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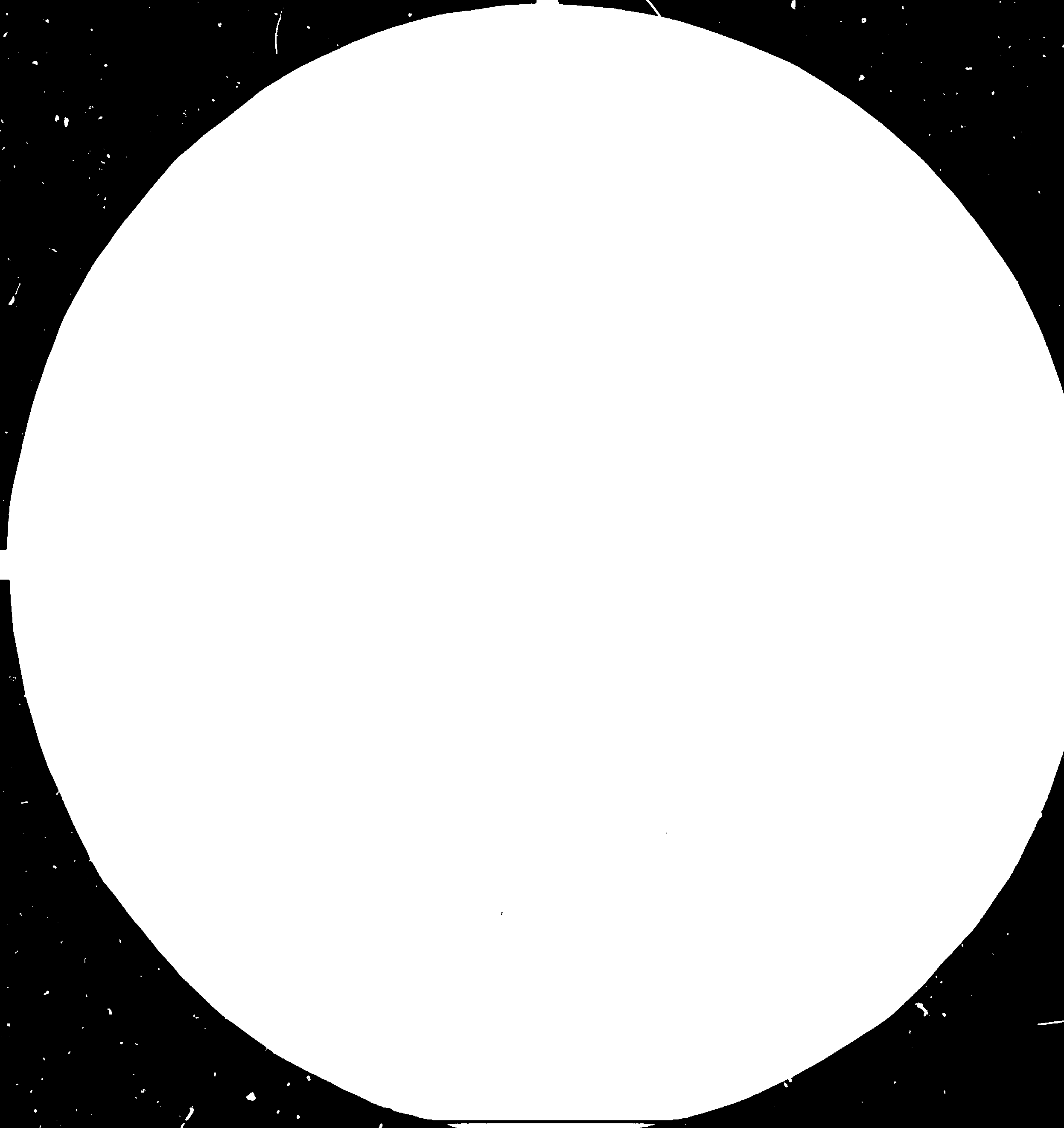

