat mixture on hot plate at 150° C. until all the carbon is oxidized; gradually increase to 400° C., and continue heating until perchloric acid is driven off. Cool solution, first in air and then in tap water; dilute with 10 ml. of cold water followed by 180 ml. of 1:2 hydrochloric acid. Complete as in lead-base bearing metal, starting with the addition of Stanreduce, but omit the addition of 135 ml. of cold water. The time of reduction is reduced to 6 minutes.[13]

Analysis of Tin-Bearing Materials

A limited number of analytical methods for tin-containing materials will be described below. These include tin salts of commerce, electroplating baths and their components or additions.

[13] *Ibid.*

Romig and Rowland[14] gave detailed descriptions of metallographic procedures for the preparation of block tin specimens and cross sections of commercial hot-dipped tin-plate coatings.

Analysis of Stannous Sulfate. Pipette a 10-cc. sample into a 500-cc. flask, dilute to about 200 cc. Add 25 cc. of 1:1 hydrochloric acid. Titrate with standard 0.1 *N* iodine solution, using starch indicator.

$$\text{cc.} \times N \times 10.74 = \text{grams per liter of } SnSO_4$$

Analysis of Stannic Sulfate. Pipette a 5-cc. sample into a 500-cc. sulfur flask. Add 100 cc. of concentrated hydrochloric acid, 30 cc. of 50 per cent sulfuric acid, 3 grams of test lead, and water to a volume of 300 cc. Stopper flask and boil for 40 minutes to reduce stannic sulfate. While boiling, submerge outlet tube in 150 cc. of saturated sodium bicarbonate and remove flask from source of heat. Bicarbonate solution is sucked into flask and thus no air enters while cooling. When the flask reaches room temperature titrate immediately with iodine. Twice the reading minus that for $SnSO_4$ leaves the amount of iodine required by stannic sulfate.

$$\text{cc.} \times N \times 15.54 = \text{grams per liter } Sn(SO_4)_2$$

Acidity of Solutions Containing Tin. The method given is that of the International Tin Research and Development Council. Precipitate tin salt with ethyl alcohol, dilute with water and titrate with 1.0 *N* sodium hydroxide, using methyl orange indicator. The result represents the acidity caused by sulfuric and sulfonic acids.

Free acidity is determined by titrating with alkali in the presence of a large excess of neutral potassium oxalate, using phenol red indicator. There is a gradual change from yellow to pink, or if back-titrating, from pink to yellow, so that a reference standard should be used. Cresol sulfonic acid can be corrected for after cresol is determined; free sulfuric acid can be calculated.

Cresol, or phenols in general, is determined by bromination under controlled and standardized conditions.

Protein or nitrogen is determined by the Kjeldahl method. The results may be converted to glue or gelatin, if source is kept constant.

Electrolytes or Plating Solutions. The following determinations apply to plating solutions or electrolytes:

Tin Concentration (Volumetric). The methods of reducing stannic to stannous chloride with nickel sheet or powdered antimony, as described in analytical texts, are suitable. For routine analysis, use reduction with sodium hypophosphite.[15] The procedure involves reduction in hydro-

[14] O. E. Romig, and D. H. Rowland, *Metals and Alloys*, **13**, 436–43 (1941).

[15] B. S. Evans, *Analyst*, **56**, 171 (1931).

chloric acid in the presence of mercuric chloride catalyst. Both reduction and titration are carried out in a carbon dioxide atmosphere. The reagents required are: (1) sodium hypophosphite, 5 grams for each test sample; (2) hydrochloric acid, 50 cc. of concentrated hydrochloric acid plus 50 cc. water; (3) saturated solution of mercuric chloride; (4) citric acid, 50 grams to 100 cc. of water (5) potassium iodide, 4 per cent solution; (6) starch indicator; (7) standard iodine solution 0.1 *N*.

A modified method to avoid external carbon dioxide is recommended. A 500-cc. flask fitted with a one-hole stopper carrying a glass outlet tube, drawn out to a jet at the outer end, is used. Dissolve a 5-cc. sample of the plating solution in 20 cc. of hydrochloric acid. Add 5 grams of hypophosphite dissolved in 80 cc. hydrochloric acid; then add 1 cc. of mercuric chloride. Boil gently for 10 minutes, add potassium iodide, citric acid, starch solutions, and 2 pieces of marble. Replace stopper with glass tube and cool quickly under tap. Remove glass tube, insert burette and titrate. Avoid agitation during cooling and titrating.

1 cc. 0.1 *N* iodine = 0.00593 gram Sn = 1.19 grams Sn per liter (in 5-cc. sample)

Tin Concentration (Gravimetric). Add a few cc. of concentrated nitric acid to 10-cc. sample and evaporate to dryness on a hot plate. Add water and filter while hot; wash the H_2SnO_3 with hot water. Dry, ignite, and heat to dull red heat; weigh residue as stannic oxide.

