IONIC CLEANLINESS TESTING RESEARCH OF PRINTED WIRING BOARDS FOR PURPOSES OF PROCESS CONTROL

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ABSTRACT
Ionic Cleanliness testing machines are designed to determine the total ionic content extractable from the printed wiring board for purposes of process control. The conductivity of the extract solution is measured and the results are expressed as sodium chloride equivalence per unit area. The problem with this method is two fold: 1.) Many of today's low residue flux and lead-free flux residues are not soluble in the extract solution. 2.) Contamination of concern is with site specific components, from which contamination does not correlate to the area of concern. The purpose of this study is to research low residue and lead-free flux structures, identify solvent compositions that will dissolve these residue types, and offer options for performing both bulk and site specific ionic cleanliness testing methods.

INTRODUCTION
Although the detection method may differ, all non-destructive cleanliness tests today require the remaining residue to be dissolved in order to measure it[1]. This is true for bulk or site specific testing. This being said, the solubility of the residue in the test solution becomes very important. The approach selected by the researchers in this study for determining the solubility, or insolubility, of current flux types focuses determining the Hansen Solubility Parameters (HSP's) for the current flux types. Once the solubility parameters for the flux types are established, a suitable solvent can be selected based upon known HSP's to fully dissolve the remaining residues for analysis. The solubility data generated in this study will be valuable in developing new and more accurate cleanliness test methods for process control and reliability prediction.

WHY IS CLEANLINESS TESTING IMPORTANT?
Many a company has learned the hard way that product reliability is directly related to the ionic cleanliness of a circuit board. The most tragic example of a suspected circuit board cleanliness failure occurred on January 27th, 1967[2] when a circuit assembly in an Apollo command module developed a short circuit in an on-board control system. The resulting fire consumed the entire module and all three astronauts on-board. There are doubtlessly many other examples of failed brake systems, pacemakers, weapons systems, and navigation satellites and other electronic systems we depend on for our everyday lives and wellbeing. This being a well established fact, much time and capital is spent every day on assembly lines worldwide to assure ionic residues are controlled.

ASSESSING CLEANLINESS TODAY
One would like to think an Apollo type failure could be avoided today by following the current IPC Electronic Industry Standards. In fact just following the current standards can leave electronic systems vulnerable to a host of failure modes related to circuit residues. Non-destructive visual inspection often misses residues under capacitors, resistors, and SMT array components. These "spot" residues are difficult analyze in a non-destructive way. Newer methods have been developed using steam or heated IPA/DI water extraction and measured by ion chromatography or electro-migration methods both of which require a trained technician or chemist and a considerable amount of time and effort. Even though these newer analytical tests have the ability to detect these hidden residues, a simpler, easier to perform test has held the top position as the most used cleanliness test performed to assess the cleanliness of electronic circuits for many years.

ROSE DEFINITION
The "ROSE" (resistivity of solvent extract) test has been the industry standard production line test for measuring the cleanliness of circuit assemblies for 37 years[3]. Originally established as a pre-conformal coat cleanliness requirement for military electronic hardware soldered with RMA and RA fluxes[4], the test was performed by flowing a 75%/25% mixture of isopropyl alcohol and de-ionized water across the surface of the circuit and measuring the drop in resistivity of the mixture. The "ROSE" test was incorporated into the

military specifications in the 1970's as a requirement for building military hardware. In the late 1980's and early 1990's, the Military adopted industry standards developed jointly through the IPC. This kept the "ROSE" test as the daily standard for class 3 (high reliability electronics). This remains as the current standard for conducting daily production tests.

NEW FLUXES AND NEW DESIGNS

This all worked quite well for some time. Then things changed and there were new fluxes and the new designs. With the introduction of surface mount, spaces became tighter. Chip cap1206's became 0201's. Then there were the new fluxes; the water soluble fluxes in the 1970's, the no-cleans of the 1990's and today's lead-free fluxes. These fluxes contain many new resins that are not necessarily soluble in the 75/25 IPA water mixture. Some have tried heating the mixture to improve solubility with limited success. Exacerbating the problem, the continual miniaturization of electronic packages is creating further problems dissolving residues in smaller and smaller spaces.

Miniaturization: Perhaps miniaturization is the most obvious trend of electronic industry. With Moore's law serving as the engine, electronic products are more versatile, running faster, and rapidly shrinking from huge floor model to tiny pocket size.

For state of art board level assembly, the mechanical hole size and pitch is 0.125 mm and 0.3 mm, respectively, while the non-mechanical via diameter and pitch is 0.05 mm and 0.175 mm, respectively. For components, among the finest are CSP with 0.3 mm pitch and 01005.[9] For portable devices, the leading edge package standoff is 0.3 mm, and the pad diameter is 0.2 mm. In the mean time, the cost of board assembly conversion has been driven down to 0.2 cents per I/O, with a board assembly escape rate of 200 ppm.[10] Miniaturization is driving multiple changes in flux technology, which ultimately influence the ability to measure in real time the cleanliness of production circuit boards.

Flux Consistency: As a result of miniaturization, the solder powder used in solder paste is shifting from type 3 (25 to 45 microns) to type 4 (20 to 37 microns), and the flux employed is more homogeneous and more thixotropic in order to achieve satisfactory consistency in printing and soldering. Also because of miniaturization, the assembly process is more vulnerable toward bridging; therefore the solder paste needs to be more slump resistant.

Oxide: In general, the volume of soldering materials, including fluxes and solder reduces in proportion with decreasing pitch. However, when the solder materials are shrunk in proportion to the pitch, the thickness of metal oxide does not shrink in proportion, as shown in Fig. 1. The metals here refer to PCB pads, component leads, and solder powder. Consequently, the amount of oxide to be removed by unit volume of flux increases with decreasing pad dimension. To compensate for this increasing work load, the fluxing capacity per unit amount of flux needs to be increased.
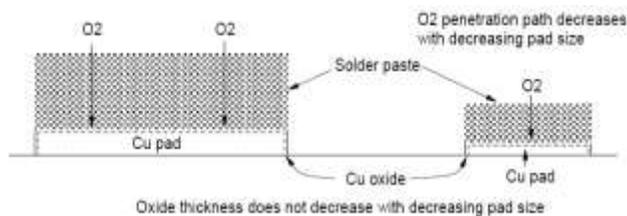

Figure 1: Relation between pad size and oxide thickness and oxygen penetration path.

