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Tin - The Occurrences, Properties, and Applications: A Literature Review

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ABSTRACT

Tin is a chemical element with the symbol Sn, atomic number of 50, atomic mass of 118.71 g/mol and belong to group 14 and period 5 in the periodic table of elements. Tin has two main allotropes, α-tin and β-tin, 10 stable isotopes, 29 unstable isotopes and 30 metastable isomers, the greatest number of any element. In nature, tin occurs primarily as the mineral cassiterite (SnO_2) in various geological formations. It is often found in association with granite rocks and alluvial deposits. Tin is purified by smelting cassiterite with carbon followed by boiling and liquation or electrolytic methods. Tin is a silvery-white metal with a relatively low melting point of 231.93°C and a boiling point of 2,602°C. It exhibits good corrosion resistance, making it suitable for use in various environments, especially when alloyed with other metals. In addition, tin is soft, malleable, ductile metal and has excellent solderability making it useful for joining other metals together in the electronic and electrical equipment. Tin has two mains oxidation states, +2 and the slightly more stable +4, and can form inorganic and organometallic compounds. Due to its remarkable physical and chemical properties make this metal attract attention and has very broad benefits. Tin is not only used in conventional technologies such as solders, cans and coins, but also in advanced technologies such as tin lithium-ion batteries, smart screens and solar cells. In future, tin will play a crucial role in advancing green technologies by enabling the development of renewable energy systems, energy-efficient processes, and environmentally friendly materials. Its versatility and sustainability make it an indispensable element in the transition towards a more sustainable future. Tin is also used as reagents in organic synthesis, such as allylic, allenic and propargylic stannanes, for forming C-C bond which are very necessary in drug synthesis and development. Tin as individual particles is not exceedingly lethal to living organisms. Elemental tin metal, its salts and its oxides present low toxicity. In contrast, certain organotin compounds are almost as toxic as cyanide. Since it is not biodegradable, organic tin can last longer in the environment.

Keyword: tin, occurrences, properties, application, organic synthesis

1. INTRODUCTION

Tin is a chemical element and the Latin name for tin is *stannum*, originally meant an alloy of silver and lead. Tin is one of the abundant natural resources in the form of minerals in Indonesia (Zalim & Munadi, 2016). Indonesia is the country with the world's largest tin reserves, with reserves of 800,000 tons and the third largest tin production, 52,000 tons, after China and Myanmar with production of 68,000 tons and 54,000 tons in 2023 (Sukoco, 2024). Tin production center areas in Indonesia include the Bangka Belitung Islands, Riau Islands, Karimun Island, Kundur, Singkep, and parts of mainland Sumatra to the west of Kalimantan. These areas are known as "The Indonesian Tin Belt." The region with the largest tin reserve and producer in Indonesia is Bangka Belitung, with almost 90% of Indonesia's total tin production.

Tin production in Indonesia is controlled by PT. Timah Tbk that has a mining area of 92%, while the remaining 8% is owned by private parties. Tin mining in Bangka Belitung by PT. Timah Tbk started in 1976 with production of 24,670; 20,079 and 14,855 tons in 2021; 2022 and 2023, respectively (Ahdiat, 2024). Uncontrolled tin mining activities began to occur in 1998 due to a paradigm shift regarding the role of tin from a strategic commodity to a non-strategic commodity, which was marked by the community being allowed to mine tin and strengthened by regional autonomy. As a result of this situation, tin mining occurs massively and uncontrollably, causing significant environmental damage, especially in Bangka Belitung. According to environmental experts, the total losses due to environmental damage caused to the tin commodity trading system in the mining business permit area of PT. Timah Tbk from 2015 to 2022 reached IDR 271.06 trillion. Environmental losses resulting from tin mining inside and outside forest areas include environmental loss costs of IDR 183.70 trillion, environmental economic loss costs of IDR 75.48 trillion and environmental restoration costs of IDR 11.88 trillion (Anonim, 2024a).

Tin is one of important metal and has high economic value due to widely used in industry since ancient times. The first tin alloy used on a large scale was bronze, made of tin (12.5%) and copper (87.5%) from as early as 3000 BC (Tylecote, 1992; Savage, 1968). After 600 BC, pure metallic tin was produced. Pewter, which is an alloy of 85–90% tin with the remainder commonly consisting of copper, antimony, bismuth, and sometimes lead and silver, has been used for flatware since the Bronze Age (Thornton et al., 2002; Kaufman, 2011). In addition, bronze, or bronze-like alloys and mixtures, were used for coins over a longer period. Ancient Chinese coins were usually made from mixtures of metals such copper, tin and lead, from bronze, brass or iron. The round metal coins with a round flat shape and square hole in the center were first introduced around 350 BC (Theobald, 2016). The beginning of the Qin dynasty (221–206 BC), the first dynasty to unify China, saw the introduction of a standardized coinage for the whole Empire (Kaufman, 2011).

In modern times, tin is used in many alloys, most notably tin-lead soft solders, which are typically 60% or more tin, and in the manufacture of transparent, electrically conducting films of indium tin oxide in optoelectronic applications. Another large application is corrosion-resistant tin plating of steel. Inorganic tin, tin-plated steel is widely used for food packaging as "tin cans," because of the low toxicity. However, some organotin compounds can be extremely toxic.

This article discusses scientifically what tin is and what its benefits are, so that tin has its own attraction and has become a very important cross-border trade commodity. Moreover, research on the use of tin in organic synthesis, especially organostannanes, is also discussed. With the hope, this article will provide inspiration for Indonesia, so that tin is not only exported in the form of tin metal, but also processed into tin derivative products which have high economic value, resulting in downstream tin industry in Indonesia.

2. THE OCCURRENCE OF TIN IN NATURE

Tin is the 49th most abundant element in Earth's crust, representing 2 ppm compared with 75 ppm for zinc, 50 ppm for copper, and 14 ppm for lead (Shu, 1982). Most tin is found in alluvial deposits, riverbeds, and former riverbeds, as a result of erosion of ore bodies containing the metal. Tin does not occur as the native element but must be extracted from various ores. Tin(IV) oxide or cassiterite (SnO_2) is the only commercially important source of tin which is made up of about 80% tin, although small quantities of tin are recovered from complex sulfides such as stannite, cylindrite, franckeite, canfieldite, and teallite. Cassiterite often accumulates in alluvival channels as placer deposits because it is harder, heavier, and more chemically resistant than the accompanying granite (Penhallurick, 1986). Cassiterite is usually black or dark in color, Figure 1, and these deposits can be easily seen in river banks. Alluvial deposits may incidentally have been collected and separated by methods similar to gold panning (Dube, 2006). Minerals with tin are almost always associated with granite rock, usually at a level of 1% tin oxide content (Anonim, 1991).

(a) (b) (c)

Figure 1. (a) Tin mining, (b) cassiterite, the main ore of tin, and (c) tin metal 99.95%.

Because of the higher specific gravity of tin dioxide, about 80% of mined tin is from secondary deposits found downstream from the primary lodes. Tin is often recovered from granules washed downstream in the past and deposited in valleys or the sea. The most economical ways of mining tin are by dredging, hydraulicking, or open pits. Most of the world's tin is produced from placer deposits, which can contain as little as 0.015% tin (Sutphin et al., 1992).

Table 1. Tin production and reserves by country in the world (Anonim, 2004b; Garside, 2024).

Country	Mine Production in 2021		Mine Production in 2022		Mine Production in 2023		Reserves	
	Tons	%	tons	%	Tons	%	tons	%
China	90,000	29.54	95,000	30.21	68,000	23.39	720,000	16.43
Myanmar	36,900	12.11	31,000	9.86	54,000	18.58	700,000	15.97
Indonesia	70,000	22.98	74,000	23.53	52,000	17.89	800,000	18.26
Peru	26,995	8.86	29,000	9.22	23,000	7.91	130,000	2.97
Kongo	16,700	5.48	20,000	6.36	19,000	6.54	130,000	2.97
Brazil	15,517	5.09	18,000	5.72	18,000	6.19	420,000	9.58
Bolivia	19,628	6.44	18,000	5.72	18,000	6.19	400,000	9.13
Australia	8,772	2.88	9,700	3.08	9,100	3.13	570,000	13.01
Vietnam	5,400	1.77	5,200	1.65	5,300	1.82	11,000	0.25
Malaysia	5,000	1.64	5,000	1.59	6,100	2.10	11,000	0.25
Russia	3,000	0.98	2,700	0.86	2,700	0.93	430,000	9.81
Rwanda	2,000	0.66	2,200	0.70	3,800	1.31	14,000	0.32
Laos	1,980	0.65	1,900	0.60	2,300	0.79	46,000	1.05
Nigeria	1,600	0.53	1,700	0.54	8,100	2.79	-	-
Other countries	1,180	0.39	1,100	0.35	1,300	0.45	310,000	7.07
Total	304,672	100	314,500	100	290,700	100	4,382,000	100

The world tin mine reserves are around 4.382.000 tons. Indonesia is the highest reserves around 800,000 tons (18.26%), followed by China (720,000 tons) and Myanmar (700,000 tons), Table 1. During last three years (2021-2023), about 305,000; 315,000; and 291,000 tons of tin were mined around the world, mostly in China (90,000, 95,000, and 68,000 tons), Indonesia (70,000, 74,000, and 52,000 tons), Myanmar (36,900, 31,000, and 54,000 tons), Peru (26,995, 29,00, and 23,000 tons), Bolivia (19,628, 18,000, and 18,000 tons), and Kongo (16,700, 20,000, 19,000 tons), Table 1. Estimates of tin production have historically varied with the market and mining technology. It is estimated that, at current consumption rates and technologies, the Earth will run out of mine-able tin in 40 years (Reilly, 2007).

