Conservation & Recycling, Vol. 9, No. 1, pp. 15 – 22, 1986.
Printed in Great Britain.

0361 – 3658/86 \$3.00 + .00
Pergamon Press Ltd.

ELECTROLYTIC REMOVAL OF TIN FROM CAN SCRAP

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Abstract—Tin in the magnetic fraction of municipal solid waste (MSW) makes this material difficult to recycle to the steel industry. An electrolytic method using stannous fluoborate – fluoboric acid for removing tin was evaluated on a laboratory scale. Optimum concentrations of tin in the electrolyte and the effects of impurities such as aluminum, copper, iron, and lead on tin removal from the electrolyte were evaluated. Operating parameters were 60 – 65 g/l fluoboric acid and 20 – 30 g/l tin using stainless steel electrodes at a current density of 60 A/ft^2. Tests were run with clean tin cans and MSW magnetics with good results. The tin content of the MSW magnetics scrap was reduced from 0.18 to 0.017 wt % tin by reshredding, magnetic separation, and air classification, followed by electrolytic removal of the tin.

INTRODUCTION

At present, in the United States, municipal solid waste (MSW) containing approximately 8% ferrous metallics is generated at a rate of 3 – 5 lb/day per person. Projections indicate approx 11 million ton/yr of this valuable ferrous scrap is being discarded [1]. Discarded MSW magnetics are equivalent to approximately 15% of the U.S. total 1982 steel production [2]. It is difficult to recycle this ferrous scrap by direct remelting because the contaminants create problems in the steelmaking furnaces and the steel end product. Copper and tin are the major metallic contaminants in MSW magnetics that are retained in the steel. They harden and strengthen steels, but also decrease ductility and cause surface hot shortness (cracking in hot rolled steel products) [3]. Lead contamination from the lead – tin solder causes problems with furnace refractories. These contaminants force any recycling of MSW magnetics in two possible directions: dilution with blast furnace pig iron or clean scrap in a 10 : 1 ratio, or removal of the contaminants before remelting.

The detinning industry could treat MSW magnetics to remove the tin and produce acceptable scrap, but most detinners, using the conventional NaOH leach, prefer not to use this tin source because of contamination by organic material and aluminum. Organics absorb tin containing leach solution and contaminate the product steel by carrying over the leach solution. Aluminum in bimetallic cans consumes the NaOH detinning solution by forming $NaAlO_2$. The formation of $NaAlO_2$ also increases solution viscosity and causes foaming, spillover, and aluminum contamination of the tin product.

An additional problem is that many resource recovery plants are not within economical shipping distances of currently operating detinning plants. This problem can probably only be addressed by detinning technology that is workable on a small scale [1,4]. In response to these problems, the Bureau of Mines has studied nonconventional detinning technology.

A Bureau funded study by Arthur D. Little, Inc. [1] reviewed existing technology and examined new concepts. It concluded that

(1) For the reasons discussed above, conventional detinning technology is not adequate to process MSW magnetics on a small scale.
(2) It is unlikely that nonupgraded MSW magnetics can be detinned economically.
(3) If MSW magnetic scrap is upgraded to reduce the nonmetallics to reasonably low levels (approx 1.5%), it may be detinned on a small scale economically by a number of processes including aqueous chemical oxidation and electrolysis.

Manuscript received 13 August 1984.

Stannous fluoborate – fluoboric acid, the solution used to make electrolytic tinplate [5], can also be used for electrolytic tin stripping. A study of this solution and its effectiveness in detinning MSW magnetics was initiated. This electrolytic process can be operated at room temperature in a wide range of tin and fluoboric acid concentrations and between current densities of 20 and 120 A/ft^2 [6]. It was chosen to avoid the high temperatures and the contamination problems of the NaOH leach. Optimum tin concentration and current density were determined, as were the effects of impurities present in MSW magnetics. Testing began with pure tin, followed by postconsumer scrap (PCS — clean tin cans) and finally by MSW magnetics. In testing with MSW magnetics, attempts were made to remove lacquer coatings, as suggested by another study [7].

The tin recovered from any detinning operation replaces a portion of import requirements. The United States currently imports about 80% of its tin and the estimated potential recovery from processing about 11 million ton/yr of MSW magnetics is 30,000 ton/yr, or half the U.S. consumption [1,8].

