

Environmental Aspects of the Industrial Use of Inorganic Tin Chemicals

Introduction

Inorganic tin chemicals are used by a diverse range of industries and employed in an equally broad range of applications. The term “inorganic tin chemicals” is applied to all tin chemicals that have no direct Sn-C – bond. The lack of this direct bonding differentiates the inorganic tins from the so-called “organotins,” where the latter is characterized by their inherent Sn-C bonding.

The inorganic tins can be broken down into two categories: tin(II) and tin (IV). Typical examples of tin(II) chemicals and their applications include:

SnCl_2	Stannous chloride	Catalyst, Electroplating, Reducing Agent, steel strip plating
SnSO_4	Stannous sulfate	Electrocolouring of Aluminium
SnF_2	Stannous fluoride	Dental Applications
$\text{Sn}(\text{BF}_4)_2$	Stannous fluoroborate	Electroplating, Steel strip plating
$\text{Sn}_2\text{P}_2\text{O}_7$	Stannous pyrophosphate	Electroplating, Dental Applications
SnC_2O_4	Stannous oxalate	Catalyst for esterification
$\text{Sn(OOC-C}_7\text{H}_{15})_2$	Stannous octoate	Catalyst for esterification and polyurethane formation
SnO	Stannous oxide	Catalyst for esterification
$\text{Sn(O}_3\text{SCH}_3)_2$	Stannous methanesulfonate	Electroplating, Steel strip plating

Typical examples of tin(IV) chemicals and their applications include:

SnCl_4	Stannic chloride	Pharmaceuticals, Glass coating, Intermediate for Organotins
$\text{K}_2\text{Sn}(\text{OH})_6$	Potassium stannate	Electroplating Stabilization of Hydrogen Peroxide for example in Hair dyeing
$\text{Na}_2\text{Sn}(\text{OH})_6$	Sodium stannate	Electroplating, Stabilization of Hydrogen Peroxide
SnO_2	Stannic oxide	Ceramics

Chemistry

In order to understand the environmental behavior of inorganic tin chemicals, a look at the most important chemical properties of the compounds is helpful.

Tin(II) chemicals:

Tin(II) chemicals are sensitive towards oxygen. During prolonged storage or exposure to air tin (II) is oxidized to tin (IV), as represented in the equation below. At the end of this process only tin (IV) species are present:



The change in oxidation state is accompanied by a change of the chemical properties. The oxidation of the tin(II) is slow, if the material is stored in a dry environment. Contact with moisture will accelerate the rate of oxidation rate. An experimental study on this behavior in electroplating bathes has been published by Jordan /1/. A more detailed study concerning the stability of stannous octoate and the effect of different stabilizers was published by Dietsch and Klötzscher /2/. Their study showed that storage of stannous octoate in direct contact with open air for 226 days resulted in the tin(II) content being reduced from 24.7 % to 12.0 %. Additionally they observed the formation of a sediment as a result of the presence of insoluble Sn(IV)-compounds.

Another example pertains to stannous sulfate solutions. Shortly after production, sulfate solution is clear and colorless. After storage, a yellowish white precipitate forms. This precipitate consists of basic stannous sulfate (a hydrolysis product) and stannic oxide. There will be no stannic sulfate present because it is not stable in its diluted form; stannic sulfate will hydrolyze immediately to stannic oxide /3/. The following equation summarizes this behavior:



In addition to oxidation, the second important reaction affecting inorganic tin degradation and its environmental fate is hydrolysis. The following equation shows briefly what happens if tin(II) chemicals come in contact with water:



First, hydroxides form, resulting in the generation of a white precipitate. The hydroxide is only an intermediate product and subsequently slowly dehydrates to a black stannous oxide. Elevated temperatures and an alkaline environment accelerate this process. At 80°C the hydrolysis leads immediately to stannous oxide.

The hydrolytical stability of the tin(II) chemicals decreases with an increased dilution in water. Stability of tin(II) chemicals is increased via the addition of small amounts of acid.

For example the attempt to dissolve crystalline SnCl_2 or SnSO_4 in pure water results in a turbid solution. The turbidity is a sign of the formation of oxides, which have a very limited solubility in water. If a SnCl_2 solution (this is true for most water soluble tin(II) salts) is diluted with water, the tin will precipitate and the solution will become turbid. This behavior can only be suppressed in the presence of a strong complexing agent.

Tin (IV) chemicals

Unlike the tin (II) chemicals, oxidation is not a concern with the tin(IV) chemicals. The hydrolysis reaction is the major decomposition reaction and is strongly influenced by pH. The stannates are alkaline substances and decreasing the pH to 7 initiates the precipitation of stannic oxide hydrates.

Stannic Chlorides hydrolysis at a $\text{pH} > 1.5$. Decomposition takes place in steps until a $\text{pH} = 7$ is reached; precipitation is complete at this point.

Modes of entry into and behavior in the environment

Due to the different applications of inorganic tin chemicals there are several ways by which tin can enter the environment. Examples include:

- plating chemicals: landfill of plating sludges or tin cans
- catalysts: leaching out or weathering of polymers or -oleochemical technical fluids
- $\text{SnF}_2 / \text{Sn}_2\text{P}_2\text{O}_7$: direct introduction into municipal sewer systems;
regulations in the EU allow a max. 1 mg Sn/m³

There are many studies available /4/ that focus on the effects of organotin chemicals in the environment. This is not the case when it comes to inorganic tin chemicals.

From the chemical viewpoint, the question regarding the fate of inorganic tin chemicals in the environment can be looked at from the perspective of the behavior of the tin (II) or tin(IV) cations.