Wgt. SnO_2 x 0.7876 = wgt. metallic Sn (in 10-cc. sample)

Free Caustic Soda Concentration. To a 5-cc. sample add 25 cc. of distilled water and 50 cc. of barium chloride solution (10 per cent), shake thoroughly, allow to stand 15 minutes, add a few drops of 1 per cent alcoholic thymolphthalein indicator and titrate with vigorous shaking until blue color starts to be discharged. Add further drop of indicator and continue titrating. The end point is reached when color changes to practically white.

1 cc. 0.1 *N* hydrochloric acid = 0.004 gram caustic soda (in 5-cc. sample)

Sodium Acetate. Place a 25-cc. sample in a 500-cc. distilling flask fitted with a two-hole stopper and a few glass beads on bottom. One hole carries tap funnel with long stem, the other, a thermometer. Connect sidearm to condenser. Add 150 cc. of distilled water to the sample in the flask and 50 cc. of 50 per cent sulfuric acid solution and distill into a 500-cc. Erlenmeyer flask containing about 50 cc. of distilled water. Distill up to about 127° C. and add more water. Continue distilling until about 250 to 300 cc. of water has distilled over or the final distillate is neutral. Titrate the distillate with 0.5 *N* sodium hydroxide and thymolphthalein indicator.

1 cc. 0.5 *N* sodium hydroxide = 0.0410 gram sodium acetate or 1 cc. 0.5 *N* sodium hydroxide = 1 64 grams per liter sodium acetate (in 25-cc. sample)

Check distillate for sulfates using 10 per cent barium chloride solution The presence of sulfates is an indication that sulfuric acid boiled over; the procedure must then be repeated.

Sodium Carbonate. This determination is required only for solutions in operation for a long period.[16]

Bivalent Tin. Acidify a 25-cc. sample with 20 per cent hydrochloric acid and titrate direct with 0.1 *N* iodine solution.

1 cc. of 0 1 *N* iodine solution = 0 00593 gram Sn = 0 2372 gram per liter (in 25-cc sample)

Sodium Stannate Impurities. The following procedures are recommended for the detection of impurities in sodium stannate.

Antimony or Arsenic. Place copper strip[17] (cleaned by dipping in nitric acid) in a 1-gram sample of solid sodium stannate used in making up bath dissolved in hydrochloric acid. On warming, metallic antimony or arsenic will precipitate as a gray coating on the copper. In small amounts, antimony gives the solution a characteristic purple color (Cu_2Sb). On a 1-gram sample of stannate dissolved in 5 cc. of water and 5 cc. of hydrochloric acid, it is possible to detect antimony or arsenic present to the extent of 0.2 per cent or over. Metallic precipitate must not be confused with a slight blackening which occurs when copper tends to dissolve in hydrochloric acid in the presence of an oxidizing agent, for example, nitrate or peroxide.

Lead. Dissolve sample of solid stannate in a few cubic centimeters of 5 per cent caustic soda solution; filter and add 1 to 2 drops of dilute ammonium sulfide solution. A 1-gram sample of stannate containing 0.05 per cent lead or more will, when dissolved in 10 cc. of water, give a black precipitate.

Tin Coatings—Corrosion Tests for Porosity. Studies on the porosity of tin coatings have been described by Macnaughtan, Clarke and Prytherch,[18] Egeberg and Promisel,[19] Vaurio, Clark and Lueck,[20] and Hoare.[21] A number of these determinations are listed below.

[16] F. F. Oplinger, and Fred Bauch, pp. 329–41 in "Modern Electroplating," New York, The Electrochemical Society, 1942.

[17] S. Baier, *Intern. Tin Research Development Council*, Pub. No. 92, 9 (1939).

[18] D. J. Macnaughtan, S. G. Clarke, and J. C. Prytherch, *Intern. Tin Research Development Council, Tech. Pub.*, **A**, No. 7 (1935).

[19] B. Egeberg, and N. E. Promisel, *Metal Cleaning Finishing*, **10**, 270–2, 274, 337–8 (1938).

[20] V. W. Vaurio, B. S. Clark, and R. H. Lueck, *Ind. Eng. Chem., Anal. Ed.*, **10**, 368–74 (1938).

[21] W. E. Hoare, *Quart. Rev., Intern. Tin Research Development Council*, No. 2 (July, 1939).

Hot Water Test. The specimen is cleaned and immersed in an upright position in distilled water at 95° C. for 6 hours. Reddish-brown spots appear at pores or discontinuities in the plated surface.

Hydrogen Evolution Test. The test specimen is immersed in normal hydrochloric acid at 135° F., and the time measured for the collection of 5 cc. of hydrogen.

Copper Sulfate Test. The specimens are immersed in boiling dilute solution of copper sulfate. Pores are revealed by rust and copper spots.