Oxygen Penetration Path: While the pitch and pad size decreases, the oxygen penetration path through flux or solder paste also decreases, as also shown in Fig. 1. This inevitably results in a more rapid oxidation of both flux materials and metals covered by the flux if soldered under air. Hence, a flux with greater oxidation resistance as well as a greater oxygen barrier capability is needed for finer pitch applications. Symptoms such as graping (see Fig. 2) and head-in-pillow become common if the flux is not upgraded in terms of those properties. In Fig. 2, the reflow was adequate when the dot size was large. However, graping occurred when the dot size was small.
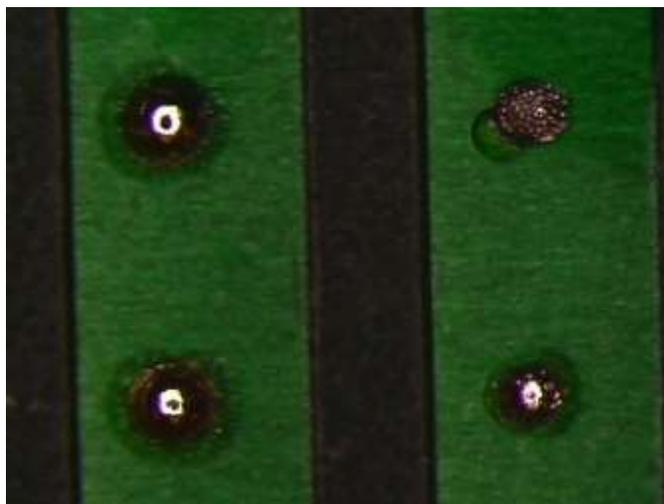

Fig. 2 Example of graping phenomenon observed for small dot sizes.

Flux Burn Off: In general, the vaporization rate of liquid increases with increasing exposure area per unit volume. For the same token, the flux burn-off increases with decreasing flux quantity deposited.[11] To offset this unfavorable trend, the flux employed for finer pitch needs to be more nonvolatile, hence more resistant to flux burn-off.

Wetting Speed: Although good wetting is a desired feature at soldering, and fast wetting is also desired at wave soldering or hand soldering, fast wetting is actually causing problem at reflow soldering. At SMT assembly, defects due to unbalanced wetting force, such as tombstoning or swimming, increases with decreasing component size, partly due to increasing sensitivity toward misregistration. Under this situation, fluxes with a slower wetting speed would allow

more time for the wetting force to be balanced, therefore promise a lower defect rate.[12]

Spattering: Miniaturization brings the solder joints closer to the gold fingers, hence is more vulnerable toward solder spattering. Spattering can be caused by moisture pickup of the solder paste. It can also be caused by fast solder coalescence action. To minimize solder spattering, fluxes with low moisture pickup and slow wetting speed should be employed.[13]

Soldering Under Air: As stated earlier, the cost of board assembly conversion has been driven down to 0.2 cents per I/O. Low cost driver is pushing the industry hard to have soldering done under air. Although miniaturization is causing solder fluxing more difficult due to more oxides and easier oxygen penetration, the assembly manufacturing houses are reluctant to use nitrogen and are pushing the challenge to solder and flux suppliers. As a result, the flux desired should exhibit the following properties: (1) a great oxidation resistance to prevent the flux from being oxidized, and (2) a great oxygen barrier capability to protect parts and solder from being oxidized.

Lead Free: The environmental consideration has driven electronic industry toward lead-free soldering operation, with July 1st, 2006 being the milestone date for European conversion dictated by RoHS. This European environmental legislation actually initiated a global lead-free conversion. As of today, about 60% of the global solder paste shipments were lead-free already.

Although some other alloys such as eutectic BiSn, eutectic SnZn or their modification are also in use, the main stream lead-free solder alloys adopted by electronic industry include Sn-Ag-Cu (SAC), Sn-Ag (SA), Sn-Cu (SC), and modification of those alloys.[14] As to PCB surface finish, the prevailing choices include OSP, HASL, immersion Ag, ENIG, and immersion Sn.

High Temperature: The main stream lead-free solders exhibit a melting temperature ranging from 217 to 227°C. Thus, the soldering temperature typically is 20-40°C higher than that of eutectic SnPb. Use of a higher soldering temperature generally causes more flux thermal decomposition, more flux burn-off, and more oxidation of fluxes and metals. To avoid problems caused by the higher soldering temperature, fluxes with the following features are desired: (1) a higher thermal stability, (2) a higher resistance against burn-off, (3) a higher oxidation resistance, and (4) a higher oxygen barrier capability.

Poor Wetting: The surface tension of lead-free alloys (0.55-0.57N/m for SAC) is about 20% higher than Sn63Pb37 (0.51N/m).[15] This consequently results in a poorer spreading and wetting for lead-free alloys.[13] This deficiency in alloy wetting is mainly compensated with new development of fluxes with a better wetting. In general, lead-free fluxes with adequate wetting exhibit the following features: (1) a lower

surface tension facilitating a better solder spread [4], and (2) a higher flux capacity and/or higher flux strength.

Large Dendrite: Due to the high tin content, lead-free alloys typically display a joint with large dendrite formation, as exemplified by Fig. 3.[16] Although large dendrite not necessarily causes early failure,[14] combining with anisotropic nature of tin crystal lattice and unfavorable grain orientation does pose reliability concern.[17] This reliability concern can be alleviated by forming solder joint with refined grain structure. Besides employing alloys with grain refining additives [18], use of proper flux chemistry can also achieve a similar result.[16]

Fig. 3 Surface dendrite structure of Sn95.5Ag3.5AgCu1.0 solder joint [9].

Miniaturization and lead-free soldering increase the flux innovation demands. Changes in flux compositions and soldering profiles increase ionic cleanliness complexities. To understand the magnitude of these complexities, nine flux residues were evaluated in this study. Two of the fluxes were organic acid based (water-soluble), one designed for tin-lead and the other for lead-free. One flux was rosin. Six fluxes were no-clean, four designed for tin-lead and two designed for lead-free.

ROSE PROBLEMS

There are problems with the ROSE test[5]. As mentioned previously, the test method relies on dissolving the flux residue to measure the effect on the resistivity. The electronic assembly drivers of miniaturization and the new flux technologies needed to achieve high yields further complicates this issue. If the residue is not dissolved, then the remaining residue is not detected by the ROSE method. This limitation leaves companies producing high reliability military and medical hardware with significant exposure. The main problem with the ROSE test today is that it is limited to isopropyl alcohol and water, and under current processing conditions, these solvents do not adequately dissolve most of today's fluxes trapped under SMT components.

HYPOTHESES
H$_1$: The IPA 75%/H$_2$O 25% will not adequately dissolve many of today's flux technologies.
H$_2$: A new test solvent that dissolves all flux technologies (water soluble, no-clean, rosin, and lead-free) is needed.

PREDICTING SOLVENT ACTION
Scientist's postulate that the solvency behavior of a pure solvent is proportional to the cohesive energy of the solvent and that this energy is proportional to heat of vaporization of the solvent and calculated from the equation below. The cohesive energy density is the amount of energy needed to completely dissolve one unit volume of molecules from their like molecules, which is equal to the heat of vaporization divided by molar volume.[21]

$$\text{Cohesive Energy} = c = \frac{\Delta H - RT}{V_m}$$

Where

ΔH = heat of vaporization
R = gas constant
T = temperature
V$_m$ = the molar volume of the solvent
Equation 1: Cohesive Energy

Hildebrand Solubility Parameters
In 1936, the Hildebrand solubility parameter was introduced by Joel Hildebrand. He proposed that the solvent's behavior to affect solids could be predicted by looking at the square root of the cohesive energy of that solvent. For a material to dissolve, in this case flux residue, the cohesive energy of the molecules must be overcome by molecules that have similar solvency behavior.[21] This parameter (δ) can be calculated as shown in equation 2 below.

$$\delta = \sqrt{((\Delta H_v - RT)/V_m)}$$

Equation 2: Hildebrand Solubility Parameter

The units of Hildebrand solubility were originally expressed as (δ/cal$^{1/2}$ cm$^{-3/2}$). With the advent of the metric system the units are now (δSI/MPa$^{1/2}$). For conversion, one δSI equals roughly two δ (2.0455 to be exact).

