Introduction and Prospect of Tin Chemical Products

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目录
CONTENTS

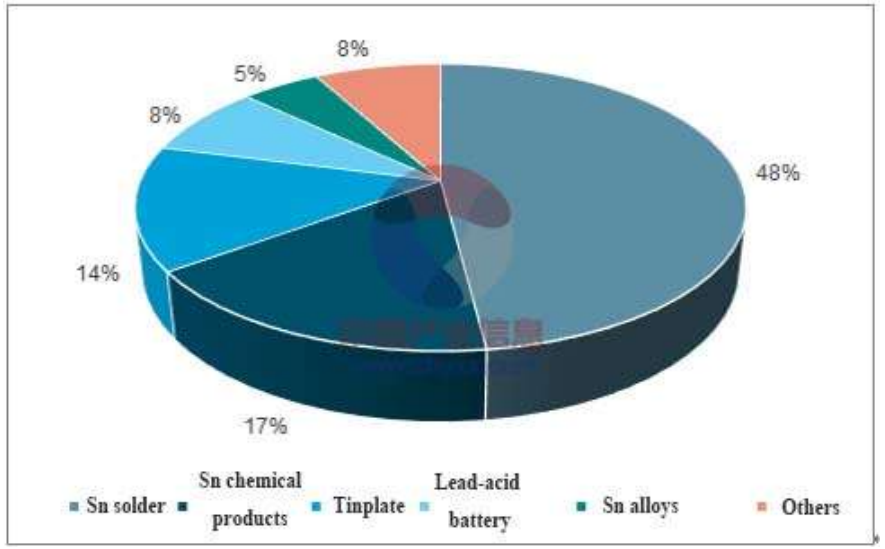
PART 01

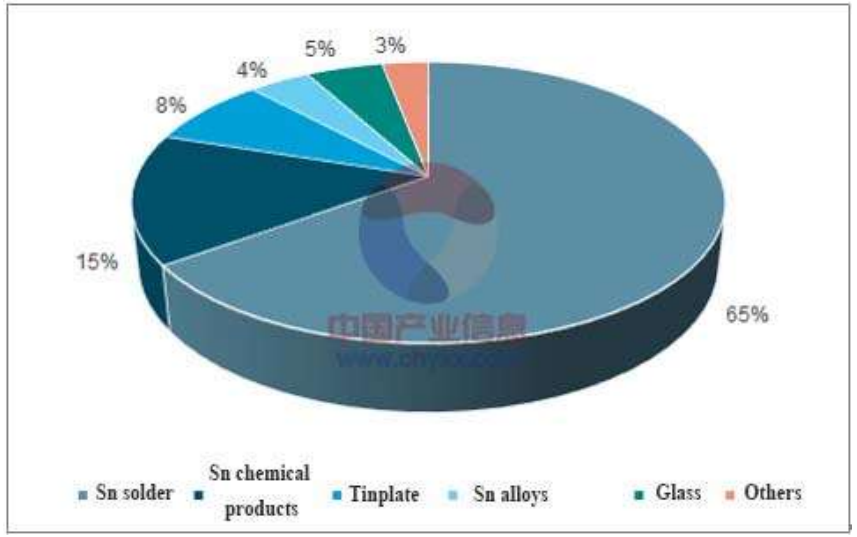
Introduction of Tin chemical industry

Characteristics of tin

Element of the carbon group; 3 common chemical valence, 0, +2 and +4; Inorganic compounds and organic compound can be generated.

The melting point of Sn is 232℃. It is an ideal soldering material for electronic industry. Sn is non-toxic and is an ideal additive for food and drug.