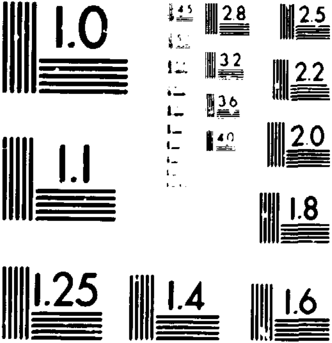

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Distr.
LIMITED

ID/WG.428/1
23 August 1984

ENGLISH

United Nations Industrial Development Organization

Workshop on Tinplate Production in the
Asia and the Pacific Region,

Jamshedpur, India, 2 - 6 April 1984

RECOVERY AND RECYCLING OF TIN IN TINPLATE PLANT*

by

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V.84-89443

Increasing price of tin coupled with difficult economic and market conditions dictate that the tinplate industry give adequate consideration to improve the economy of operations through recovery and recycling of tin metal from in-house waste products.

Tinplate industry, whether based on the old hot dip system or the new electrolytic one, provides ample opportunities for recovery and recycling of the costly metal and thereby substantially contributes to the economic operation of the plant.

SOURCES OF TIN LOSSES THROUGH WASTE PRODUCTS

In general, tin bearing waste products can be classified into the following two categories:

[A] Materials of predominantly metallic in nature such as -

- (a) Tinplate waste of tinning and canning operations;
- (b) Tin dross or scruff.

[B] Materials of predominantly oxidic in nature such as -

- (a) Tin ash;
- (b) Tin slags;
- (c) Tin sludge (from ETP lines) etc.

Of the above, tinplate scrap arising out of substandard tinplates, tinplate trimmings etc. are common to hot-dip tinning plants as well as E.T.P. units. However, by and large it is of greater relevance to the former, because of thicker coatings of tin on the hot-dipped tinplate wherein the tin content may be as high as 0.75% to 1.6%.

If the plant is involved in down the line activities of can manufacture etc., then additional tinplate scrap becomes readily available at site for recovery unit. In addition to these clean cans, spoiled during manufacture, used cans from consumers additionally boost up the secondary metal recovery.

Extraction and recovery of tin from the tinplate scrap is termed as 'detinning'. It not only recovers a very valuable metal for reuse but detinning also makes the ferrous scrap acceptable as a melting stock. For after detinning the tin content of the scrap comes down to a level of 0.02 to 0.06% by weight which includes the tin content of the base steel. The detinned scrap is also particularly suitable for copper recovery by cementation process from leach liquors, because of its active surface.

In most of the developed countries, especially in USA, the detinning industry has been in existence for almost three quarters of the present century. There are two main reasons for this industry's existence. First, there is a negligible quantity of tin containing minerals in these countries and all the tin must be imported. Secondly, tin is an injurious contaminant in steel, so tinplate scrap cannot be remelted to make steel directly.

Further, a third dimension, has been added to these factors, that is as the public becomes more ecology conscious, the problem of disposal of used tin cans is becoming more and more urgent, in almost all the countries[1].

Economic Aspects and Raw-material Availability

Tinplate, the basic raw-material for containers and can manufacturing industry is mild steel sheet commonly about 0.25 mm thick with coating of tin varying from 0.75% to 1.6% of its weight.

Of the two processes of tinplate manufacture, hot dipped and electrolytic tinning, the former where it still survives, gives a considerably heavier coating of tin than the latter.

Since last World War, heavy emphasis has been placed upon the development of an electrolytic tinplate, which would greatly reduce the tin requirement for tinplate. The development of appropriate electrolytic tin plating facilities and with the continued improvement in, and use of lacquers as an additional lining for the tin can, the average recoverable tin content of tinplate has come down from 35-40 lbs of tin per gross ton of hot dipped tinplate to the present day figure of about 7.5 lbs of tin per gross ton of electrolytic tinplate[2].