According to the Ministry of Energy and Mineral Resources, Republic of Indonesia, the tin producing regions in Indonesia are Bangka Belitung, Riau, Riau Islands, West Kalimantan and North Sulawesi with production of 70,370; 10,000; 5,000; 2,500 and 2,000 tons per year respectively (Anonim, 2024b; ESDM, 2020).

Generally, tin is produced by carbothermic reduction of the oxide ore, cassiterite, with carbon or coke. Both reverberatory furnace and eolectric furnace can be used (Schrader, 2012; Barry, 2017). Tin is smelted at temperatures of up to 1370°C with carbon to produce low purity tin and CO_2 gas. It is then refined to high purity (>99%) tin metal through boiling, liquation, or electrolytic methods.

$SnO_{2(s)}$ + C Arc furnace → $Sn_{(s)} + CO_{2(g)}$

3. PROPERTIES OF TIN

3.1 Physical Properties of Tin

Tin is a chemical element with symbol of Sn, atomic number of 50, and atomic mass of 118.71 g/mol. Tin is a silvery-white, soft, malleable, ductile metal, Figure 1, with the Mohr's hardness of 1.5, melting point of 231.9°C, and boiling point of 2,602°C. Tin has an atomic radius of 162 pm, atomic volume of 16.3 (ml/mol), covalent radius of 141 pm, ionic radius of 71 pm for +4 and 93 pm for +2, specific heat of 0.222 J/g mol at 20°C, fusion heat of 7.07 kJ/mol, evaporation heat of 296 kJ/mol, Pauling's negativity number of 1.96, first ionizing energy of 708.2 kJ/mol, oxidation state of +2 and +4, and lattice constant of 5.820 Å (Holleman,1985; Anonim, 2024c).

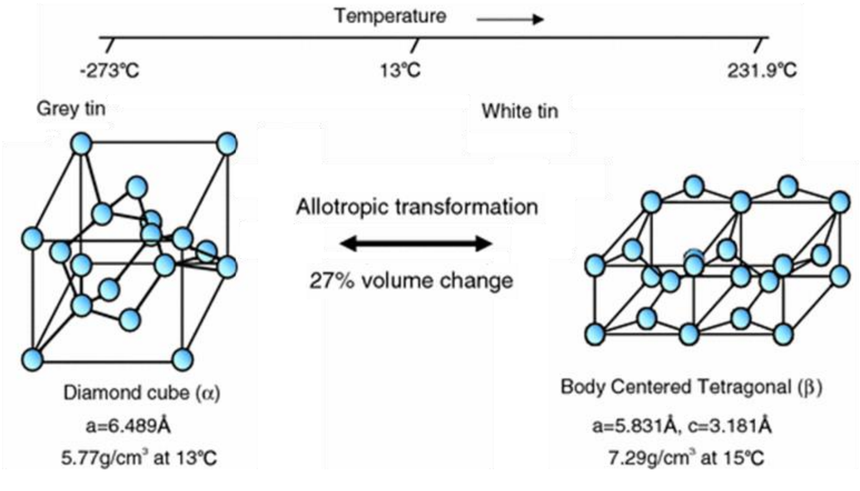


Figure 2. The α- and β-allotropes of tin (Plumbridge, 2007).

Tin has two main allotropes, α-tin and β-tin, (Plumbridge, 2007), Figure 2. At low temperatures, -273°C, tin has an α-structural form known as gray tin. It has the diamond cubic crystal structure and density of 5.75 g/cm^3. Alpa-tin does not have metallic properties because its atoms form a covalent structure in which electrons cannot move freely, as do diamond and silicon. Alpa-tin is a dull-gray powdery material with no common uses other than specialized semiconductor applications (Holleman,1985). At room temperature, the stable allotrope is β-tin, a silvery-white and malleable metal, which has the body-centered tetragonal crystal structure and density of 7.31 g/cm^3. At temperature above 161^{o}C and pressures above several GPa, tin exist in the form of γ- and σ-tin (Molodets & Nabatov, 2000).

In cold conditions, around 13^{o}C, β-tin tends to transform spontaneously into α-tin, a phenomenon known as tin pest or tin disease (Anonim, 2024d; Bashyal, 2024). Commercial grades of tin (99.8% tin content) resist transformation because of the inhibiting effect of small amounts of bismuth, antimony, lead, and silver present as impurities. Alloying elements such as copper, nickel, iron, zinc, magnesium, and other elements increase the hardness of tin (Nnakwo et al., 2017; Nnakwo, 2017). Nnakwo et al., 2017 reported that addition of nickel and iron significantly improved the percentage elongation, ultimate tensile strength, hardness and impact strength of tin bronze. Maximum percentage elongation and impact strength of 36.5% and 34 J respectively were obtained by the sample containing 0.2%wt iron content while optimum ultimate tensile strength and hardness values of 300 MPa and 275 MPa respectively were obtained by the sample containing 1%wt nickel content (Nnakwo et al., 2017). In addition, the hardness values of Cu-Sn-Zn and Cu-Sn-Mg alloys increased as the zinc and magnesium content increased to 0.8%wt and decreased with further increase in the dopants content. Maximum percentage elongation and impact strength of 17.3% and 63 J respectively were obtained by the sample containing 1wt% zinc while optimum hardness and ultimate tensile strength values of 285 MPa and 312 MPa respectively were obtained by the sample containing 0.8%wtand 1wt% magnesium respectively (Nnakwo, 2017). Tin easily forms hard, brittle intermetallic phases that are typically undesirable. It does not mix into a solution with most metals and elements so tin does not have much solid solubility. Tin mixes well with bismuth, gallium, thallium, and zinc, forming simple eutectic systems (Schwartz, 2002). Tin becomes a superconductor below 3.72 K (Dehaas, 1935) and was one of the first superconductors to be studied (Meissner, 1933).

3.2 Chemical Properties of Tin

Metallic tin does not easily oxidize in water and air, but can be corroded by acids and alkalis. With diluted hydrochloric acid (HCl), tin reacts slowly, but it reacts rapidly with concentrated acid to produce tin (II) chloride and hydrogen gas.

$$Sn_{(s)} + 2\ HCl_{(aq)} \rightarrow SnCl_{2(s)} + H_{2(g)}$$

In presence of strong alkaline solution, tin reacts to form sodium hexahydroxystannate (IV) salts and hydrogen gas.

$$Sn_{(s)} + 2\ NaOH_{(aq)} + 4\ H_2O_{(l)} \rightarrow Na_2[Sn(OH)_6]_{(aq)} + 2\ H_{2(g)}$$

When heated tin reacts with chlorine to generate tin (IV) chloride.

$$Sn_{(s)} + 2\ Cl_{2(g)} \rightarrow SnCl_{4(s)}$$

At room temperature, tin does not react with oxygen. However, when the temperature is elevated, tin reacts with oxygen to form tin dioxide, SnO_2.

$$Sn_{(s)} + O_{2(g)} \rightarrow SnO_{2(s)}$$

Tin can be highly polished and is used as a protective coat for other metals (Holleman, 1985), a protective oxide layer prevents further oxidation (Craig & Anderson, 1995). Tin acts as a catalyst triggering a chemical reaction of a solution containing oxygen and helps to increase the speed of the chemical reaction that results (Crutchlow, 2021).

The atomic number of tin is 50, it means tin has 50 protons in the nucleous and 50 electrons in the cells with electronic configuration of $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^{10}$, $4p^6$, $5s^2$, $4d^{10}$, $5p^2$. Tin is a post-transition metal in group 14 and period 5 of the periodic table of elements. Tin shows a chemical similarity to both of its neighbors in group 14, germanium and lead, and has two main oxidation state, +2 and the slightly more stable +4. Tin is the 49th most abundant element on the earth and has 10 stable isotopes. Ordinary tin is composed of ten stable isotopes, the greatest number of any element, due to its atomic number of 50 which is a "magic number" in nuclear physics. Twenty-nine unstable isotopes have been recognized and 30 metastable isomers exist. The ten stable isotopes are Sn^{112}, Sn^{114}, Sn^{115}, Sn^{116}, Sn^{117}, Sn^{118}, Sn^{119}, Sn^{120}, Sn^{122} and Sn^{124} with abundances of 0.97, 0.66, 0.34, 14.54, 7.68, 24.22, 8.59, 32.58, 4.63 and 5.79 %, respectively (RSC, 2024). Tin-120 makes up almost a third of all tin. Tin-118 and tin-116 are also common. Tin-115 is the least common stable isotope. The isotopes with even mass numbers have no nuclear spin, while those with odd mass numbers have a nuclear spin of ½.

Tin is one of the easiest elements to detect and analyze by NMR spectroscopy, which relies on molecular weight and its chemical shifts are referenced against tetramethyltin, $Sn(CH_3)_4$. Tetramethyltin is a liquid (b.p. 74–75 °C) in normal atmospheric conditions and at room temperature has a vapor pressure of a mere ~100 mm Hg. In the gaseous states it is a highly symmetrical molecule which belongs to the T_d point group; its four equivalent methyl groups being joined together in a tetrahedral molecule (Makulski, 2012).

The neutron capture cross sections of the stable isotopes ^{114}Sn, ^{115}Sn, ^{116}Sn, ^{117}Sn, ^{118}Sn and ^{120}Sn have been measured using neutron energy of 3 to 225 keV. The capture cross sections for fast neutron energy at interval 40-50 keV for the isotopes were 106.1, 303.9, 65.8, 258.5, 42.0 and 24.3 millibarns, respectively (Wisshak, 1995).

