THE WORLD OF ORGANOTIN CHEMICALS:
APPLICATIONS, SUBSTITUTES, AND THE ENVIRONMENT

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Introduction

Organotin chemicals are those compounds containing at least one bond between tin and carbon. This paper presents a brief overview of some of the major commercial organotin chemicals, their applications and substitutes, as well as the environmental pressures coming to bear on these products. As the world of organotin chemicals is quite extensive and diverse, this paper will briefly discuss some of the major commercial uses concentrating on the alkyltins (methyltins, butyltins, octyltins), with a brief mention of phenyltins and cyclohexyltins used in certain applications. The majority of organotin uses are comprised of five major commercial applications: PVC Heat Stabilizers, Biocides, Catalysts, Agrichemicals, and Glass Coatings. These uses account for approximately 20K tons of tin consumption per year.

There has been a great deal of public attention focused on the toxicological and ecotoxicological aspects of organotins recently. There is special concern over the use of tributyltin (TBT) because of its biocidal properties. However, clear distinctions must be drawn between the triorganotin compounds which have three tin-carbon bonds used as biocides and pesticides, and the mono- and diorganotin compounds, which have one and two tin-carbon bonds respectively, used in stabilizer, catalyst, and glass coating applications. The latter exhibit no biocidal properties in contrast to the TBT compounds. There are certain mono- and dialkyl tins that have been approved as PVC stabilizers for food contact throughout the world. It is highly inappropriate to generalize that all organotin chemicals have similar toxicological and environmental properties, yet this is happening more frequently. One of the goals of Product Stewardship is to help customers, regulators, and stakeholders in general to understand the distinctions.

Major Applications of Mono and Diorganotin Chemicals

1. PVC Heat Stabilizers

Mono- and diorganotins are used extensively as heat stabilizers for processing polyvinyl chloride (PVC). The primary purpose of these tin stabilizers is to reduce the polymer backbone degradation of the PVC. They do this by scavenging the HCl lost during processing at high temperatures and stabilizing the unstable chloride sites in the PVC molecule.

Tin mercaptide stabilizers are some of the most effective PVC stabilizers available. They contain both tin and sulfur. Tin, acting as a base, reacts with the HCl initially released during PVC processing. The strength of this base is critical so it will not extract HCl from the PVC, but only react with the HCl that is already released. Only a very few bases have the right balance of reactivity to allow this. The mercaptan, a weak sulfur-containing acid, reacts with the unstable chloride sites on PVC to heal the polymer and reduce further decomposition. The high molecular weights and ester function in the mercaptan ligands also promote solubility of the stabilizer in PVC and provide lubrication during polymer processing.

There are three major types of tin stabilizers. They are distinguished by their respective alkyl groups: octyl, butyl, and methyl.

Octyltin stabilizers have the lowest tin content and are somewhat less efficient. However, they are approved for food contact applications by most regulatory authorities worldwide.

Butyltin stabilizers have been the dominant type used until methyltins were introduced.

Methyltin stabilizers have a higher tin content and lower raw material cost compared to the other two types. Some formulations (mercaptides) have also been approved for food contact applications.

The ligands (the chemical group attached to the tin atom) are used to differentiate the various tin stabilizers. The primary ligands are thioglycolic acid esters, reverse esters, and carboxylic acids.

The main applications for tin stabilizers are building products, such as pipe and fittings, and siding and profiles (windows, etc.), packaging, and flexible PVC.

The substitutes for tin stabilizers are manufactured from lead or mixed metals such as Calcium/Zinc. Lead stabilizers have the benefit of low cost but are declining in use due to environmental concerns. Tin and mixed metal stabilizers, in fact, are replacing them. Mixed metal stabilizer technology is more expensive than tin, and less effective in stabilization.

It is estimated that between 12 to 13K tons of tin are used annually in tin stabilizers worldwide. This market is expected to grow about 4% annually.

2. Catalysts

Catalysts are used to speed up chemical reactions, especially polymerization. The most common applications for mono-and diorganotin catalysts are in chemical synthesis and the curing of coatings.

In chemical synthesis, the organotins are used for the esterification and transesterification of mono- and polyesters. These products are then used for plasticizers, synthetic lubricant manufacturing, and polyester polyol production, as well as some coating applications.

As curing catalysts, one of the largest uses of organotins is in electrocoat (E-coat) coatings. These electrocoating products are sold into a wide range of applications, with the largest being automotive, where they provide excellent rust resistance. The catalysts are also used in urethane coatings as well as polyurethane foam production. Other applications include curing silicones and silanes.