Tinplate scrap for recovery of secondary tin, as well as the reclamation of a high grade steel scrap, is available from mainly three types of sources:

[1] Tinplate scrap at the plant of tinplate manufacture;

[2] Scraps generated at the various can and container making facilities; and

[3] The used and discarded cans and containers.

An estimated 10-15% of the tinplate used in making can etc. is left as scrap in the form of punch press skeleton sheets, punchings, trimmings etc. Similarly about 2 to 3% of the scrap arises in the form of side cuttings etc. during the production of tinplate itself. These furnish a relatively large tonnage of fresh and uniform raw-material for the detinning industry. In addition, used tin cans comprise a vast potential source of the material.

On the basis of the present established capacity, amount of tinplate scrap that may be available in India for recovery of tin can be estimated at about 50,000 tonnes per annum accounting for about 300-400 tonnes of recovered tin.

RECOVERY PROCESSES

Before the last World War, most of the tin was recovered as stannic chloride. This compound was used quite extensively in the silk industry. With the sharp decline in the supply of silk during and after the War, there was an immediate increase in the production and consumption of secondary tin as the final form of recovered tin and currently about 85-90% of the recovery is being marketed as metal[3].

Process for recovery of tin in metallic form fro scrap tinplates consist essentially of the following steps:

[a] Cleaning the scrap in dilute caustic soda solution.

[b] Dissolution of the contained tin coat in a stronger solution of caustic soda with some oxidising agent, and formation of sodium stannate.

[c] Recovery of metallic tin from sodium stannate, with or without crystallisation and purification of sodium stannate.

Variation or elimination of one or more of the steps, and addition of some minor treatment to the above general process form the major part of the subject matter of a large number of patents and processes worked on a commercial scale.

Among the more recent processes, the one patented by Wakae Hosoda and Masao Mukai[4] specifies an aqueous solution of 300-500 gm of caustic soda with 50-150 gm of sodium nitrate per litre at 105-125°C for dissolution of tin from scrap. According to the processes patented by Jean Marie Gustave Creusot[5] the tinplate scrap is compressed into briquette form and sprayed with a caustic soda solution containing lead oxide or sodium nitrate. Additional oxidising action is derived from the air streaming through the vacant spaces in the briquettes.

The recovery of tin from the solution is usually done by electrolysis. There are, nevertheless, some processes in which tin is recovered by chemical reduction. A.J.Krombhols[6] describes a method in which the separated sodium stannate is treated with sulphuric acid to obtain tin hydroxide which is reduced with anthracite coal at 2200°F to obtain 99.94% tin. B.Chatterjee[7] describes a method where tin is removed from scrap as tin chloride by treatment with dry chlorine. Tin chloride is next treated with a more electropositive metal, for instance zinc, when tin precipitates out as a powder. This powder can be melted into lumps.

The Central Electrochemical Research Institute, Karaikudi, India, has developed a chemical process in which the tin from the coating is dissolved out in hot, concentrated hydrochloric acid in presence of an inhibitor to prevent the attack on the steel substrate. The dissolved tin is later displaced from the solution.

It may be noted that during electrolytic deposition of metallic tin, the evolved oxygen usually goes to waste. There have been some attempts to utilize this oxygen for dissolution of tin. Frederick A. Lowenheim's patent[3] describes a process in which the anodically evolved oxygen is utilised for dissolution and oxidation of tin to stannate radical. The metal is recovered by electrolysis directly from the bath containing dissolved stannate.

Electrolytic Detinning

The latter method has several attractive features. In the first place, it utilizes anodically evolved oxygen for dissolution of tin and thus affects economy in chemicals. Secondly, it bypasses the stage involving crystallisation, purification and re-dissolution of sodium stannate, prior to recovery of tin from it. This makes all the equipment relating to this stage unnecessary. Under Indian conditions such simplification in method and equipment is desirable and it is therefore worthwhile to examine the method for commercial application. A programme of experiments was therefore worked out to carry on the investigation at the National Metallurgical Laboratory, Jamshedpur, India.