Electrolytic Test. The specimen is made the anode in 0.05 to 0.1 *M* solution of sodium bisulfide for 10 minutes. If the specimen is of uniform shape so that its area can be determined, it may be stripped in concentrated hydrochloric acid containing 20 grams per liter of antimony trioxide. Weigh specimen before and after stripping. Tin may also be stripped by treating anodically in 5 to 10 per cent sodium hydroxide solution. For heavier deposits (over 0.0002 in.) select a diameter on a part which can be measured with a micrometer before and after plating or stripping. This type of test is applicable to round objects, but not flat ones.[22]

Ferricyanide or Preece Test. Place a piece of filter paper saturated with ferricyanide solution next to the tin side of a plated specimen, establishing close contact with a soft brush dampened with reagent. Brush at intervals to keep moist. Dark blue spots appearing at defective points are best observed with low-power lens after superimposing ruled glass sheet over the paper removed from the specimen.

Ammonia Fume Test. For testing the porosity of a tin coating on brass, copper or bronze, place the specimen on an inclined and cooled shelf in a closed box at room or elevated temperatures. At the bottom of the box there is an open container of ammonium hydroxide. Ammonia fumes will attack base metal through any pores in the plate. The specimen is considered nonporous when no dark spots appear on the plate after approximately four hours.

Tin Coatings—Thickness Tests.[23] Tests for the thickness of tin deposits should be interpreted with reservation, in view of the softness of the metal.

Clarke's Method for Tin Coatings on Steel. Clean the surface of the specimen with organic solvent and weigh to the nearest milligram. Solution required: 20 grams of Sb_2O_3 dissolved in 1,000 ml. of cold hydrochloric acid (sp. gr. 1.146). Place the specimen in a suitable volume of solution and allow it to remain one minute after gas evolution ceases. Wash surface immediately in running water, mop with a wet soft cloth to remove antimony deposit, dry, and weigh again. Initial weight minus final

[22] P. R. Pine, *Trans. Electrochem. Soc.*, **80**, 631–44 (1941).

[23] *Sheet Metal Inds.*, 625 (April, 1943).

weight equals weight of tin coating on area (see conversion factors in Tables 57 and 58).

Tin Coatings on Brass and Copper. Essentially the same method is used as that above for coatings on steel. The solution attacks brass and copper, but the dissolution time is sufficiently short, so that this source of error may be ignored. Unless the tin coating is very thin, the above method is reliable.

Cuprous Chloride Method for Hot-Dipped and Electrodeposited Tin Coatings on Copper. Solution required: 12 grams of cuprous chloride dissolved in 40 ml. of water and 50 ml. of concentrated hydrochloric

TABLE 57. THICKNESS AND WEIGHT OF TIN ON TIN PLATE

THICKNESS		WEIGHT COATING ON EACH FACE				TIN-PLATE COATING
(in.)	(mm.)	(g./sq. in.)	(g./sq ft.)	(oz./sq ft.)	(g./sq in.)	(wt./basis box)
0.0005	0.00127	0.00597	0.859	0.0303	9.25	13.2 oz.
0.0001	0.00254	0.0119	1.72	0.0606	18.5	1 lb., 14 oz
0.0003	0.00762	0.0358	5.15	0.182	55.5	4 lb., 15.2 oz
0.0005	0.0127	0.0597	8.69	0.303	92.5	8 lb., 4 oz.
0.00075	0.0191	0.0895	12.9	0.454	139	12 lb., 6 oz.
0.001	0.0254	0.119	17.2	0.606	185	16 lb., 8 oz.

Basis box (Great Britain) or base box (United States) unit area equals 31,360 sq in. of sheet (*e.g.* 56 sheets 28 in. by 20 in. or 112 sheets 20 in. by 14 in.). Area of coated surface in basis box 62,720 sq in. Coating weight on tin plates usually expressed as lb. per basis box (Great Britain and United States) and g. per sq m (European continent). One g. per sq. in. equivalent to 1.43 oz. avoir. per basis box.

Selected area of tin coating may be protected from solution by a coating of nitrocellulose varnish. Applied after first weighing and removed with acetone before final weighing.

In stripping hot-dipped tin coatings, certain amount of iron dissolved as FeSn alloy. Apply following adjustment to calculated thickness: 0.000004 in. (0.0001 mm. or 1 oz. per basis box) to be deducted.

acid. Heat the solution with small pieces of copper until almost colorless. If the process is slow, add pieces of scrap tinned copper. Rapid addition reduces cupric chloride. Place a layer of paraffin on the surface of the solution to prevent oxidation of cuprous chloride. Maintain temperature at 90 to 100° C. Weigh the degreased specimen and then immerse it (through the paraffin) in the hot solution for 10 to 15 minutes. Brush off copper deposit. Wash in water, then alcohol; dry in warm air and reweigh. This method is accurate to ±5 per cent.

