Using Hansen Solubility Parameters for Identifying Safer Solvent Alternatives

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Presentation Topics

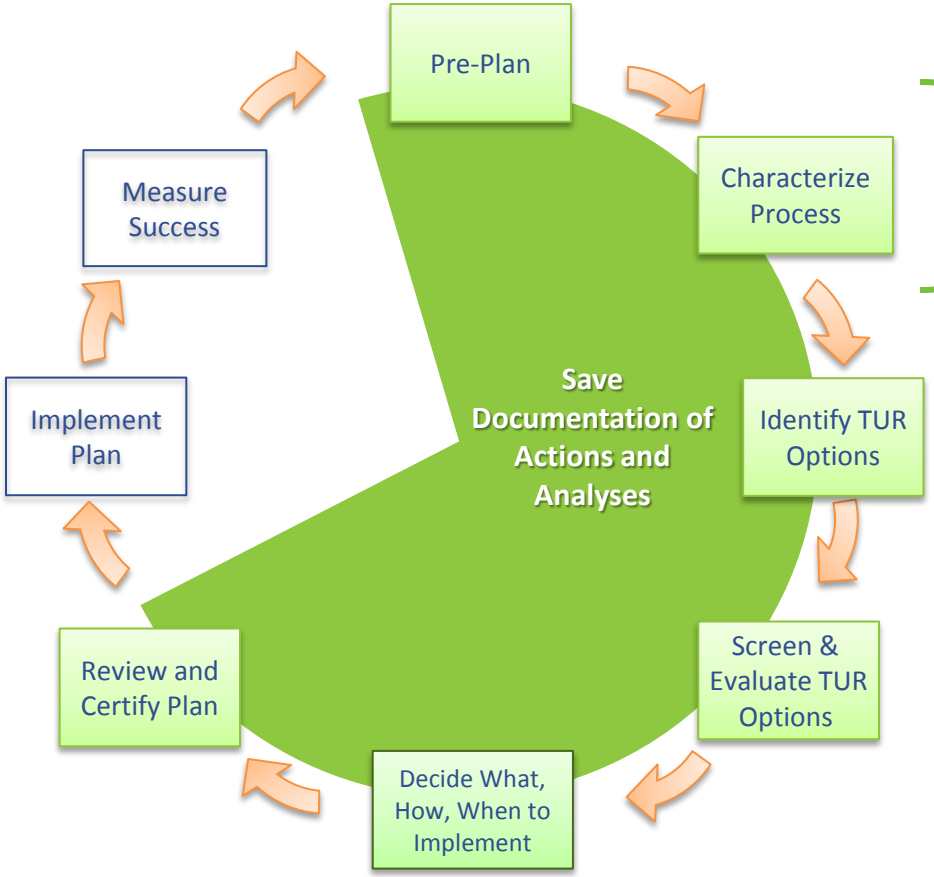
- Overview of Hansen Solubility Parameter Theory
- Hansen Solubility Parameters in Practice Software
- Methodology for identifying safer solvents
- Examples: safer paint strippers and safer contact adhesives

Use of Toxic Solvents

Problem: Solvents with toxic properties are used for numerous applications: adhesives, spot removers, coatings, paint thinners, dry cleaning, nail polish removers, etc.

Solution: The Toxics Use Reduction Institute (TURI) in partnership with UMass Lowell faculty and students are utilizing the Hansen Solubility Parameters in Practice (HSPiP) Software to identify safer solvent and solvent blends to provide safer alternatives to the use of toxic solvents.

The TUR Planning Cycle



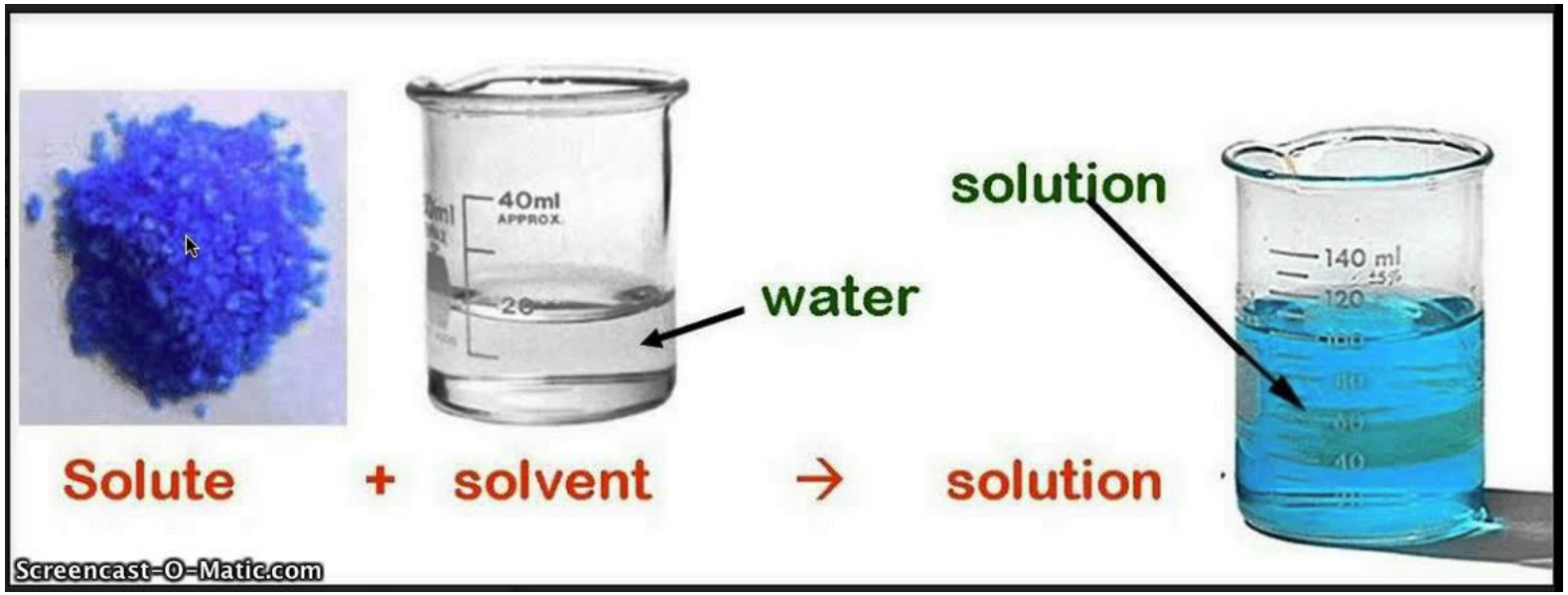
Solvent use identified, for example: toluene, xylene, methanol, acetone, hexane, methyl ethyl ketone (MEK), methylene chloride, etc.

Identify safer solvent options and screen out options that are not financially and technically feasible

Hansen Solubility Parameters - Theory

Creating a Solution

Solute + Solvent = Solution



- Solute is the substance being dissolved, solvent is the substance that dissolves it. Both substances must be similar to dissolve the solute.

Hansen Solubility Parameters

- Hansen Solubility Parameters (HSP) is based on three intermolecular forces, focusing on the specific requirements for solubility.

- Based on “like dissolves like”, the more similar the solvent and solute, the more likely the ability to dissolve the solute.

Inter-molecular forces

Dispersion force (also called London Force)

- The electron cloud surrounding an atom is, on average, evenly distributed around the atom.
- However at a given moment, the electron distribution may not be even.
- This causes a temporary, non-localized (disperse) polarization force.

Polar force (also called dipole-dipole force)

- Dipole moments are created when atoms of the same molecule have different electronegativities.
- This causes a permanent polarization, from a specific, fixed location.