DEVELOPMENTAL WORK AT N.M.L. TO RECOVER TIN FROM TINPLATE SCRAP (9)

The National Metallurgical Laboratory developed a process for electrolytic recovery of tin from the tinplate scrap. The electrolysis is carried out with a caustic soda bath, mild steel sheets and stainless steel sheets have been used as cathodes and the tinplate scrap, packed in the form of rectangular Bundles, serve as the anode. Following results have been obtained in laboratory scale experiments, at the rate of treatment of approximately 25 kgs of tinplate scrap per electrolytic run of one hour duration:

Recovery of metallic tin as cathode deposit plus the tin in dissolved form in the electrolyte	..	96%
Current efficiency at the cathode	..	90.8%
Current density (D.C) at cathode	..	Av. 14 amp/mtr^2
Purity of the tin deposit	..	Above 99%
Tin content of the detinned scrap	..	0.04% to 0.06% maximum

The process as developed in the National Metallurgical Laboratory, consists of the following steps:

[a] Compaction of the waste tinplate trimmings etc.

[b] Pretreatment for removal of organic coatings, if any.

[c] Treatment of thus compacted tinplate waste in an electrolytic cell with caustic soda solution, to recover tin as cathode deposit.

[d] Washing the detinned scrap bundle free from caustic soda, for ultimate utilization as high grade steel scrap.

Almost all the major detinning operations in India are being carried out through the alkaline electrolytic process, as developed in NML. A few of the firms are listed here:

(1) M/s. Detinners Limited, Bombay.

(2) M/s. P.M.Industries, Subhas Road, Aligarh.

(3) M/s. Tin Scrap Industries, Kanpur; etc.

RECOVERY FROM TIN BEARING SCRUFF, SLAG, SLUDGE ETC.

It may now be desirable to describe btiefly the recovery of tin from such waste products in a tinning plant as are non-metallic in nature such as the sludge that is periodically obtained from E.T.P. line tanks or tin scruff from hot dip tinning lines etc.

Production of hard head (containing upto 10% Fe) either in the hot dip tank or obtained during refining is a regular feature not only in hot dip lines but also during the pyrotreatment of sludges that are produced.

Recovery of tin from tin scruff

Earlier work on the recovery of tin from tin scrap have been reported by V.D.Mishin & V.I.Smirnov[10]. The heavy metal (Sn-Fn alloy containing 90-94% Sn, 6-10% Fe and some lead, copper and other metal) and oil scrap (burned cotton seed oil containing 20-40% Sn, flux and other impurities) are tested separately. The heavy metal scrap is treated at moderate temperature while oil scrap at 270-280°C. Flux scrap is treated by hydrometallurgical method where Zn is removed as $ZnCl_2$, which is reused as flux. The slimes left are mixed with Fe-Sn alloy and treated further.

A modified liquation technique was developed by P.Vajragupta & P.Suwanrut[11] in the year 1969 for recovery of tin from tin house scruff metal or hard-head containing 10% Fe and 15% ocluded flux (palm oil and moisture). The scruff is heated to 950°C followed by rapid cooling tc suppress the formation of Fe-Sn_2 and FeSn and then subjecting it to the ordinary liquation and drossing process of refining. By this process it is possible to recover 85% of the original tin content and with subsequent remelting of irony dross, an overall recovery of 82% is obtained.

D.A.Wilson & P.M.Sullivan[12] have developed a process for recovery of tin from hard-head by selective oxidation of iron. Molten melt or hard head at about 1000°C is blown with air and the oxidised iron is removed by putting a fluid flux cover of silica, lime and borax in the ratio of 43:17:40 per cent respectively. Tin recovery is of the order of 96-98%. The product contains 0.1 to 2.0% Fe, which is reduced to 0.06% by filteration at 250°C.