CELL DESIGN AND EXPERIMENTAL PROCEDURE

The material to be detinned was divided equally and placed in two stationary stainless steel wire mesh baskets that served as anodes. Two baskets were used to obtain a uniform tin deposit on the entire cathode. A solid piece of stainless steel with a known exposed area for determining cathode current density was the cathode. The two wire baskets were 2.5 cm apart, and the cathode was between them. The total electrolyte volume was 2 l, and the solution was circulated with a stainless steel stirring rod. The cell's potential varied between 1 and 3 V, depending on the type of material tested. The cell operated at room temperature. In initial testing, the material used was pure tin, but later tests used PCS and MSW magnetic scrap. Tests were conducted for the theoretical time necessary for complete tin removal. The final tin content of the scrap was computed by subtracting the amount of pure tin deposited from the amount of tin initially present in the scrap and correcting for the tin concentration in the electrolyte.

ELECTROLYTE EXPERIMENTS

Determining electrolyte composition

Electrolytic removal of tin using an aqueous stannous fluoborate – fluoboric acid electrolyte was evaluated using operating conditions similar to those used to plate tin on steel [9]. The cell uses a pure tin anode. The variables studied were cathode current efficiency, current density, and electrolyte composition.

The tested fluoboric acid concentration in the electrolyte ranged from 28 to 174 g/l and the tin concentration from 12.1 to 40.0 g/l. Good tin deposits (cathode current efficiency >90% and minimal amounts of sponge and powder) were obtained when the tin concentration was greater than 25 g/l with current densities at or below 60 A/ft^2. Gassing occurred at the higher current densities and low tin levels. The formation of gas is reflected in lower cathode current efficiencies (see Fig. 1). The acid concentration had little effect on cathode current efficiency because at all acid levels tested, cathode current efficiency is above 90% when the tin concentration and the current density are in acceptable ranges. Tests were also conducted using gelatin and beta naphthol additions to the electrolyte. Based on these results, the following electrolyte composition was chosen:

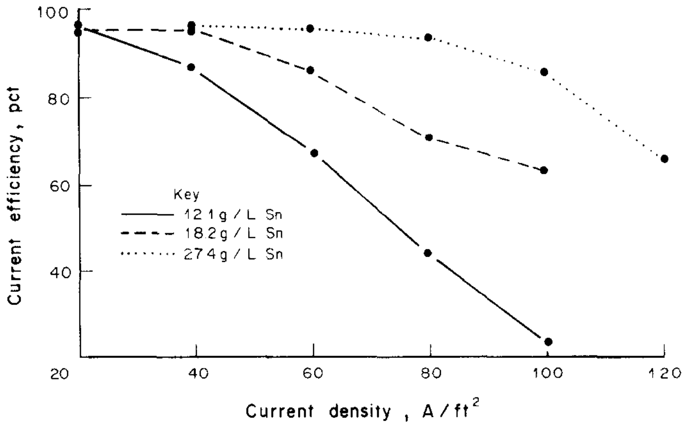

Fig. 1. Current efficiency versus current density (low acid concentration — 28 g/l HBF_4).

HBF_4 = 60 – 65 g/l
Tin = 25 – 30 g/l
Gelatin = 6 g/l
Beta naphthol = 1 g/l

Since acid concentration had little effect on cathode current efficiency, a moderately low acid concentration was selected from the concentrations used in tin plating. Gelatin and beta naphthol are additives that are used to obtain good throwing power and good tinplate appearance. The concentrations used are also representative of commercial practice.

Effects of impurities in the electrolyte

Impurities were investigated to determine their effect on cathode current efficiency and the quality of the tin deposit. The cell used a pure tin anode. The impurities aluminum, copper, and iron were dissolved into the electrolyte using the elemental metal or oxide; lead was dissolved as $PbCO_3$. The anode current efficiency was assumed to be 100% and deviations in cathode current efficiency are attributed to the presence of the impurity. The effect of each impurity on current efficiency at 60 A/ft² is summarized in Table 1.

Table 1. Effect of impurities on cathode current efficiency at 60 A/ft²

Impurity	Impurity conc. (g/l)	Avg. tin conc. (g/l)	Cathode current efficiency (%)
None	—	36.5	96.9
Aluminum	12.5	31.9	97.1
	4.7	30.9	96.3
Iron	32.0	30.9	96.1
	11.0	31.6	95.6
Lead	9.0	34.0	94.9
	6.7	32.0	95.1
Copper	.86	30.0	95.6

Copper and lead codeposit with tin to a much greater degree than aluminum and iron. The impurity levels are, in weight percent, copper, up to 3; lead, up to 10; aluminum, <0.02; and iron, <0.40. These impurities have little, if any, effect on the cathode current efficiency at the concentrations tested. Aluminum in concentrations above 12.5 g/l forms a sludge containing AlF_3 and $AlF_3 \cdot 3H_2O$. The concentration of aluminum in the electrolyte is therefore self limiting.