Global/Chinese tin consumption distribution

Tin consumption distribution

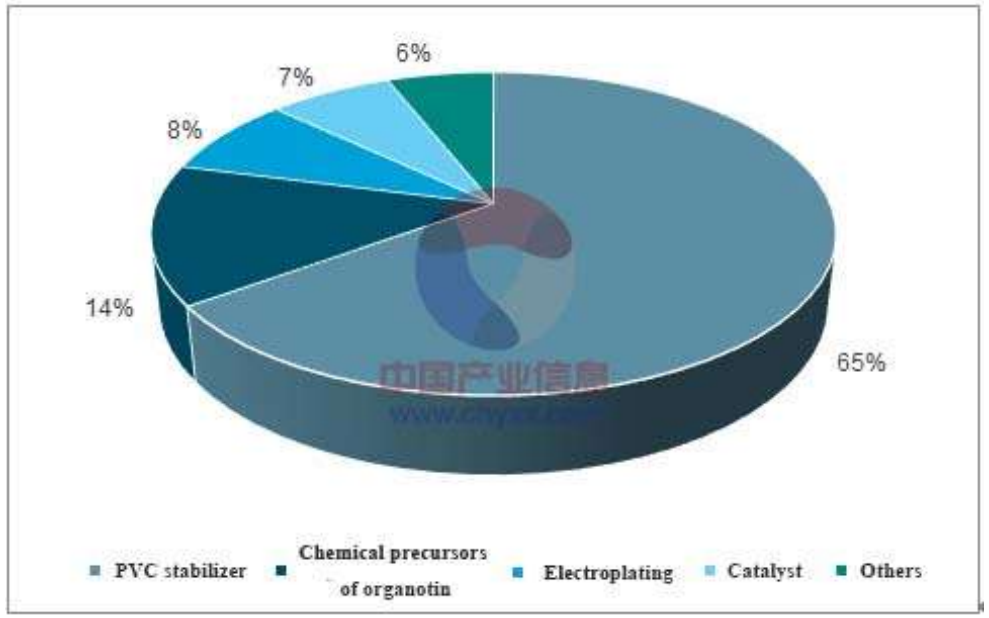
Chemical industry is the second largest industry in tin consumption, next only to solder manufacturing industry.

Global tin consumption in 2016 was 348,900 tons, 59,000 tons were consumed by chemical industry, among which 23,500 tons were consumed by China. The added value is nearly 10 billion.

PART 02

Introduction of Tin chemical products

Tin chemical products



Tin consumption distribution in chemical industry

PVC stabilizer and intermediate: Organotin mercaptide, alkyl tin chloride, stannic chloride

Electroplating auxiliaries: stannous chloride, sodium stannate, stannous sulfate

Catalyst: SnO_2, stannic chloride, tin carboxylate.

Ceramic/glass: SnO_2, metastannic acid

Flame retardant: zinc stannate, zinc hydroxystannate

…

Inorganic tin - Stannous oxide

1. Properties: SnO, blue-black metallic crystal powder, when heated to 220℃ in the air, SnO_2 is formed.
2. Preparation method: stannous salt → stannous hydroxide → stannous oxide (dissolve refined tin in hydrochloric acid, then adjust PH to 9 with ammonia, heat preservation at 60-70℃ with diluted ammonia after washing)
3. Main applications: the preparation of catalyst, reducing agent and stannous salt; the preparation of stannous fluoborate and other soluble stannous salts in electroplating.

Inorganic tin - Stannic oxide

1. Properties: stannic oxide, SnO_2; white, light yellow or light gray, tetragonal, hexagonal or oblique crystal powders.
2. Preparation method: mainly prepared by sol-gel method, co-precipitation and electrochemical deposition; first prepare stannic hydroxide, then burn it for SnO_2.
3. Main applications: often used in enamel and electromagnetic materials, the manufacture of opal glass, tin salts, porcelain colorants, fabric mordants and weighting agents, polishing agents for steel and glass; SnO_2 electrode is widely used in the smelting of advanced optical glass and electrolytic aluminum industry.

Inorganic tin - Stannous chloride

1. Properties: $SnCl_2$, White, monoclinic crystal
2. Preparation method: can be made from Sn reacting with concentrated hydrochloric acid or SnO reacting with hydrochloric acid.
3. Main applications: reducing agents, rubber activators, mordant dyes, electroplating sensitizers and food antioxidants.

Inorganic tin - Stannic chloride

1. Properties: $SnCl_4$, anhydrous stannic chloride is a colorless liquid, and the gas molecule is a tetrahedral structure. White smoke with a strong irritant will be produced when exposed to humid air, for $SnCl_4$ reacts with the water in the air and decompse into hydrochloric acid and stannic acid.
2. Preparation method: can be made from Sn reacting with chlorine
3. Main applications: raw materials for preparing organotin compounds, mordant dyes, condensation agents, catalysts for cationic polymerization, also be used in electroplating and glass industries.

Inorganic tin - Stannous sulfate

1. Properties: $SnSO_4$, White or light yellow crystal powders, soluble in water and dilute sulphuric acid.
2. Preparation method: prepared by excess tin reacting with sulfuric acid.
3. Main applications: bright electroplating on metal surface, plating metal materials, coloring and mordant dyes for textile in printing and dyeing industry, etc.