Hydrogen bonding force

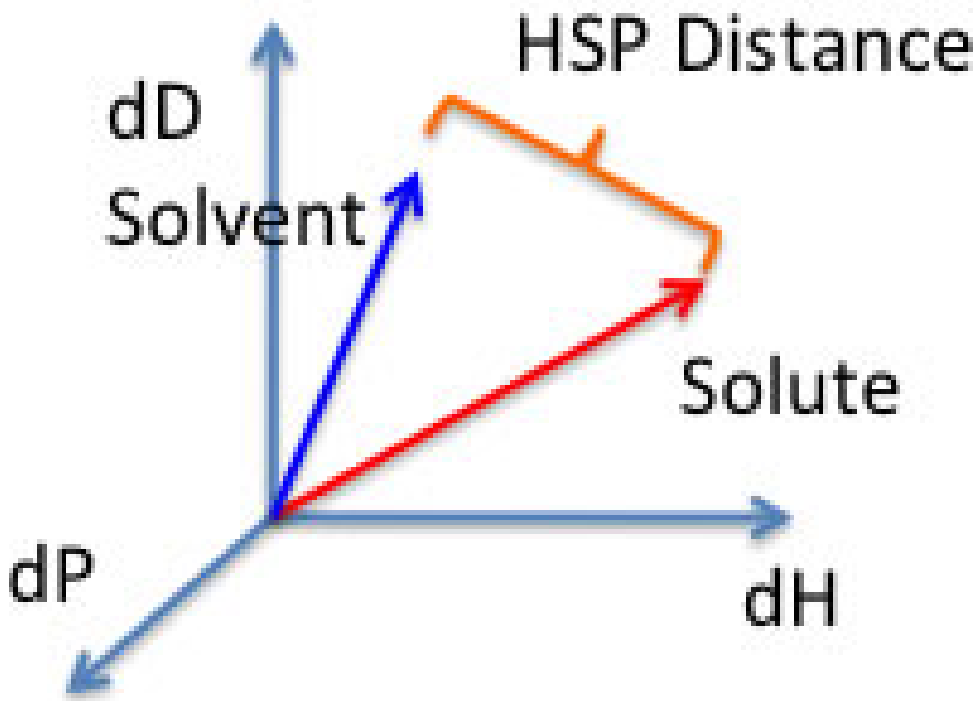
- Occurs in molecules containing highly electronegative elements (i.e. F, O, or N) directly bound to hydrogen.
- This force exists between hydrogen atoms and other atoms present in adjacent molecules.

Strength of forces (on average): hydrogen bonding > polar > dispersion

Hansen Solubility Parameters in 3D Space

The solvent and solute can be characterized in 3 dimensional space using the three Hansen Solubility Parameters.

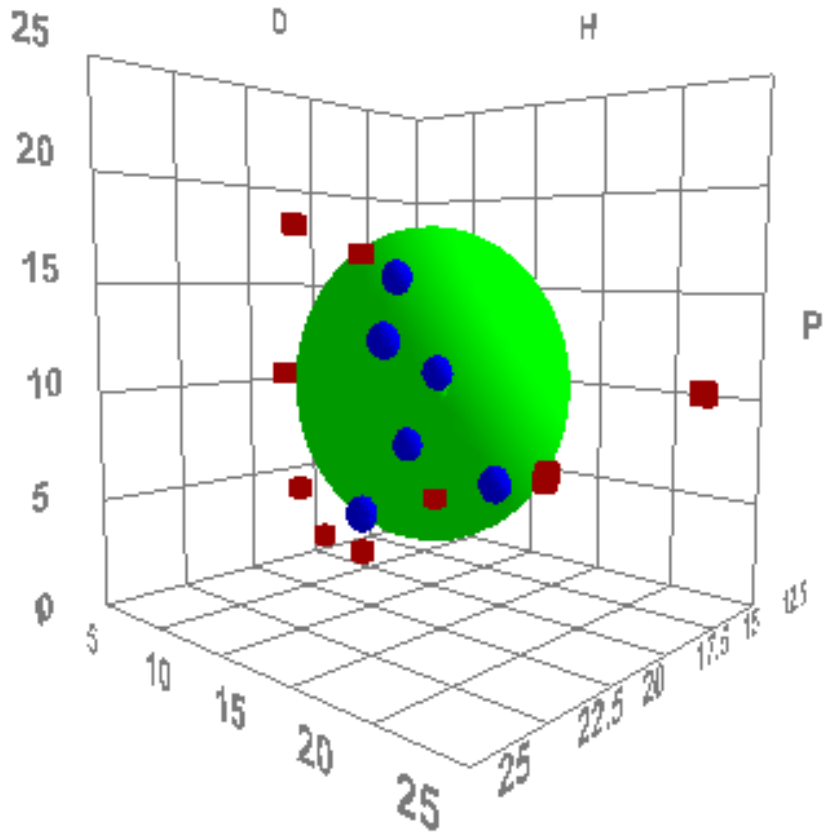
δd – Dispersion force
δp – Polar force
δh – Hydrogen-bonding force



"Like dissolves like" – the smaller the HSP distance between the solvent and solute, the more likely the solute can be dissolved.

Source for figure: https://pirika.com/NewHP/PirikaE/polymer-solvent.html

“Like dissolves like”

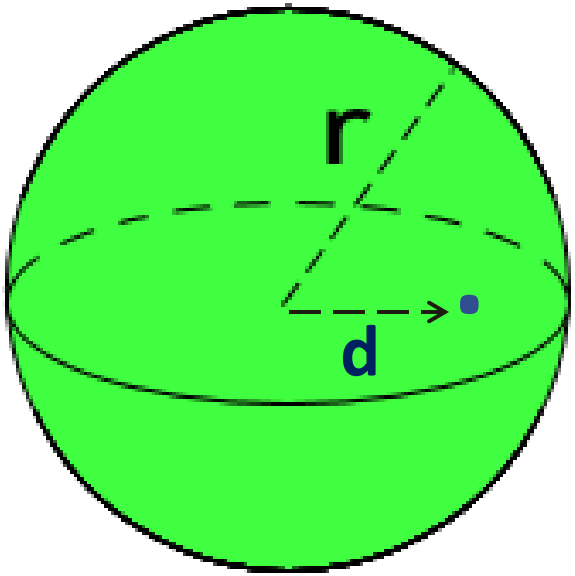


Green Sphere: 3D HSP space in which a solvent will dissolve the solute (i.e. polymer)

Blue Dots: solvents that will dissolve the solute (inside or on surface of the green sphere)

Red Cubes: solvents that will not dissolve the solute (outside of the green sphere)

Solute
HSP
sphere



The RED number is the Relative Energy Difference and is calculated as follows:

$$\text{RED} = \frac{\text{distance (d) of your solvent (or solvent blend) to target HSP}}{\text{radius (r) of the target HSP Sphere for the solute}}$$

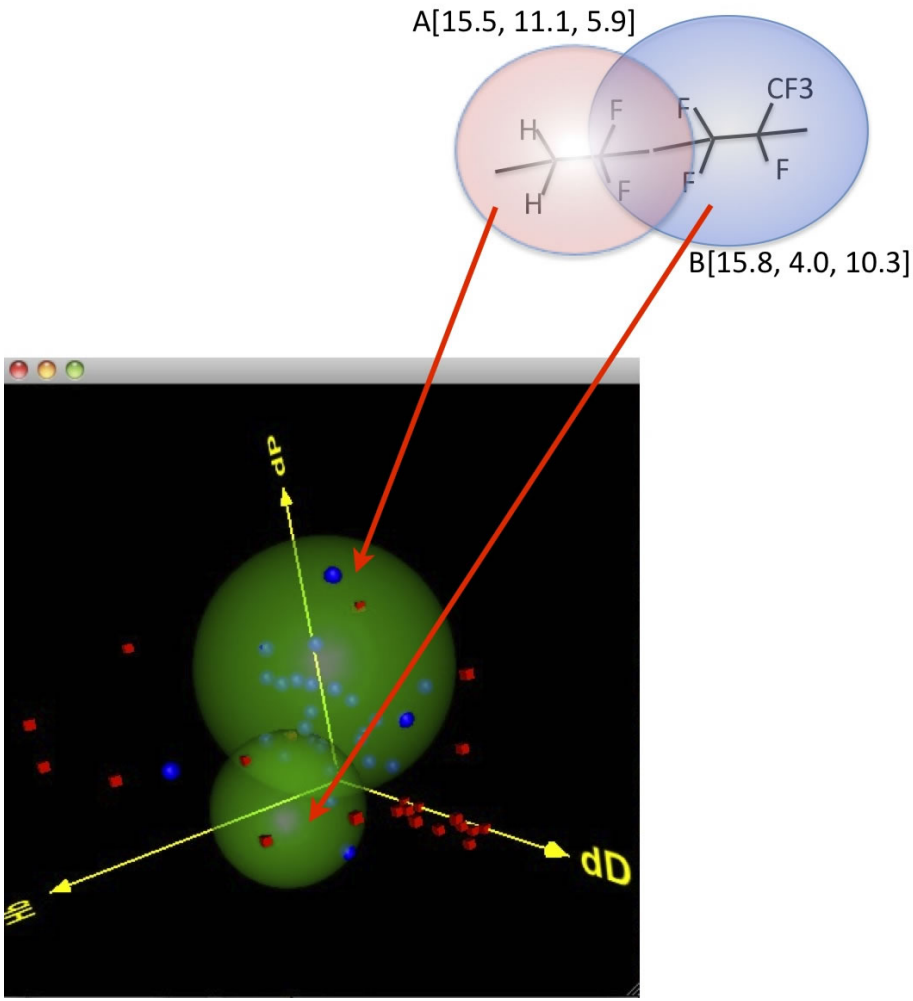
A perfect solvent has a RED of 0.