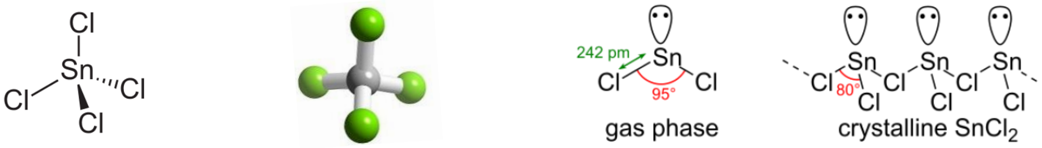
Tin has 31 unstable isotopes, ranging in mass number from 99 to 139. The unstable tin isotopes have half-lives of less than a year except for tin-126, which has a half-life of about 230,000 years. Tin-100 and tin-132 are two of the very few nuclides with a doubly magic nucleus which despite being unstable, as they have very uneven neutron-proton ratio, are the endpoints beyond which tin isotopes lighter than tin-100 and heavier than tin-132 are much less stable (Walker, 1994). Another 30 metastable isomers have been identified for tin isotopes between 111 and 131, the most stable being tin-121, with a half-life of 43.9 years (Audi et al., 2003).

The relative differences in the number of tin's stable isotopes can be explained by how they are formed during stellar nucleosynthesis. Tin-116 through tin-120 are formed in the *s*-process (slow neutron capture) in most stars which leads to them being the most common tin isotopes, while tin-122 and tin-124 are only formed in the *r*-process (rapid neutron capture) in supernovae and are less common. Tin isotopes 117 through 120 are also produced in the *r*-process. Tin isotopes 112, 114, and 115, cannot be made in significant amounts in the *s*- or *r*-processes and are among the p-nuclei whose origins are not well understood. Some theories about their formation include proton capture and photodisintegration. Tin-115 might be partially produced in the *s*-process both directly and as the daughter of long-lived indium-114 (Cameron, 1973).

4. TIN COMPOUNDS

4.1 Inorganic Compouns

In the great majority of its compounds, tin has the oxidation state II or IV. Compounds containing bivalent tin are called stannous while those containing tetravalent tin are known as stannic. Halides compounds are known for both oxidation states. For Sn(IV), all four halides are well known such as SnF_4, $SnCl_4$, $SnBr_4$, and SnI_4. Sn(IV) halides have tetrahedral molecular geometry as a consequence of the sp^3 hybridization of the tin atom, Figure 3. The three heavier members are volatile molecular compounds, whereas the tetrafluoride is polymeric. All four halides are known for Sn(II) also such as SnF_2, $SnCl_2$, $SnBr_2$, and SnI_2. All are polymeric solids. Of these eight compounds, only the iodides are colored (Holleman & Wiberg, 2001).



Tin tetrachloride

Tin dichloride

Figure 3. Molecular structure of tin(IV) chloride and tin(II) chloride in gas phase and crystal solid.

Tin(II) chloride, also known as stannous chloride, is the most important commercial tin halide. Illustrating the routes to such compounds, chlorine reacts with tin metal to give $SnCl_4$ at 115°C whereas the reaction of hydrochloric acid and tin produces $SnCl_2$ and hydrogen gas. Alternatively, $SnCl_4$ and Sn combine to stannous chloride by a process called comproportionation (Greenwood & Earnshaw, 1997).

$Sn_{(s)} + 2\ Cl_{2(g)} \rightarrow SnCl_{4(l)}$ and $SnCl_{4(l)} + Sn_{(s)} \rightarrow 2\ SnCl_{2(g)}$

Tin can form many oxides, sulfides, and other chalcogenide derivatives. The dioxide SnO_2 forms when tin is heated in the presence of air (Holleman & Wiberg, 2001). SnO_2 is amphoteric, which means that it dissolves in both acidic and basic solutions (Taylor, 1942). Stannates with the structure $[Sn(OH)_6]^{2-}$, like $K_2[Sn(OH)_6]$, are also known, though the free stannic acid $H_2[Sn(OH)_6]$ is unknown. Moreover, sulfides of tin exist in both the +2 and +4 oxidation states such as tin(II) sulfide and tin(IV) sulfide. Cylindrite ($Pb_3Sn_4FeSb_2S_{14}$), franckeite ($Pb_5Sn_3Sb_2S_{14}$) and teallite ($PbSnS_2$) are examples of tin-bearing sulfide minerals.

Chalcogenides are compounds containing one or more chalcogen elements, e.g., sulfur (S), selenium (Se), and tellurium (Te). It is usually represented as (M_aX_b), M is an element of Group IV, Group III, Group VI, or transition metal and X: S, Se, or Te (Nande et.al., 2023). The *chalcogenides* are narrow band-gap semiconductors that have been extensively used in optoelectronics, thermoelectric energy conversion.

Stannane (SnH_4), with tin in the +4 oxidation state, is unstable. However, organotin hydrides are well known, e.g. tributyltin hydride ($Sn(C_4H_9)_3H$) (Holleman, 1983). These compound release transient tributyltin radicals, which are rare examples of compounds of tin(III) (Gaur, 1973).

4.2 Organotin Compounds

Organotin compounds, also known as stannanes, are chemical compounds with at least one covalent tin–carbon bonds (Sn-C) (Elschenbroich, 2006). Of the tin compounds, the organic derivatives are commercially the most useful (Graf, 2000). Some organotin compounds are highly toxic and have been used as biocides. The first organotin compound to be reported was diethyltin diiodide, $(C_2H_5)_2SnI_2$, reported by Edward Franklannd in 1849 (Thoonen et al., 2004).

A large number of organotin compounds has been synthesized. Important organotin compounds can belong to any of four classes. These classes are related to the number of organic groups, namely monoorganotins, diorganotins, triorganotins, tetraorganotins and with one, two, three, and four alkyl or aryl groups, respectively. Figure 4 shows some common organotin compounds. They are widely used as polyvinyl chloride (PVC) stabilizers, biocides, or antifouling paints and have given rise to ubiquitous environmental contamination.

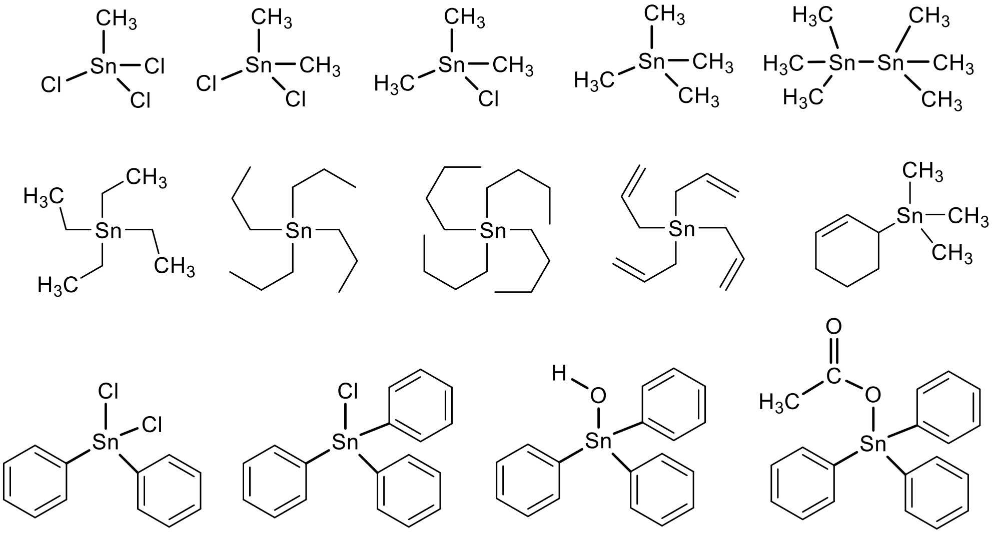


Figure 4. Molecular structure of some organotin compounds.

Most organotin compounds are colorless liquids or solids that are stable to air and water. They adopt tetrahedral geometry. Tetraalkyl- and tetraaryltin compounds can be prepared using Grignard reagents (Graf, 2000).

$$SnCl_4 + 4\ RMgBr \rightarrow R_4Sn + 4\ MgBrCl$$

The symmetrical tetraorganotin compounds, especially tetraalkyl derivatives, can then be converted to various mixed chlorides by redistribution reactions (Graf, 2005).

$$R_4Sn + 3\ SnCl_4 \rightarrow 4\ RSnCl_3$$

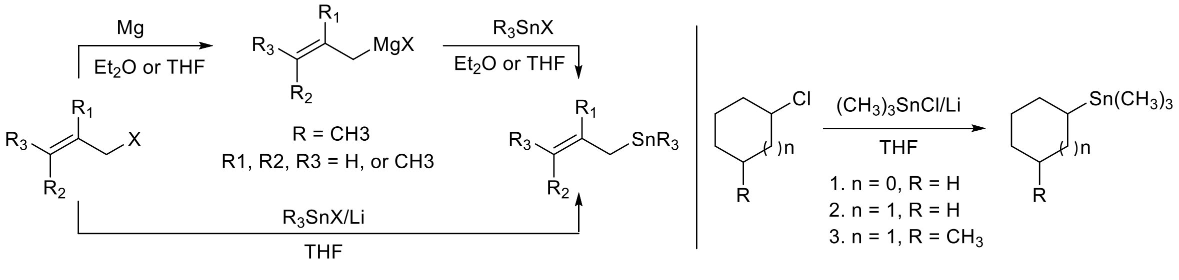
$$R_4Sn + SnCl_4 \rightarrow 2\ R_2SnCl_2$$

$$3\ R_4Sn + SnCl_4 \rightarrow 4\ R_3SnCl$$

The mixed organo-halo tin compounds can be converted to the mixed organic derivatives, as illustrated by the synthesis of dibutyldivinyltin (Seyferth, 1959):