The primary use of the Hildebrand solubility parameter was to predict the affect of solvents on materials. From selecting solvents to strip paints, to removing machining oils, this approach shortened and improved the formulation process. Furthermore, this approach could be used to avoid damaging certain materials of construction, such as epoxy fiberglass under the paint.

The Cleaning Universe
A good analogy is to think of all the thousands of solvents as points in 3 dimensional spaces, like stars in the night sky.

The stars in this universe are arranged such that the stars closest to one another have similar solubility properties. Now imagine we can plot the residues to be removed and the materials of construction the widgets are made from in the same space such that if the residue or a widget material close to a solvent point we could predict the dissolution or deterioration of the material. This would be quite useful in both selecting a solvent to clean the residue of interest and avoid solvent selections that would deteriorate the materials of construction.

Along Comes Hansen
This is precisely the concept introduced by Dr. Charles Hansen in 1966. He proposed the Hildebrand solubility parameter could be broken into three parts. The Hildebrand approach is much like looking into the night sky and seeing two stars that appear to be close. They could be close, or one could be light years behind the other. Dr. Hansen added three parameters to establish true location in this three dimensional relationship.

The Hansen parameters estimate three important forces that influence solubility and that the sum of the squares of these equaled the Hildebrand solubility parameter squared as given in the equation below.

$$\delta_t{}^2 = \delta_d{}^2 + \delta_p{}^2 + \delta_h{}^2$$

Where:
$\delta_t{}^2$ = total Hildebrand solubility parameter
$\delta_d{}^2$ = dispersion force component of solubility
$\delta_p{}^2$ = polar force component of solubility
$\delta_h{}^2$ = hydrogen bonding force component of solubility

The Components of Hansen Space
The first is the dispersive/cohesive force (δ_d). In non-polar solvents this force predominates. It is a measure of the molecule to molecule interaction created by momentary differences in electron distribution. The energy of vaporization can be used to estimate the dispersive force. The second parameter in Hansen space is an estimate of the polar cohesive force (δ_p). It is the force created by the permanent differences electron densities created when electron rich and electron poor atoms are found in the same molecule. The polar force can be estimated from the dipole moment of the molecule. The third force of Hansen space is the hydrogen bonding parameter (δ_h). It is a measure of the ability to exchange electrons though hydrogen bonding. It can be estimated from the heat of mixing, or can be calculated as the sum of everything not included in the first two parameters. Table 1 provides an overview of HSPs for common solvents.

Solvent	δ_d Dispersive Force parameter	δ_p Polar Force parameter	δ_h Hydrogen Bonding Force parameter
Acetone	15.5	10.5	7.0
D-Limonene (terpene)	16.6	0.6	0.0
HFC 43-10mee	12.9	4.5	5.3
Hydrocarbons (C7-11) 25% aromatics	15.8	0.0	0.0
Isopropyl Alcohol	15.8	6.1	16.4
Methyl Acetate	15.5	7.2	7.6
Methyl Ethyl Ketone	16.0	9.0	5.1
Methylene Chloride	18.2	6.3	2.9
N-Methylpyrrollidone	18.0	12.2	7.2
N-Propyl Bromide	16.0	6.5	4.7
Perchloroethylene	19.0	6.5	2.9
Trichloroethylene	18.0	3.1	5.3
Water	8.6	13.4	25.8

Table 1: Hansen Parameters for common solvents (source BFK Solutions newsletter[5])

Charting Solvents in Hansen Space

Representing 3D space on a sheet of paper can be a challenge. At best, you have to use your imagination to visualize the data. Software is available to allow "point of view" rotation to assess the 3D data. Figure 4 shows a single point of view look at solvents plotted in Hansen space.
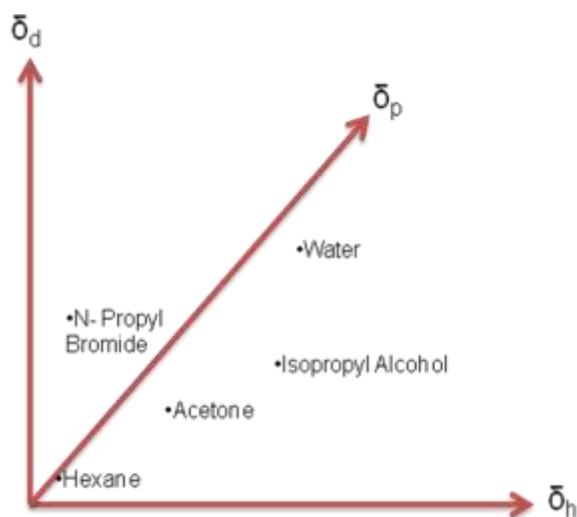
Figure 4: 2D representation of 3D Hansen Space

Looking at the data represented in Figure 4, it is apparent that hexane has a lower polar force than water. It would be difficult to judge if acetone was greater than n-propyl bromide. Traditional two dimensional (x,y) charts can be used to evaluate Hansen data but this requires two charts to tell the full story.

Teas Charts

Teas Charts were developed by J P Teas to allow a 2D view of 3D data. Figure 5 shows a generalized view of solvent classes plotted with a Teas graph[7]. The three axes of the chart represent the percentage of each of the three Hansen solubility parameters.
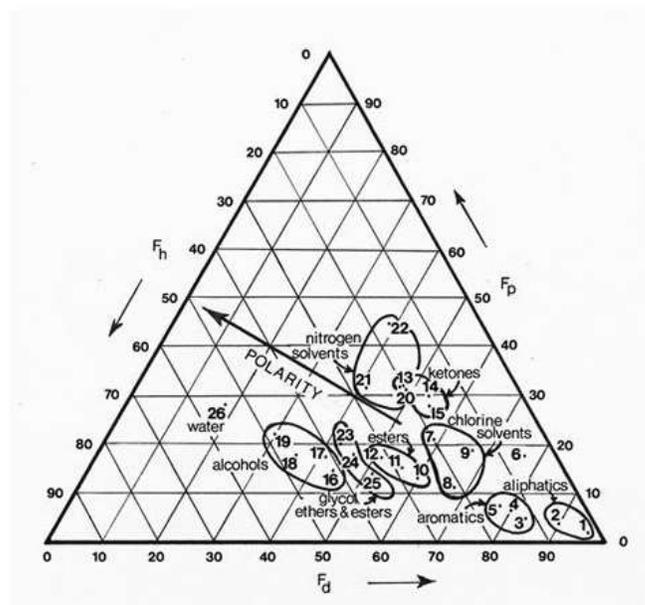

