Tin Chemicals Roadmap 2015

Challenged but growing

Roadmap

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Executive Summary

Tin chemicals represented 16.5% of tin use in 2013 and may grow by around 7% in 2014 to become the second largest use of tin. Some products are sensitive to substitution with tin price and regulation both significant threats, especially in Europe. There are some concerns over tin supply, including ethical sourcing regulation, but the industry is responding robustly.

The largest use sector is PVC stabilisers where tin products have particular technical merit. Strong regulatory pressures and competition from cheaper calcium-zinc alternatives have significantly decreased markets in Europe but growth in China and SE Asia is strong based on increased PVC use there. Continued phase out of lead stabilisers may benefit tin particularly in China and especially for potable water pipes. Methyltin products are likely to become the focus of future use as butyltins are being phased out and octyltins are now under some pressure.

Catalyst markets are under similar regulatory pressures in Europe and some producers are marketing 'tin-free' products. The major product, stannous octoate, may also have issues with the octoate component. However markets for their application in silicones and polyurethane are strong and competitive products are still more expensive. The very many smaller catalytic uses of tin continue to abound, including organic synthesis and some remarkable examples in carbon capture.

Tin has a wide variety of glass coatings applications including flat glass, bottles and displays, using different precursors. Application markets are strong, driven by increases in construction, packaging and electronics use, particularly amongst middle classes in emerging economies, as well as increased energy saving and need for more displays. However large areas of glass are required to make a significant impact on tin use. Organotin variants are more efficient, though more expensive, but some 'tin-free' products are now seen here too.

A number of tin chemical variants are used in the traditional markets for electroplating including engineering, tinplate, wires and giftware. In general the high price of tin has brought this market into gradual decline in recent years, although some specialist innovative applications may grow. A supplier in China recently reported strong growth in sales.

Other traditional markets such as ceramics and pigments are likely to be relatively stable, with some gains from newer products compensating for declines in more traditional uses.

Other uses include cement additives, brake pads, fire retardants and a number of medical applications. New use may focus on a range of energy and electronics materials including lithium-ion batteries, solar cells, thermoelectric materials and photocatalysts.

Background

Global refined tin usage in 2013 is reported to be almost 350,000 tonnes per annum, the vast majority finding application in metallurgical uses, primarily solders and tinplate[1]. Tin use in chemical applications, although challenged in a number of ways, still remains one of the fastest growing areas. 2014 growth has been estimated at 7% and, if so, it will overtake tinplate as the second largest user of tin.

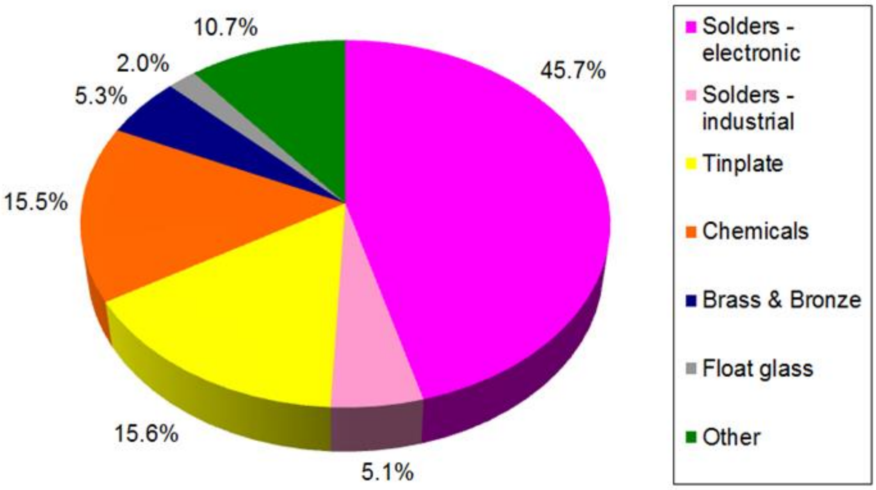

Figure 1 - World refined tin use by application, 2013

Tin price is often referred to as a challenge for the market and of all tin use sectors tin chemicals is the most sensitive to substitution. Regulation has pressured development of alternatives to tin and this has significantly increased the threat of price-based substitution. However, recent price crashes for several commodities including tin should have mitigated this concern, albeit with some uncertainty about the longer term.

