1. Introduction

1.1 History and Properties of Tin [1-3]

Tin is one of the world ' s most ancient metals .It was being used to make bronze weapons and tools. The Romans used tined copper vessels. Tinned sheet for metal containers and tools were made. It appeared in England and Saxony about the middle of the seventeenth century. Although tinplate was not manufactured in United State until the early nineteenth century, production increased rapidly and soon out stripped all other countries.

Tin in some form has been associated with the economic and cultural growth of civilization. Food preservative and canning developed rapidly with the invention of tin – coated steel; transportation and high speed machinery became a reality with the invention of tin-base bearing metals. The casting of type metal was an important advance in printing technology; bonze alloy became weapons, tools, and architectural object; tin alloys are used in organ pipes and bell; and telecommunication and electronic equipment depend upon the tin-lead soldered joint. In modern technology, new uses of tin include the plating of protective coatings, nuclear energy, plastics and other polymers, agriculture, biochemistry, electronic packaging and glassmaking.

The distribution of tin consumption, as shown in Table 1.1, and the world trading in tin occurs mostly at Penang, London, and New York, as show in Table1.2. Most of the world' s tin produced in Southeast Asia.

There are nine different type of tin – bearing minerals found in the earth ' s crust, only cassiterite, Sn_2O, is importance. Complex tin sulfide minerals such as stannite, $CuS.FeS.SnS_2$; teallites, $PbSnS_2$; cylinderrite, $PbSn_4FeSb_2S_{14}$; and canfieidite, Ag_8SnS_6 , are found in the lode deposits of Bolivia and Cornwall associated with cassiterite and granitic rock, in the lode mines, the ores often contain 0.8 – 1.0 wt % of tin metal. The important tin – producing countries are Malaysia, Bolivia, Indonesia, Nigeria, Thailand, Zaire, People Republic of China.

Table 1.1 Distribution of 1980 tin consumption, Metric Tons[1]

Product	USA	Japan[b]	FRG	France	UK	Combined
Tinplate	16,345	11,997	4,329	4,885	3,155	40,712
Solder	15,681	10,878	2,446	2,678	892	32,512
Bronze	7,478	1,521	375	493	1,245	11,112
Babbitt	2,380	855	376	332	1,472	5,415
Tinning	2,577	1,396	549	262	844	5,628
Chemicals	48,00	1,649	2,050	510	1,282	10,291
Other	7.163	2,583	4,146	899	1,010	15,801
Total	56,362	30,879	14,271	10,059	9,900	121,471

Table 1.2 World Tin Production, Metric Tons [1]

Year	World	Malaysia	Thailand	Indonesia	Bolivia	Brazil	Zaire	UK
1925	165,600	57,746	8,335	33,831	37,763	-	982	2,700
1950	164,800	58,694	1,530	32,617	31,714	183	11,947	904
1960	138,700	52,813	12,275	22,958	20,543	1,581	9,350	1,218
1965	154,400	64,692	19,353	14,935	23,407	1,220	6,311	1,334
1970	185,800	73,794	21,779	19,092	30,100	3,610	6,458	1,722
1975	177,700	64,364	16,406	25,346	28,324	5,000	4,562	3,330
1978	196,900	62,650	30,186	27,410	30,881	6,320	3,450	2,802
1979	200,700	62,995	33,962	29,440	27,781	6,645	3,300	2,374
1980	199,300	61,400	33,680	32,527	27,271	6,756	3,159	3,028

The most important source of cassiterite in Thailand was in the Southern part in every province. In the Middle part it were found in Kanjanaburee, Rachaburee, Pechaburee, and in The Northern part in Utaithanee, Tak, Kumpangpech, Lumpang, Chiang Mai, Chiang Rai, and Mae Hong Son.