A solvent just on the surface of the Sphere has a RED of 1.

If RED > 1 then incompatible, if RED < 1 then compatible.

Relative RED values are useful. If you have a solvent of RED 0.2 and another of 0.4 you know (a) that neither is perfect and (b) that the first one is better.

Applications with Multiple Solutes

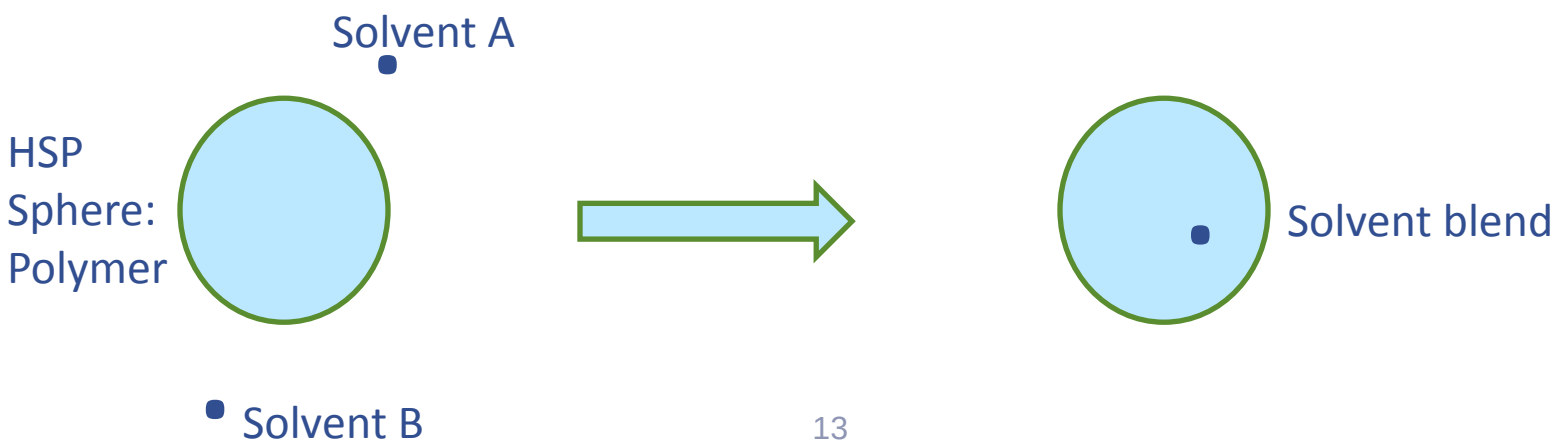


Junction Value - the sweet spot which would define the solvent HSP values most likely to interact well with each of the solutes (i.e. polymers).

Source: https://www.pirika.com/NewHP/PirikaE2/Sphere-Dbl.html

Solvent Blends - Example

Solvent	Volume %	D	P	H
Solvent A	50%	12	4	21
Solvent B	50%	18	11	3
Solvent Blend		15	7.5	12



Hansen Solubility Parameters in Practice (HSPiP) Software

HSPiP 4th Edition 4.1.07 Licensed to: TURI Group License

File Dist. Diff. Adh./Visc. Force Fit Teas HPLC IGC GC Temp. Evap. FindMols Grid DPC PowerTools Help

GRAS

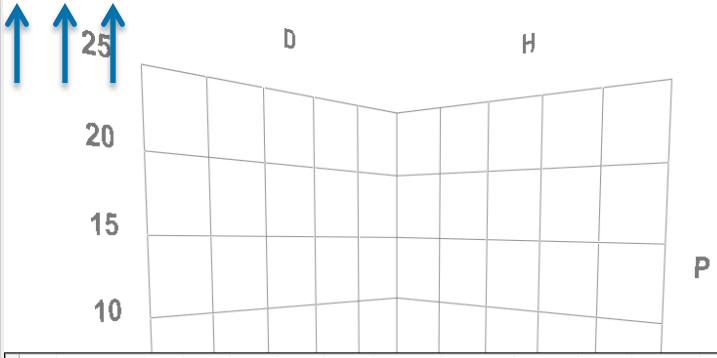
Double-Click Radius 4.0 ESC Alert Limit MVC GA "Inside" 1

Total Compounds = 79

Both only Hide unused SRC SSel D/A Search_Text Master 10K MyDB

No.	Solvent	δD	δP	δH	Score	RED	MVol
1	Acetic Acid	14.5	8	13.5	-	-	57.6
2	Aconitic Acid	17.4	8.8	16.6	-	-	124.8
3	Adipic Acid	17.1	10	16.3	-	-	133.9
4	l-Ascorbic Acid	18	11.7	25.5	-	-	124.8
5	Ascorbyl Palmitate (Palmitoyl l-Ascorbic)	17	9.1	11.1	-	-	382.8
6	Benzoic Acid	20	6.9	10.8	-	-	112.4
7	Biotin	18.2	15.9	15.2	-	-	193.2
8	Butylated Hydroxyanisole (Bha)	17.6	4.8	7.9	-	-	182.1
9	Caffeine	19.5	10.1	13	-	-	157.9
10	Caprylic Acid	15.7	3.3	8.2	-	-	162.1
11	Carbon Dioxide	15.7	6.3	5.7	-	-	37.2
12	Carboxymethyl Cellulose	18.2	17.7	18	-	-	100
13	Carnauba Wax	16.9	1.2	5.5	-	-	816
14	Carotene (Beta - Carotene)	17	2.5	4	-	-	587.3
15	Cellulose Acetate	18.3	16.5	11.9	-	-	100
17	Cholic Acid	18.3	4.6	10.8	-	-	369.8
16	Citric Acid	17.5	8.7	20.6	-	-	127.7
17	Clove Oil (As Eugenol)	19	7.5	13	-	-	154
18	Coconut Oil (As Lauric Acid)	16	3	7	-	-	228.2
19	Desoxycholic Acid	18.4	3.6	10	-	-	368.1
21	Diacetyl	15.7	5.1	6.8	-	-	87.8
23	Erythorbic Acid (d-Isoascorbic Acid)	18	11.7	25.5	-	-	124.8
24	Ethyl Formate	15.5	8.4	8.4	-	-	80.9
25	Formic Acid (Packaging)	14.6	10	14	-	-	37.9
26	l-Glutamic Acid	16.8	10.5	17.2	-	-	117.2
27	Glycerin And Glycerides	17.4	11.3	27.2	-	-	73.4
28	Glycocholic Acid	18.2	6.2	11.8	-	-	403.3
29	Glycyrrhiza	18	12	12	-	-	800
30	Hydrogen Peroxide	15.5	12.2	42.7	-	-	23.6
31	Inositol	18	12	20	-	-	114.6
32	Invert Sugar	18	12	20	-	-	100
33	Isopropyl Citrate (As Monoglyceride)	16.8	8.4	17.4	-	-	181.5
35	Lactic Acid	17	8	24	-	-	76.7

