COULOMETRY: A PROMISING METHOD FOR QUANTIFYING ORGANIC RESIDUE ON SMCs AFTER CLEANING

Dr. J. K. (Kirk) Bonner and Mr. J. M. (Marv) Lewis
Buffalo Research Laboratory
Allied-Signal Corporation
Buffalo, NY 14210

INTRODUCTION

Now that SMT has finally arrived, reflow soldering is becoming much more common. Both infrared and vapor phase reflow systems are now in common use. Solder pastes are routinely used in conjunction with the reflow soldering operation. The pastes are applied to the solder pads either with a screen or a metal stencil, the SMCs mounted on top, the resulting assembly preheated and reflowed and then cleaned.

Solder pastes are complex mixtures, chemically speaking. In addition to containing solder powder (typically 85-92 weight percent of the paste), flux activators, and a suitable binder such as rosin, they also contain thickening agents to maintain a high viscosity during application and reflow, and a high boiling solvent to increase tack time. The thickening agents are normally derivatives of hydrogenated castor oil, the triglyceride of ricinoleic acid. The residues from paste remaining on the assembly after reflow are difficult to remove, regardless of what cleaning technology is employed.

Concomitant with the problem of cleaning solder paste residues is the problem of verifying cleanliness. Previously, for conventional through-hole boards, the industry has relied on ionic contamination testing to determine assembly cleanliness. However, SMT brings its own problems to cleanliness verification. There is considerable evidence that the test solution used in ionic contamination testing, viz., a 75% IPA/25% water by volume mixture, will not readily penetrate and remove paste residues under low standoff SMCs. Even if the IPA/water test solution could penetrate under the SMCs, the thixotropic residues are not soluble in this test medium and leave a white residue after being exposed. Further, most pastes employ an RMA flux so ionic readings, even if attainable, are generally quite low. Many people in the industry are using qualification testing by desoldering the components and examining them visibly for evidence of paste residues. This method is subject to all the drawbacks of qualitative testing. Comparisons are very difficult to make.

Coulometry, a method that has already found application in the finishing industry [1,2], offers a way to quantify the amount of paste residues on surface mount components (SMCs) after reflow and cleaning. The method is rapid, simple, reproducible, and quantitative. See Figures 1 and 2 for a depiction of the equipment. Coulometry involves the combustion of sample carbon and its conversion into carbon dioxide (CO_2) inside a tube furnace held at 400° - 550°C. Once the sample carbon is converted into carbon dioxide, the carbon dioxide is reacted with ethanolamine to form a carbamic acid [$HOCH_2CH_2NHCOOH$], and the carbamic acid is titrated coulometrically. The amount of carbonaceous residue is expressed in milligrams of carbon per sq. meter (mgC/m^2) or in milligrams of carbon per sq. foot (mgC/ft^2). It is easy to convert the last figure into micrograms of carbon per sq. inch

($\mu gCin^2$). Since coulometry involves the combustion of carbonaceous material, it is not a suitable method for epoxy board material nor for epoxy components. It can, however, be employed to great success with ceramic chip carriers, and the data presented in this paper were collected from the combustion of carbonaceous residue on ceramic carriers.

Methodology

The surface mount assemblies (SMAs) used in these experiments were Type I assemblies with SMCs on the top side only. All components were LCCCs (leadless ceramic chip carriers). For the fully populated assembly, the components were:

8	20-Terminal	LCCCs
6	28-Terminal	LCCCs
6	44-Terminal	LCCCs
6	52-Terminal	LCCCs
6	68-Terminal	LCCCs
6	84-Terminal	LCCCs
38	SMCs total/board	

This assembly is depicted in Figure 3. 60/40 tin/lead RMA paste (90% solder) was applied using a 0.010" metal stencil. In some cases the paste had 0.005" lead sphere standoff material incorporated in it and in other cases it did not. See Test Protocols. The components were mounted manually using a template. The assembly was preheated for 30 minutes at 175°F. The assemblies were then refloved in a vapor phase reflov unit set at 0.5 min. reflov time and 1.0 min. dvell time. Several different test protocols were employed. These are described below:

TEST PROTOCOLS

PROTOCOL 1

1. High pressure cleaning simulating 10 ft/min conveyor speed.

2. Nozzle pressure 140-150 psig.

3. Number of passes under the high pressure nozzle: 100,50,25 and 12.

4. Test board fully loaded:

8	20-pin LCCCs
6	28-pin LCCCs
6	44-pin LCCCs
6	52-pin LCCCs
6	68-pin LCCCs
6	84-pin LCCCs
38	SMCs total/board

5. RMA paste with no standoff/0.010" metal stencil

6. Genesolv®DE - cleaning solvent

PROTOCOL 2

1. Same as 1.

2. Same as 1.

3. 100, 50 and 25.