1.2 Chemical Properties of Tin [1, 2, 5]

Tin falls between germanium and lead in Group IVA of the periodic Table, which has atomic number 50, atomic weight 118.69. It has ten natural occurring isotopes as seen in Table 1.3

Table 1.3 The Natural Isotopic Composition of Tin[2]

Isotope	112	114	115	116	117	118	119	120	122	124
% abundance	1	0.68	0.38	14.4	7.54	24.1	8.62	32.5	4.7	5.9

Tin is amphoteric and reacts with strong acid and strong bases, but is relatively resistant to nearly neutral solution. Distilled water has no effect on tin, oxygen greatly accelerates corrosion in aqueous solutions, In the absence of oxygen, the high redox potential of tin (0.75 V) causes a film of hydrogen to be retained on surface which retards acid attack. The metal is normally covered with a thin protection oxide film, which thickens with increasing temperature.

Tin does not react directly with nitrogen, hydrogen, carbon dioxide, or gaseous ammonia. Sulfur dioxide, when moist, attacks tin. Chlorine, bromine, and iodine readily react with tin; with fluorine, the reaction slow in room temperature. The halogen acid attacks tin particularly when hot and concentrated. Hot sulfuric acid dissolves tin, especially in the presence of oxidizers. Although cold nitric acid attacks only slowly, hot nitric acid converts it to an insoluble hydrated stannic oxide. Sulfurous, chlorosulfuric, and pyrosulfuric acids react rapidly with tin. Phosphoric acid dissolves tin less readily than the other mineral acids. Organic acids such as lactic, citric, tartaric, and oxalic attack tin slowly in the presence of air or oxidizing substances.

Dilute solutions of ammonium hydroxide and sodium carbonate have little effect on tin, but strong alkaline solution of sodium or potassium hydroxide, cold and dilute, dissolve tin to form stannates.

Neutral aqueous salt solution react slowly with tin when oxygen is present but oxidizing salt solution, such as potassium peroxysulfate, ferric chloride and sulfate, and aluminum and stannic chlorides dissolve tin. Nonaqueous organic solvents, lubricating oils, and gasoline have little effect.

1.3 Tin Compounds [1,4,5,8]

Tin has a valence of + 2 in stannous compounds and +4 in stannic compounds. Types of tin compounds include ones containing tin (II) and tin(VI) compounds. Complex stannites ($MSnX_3$) and stannates ($M_2Sn X_6$), coordination complexes, organic tin salts where tin is not bonded through carbon, and organotin compounds, which contain one-to-four carbon atoms bonded directly to tin.

Tin compounds are used for a wide variety of purposes, eg, catalysts, and stabilizers for many materials including polymer; biocidal agent, eg, bactericides, insecticides, fungicides; wood preservatives, acaricides, and antifouling paint; ceramic opacifiers; textile additives; in metal finishing operation; as food additive; and in electroconductive coatings.

Tin compounds on a commercial scale include tin(II) compounds and tin(IV) compounds. Consumption of tin compound for chemical applications by five countries from 1975 – 1980 was shown in Table 1.4.

Table 1.5 Consumption of Primary Tin for Chemical Application, Metric Ton[4]

					USA	
year	France	FRG	Italy	UK	Primary	Secondary
1975	345	492	650	1210	2735	1263
1976	330	998	700	1463	4718	903
1977	420	1137	650	1468	4655	1072
1978	540	1414	600	1374	4557	
1979	590	1894	500	1305	4797	
1980	700	2050	450	1282	4800	

Approximately 80 % of inorganic tin chemical consumption is accounted for by tin chlorides and tin oxides. The tin chloride is the greatest commercial importance they are stannous chloride and stannic chloride. Both of stannous chloride and stannic chloride are best prepared by the reaction of chlorine with tin metal.

1.3.1 Stannous chloride is available in two forms: anhydrous stannous chloride, Sn_2Cl, and stannous chloride dihydrated, $SnCl_2.2H_2O$, also called tin crystals or tin salt. Both forms are sometime used interchangeably; however where stability, concentration and adaptability are important, anhydrous stannous chloride is the preferred material. Even after long storage change in stannous tin content of anhydrous stannous chloride are extremely low.

