"Using Hansen Space to Optimize Solvent Based Cleaning Processes for Manufacturing Electronic Assemblies"

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Take the Guess Work Out of Solvent Selection

Sometimes you just cannot clean with water. Good examples of this are: circuits with batteries attached, cleaning prior to encapsulation, ionic cleanliness testing, and non-sealed or other water sensitive parts. High impedance or high voltage circuits need to be cleaned of flux residues and other soils to maximize performance and reliability and, in these types of circuits; water can be just as detrimental as fluxes. When solvent cleaning is called for, Hansen solubility parameters can help target the best solvent or solvent blend to remove the residue of interest, and prevent degradation of the assembly being manufactured. In short, using this approach can time, manufacturing cost and reduce product liability.

What is an optimized cleaning process?

Is it based solely upon removing the residue, or is it more? Of course it is more. We do not want to remove the labels or other parts markings, or degrade or damage the substrate of individual components. It is not desirable to swell elastomers or create new residues or otherwise affect the product being built.

Dissolving manufacturing residues, without affecting the materials of construction, is difficult when working with organic solvents and solvent blends. Water being the great solvent that it is, is all around us. We generally design our widgets to be compatible with water. On the other hand, solvents and solvent blends are not routinely found in the environment in which our widgets are used. Why would a designer design a widget to be tolerant of organic solvents? Even if a designer wanted to have his widget resist a certain solvent, there are thousands of solvents and an infinite number of solvents blends.

Predicting Solvent Action

Scientist 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 could be calculated from the equation below.

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

Where

ΔH = heat of vaporization
R = gas constant
T = temperature
V_m = the molar volume of the solvent

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. This parameter (δ), can be calculated as shown in equation 2 below.

$$\text{Hildebrand Solubility Parameter} = \delta = \sqrt{c} = \left(\frac{\Delta H - RT}{V_m} \right)^{1/2}$$

The units of Hildebrand solubility were originally expresses as ($\delta/cal^{\frac{1}{2}} cm^{-3/2}$). With the advent of the metric system the units are now ($\delta SI/MPa^{\frac{1}{2}}$). 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 space, 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 shows the (SI) Hansen parameters for several 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)

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 1 shows a single point of view look at solvents plotted in Hansen space.
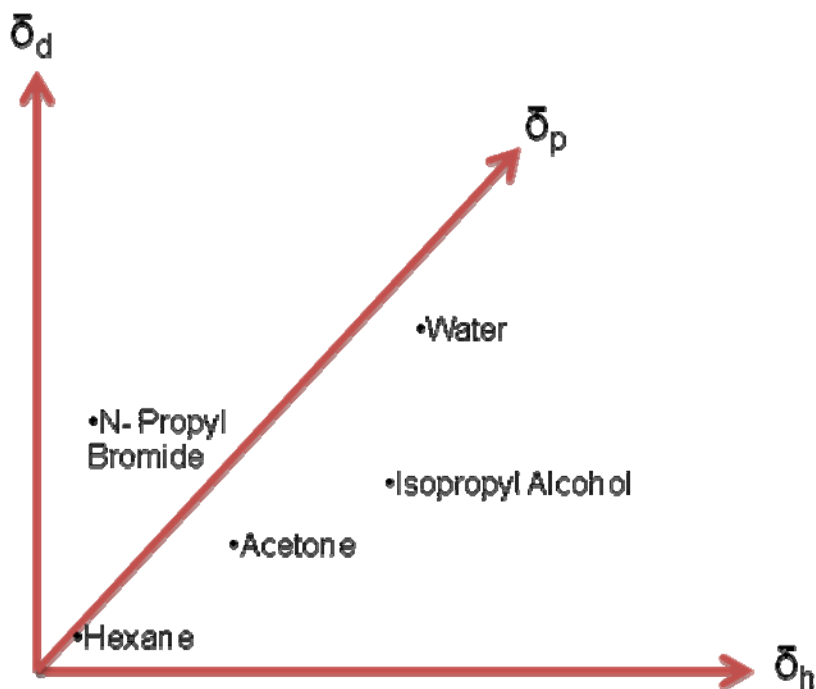

Figure 1: 2D representation of 3D Hansen Space (single point of view)