4. Same as 1.

5. RMA paste with 0.005" standoff/0.010" metal stencil.

6. Same as 1.

PROTOCOL 3

1. High pressure cleaning simulating 20 ft/min conveyor speed.

2. Same as 1.

3. Same as 2.

4. Test board partially loaded:

8	20-pin LCCCs
6	28-pin LCCCs
6	52-pin LCCCs
6	84-pin LCCCs
26	SMCs total/board

5. Same as 2.

6. Same as 1.

PROTOCOL 4

1. In-line defluxer cleaning with conveyor speed at 1.25 ft/min.

2. Standard spray pressures were used, viz:

Pre-clean	top	5 psig
"	bottom	3 psig
Recirculating	top	11 psig
"	bottom	9 psig
Distillate	top	5 psig
"	bottom	4 psig

3. While the run was being made, the conveyor was stopped while the SMA was under the recirculating spray manifolds (which also were oscillating). The amount of time the conveyor was stopped was 8 min., 4 min., and 2 min.

4. Same as 3.

5. Same as 2.

6. Genesolv®DFX - cleaning solvent.

The use of the high pressure spray nozzle has been previously described in the literature [3,4].

After cleaning the SMAs were desoldered. The components were divided into sets and run in the Coulometer, and the Coulometer furnace was set at 400°C. It was determined in a prior experiment that increasing the furnace temperature will not affect the amount of carbon residue detected. It will, however, reduce the test time. The bare boards were tested in a suitable solvent extract resistivity test unit for residual ionic contamination. The LCCC sets in the Coulometer consisted of:

1. 8 20 pin LCCCs
2. 6 28 pin LCCCs
3. 3 44 pin LCCCs
4. 3 52 pin LCCCs
5. 3 (sometimes 2) 68 pin LCCCs (2 or 3 sets)
6. 3 (sometimes 2) 84 pin LCCCs (2 or 3 sets)

Results and Discussion

Blank values were determined first; the average blank value was found to be 5.7 $\mu gC/in^2$.

The data for Protocol 1 are presented in Table 1. The results are expressed in (1) number of micrograms of carbon per sq.in. (#$\mu gC/in^2$), (2) number of micrograms of carbon per component (#μgC/component). This later figure was found by multiplying the number of microgram of carbon per sq. in. (#$\mu gC/in^2$) by the area of the component in sq.in. In addition, an overall average for all components, expressed in $\mu gC/in^2$; is given for each number of passes (or time halted under the spray manifold - Table 4). Also, the average ionic reading for the bare boards tested is reported in micrograms of sodium chloride or equivalent per sq.in. ($\mu gNaCl/in^2$) for each number of passes. The data for Protocol 2 are presented in Table 2; for Protocol 3 in Table 3; and for Protocol 4 in Table 4. These data are averages over the individual data for the different sets run in the Coulometer. All data presented in Tables 1-4 are corrected of the blank reading, viz., 5.7 $\mu gC/in^2$.

Perusing the data, in Tables 1 - 3, better cleaning results when

- The paste had a built-in standoff of 0.005".
- The simulated conveyor speed in the high pressure unit was 10 ft/min as opposed to 20 ft/min.
- The number of passes under the high pressure nozzle was increased.

Table 4 suggests that cleaning of SMAs with 0.005" standoff is achievable at slow conveyor speeds without high pressures provided there is plenty of flushing action by the solvent.

It is also clear from perusing the data in Tables 1-4 that the ionic contamination test alone was not adequate to distinguish different cleaning protocols. Other work indicates it is also not a sufficient test to distinguish the cleaning effectiveness of different solder pastes.

Conclusion

The coulometric method presented here is definitely a viable method for quantifying residual carbonaceous material left on SMCs after cleaning. As such, it can be used to compare either different solder pastes or cleaning protocols. Based on a comparison with visual observation, an overall average of 20.0 micrograms of carbon per sq. in. (20.0 $\mu gC/in^2$) is suggested as the cutoff point for a pass/fail test. Although the test is destructive and requires the use of ceramic components only, it could be used as a cleanliness test for SMA acceptability and quality control. This could be done in either of two ways. One way would be to have a dummy assembly with LCCCs go through the process and then use the LCCCs in conjunction with coulometry as a qualification check. Another way would be to have two strategically placed LCCCs per board and use them in conjunction with coulometry. In the latter method some board real estate would have to be sacrificed.