Anhydrous stannous chloride, a water – soluble white solid, is most economical source of stannous tin and is especially important in redox and plating reduction. Anhydrous salt may be prepared by direct reaction of chloride solution with tin metal followed by dehydration.

Stannous chloride dihydrate, a white crystalline solid, is prepared either by treatment of granulated tin with hydrochloric acid followed by evaporation and crystallization, or by reduction of a stannic chloride solution with the cathode or tin metal followed by crystallization.

1.3.2 **Stannic Chloride** is available commercially as anhydrous stannic chloride, $SnCl_4$, and stannic chloride pentahydrate, $SnCl_4.5H_2O$; and in proprietary solutions for special applications. Anhydrous stannic chloride, a colorless fuming liquid, fumes only in moist air, with the subsequent hydrolysis producing finely divided hydrated tin oxide or basic chlorine. It is soluble in water and many organic solvents. With water, it forms a number of hydrates, of which the most important is the pentahydrate.

Stannic chloride is made by the direct chlorinating of tin at 110 –115 °C. Any stannic chloride formed in the process is separated from the stannic chloride by volatilization and subsequently chlorinated to stannic chloride. The latter is inert to steel in the absent of moisture and is shipped in plain steel in drums of special design. Since prolonged contract with skin causes burns, goggles and protective clothing should be used in the handling of stannic chloride. Stannic chloride, like stannous chloride, also forms many complexes.

The main uses of stannic chloride are as a raw material for the manufacture of other tin compounds, especially organotins, and surface treatment of glass and other nonconductive substrate gives it strength, abrasion – resistance, and conductivity.

Stannic chloride pentahydrate is white, crystalline, deliquescent solid that is soluble in water or methanol and stable at 19 – 56 °C. It is used in place of the anhydrous stannic chloride where anhydrous condition are not mandatory. It is easier to hand than fuming anhydrous liquid form. The pentahydrate is prepared by dissolving anhydrous stannic chloride in hot water, thereby forming the pentahydrate at a temperature above the melting point and crystallizing by cooling. The cake is broken into small lumps for packaging.

1.4 Organotin Compounds [1,2,4]

Organotin compounds have developed from being laboratory curiosities to the large-scale industrial chemicals. First commercial significant property of organotins to become recognized, was ability of diorganotins used as stabilizers for poly(vinyl chloride), PVC, which was degraded under the influence of heat and UV light. Its were used in U.S.A. in the 1940s, in U.K. in 1951s and in the west of Europe and Japan in the middle of 1950s. The high biocidal activity of the triorganotins is one of the most applied areas of their usefulness. In addition, organotins are widely used as catalyst and curing agents and in the treatment of glass.

World production of organotin compounds was started to be running at 1,000 – 2,000 tones by 1957 mainly for dibutyltin stabilizer for PVC. More sophisticated compounds were soon developed, in particular, triorganotin compounds were shown to be extremely efficient heat stabilizers for PVC.

The biocidal uses of organotin compounds stemmed from the systematic study of these compounds sponsored at Institute for Organic Chemistry, TNO, Utrecht, by the International Tin Research Council in 1950. The research team at TNO under the leadership of Professor G.J.M. Van der Kerk made important contributions to the study of the organometallic chemistry of tin, synthesizing new compound, and establishing their characteristics. In particular the powerful biocidal properties of triorganotin derivatives were established. By the middle of 1960s world annual production of organotins had risen to around 10,000 tonnes

In 1959 the seeds of another important use of organotin compounds were sewn, when the Osmose Wood Preserving Company of America began active investigation into the possibilities of organotins for wood preservation. As a result of these studies, the company marketed a commercial organotin-based wood preservative in 1960s. This stimulated major developments in Europe and organotins became firmly established in the field of wood preservation over the next decade in many parts of the world. In the early 1960s organotin compounds began to find use in antifouling paint systems for ships in view of their biological activity against a wide spectrum of fouling organisms. The subsequent develop of more effective coating with long-term activity has led to a marked in crease in the uses of organotins for antifouling systems and today this market is growth area.