δP v δH δH v δD δP v δD



All chemicals

No.	Name	δD	δP	δH	MVol	CAS	SMILES	Formula	MWt	Density	MPt	BPt	RI	VP@25	RER	TEa	TEm	LogOHR	MIR	LogKow
1	Acetaldehyde	14.7	12.5	7.9	56.5	75-07-0	CC([H])=O	C2H4O	44.05	0.788	-123	21	1.328	900	2338.54	0.00081	-0.7224	-10.8	6.539	-0.34
2	Acetaldoxime	16.3	4	20.2	61.2	107-29-9	C/C=N/O	C2H5NO	59.07	0.965	47	115	1.415	(13.04)	(37.84)	-	-	-11.66	(-99999...	-0.13
3	Acetamide	17.3	18.7	19.3	59	60-35-5	CC(N)=O	C2H5NO	59.07	0.998	81	221	(1.405)	0.02	0.041	0.00057	-0.7143	(-99999...	(-99999...	-1.26
4	Acetanilide	20.6	14.4	13.5	131	103-84-4	CC(=O)NC1...	C8H9NO	135.17	(1.089)	115	304	1.53	(0.000)	0.001	0.0005	-0.7143	(-10.868)	(-99999...	1.16
5	Acetic Acid	14.5	8	13.5	57.6	64-19-7	CC(O)=O	C2H4O2	60.05	1.049	17	118	1.37	15	39.654	0.00059	-0.7316	-12.13	0.685	-0.17
6	Acetic Anhydride	16	11.7	10.2	95	108-24-7	CC(OC(C)=...	C4H6O3	102.09	1.082	-73	140	1.389	5.273	23	0.00068	-0.7301	(-99999...	(-99999...	0.27
7	Acetone	15.5	10.4	7	73.8	67-64-1	CC(C)=O	C3H6O	58.08	0.791	-95	56	1.356	231.515	560	0.0008	-0.701	-12.65	0.356	-0.24
8	Acetonecyanhydrin	16.6	12.2	15.5	91.8	75-86-5	CC(C)(O)C#N	C4H7NO	85.11	0.928	-20	171	1.398	0.827	3.492	0.00063	-0.7143	(-12.434)	(-2.761)	(-0.55)
9	Acetonemethyloxime	14.7	4.6	4.6	96.7	3376-35-0	CC(=NOC)C	C4H9NO	87.12	(0.816)	(-46)	(66)	(1.395)	89.517	398.189	-	-	(-99999...	(11.773)	(2.18)
10	Acetonitrile	15.3	18	6.1	52.9	75-05-8	[H][C@@][(...	C2H3N	41.05	0.786	-44	82	1.342	86.567	230	0.00077	-0.7187	-13.58	(-2.007)	-0.34
11	Acetophenone	18.8	9	4	117.4	98-86-2	CC(C1=CC=...	C8H8O	120.15	1.028	20	202	1.534	0.304	1.642	0.00057	-0.7094	-11.56	(-99999...	1.58
12	Acetoxime	16.3	3.7	10.9	80.2	127-06-0	CC(=NO)C	C3H7NO	73.09	0.901	61	135	(1.446)	(4.108)	(14.41)	-	-	(-99999...	(1.939)	0.12
765	1-Acetoxy-1,3-Butadiene	16.1	4.4	8.3	118.4	1515-76-0	CC(=O)OC=...	C6H8O2	112.13	0.945	(-59)	(131)	1.469	(8.566)	(47.20)	-	-	(-9.876)	(10.771)	(1.35)
1116	Acetyl Salicylic Acid	19	6.9	9.7	149.4	50-78-2	CC(=O)OC1...	C9H8O4	180.16	(1.267)	141	291	1.562	(0.000)	(0.000)	-	-	(-99999...	(-99999...	1.19
785	2-Acetyl Thiophene	19.1	12.2	9.3	108	88-15-3	CC(C1=CC=...	C6H6OS	126.18	1.168	10	214	1.565	(0.706)	(3.509)	-	-	(-11.337)	(-99999...	1.25
1219	Acetyl Triethyl Citrate	16.6	3.5	8.6	279.9	77-89-4	CCOC(=O)C...	C14H22O8	318.32	1.137	(2)	(326)	1.439	(0.000)	(0.000)	-	-	(-11.061)	(-1.580)	(1.33)
17	Acetylacetone	16.1	10	6.2	103.1	123-54-6	CC(CC(C)=O...	C5H8O2	100.12	0.957	-23	137	1.447	9.302	44.114	0.00056	-0.7495	-11.94	1.006	0.4

Spherical D-Min 15 P-Max 25 H-Max 25

10,000+ chemicals (solvents) in the HSPiP database with associated chemical properties: HSP, Density, Mvol, Bpt, Mpt, RER, vapor pressure, etc.

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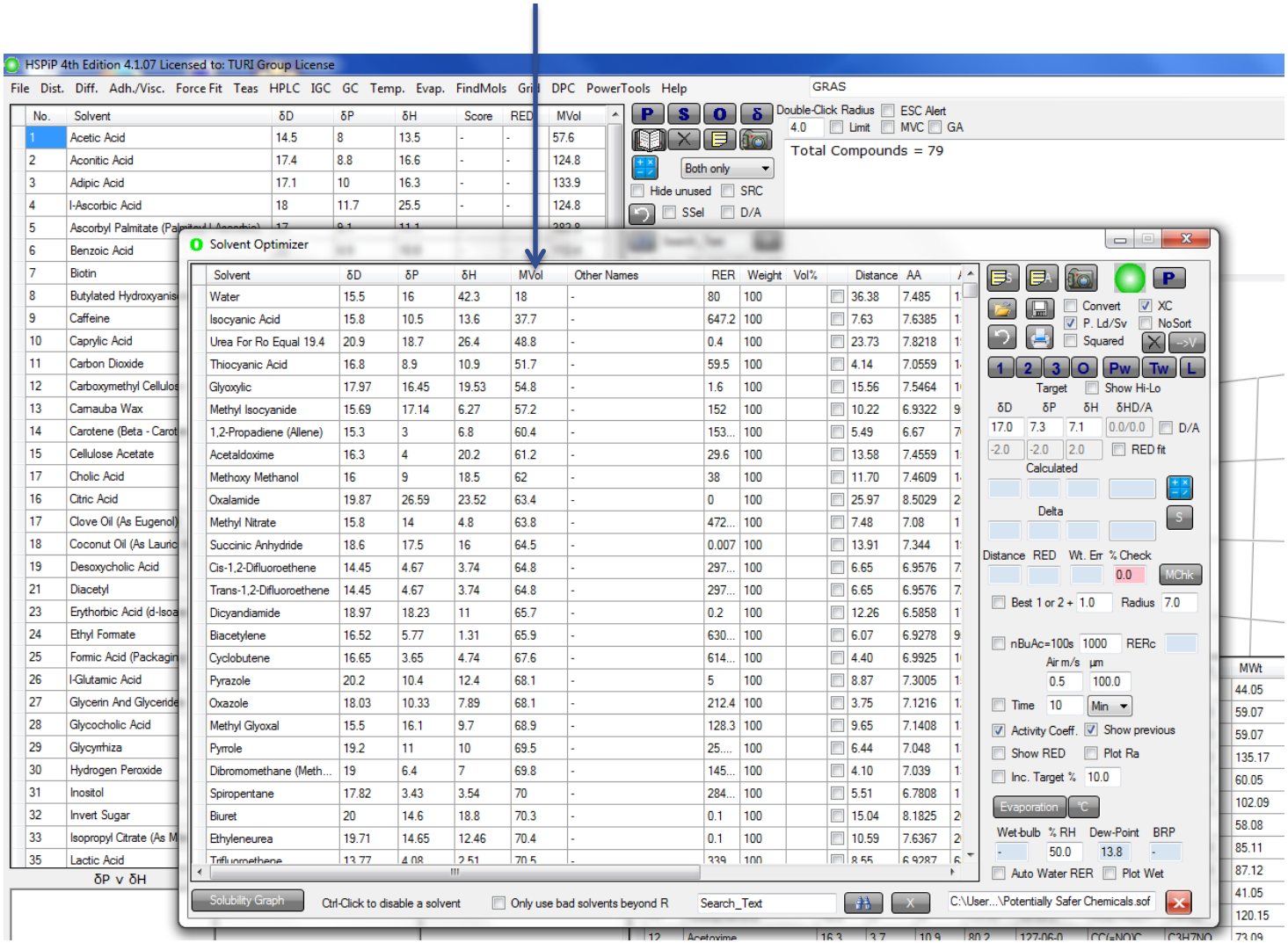