Some of the more common organotins used as catalysts are:

Hydrated Monobutyltin Oxide
Butyl Chlorotin Dihydroxide
Butyltin tris (2-ethylhexoate)
Dibutyltin diacetate
Dibutyltin oxide
Dibutyltin dilaurate
Butyl Stannoic Acid
Dioctyltin dilaurate
Dioctyltin maleate

Although not technically classified as organotins, since they do not have a tin-carbon bond, other tin chemicals such as stannous oxide, stannous oxalate, and stannous bis(2-ethylhexoate) are used extensively in chemical synthesis as catalysts.

Outside of tin-based chemistry, substitute products are limited in the area of urethane/E-coat catalysts. There are some Bismuth and Beryllium based catalysts, but none have been successful in penetrating the market to date due to a lack of cost/performance benefit.

For polyester production, again, the substitutes are few. There is limited non-tin substitution (particularly in the U.S.), which is usually in the form of titanates when it exists.

Plasticizers (monoesters) are typically produced at lower temperatures and lend themselves more readily to the use of acids and titanates as catalysts. Sulfuric and sulfonic acids are regularly used in these production schemes. The advantages of tin-based products are normally seen at higher temperatures. Monoesters produced for synthetic lubricant applications are typically manufactured at higher temperatures and better lend themselves to the use of tin catalysts.

3. Glass Coatings

Monoorganotins are used on glass containers in Hot End Coatings (HEC). In HECs a metallic oxide is deposited on the hot glass surface of bottles thereby preventing microfissures. The predominant chemical used is monobutyltin trichloride (MBTC) although some inorganic stannic chloride ($SnCl4$, also known as tin tetrachloride) is used.

In the various container markets, glass bottles are beginning to be displaced by ones produced from PET. This trend is expected to continue.

On flat glass, mono- and diorganotins, deposited by chemical vapor deposition (CVD), are used in the manufacture of Low E glass. They reduce the heat loss through the metallic oxide coating deposited on the glass surface. Here, MBTC as well as dimethyltin dichloride (DMTC), are the dominant products. As with containers, stannic chloride is also used in less sophisticated processes.

Major Applications of Triorganotin Chemicals

4. Biocides

Tributyltin (TBT) is unique among the organotins in that it is used as a biocide. The monobutyl- and dibutyltins do not exhibit these properties.

Marine Antifoulant Paints

In the marine antifoulant (MAF) paint market, tributyltin is used as a biocide in paint formulations. These paints are then used to protect the underwater surface area of a ship's hull against barnacles, algae, etc. in order to avoid increased fuel consumption and premature drydocking. Triorganotins were introduced for this application 30 to 40 years ago. Originally tributyltin oxide (TBTO) was freely dispersed in what were called Free Association Paints (FAP). These paints had uncontrolled, rapid leaching rates of the biocide.

In response to the negative performance and environmental effects (which will be discussed later) of FAPs, tributyltin methacrylate copolymer systems were developed which had self-polishing behavior. These revolutionary new systems, called Self-Polishing Copolymers (SPC) had controlled, uniform leach rates of the biocide by incorporating the tributyltin biocide into the polymeric binding system of the paint formulation.

Throughout the 1980s many countries worldwide began restricting the use of TBT paints because of their environmental impact resulting from the misuse of the product in pleasure craft and other small coastal vessels. In the late 1980s, the Organotin Antifoulant Paint Control Act was passed in the United States which restricted the use of TBT paints to vessels greater than 25 meters in length. It also specified the allowable leach rates of MAF paints sold in the US as well as restrictions on applications and waste disposal. Presently, the International Maritime Organization (IMO) has proposed a worldwide ban on TBT MAF paints commencing with a ban on its application to vessels as of January 1, 2003 and a total ban on its presence on vessel hulls as of January 1, 2008.

Extensive research and development for replacement products for TBT paints has resulted in MAF paints based on binder systems made from copper acrylates, silylacrylates, and zinc acrylates. However, these SPC systems require the addition of co-biocides and booster biocides. These systems are still reportedly inferior to the TBT systems and continue to undergo further development in order to match the five to seven year performance of TBT. Questions are also beginning to surface surrounding the environmental impact of the replacement biocides.

Second generation replacement products are in the early stages of development. These products, based on silicones and fluoropolymers, are called non-stick or foul release coatings and contain no biocides at all. These paints produce surfaces to which fouling organisms will not stick, or can be easily cleaned off by brushing, water spray, or the vessel's own movement through the water.

Other Biocidal Uses

TBTO and tributyltin naphthenate (TBTN) are also used for industrial wood treatment and preservatives. This use is declining and mainly concentrated in tropical areas.

TBTO is used in formulations in the US for industrial cooling tower water treatment to control slime, algae, and fungi. This use is quite small and is also declining as other biocides continually replace TBTO.