1.5 Classes Of Organotin Compounds [5-11]

There are four classes of organotin compounds known and widely used in laboratory and many kind of industry:

1) Tetraorganotins, R_4Sn , those with four Sn-C bonds,
2) Triorganotins, R_3SnX, those with three Sn-C bonds,
3) Diorganotins, R_2SnX_2, those with two Sn-C bonds,
4) Monoorganotins, $RsnX_3$, those with one Sn-C bond.

1.5.1 Tetraorganotin compounds

The tetraorganotins are important compounds, which are the starting materials for many of the industrially important mono-, di-, and triorganotins. The most widely uses in preparations of tetraalkyl- and tetraaryltin compounds is the reaction of stannic chloride with tetrahydrofuran-based Grignard reagents or organoaluminum compounds: as in equation 1-1 and 1-2.

$$4\ RMgX + SnCl_4 \xrightarrow{THF\ or\ R_2O} R_4Sn + 4\ MgXCl \text{ --------(1-1)}$$

$$4\ R_3Al + 3\ SnCl_4 \xrightarrow{R_3N\ or\ R_2O} 3\ R_4Sn + 4\ AlCl_3 \text{ ---------(1-2)}$$

Excess alkylating reagent is required if the tetraorganotin is desired as the exclusive product. In commercial practice, The stoichiometry is kept at or below 4:1,since the crude product is usually redistribution to lower organotin chlorides in subsequent step ether is used as the solvent. The used of diethyl ether in Grignard reaction has been generally replaced with tetrahydrofuran.

Organolithium and organosodium reagent can also be used to prepare tetraorganotins:

$$4\ RLi + SnCl_4 \longrightarrow R_4Sn + 4\ LiCl \text{ ------------------(1-3)}$$

$$4\ RNa + SnCl_4 \longrightarrow R_4Sn + 4\ NaCl \text{ ----------------(1-4)}$$

The Wurtz reaction in equation 1.5, which relies on *in situ* formation of an active organosodium species, is also useful for preparing tetraorganotin compounds and practiced commercial. Yields are usually only fair and variety of by –product, including ditins, also form:

$$SnCl_4 + 8\ Na + 4\ RCl \longrightarrow R_4Sn + 4\ NaCl \text{ ------------(1-5)}$$

The Wurtz reaction is the preparation of tetrabutyltin form activated magnesium chips, butyl chloride, and stannic chloride in hydrocarbon mixture. Only a small amount of tetrahydrofuran is required for the reaction to proceed in high yield.

The use limitation of an active metal organometallic, eg, Grignard or organolithium reagent, allow preparation of only tetraorganotins, which have no functional groups reactive to the organometallic reagent on the molecule.

1.5.2 Triorganotin Compounds

Triorganotin and diorganotin compounds constitute by far the most important classes of organotin compounds.

Preparation of triorganotin chloride, which the general formula R_3SnCl are the basic starting materials for other triorganotins. They are generally prepared by Kocheskov redistribution from the crude tetraorganotin: as equation

$$4\ R_4Sn + SnCl_4 \longrightarrow 4\ R_3SnCl \text{ ---------(1-6)}$$

Triorganotin compounds are widely used as industrial biocides, agricultural chemicals, wood preservatives, and marine antifoulants. The triorganotin compounds that are most useful as biological control agents, in general, are the tributyltins, triphenyltins, and tricyclohexyltins. Tributyltin compounds, especially the oxide and benzoate, are used as antimicrobials and slimicides for cooling-water treatment and hard-surface disinfectants.

