Recovering J-STD-006C Quality Bar Solder from Dross Recovery Systems
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Alpha an Alent plc Company

Introduction

Wave or Machine soldering was patented in 1958 by the Electrovert Company. Wave soldering revolutionized the process of soldering through hole components to printed wire boards. The number of components that can be soldered per man hour increases exponentially versus soldering with a hand held iron using cored wire.

One drawback of the wave soldering process is the generation of solder dross. Dross is oxidized metal that is incapable of forming intermetallic compounds with the metallization used on circuit boards and component lead finishes. It is generated wherever molten, liquid phase solder alloy is exposed to oxygen in the atmosphere. Dross production accelerates as turbulence generated in the wave process mixes oxygen below the surface of the solder bath.

Solder dross that adheres to the surface of a printed circuit board is a cosmetic defect that very few would accept under visual inspection. It is a dull, grainy material that does not melt when heated above the alloy melting point. Dross included in a solder joint will make the joint less conductive, weaker and more prone to mechanical and thermal cycling failure. Dross is less dense than molten solder so it is commonly found on the surface of a molten solder bath, and is easily picked up by protrusions from the bottom side of the circuit board.

Dross is removed from the molten bath by manual skimming. Solder dross skimmings are collected and sold to materials recyclers who consolidate and/or process large volume batches. In the skimming process, un-oxidized molten solder alloy is entrapped in the dross. Profitable recycling requires recovery of very high percentages of the un-oxidized solder alloy. Chemically reducing metal oxide to the metallic form is another high source of value in the recycling process. If the boards or components used in the wave soldering process had gold or palladium plated surfaces, there is even more value available by recovering these precious elements. The most competitive processors are able to pay for scrap purchases with highly refined J-STD-006 compliant solder alloys demanded by the electronics industry.

With the increase in the value of metals used in solder alloys, there are several new small batch machines designed to separate metallic solder alloy from dross skimmed from a solder bath.

This “do-it yourself” option should be analyzed carefully to assure that the inherent batch to batch variations in materials recovered from the wave soldering process yield industry standard compliant materials. Also, without the ability to reduce metal oxides (dross) back to the metallic form, and the ability to recover high value gold or palladium, separating dross from solder alloy and paying for the disposal of the metal oxide remains may not be the best method of managing metals value. New health and safety issues arise when the spent oxide powder begins to be is removed and collected from this type of process.
Discussion and Analysis

Among the many diverse drivers in the electronics assembly market, process yields, miniaturization, increasing product functionality, manufacturing costs, and environmental impact are on nearly every technology roadmap. Miniaturization, product functionality as well as manufacturing costs have driven the market away from printed through hole (PTH) towards surface mount technology (SMT) processing. Assemblies requiring high yield and high throughput PTH processing must look at dross management to reduce manufacturing cost and minimize environmental impact.

Metals pricing and the push for lead-free assemblies has had a tremendous effect on wave soldering metals costs. The 10 year price history of silver and the 25 year history of tin are shown in figures 1 and 2.

Figure 1- 10 year price history of Silver

Although the recent price of silver has dropped below $18 U.S per Troy ounce for the first time since 2010, it is nearly double the price level before the RoHS (lead free) transition began in 2006.

Figure 2- 25 year price history of Tin
Tin’s price rose well beyond its historical range after the implementation of RoHS in July 2006. High silver and tin prices increase the economic benefit of recovering a higher percentage of metal from wave soldering dross skimmings.

The most efficient and cost effective method of obtaining the full value of metal from dross skimming is to store the material in containers provided by a solder manufacturer. Once an economic volume of skimming is collected, the solder manufacturer will make the pick-up and pay all freight. The most competitive solder manufacturers can recover the solder alloy, reduce oxides to their metallic form, and recover precious metals dissolved in the alloy.

Publicly held companies who have this technology are also held to a higher level of financial transparency and accountability.

**In House Metals Recovery**

Since the spike in tin and silver prices in the mid to late 2000s, several companies have developed equipment designed to separate or “sweat” metallic alloy from dross. At high tin and silver prices, there is more incentive the value of the recovered metal, and price of purchases avoided make this seem to be more attractive versus lower metals pricing. There are several questions that should be answered before a large, high reliability electronic assembler decides to become an in house metal recycler.

- Is the solder that is recovered always compliant with the industry standard for purity that is currently used?
- How much will each lot cost to certify to J-STD-006 standards?
- Does the level of dross inclusion meet or exceed the standard currently met by my bar supplier?
- Is there more or less lot to lot variation in alloy composition/impurity levels than currently met by my solder supplier?
- How much does it cost to dispose of metal oxides that are currently processed by my solder supplier?
- How much precious metals recovery will be lost when the in-house method is implemented?
- What local, state and federal permits are needed to recycle scrap?
- What Health, Safety and Environmental permits are required to handle the metal oxide powder after the solder alloy is separated from the dross?
To remove dross from a solder bath, simple, manual tools are commonly used. Slotted spoons, spatulas or a more custom engineered dross skimmer like the American Beauty 602 are illustrated below.