A pyrometallurgical method has been developed in 1958 by V.N.Maksaev et al[13], to recover tin from dross, which arises during refining of crude tin. The dross is introduced in a slag bath containing 15% Al_2O_3 in an electric arc furnace at 1800°C, when the dross is completely melted, liquid tin and excess slag are tapped. Some slag is left and further portion of dross is added. Formation of crust is avoided by addition of soda ash. High iron in the dross causes formation of hard which decreases the yield of Sn. This is prevented by addition of silicon to the melt. Recovery of Sn is only 78-80%. Some tin is left in slag, which is treated with Sn-Fe (hard head) separately.

Recovery of tin from slag

Recovery of tin from slag have been reported by number of authors. The slag arising from tin smelting practice are subjected to a batch-wise combustion-heated fuming treatment, in which tin is vaporised as stannous sulphide from the remaining components of the slag. The sulphide vapour is burnt off to produce stannic oxide and sulphur dioxide. In a small experimental plasma furnace more than 80% of tin has been recovered from low grade (3-4% Sn) slag at feed rate of 9 kg/hr for total energy inputs of 4-5 KWH/kg[14] of slag.

Pommier & Escalera[15] have worked out a leaching and electrowinning process on the laboratory scale for treating the complex Sn-fumes arising from the rotary furnace fuming of low grade concentrate. The fume consists of oxides and sulphides of Sn, Pb, Tu, As, Sb together with traces of Bi and Cu, is leached with $NaOH/Na_2S$ solution at 85°C and then the Sn is extracted from the leach solution by electrolysis using steel anodes at 90°C. Advantage of the process is the increasing current efficiency at current densities well above those used in any other tin electrolysis.

Work on improvement in recovery of tin from tin bearing material have also been reported in British Patent[16]. Materials containing 20% maximum tin and oxides of iron, silicon, aluminium and magnesium in which ratio of the combined amounts by weight of CaO, Al_2O_3, MgO and FeO to SiO_2 is greater than one and the ratio of Fe to Sn is 1.5 to 1.0 min are melted with ferro-silicon. The molten mass is cooled in a mould whereby 97-98% tin is recovered leaving the top portion Fe-Si rich in Fe. Al-Si-Fe mixture has also been used instead of silicon.

Recovery of tin from anode slime

Tin is recovered from anode slime (generated from sulphate electrolysis of crude tin) either by melting down the slime with $NaOH/NaNo_3$ mixture and dissolution of the soda slag in hot water or by prolonged stirring of the slime with hot $NaOH/NaNo_3$ stirring. Tin of high purity is obtained from the solution by electrolysis using insoluble electrodes.

ROLE OF NATIONAL METALLURGICAL LABORATORY

NML has carried extensive work on the recovery of tin values from the various secondary tin resources available in the country. Processes for the treatment of following secondary resources were developed, tested and confirmed on large scale:

[1] Tin sludge from E.T.P. lines
[2] Sponge tin from detinning units
[3] Tin dross from hot dip tinning units
[4] Tin scruff from hot dip tinning units
[5] Tin slag from smelting units

In each case a metal recovery of over 95% with a minimum purity of 99.5% was obtained by using simple pyrometallurgical routes. The process for the treatment of tin sludge is already being commercially exploited and the process for sponge tin has been licensed to a firm in Calcutta. A brief summary of each of the above processes is given below:

Recovery of tin from tin sludge from ETP lines

The sludge is obtained from electrolytic tin plating lines. During electrolytic tinplating operations, the soluble stannous salts of the electrolyte get oxidised into insoluble stannic salts due to atmospheric oxidation. These insoluble tin salts alongwith other impurities settle in the bottom of the electrolytic tank and are removed periodically in the form of slime which is known as tin sludge. On an average tin sludge contains about 40-50% tin on dry basis. A simple pyrometallurgy process consisting of roasting, smelting and fire refining was developed for the treatment of tin sludge obtained from E.T.P. lines of M/s. Tinplate Company of India Limited. The process guarantees a minimum purity of 99.75% tin with a recovery of 95% of the tin contained. As mentioned earlier, the process is already being commercially exploited and the metal so recovered at NML, is being reused by M/s. Tinplate Company of India Limited in their E.T.P. lines.