Supply of tin has also been referenced as an issue, although in reality this is more short-term, since ultimately there is still plenty of tin available, especially with increase in recycling. This has been recently illustrated by a new surge in tin supply from Myanmar for example. However, investment in most of the several new tin mine projects will require a higher tin price. Conflict minerals certification issues relating to tin from DRC Congo have concerned US-based companies in particular, and now there is new highlighting of ethical

[1] ITRI Tin Use Survey, unpublished, 2013

mining issues in Indonesia, the world's second largest supplier. The tin industry is responding robustly to these challenges by the introduction of traceability programmes and stakeholder engagement schemes.

Tin chemicals are used in a wide variety of applications related to basic commodity markets such as plastics, adhesives, glass and metal plating which are linked to global economic trends. In line with other commodities the current markets are quite strongly polarised – flagging in Europe in particular but strongly driven by the growth in emerging economy middle classes in Asia and China. Construction and automotive markets are two examples of particular relevance.

PVC Stabilisers

Global demand for PVC is forecast to grow strongly, at 3.9% per annum[2] until 2020 reaching greater than 49 million tpa[3]. The major increase is in Asia, especially in the Chinese construction sector. Other markets are much weaker. The corresponding market for PVC heat stabilisers will reach 1.1 million tpa in 2020[4], although demand has been static in Europe, North America and Japan. Overall the growth rate for PVC stabilisers is about 4% per annum and 8-10% in China.

Substitution of PVC with other polymers e.g. PET will continue to happen and will gradually erode some market volume, although the cost effectiveness of PVC will ensure this stays at a minimum rate.

Phase out of lead stabilisers, already largely complete in Europe, will give some opportunity for tin stabilisers, especially in potable water pipes. However cheaper calcium-zinc products are taking significant market share even though in some cases they have inferior performance. Calcium stabilisers had 65% market share in Europe in 2012 and ESPA predict they will have 80% share by 2016[5].

Tin stabilisers are mainly used in rigid PVC, with only 5% use in flexible products. ITRI estimates that tin stabilizer markets will grow by an average of 5-10% in the short to medium term, mainly in China. Tin stabiliser production in China is estimated to be over 50,000 tpa, probably accounting for ca. 9,000 tpa tin. Tin has 10% share of the Chinese stabiliser market[6]. Markets in India, the Middle East and Africa are expected to grow in the medium term.

However tin stabiliser markets are static in the US and in Europe will decline from 8% in 2014 to 6% market share by 2016[7]. In North America they still have the dominant share in rigid PVC, particularly in pipe and profile markets, and to a lesser extent PVC film.

All stabilisers are made from $SnCl_4$ precursors, reacting with alkyl chloride or alkyl aluminium compounds.

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[2] Ceresana, "*Market Study: Polyvinyl Chloride (3rd Edn)*", July 2014
[3] GBI Research, *"Polyvinyl Chloride (PVC) Global Market to 2020 - Growth from Asia-Pacific Construction, Packaging and Electrical Sectors Continues to Drive Demand"*, August 2012
[4] Global Industry Analysts Inc., *"Heat Stabilisers – A Global Strategic Business Report"*, March 2014
[5] Nanni, E., *"The sustainable use of additives"*, PVC Formulation 2013, Dusseldorf, Germany
[6] ITRI, unpublished data, 2014
[7] Compounding World, *"Building a stable future"*, June 2013, p17

Butyltin products were the dominant type used until methyltins were introduced in the 1980s and later octyltins. The main ligand types are thioglycollic acid esters (often referred to as 'thiotins' or 'tin mercaptides') and carboxylic acids, mainly maleates and dilaurates. It is widely recognised that the sulphur-containing thiotins are the most efficient heat stabilisers available for PVC and are particularly prominent in PVC packaging for foodstuffs.

Di-butyltins have been under pressure for some time in Europe from the Dangerous Substances Directive 67/548 EEC (DSD)[8]. They were banned from use in all but a few exceptions since January 2012 and completely from January 2015.There is concern about increasing regulatory pressure in the America's, especially Canada, that could lead to a similar market impact there in the medium term.

Octyltins have the lowest tin content and are somewhat less efficient, but they have been assumed to be generally safe and are approved for food contact applications by most regulatory authorities worldwide. Di-octyltins have however been restricted from use by the general public in skin contact applications such as gloves and footwear, since January 2012 under the DSD Directive, now transferred to Annex XVII of REACH.