If polymers containing tin(II) chemicals undergo oxidation or hydrolysis degradation it is very likely that the tin(II) will precipitate out as stannic oxide. The same is true for tin(II) contaminated waters leaching from landfills tin(II) bearing plating sludges.

As far as the tin(IV) chemicals are concerned they are hydrolyzed to the stannic oxide.

Any conclusion about the toxicological effects of such a liberation has to take that into account.

Stannic oxide occurs in its natural form as cassiterite. Cassiterite is mined extensively for it is the main raw material for most tin chemicals. The solubility of SnO₂ in water, diluted acids, and caustic is very low. Especially in its aged form, SnO₂ is a nearly inert material.

Toxicological Aspects

Metallic tin is generally considered to be non-toxic. Tin has been used for centuries in making plates, jugs or drinking vessels. It has been shown that large amounts of tin salts in the digestive system causes negligible harm /5/. Orally introduced inorganic tin is poorly absorbed by animals and humans /6/. 99% of ingested tin will leave the body by normal discharge methods. Less than 1 % will be absorbed by the various tissues (e.g. liver, kidney). When present in a dust form, inorganic tin chemicals can accumulate in the lung and lead to irritation of the respiratory tract. For the occurrence of a “stannosis,” an exposure of 8.6 – 14.9 mg/m³ over a long period (i.e. many years) is necessary. The illness does not lead to a decrease of the lung function /7/.

In the MAK-List (TRGS 900), the maximum allowable tin concentrations at the workplace is 2 mg/m³ (calculated as tin, measured as total dust). Tin is categorized as II-1.

The low toxicity of inorganic tin chemicals can be seen from the following table /8/ which lists acute oral LD₅₀ values [mg/kg] for rats exposed to various tin compounds:

SnF ₂	188
SnCl ₂	700
Sn(OOC-C ₇ H ₁₅) ₂	5870
SnC ₂ O ₄	3400
SnO	> 10000
SnO ₂	> 20000

A more detailed description can be found in /6/.

Stannous fluoride and pyrophosphate have been used for a long time in the dental healthcare profession as a protective agent against the dissolving of dental enamel by lactic acid. These chemicals are components of toothpastes, mouthwashes and topical solutions /6/. Interest in the use of stannous fluoride and pyrophosphate by the dental healthcare profession is increasing, as evidenced by the number of new patents issued in the past few years /9/.

The Food and Drug Administration (FDA) regulates tin chemicals in various applications.

An example includes the regulation of stannous octoate used as a catalyst or crosslinking agent in resin applications that involved direct contact with food products. 21-CFR 175.300 sets the maximum amount of tin used in these products at 1% stannous chloride is found in the FDA's GRAS (Generally Recognized As Safe) listings as acceptable for use as an antioxidant in food applications at levels not exceeding 0.0015 %. /10/. Furthermore, stannous chloride is listed as an acceptable food additive for color retention of glass-packed asparagus at levels not exceeding 20 ppm /11/. These examples are application-specific and cannot extrapolated to other applications. However, given the fact that certain inorganic tin chemicals can be found in the FDA's listings, indicates that there are no significant toxicological characteristics related to their use.

Summary

Inorganic tin chemicals oxidize and hydrolyze to stannic oxide, if liberated into the environment. The toxicological risks are considered to be low.

The main pathways for inorganic tin degradation related to the presence in the environment are oxidation and hydrolysis. Review of the relevant European and North American regulations indicates that the toxicological risks inherent in the use of inorganic tin chemicals is low.

Literature:

- /1/ M. Jordan, Die galvanische Abscheidung von Zinn und Zinnlegierungen, Leuze Verlag, 1993, p. 62ff, 80 ff
- /2/ E. Dietsch, I. Klötzscher, Plaste und Kautschuk, 22 (1975) 726
- /3/ M. Ahmed, H. Fjellvag, A. Kjekshus, Acta Chim. Scan. 52 (1998) 305
- /4/ S. Nicklin, M. Robson, Appl. Organomet. Chem. 2 (1988) 487;
Y. Arakawa, O. Wada, Met. Ions Biol. Syst. 29 Biological Properties of Metal Alkyl Derivatives, 1993, 101-36;
M. Musmeci, G. Madinia, M. Giudice, A. Silvestri, G. Ruisi, R. Barbieri, Appl. Organomet. Chem. 6 (1992) 127;
I. Boyer, Toxicology, 55 (1989) 253
- /5/ Ullmann's Encyclopedia of industrial chemistry, VCH, 5th edition, A27, 79
- /6/ J. Tsangaris, D. Williams, Appl. Organomet. Chem. 6 (1992) 3
A. Bessmertnyi, N. Grin, Gig. Sanit. 1986, 82 (CAS 105 : 74010)
- /7/ W. Wirth, C. Gloxhuber, Toxikologie, Thieme-Verlag, Stuttgart, 1985
R. Ludewig, K. Lohs, Akute Vergiftungen , Ratgeber für toxikologische Notfälle, G. Fischer-Verlag, Stuttgart, 1981
M. Daunderer, Metallvergiftungen , Diagnostik und Therapie, Teil III, Bd. 9, Ecomed-Verlag, 1988
- /8/ S. Blunden, P. Cusack, R. Hill, The Industrial Uses of Tin Chemicals, Royal Society of Chemistry, ISBN 0-85186-927-0, p. 35
MSDS Data Sheets of Goldschmidt or other producers
- /9/ Application / Literature overview on this topic is available from Goldschmidt
- /10/ FDA, 21 CFR 184.1845
- /11/ FDA, 21 CFR 172.180