Several nondestructive tests (NDTs) for cleanliness are also being pursued at Allied-Signal's BRL Laboratory in Buffalo. Among these are: differential refractometry, high performance liquid chromatography (HPLC), and spectrophotometry. One, or several, of these methods may also prove viable as a cleanliness test for SMAs.

REFERENCES

1. King, Arthur E. "Direct Determination of Carbon on Metal Surfaces." SME Technical Paper, FC78-584.

2. Coulometrics, Inc. Technical Bulletin on coulometry.

3. Bonner, J.K. (Kirk) and Osterman, H. (Hank) F. "A New Process for Cleaning Surface Mount Assemblies." Proc. Nepcon West '87.

4. Bonner, J. K. (Kirk) and Osterman, H. (Hank) F. "Effective Cleaning of Surface Mount Assemblies." Proc. Expo SMT '87.

TABLE 1

CARBON RESIDUE AND IONIC RESIDUE AFTER CLEANING - PROTOCOL #1

TERMINAL COUNT	NO. OF PASSES	#µgC/in^2	#µgC/component	#µgNaCl/in^2 (Board Only)
20	100	31.3	3.83	
28		34.0	6.88	
44		25.0	10.56	
52		18.8	10.58	
68		16.0	14.44	
84		16.7	22.09	
Overall Ave.		23.6	11.40	1.2
20	50	102.1	12.51	
28		219.9	44.53	
44		31.9	13.48	
52		70.1	39.43	
68		47.2	42.60	
84		85.4	112.94	
Overall Ave.		92.8	44.25	1.2
20	25	58.3	7.14	
28		527.1	106.74	
44		338.9	143.19	
52		319.4	179.66	
68		93.8	84.65	
84		77.8	102.89	
Overall Ave.		235.9	104.05	2.4
20	12	406.3	49.77	
28		777.1	157.36	
44		353.5	149.35	
52		293.1	164.87	
68		175.7	158.57	
84		193.1	255.37	
Overall Ave.		366.5	155.88	2.4

TABLE 2

CARBON RESIDUE AND IONIC RESIDUE AFTER CLEANING - PROTOCOL #2

TERMINAL COUNT	NO. OF PASSES	$\mu gC/in^2$	μgC/component	$\mu gNaCl/in^2$ (Board Only)
20	100	19.8	2.42	
28		21.2	4.29	
44		20.5	8.66	
52		18.8	10.58	
68		13.5	12.18	
84		12.8	16.93	
Overall Ave.		17.8	9.18	0.8
20	50	21.2	2.60	
28		23.3	4.72	
44		18.4	7.77	
52		16.7	9.39	
68		13.1	11.02	
84		12.7	16.80	
Overall Ave.		17.6	8.85	1.9
20	25	27.8	3.41	
28		47.6	9.64	
44		17.9	7.56	
52		22.9	12.88	
68		14.5	13.09	
84		17.9	23.67	
Overall Ave.		24.8	11.71	1.3

TABLE 3

CARBON RESIDUE AND IONIC RESIDUE AFTER CLEANING - PROTOCOL #3

TERMINAL COUNT	NO. OF PASSES	#µgC/in^2	#µgC/component	#µgNaCl/in^2 (Board Only)
20	100	26.0	3.18	
28		23.3	4.72	
44		-	-	
52		34.4	19.35	
68		-	-	
84		16.3	21.56	
Overall Ave.			12.20	2.1
20	50	31.3	3.83	
28		29.5	5.97	
44		-	-	
52		40.3	22.67	
68		-	-	
84		24.3	22.14	
Overall Ave.		31.4	16.15	2.0
20	25	81.6	10.00	
28		37.5	7.59	
44		-	-	
52		49.7	27.96	
68		-	-	
84		18.1	23.94	
Overall Ave.		46.7	17.37	2.0

TABLE 4

CARBON RESIDUE AND IONIC RESIDUE AFTER CLEANING - PROTOCOL #4

TERMINAL COUNT	TIME UNDER RECIRCULATING Spray (Min)	#µgC/in^2	#µgC/component	#µgNaCl/in^2 (Board Only)
20	8	20.1	2.46	
28		11.5	2.33	
44		-	-	
52		17.7	9.96	
68		-	-	
84		8.7	11.51	
Overall Ave.		14.5	6.57	0.4
20	4	21.9	2.68	
28		16.7	3.38	
44		-	-	
52		19.4	10.91	
68		-	-	
84		11.1	14.68	
Overall Ave.		17.3	7.91	0.7
20	2	25.3	3.10	
28		16.3	3.30	
44		-	-	
52		17.0	9.56	
68		-	-	
84		14.6	19.31	
Overall Ave.		18.3	8.82	0.9