Screen out chemicals with undesirable properties for a particular application

- Sort by parameter of interest: For example, select the column "Mvol" (Molecular Volume)

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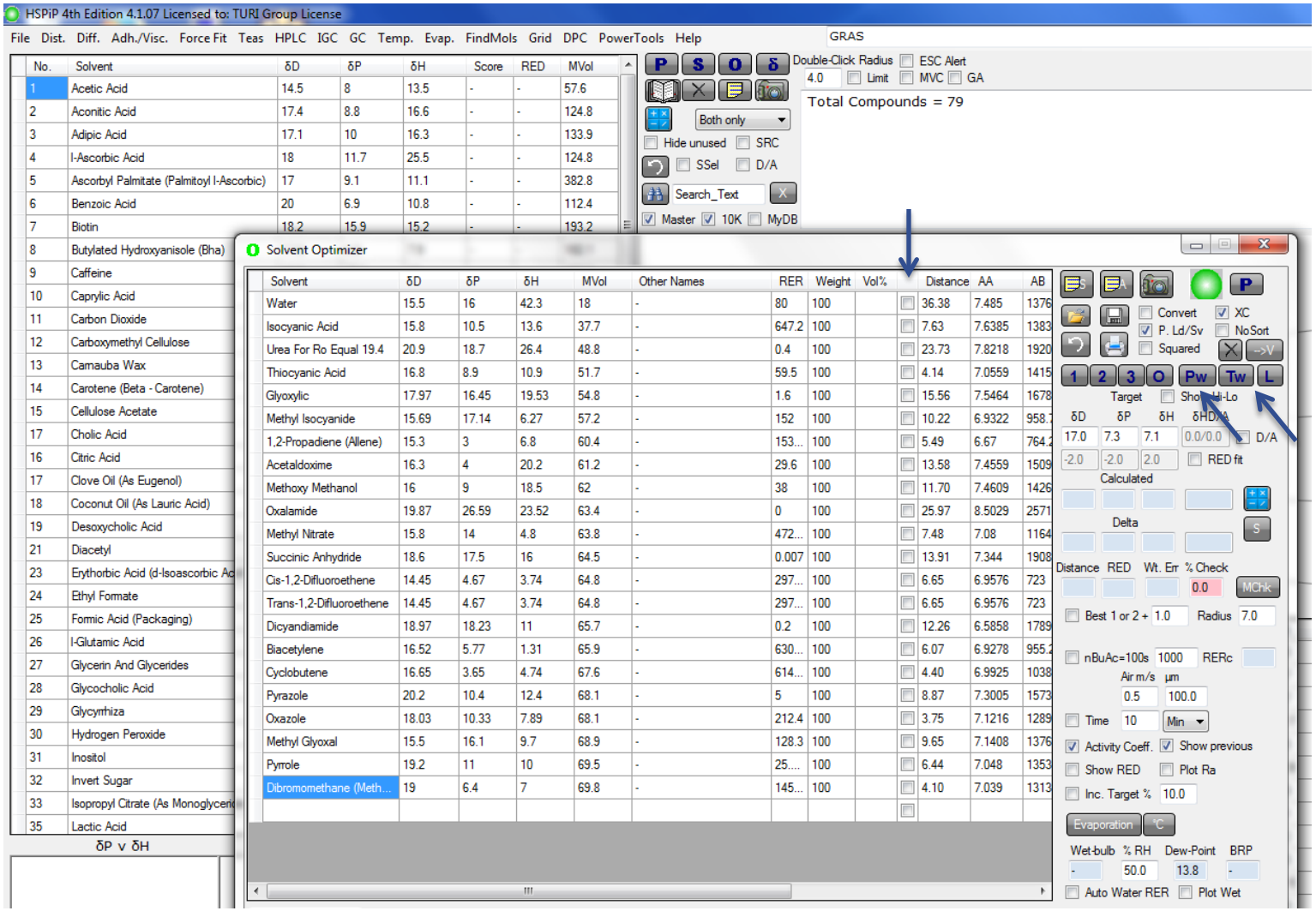

Determine solvent blends using an HSP target value

- Check off the desired solvents
- Select the “Pw” (pairwise) button (or “Tw” button for triplet wise combinations)