Now REACH[9] and CLP[10] classification procedures are starting to pressure di-octyltin products too. For example dioctyltin bis(2-ethylhexyl mercaptoacetate) – DOTE - was REACH registered in November 2010 with classification as a 'suspected human reproductive toxicant' but this was modified by ECHA[11] in October 2013 to 'presumed human reproductive toxicant' – Reproductive Toxicity Category 1B. Since December 2014 DOTE was included in the SVHC Candidate List. DOTE is also categorised as Reproductive Toxicity Category 1B.

Mono-octyltin is not classified as toxic and methyltins are for now accepted to have low toxicity, although there are increasing concerns that both mono and di-methyltins may be subject to a stricter classification in Europe.

Mono-organotins and methyltins are still strongly supported by producers, some of whom are increasing capacity, especially in China. However some feel that if regulations become more stringent, this could significantly impact the use of tin PVC stabilisers.

Given the narrowing opportunities, European PVC producers themselves have been made to reconsider the whole tin stabiliser franchise and are giving more focus to non-tin options for stabilisation, and this has also begun in the Americas. Many stabiliser producers are developing and promoting non-tin alternatives into the market. Although these alternatives

[8]Note that the Dangerous Substances Directive 67/548 EEC Directive will be repealed by Regulation (EC) No 1272/2008 in June 2015, introducing the Globally Harmonised System of Classification and Labelling of Chemicals (GHS), meaning changes to previous categorisations.
[9]Regulation (EC) No 1907/2006 on Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH),
[10] Regulation (EC) N° 1272/2008 on Classification, Labelling and Packaging of substances
[11]ECHA: European Chemical Agency, Helsinki

cannot meet all the technical demands at this time, there is an ongoing gradual growth at the expense of tin products.

There is a similar risk that, aside from regulation, sustainability professionals from large user corporations will make their own much broader judgements and already some are issuing supply chain notices on chemical use that include organotins. Danfoss, for example – a leading supplier of components and solutions for engineering products - have published a 'Negative List of Chemicals'[12]including all organotins, stating that their suppliers and subcontractors 'must not use any chemicals listed in processes manufacturing parts for Danfoss'. They are also required to report on any such substances present in materials and products supplied.

Increasing regulation in lower cost countries such as China is forcing investment into safety, environmental and health controls, which will bring additional costs thereby impacting on their ability to compete on a global scale.

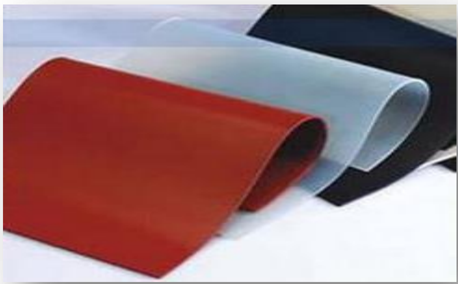
Despite all this, the positive potential in China and other emerging economies is still encouraging some major stabiliser producers to actively develop new products. The focus is on additives with lower tin contents, reducing cost, improved functional performance and enabling higher throughput for extrusion applications.

Certain organotin products have also been found to be effective in stabilising halogenated polymers used in thermoplastics such as ABS co-polymer and polyolefins and this could perhaps be a significant spinoff market.

There is also industry interest in production routes directly from tin metal using alkyl chlorides.

[12] Danfoss website, 'Negative List of Chemicals', March 2014 http://tinyurl.com/npad8w7

Catalysts



Tin catalysts are commonly used in certain types of silicone rubber products such as RTV (Room Temperature Vulcanising) silicones, for example in household silicone sealants and moulds for casting resins, waxes, gypsums or even lead. They are also used in polyurethane for flexible and rigid foam, as well as solid products and coatings.

The silicone rubber market is seen as robust due to its specialist high performance products, benefitting particularly from a general shift towards solvent-less products, especially in Europe. As with other polymers Asia-Pacific is expected to see the fastest growth, of over 5.0% through to 2017[13].

Market characteristics and forecast for the polyurethane market are quite similar to the PVC market, with decline in the US and similar markets more than compensated by significant growth in Asia-Pacific and other emerging markets, with overall forecasted growth at 5.1% to 2020[14]. Recent demand for rigid insulation foams in 'green' buildings has greatly increased use in this sector and this may be the strongest growth potential for tin.

By far the largest catalyst use, in polyurethanes particularly, is stannous octoate – tin (II) 2-ethylhexanoate. It is not an organotin and has a simpler production method using either SnO or $SnCl_2$ precursors. Some major catalyst producers state that tin is being 'phased out' alongside mercury and lead catalysts due to 'legislation and hazardous characteristics', 'legislated out due to environmental concerns' or replaced due to 'intense scrutiny in Europe over tin toxicity'. Evonik have drawn attention to some potential issues with the octoate form and are now marketing a tin alternative – KOSMOS 27 – based on tin (II) isononanoate for flexible foam applications.