Figure 5: Teas chart of Hansen solubility parameters for general solvent classes

Computer Generated "3-D" charts

Figure 6 illustrates a chart that places solvent properties into a three dimensional sphere, which is the heart of HSP. The sphere positions solvents in relationship to their ability to dissolve the contaminant, in this case flux residue. The solvents inside the sphere dissolve the contaminant and none of those outside the sphere dissolve the contaminant.[8] The objective is to identify a group of relevant solvents that work best on the specific flux residue. The broader the range of dispersive, polarity, and hydrogen bonding properties away from the sphere the least amount of work those solvents have on the selective soil.
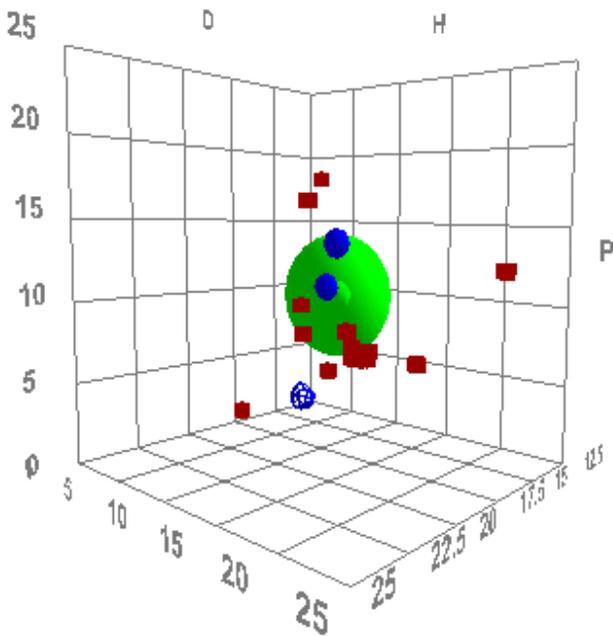
Figure 6: The Interaction Sphere is at the heart of the HSP theory.

Figure 7: Grading Scale Sample Illustrations

Score	Description
1	Easily dispersed, very stable dispersion
2	Takes a bit of effort to disperse, reasonably stable
3	Disperses but fairly soon starts to settle
4	Pretty reluctant to disperse
5	Some hint of dispersal
6	Just sits and laughs at the solvent

Table 2: Grading Scale

METHODOLOGY

To determine the HSP's for a given residue (water soluble flux, rosin flux, no-clean flux, lead-free no-clean flux), a simple series of tests were performed. For tests performed in these experiments, samples of the various flux residues were heated to peak reflow temperatures and held at that temperature until low boiling solvents were removed (approximately 5minutes) and cooled to room temperatures. An alternative method of preparing samples would be to cut up a soldered assembly and use these small samples for testing. Using the prepared residues the following test is performed. Each material of interest was exposed to a group of 20 solvents selected to represent specific regions of Hansen space. In this test, a "shaker table" and 24 position test rack was used to hold and agitate the samples for a fixed time. A one hour exposure at room temperature was used for determining the HSP of each flux residue presented in this study

The objective is to define the sphere which says "all or most of the solvents inside the sphere dissolve the flux and none or few of the solvents outside the sphere fully dissolve the flux residue.[19] The twenty solvents selected to characterize the flux residues exhibit a broad range of dispersion, polarity, and hydrogen bonding parameters. The residues from the nine fluxes in the study were added individually to each of the twenty test solvents at roughly 3% by weight.

The samples were prepared using 12 ml sample vials. Visual results were used to grade the rate of dispersion (Figure 7). Table 2 documents the grading scale used.[19] A score of 1 is very close to the center of the sphere while a six is very far outside the sphere radius. The smaller radius that gives the closest fit to a 1.0 is optimal.
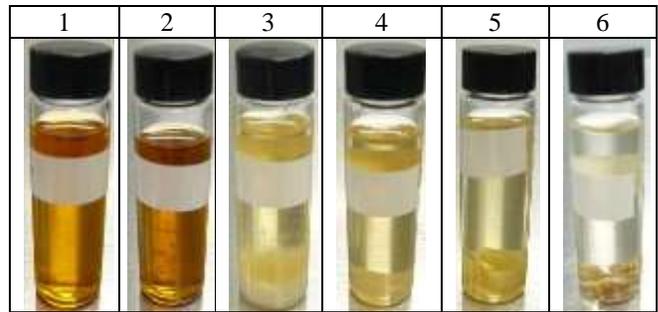
Upon completion of the test, the samples were graded and entered into the HSPiP software. Analyzing the results of all 20 solvents tested on the specific flux residue type gives the location of the "interaction zone" where dissolution occurs.[8] The software program performs a calculation to find the best fit of the data. Inside solvents (blue circles) are within the radius and all outside solvents (red squares).[19] There are some solvents that will disperse the soil but are categorized as "wrong solvents" since their HSP parameters are outside the interaction zone. Such wrong solvents are marked with a "*" and represented as blue open circles for soils inside that are outside the sphere and red open circles for outside solvents that are inline the sphere. This test procedure establishes the Hansen Solubility Parameter for the specific flux residue tested.

Interaction Zone

The interaction zone indicates the region where other solvents can be found that could effectively remove the residue. Even though we did not test with these solvents, we now know they too have a high probability of removing the residue. This area of positive interaction in the Hansen plot is interaction space for that material. Depending on the material, this area can be large or small and is usually spherical or oval in shape. The size of the interaction zone is indicated by the Interaction Radius (R), which is the average radius of the zone. The center of the material interaction zone is used to set the Hansen parameters for that solid material (Figure 7).
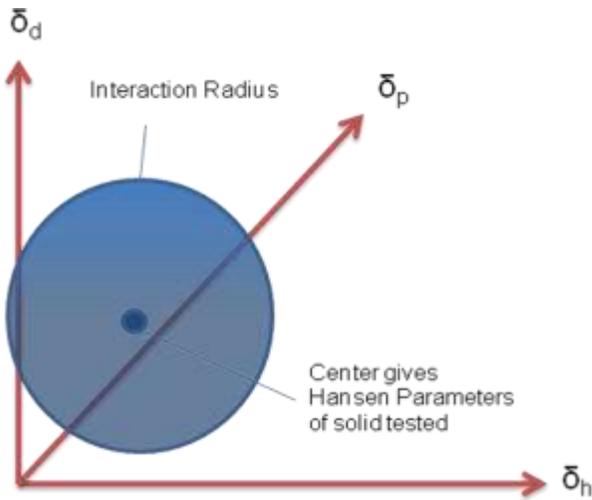
Figure 8: Interaction Radius of the Soil Tested

RED Number

Relative Energy Distance (RED) is the Hansen Solubility Distance between the given solvent and the reference value, divided by the radius that defines the goodness of fit.[19] The equation for the RED number is the ratio of the distance Ra (distance between the given solvent to the reference value) divided by the Ro (interaction radius). The *RED number* reflects the relative energy difference.[8] A RED number of 0 has no energy difference. RED numbers less than 1.0 are considered inside solvents, which indicate high affinity. RED numbers equal to or close to 1.0 are considered a boundary condition; which indicates that the solvent will disperse the soil. Progressively higher RED numbers indicate progressively lower affinities that indicate that these materials are the wrong solvents.

$$RED = Ra/Ro.$$

The distance between flux soils based on their respective partial solubility parameters indicates the boundary regions that those soils find in today's electronic assembly process.[8] What this means is that some flux soils will have a higher affinity for cleaning agents that are inside the interaction zone. Cleaning agents that exhibit a boundary condition or are the wrong solvent for the soil will not clean as well.