5. Agrichemicals

There are five main triorganotin ingredients used as pesticides for crop protection:

Triphenyltin Hydroxide	(TPTH or Fentin Hydroxide)
Tricyclohexyltin Hydroxide	(TCTH or Cyhexatin)
Tricyclohexyltin Triazole	(TCTT or Azocyclotin)
Trineophenyltin Oxide	(TNTO or Fenbutatin Oxide)
Triphenyltin Acetate	(TPTA or Fentin Acetate)

These products are used primarily as fungicides and acaracides.

Fungicides - pesticides which kill or inhibit the growth of fungi
Acaracides - pesticides which kill mites and ticks (acarides)

As fungicides, TPTA and TPTH are used primarily for high value crops. Tin fungicides are used when the possibility of disease is very high, which justifies the added costs. They are used on potatoes, sugar beets, and pecans.

As acaracides, the efficiency of TCTH, TCTT, and TNTO is excellent. They are also not considered susceptible to resistance development. They are used on citrus, top fruit, vines, vegetables, and hops.

There are substitute products available, depending on the market segment. For example on potatoes, a substitute for TPTH is propamocarb hydrochloride / chlorothalonil and dimethomorph / mancozeb. On sugar beets, tetraconazole can be used. Substitutes for TCTH include dicofol, hexythiazox, propargite, pyribaden, and tebufenpyrad.

The organotin products typically have a cost advantage for growers when one considers the rate at which the product is applied, the cost of the product itself, and the number of days between sprayings. However, a single treatment method is not normally used. Growers typically rotate two or three treatment types in order to avoid the buildup of resistance to any one fungicide.

Environmental Pressures

1. Tributyl Tin and the History of Antifoulant Paints

In the early 1970's, tributyltin (TBT) was introduced as an ingredient in marine antifouling (MAF) coatings for general use on sea-going vessels. TBT soon became the most cost-effective technology for antifoulant protection of deep-sea vessels. It was so effective that TBT-based antifoulant paint spread to non-essential uses such as pleasure craft, coastal vessels, and fresh watercraft.

In the early 1980s countries such as France and the UK began regulating the use of TBT-based MAF paints. After reports in the mid 1980s of TBT causing imposex in dogwhelks and chambering in oysters, environmental concerns mounted over potential impact of TBT-based antifouling paints and led to regulatory measures in countries worldwide by the late 1980s.

Following the lead of many countries, the US passed the Organotin Antifouling Paint Control Act (OAPCA) in 1988, restricting use of TBT-based MAF paints to ships larger than 25 meters or those with aluminum hulls, while limiting the TBT release rate. The US EPA then mandated a Long Term Monitoring Program as a requirement for pesticide registration in the US.

As a result of concerns over release rates of TBT in free association paints, TBT-based Self-Polishing Copolymers (SPC) were developed to control release rates. This technology is now the standard within the industry.

Meanwhile, various Japanese paint and chemical companies developed alternative tin-free technologies and subsequently banned TBT paints in Japan. This action placed Japan in an uncompetitive position for maintenance and repair of ships, whereby they lost considerable market share. Japan began pushing heavily for the worldwide ban of TBT to “level the playing field”.

In 1990, the International Maritime Organization (IMO) of the United Nations’ Marine Environment Protection Committee (MEPC) adopted a resolution that recommended governments adopt measures to restrict the use and release rate of TBT-based antifouling paints. The MEPC is made up of IMO member countries with shipping/maritime interests. MEPC has proposed a worldwide application ban on TBT-based antifoulant paints to commence January 1, 2003, with a total use ban as of January 1, 2008. This proposal will be sent to a diplomatic conference in 2001 to agree on all details and resolve all issues. It will then be presented to the IMO General Assembly for final approval in late 2001. There is much uncertainty whether all of the issues can be resolved in time for individual country ratification of the treaty and passage of domestic legislation prior to the 2003 date.

Regulations put into effect in the late 1980s and early 1990s, as well as the widespread use of SPC technology, have helped reduce TBT levels worldwide. The situation today is that the science does not support a ban. The Consortium of Tributyltin Manufacturers has been very active in trying to educate the stakeholders and delegates to the MEPC on the issues:

- No proven alternatives are now available that match TBT-based paints
- Tin-Free does not necessarily mean environmentally sound
- Existing alternative products do not meet US VOC emissions restrictions
- The premature ban of TBT-based antifouling paints will have severe economic consequences to the shipping industry
- No criteria for evaluating alternatives have been established.

2. Butyl and Methyl Tin Pressures

As we have seen, the family of organotin compounds covers a spectrum of products used in a wide variety of applications varying from use of its toxicity as a biocide, to stabilizer use in the PVC industry for food contact applications. Although this wide application is a technical advantage, it makes the organotin range also vulnerable to confusion and misconceptions by lay persons.