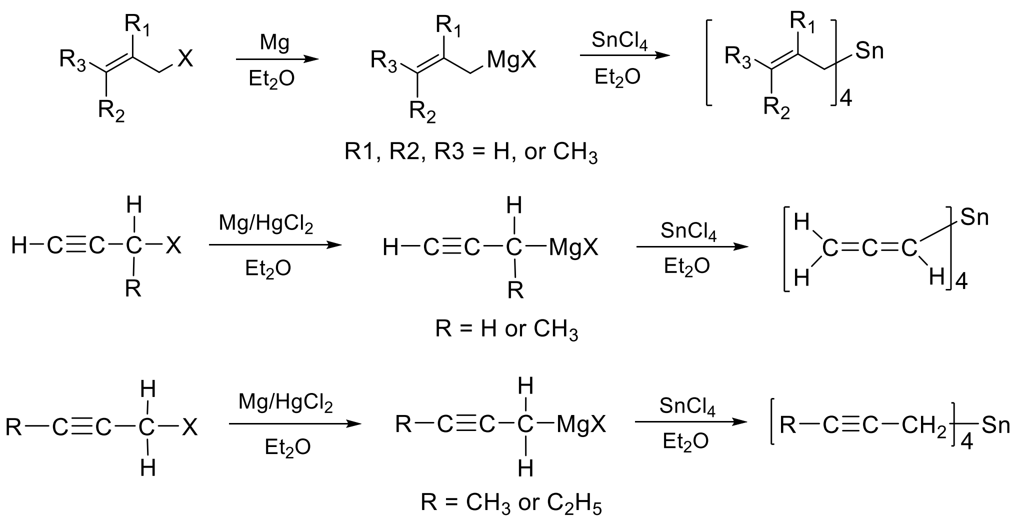
$$Bu_2SnCl_2 + 2\ CH_2{=}CHMgBr \rightarrow Bu_2Sn(CH{=}CH_2)_2 + 2\ MgBrCl$$

Allylic, allenic and propargylic tin refer to specific arrangements of carbon atoms in organic compounds, often characterized by the presence of unsaturation (double or triple bonds) adjacent to a tin atom. Both acyclic and cyclic allylic organotin compounds have been synthesized from allylic magnesium halides with organotin halides (Abel & Rowley, 1975) and from allylic halides with organotin lithium reagents by treatment of organotin halides with lithium metal in tetrahydrofuran (Muderawan, 1977), Scheme 1. Whereas, tetraallylic, tetraallenic and tetrapropargylic tin were prepared from the corresponding allylic chloride with tin tetrachloride via the Grignard reaction (Muderawan, 1977; McCluskey et al., 1998), Scheme 2. These organotin compounds are valuable intermediates in organic synthesis due to their ability to participate in a variety of reactions, providing a way to introduce functionality into molecules selectively.



(a) (b)

Scheme 1. Preparation of (a) acyclic and (b) cyclic allylictin compounds.



Scheme 2. Preparation of tetraallylic, tetraallenic and tetrapropargylictin compounds.

On the other hand, divalent organotin compounds are uncommon, although more common than related divalent organogermanium and organosilicon compounds. The greater stabilization enjoyed by Sn(II) is attributed to the inert pair effect. Organotin(II) compounds include both stannylenes (formula: R_2Sn, as seen for singlet carbenes) and distannylenes (R_4Sn_2), which are roughly equivalent to alkenes. Both classes exhibit unusual reactions (Peng et al., 2009).

5. APPLICATION OF TIN

Tin is a metal that plays a crucial role in our day-to-day lives. It has played a major role in the past, is significant in our present, and will be vital for our future. There were more than 20,300 scientific papers and patents on tin related technologies published in the last five years (2019-2023) demonstrating a strong future for this versatile element. Study of tin users carried out by the International Tin Association (ITA) estimated that global refined tin use share in 2022 was 376,900 tons (Anonim, 2023). Solder still accounts for the largest global share of tin use, increasing marginally to 50% in 2022, followed by chemicals (16%), tinplate (12%), batteries (7%), tin-coper alloy (7%), and other applications (8%), Figure 5.

Figure 5. Uses and applications of tin.

Moreover, tin has a wide range of technical properties that mean its uses extend to many areas of everyday life. It can adapt well to meet emerging needs for new materials that can generate, store and deliver tomorrow's energy. ITA has identified nine technology opportunities for tin in lithium-ion batteries, mainly in high-capacity anode electrode materials, but also in solid-state and cathode materials. At the same time the fascinating technical properties of tin are already delivering a wide and growing range of research and development projects across green energy technologies as well as new electronic materials. Over the next decade tin has many opportunities in lithium ion and other batteries, solar PV, thermoelectric materials, hydrogen-related applications and carbon capture. Tin-copper products should also benefit from development of electric vehicles and renewable energy infrastructures.

5.1 Solders

Tin has been used in alloys with lead as solder in the form of tin lead wire for long time. Tin-lead wire is a eutectic mixture at the weight proportion of 62% tin and 38% lead, with a single melting temperature of 183 °C (D'Amelia et al., 2012; Long et al., 2017). It is widely use to joint two metals together. Such solders are primarily used for joining pipes or electrical circuits. Soldering is performed in a wide range of industries including plumbing, electronics, heating or air condenser, and manufacturing processes. Tin-lead wire solder has some benefits, such as ideal for application due to delicate temperature for soldering, suitable used for electronic where heat sensitive components will begin to melt, good electrical properties, and corrosion resistance properties. Tin as solder will glue together all of the electronic and electrical equipment required for a 5G-supported smart communications future.

5.2 Tin Plating

The metal coating process is one way to improve performance, prevent corrosion, beautify the appearance, and improve the surface of the material. The methods commonly used in the metal coating process are electroplating, electroless plating, hot dipping, physical vapor deposition (PVD), and chemical vapor deposition (CVD). Tinning is a metal coating method where the coating metal is white tin (Sn), which is known as tin plating (Sutrisno, 2022). There were commonly used methods of applying tin plating, one of them is electroplating. Tin electroplating is the process of depositing tin to the surface of a material via an electrical current in an electrolyte solution (Edi Septi et al., 2023).

Tin plating is used by ancient civilizations and is still being used in the modern era. Different industries which include electronics, solar, mechatronics, hardware, and many more, use tin plating for several purposes. Tin bonds readily to iron and is used for coating lead, zinc, and steel to prevent corrosion. Tin-palted steel containers are widely used for food preservation, and this forms a large part of the market for metallic tin. Copper cooking vessels such as saucepans and frying pans are frequently lined with a thin plating of tin, by electroplating or by traditional chemical methods, since use of copper cookware with acidic foods can be toxic.

5.3 Specialized Alloys

Alloy is a combination of two or more elements, one of which must be a metal. The result of this mixture is a material whose properties such as the ability to conduct electricity, malleability and ductility are significantly different from those of the constituent elements. Tin in combination with other elements forms a wide variety of useful alloys (Hampshire, 2001). Tin is most commonly alloyed with copper. Bronze is a durable alloy made by mixing copper (Cu) and tin (Sn) around 12-12.5%. Bell metal is also a copper-tin alloy, containing 22% tin and 78% copper. Besides its traditional use in weapons and tools, bronze was widely *used* in coinage.

Niobium-tin Nb_3Sn alloy has been synthesized and is being utilized as superconductor. A superconductor is a type of material that conducts electricity with zero energy loss or resistance when cooled to a certain temperature. Niobium-tin Nb_3Sn superconductors have significant applications in constructing high-field (>10 T) magnets. The niobium-tin compound Nb_3Sn is commercially used in coils of superconducting magnet for its high critical temperature (18 K) and critical magnetic field (25 T). A superconducting magnet weighing as little as two kilograms is capable of producing the magnetic field of a conventional electromagnet weighing tons (Geballe, 1993).

Niobium-tin conductors have been used for high energy physics, fusion, MRI and NMR applications made by different techniques (Gregory, 2008). Bruker produces high-grade Nb_3Sn-based wires for applications in medical, scientific, and industrial engineering (Bruker, 2024). Today, Nb_3Sn wires are applied at a large scale in high field nuclear magnetic resonance spectrometry (NMR), high energy physics and fusion research. Nuclear Magnetic Resonance (NMR) Spectroscopy is the most prominent application of Nb_3Sn wires. Magnets delivering field strengths in excess of 20 Tesla are employed in NMR systems. The Nb_3Sn conductors are also utilized in all major particle accelerator and fusion research projects, which will in future require magnets exceeding 12 Tesla.

5.4 Tin Lithium-ion Batteries

Tin and tin oxide (SnO2) material has been applied in lithium-ion batteries with a high specific capacity. Tin forms several inter-metallic phases with lithium metal, making it a potentially attractive material for battery applications. Large volumetric expansion of tin upon alloying with lithium and instability of the tin-organic electrolyte interface at low electrochemical potentials are the greatest challenges to employment in commercial cells (Mou et al., 2020; Weeks et al., 2019). Moreover, SnO_2-based anodes in lithium-ion batteries have drawn considerable attention because of their high theoretical capacity, resources availability, environmental benignity, low cost and operating potentials (0.3 – 0.5 V) versus Li+/Li in charge and discharge processes (Li, 2019, Lin, 2013, Li, 2015). The chemical reaction of SnO_2 with lithium electrodes involves the following two steps.

$$SnO_2 + 4\ Li^+ + 4e^- \rightarrow Sn + 2\ Li_2O$$

$$Sn + x\ Li+ + xe^- \rightarrow Li_xSn\ (0 \le x \le 4.4)$$

Researchers have announced a performance breakthrough for their innovative 3D tin electrodes in lithium-ion batteries (Sun, 2019). The new technology stored several times the energy of currently used commercial high-capacity anodes, as well as recording the highest power rating so far reported for such a high energy anode. An electrode with a 20%v/v Sn loading exhibits a high volumetric/areal capacity of ~879 mA h/cm^3/6.59 mA h/cm^2 after 100 cycles at 0.5 C and a good rate performance of about 750 mA h/cm^3 and 5.5 mA h/cm^2 (delithiation) at 10 C in a half-cell configuration. The 3D Sn/C anode also shows good compatibility with a commercial lithium cobalt oxide (LCO) cathode in a full cell configuration.