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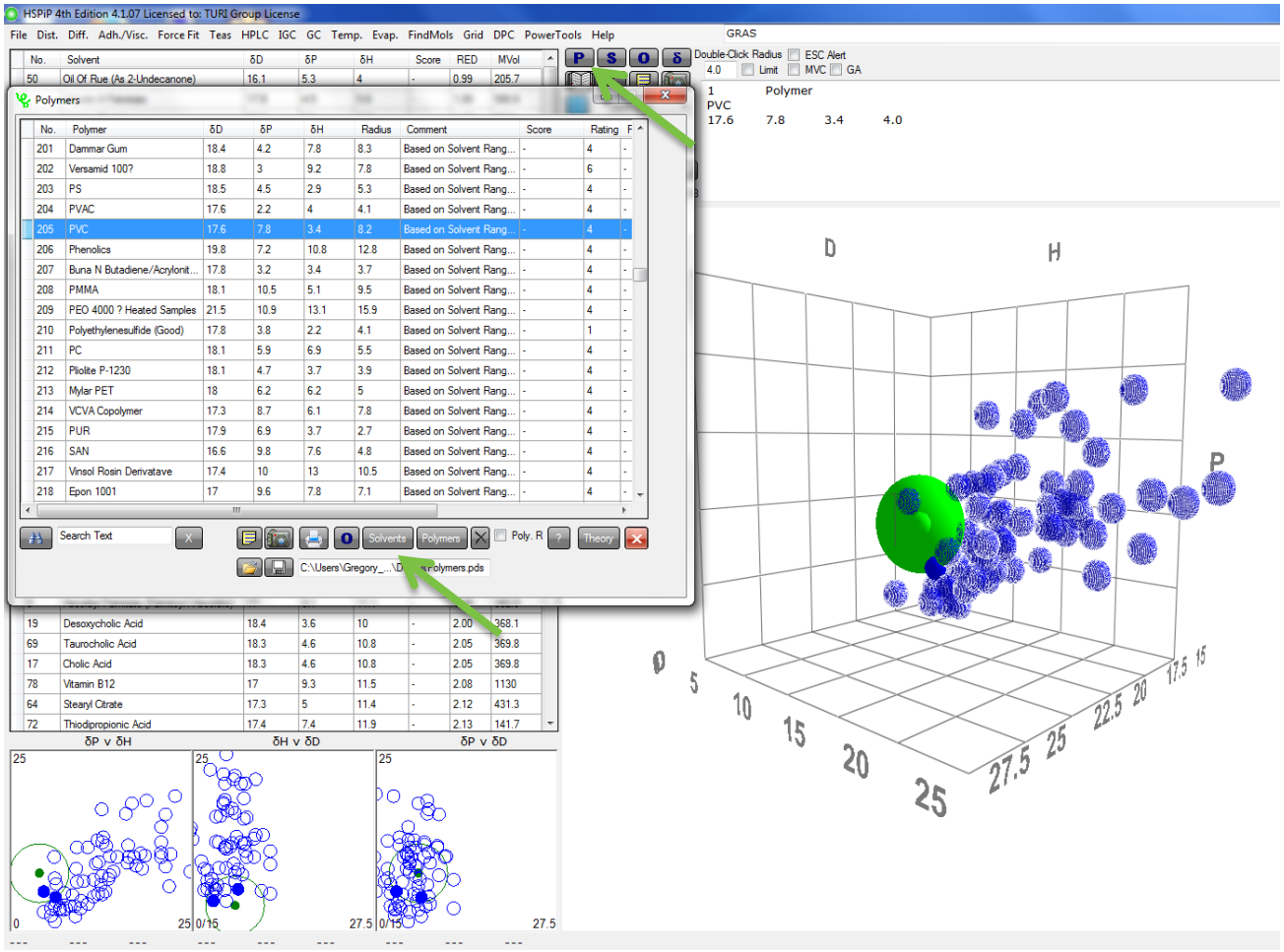
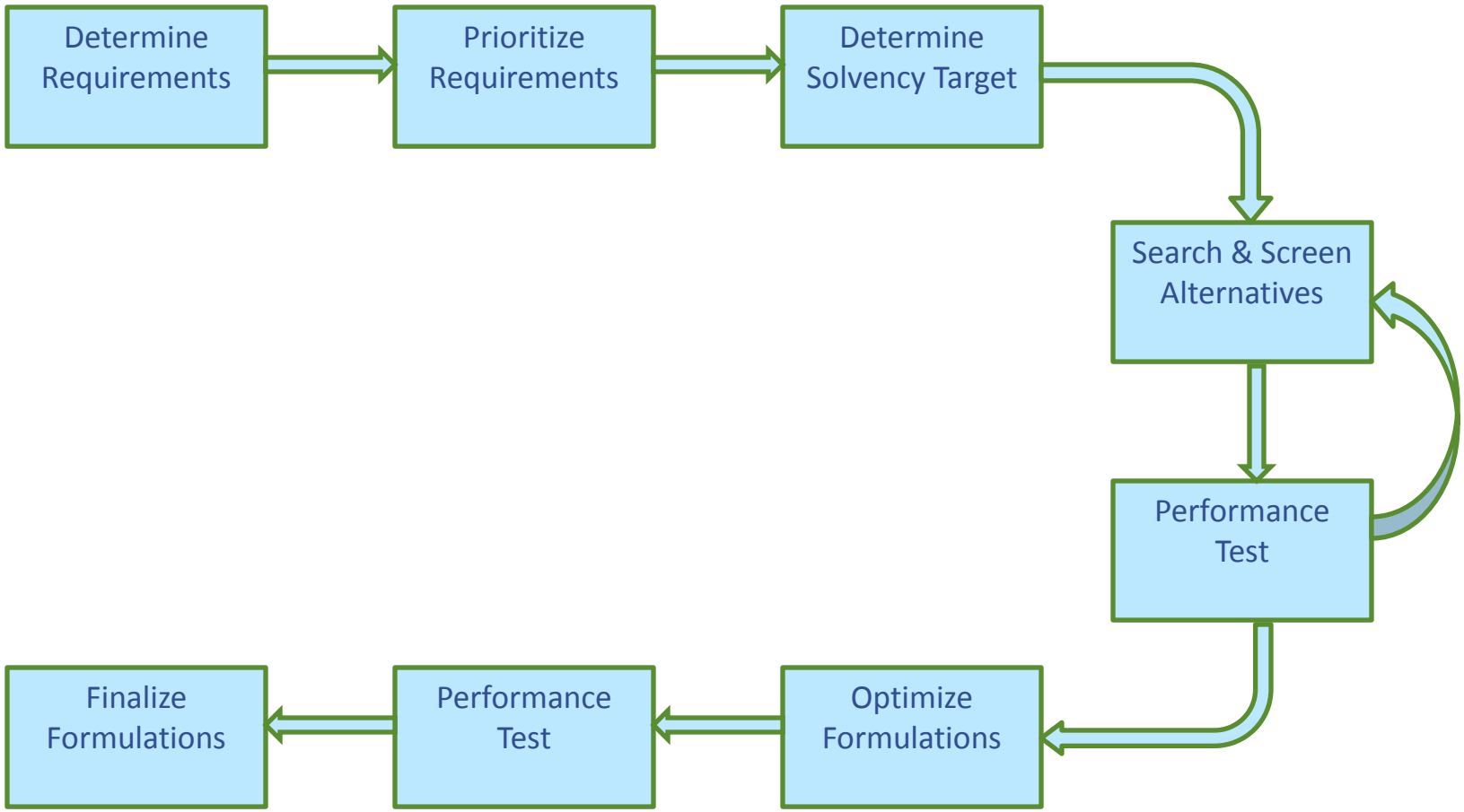


Find solvents that will dissolve a certain polymer

- Open Polymer form (600+ polymers)
- HSP green sphere for selected polymer and selected solvents (blue dots) shown in 3D space, solvents sorted by RED value

Safer Solvents Identification and Evaluation



TURI Examples

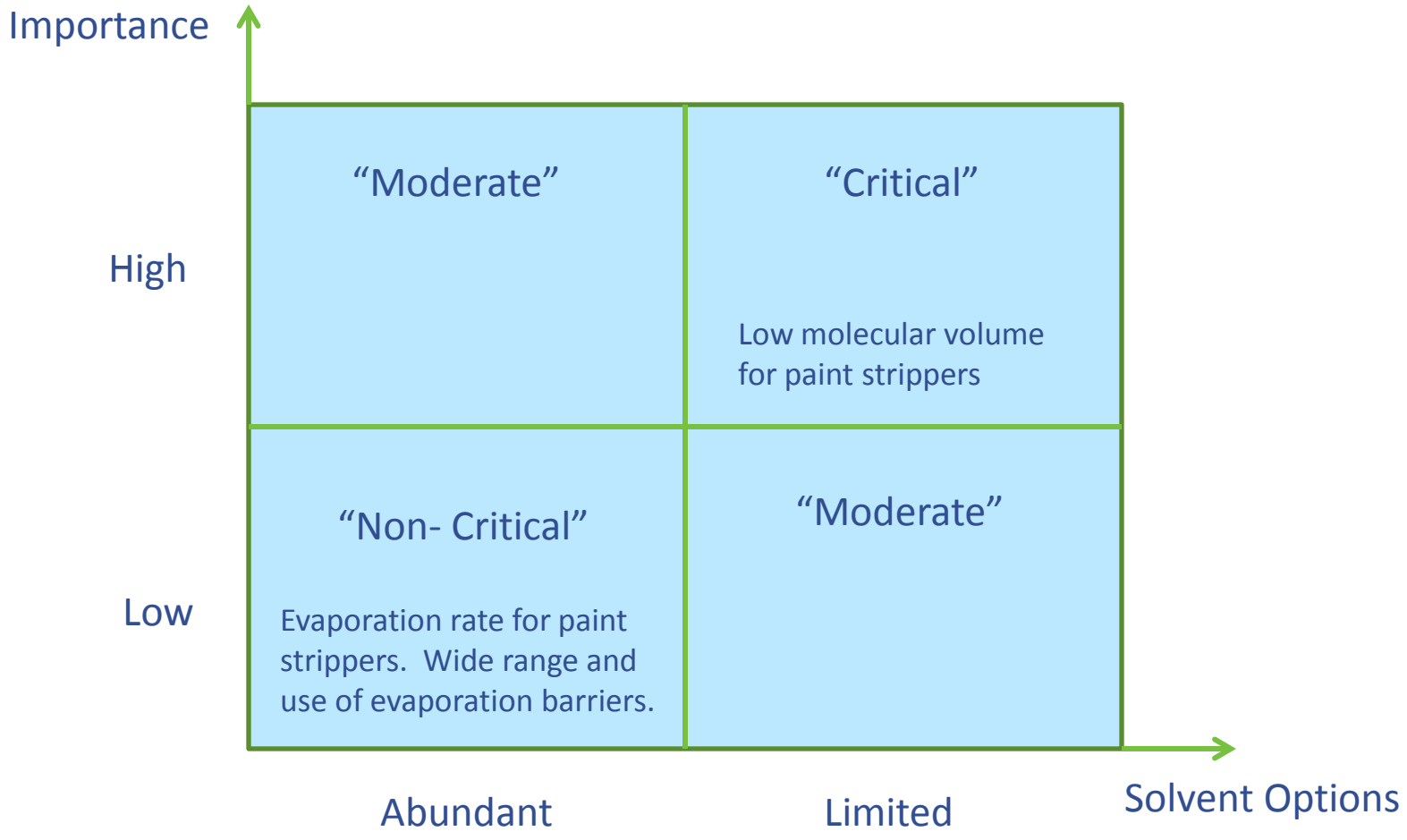
Application	Toxic Solvent(s)	Solute
Paint stripping	Methylene chloride	Various paints/coatings
Contact adhesives	Hexane and toluene	Rubber and resin

Determine Requirements

Categories	Examples
Cost	$ per pound, $ per gallon, etc.
Performance (requires testing to evaluate)	Material compatibility, solutes to dissolve, time to dissolve, strength requirements, etc.
Physical properties (inherent to individual solvents)	Evaporation rate, color, specific gravity, odor, etc.
Regulatory/environmental	HAPs free, VOC content, etc.

