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Tin – an urgent need in industry and its recycling

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The aim of this work is to draw attention to urgent need of tin in industry, the characterization of the waste with tin content, its origin and composition. This study describes the ways of waste treatment with tin content. The treatment generally depends on the amounts of tin and the form in which the waste is. The paper also discusses possible ways of tin waste treatment, which are used by different companies in the world.

The amount of waste produced is naturally increasing due to the continuous development of new technologies in present society and continuously growing industrialisation. In 2012 European Union (EU – 28) produced 2 515 mil. tons of waste representing 4 984 kg per person (4% defined as hazardous waste) [1]. The Slovak Republic produced 9.8 million tons of waste in 2012 [2] .

The current policy of the Slovak Republic is governed by „Hierarchy of objectives and waste management which contains 5 points, namely:

- waste prevention,
- preparation for reuse,
- recycling,
- other recovery – eg. energy recovery,
- disposal [3].

At the beginning of 2014, fees for depositing waste at dumps increased [4] and this is why the society is forced to seek new alternative options for utilising waste as a secondary raw material. Recycling is also one such option which saves natural resources (primary raw materials), energy and, last but not least, it minimises the amount of waste deposited at waste dumps.

In 2013, 3.7 mil. tons of waste were recovered (excluding municipal waste) which represents nearly 46% of the total amount of waste. Quite significantly to the recovery of waste R04 activity, recycling and reclamation of metals and metal compounds also contributed with approx. 14% share [2].

The aim of this paper is to state the method of waste treatment with tin contain in practice, to outline alternative method of treatment and draw attention to the need and indispensability of tin for the following reasons:

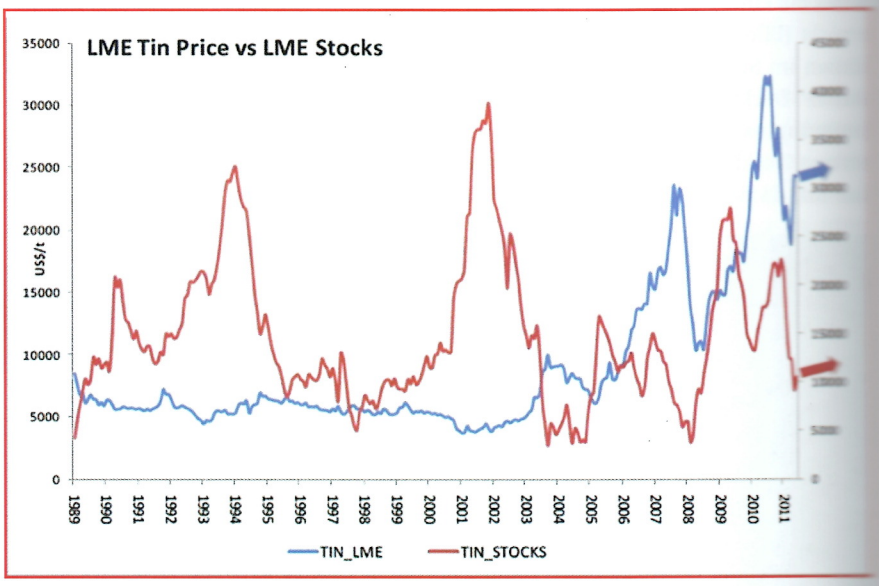

Fig. 1: Development of prices and stocks of tin [7]

- currently insufficient reserves,
- continuously increasing price of tin,
- need for tin in various industries due to specific and irreplaceable characteristic.

Current situation

Demand for metal is increasing worldwide due to its use in various industries. Replacing metal with other materials is usually problematic. The main problem is that every metal has its own specific properties. According to [5] that, from the total amount of metal used in industry as many as 62 metals cannot be replaced with materials that would meet 100% of the required properties. In 2011, the European Commission issued a report on the list of critical metals, which are currently necessary for meeting European Union (EU) energy policy. At that time, the EU adopted the SET Plan (Strategic Energy Technology Plan), which prefers the use of alternative energy sources without fossil fuels such as wind power, solar energy, geothermal energy etc. 14 critical metals necessary for applying and developing this energy were defined in order of their importance: tellurium, indium, tin, hafnium, silver, dysprosium, gallium, neodymium, cadmium, nickel, molybdenum, vanadium, niobium and selenium [6].

Tin plays an irreplaceable role in various industries. Global demand for this metal is currently growing (Fig. 1) [7].