Tin lithium-ion batteries should benefit from development of electric vehicles and renewable energy infrastructures. The proliferation of electronics in vehicles, and the growth in electricity generation and storage infrastructure, will need to accompany the growth of electric vehicles, both present exciting opportunities for future tin demand growth. Research on potential new market opportunities for tin in lithium-ion batteries conducting ITA concluded that if tin does gain market share, lithium-ion batteries could grow to represent a significant new tin use in the 2025-2030 timescale (ITA, 2019).

5.5 Optoelectronics, Solar Cells and Touchscreens

Optoelectronics is the study and application of light-emitting or light-detecting devices. Tin indium oxide (ITO) are electrically conductive and transparent, and are used to make transparent electrically conducting films with applications in optoelectronics devices such as liquid crystal displays, photovoltaic, and energy storage (Kim, 199; Dalapati, 2021). Optoelectronics is quickly becoming a fast emerging technology field that consists of applying electronic devices to sourcing, detection, and control of light. These devices can be a part of many applications like telecommunications, military services, automatic access control systems, medical equipment, etc.

Since this field is so broad, the range of devices that fall under optoelectronics is vast, including image pick up devices, LEDs and elements, information displays, optical storages, remote sensing systems, and optical communication systems. The most common optoelectronic devices that feature direct conversion between electrons and photons are LEDs, photo and laser diodes, and solar cells.

Moreover, tin can form many oxides, sulfides, and other chalcogenide derivatives. Chalcogenides are one of the main compounds applied as absorbers of highly efficient photovoltaic devices based on thin-film technology (Dias et al., 2021; Hajijafarassar, 2020; Li & Gu, 2020). Current research shows that chalcogenide is a semiconductor and can be used for solar cells. Chalcogenide solar cells are solar cells that use chalcogenide, an organometallic halide semiconductor, as a light-absorbing material and belong to the third generation of solar cells.

To date, most solar cells have been made from silicon, as this material is very good at absorbing light. However, silicon panels are expensive to manufacture. Scientists have been working on a structure made up of chalcogenide to make it an alternative to silicon. Chalcogenides are the materials containing at least one group VI element such as Sulphur (S), Selenium (Se), and Tellurium (Te), along with network forming group III-IV elements such as Gallium (Ga), Germanium (Ge), Stannum (Sn), Arsenic (As), Antimony (Sb), Silicon (Si), Phosphorus (P), etc. (Khan, 2021). Then, it can be modified into several types of chalcogenides, such as I–III–VI$_2$, I$_2$–V–VI$_4$, I$_2$–II–IV–VI$_4$, and I$_2$–IV–VI$_3$. This modification is carried out to obtain material properties as expected. With this wide variety of chalcogenides, it has varied physical and chemical properties. These are the covalently bonded semiconductor materials having optical bandgap in the range of 1–3 eV, corresponding to their compositions (Savage, 1982). True chalcogenide, a mineral found in the earth, is made up of calcium, titanium and oxygen molecules that have been specially arranged. Materials with the same crystal structure are called chalcocite structures. Figure 6 shows crystal structure of quaternary chalcogenides with molecular structure of $Cu_2BIICIVX_4$ (Wang et al., 2019). Chalcogenide structures are ideally suited as the active layer for light absorption in solar cells, as they absorb light more efficiently than silicon and at a lower cost.

The optical studies of chalcogenide thin films are one of the leading research areas that supports promising photonic applications for future prospectives. Thin film solar cells based on Cu_2ZnSnS_4 (CZTS) and the related sulfur selenium alloy $Cu_2ZnSn(S,Se)_4$ (CZTSSe) were strongly investigated in the last 10 years. More recently, chalcogenide photovoltaic absorbers potentially able to face TW range applications better than CZTS and CZTSSe due to the higher abundance of their constituting elements are getting considerable attention. They are based on both MY_2 (where M = Fe, Cu, Sn and Y = S and/or Se) and Cu_2XSnY_4 (where X = Fe, Mn, Ni, Ba, Co, Cd and Y = S and/or Se) chalcogenides (Le Donne, 2019).

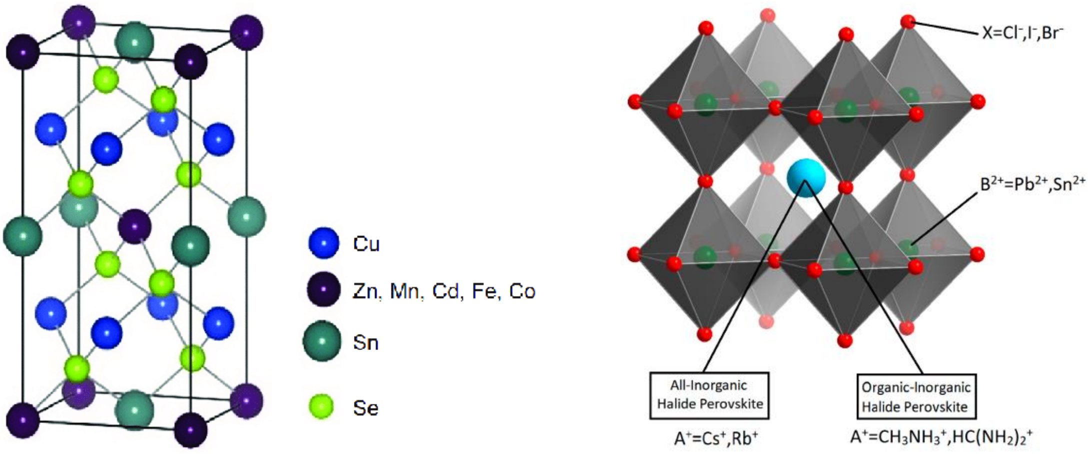


Figure 6. Crystal structure of quaternary chalcogenides $Cu_2BIICIVX_4$ (B = Zn, Cd, Mn, Hg; C = Si, Ge, Sn; X= Se, S, Te) (Wang et al., 2019) and ABC structure of perovskite (Dai et al., 2021).

Another application of ITO is in touchscreen technology. A touchscreen is a type of display that can detect touch input from a user. It consists of both an input device or touch panel and an output device or visual display. Indium-Tin Oxide (ITO) exhibits several properties that make it ideal for use in capacitive touchscreens. ITO is used as a clear conductive layer on almost all electronics devices that have a display. Touchscreens are prominently employed in smartphones, personal computers, televisions, and car navigation due to their compactness, reliability, and low power consumption. The display is often a liquid crystal display (LCD), an active-matrix organic light emitting diode (AMOLED) or an organic light emitting diode (OLED) display.

ITO is a material consisting of three elements: indium, tin and oxygen. The ratio of these three elements can vary depending on the type of ITO with a melting point in the range 1526–1926 °C. These three elements are mixed together to create a transparent material known as ITO. In ITO, tin acts as a cationic dopant in the In_2O_3 lattice and as a substitute on the indium sites to bind with the interstitial oxygen (Thirumoorthi & Prakash, 2016). ITO is a well-known n-type degenerate semiconductor with an optical band gap of 3.5-4.3 eV and has a high transmission in the near infrared and visible regions of the electromagnetic spectrum (Yu et al., 2016). ITO properties are high optical transparency, good electrical conductivity, chemical inertness, hardness and excellent substrate adherence (Sofi et al., 2017). ITO is applied over the top layer of capacitive touchscreens, thereby allowing the touchscreen to function as intended.

5.6 Hydrogen Production and Fuel Cells

The hydrogen economy is still largely in the future as a concept, but there are already some uses and an increasing investment in visionary projects. It has been reported that Ga-In-Sn-Bi alloy-activated Al-H_2O reaction to generate hydrogen gas exhibited excellent rate stability and durability with a hydrogen productivity of 92%, making it a preferred hydrogen source for fuel cells. Adding Sn not only can enhance the hydrogen generation rate but also accelerates oxidation of the liquid metal alloy (Xu et al., 2020). Moreover, tin has already been shown to have potential to significantly reduce the costs and sustainability of hydrogen production technologies, notably in use as a liquid metal to strip carbon from methane and as an oxide or sulphide photocatalyst to split water in sunlight (Cheng et al., 2017). Thus, hydrogen production using tin seems to be an important part of society's move to curb global warming and against climate change.

On the other hand, fuel cells are used to combine hydrogen and oxygen over a catalyst to produce electricity and tin has been shown to make an important contribution to some key components in the technology. Liquid tin was first used as an electrode in a type of fuel cell that was able to convert any type of hydrocarbon gas feed and at the same time act as catalyst the recombinant reaction (Luo et al., 2020). Other developments have used tin, its alloys and compounds in various physical parts of the fuel cell, including tin pyrophosphate as a medium temperature fuel cell membrane (Huang et al., 2018).

5.7 Carbon Capture Catalyst

The race is on to find and develop catalysts that can convert climate change gases, notably carbon dioxide, to useful industrial chemicals such as formate. Although there are numerous candidates, tin has a special ability to reform and join organic compounds that can be exploited, using sunlight or electrochemistry. An increasing number of studies are using tin as the active component, or as a promotor in other catalyst systems. It has been reported that the coating of Sn-Co on a porous copper scaffold resulted in the fabrication of a promising electrochemical catalyst, which can greatly increase the electrocatalysis selectivity for CO_2 reduction to formate in an aqueous $NaHCO_3$ solution (Hu et al., 2020). Tin-based catalysts offer an incredibly efficient conversion of the greenhouse gas CO_2 to the valuable formic acid. Thus, tin-based catalyst offers the chance to not only reduce the severity of climate change but also produce a valuable product.