Looking at the data represented in Figure 1, 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 2 show a generalized view of solvent classes plotted with a Teas graph. The three axes of the chart represent the percentage of each of the three Hansen solubility parameters.
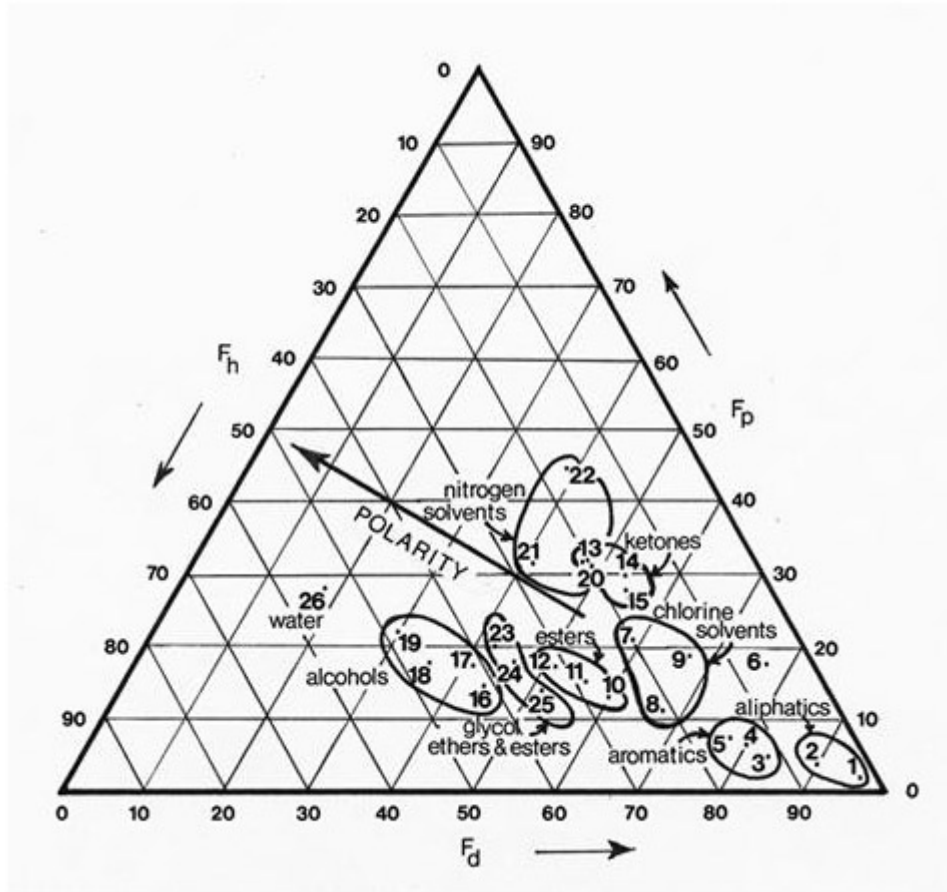
Figure 2 Teas chart of Hansen solubility parameters for general solvent classes

Determining Hansen Parameters for Solids
The key to optimizing a cleaning process is to know where the residues and the materials of construction plot in Hansen space. To determine this, a simple series of tests can be performed. Using the residues to be cleaned and/or the materials of construction wished not to be affected, the following test is performed. Each material of interest is exposed to a group of solvents selected to represent specific regions of Hansen space. A special rotating jig is used to hold and agitate the samples for a fixed time. The time selected should be based on how long the cleaning exposure is or how long you want the material to resist the solvent. Most of Hansen parameter found in data sheets is based on tests performed at room temperature. If you plan to use heated solvent in your cleaning process, test longer at room temperature if you wish to compare results to published data.

Visual, dimensional, or gravimetric measurements can be used to grade the result. The simplest is pass/fail. It did or it did not dissolve the residue. It did or did not affect the part, remove the label, or swell the elastomer. Once the test is complete and the pass fail data is gathered, the results are posted in Hansen space at the location of the solvent tested.

Residue removal, with a given solvent, 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). It 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.
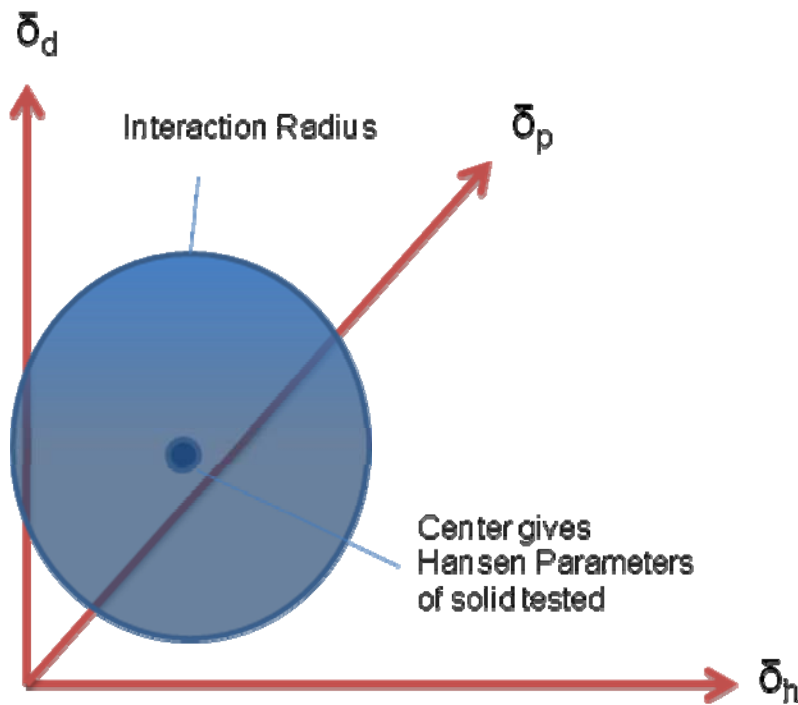

Figure 3 Plot of Hansen interaction for a solid material

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Table 2 shows typical Hansen parameters some common materials of construction.