Inorganic tin - Zinc stannate, Zinc hydroxystannate

1. Properties: $ZnSnO_3$, $ZnSn(OH)_6$, White monoclinic crystal powers.
2. Preparation method: co-precipitation, reacting sodium stannate with zinc salt and heating.
3. Main applications: environmentally friendly products of flame retardants and smoke inhibitors in the plastic industry, ideal material to replace antimony trioxide.

Inorganic tin

Name	Applications
Sodium stannate	Most importantly, it is used for electroplating tin and its alloys; it is also used for immersion tin plating to form a bright coating on automotive aluminum alloy pistons; the substrate, pigment and catalyst for ceramic capacitors.
Stannic disulfide	Bronze coloring agent for wood and gypsum; pigments.
Potassium stannate	Electroplating solution for alkaline tin plating; substrate of ceramic capacitor; catalyst.
Stannous acetate	Catalyst for high-pressure hydrogenation of coal; accelerant for textile printing and dyeing.
Stannic arsenate	Effective insecticides for animals.
Stannous arsenate	Highly effective non-toxic catalysts and stabilizers in plastics and rubber products.
Stannous fluoborate	Ingredients for dental medicament; toothpaste additives to prevent dental caries; radiopharmaceuticals scanning agents.
Stannous pyrophosphate	Plating bath for tin alloy; radiopharmaceuticals scanning agent.

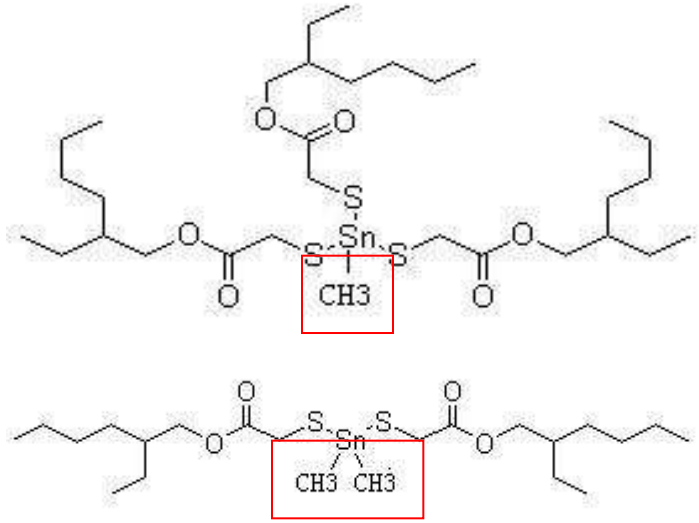
Organotin - Tin carboxylate

1. Properties: White or light yellow paste, unstable and easy to be oxidized.
2. Preparation method: can be made from reacting stannous oxide with octanoic acid
3. Main applications: Basic catalyst for polyurethane foam, room temperature curable silicone rubber, polyurethane rubber, catalyst for polyurethane coating.

Organotin - Alkyl tin mercaptide

Largest consumption among all the tin chemical products

1. Representative products: Butyltin mercaptide, methyltin mercaptide, octyltin mercaptide
2. Main applications: PVC heat stabilizer
3. Supporting intermediates: $SnCl_4$, alkyl tin chloride
4. Molecular structure:



Methyltin: CH_3—

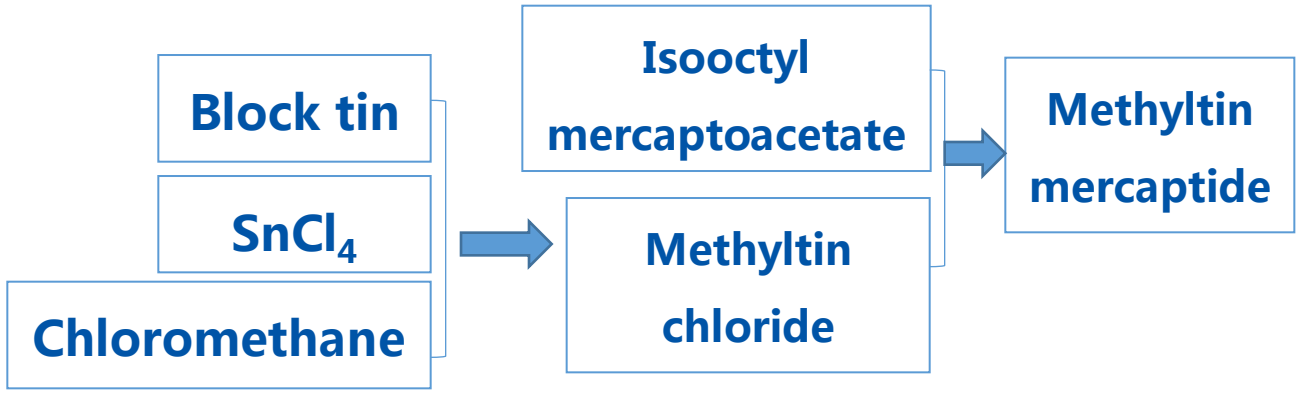
Butyltin: CH_3（CH2）$_2CH_2$—

Octyltin: CH_3（CH2）$_6CH_2$—

Organotin - Alkyl tin mercaptide

5. Preparation method

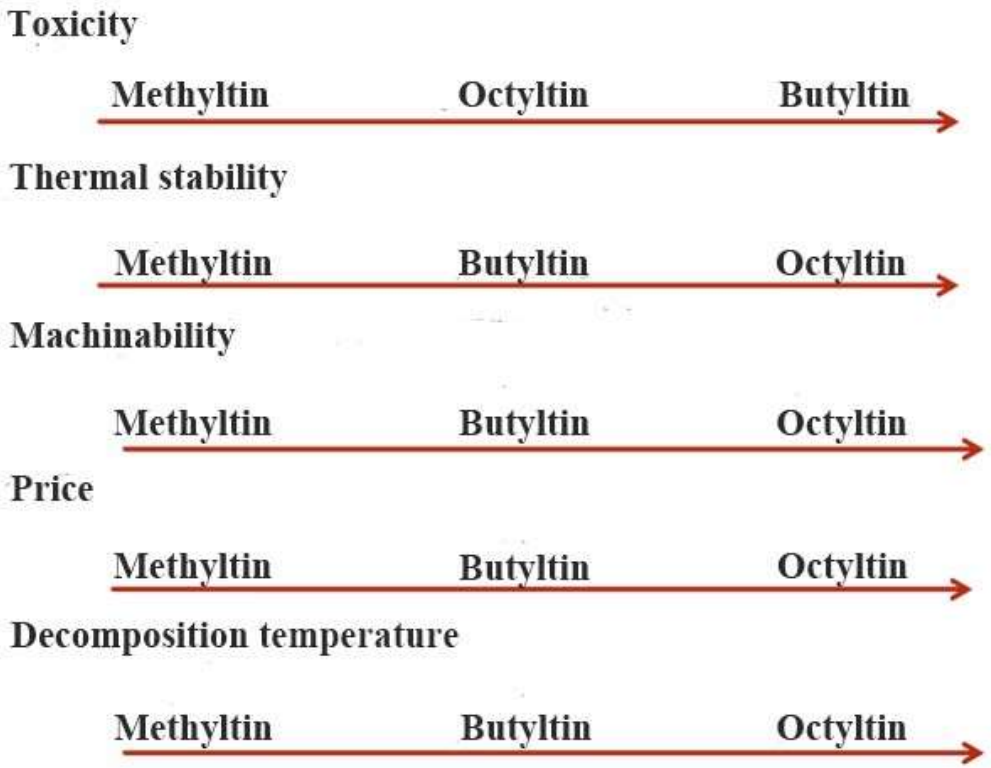
a.Methyltin mercaptide



b. Butyltin/Octyltin mercaptide

6. Application differences

(Increase along the arrow direction)



Organotin - Alkyl tin mercaptide

7. Main parameters of conventional varieties

Parameter	Methyltin	Butyltin	Octyltin
Appearance	Transparent oily liquid	Light yellow transparent oily liquid	Yellow transparent oily liquid
Sn content (%)	19.2	17.5	15.2
Chroma (Pt-Co)	25	100	250
Specific weight (25℃ , g/cm^3)	1.18	1.12	1.08
Refractivity	1.51	1.50	1.50
Replace one (%)	25	25	25
Replace three (%)	0.1	0.2	0.2
Environmental protection	FDA	-	FDA

Organotin - Alkyl tin mercaptide

8. Chinese consumption and production capacity

There are 12 manufacturers in China, mainly produces methyltin mercaptide , with a capacity of about 75,000 tons. The most representative manufacturers in China are Hubei Benxing Chemical Co., Ltd. and Yunnan Tin Chemical Co., Ltd.

Chinese domestic consumption is about 35,000 tons, accounting for 15% of the consumption for PVC stabilizer.