5.8 Tin-based Drugs

Tin-based drugs, specifically organotin compounds, have been explored for various medical applications, primarily in cancer treatment and antifungal therapy (Linder & Hazegh-Azam, 1996). One notable example is tributyltin (TBT), which was once investigated as a potential anticancer agent due to its ability to inhibit the growth of tumor cells. Another organotin compound, tetrabutyltin (TeBT), has shown promise as an antifungal agent. It has been studied for its ability to inhibit the growth of fungal pathogens, particularly those resistant to other antifungal drugs (Sharma & Bhalla, 2013). Moreover, tin-based compounds have been reported to have a potential as carriers for targeted drug delivery and an ability to form stable complexes with therapeutic agents and target specific tissues or cells (Voskresenska et al., 2019). However, the use of TBT and TeBT were limited by its toxicity to healthy cells and its tendency to bioaccumulate in the environment (Oehlmann et al., 2019).

Overall, while tin-based drugs have demonstrated interesting pharmacological properties, their development has been hampered by toxicity concerns and environmental considerations. As a result, research in this area has shifted towards exploring alternative compounds with improved safety profiles.

5.9 Other Applications

Punched tin-plated steel, also called pierced tin, refers to an artisan technique where tin-plated steel sheets are perforated with patterns or designs using a punching tool for creating functional and decorative housewares. This craft dates back centuries and has been used in various cultures for both functional and decorative purposes. Tin-plated steel is a durable material that provides strength, while the tin plating adds corrosion resistance and a shiny surface.

Historically, punched tin has been used in the creation of lanterns, pie safes, decorative panels, and even furniture. The punched holes allow light of a candle shining through the pierced design creates a decorative light pattern and designs in the room where it sits, Figure 7a. In addition to its decorative applications, punched tin has also been used for practical purposes such as ventilation in cabinets or as a means of cooling food in pie safes. Today, punched tin remains popular for its rustic charm and versatility in home decor. Artisans continue to create intricate designs, ranging from traditional motifs to modern patterns, making punched tin a timeless and unique addition to any space.

(a) Punched tin lanterns (b) Decorative tin panel (c) Pie safe tin

Figure 7. Some type of intricate designs using punched tin.

Tin(II fluoride is added to some dental care products as stannous fluoride, SnF_2. Stannous fluoride has played an important role in fighting dental decay (Meshri, 2000). Tin(II fluoride can be mixed with calcium abrasives while the more common sodium fluoride gradually becomes biologically inactive in the presence of calcium compounds (Hattab, 1989). It has also been shown to be more effective than sodium fluoride in controlling gingivitis (Perlich et al. 1995).

Tin is also used as a target to create laser-induced plasmas that act as the light source for extreme ultraviolet lithography (Harilal et al., 2018; Sandhu & Sharma, 2019). When a high-intensity laser pulse is focused onto a tin target, it can create a very hot and dense plasma due to the extreme conditions generated by the laser energy. This plasma can be studied for various applications including fusion research, astrophysics simulations, and laser-produced plasma sources for extreme ultraviolet (EUV) lithography used in semiconductor manufacturing. Tin is preferred for some of these applications due to its relatively low ionization energy and high laser absorption efficiency.

On the other hand, the organotin compounds are most heavily used. Worldwide industrial production probably exceeds 50,000 tonnes (Ebdon, 2001). These compounds find their applications in several industries ranging from automotive, defense, wearable, manufacturing, and more. The mono, di, or tri substitutes of the organotin compounds are mainly used in the wearable industry as they are used in footwear and clothes manufacturing. The major commercial application of organotin compounds is in the stabilization of PVC plastics. In the absence of such stabilizers, PVC would rapidly degrade under heat, light, and atmospheric oxygen, resulting in discolored, brittle products. Tin scavenges labile chloride ions (Cl^-), which would otherwise strip HCl from the plastic material (Atkins et al., 2006). Typical tin compounds are carboxylic acid derivatives of dibutyltin dichloride, such as the dilaurate (Wilkes et al., 2005).

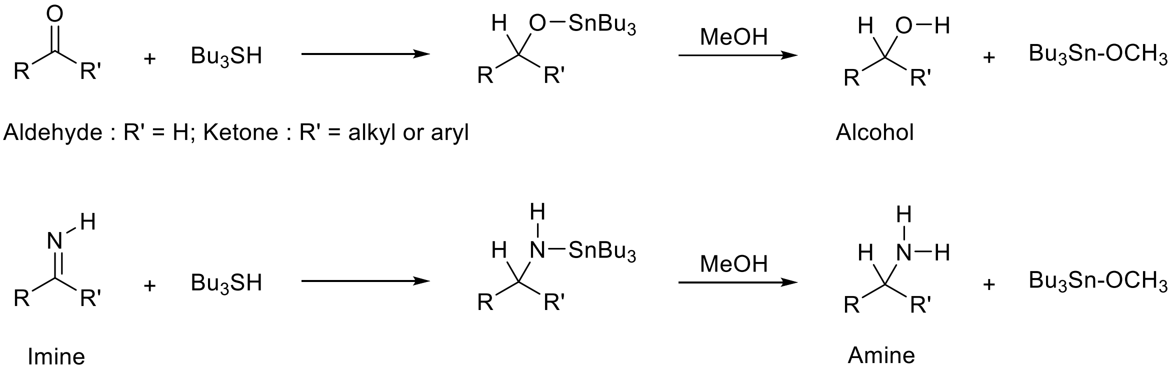
Some organotin compounds are relatively toxic, with both advantages and problems. They are used for biocidal properties as fungicides, pesticides, algaecides, wood preservatives, and antifouling agents (Atkins et al., 2006). Tributyltin oxide is used as a wood preservatives (Hon & Shiraishi, 2001).[99] Tributyltin is also used for various industrial purposes such as slime control in paper mills and disinfection of circulating industrial cooling waters (Antizar-Ladislao, 2008). Tributyltin was used as additive for ship paint to prevent growth of fouling organisms on ships, with use declining after organotin compounds were recognized as persistent organic pollutants with high toxicity for some marine organisms (Eisler, 1989).

6. TIN IN ORGANIC SYNTHESIS

Tin compounds are widely used in organic synthesis due to their versatile reactivity and ability to participate in various chemical transformations. Some common uses of tin in organic synthesis include tin-mediated reaction, stannylation and allylation, tin-catalyzed reaction, tin-mediated cyclization, coupling reaction, and as protecting group.

6.1 Tin-Mediated Reductions

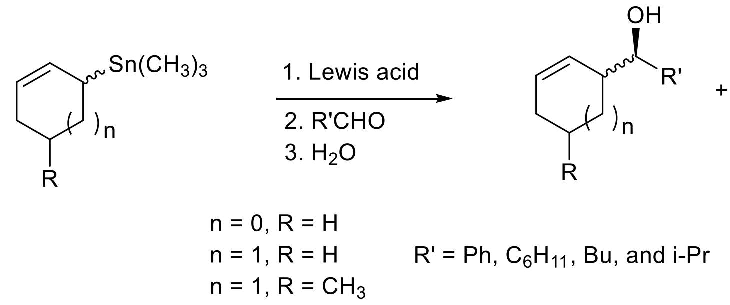
The tin-mediated reduction of aldehydes, ketones and imines is a chemical transformation that involves the use of tin compounds as reducing agents to convert aldehydes, ketones and imines into their corresponding alcohols or amines, respectively (Tsuji et al., 1969; Gallagher et al., 1986; Ley et al., 1998). Tributyltin hydride (Bu_3SnH) is a commonly used reagent for these transformations (Brown et al., 2004).



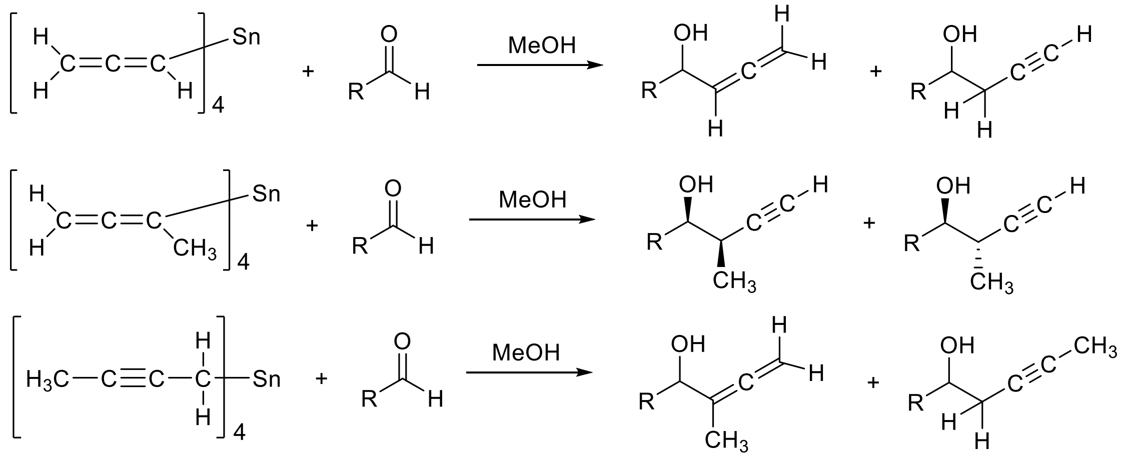
Scheme 3. Reduction of aldehydes, ketones and imines with tributyltin hydride.

6.2 Stannylation and Allylation

Tin compounds, such as diorganotin reagents (e.g., R_2SnCl_2), are used to introduce tin functionalities into organic molecules. Stannylation reactions are valuable for installing tin-containing groups, which can serve as handles for further transformations. Carbonyl compounds, such as aldehydes and ketones, can undergo allylation with allylic stannes to yield the corresponding alcohols via Lewis acid activation of the electrophile or via transmetallation, depending on the Lewis acid (Marshall, 2000; Muderawan, 1998), Scheme 4. Methyltin trichloride (CH_3SnCl_3) and indium(III) chloride ($InCl_3$)proved useful in deciphering the stereochemistry of transmetalation with allylic stannanes. Wereas, tetraallylic, tetraallenic and tetrapropagilic stannanes reacted to carbonyl compounds promoted by solvent to give corresponding alcohol, respectively (McCluskey, 2003), Scheme 5.