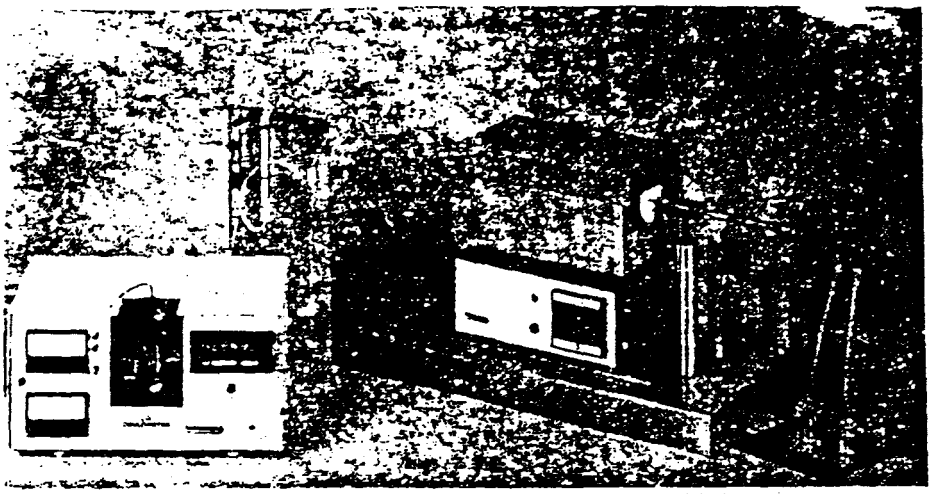

FIGURE 1. TOTAL CARBON APPARATUS WITH COMBUSTION TUBE AND COMBUSTION FURNACE

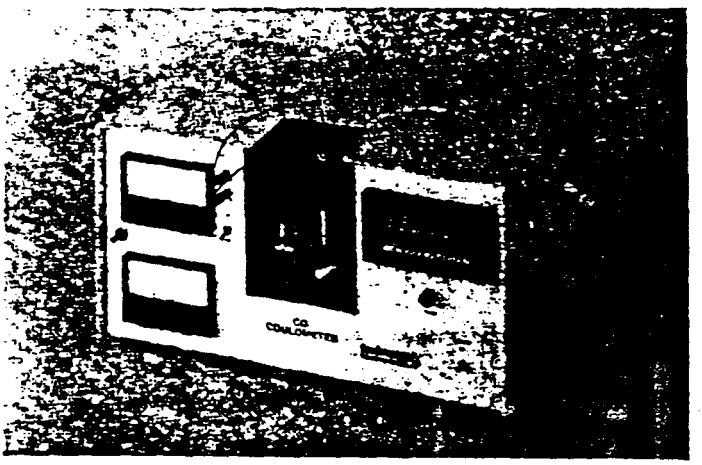

FIGURE 2. COULOMETRIC CELL FOR TITRATING CABON DIOXIDE

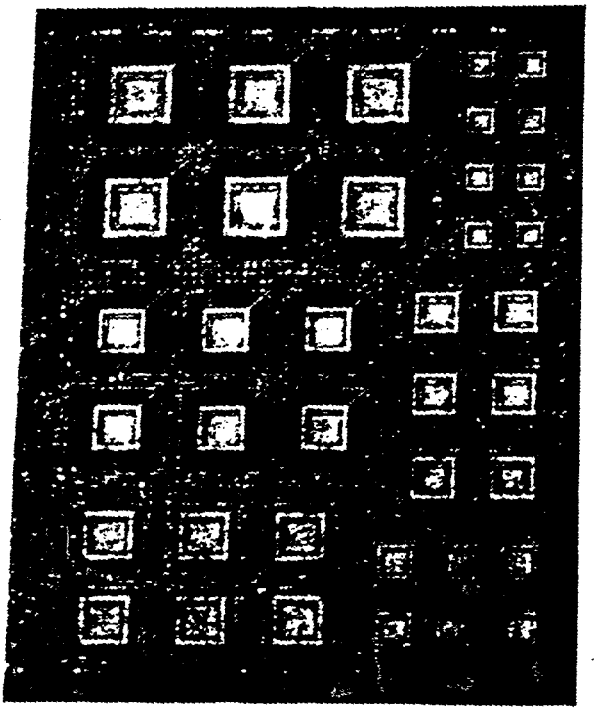

FIGURE 3. SURFACE MOUNT ASSEMBLY (FULLY POPULATED) USED