Recovery of tin from sponge tin

Sponge tin is obtained during electrolytic detinning of tinplate scrap and used tin cans. The metal obtained is not suitable for any application without its further reprocessing. As per the earlier local practice the sponge tin obtained by detinning, was being melted with excess charcoal after drying and magnetic separation to get tin metal with only 50% recovery and high tin containing slag (over 20% tin). The tin slag was being sent abroad for its further reprocessing on toll basis. NML developed a process by which it is possible to extract about 95% tin metal in a single smelting operation and the resulting slag is very low in tin content ($< 0.5\%$) and can be discarded. This has stopped the further export of the tin slag for its reprocessing. The process has been licensed to M/s. Detinners Private Limited, Calcutta.

Process for recovery of tin from tin dross

Dross is collected as skimmings from various tinning operations. It contains considerable tin oxide formed due to oxidation of tin bath during hot dip tin coating. Dross contains varying amount of tin ranging from 20% to 90% tin depending upon the source and nature of its generation and collection. NML has developed a process for the recovery of tin metal from dross by which it is possible to recover over 90% tin metal contained in the dross with a minimum metal purity of 99.5%. The process has been tested and confirmed on commercial scale at NML and transfer of this technology to industry is in progress.

Recovery of tin from tin 'scruff'

"Scruff" is obtained during hot-dip tinplating operation collected from hot tin bath. The scruff contains about 60-80% tin mostly in the form of inter-metallic compound with iron. The existing process being adopted for the treatment of this scruff were as follows:

[1] The scruff was first treated in liquation furnaces at about 400°C to liquate out any free tin metal present in the scruff. At the same time iron-tin inter-metallic compound gets converted into its component oxides.

[2] The residue obtained after liquation (oxides of iron and tin) known as dross was being treated separately by the conventional smelting and refining techniques. The overall metal extraction by this process was only 90%.

A simple single stage smelting and refining process was developed at NML and patented for the treatment of scruff with over 95% metal recovery. The special features of NML developed process is:

(1) Higher metal recovery
(2) Low processing cost
(3) Higher profitability even on smaller scale

Recovery of tin from tin slag

Tin slag is obtained from melting operation of tin containing materials during its processing for recovery of tin. If the melting operation is not perfect, high tin losses in slag may result. As the efforts for recovery of tin values from secondary sources are not properly organised and systematic, tin slags of varying composition ranging from 5% to 30%, tin are available in the country.

Therefore NML developed a process for the recovery of tin metal from these slags. The process consists of single stage smelting with proper addition of flux and reductant to recover entrapped tin metal and to reduce the oxide and to produce a low tin containing slag ($<$0.5%) which can be discarded.

CONCLUSION

The tinplate scrap, when arising either as cutting and clippings and defective sheets in the manufacture of tinplate itself or during the making of can and containers, is available in loosely packed bundles. In the case of the Tinplate Company of India Limited, Jamshedpur, they supply the rejects and cuttings in rectangular bundles of coils 50 kgs each measuring approximately 75 x 50 x 50 cm. As such, these can be directly put in the electrolytic tank as anodes. For the used cans and containers, pretreatment like removal of paints and enamels and shredding may be necessary. However, the overall recovery of tin in the form of metal and as compounds like sodium stannate, tin oxide etc. recoverable from the electrolyte, and also the recovery of clean detinned steel scrap, have bright prospect and the extent of profitability of such recovery on large and organised scale in developing countries like India may be examined by preparing detailed project report. The same is also true of incorporating recovery units for processing of sludges, scruff and slags which can yield the tin values and boost up the sagging economy of tinplate industry.

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