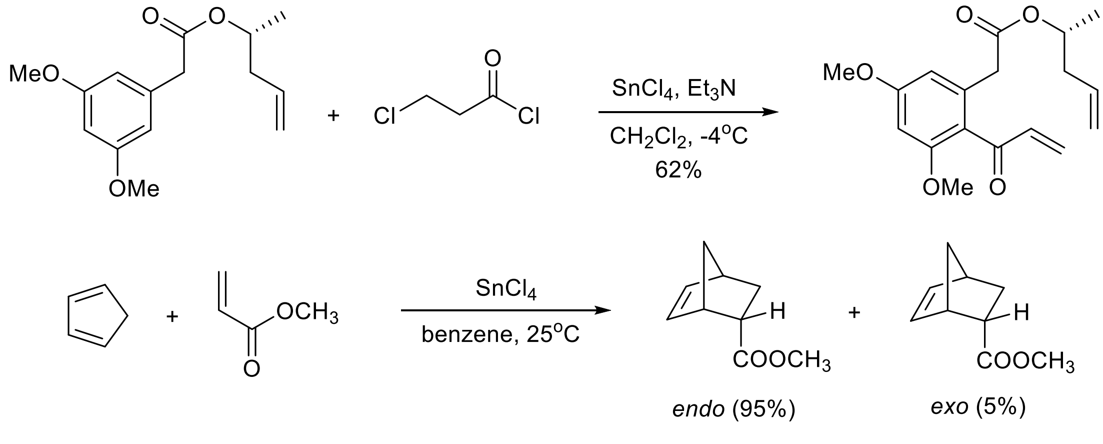
Scheme 4. Reaction between allylic stannanes and aldehydes and ketones mediated by Lewis acid.



Scheme 5. Reaction between tetraallylic, allenic and propargylic stannanes with carbonyl compounds.

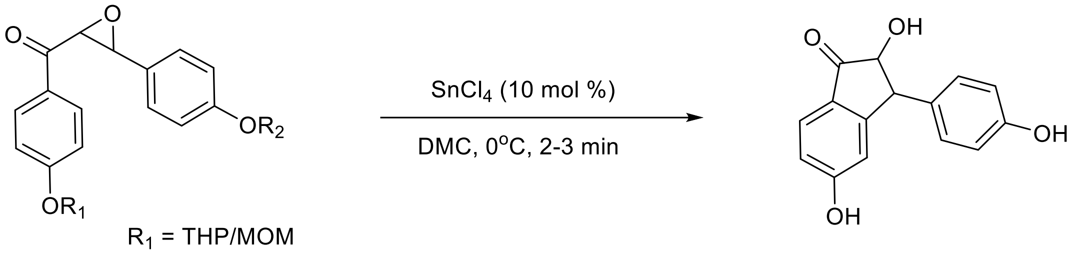
6.3 Tin-Catalyzed Reactions

Tin salts and organotin compounds can catalyze various organic transformations. For example, tin(IV) chloride (SnCl4) is used as a Lewis acid catalyst in reactions like Friedel-Crafts acylation (Li, 2021) and Diels-Alder reactions (Sauer, 1967), Scheme 6.



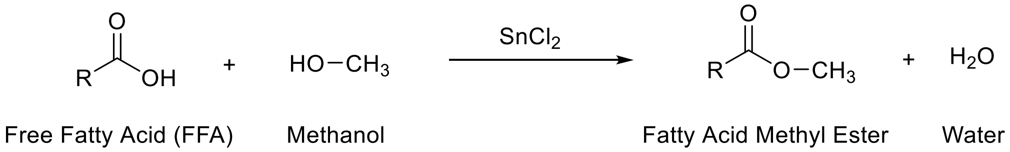
Scheme 6. Friedel-Crafts acylation and Diels-Alder reaction catalyzed by tin(IV) chloride.

Moreover, $SnCl_4$ catalysts provided a rapid and efficient detetrahydropyranylation and demethoxymethylation of phenolic ethers and a sequential one-pot intramolecular Friedel–Crafts alkylation of chalcone epoxides under mild reaction conditions (Ahmed et al., 2015). The reaction took 2-3 min to give the phenols and 1-indanones in an excellent yield (90-98%) at 0 °C without affecting other functional groups. With these catalysts, this protocol gave regioselective products as *trans*-3-aryl-2-hydroxy-1-indanones in an excellent yield (76-98%) and an enantiomeric excess of up to 99.9% under the same conditions.



Scheme 7. SnCl4 catalyzed intramolecular Friedel-Crafts alkylation.

In addition, tin(II chloride has been used as catalyst in transesterification of high free fatty acid (FFA) Jatropha oil to produce biodiesel (Kusumaningtyas et al., 2014), Schame 8. The optimum reaction conversion was obtained at 60 °C with the catalyst loading of 10% w/w oil and molar ratio of methanol to oil of 120:1.

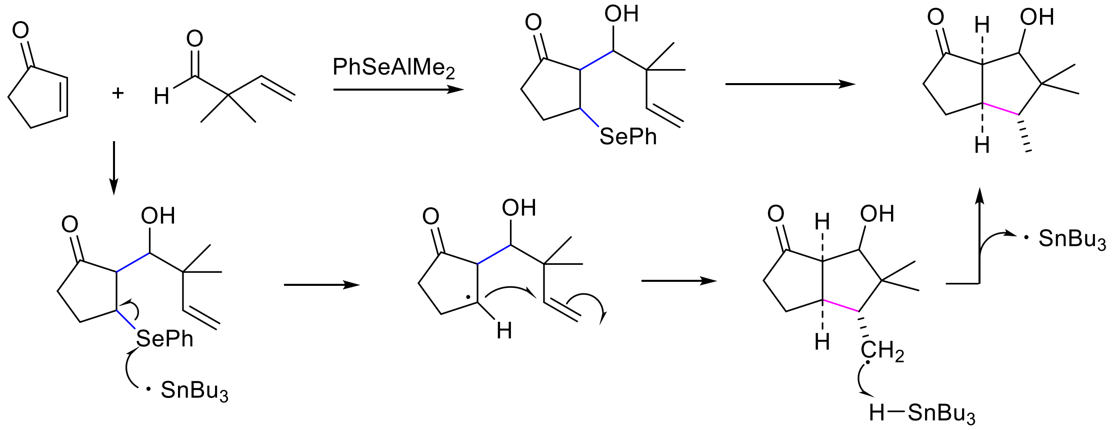


Scheme 8. Tin(II) chloride catalyzed esterification of FFA Jatropha oil.

6.4 Tin-Mediated Cyclizations

Tin compounds can facilitate cyclization reactions in organic synthesis. For instance, the use of organotin compounds in radical cyclizations allows for the construction of cyclic compounds with high stereoselectivity.

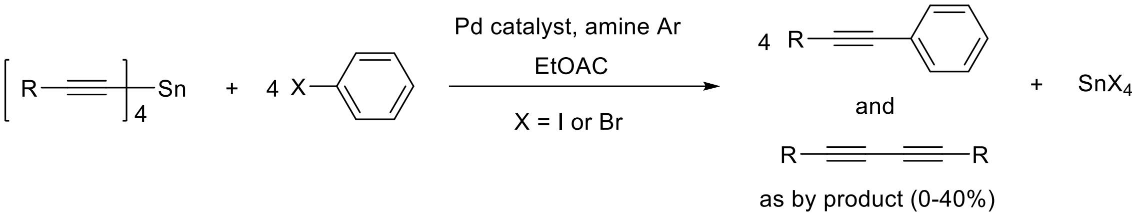
Tin compounds have been used in radical annulation (Malik, 2021), Scheme 9. Tin-based radical annulation method is the most common and widely used procedure for the synthesis of a wide range of organic compounds with medicinal significance. Stereoselective tin-mediated radical cyclization reactions encourage chemists to construct many other molecules of interest following the principles involved in these reactions.



Scheme 9. Tin mediated radical cyclization.

6.5 Stille Coupling

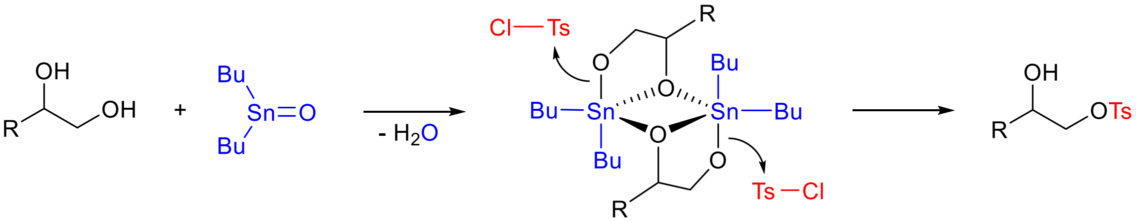
The Stille coupling reaction, named after chemist John Stille, involves the cross-coupling of an organotin compound with an organic halide or pseudohalide in the presence of a palladium catalyst. This reaction is widely used in the synthesis of complex organic molecules, especially in pharmaceutical chemistry. Tetraorganotin compound suach as tetraalkynylstannanes easily react with a variety of aryl iodides and bromides under Stille conditions according to the following scheme (Levashov, 2017).



Scheme 10. The reaction of tetraalkynylstannanes with aryl halides.