9. Major manufacturers

Global: PMC（ARKEMA、DOW）、GALATA、TIMAH、 REAGENS 、SONGWON

China: Hubei Benxing, Yunnan Tin Chemical, Hubei Nanxing, Zhejiang Tiandao, Zhejiang Shengchuang, Jianhua Dongxu, Xinaote, Zhejiang Himpton, Shandong Xingyu, Tai’an Blue Sky, Weihua Yihua, Nantong Advance.

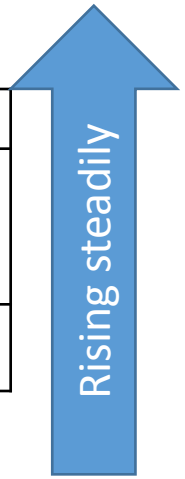
Other organotin

Variety	Application
Triphenyltin compounds	Insecticide, disinfectant
Tributyltin oxide	Bactericide, algicide
Alkyl tin chloride	SnO_2 coating precursors for glass, stabilizer intermediates
Tin alkyl maleate	PVC stabilizer
Tin alkyl laurate	PVC stabilizer, polyurethane catalyst

Prospect of Tin chemical industry

Tin consumption of Chinese tin chemical industry in 2013-2017 (source from ITA)

	2013	2014	2015	2016	2017
Tin consumption of Chinese tin chemical industry (ton)	20,300	21,600	21,300	22,700	24,300
Growth rate		6.40%	-1.39%	6.57%	7.05%



Prospect of tin chemical industry

1. There are many kinds of inorganic tin, but the consumption of individual variety is small. —— different fields will have different situations :

a. The increasing application of environmental friendly flame retardants will promote the upgrading of zinc stannate and zinc hydroxystannate.

b. Tin consumption of high-end glass and catalyst products will continue to grow.

c. Tin consumption of electroplating and ceramic industry will be stable for a short time, and will be in a downward trend for a long time.

Prospect of tin chemical industry

2. There are less kinds of organotin, but the consumption of individual variety is large:

a. The overall growth of PVC products led to the growth of stabilizers. In 2017, Chinese PVC consumption was 17,700,000 tons, and is growing every year.

b. Ban on lead has been published successively in China, 70% of the market share released by lead salts will be partly taken by the organotin products.

c. Due to the influence of raw materials and environmental safety, organotin industry has maintained high production capacity but relatively low profit margin in a certain period of time. The sales and supply tend to be balanced.

Prospect of tin chemical industry

3. Trends of organotin technology: the technology is rather mature, but personalized products will be the future development priority.

a. The PVC stabilizer industry will gradually concentrate on organotin mercaptide, and methyltin mercaptide will be the focus rather than butyltin and octyltin mercaptide. Methyltin mercaptide takes un 95% of the Chinese market, more customers in Europe and the United States are proposing alternates and related solutions.

b. With the development of lead-free process, the use of stabilizers in engineering plastics will be the focus of the development of organotin stabilizers, and low-content products will be the focus.

c. For CPVC stabilizer, besides organotin mercaptide, new high-efficiency organotin will be the research focus.

d. The breakthrough of new heat stabilizer technology will affect the development of organotin stabilizer to a certain extent.

e. The entry requirements of organotin technology is relatively high, the competitiveness of conventional products is gradually weakening, personalized and differentiated products will be the focus of development.

Prospect of tin chemical industry

4. Regulatory issues in organotin:

a. **EU Standard EN71-3: Restricted the total content of organotin and tin (maximum 12ppm) in the products → the application of organotin in PVC products is limited.**

b. **Substances of very high concern (SVHC): limited the use of butyltin and octyltin → accelerated the alternative use of methyltin.**

c. **ASTM and NSF for North American products: Except for organotin systems, other systems are difficult to pass → the application of organotin in North American will grow steadily.**

Prospect of tin chemical industry

5. Influence of tin on tin chemical industry

a. Effect of the quality of block Sn: more than 60% of the cost of organotin stabilizer is the cost of Sn; 99.9% of the general refined Sn can be used as stabilizer, while it is still urgent to produce specialized Sn for stabilizer to control specific impurities and reduce costs.

b. Influence of the trading mode of block Sn: block Sn producers → platforms (traders) → block Sn users, better communicate is necessary for them to cooperate and reduce intermediate expenditures.

行业领跑者
industry leader

Hubei Benxing Chemical Co., Ltd.

The largest organotin producer in China with an annual output of 25,000 tons of methyltin mercaptide, and is supporting a project of 20,000 tons Isooctyl mercaptoacetate per year.

Sincerely welcome experts and friends to visit us.

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Thank you for your listening!

Thank you for your time!