DATA FINDINGS

HSP encodes the principle that "like dissolves like."[8] Nine flux soils were characterized in this study. Two of the soils were water soluble, with one designed for eutectic tin-lead alloys and the other designed for lead-free alloys. Six of the soils were no-clean, with two of the no-clean designed for lead-free. One of the soils was rosin. The characterization was based on thermodynamic effects of the solvent for the specific flux soil tested. The calculation of the soil characterizes the material according to its sphere. Inside the sphere interacts well with the

solvents and outside the sphere the solvent is incompatible.[8] The characterization is done at room temperature. From this characterization, the flux soils Hansen Solubility Parameters of dispersion, polarity and hydrogen bonding were established (Figure 8).

To regress a bit, the Navy sponsored early development of ionic testing in the 1970s. The fluxes used to establish the baseline were rosin mildly active (RMA) and rosin active (RA). The solvent reagent was a 75/25 volume to volume mixture of IPA and water. The Hansen Solubility Parameter established for rosin is illustrated in Figure 9. From the solvents used, there were a number of inside solvents (blue solid circles), outside solvents (red solid squares), inside solvents that should be outside the radius (blue open circles), and outside solvents that are inside the radius (red open squares). From this data analysis, the software calculates the HSP for rosin.
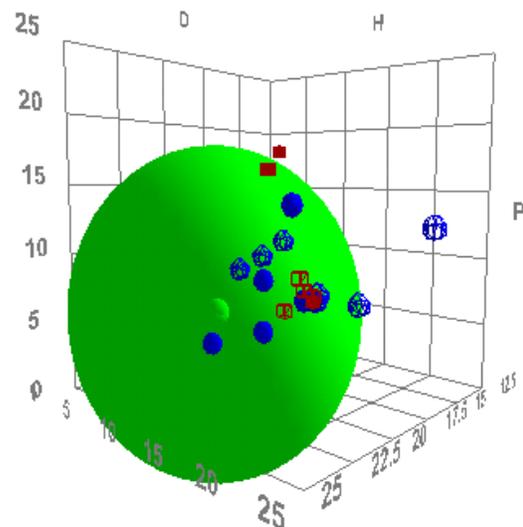

Figure 9: Solvent Interaction with Rosin

Six no-clean flux residues were tested to establish their HSPs. The data findings indicate different solubility parameters for the each of the soils. This finding gets into the heart of the problem that IPA/H_2O is outside the radius on many of the no-clean materials tested. Figures 10-15 illustrate the solubility parameters differences from the six no-clean soils tested.
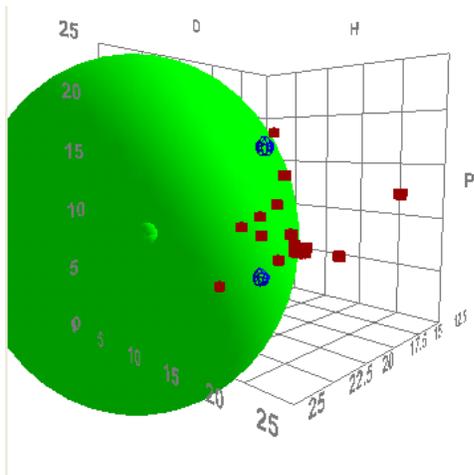
Figure 10: Interaction Zone for No-Clean # 1 designed for Eutectic Tin-Lead

Notice how none of the twenty solvents were a perfect fit in dissolving this soil. There were a few soils that dispersed the soil but the software classified them as inside solvents outside the radius. The HSPiP software gives you a choice of selecting whether the solvent is inside the radius based on the score. This data is based on a score of 1 being inside the sphere and a score outside of 1 is outside the sphere. If we were to select one and two being inside sphere, there would be slightly more inside solvents.
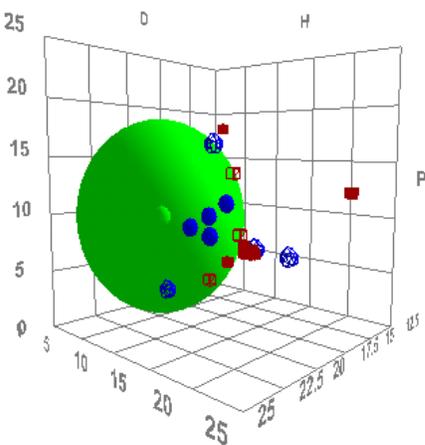
Figure 11: Interaction Zone for No-Clean #2 designed for Eutectic Tin-Lead

The no-clean flux residue represented in Figure 11 showed a much different solubility parameter than did the flux residue illustrated in Figure 10. Notice the increased number of the solvents that are inside the radius for No-Clean #2 as opposed to No-Clean #1. Keep in mind that the solubility matrix is different for each of these soils.
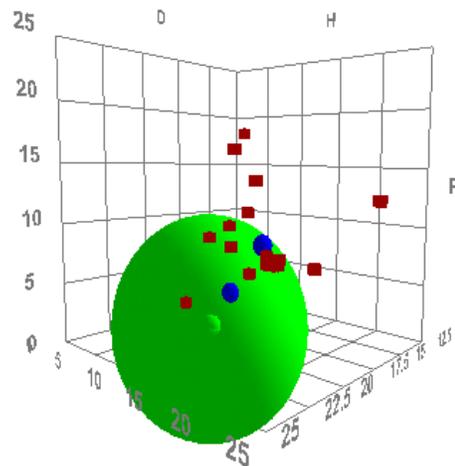

Figure 12: Interaction Zone for No-Clean #3 designed for Eutectic Tin-Lead

The no-clean flux residue represented in Figure 12 also showed a different solubility parameter from the other soils tested. Notice how each of the flux soils illustrated require a high level of dispersion to solubilize the residue. The soil illustrated in Figure 12 is dissolved with a limited number of test solvents with a wide range of the test solvents being outside the sphere.
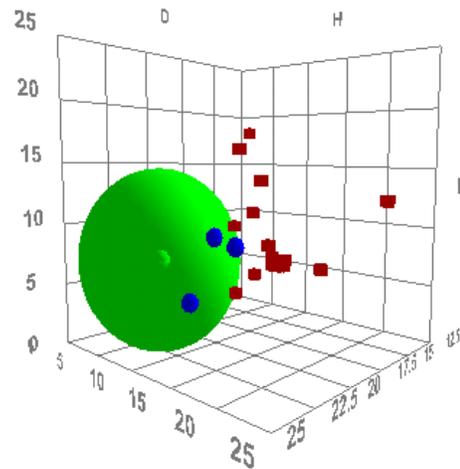

Figure 13: Interaction Zone for No-Clean #4 designed for Eutectic Tin-Lead

The no-clean flux residue represented in Figure 13 was similar to the soil represented in Figure 11. A relatively small number of the solvents tested were inside the radius with many outside. The data set indicates that this soil may be difficult to clean.
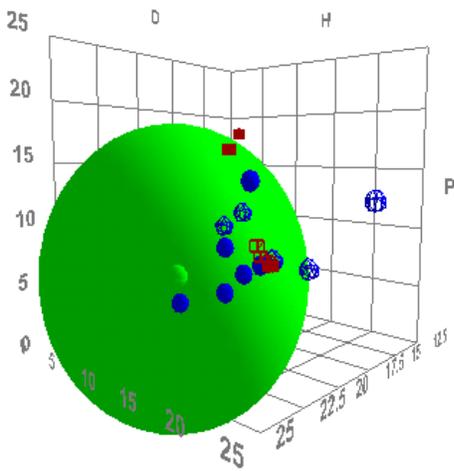
Figure 14: Interaction Zone for No-Clean #5 designed for Lead-Free