DETINNING TESTS

Results for PCS

Postconsumer scrap was shredded in a hammer mill with $\frac{1}{2}$-in. grates. The shredded PCS contained many balled pieces, resulting from too long a residence time in the milling zone before passing through the grates. A shear-type shredder would produce a better sample for detinning, but one was not available. Total shredded sample weight was 5000 g (about 11 lb) with an average bulk density of 1.44 g/cm^3 (89.8 lb/ft^3). The shredded scrap was split using a riffle splitter from which analytical samples were taken as well as samples for detinning. The analysis is listed in Table 2.

Table 2. Composition of postconsumer scrap

Sample	Sample weight (g)	Concentration (wt %)			
		Aluminum	Copper	Lead	Tin
PCS 1	4.4	0.02	0.02	1.32	0.32
PCS 2	4.5	0.02	0.03	0.30	0.36
PCS 3	7.5	0.02	0.04	0.65	0.25
PCS 4	6.9	0.01	0.03	0.35	0.27

Sample preparation and cell operation with PCS were as follows: Material for testing was riffle split into samples between 150 and 200 g. Before the scrap was detinned, it was screened to 100% plus 20 mesh to prevent the fines from falling through the wire mesh basket. The fines (<1 wt % of the sample) were discarded. Stripping time was based on the tin content of the postscreened weight, assuming an average of 0.30 wt % tin and a current density of 60 A/ft^2. The final tin content of the detinned scrap ranged from 0.035 to 0.009 wt %, with an average of 0.014 for 32 tests. The treated scrap's tin content did not increase greatly as the tests proceeded, showing no inefficiency of tin stripping with time.

Impurity buildup from detinning PCS was also studied during these tests. The concentrations of copper, iron, and lead were determined in the electrolyte and in the tin deposit. Lead was the highest tin deposit impurity, present up to 0.15 wt %. This value remained relatively constant, while the lead in the electrolyte increased linearly up to 0.223 g/l during the 32 detinning test runs. The same trend was observed with iron. The iron contamination of the tin deposit never exceeded 0.05 wt %, while the iron concentration in the electrolyte increased linearly up to 1.62 g/l during the 32 runs. Copper was detected in very small quantities (0.0007 g/l) in the electrolyte. The small level present (<0.2 wt %) in the tin deposit would not significantly affect the value of the tin product.

The cell operated on a problem-free basis with PCS for 32 consecutive tests, approximately 5 h of operation. During this time, cathode current efficiency remained at approx 95%. Gassing was minimized, and all tin deposits were rated good to fair on the basis of appearance. A good deposit is smooth and contains no spongy or powdery areas. The tin electrolyte concentration remained at 28±2 g/l throughout the tests, indicating that tin was not being stripped from the electrolyte.

RESULTS OF DETINNING MSW MAGNETICS

About 45.5 kg (100 lb) of MSW magnetic scrap was obtained from the Resource Recovery Unit of the Ontario Ministry of the Environment in Toronto, Canada. The scrap had already been shredded, magnetically separated, and air classified. It was reshredded in the same manner as PCS, then again subjected to magnetic separation and air classification to remove aluminum and organic wastes entrapped in the original sample. Riffle splitting was then done to obtain samples for analysis. Their composition is listed in Table 3. The aluminum and copper contents vary greatly from sample to sample. The variations in lead and tin content are small, considering the heterogeneous nature of the material (see Fig. 2). The average bulk density for this material is 1.62 g/cm^3 (101 lb/ft^3).

Table 3. Composition of shredded MSW magnetics

Sample	Sample weight (g)	Concentration (wt %)			
		Aluminum	Copper	Lead	Tin
MSW 1	10.8	0.01	0.02	0.39	0.16
MSW 2	11.9	2.91	0.11	0.37	0.16
MSW 3	17.8	0.01	0.04	0.46	0.22

The scrap was blended, coned, and quartered. To have representative sampling, riffle-split portions were then taken for the individual tests. MSW magnetics sample size and preparation, cell operation (current density 60 A/ft^2), and starting electrolyte composition were identical to that used when detinning PCS.