Dibutyltin diacetate and dibutyltin dilaurate, made from $SnCl_4$ precursor, are also typical catalysts. An example would be the 'XIAMETER® RTV-3010-S' catalysts for silicone rubber from Dow Corning. As above, there are now sustainability concerns over dibutyltins in Europe particularly and this has led to several producers as Evonik , BASF, Tosoh Europe, King Industries and Umicore Speciality Materials either switching to alternative stannous octoate products or developing some 'tin-free systems'. However, dibutyltin catalysts are still very widely used outside Europe and there is no indication yet of any effect on Asian markets.

Methyltin products, also made from $SnCl_4$ precursor, such as 'METATIN' from Dow Corning – dimethyltin dineodecanoate – can also be used for polyurethanes, silicones and polyester

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[13] Global Industry Analysts Inc, *"Silicone - Global Strategic Business Report"*, August 2011
[14] Jahan, R., BASF, *BASF Polyurethanes Division presentation*, September 5th 2012

systems. They are particularly useful for high-temperature esterification and polyesterification.

Competitive products in various product types include bismuth, zinc, zirconium and amine catalysts. Bismuth carboxylate would be typical. Many of these are currently more expensive than tin and it is expected that the rate of change will be mainly governed by this factor. Once these new technologies can achieve the technical performance at a competitive cost, the switch may be rapid.

Despite these challenges some tin chemicals producers are still very positive about growth in tin polymer catalysts, although generally outside Europe.

There are very many smaller scale catalytic uses of tin and it is commonly used in organic synthesis reactions. A recent commercial example has been in Vitamin-E production. Research papers have highlighted potential use in synthetic crude oil generation from oil sand bitumen and production of some novel polymers. Some remarkable recent work has shown that tin alkoxides can be used in carbon capture to convert carbon dioxide to polyurethane plastic.

Glass coating

A wide range of tin (IV) oxide glass coatings are in use, made by spray pyrolysis or Chemical Vapour Deposition (CVD), usually from $SnCl_4$ but also from $SnCl_2$ and organotin compounds.

Very thin films are used for scratch resistance on catering glass, bottles and jars.

Slightly thicker films are iridescent and sometimes used for decorative purposes on ceramics or glass surfaces.

Increasingly important are thicker films – greater than 1 micron – used as conductive films for applications such as de-icing windscreens, electroluminescent displays and RF shielding. Electrical conductivity can be enhanced using doping with fluorine, boron or antimony. The largest such use in in low-emissivity 'e-glass' used in 'green' buildings to reduce energy losses. More rarely thick films of tin oxide and antimony tin oxide (ATO) on glass are made from sol-gel precursors, particularly for applications such as solar cells.

Flat glass was used 80% in buildings for windows, 10% in automotive windows and 10% in solar panels and other applications in 2011[15]. US and Europe production of flat glass are still badly affected by the recent economic downturn but emerging markets are expanding quickly. China has 50% of global production capacity, expected to grow at 8.2% annually to 2016[16]. Asia-Pacific accounts for 60% of demand and is expected to continue providing the fastest growth. Overall world demand is forecast to rise by 7.1% to 2016, faster than historical rates of 4-5% per year[17].

Glass bottles remain the leading packaging for alcoholic drinks but its market forecasts vary widely by region. Mature regions such as the US and Europe will remain flat due to tightening economic climates and health concerns, whilst strong growth of 5% to 2017 is predicted for Asia-Pacific overall, despite competition from PET and metal in some applications, with India just behind China in forecasted demand.[18]

Market trends for glass displays and for energy saving are also driving growth in high end markets, although very large areas of glass are needed to make a significant impact on tin use.