6.6 Tin in Protecting Group Chemistry

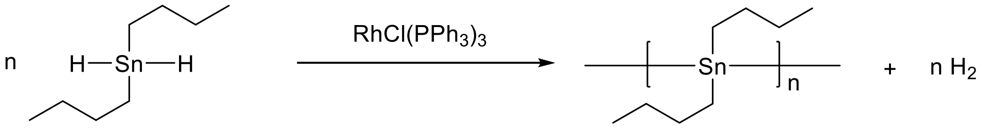
Tin-containing protecting groups are used to temporarily mask reactive functional groups in organic synthesis. These protecting groups can be selectively removed under mild conditions, allowing for the controlled manipulation of functional groups in complex molecules. Organotin derivatives have been used extensively as intermediates for the regioselective substitution of the hydroxyl groups of diols, polyols and carbohydrates. Two types of tin derivatives have been used mainly to achieve these reactions; dialkylstannylene acetals are formed by reaction of dialkyltin oxides with diols; tributyltin ethers are formed by reaction of bis(tributyltin) oxide with alcohols (Grindley, 2008). Dibutyltin oxide reacts with 1,2-diol to form dibutylstannylene dimer. Upon treatment of the dibutylstannylene with TsCl and triethylamine, tosylation occurred selectively at the primary alcohol of the 1,2-diol, Scheme 11.



Scheme 11. Regioselective substitution of the hydroxyl groups of diols.

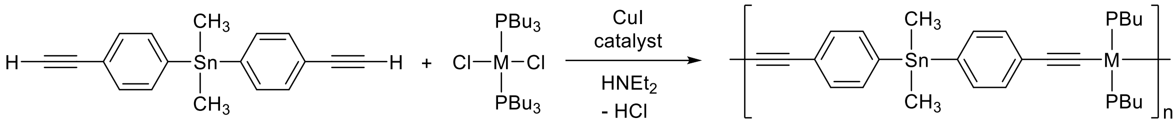
6.7 Tin in Polymer Chemistry

Polystannanes are organotin compounds with the formula $(R_2Sn)_n$. Dialkytin dihydrides (R_2SnH_2) were reported to undergo dehydropolymerization in the presence of Wilkonson's catalyst to form poly(dibutylstanne) without cyclic by products, Scheme 12. The polymers were yellow with number average molar masses of 10 to 70 kg/mol and a polydispersity of 2-3 (Choffat et al., 2005). The poly(dialkylstannane)s were found to be thermotropic and displayed first-order phase transitions from one liquid-crystalline phase into another or directly to the isotropic state, depending on the length of the side groups. Like polysilanes, polystannanes are semi-conductive. Temperature-dependent, time-resolved pulse radiolysis microwave conductivity measurements of poly(dibutylstannane) yielded values of charge-carrier mobilities of 0.1 to 0.03 $cm^2 V^{-1} s^{-1}$, which are similar to those found for pi-bond-conjugated carbon-based polymers.



Scheme 12. Synthesis of pure linear poly(dibutylstannane) using dibutylstannane in presence of Wilkinson's catalyst.

In addition, organometallic polymers containing tin and transition metals have been synthesized by polycondensation between dimethyldi(4-ethynylphenyl)tin and transition metal halides using cuprous iodide as a catalyst in diethylamine (Tahara et al., 1987), Scheme 13. The polymers, in which tin and transition metals are regularly linked by a conjugated system through M-C bonds.



Scheme 13. Synthesis of organometallic polymers containing tin and transition metals.

Moreover, tin and organotin polymers display two kinds of supramolecular assembling forces: (i) non-covalent associations and (ii) covalent bonds. The last one can be weak or strong intermolecular connections, being easily extinguished in solution or unaffected by solvation, rendering in this case insoluble compounds (Dos Santos & de Lima, 2020). Some polymeric triorganotin carboxylates were obtained from the reaction of sodium 4-phenylbutyrate, NaOPhb with R_3SnCl (R = Me, Bu or Ph), yielding $[R_3Sn(OPhb)]n$ (R = Me, Bu or Ph). Analogous reactions of sodium valproate, NaOVp, with Me_3SnCl yielded $[Me_3Sn(OVp)]_n$ (Dos Santos & de Lima, 2020), Figure 8.

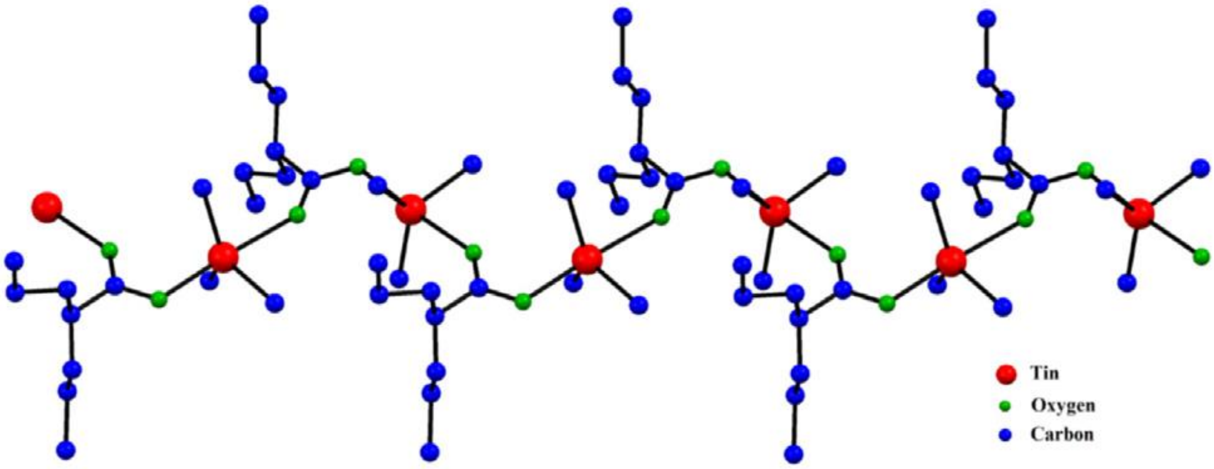


Figure 8. Polymeric structure of compounds $[Me_3Sn(OVp)]_n$ (Dos Santos & de Lima, 2020).

7. TOXICITY AND ENVIRONMENTAL EFFECTS OF TIN

Tin as individual particles or atoms is not exceedingly lethal to living organisms. Elemental tin metal, its salts and its oxides present low toxicity. Cases of poisoning from tin metal, its oxides and its salts are almost unknown. Tin-plated steel cans are still widely used for food preservation. In contrast, certain organotin compounds are almost as toxic as cyanide (Graf, 2000). Since it is not biodegradable, organic tin can last longer in the environment. Microorganisms typically face difficulties when attempting to degrade tin compounds that have accumulated on water sediments for an extended period.

Exposure to tin in the workplace can occur by inhalation, skin contact, and eye contact. The US Occupational Safety and Health Administration (OSHA) set the permissible exposure limit for tin exposure in the workplace as 2 mg/m^3 over an 8-hour workday. The National Institute for Occupational Safety and Health (NIOSH) determined a recommended exposure limit (REL) of 2 mg/m^3 over an 8-hour workday. At levels of 100 mg/m^3, tin is immediately dangerous to life and health (NIOSH, 2019).

The EU banned the use of organotin compounds in 2003 (EU, 2003), while concerns over the toxicity of these compounds to marine life and damage to the reproduction and growth of some marine species (Atkins et al., 2006) (some reports describe biological effects to marine life at a concentration of 1 nanogram per liter) have led to a worldwide ban by the International Maritime Organization (Dürr, 2008). Many nations now restrict the use of organotin compounds to vessels greater than 25 m long (Atkins et al., 2006). The persistence of tributyltin in the aquatic environment is dependent upon the nature of the ecosystem (Maguire, 1987). Because of this persistence and its use as an additive in ship paint, high concentrations of tributyltin have been found in marine sediments located near naval docks (de Mora et al., 1995). Tributyltin (TBT) has been used as a biomarker for imposex in neogastropods, with at least 82 known species (Axiak, 2003). With the high levels of TBT in the local inshore areas, due to shipping activities, the shellfish had an adverse effect (Maguire, 1987). A high level of TBT can damage mammalian endocrine glands, reproductive, and central nervous systems, bone structure and gastrointestinal tract (Roach, 2018). Not only does tributyltin affect mammals, it affects sea otters, whales, dolphins, and humans (Roach, 2018).

Despite their utility, it is worth noting that some organotin compounds have raised environmental and health concerns due to their toxicity and potential bioaccumulation. Consequently, there has been ongoing research into developing alternative methods that minimize the use of tin or replace it with less toxic alternatives in certain applications.

8. CONCLUSION

Tin is a versatile and commodity metal with a wide range of applications across various industries including soldering, metallurgy, packaging, alloys, and electronics. Apart from being a metal, tin can also be in the form of both inorganic and organic compounds. Tin compounds are used in various chemical applications, such as catalysts in organic reactions, stabilizers in plastics, and reagents in organic synthesis. In conclusion, tin is a vital element with widespread applications due to its favorable properties such as corrosion resistance, malleability, and low toxicity. From everyday items like food containers to high-tech electronics, tin plays a crucial role in day-to-day lives as well as in modern industry and manufacturing processes. It has played a major role in the past, is significant in our present, and will be vital for our future. Its importance in modern manufacturing and everyday life underscores its enduring relevance in the global economy.

Indonesia is one of the countries with the world's largest tin reserves and the third tin producers. Because of tin is a critical component of high-tech hardware, electrical vehicles and robotics, then tin has prospect of increasing Indonesia's economic growth. To achieve this goal, thin-based technology must be developed in Indonesia. However, even though Indonesia has the largest tin reserves and is the world's third tin producer, the advanced tin-based technology has received little attention and has not developed. Indonesia faces serious problems in tin management and development of tin to be component of high-technology.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest in publication of this article.

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