The testing of MSW magnetics was divided into four parts. In the first experiments, the shredded MSW magnetics were given no further treatment other than reshredding, magnetic separation, and air classification. In the second, they were chemically delacquered by soaking in acetone for 4 days followed by lacquer thinner for 2 days, washed with fresh acetone, then air dried. In the third, MSW magnetics were roasted for 30 min at 350°C. Finally, MSW magnetics were flash-roasted by placing the samples cold in a furnace already heated to 400, 500 or 600°C for residence times of 2, 5, 10 or 15 min, and then removed and allowed to cool.

The detinning results on all the different pretreatments of MSW magnetics were good, producing acceptable steel scrap for remelting. During most of these tests, cathode current efficiency was above or close to 90%, and tin deposits were of acceptable quality. The average final tin content of MSW magnetics that had only been shredded and magnetically separated with no further treatment was 0.017 wt %. None of the pretreatments appear to significantly affect tin removal.

Table 4 lists copper and tin values for some of the grades of steel scrap that are currently marketed [10]. The fluoborate detinned MSW appears comparable to detinned bundle or No. 2 bundle scrap. A representative lead analysis for shredded auto scrap is 0.01 wt %. Detinned MSW would contain more lead.

Table 4. Copper and tin content in steel scrap [9]

Scrap type	Conc. (wt %)	
	Copper	Tin
No. 1 heavy melting	0.16	0.011
No. 1 factory bundle	0.06	0.005
Shredded auto	0.22	0.021
Detinned bundle	NA	0.04
No. 2 bundle (nonauto)	0.38	0.038
No. 2 bundle (auto)	0.48	0.08

NA — Not available.

Fig. 2. Shredded MSW magnetics.

Analytical data for the tin deposit and electrolyte are listed in Table 5. The impurity levels varied depending on the type of pretreatment. All tin deposits contained less than 1.0% total impurities. Aluminum and lead are the most abundant elements in the tin deposits but are found in lower concentrations than iron in the electrolyte. Copper content is small in both the tin deposits and the electrolyte, but the deposit's copper content is significant when considering the amount of copper in the electrolyte.

Table 5. Impurities in tin deposits and electrolytes during electrolytic stripping of treated and untreated shredded MSW magnetics

Type of pretreatment	Tin deposit impurities (wt %)				Electrolyte impurities (g/l)			
	Aluminum	Copper	Iron	Lead	Aluminum	Copper	Iron	Lead
None	0.141	0.010	0.043	0.139	0.146	0.002	0.668	0.064
Acetone – lacquer thinner	0.206	0.012	0.042	0.098	0.160	0.0014	0.608	0.054
Roast at 350°C for 30 min	0.099	0.010	0.032	0.197	0.154	0.0018	1.64	0.160
Roast at 400°C for								
2 min	0.122	0.005	0.025	0.045	0.042	0.0010	0.200	0.022
5 min	0.143	0.007	0.062	0.078	0.086	0.0009	0.760	0.069
10 min	0.107	0.009	0.027	0.159	0.148	0.0013	1.05	0.130
15 min	0.107	0.010	0.024	0.224	0.210	0.0014	1.85	0.178
Roast at 500°C for								
2 min	0.058	0.008	0.036	0.066	0.063	0.0009	0.400	0.0238
5 min	0.064	0.007	0.104	0.147	0.176	0.0010	1.10	0.0854
10 min	0.076	0.010	0.110	0.371	0.250	0.0010	2.60	0.210
15 min	0.063	0.011	0.034	0.412	0.358	0.0009	11.3	0.256
Roast at 600°C for								
2 min	0.085	0.006	0.057	0.098	0.051	0.0008	1.34	0.030
5 min	0.071	0.006	0.032	0.243	0.133	0.0010	11.3	0.16
10 min	0.073	0.008	0.039	0.381	0.220	0.0008	21.9	0.41
15 min	0.043	0.007	0.043	0.773	0.270	0.0008	29.8	0.57

Pretreatment of the MSW with acetone – lacquer thinner before detinning did not significantly affect either the tin deposit or the electrolyte. Roasting does not appear to significantly improve deposit quality, and many of the roasts were deleterious. The iron content in the electrolyte increases when roasted scrap is used. This is probably due to the formation of rust (iron oxide). Also, lead concentration increases in both the electrolyte and tin deposit when roasted scrap is detinned.

The metal produced meets the ASTM specification for Grade E tin (99% tin). This material is used in cast bronzes, bearings, and lead-base alloys. The aluminum content makes the material unacceptable for use in solder and tinning [11].

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