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[15] NSG Group, *"Markets and Growth"*, webpage http://www.nsg.com/en/our-businesses/buildingproducts/marketsandgrowth

[16] Devlin K., *"Brave New World of Glass"*, webpage http://glassmagazine.com/article/commercial/brave-new-world-glass-1412178

[17] Ispy Publishing, *"Glass Market Intelligence Report, Report 1 – 2013"*, 2013

[18] Dussimon, K., "SPECIAL REPORT: Global glass bottle markets", July 11th 2013, webpage http://www.thedrinksreport.com/news/2013/14995-special-report-global-glass-bottle-markets.html

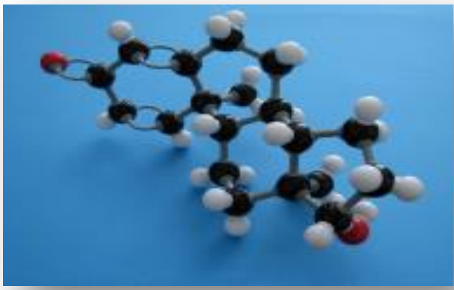
Organotin use in glass applications is subject to similar pressures as in other applications, with, for example, producer Evonik referring to 'a trend of avoiding the use of tin-containing compounds in glass coatings' with a tin-free variant in its VESTANAT range[19] (Evonik PR, 2013).

Although more expensive, organotins are more efficient than inorganic tin precursors, with less tin losses and higher quality coatings. Although butyltins are still widely used, monomethyltin products are likely to be the focus of future organotin use in this sector.

More recently alkoxides have also been used in sol-gel processes for glass coating in very high end applications.

[19]Evonik, *"Evonik: Unlimited play of colors and effects with glass".* March 19th 2013, webpagehttp://corporate.evonik.com/en/media/search/pages/news-details.aspx?newsid=34215

Electroplating



Tin and tin alloy plating are amongst several surface finishes used to give decorative or corrosion protection to metal parts used in a wide variety of sectors such as furnishings, engineering, wires, giftware and sports goods for example.

Stannous sulphate, stannous chloride or stannous fluoroborate are commonly used in acid tin plating baths, for example in plating automotive pistons or steel wire. Stannous methane sulphonate is used to supply tin in Methane Sulphonic Acid (MSA) for high-speed plating systems used in electronics or tinplate.

Anodising architectural aluminium has grown to be a major use of stannous sulphate in the US over the last 15 years.

Stannates, either sodium or potassium, are used for some niche electroplating applications, for example aluminium pistons. They can be used as cheaper alternatives to some silver or nickel processes in electronics. Their electroplating processes are alkaline and more difficult to control, with potassium stannate being more effective. Sodium stannate is widely used in copper-tin and zinc-tin systems.

Higher tin prices have impacted this market and there has been a significant decline generally, although some ground has been gained in specialised applications for substitution of less environmentally acceptable solutions and high end uses that are tailored to specific customer requirements. A supplier in China recently reported strong growth in sales.

Ceramics & pigments

Tin oxide has been used for millennia as a white opacifier for glazes and, although more recently it has been largely replaced by cheaper alternatives, it is still used in the highest quality artware.

It can also accommodate other metal ions into its lattice to produce a number of high temperature pigments including tin-antimony greys, tin-chromium pinks and purples and ‘Purple of Cassius’ which incorporates colloidal gold. More recently new niobium-tin yellows and rutile tin-zinc oranges have been launched as robust replacements for less sustainable products such as lead chromate road marking paints and some nickel pigments used in food contact.

Conductive electrodes can be made from sintering tin oxide, often with a small amount of copper and antimony doping. These inert anodes are most widely used to melt lead crystal glass. These electrodes can also destroy organic molecules in water and so be used in disinfectant or decontamination technologies. In sol-gel form conductive Antimony Tin Oxide (ATO) can be used as an anti-static treatment for displays, plastics or textile fibres.

Silver-tin oxide sintered products are also widely used in electrical contacts for relays and automotive application.

Tin oxide is also used as a catalyst material, particularly for carbon monoxide oxidation and other similar reactions. It is also used as a catalyst support, particularly with precious metals, for application in CO_2 lasers and air purification systems. Absorption of carbon monoxide and organic substances on the tin oxide surface changes electrical resistance and so tin oxide and its variants are commonly used as gas sensor materials.

Tin oxide is also an abrasive and used in some polishing applications, including stone polishing and LCD screens. It is also use in tyres and some friction materials to improve performance.

Most of these markets are likely to be relatively stable, with some gains from newer products compensating for declines in more traditional uses.

Cement

Since January 2005 an EU regulation on chromium in cement has created a market for stannous sulphate, or stannous chloride, additives to reduce the chromium to a non-allergenic form.

Mainly used for high end applications tin did achieve a quite reasonable 20% market share, but has now lost significant ground to cheaper iron sulphate alternatives that have been technically improved. Dramatically rising tin prices since 2005 have been a major factor.

As yet there is no evidence of regulation outside the EU, but the very significant use of cement in emerging economies such as China and India may hold promise for new tin use in the next 5-10 years.