Sources: literature search, industry partners, etc.

Prioritize Requirements



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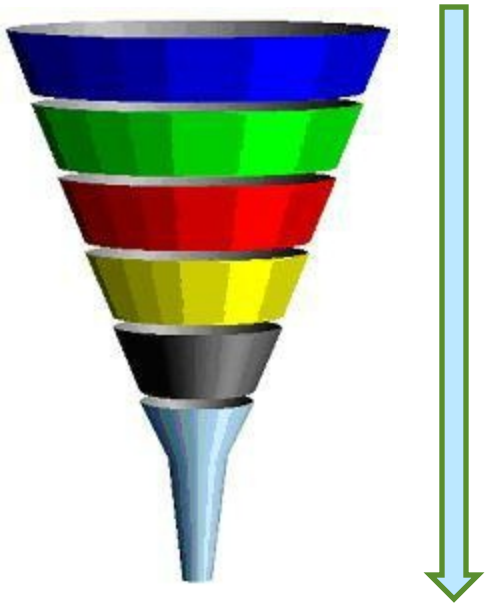
Search and Screen Alternatives

- Thousands of different solvents to consider
- Numerous solvent requirements to consider
- Binary, ternary, and quaternary blend possibilities
- Iterative process: initial screen, revised screen, etc.
- Use of software tools to assist: Hansen Solubility Parameters in Practice (HSPiP), MS Excel

10,000+ solvents



2 – 4 solvents in final solvent blend

Search and Screen Alternatives

Example:
Specific gravity requirement of 0.80 to 0.90

Initial screen:
Look for solvents with specific gravity of 0.80 to 0.90

Revised screen:
Look for solvents with specific gravity of 0.70 to 1.0.
For example: one solvent at 50% with specific gravity of 0.75 and another solvent at 50% with specific gravity of 0.95

Subsequent revised screen:
Look for solvents with specific gravity of 0.5 to 1.4.
For example: one solvent with specific gravity of 0.80 at 95%, and one solvent with a specific gravity of 1.4 at 5%.

Determine Solvency Target

Target HSP Parameters – Paint Stripper Example

1) Based on target chemical D, P, H value

methylene chloride: 17, 7.3, 7.1

However, the chemical is used as part of a solvent blend.

2) Based on target product (solvent blend)

Paint Stripper product formulation X (low methylene chloride content, methanol, toluene, and acetone)

Paint Stripper product formulation Y (high methylene chloride content methanol, and toluene)

However, the products may not be optimized for the target application.

Target HSP Parameters – Paint Stripper Example

Create an model in MS Excel based on polymer HSP values included in the HSPiP database. The model contains HSP values for 59 different types of paints/coatings from various manufacturers (including alkyd, amino resin, cellulose acetate, epoxy, polyacrylate, polyamide, polyester, polyurethane, polyvinylbutyral, chlorinated polypropylene, polyvinylacetate, shellac, silicone, and methacrylate).

Polymer/Product Name	D	P	H	Radius	Polymer Type
Desmophen 1100	16	13.1	9.2	11.4	Polyester
Epikote 828	23.1	14.6	5	20.5	Epoxy
Desmolac 4200	18.7	9.6	9.9	8.2	Polyurethane

Target HSP Parameters – Paint Stripper Example

For each solvent or solvent blend that you enter into the Excel model, it will provide the following output:

% Effectiveness: the percentage of the 59 coatings that the solvent blend will dissolve.

Average distance: the average distance from the HSP sphere center for each of the 59 coatings.

Create HSP Spheres for Contact Adhesives

No existing polymer HSP data for specific rubber and resins used in target contact adhesives.

Contact adhesive 1: Rubber A, Resin B
Contact adhesive 2: Rubber C, Resin D

Add polymer samples and solvent into test tubes

Create HSP Spheres for Contact Adhesives

Repeat for 20 – 30 different solvents

After 24 hour dwell time, record results.

Score = 1 (polymer dissolves, inside sphere)
Score = 0 (polymer does not dissolve, outside sphere)

Enter values into HSPiP software to create the 3D HSP sphere

HSP Sphere for Rubber X

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File Dist. Diff. Adh./Visc. Force Fit Teas HPLC IGC GC Temp. Evap. FindMols Grid DPC PowerTools Help

Test Solvents ITW Sphere NEO with scores oct 27 2015 final

No.	Solvent	δD	δP	δH	Score	RED	MVol
7	Acetone	15.5	10.4	7	0	1.672	73.8
10	Acetonitrile	15.3	18	6.1	0	2.767	52.9
102	n-Butyl Acetate	15.8	3.7	6.3	0	1.036	132.6
156	Chloroform	17.8	3.1	5.7	1	0.283	80.5
9999	DBE	16.2	4.7	8.4	0	1.158	135.3
267	Diethylene Glycol Monobutyl Ether	16	7	10.6	0	1.761	170.4
303	Dimethyl Sulfoxide	18.4	16.4	10.2	0	2.619	71.3
306	1.4-Dioxane	17.5	1.8	9	1	0.978	85.7
16615	Dipropylene Glycol Monomethyl Ether	16.1	6.7	10.4	0	1.651	153.9
325	Ethanol 99.9%	15.8	8.8	19.4	0	2.991	58.6
326	Ethanolamine	17	15.5	21	0	3.738	60.3
328	Ethyl Acetate	15.8	5.3	7.2	0	1.106	98.6
417	Hexane	14.9	0	0	0	1.826	131.4
481	MEK	16	9	5.1	0	1.327	90.2
456	Methanol	14.7	12.3	22.3	0	3.588	40.6
464	Methyl Acetate	15.5	7.2	7.6	0	1.340	79.8
521	N-Methyl Pyrrolidone	18	12.3	7.2	0	1.778	96.6
524	Methylene Dichloride	17	7.3	7.1	1	0.910	64.4
9999	N Butyl Acetate 50%, Tce 50%	17	4.7	3.1	1	0.000	0
592	PMA	15.6	5.6	9.8	0	1.580	137.1
570	2-Propanol	15.8	6.1	16.4	0	2.476	76.9
584	Propylene Carbonate	20	18	4.1	0	2.870	85.2
615	TCE	18.3	5.7	0	1	0.996	102.8
617	Tetrahydrofuran	16.8	5.7	8	1	0.918	81.9
637	Toluene	18	1.4	2	1	0.704	106.6
9999	Toluene 50%, Methylene Dichloride 50%	17.5	4.3	4.6	1	0.267	100
1059	Undecane	16	0	0	0	1.645	212.2