Fig. 1 shows the decrease in stocks and the continuously rising price of tin. In 2000, the price of tin was around USD 11.000/t which was caused by the global economic crisis. In 2010, the price of tin reached a record of USD 33.000/t. The current price of tin (03.01.2017 is USD 21.290 USD/t [8].

The global tin consumption for this metal is growing every year (Fig. 2). The latest US Geological Survey estimates the state tin stocks at 4.800.000 tons. With the current production of 296.000 t per year (2014), tin stocks are currently estimated to last 16 years [9] .

Continuously increasing price of tin, currently insufficient reserves and the increased consumption of this metal indicate the need to also obtain the tin from waste - a secondary raw material - by recycling [9].

Industrial use of Tin

Because of its properties tin is a frequently used metal. In the past, tin was used for the production of containers. However, its

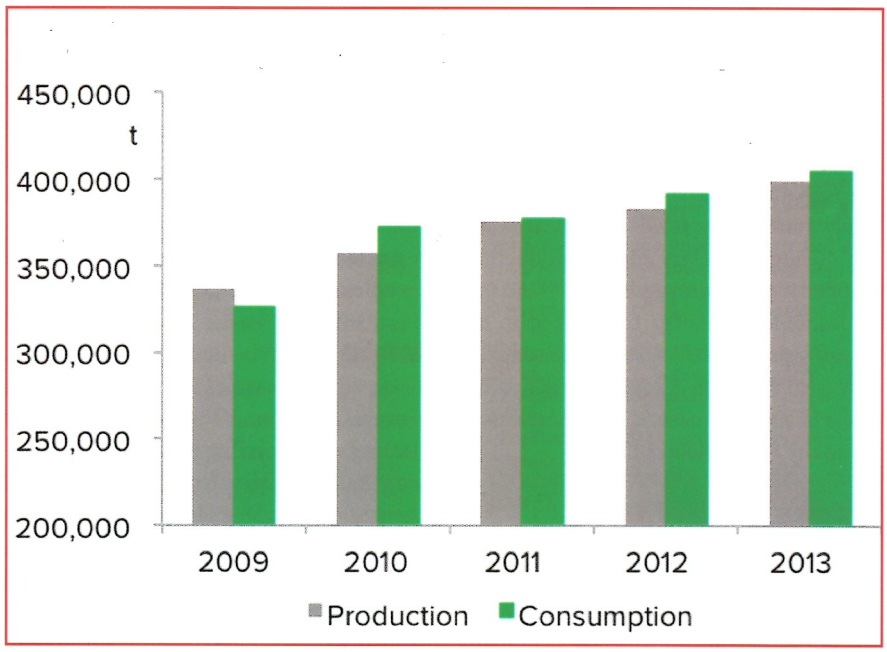

Fig. 2: Development in production and consumption of tin [9]

use is much wider, e.g. in the production of bronze, tin coated sheeting and as solder. Insufficient stocks are causing tin to be used less and less and there are efforts being made to replace it with another material. However, there are areas in which tin is irreplaceable. One such area is the electrical industry (solders) [10].

(RoHS) on hazardous waste that is present in electrical and electronic equipment (WEEE). The main purpose was to reduce the amount of WEEE, increase recovery of metals by recycling and reduce impact of production process on the environment. The result is the prohibition the use of some toxic substances and lead from 1. July 2006

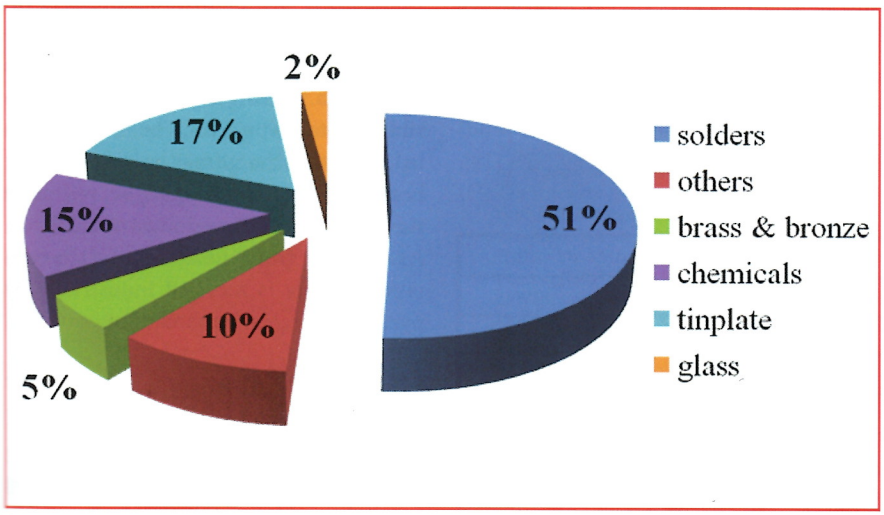

Fig. 3: Tin consumption in 2011 [11]