Brake pads

The use of tin in brake pads is also a relatively new application of significant size. Friction materials including tin sulphide variants are used, especially in high end applications, and are starting to replace the more common antimony sulphide products.

Although lead sulphide products have been largely phased out in Europe and the US they are still used elsewhere. Increasing sustainability sensitivities within automotive industries will continue to pressure replacement of lead and antimony products. It has long been known that antimony sulphide can oxidise to the suspect carcinogen antimony trioxide and be released into the atmosphere from vehicles and this should be a strong driver to overcome the price differential with tin in the future.

A variant of this technology uses a blend of tin powder and iron sulphide to produce tin sulphide in-situ with the heat and pressure of braking. New pressure on use of copper in friction materials may boost this particular solution, which is performing well in tests.

Other uses

There are in fact at least 100 smaller uses of tin chemicals, showing the versatility of this little-known element. Collectively they provide some robustness to the tin market since they are often exploiting unique technical properties.

Biocides have been a traditional use of tin chemicals over many years and some organotins are still in use. However these have largely been replaced by cheaper and safer alternatives to the particular products used in applications such as anti-fouling paints for ships, pesticides and wood preservatives.

However some newer types of tin technologies are showing promise in anti-microbial use. Tiny additions of stannous chloride have been shown to reduce fouling in municipal water systems and stannous fluoride has been successfully launched as a veterinary medicine. Both have been used in toothpaste and dental products for some time as highly effective anti-microbial agents as well as dentine strengtheners. Stannous pyrophosphate is also used with dentifrices.

The reducing properties of these stannous compounds are also used in a number of ways, including, for example, use with Technetium 99 radiographic diagnostic agents. A larger scale and more recent use of this property is addition of stannous chloride to fracking fluids where it solubilises iron and prevents clogging of fluid flow channels.

There has been a recent revival of interest in use of tin compounds as anti-cancer agents, with thousands of published papers. Tin has been hailed as potentially the biggest breakthrough since the introduction of platinum drugs 50 years ago. Tin ethyl etiopurpurin has also been introduced in treatment of eye disease. Tin porphyrins are used to treat jaundice in babies.

Hydrated tin oxide can coordinate metals and is used, for example in chromatography of radionuclides, including in the medical field. It is also used to remove metals from petroleum feedstock in refineries, preventing coking on catalyst beds. It is added as a stabiliser to hydrogen peroxide to absorb trace metals.

Tin-based fire retardants have been developed over a number of decades and are highly effective alternatives to antimony products currently used, especially for smoke suppression. Cost is the major obstacle to wider use but this market could have very significant growth potential if there was more regulatory pressure on antimony use. For now zinc stannates and hydroxystannates are growing in use in niche applications, particularly those where smoke is important. New markets are opening up in halogen-free fire retardant systems, for which tin has been shown to be effective in reducing filler loadings. Sol-gel products based on tin oxide can also be used in textiles and rubbers for example.

Energy uses

Tin is proving a strong candidate for a number of new energy and electronics materials uses, linked to its ability to create, harvest, conduct and store energy in combinations with other metals and materials.

Probably the largest potential is for use in lithium ion batteries, where impregnation of carbon anodes with stannic/stannous chloride or nanotin oxides can significantly increase charge storage capacity. Early tin products were launched but withdrawn due to competition from silicon. However, there is still a very significant amount of published development work, some of which is focussed on the complementary use of tin with silicon and the potentially huge hybrid car market may still be open. Nanotin oxides are also being evaluated for next generation magnesium and sodium ion battery anodes and for textile-based wearable electronics.

Some work is starting to be published on tin supercapacitor materials. Tin-niobium is already used in superconductors and now there is new work on stannene – theoretically 100% conductive and a better possible replacement for silicon in computer chips and displays than graphene.

There has been much publicity of tin-based solar cell materials as low cost and abundant alternatives to current materials. Copper Zinc Tin Sulphide (CZTS) is a leading candidate and tin perovskite materials may be used in architectural glass.

Complex oxides, sulphides and tellurides including tin are rapidly being developed as new thermoelectric materials that can harvest wasted heat from sunlight, car exhausts or even the human body.

Polyvalent tin oxides can also be photocatalytic and a significant research effort is focussing on applications such as water splitting to produce hydrogen, dye bleaching and self-cleaning windows. Similar materials can be used in electrocatalytic applications such as fuel cells. They can also be photo and electro-luminescent.

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