1.5.3 Diorganotin Compounds

Diorganotin can be obtained by halogenation of fully substituted tetraorganotin compounds, or by various reactions starting form metallic tin or its organic compounds

Rearrangement reaction between tin(IV) halides and tetra-alkyls or –aryls, R_4Sn, are an especially useful method of preparing organotin halides. In theory a particular halide might be obtained by taking R_4Sn and SnX_4 in suitable proportions:

$$3\ R_4Sn + SnCl_4 \longrightarrow 4\ R_3SnCl \text{ ----------(1-7)}$$

$$R_4Sn + SnCl_4 \longrightarrow 2\ R_2SnCl_2 \text{ ---------(1-8)}$$

$$R_4Sn + SnCl_4 \longrightarrow 4\ RSnCl_3 \text{ ----------(1-9)}$$

The largest single industrial application for organotins is in the stabilization of poly(vinyl chloride), PVC, which are added to PVC to prevent its degradation by heat (180-200 ° C) during processing and by long-term exposure to sunlight. Dialkyltin compounds are the best general-purpose stabilizers for PVC, especially if colorlessness and transparency any required.

1.5.4 Monoorganotin compounds.

Monoorganotin halides are the basic raw materials for all other triorganotin compounds and are generally prepared by Kocheshkov redistribution from the tetraorganotin, eg, tetrabutyltin or the higher organotin halide:

$$R_4Sn + SnCl_4 \longrightarrow 4\ RSnCl_3 \text{-----------------} (1\text{-}10)$$

$$R_2SnCl_2 + SnCl_4 \longrightarrow 2\ RSnCl_3 \text{---------------} (1\text{-}11)$$

The oxidative addition of aliphatic organic halides to stannous chloride has long been of interest for the preparation of monoorganotin trihalides:

$$SnCl_4 + RCl \longrightarrow RSnCl_3 \text{---------------------} (1\text{-}12)$$

The use of monoorganotins in PVC stabilizers generally less effective than dialkyltin derivatives, monoalkyltins added to the dialkyltins in amounts of 5 - 20 wt % exert a synergistic effect on stabilizer effectiveness, preventing early yellowing. The other use of monoorganotins as in the hot-end coating of glass to improve the abrasion resistance and bursting strength of glass bottles has been patented.

1.6 Bis(tributyltin) Oxide. [1,9,12-15]

Bis(tributyltin) oxide is one kind of trialkyltin compounds, which were first proposed for use as wood preservatives in 1954 by Van der Kerk and Luijten, who carrying out a systematic investigation into the biocidal properties of organotins at the Institute of Organic Chemistry TNO, Utrecht, Holland under sponsorship of the International Tin Research Institute. These workers discovered the high fungicidal activity of tributyltin compounds and, by the late 1950's, bis(tributyltin) oxide was already in commercial use as a wood preservative. In 1959 Oswood Preserving Company in U.S.A. introduced bis-(tributyl) oxide as a wood preservative which the formation contained the organotin in base of colorless mineral oil and was applied by brushing, spraying or dipping. The product was marketed under the name "Oz". Osmose is still marketing organotin-based wood preservatives today. Bis(tributyltin) oxide became widely adopted as wood preservative in many countries, its rather long chemical name being shortened commercially to "T.B.T.O.". It has a number of advantages for this application. As a colorless liquid, it is easily applied in a suitable organic solvent and it does not discolour wood or increase its flammability. Moreover, normal oil-based or water-based paint systems can be used over treated timber and the colour and adherence of the paint films are unimpaired.

Another area where T.B.T.O. has potential is in cooling water systems, to inhibit the growth of algae, fungi and bacterial slime. These organisms can cause serious problems due to restriction of water flow, loss of heat transfer and corrosion. An important use of triorganotin compounds is in antifouling paints and a number of sophisticated systems based on these chemicals have been developed. The aim of these paint systems is to provide long-term protection against marine organisms, which attach themselves to the hulls of vessels, thus reducing their operating efficiency. Tributyltin oxide is not widely used for protecting large commercial vessels, since its leaching rate from the paint is too rapid to allow long-term protection. However, it is still much used in antifouling paints for the yacht and the dinghy trade, where an application is only required to last through the summer months. An added advantage for aluminium-hulled boats is that it does not set up bimetallic corrosion, as is possible when copper-containing paints are used.