Material of Construction (solid)	δd Dispersive Force parameter	δp Polar Force parameter	δh Hydrogen Bonding Force parameter	R Interaction radius
Cellulose Acetate	18.6	12.7	11.0	7.6
Chlorinated Polypropylene	20.3	6.3	5.4	10.6
Epoxy (cured)	20.4	12.0	11.5	12.7
Isoprene Elastomers	16.6	1.4	-0.8	9.6
Cellulose Nitrate	15.4	14.7	8.8	11.5
Polyamide	17.4	-1.9	14.9	9.6
Poly isobutylene	14.5	2.5	4.7	12.7
Ethyl Methacrylate (cured)	17.6	9.7	4.0	10.6
Methyl Methacrylate (cured)	18.6	10.5	7.5	8.6
Polystyrene	21.3	5.8	4.4	12.7
Polyvinyl acetate	20.9	11.3	9.6	13.7
Poly vinyl butyral	18.6	4.4	13.0	10.6
Poly vinyl chloride	18.2	7.5	8.3	3.5
Polyester (saturated)	21.5	14.9	12.3	16.8
RMA Flux (reflowed)	9.1	2.3	4.9	8.3

Table 2 Hansen Parameters for common solid materials (source John Burke and Ken Dishart)

Solvent Blends

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.

For example, a mixture of 75% isopropyl alcohol and 25% water is often used for ionic cleanliness testing of finished circuit assemblies. The Hansen solubility parameters can be calculated for the 75/25 mixture as shown in table 3 below. The fractional parameters are summed to give the parameters of the mixture.

	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

Optimizing the Cleaning Process

Let's now go back to the original premise of the paper. Once the Hansen solubility parameters of the soil(s) to be cleaned is known, a solvent or solvent blend can be selected based on Hansen solubility parameters best matching the soil(s) and avoiding solvents that might affect the materials of construction comprising the electronic module being cleaned. In this way, we can clean the soils and avoid any potential deterioration of the module for normal exposure times.

If the interaction zones of the cleaning agent and a material of construction overlap, then a directional approach should be used. Select cleaning agents in the cleaning interaction zone on the side opposite the overlap. This avoids the potential interaction with the module.

Using Hansen Parameters to Avoid "White Residues"

Partially cleaned residues form by definition at the edge of the interaction zone because they are partially soluble. This gives rise to the notorious "white residue". It also explains why this residues composition is so elusive. The residue will vary in composition depending on the soil and the cleaning agent. Reflow rosin residues cleaned with a 75/25 mixture of IPA/water often leave significant quantities of this white stuff. Hansen theory suggests that 100% IPA would do a better job of cleaning rosin residues than the 75/25 mixture. The Teas chart below shows the location of the solvents relative to the RMA interaction zone.
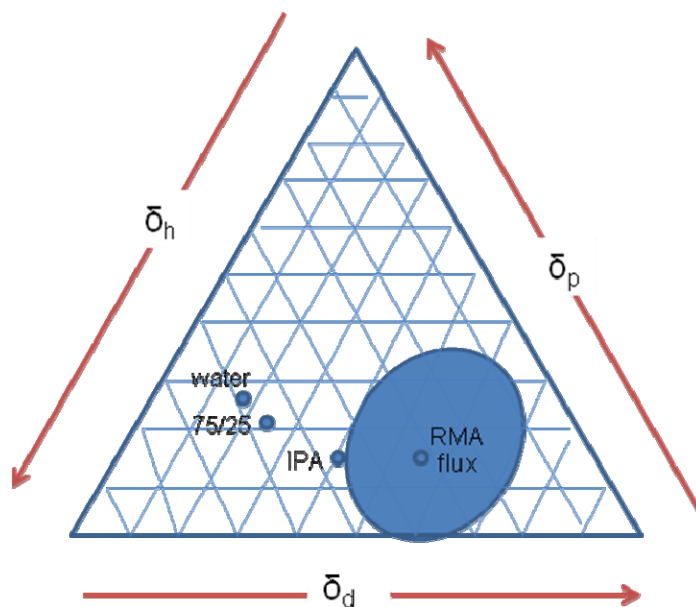
Figure 4 Teas chart comparing the interaction zone of RMA flux to solvents

It is visually obvious that the 75/25 mixture is much more likely to partially dissolve the residue and leave a white residue than the 100% IPA cleaning agent. While IPA is on the

edge of the RMA interaction zone, it may or may not clean the residue without leaving some kind of residue. It is likely the interaction zone of the RMA flux will tighten with higher reflow temperatures. So to, the interaction zones may increase with temperature.

Summary
Determining the Hansen solubility parameters to optimize cleaning can save the electronics industry a lot of money and time. Process development time can be reduced by knowing where your residue(s) of interest lie in relationship to the solvents of Hansen space. Determining where the materials of construction lie relative to proposed solvent can help avoid cleaning agents and process parameters that could degrade the performance or reliability of the products we build. This tool is one every Process Engineer involved in cleaning should use.

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John Burke,AIC book Volume 3, 1984

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