Sodium Plumbite Method. This procedure is used to determine the thickness of the free tin part of the coating, leaving the tin-iron or tin-copper alloy layer unattacked. Solution required: 60 grams of lead ace-

tate; 100 grams of sodium hydroxide; 750 ml. of water. Make up solution at 60° C. The specimens are cleaned, degreased and weighed, then immersed in the boiling solution for about 5 minutes. Brush off the lead deposit. Plunge immediately into cold water. If free tin is left, replace specimen in solution. Wash, dry, reweigh. The time of immersion should not be too long, so as to avoid even slight attack of alloy layer by the solution. For hot-dipped tin the optimum time is 0.07 gram per sq. m. per minute.

Nitric Acid-Hydrochloric Acid Method. This test is suitable for steel-base materials of large size. Solution required: 5 volumes of concentrated

TABLE 58. THICKNESS AND WEIGHT OF TIN ON TIN PLATE

THICKNESS OF COATING			WEIGHT OF COATING ON EACH FACE				
(oz./box)	(in.)	(mm)	(g./sq. in)	(g./sq. ft)	(oz /sq ft.)	(oz./sq. m)	(g./sq. m.)
1	0 000004	0 000096	0 000452	0 0651	0 00230	0.0247	0.701
2	0 000008	0 000192	0 000904	0 130	0 00459	0.0494	1.40
3	0 000011	0 000289	0 00136	0 195	0 00688	0.0741	2.10
4	0.000015	0.000385	0 00181	0 260	0.00917	0.0987	2.80
5	0 000019	0 000481	0 00226	0 325	0 0115	0.123	3.50
6	0.00002	0 000577	0 00271	0.391	0.0138	0 149	4.20
7	0 000024	0 000674	0 00316	0.456	0 0161	0 173	4.90
8	0 00003	0 000770	0 00362	0 521	0 0184	0.198	5.60
9	0.000034	0 000866	0 00407	0 586	0 0207	0 223	6 31
10	0.000038	0 000962	0.00452	0.651	0 0230	0.248	7.01
11	0.00004	0.00106	0 00497	0.716	0.0253	0.272	7.71
12	0 000046	0 00115	0 00542	0.781	0 0275	0 296	8 41
13	0 00005	0.00125	0 00588	0.846	0 0298	0 321	9 11
14	0.000054	0.00135	0.00633	0 911	0.0321	0.346	9.81
15	0.000058	0 00144	0 00678	0.976	0.0344	0 370	10 5
16	0.00006	0 00154	0 00723	1 04	0 0367	0 395	11 2
20	0.000077	0.00192	0.00904	1.30	0 0459	0.494	14 0
24	0.00009	0.00231	0 0109	1 56	0 0551	0.593	16 8

hydrochloric acid; 1 volume of concentrated nitric acid; 15 volumes of water; operated at room temperature. The solution dissolves tin slowly and attacks the base only slightly.

Dropping Test (Hull and Strausser). The dropping test is used for the measurement of tin coatings on steel, brass and copper. Solution required: 12 grams of trichloracetic acid; 1,000 ml. of water. A 250-ml. separatory funnel is connected by about 8 inches of rubber tubing to a glass stopcock. The lower end of the funnel is drawn to a jet with an orifice delivering an 0.05-ml. drop. A glass dish is placed below the orifice and the specimen is supported so that drops strike the point to be tested and run off at a 45° surface angle. The funnel is filled with solution at

about 25° C. and the stopcock is adjusted so that the rate of discharge is about 100 drops per minute. The specimen is cleaned, degreased and held in position. The number of seconds to remove coating at the site of drops is recorded. The end point is noted by the appearance of the color of the base metal. Thickness is calculated from the relationship: 10 seconds equivalent to 0.0001-in. thickness of tin. The method is accurate to 15 per cent, and is applicable to coatings of 0.0001- to 0.001-in. thickness.

Iodine Titration. This test is used for tin coatings on steel, copper or brass base. The detinned specimen must be removed from the solution before the tin is titrated. Place specimen in 40 ml. of concentrated hydrochloric acid, and heat. Run in oxygen-free carbon dioxide throughout experiment to prevent oxidation of tin. When dissolution is complete, cool flask in running water and titrate with standard iodine solution, using starch as indicator. Apparatus consists of conical flask fitted with a three-hole rubber stopper: one carries tube for carbon dioxide, the second, the tap funnel, and the third allows insertion of burette. During the dissolution the openings are closed off with a glass rod. It is sometimes convenient to adjust the standard solution so that 1 ml. is equivalent to 0.00579 gram of tin. Thus, if sample having a total surface of 8 sq. in. is used, 1 ml. of solution will be equivalent to 0.1 lb. of tin per base box.

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