Tributyltin oxide finds use as a preservative in adhesives used for securing tiles and vinyl coverings and in cellulose-based fillers for domestic use. The secure fixing of wall coverings and tiles to floors and ceilings depends upon the adhesive maintaining its activity over long periods. However, such pastes are vulnerable to bacterial attack, which can reduce the adhesive properties. Small amounts of the organotin compound can prevent this bacterial attack and are often used for this purpose.

There are a number of other applications for which T.B.T.O. has potential, in combating the spread of the tropical illness Bilhazia, rubber pellets impregnated with T.B.T.O., have been used as molluscicides to prevent snail-borne transmission of the parasites which cause the diseases. These rubber pellets float on water frequented by the snails and slowly release a dose of toxicant, which is fatal to the snails but does minimum damage to other marine life. A number of trials have been conducted with this material in Africa and South America. This slow-release concept has also been put to use in protective rubber panels used to prevent marine fouling of sonar buoys used in early-warning defence systems.

1.6.1 Physical Properties of T.B.T.O. (17)

1. Colorless oil-like liquid
2. Molecular weight is 596
3. Boiling point at 180 ° C/2 mm Hg
4. Freezing point below – 45 ° C
5. Specific gravity at 25 ° C is 1.17
6. Flash point above 100 ° C
7. Refractive index at 20 ° C is 1.488

8. Low solubility in water below 0.1 %
9. High solubility in organic solvent
10. Low volatility

1.6.2 Biocidal activity of T.B.T.O.[12-14,18-20]

T.B.T.O. is the one type of triorganotin compounds, which have general formula R_3SnX (where R is an alkyl or aryl group and X is function group, usually inorganic), are powerful biocides. The group X does not significantly influence these biocidal properties, which depend largely upon the length of the carbon chain in the group R. For insects, the trimethytins are usually the most toxic, for mammals the triethyltins and for fungi the tributyltins have maximum toxicity. Obviously for a compound to be useful as an industrial biocide it must have low toxicity against humans. The diagram in Figure 1.2 shows the toxicity to insects, mammals and fungi for triorganotin compounds where X is acetate, as a function of the carbon chain length in alkyl group R. It can be seen that the widest separation between mammalian toxicity and biocidal action against fungi occurs for butyl group: as shown in Figure 1.1.