The recent environmental issues surrounding tributyltin have been increasing environmental pressures on all butyltin compounds and other organotins in general. Focus is increasingly shifting to organotin stabilizers used in PVC, in an attempt to attack PVC from a variety of angles (e.g., chlorine, dioxin, and phthalates).

In Europe and Japan, increasing pressures have been mounting on PVC additives. Organotin stabilizers (predominantly the butyltins) have come under scrutiny. Countries such as Japan, Germany, The Netherlands, Denmark, and Sweden have initiated studies into organotins and some have already passed regulations restricting use of organotin stabilizers. Denmark seems to have concentrated efforts on evaluating the human health hazards, while Sweden has concentrated on assessing the environmental risks. Because the industry has reacted positively by presenting helpful toxicological information, neither Sweden nor Denmark have yet called for a ban, but Scandinavian sales are restricted to no more than 1994 levels.

In Germany, the VDA (German Automobile Manufacturers Association) was considering a ban on all organotins in automobile manufacture based on the environmental issues surrounding tributyltin. The industry provided the VDA with sound technical information distinguishing among the various classes of organotins and the VDA agreed not to ban organotins from automobile manufacture.

Articles have begun appearing in international scientific journals that imply that butyltins may be a human immune system, or hormone, disruptor. A university study dealt with the effects of butyltins on natural killer cell activity in human blood samples. Another article presented the results of a survey of butyltin compounds measured in the blood of human volunteers. According to the articles, sources of butyltin are hypothesized as coming from PVC compounds and fish contaminated with TBT from antifoulant paints.

In Japan detection of butyltin, as well as tributyltin, compounds was reported in silicon-treated baking paper and foodstuffs prepared using the paper. This has lead to increased concern in Japan over TBT content in stabilizers and the immune toxicity of dibutyltin. Immediately following this, MITI urged manufacturers to adjust the MSDSs of organotin stabilizers and catalysts accordingly.

Environmental groups such as Greenpeace and World Wildlife Federation have been increasing their attention on organotins.

3. Trade Associations and Advocacy Efforts

The Organotin Environmental Programme Association (ORTEPA) is a non-profit association of world manufacturers of organotin compounds. The objectives of the Association are to promote and foster the dissemination of scientific and technical information on the toxicological and environmental effects of organotin compounds. The Association cooperates with governments, industry and private agencies to provide greater appreciation of the available scientific and technical information toxicological and environmental aspects of organotin compounds.

In order to address many of the environmental concerns over organotins ORTEPA has established a database of technical and environmental information relating to organotin compounds.

One of ORTEPA's objectives continues to be to fund, cofund, and support future research efforts where specific needs are identified. One recent effort was commissioning the Institute for Toxicology of the GSF (Forschungszentrum fur

Umwelt und Gesundheit) to compile a comprehensive, and independent, review of all available toxicological and ecotoxicological data on organotin stabilizers.

The global chemical industry, through its International Council of Chemical Associations (ICCA) has launched a global Initiative on High Production Volume (HPV) chemicals. The US EPA has launched a similar initiative. The goal of the ICCA Initiative is to prepare harmonized, internationally agreed data sets and initial hazard assessments under the Screening Information Data Set (SIDS) Program of the OECD (Organization for Economic Cooperation and Development). The key element of these initiatives is the improvement of the current database of approximately 2,000 HPV chemicals based on information gathering and where appropriate by additional testing by the end of 2004. Most of the organotins are included on this HPV list.

Members of ORTEPA have assembled a consortium of companies to share the multimillion-dollar financial burden of the testing requirements for the HPV/ICCA testing program involving organotin stabilizer products and raw materials. They will collect hazard information and, where appropriate, conduct tests needed to supplement available information.

Summary

Recently there have been a number of concerns raised regarding possible human health effects associated with organotins. Unfortunately, many of these allegations fail to consider the weight of scientific evidence and important scientific research conducted over the last decade.

Organotin compounds are versatile agents in a wide range of industrial applications. They have been safely used for decades as catalysts in certain polyurethane, polyester and silicone systems, and as stabilizers in PVC processing technology. Clear distinctions must be drawn between triorganotin compounds used as biocides and pesticides, and those mono- and dialkyltins used, for instance, as polymer additives, which exhibit no biocidal properties. As such, it is inappropriate to categorize all tin compounds as having equivalent toxicological and ecotoxicological profiles.

Conclusion

Although organotins have a wide range of applications due to their versatility, this advantage can also lead to confusion and misconceptions about organotins in general. It is inappropriate to generalize that all organotins have similar properties. When used responsibly and safely, they can provide performance and value in a variety of end uses.