P S O δ Double-Click Radius ESC Alert

6.0 Limit MVC GA

Both only

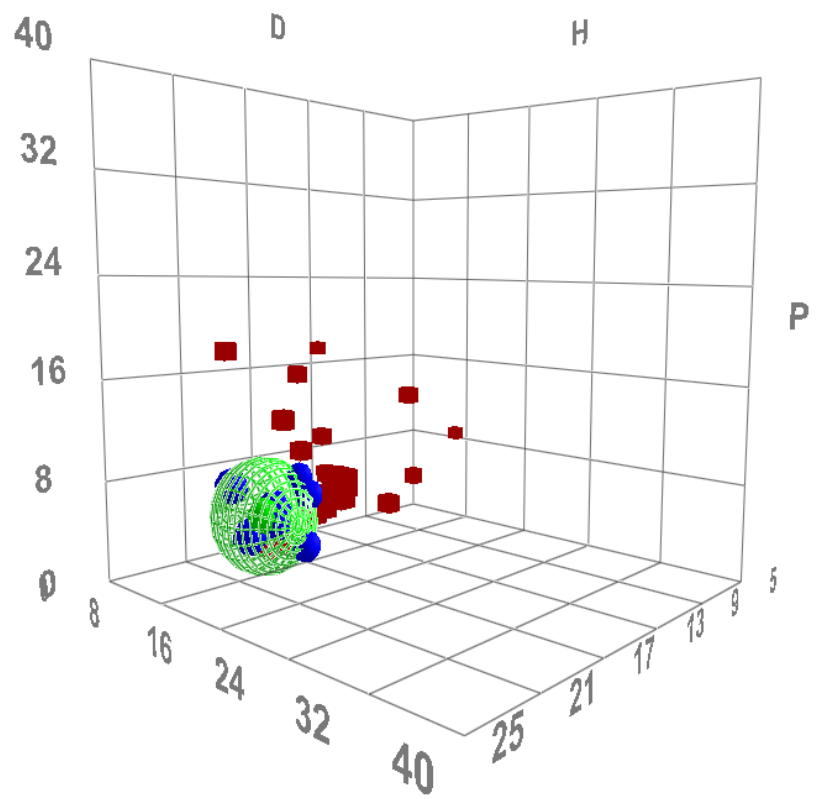
Hide unused SRC

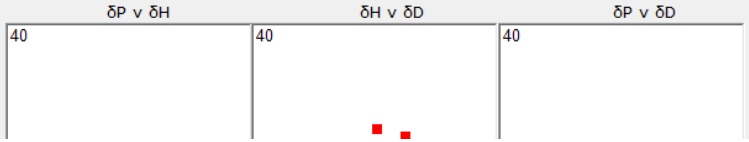
SSel D/A

Search_Text X

Master 10K MyDB

In= 8 Out= 19 Total= 27
D= 18.11 P=3.76 H=4.55
Tot = 19.05
R= 5.0
Fit= 1.000
Core= ±[0.40, 1.10, 0.60]
Wrong In= 0





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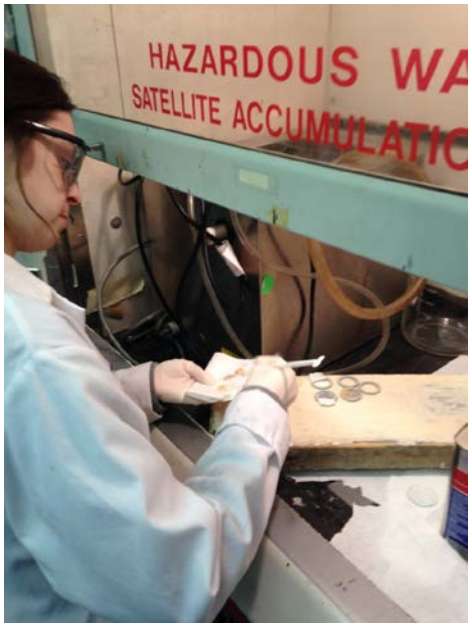
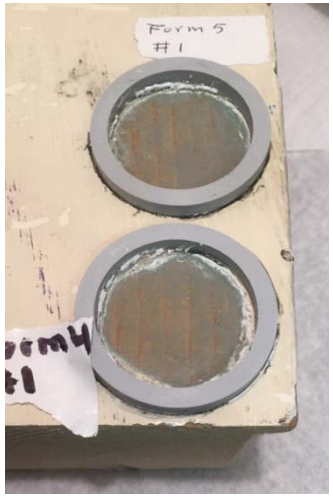
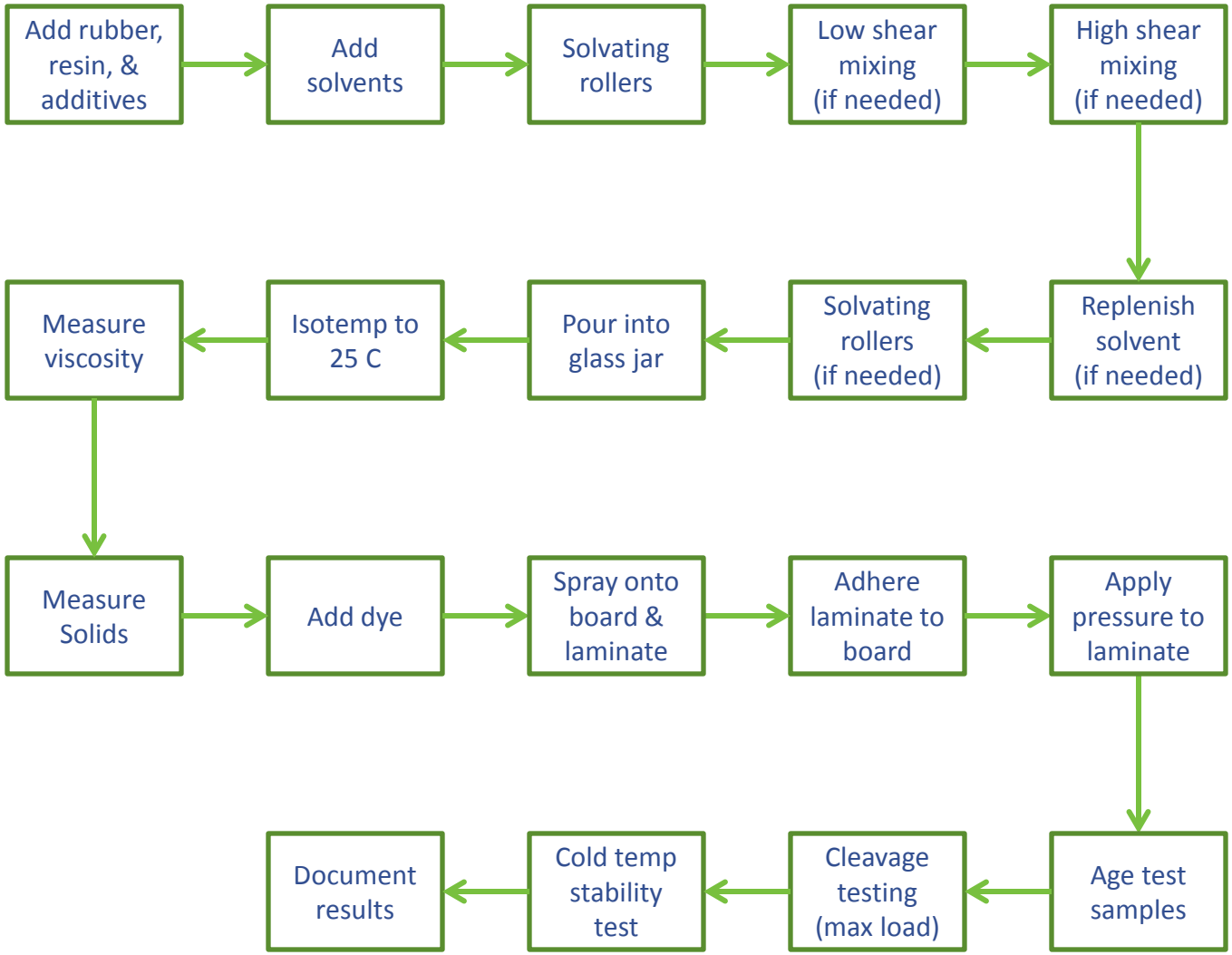
Performance Test: Paint Stripper





- Glue a ring gasket on the test area of the test vehicle
- Use a clean pipette to add approx. 1.5 ml of solvent blend inside the ring gasket
- Cover the gasket with lab watch glass
- Start timer to initiate dwell time
- Record initial cracking time
- After dwell time: remove watch glass
- Lightly scrape off coating residue with plastic scraper & record substrate exposure

Performance Test: Contact Adhesive



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Optimize Formulations

- Narrow down to a limited number of preferred target solvents
- Determine key criteria
- Develop MATLAB scripts with constraints
- Utilize MATLAB to optimize the formulations based upon key criteria

Contact adhesive MATLAB Script includes the following:

- Cost ($/L)
- VOC level (g/L)
- Density
- HSP parameters (D, P, H)
- HSP distance from the polymer
- HSP distance from the resin
- Whether it falls in the solubility sphere
- Include 7 target solvents

Finalize Formulation

Select the final formulation that meets all requirements, passed all performance tests, and has been optimized.

Contact

Questions about:

- Hansen Solubility Parameters
- Hansen Solubility Parameters in Practice (HSPiP) software
- Identifying and evaluating safer solvents

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