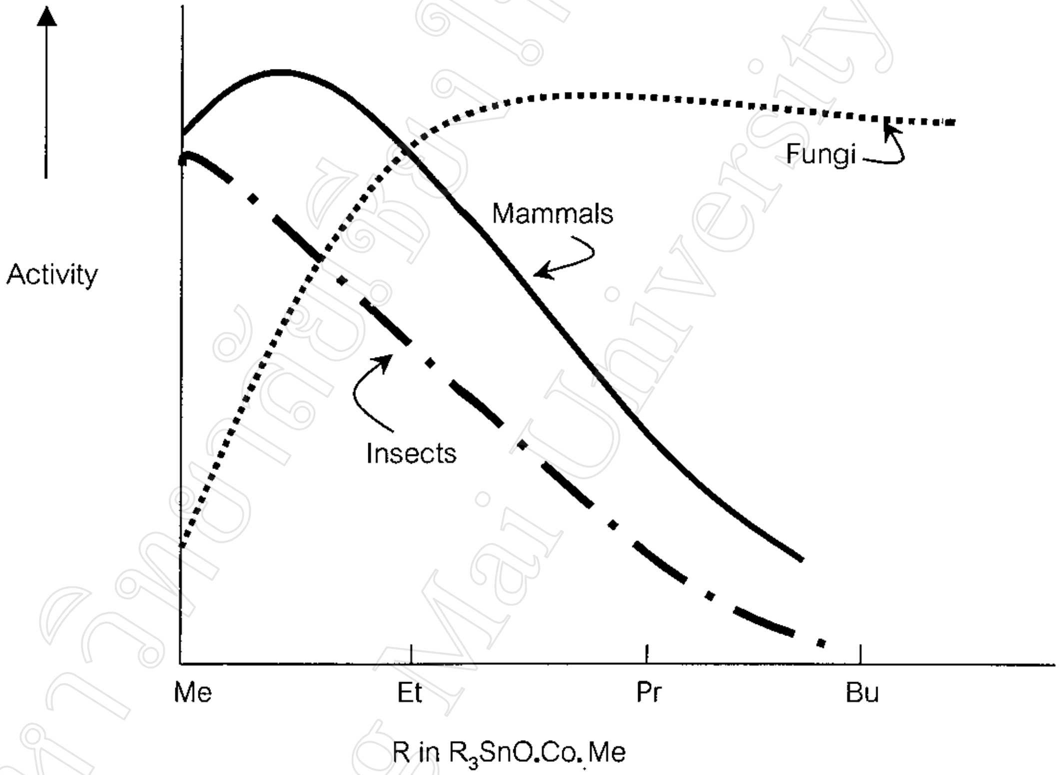

Figure 1.1 Dependence of the biological activity of tri-n-alkyltin acetate on the nature of alkyl group for different species.[13]

T.B.T.O. is active against a wide range of fungi and gram- positive bacteria. Typical values are shown in Table 1.5

The acute oral toxicity (LD_{50}) for rats is approximately 200 mg/kg with a high fungicidal activity. In a 4-week inhalation study no harmful reaction were observed in rats exposed to vapour practically saturated with T.B.T.O. From the respective for humans can be derived. This accepTable room air concentration can be compared with results of a model study, in which changes in concentration with time over wood blocks coated with preservatives containing 1.5 and 3.0 % T.B.T.O. were measured. From this it is concluded that there are no objections to a large surface application of wood preservatives of tested composition in room interiors. And approximately 20 years of industrial use, There have been no reported cases of serious toxic of the eyes and respiratory tract, Which are most commonly associated with pure compounds or concentrate solution

Table 1.5 Biocidal Properties of Tributyltin oxide

Organism		Minimum concentration (ppm) for complete inhibition of growth
Fungi	*Aspergillus niger*	0.5
	Chaetonium globosum	1.0
	Penicillium expansum	1.0
	Pullularia pullulans	0.5
	Trichoderma viride	1.0
	Candida albicans (yeast-like)	1.0
Gram- positive bacteria	*Bacillus mycoides*	0.1
	Micrococus pyogenes var, aureus	1.0
	Bacterrium ammoniagenes	1.0
Gram-negative bacteria	*Pseudomonas aeruginosa*	>500
	Aerobacter aerogenes	>500

Table 1.6 Findings in feed studies with T.B.T.O. in Juvenile rats [13]

Study period	Animal / group	Does (ppm)	Salient findings
4 weeks (dose rang-finding)	5 males and 5 Females	4	No substance-related effects observed
		20	No substance-related effects observed
		100	Food consumption and weight gain ↓ , absolute thymus weight ↓ (M)
		500	High mortality, apathy, emaciation, thymus and lymph node weight ↓ (M+F), depletion of lymphocytes in lymphatic organs, atrophy of thymus and lymph node
13-14 weeks (subchronic study)	10 males and 10 females	0	No effects observed
		4	No substance-related effects observed
		20	Slight prolongation of coagulation times (M), Food consumption ↓ (F)
		100	Food consumption and weight gain ↓ , serum alkaline phosphatase ↑ albumin ↑ (F), γ- globulin ↓ (F), weight of thymus , lymph node and thyroid ↓ , adrenal weight ↓ (M)