The no-clean flux residue represented in Figure 14 has a larger number of inside solvents. Lead-free flux compositions require higher molecular weight resins that hold up to higher temperature profiles. The residue after boiling down was pliable (soft). The characteristic of this residue was easier to dissolve.
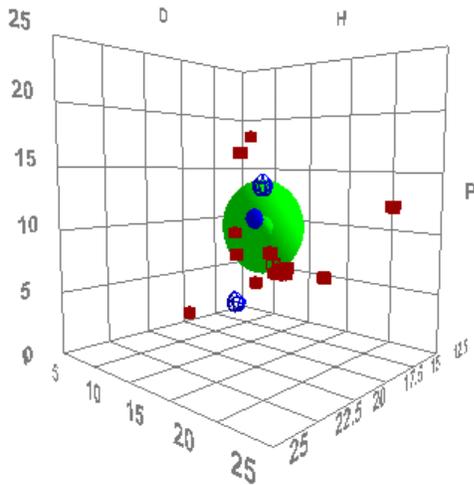

Figure 15: Interaction Zone for No-Clean #6 designed for Lead-Free

The no-clean flux residue represented in Figure 15 shows a different solubility parameter than the other no-clean flux residues. Notice how this residue requires increase polarity and hydrogen bonding properties. Similar to the other soils tested, a number of the solvents were outside the sphere.

Two water soluble flux residues were tested. The water soluble soils make a shift toward increased polarity and hydrogen bonding properties and less dispersive properties. This is expected since these soils are designed to be clean with water only. Figures 16 and 17 illustrate the findings from these two soils.
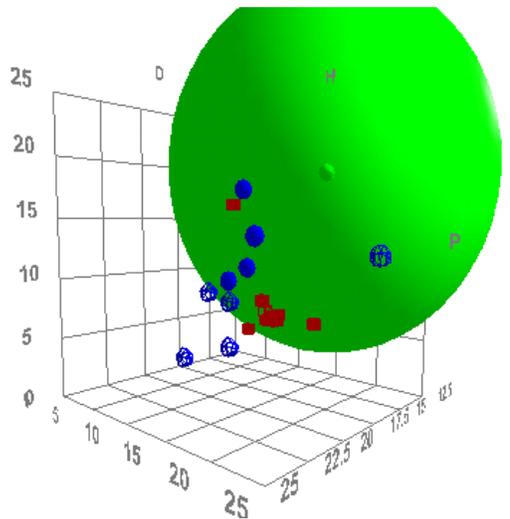

Figure 16: Interaction Zone for Water soluble flux designed for Lead-Free

The water soluble flux residue represented in Figure 16 shows greater polarity and hydrogen bonding properties. Of the 20 solvents tested, only the oxygenated solvents and water represented inside solvents with the aromatic, aliphatic, chlorinated, and ketones representing the outside solvents.
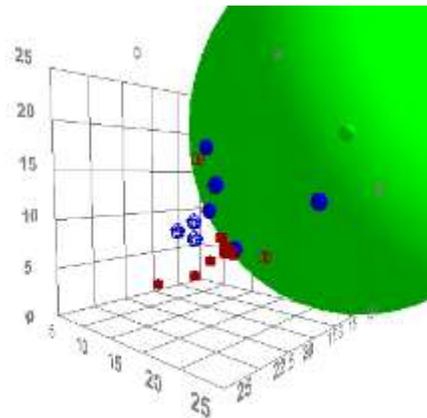

Figure 17: Interaction Zone for Water Soluble #2 designed for Eutectic Tin Lead

The water soluble flux residue represented in Figure 17 shows high polarity and hydrogen bonding properties. Similar to water soluble #1 only oxygenated solvents and water represented inside solvents.

The data findings indicate that the no-clean and rosin flux residues contain non-polar constituents that require organic materials to disperse (attract) the soil to the solvent. The no-clean and rosin flux residues also contain polar cohesive energy, which indicates that a portion of the residue may be water soluble. The third source of cohesive energy shows a moderate attraction of the no-clean and rosin flux residues among molecules because of hydrogen bonding. As expected, the water soluble flux

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residues show a higher cohesive polarity and hydrogen bonding and weaker dispersion energies.

The thermodynamic properties of each the soils are different. The calculated HSPs for each of the soils are represented in Figure 18. The differences in the HSPs clearly indicate that soils exhibit different solubility parameters. The data also suggests that those soils outside the solubility sphere for IPA/H_2O may not dissolve when undergoing ionic testing. When this occurs, a low ionic reading would be expected.

No.	Solvent	δD	δP	δH	Scor
1	Rosin #1	21.41	6.25	10.28	-
8	No-Clean #5 LF	21.36	6.03	9.25	-
5	No Clean #4	22.37	7.27	4.70	-
3	No Clean #3	19.26	1.51	12.82	-
4	No Clean # 2	19.61	9.63	4.55	-
2	No Clean #1	24.49	8.63	5.51	-
9	No-Clean #5 LF	16.60	10.19	10.08	-
6	Water Soluble #2	11.10	19.67	22.18	-
7	Water Soluble #1	8.65	20.07	8.53	-

Figure 18: HSPs calculated for the nine flux residues

IPA75%/H_2O25%

	Δd	Δp	δh
100% Isopropyl Alcohol	**15.8** x.75 = 11.85	**6.1** x.75 = 4.6	**16.4** x.75 = 12.3
Water	**8.6** x.25 = 2.15	**13.4** x.25 =3.3	**25.8** x.25 = 6.5
75/25 IPA/Water mix	**14.0**	**7.9**	**17.8**

Table 3: Calculation of Hansen Parameters for a 75/25 IPA/water mixture

Figure 8: HSPs for Flux Soils Tested

ACCEPT OR REJECT RESEARCH HYPOTHESES
To accept or nullify the research hypothesis that IPA 75%/H_2O25% will not adequately dissolve many of today's flux technologies, a second set of tests were conducted. Each of the research flux residues were exposed to the IPA75%/H_2O25% reagent. The following sets of samples were run:

1. IPA75%/H_2O @ 68-78F (20-25C)
2. IPA75%/H_2O @ 100-110F (37-43C)
3. IPA75%/H_2O @ 165-180F (74-82C)

Kinetics versus Thermodynamics
The Hansen Solubility parameters are driven by thermodynamics. In this example, thermodynamics determines whether the cleaning agent (solvent) will dissolve or disperse the flux soil at ambient conditions. Flux is a solid at room temperature, but reaches its liquid state at or below the soldering temperature. Applying kinetics in the form of heat and impingement energy can change the solubility parameters and the size and location

In the 1970's when the Navy developed the current ROSE method using rosin as the primary soil, the standard reagent call out in Mil-P-28809 was a mixture of 75% isopropyl alcohol and 25% water. This remains the primary solvent mixture currently used today for ionic cleanliness testing of finished circuit assemblies. The Hansen solubility parameters can be calculated for the 75/25 IPA/H_2O mixture as shown in table 3 below[8]. Hansen parameters can also be estimated mathematically for solvent blends by summing the individual parameters for each unique solvent in the blend, divided by the volume fraction of that solvent in the blend. The fractional parameters are summed to give the parameters of the mixture.