Electrical industry

Fig. 3 shows that 52% of worldwide production of tin is consumed in the electrical industry for the production of solders [11]. Currently, in the electrical industry lead-free solders with a tin content from 90 – 95% Sn are used [12, 13]. The main reason was the fact that in 2003, the European Parliament and the Council of the European Union published Directive 2002/96/EC

[14]. End of life of electrical and electronic equipment becomes the waste, which is a valuable secondary raw material.

Tinplating

Another potential use of tin, which is still applied in the world, is tinplating of steel sheet. Tinplating can be divided into:

- hot-dip tinplating – cleaned object passes through the flux due to final cleaning and subsequently is dipped into molten metal where base metal (steel) reacts with the molten metal [15].
- electrolytic tinplating – consist of chemical degreasing of steel coils in alkaline solution and electrolytic degreasing in an alkaline electrolyte. The next step is electrolytic tinplating in an aqueous solution of methanesulphonic acid, phenolsulphonic acid, hydrochloric acid etc. [15, 16].

Tinplate use is versatile, but most tinplate is used in the automotive and food industry. The reason is health and corrosion resistance [17].

Alloy production

Tin alloys called bronzes are copper alloys with other metal such as zinc (in the past only copper alloy with tin). Bronzes are usually referred to by their main additive – aluminium bronze, tin bronze etc. The content of copper and tin in tin bronze is min. 99.3%. The colour depends on the amount of tin in the alloy, it can vary from red, yellow to white. 5% of tin is used for production of alloys from the worldwide production [18].

Chemicals

Chemicals containing tin are used in daily activities. In general, chemicals can be divided into organic and inorganic. In the construction industry as an additive to PVC products (windows, doors), the organic chemicals are used the most. The main reason is to avoid the degradation of these products from the effect of sunlight. Inorganic Tin chemicals are used as a catalyst for a wide variety of industrial processes, e.g. fire retardant and catalyst for the production of ceramics or cement. Tin catalysts are also used in production of polyurethane foam, which is currently used for the insulation of modern buildings, "Green buildings". These buildings efficiently use natural resources and they are environmentally friendly throughout its lifetime - from design to disposal of building [19].

Tin recycling

Tin is widely used and the reason is the diversity of waste, such as waste from electrolytic tinplating, waste – alloys, WEEE, where tin is located on PCB as solder. Tin is also a part of waste generated during

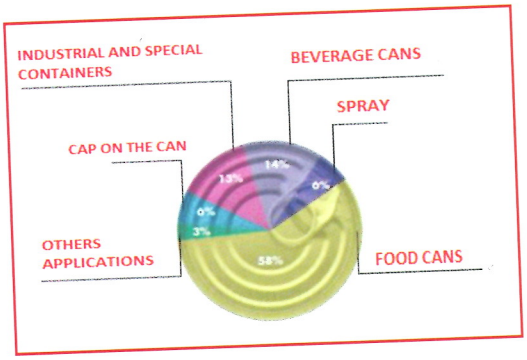

Fig. 4: Use of tinplate [17]

secondary production of copper. In practice, there are some secondary copper industries, where WEEE is melting charge. The reason is that WEEE contains a high amount of copper, so that it is an important secondary raw material. WEEE contains other more important components, such as copper, which are during the process of secondary copper production accumulated in the waste – slag, dust etc. Table 1 shows the weight content of tin in the waste [18, 20, 21, 24].

The largest amount of waste is generated waste of electrical and electronic equipment at end-of-life. In recent decades, the amount of waste WEEE tripled [25, 26]. In general, three ways of tin waste treatment exist – pyrometallurgy, hydrometallurgy or combination of both. Pyrometallurgical treatment is less demanding on technology suitable for more heterogeneous batch and for a large amount of batch. The disadvantages of pyrometallurgical treatment are the processing of toxic gases, dust, noise and inability of the separation of pure components. Hydrometallurgical treatment is suitable for a smaller amount of batch and by using this method of treatment; it is possible to separate the pure components. The disadvantages are the higher demand on complex technology, obligation of homogeneous batch, complicated management and process control [26].