M: male animals, F: female animal, ↓ : decrease , ↑ : increase, ppm: mg/kg diet

1.7 Methods of Preparation of Bis(tributyltin) oxide [9,12,15]

There are several basic methods for the preparation of T.B.T.O., however virtually all of them are based on starting from tetrabutyltin which can be prepared by several known methods, these are shown in Figure 1.2

$$4\ BuCl + 8\ Na + SnCl_4 \longrightarrow Bu_4Sn + 8\ NaCl$$

$$4\ BuMgCl + SnCl_4 \longrightarrow Bu_4Sn + MgCl_2$$

$$4\ Bu_3Al + 3\ SnCl_4 \longrightarrow 3\ Bu_4Sn + 3\ AlCl_3$$

$$4\ BuCl + Mg_2Sn \longrightarrow Bu_4Sn + 2\ MgCl_2$$

$$SnH_4 + 4\ C_4H_8 \longrightarrow Bu_4Sn$$

Figure 1.2 Tetrabutyltin preparation.[15]

The tetrabutyltin is used to prepare tributyltin chloride by redistribution or cleavage and the resultant tributyltin halide is subjected to alkaline hydrolysis to yield T.B.T.O. as shown in Figure 1.3 and 1.4

$$Bu_4Sn + SnCl_4 \longrightarrow 4\ Bu_3SnCl$$

$$Bu_4Sn + HA\ \text{(mineral acid)} \longrightarrow Bu_3SnA$$

$$2\ Bu_3SnCl + 2\ NaOH \longrightarrow (Bu_3Sn)_2O + NaCl$$

Figure 1.3 Reaction scheme for preparation of T.B.T.O. from tetrabutyltin.[15]

$$Bu_3SnCl + NaOH \longrightarrow Bu_3SnOH + NaCl$$

$$2\ Bu_3SnOH \longrightarrow (Bu_3Sn)_2O + H_2O$$

Figure 1.4 Alkaline hydrolysis of tributyltin chloride.[15]

The commercial process is base on the basic starting raw materials, butyl alcohol, hydrogen chloride, tin and magnesium, Shown in Figure 6 is the entire theoretical process chemistry. A Flow scheme of the process is given in Figure 1.5

$$
\begin{aligned}
&\mathrm{Sn} + 2\,\mathrm{Cl_2} \longrightarrow \mathrm{SnCl_4}\\
&\mathrm{BuOH} + \mathrm{HCl} \longrightarrow \mathrm{BuCl} + \mathrm{H_2O}\\
&4\,\mathrm{BuCl} + 4\,\mathrm{Mg} \longrightarrow 4\,\mathrm{BuMgCl}\\
&4\,\mathrm{BuMgCl} + \mathrm{SnCl_4} \longrightarrow \mathrm{Bu_4Sn} + 4\,\mathrm{MgCl_2}\\
&3\,\mathrm{Bu_4Sn} + \mathrm{SnCl_4} \longrightarrow 4\,\mathrm{Bu_3SnCl}\\
&2\,\mathrm{Bu_3SnCl} + 2\,\mathrm{NaOH} \longrightarrow (\mathrm{Bu_3Sn})_2\mathrm{O} + 2\,\mathrm{NaCl}
\end{aligned}
$$

Figure 1.5 Commercial process chemistry for production of T.B.T.O. [15]

This research was intended to prepare T.B.T.O. from cassiterite as a starting raw material. Since the purpose was use T.B.T.O. as a wood preservative which no need to be pure substance for application. It success the cost will be very low. There is only one report by Noppawan Auchariyapitak [17] to attempt to prepare T.B.T.O. from cassiterite directly but without success. So in this work the attempt was carried out with different aspect. First to study the two methods, Grignard method and Wurtz method, which were used in the preparation of bis(tributyltin) oxide, T.B.T.O., from anhydrous stannic chloride, $SnCl_4$, as starting material. Second compare the yield, advantage and disadvantage of the two methods, and third to select the better of two methods to prepare T.B.T.O. by using cassiterite, SnO_2, as a starting material.

1.8 Objective of the study.

(1) To study the two methods which, were used in the preparation of bis(tributyltin) oxide compound, Grignard reaction and Wurtz method.

(2) To prepare bis(tributyltin) oxide by two methods and select the best method for prepare the bis(tributyltin) oxide by use cassiterite as starting material.