There are a wide range of flux technologies currently in use in today's electronic assembly environment. Many of these flux technologies may or may not be located inside the IPA/H_2O sphere or near the boundary line condition. Other flux technologies may be located outside the sphere. This creates a problem for developing one optimal solvent mixture such as IPA75%/H_2O25% that provides good cleaning properties for all flux materials currently in use today.

of the interaction zone. How does the Hansen Solubility parameters of IPA75% / H_2O25% (reagent) change when the reagent is heated to 100°F (30°C) as allowed in some equipment or at 175°F (80°C) as prescribed in the IPC ion chromatograph protocol?

This experiment is slightly different from the first experiment used to establish the Hansen Solubility Parameters for the nine flux residues. In this experiment, the same grading scale will be used to determine the solubility parameters for IPA/H_2O at various temperatures.

The data finding for IPA/H_2O @ 25°C show the majority of the flux residues have RED numbers greater than 1. The software calculated the water soluble fluxes and one lead-free no-clean as the only solvents within the interaction zone. Rosin was close to the interaction zone. IPA/H_2O @ 25°C would be considered as the wrong solvent for measuring ionic cleanliness of 5 out of six of the no-clean residues tested in this study. This finding accepts the first hypothesis that IPA/H_2O @ 25°C is the

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wrong solvent for testing ionic cleanliness of many of today's flux residues. Figure 19 illustrates the data findings.
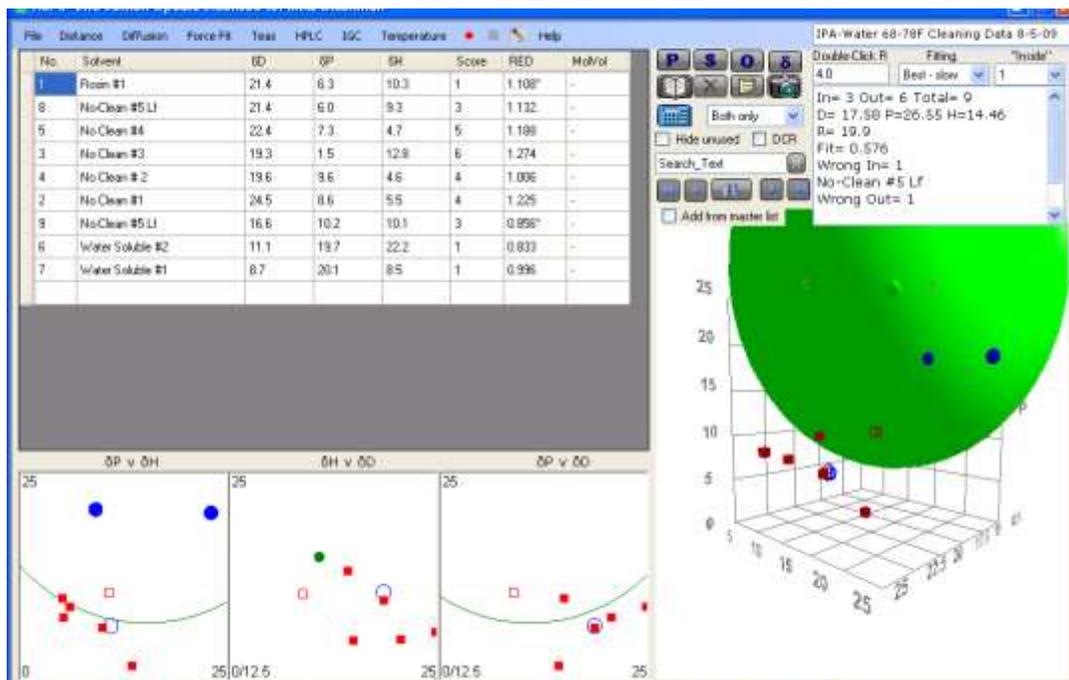

Figure 19: Flux Set Interaction with 75%/25% IPA/H₂O @ 25°C – 6 of 9 fluxes outside interaction zone

The data findings for IPA/H$_2$O @ 40°C also show the majority of the flux residues have RED numbers greater than 1. Similar to the 25°C data, the software calculated the water soluble fluxes and lead-free no-clean as the only solvents within the interaction zone. This finding accepts the first hypothesis that IPA/H$_2$O @ 25°C is the wrong solvent for testing ionic cleanliness of many of today's flux residues (Figure 20).
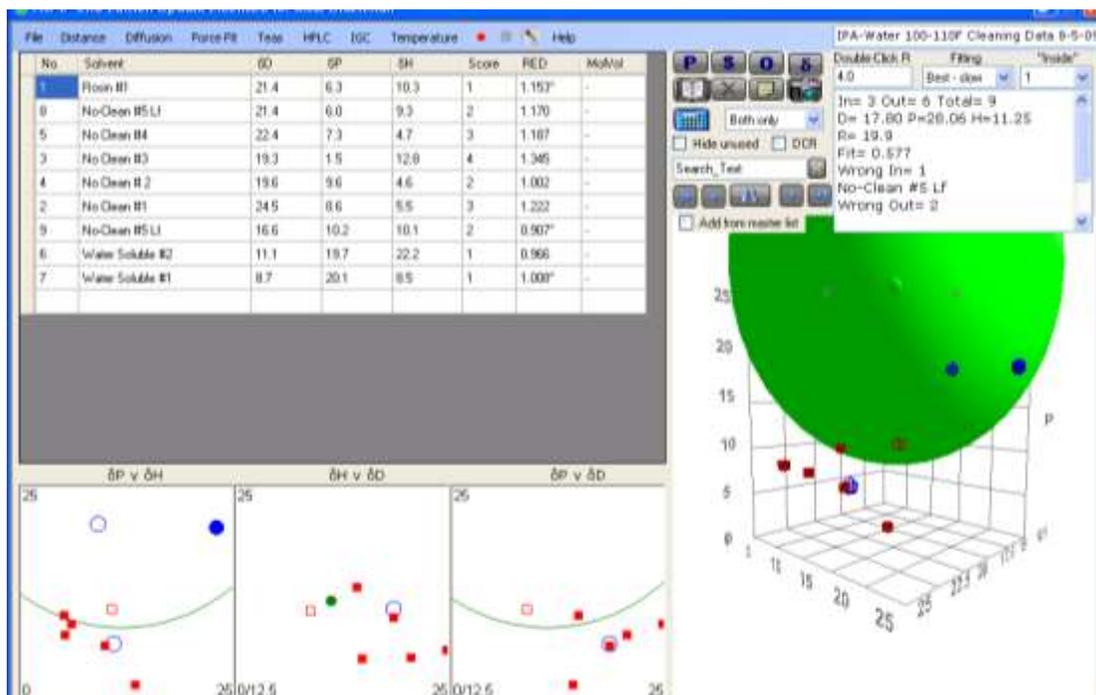