In practice, treatment of tin-containing is typically carried out by pyrometallurgy as set out at the following sections. The reason is that the tin waste is not treated separately, but it is recycled with other waste e.g. during secondary copper production. Copper is the main product and tin as an undesirable element is transferred to the waste - slag, dust. Waste containing tin may also be treated together with other waste of a similar nature, for example as in company Fenix Metal LTD.

Waste	Amount of Sn (%)
Flue dust from the secondary production of copper	0,4 - 30
Slag from the secondary copper production	0,38 – 0,8
Sludge from electrotinning	50 - 70
WEEE	~ 4
Bronze	max. 20
Tin brass	max. 2,5
Tinplate	1 – 2 g/m²
Tin ore	max. 1

Table 1: Weight content of tin in the waste [18-21, 24]

Metallo – Chemique N.V.

Metallo – Chemique N. V. is a Belgian company dealing with recycling and refining of non-ferrous metals. This company includes a company Elmet S.L.U. in Spain. This company deals with treatment of secondary raw materials with copper content and production of blister copper, which is further treated in Belgium. Company Metallo – Chemique N.V. recycles 350 000 tons of secondary raw materials per year. From these secondary raw materials, it is possible to gain non-ferrous metals or its compounds for sale. The main products of this company are pure copper, lead, nickel, tin and zinc oxide [27, 28]. Tin is obtained after a process of treatment slag containing lead and tin. Lead is removed from lead-tin alloy by vacuum distillation and the product is tin with purity 99, 93 – 99, 95% [28].

Umicore N.V.

Umicore N.V. is a Belgian company with a worldwide coverage (38 countries). The company is able to recycle 17 precious and non-ferrous metals recycled of WEEE, fuel elements, automotive and industrial catalysts [29]. Recycling process is divided into two branches: branch of recycling base elements and branch of recycling precious metals. Tin is obtained in the branch of base metals. The process begins in the blast furnace during lead melting due to the tin content in the feed material. The separation of tin and lead occurs during the refining of lead. Tin is obtained in the form of a complex compound [30].

Aurubis AG

Aurubis AG is one of the largest companies dealing with recycling of copper. The company has manufacturing facilities around the world, including Slovakia. In addition to highly pure copper, Aurubis AG produces metals alloys based on tin, lead, zinc and selenium. Tin is set into the process of copper production as solder that is present in the WEEE [31]. WEEE is crushed and then set in a blast furnace. The product of melting is blister copper with tin and lead content. Tin and lead passed into slag during converting process. The product of recycling slag in retort furnace is alloy of tin and lead [32].

Fenix Metal LTD

Company is dealing with treatment of tin waste and production of the final marketable product. Tin is recycled by vacuum distillation. During this process, it is possible to obtain a pure tin. The content of tin in the melting charge may be less than 15%, because of this may company recycle more tin waste from various industries [33].

As apparent from the above, the tin-containing waste is recycled industrially by pyrometallurgical method.

Conclusion

Waste containing tin is possible in quantitative terms to divide into the following groups:

- flue dust from the secondary production of copper,
- waste of electrical and electronic equipment,
- waste of tinplate,
- waste of electrotinning,
- waste of bronze.

This waste can be classed as valuable secondary raw material because of metal content. Compared with the primary raw materials – ores, the metal content in waste is many times higher. The main reason for recycling of waste is a hazard-

ous characteristic of this waste. It contains compounds of heavy non-ferrous metals which are risky for human and environment. Recycling of waste with tin content is important not only for high tin content, but also because of tin price. Currently, the price of tin is 16 050 $ per tonne [8].

Price of tin is increasing, but the stocks of tin are decreasing. The European Union has recognized the needs of tin for itself, and therefore determined the list of critical metals, which are necessary for the needs of energy industry, where tin inherently belongs. Finally, it is necessary to consider the treatment of waste containing tin because of the high financial potential that is hidden in this waste.

Treatment of waste containing tin in practice is carried out by pyrometallurgical processing methods. Waste of electrical and electronic equipment is typically treated in the secondary production of copper pyrometallurgical method. Company FENIX Metal LTD treats a variety tin waste by pyrometallurgical method. In the area of waste treatment with tin content, there will be need to focus on the hydrometallurgical method of recycling. Hydrometallurgical processing appears to be preferred, especially on account of the hydrometallurgical treatment it is appropriate, because of the flexibility, less investment for the operation, the formation of SO_2 is eliminated, which means that the hydrometallurgical processing does not pollute the atmosphere. Finally, it should be noted that the hydrometallurgical treatment is suitable for processing of secondary raw materials – waste [26].

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