When dross is removed by skimming the surface of the molten solder bath, solder alloy is also dragged out. Because this process is manual and quite frequent, there will be material and process variation with each operator, and probably more variation from operator to operator.

Operator technique and solder bath composition will certainly vary. One operator may skim dross a little faster than the next. The depth that the dross tool is submerged into the liquid phase of the alloy bath will also vary the ratio of metal oxide to solder alloy collected by the technician. Pot temperature, temperature of the skimming tool, and level of copper in the alloy are also variables that will affect what is in the material removed from the solder bath.

If the plated through hole line being used has a mix of assembly types with variations in board finish/through hole metallization and variable component mixes, there will be variation on the elemental composition of the dross and alloy that is being collected. For example, copper OSP boards will elevate the copper level, ENIG boards will contribute gold and nickel to the dross content. Palladium bearing component lead finishes will increase the level of palladium in the primarily tin based scrap.

Dross Recovery Systems

Since the price of tin and silver jumped in 2005-2007, an increasing number of equipment vendors have offered small scale equipment to extract solder from this dross/solder mix.

These systems are fed with skimmings from one or more wave soldering machines. The dross/alloy mixture is heated above the melting point of the solder. The molten material is separated and cast into molds. This becomes the new feedstock for the wave soldering process.
Bar Solder Manufacturing

There are several commonly used bar solder alloys used in wave soldering today. Since the implementation of RoHS in July of 2006, a vast majority of the alloy used converted from 63% tin/37% lead to alloys of tin/silver/copper (SAC). The dominant alloy was SAC 305 (3% Silver, 0.5% Copper, balance tin) until the price of silver skyrocketed in 2007. Since then, up to 40% of the lead free wave soldering alloys used have a lower silver content.

Both tin/lead and lead free bar solder are produced by introducing combinations of high purity tin/silver/copper or tin/lead into a heated vessel, melting the metals into the desired alloy. High purity metals are generally recycled metals that are purified using any of a number of refining techniques, including electrolytic refining and vacuum chamber purification.

Alloying metals inherently produces some level of dross. Molten metal is exposed to atmospheric oxygen. Electronic grade solders are treated to remove this dross. Lower quality solder will have levels of dross inclusions in the solidified bar solder. This dross quickly floats to the top of a wave soldering pot and increases the amount of dross required to skim from the bath.

Alpha created a test method over 20 years ago to measure the amount of dross inclusions in a sample of bar solder. A sample of bar solder is placed in a heating vessel and covered with liquid flux. The liquid flux acts as an oxide barrier to prevent dross generation during the melting process. Dross inclusions from the test sample will float to the top of the flux layer. The dross is collected, dried and weighed.

Alpha’s Vaculoy process was developed to greatly reduce or eliminate dross inclusions in solder as bars are being formed. If one attempts to heat/sweat a sample of dross/alloy skimmed from a wave soldering pot, dross will remain in the bulk of the solder. A bar cast from this material would have little chance to create less dross inclusions than a bar produced using the Alpha Vaculoy process. Dross inclusions are unusable oxides and the volume of inclusions is a measure of the level of defect in bar solder.

Alloy Purity

The Institute for Printed Circuits (IPC) has developed and maintains standards for impurities in electronic grade solders. J-STD-006C is the current version of the solder alloy standard that specifies the tolerances for the elements of the alloy, and the maximum level of impurities from other metallic elements. Based on the alloy, here are the tolerances for each primary constituent:

“Except where otherwise indicated, the component elements in each alloy shall deviate from their nominal mass percentage by not > 0.10% of the alloy mass when their nominal percentage is δ 1.0%; by not > 0.20% of the alloy mass when their nominal percentage is > 1.0% to δ 5.0% or by not > 0.50% when their nominal percentage is > 5.0%. Example – Component Element with Percentage < 5.0% Nominal Percentage = 3.5%
Allowable Range = 3.3% to 3.7%”
In addition to tolerances for the main constituents of an alloy, the maximum allowed metal impurity levels are also included in the industry standard. Figure 2 is Table 3-1 from the current IPC standard for electronic grade solder impurity levels.

| Percentage by Mass of Impurity Elements in Alloys |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Ag | Cd | Pb | Al | Cu | Sn | As | Fe | Zn | Au | In | Sb | Bi | Ni |
| Percentage (%) | 0.10 | 0.002 | 0.07 | 0.005 | 0.08 | 0.25 | 0.03 | 0.02 | 0.003 | 0.05 | 0.10 | 0.20 | 0.10 | 0.01 |

Figure 2

Surface finishes on PTH boards are designed to form intermetallic compounds with tin and other elements in solder alloys. This means that the metallic finishes, and copper from copper OSP boards are soluble in molten tin. Gold, copper, silver and tin (in the form of immersion tin or SnCu HASL) are all very soluble in tin. Solder bath pots are made from alloys of iron (stainless steel is primarily iron!)