Figure 20: Flux set interaction with 75%/25% IPA/H$_2$O @ 40°C – 6 of 9 fluxes outside the interaction zone

The data findings for IPA/H$_2$O @ 80°C, which is the temperature used for Ion Chromatography extractions, shows a much different result. The majority of the flux residues have RED numbers less than 1. Those with RED numbers greater than 1 successfully dispersed at this temperature. One could argue that this finding accepts and or rejects the first hypothesis that IPA/H$_2$O @ 25°C is the wrong solvent for testing ionic cleanliness of many of today's flux residues (Figure 21). The data suggests two converging effects: 1. The solvency of IPA/H$_2$O improves with increased temperature, and 2. The flux residues soften at 80°C, which renders them more soluble in IPA/H$_2$O
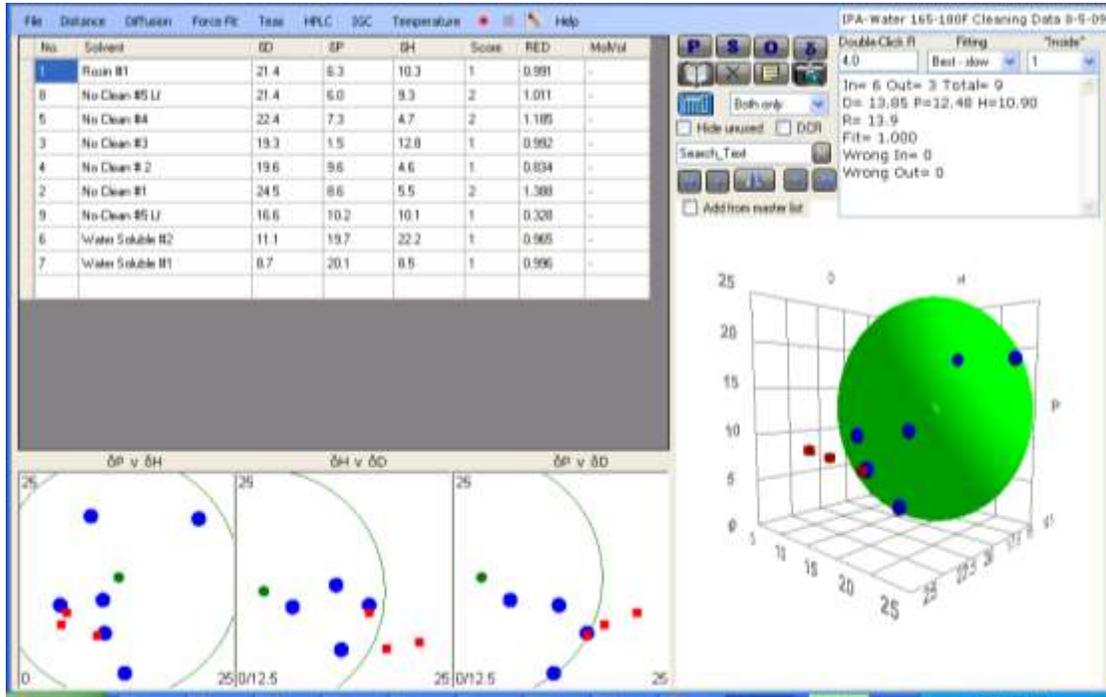

Figure 21: Flux Set Interaction with 75%/25% IPA/H$_2$O @ 80°C – 6 out of 9 flux are in the interaction zone

INFERENCES FROM THE DATA

The data findings infer that no-clean and rosin flux residues require high dispersive forces, moderate permanent dipole-permanent dipole forces, and moderate hydrogen bonding forces. Contrary, water soluble flux residue solubility parameters require moderate dispersive forces and high polarity and hydrogen bonding forces. The ideal solvent mixture requires a material that exhibits high dispersive, polarity, and hydrogen bonding.

Little innovation has taken place since the introduction of commercial instruments designed to measure the resistivity of solvent extract in the 1970's. IPA75%/H$_2$O25% was determined by the Navy in the 1970s to be the best solvent for dissolving rosin.[20] The problem is that the electronic assembly roadmap seeks higher functionality, miniaturization, increased density, and speed. In order to meet ever increasing demands, rapid innovation is occurring on all fronts. Solder material companies are under pressure to improve solderability yields. Emerging flux needs, as discussed in this document, require new material properties, which may not dissolve well with existing IPA75%/ H$_2$O reagent.

The research findings uncovered a number of key insights.

1. Since the measure of ionic cleanliness is dependent on extracting all ionic residues using the current R.O.S.E. test method, the data suggests that this method is not suitable for measuring ionic cleanliness on flux residues that are outside the IPA/H$_2$O interaction zone.

This research finding is a controversial statement. Those schooled in the no-clean solder flux technology may argue that the ionic residues are encapsulated into a no-clean residue that is not designed to be soluble in ionic test reagent IPA/H$_2$O.

On the other front, miniaturization reduces the distance between conductors. When exposed to harsh conditions, the no-clean residue may break down, and in the presence of humidity (moisture), the entrapped ionic residues may propagate and cause a failure. The data suggests that current ROSE method of measuring this effect on the manufacturing floor is not valid.

2. Temperature of the IPA/H$_2$O reagent opens up the solubility interaction zone. Ion Chromatography extractions immerse the assembly into an 80°C IPA/H$_2$O reagent for one hour. The data suggests that many of the no-clean flux residues will either

dissolve or disperse at this temperature. The solubility parameter is improved but is this practical for testing on the manufacturing floor? If so, new equipment designed to run the procedure and address flammability concerns would need to be considered.

3. The data suggests that new test solvent and test equipment needs to be designed to address today's circuit assemblies and flux technologies. There are numerous challenges with this approach.

   a. Based on the limited data set of nine fluxes, it is difficult to know whether one optimal solvent would meet all the flux types.
   b. The current method would require additional testing to develop an Industry Standard.
   c. Test instrumentation design would need improved kinetic (impingement) energy to penetrate and extract residue under small components.

FOLLOW ON RESEARCH
Kenyon (2007) cited past research which showed a dramatic difference in the release rate of the residues of rosin fluxes, water-soluble fluxes, no-clean fluxes, and lead-free fluxes. Follow on research is needed to characterize the HSP properties of the various flux soils used by electronic assemblers. Once the HSP of the soils are known, the soils can be grouped based on solubility parameters.

Hansen parameters for different flux residue soils using the IPA75%/H_2O25% reagent need to be established. On residues that are outside the interaction zone, alternative cleanliness testing protocols need to be developed. Follow on research into alternative cleaning agents that offer a better interaction zone for today's flux soils is needed.

Once the solubility parameters are known, new test instrumentation needs to be researched and innovated for running an improved procedure on the manufacturing floor. As instrumentation is developed to incorporate the kinetic energy requirements of time, heat, and energy, alternative solvent blends with better HSP properties than the current IPA/H_2O may be applicable.

Additional research applying kinetic energy to alternative solvent mixtures is needed on flux residue types that are outside the RED zone.

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