Tin/lead and lead free solder baths absorb these metallic contaminants, continuously changing the exact composition of the solder bath. The metal recovered in the dross skimmings will also include these dissolved elements. Solder recovered from small batch units will have batch to batch variation in the levels of the elements soluble in tin.

When ENIG surface finishes are used, the intermetallic joint formed with tin bearing solder is tin/nickel. The gold layer preserving the nickel passivation layer over copper is highly soluble in molten tin. This gold is easily absorbed by the tin in the solder bath. As the Ni/Sn intermetallic is formed, some level of Ni will dissolve in the tin based solder bath. The levels of gold and nickel dissolution will depend on dwell time and bath temperature.

Simple “sweating” of dross will not separate contaminates from the recovered solder alloy. Electro-deposition and vacuum distillation are often needed to make recovered dross into IPC-J-STD-006C compliant solder.

Batch to Batch Variation

Batch to batch variation is reduced as batch size increases. If 100 x 200 kg batches of solder alloy are sweated from metal oxide (dross), the tin/silver/copper ratio will vary, hopefully in a normal distribution. A large number of ENIG, HASL, ImAg or ImSn boards may make the distribution more Poisson, because the probability of having more gold, nickel, silver or tin is greater than the possibility of having less than in the original bar solder alloy.

Producing 1 x 20,000 batch of alloy will produce zero variation in alloy content, assuming homogeneity from bar to bar. But any variation from alloying to casting would be the same in either case.

The point, is large volume recovery of metal from dross is much more likely to produce consistent, known quality, and compliance with industry standards than small batch processing. Electrolytic refining or vacuum distillation are methods of correcting impurity levels. These refinement techniques are much more efficient in large volume batch quantities. They may be impossible using small batch, in-house metal recovery systems.

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That brings up one more critical issue - alloy inspection. The most efficient method of analyzing alloy for main element compliance and level of J-STD-006C specified impurities is to analyze fewer large batches versus many small batches. Using a small batch dross recovery unit may require a significant investment in out-sourced analytical services, or the capital expense of an analytical tool that requires continuous calibration and the expertise of an in-house analytical staff.

**Summary**

Small, direct recovery of solder from dross skimmings appears to be an easy way of bypassing the cost of using a solder manufacturer to purchase and recycle this material. Before initiating in-house metals recovery, one should consider the following:

- How do I generate traceable certificates of analysis/compliance documenting alloy composition and impurity level in each batch of recovered metal meets in-house or IPC-J-STD-006C standards?
- How does the dross inclusion levels of in-house recovered solder compare to best in class solder?
- How does the rate of dross generation compare with bar solder created using a Vaculoy process?
- How is the bar solder created from in-house recycling compliant with my company’s standard for alloy content and impurity levels?
- How much will it cost to dispose of metal oxides separated from the recovered solder?
- How do I recover dissolved gold, palladium or platinum absorbed in the solder bath from surface finishes/components?
- How does the mix of surface finish/components used in my assemblies affect the variation in the solder that is recycled in-house?
- How often does the small batch solder recovery system require maintenance/calibration/repair?
- What local/state/federal permits are required to recycle metals in my facility?
- What Health/Safety and Environmental controls are needed to process scrap into re-useable metal and metal oxide powder?

**Conclusions:**

- Removing dross from the Wave soldering process is important to maintain quality and throughput of wave soldering joints.
- Recovering the metal value of the dross skimmings has always been a key to minimizing bar solder cost of ownership. With the price of tin and silver doubling over historical norms, value recovery is more important than ever.
- Skimming dross from a wave solder pot is a batch process, subject to significant batch to batch variation.
- Leading producers of solder bar are able to collect and refine large batches of dross skimmings, and recover metal from oxides and the value of precious metals in the recycle stream. Small, in-house batch machines may not have that capability.
- Separating molten solder from metal oxide will result in variation in the recovered alloy composition, as well as the level of impurities specified in J-STD-006C.
- Oxides separated from solder skimmings in-house may have a net cost of disposal
- Solder produced from these small in-house recovery systems will contain more dross inclusions

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than bar solder that was produced using the Vaculoy process. The resulting bar solder will create more dross, faster than bar produced using the Vaculoy process.
- Labor and maintenance of small batch size solder bar recovery, along with greater variation in bar quality and loss of the metals in oxide and precious metal content should be considered in the total cost of ownership.

References:


2-Ibid source 1.