

Controlled Environments™

WWW.CEMAG.US

SEPTEMBER 2013

Solving the Solvent Substitution Puzzle

- IEST's First Nano Facility RPs
- Compounding Pharmacy Design Issues
- Touch Technology for Cleanroom Controls
- Installing Test Chambers
- ISPE Product Showcase

Solving the Solvent Substitution Puzzle

Trade inefficient trial-and-error testing for a systematic approach to solvent substitution and blends.

Darren L. Williams, Ph.D
Associate Professor of Chemistry
Sam Houston State University
Huntsville, Texas

The cleaning chemist's lament:

*First, they took my CFCs;
Then, controlled my VOCs.
Now, they want my 225.
Will my company survive?*

This article outlines a systemic evaluation process for making solvent substitution decisions. Environmental, safety, and health information is extracted from the MSDS and is considered along with effectiveness criteria. The heart of the process is the effectiveness evaluation that is based upon the Hansen solubility parameters. The theory and use of HSPs are illustrated in an example of solvent selection and solvent blending to remove a silicone-based high-vacuum grease.

Although there are many technical subject matter experts (SMEs), line managers, and industry personnel who are tasked with solvent selection responsibilities, there are also other industrial sectors¹ that are dealing with solvent substitution requirements (e.g. refrigeration, air conditioning, foam blowing agents, fire suppression, explosion protection, aerosols, sterilants, tobacco expansion, adhesives, coatings, and inks).

Industrial chemists and engineers have an impressive track record of “rising to the occasion” with respect to the increasing restrictions on acceptable process solvents. They have responded with continual improvement to remove ozone-depleting (OD) solvents, to reduce hazardous air pollutants (HAPs), to reduce volatile organic carbon (VOC), to avoid solvents with a high global warming potential (GWP), to reduce flammability when feasible, and to enhance worker health and safety. Consequently, the process of solvent selection has become increasingly complex.

Some good resources

The U.S. EPA has a website for their Significant New Alternatives Policy (SNAP) program that reports on the evaluation and regulation of non-ozone-depleting alternative solvents. The purpose of this program is “to allow a safe, smooth transition away from ozone-depleting compounds by identifying substitutes that offer lower overall risks to human health and the environment.”

The SNAP program is primarily focused on non-ozone-depleting replacements, but there exists an excellent resource—the **Toxics Use Reduction Institute** (TURI)²—that addresses the reduction of overall toxicity. Their broad evaluations of regulated

chemicals and suitable replacements are a valuable resource for the cleaning sector as well as other solvent-heavy sectors of industry.

But first, be practical. If a well-established business sector has a particular work-horse solvent (e.g. perchloroethylene, *n*-Propyl bromide, etc.), the first source of information should be the solvent manufacturer. A good relationship with the technical representatives is valuable. If a solvent is slated to be phased out, the supplier will be devoting a large amount of effort to maintain their market share by researching alternatives.

It may be the case, though, that a different manufacturer will have a better replacement and navigating this situation can be confusing. If one has a critical performance need or a problem soil-substrate combination, then the various manufacturers are often willing to test their alternative solvent(s) against the critical need.

However, many SMEs, chemists, and engineers are curious by nature, and they want to know what is going on behind the scenes in these solvent evaluations. Some will even want to do the evaluations themselves to satisfy this curiosity and to instill confidence in the independence of the evaluation.

This article addresses this “need to know” by briefly describing:

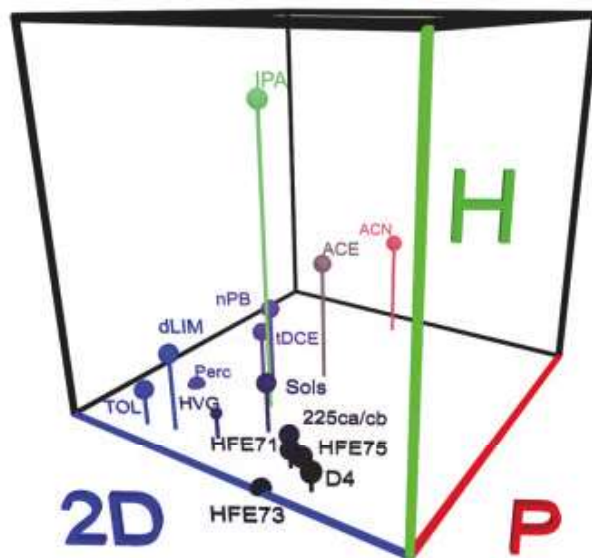


Figure 1: A Hansen solubility parameter plot for several popular solvents and a particular soil—a high-vacuum grease (HVG). The solvents and soil are plotted at coordinates $(2\delta_D, \delta_P, \delta_H)$ so that the interaction region is spherical. The data points are colored according to the relative magnitudes of δ_D (blue), δ_P (red), and δ_H (green) such that similar colors interact strongly—like dissolves like.

1. The Hansen solubility parameters of soils and solvents
2. The selection of solvents to fit within an environment, health, and safety (EHS) profile
3. The blending of solvents to maximize performance within an EHS envelope

Theory

Solvent-soil interactions

The cleaning solvent and the soil must spontaneously “like each other.” It is best if the solvent and the surface spontaneously like each other, too, because this allows the fluid to wet the surface lifting the soil into the bulk solvent. The thermodynamic property that governs spontaneity (at constant pressure) is the Gibbs free energy, and a negative Gibbs energy of mixing (ΔG_{mix}) indicates that the substances like each other enough to mix spontaneously.

The ΔG_{mix} can be written (Eq. 1) in terms of the enthalpy of mixing (ΔH_{mix}), the entropy of mixing (ΔS_{mix}), and the temperature of the system (T). Notice how increased temperature favors mixing by reducing ΔG_{mix} :

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

The entropy of mixing can be written in terms of the volume fractions of each of the components (Eq. 2):

$$\Delta S_{mix} = -n_T R(x_1 \ln x_1 + x_2 \ln x_2)$$

In Eq. 2, n_T represents the total number of moles of molecules present in the system, R is the gas constant $8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$, V_T is the total volume, and the x_i are the volume fractions (v_i / V_T) of the mixture components. It is interesting to note that all the volume fractions are by definition less than one. This causes all the natural logarithms to be negative, resulting in a positive entropy of mixing. It is always entropically favorable to form mixtures.

If substances do not spontaneously mix, it is due to the enthalpy of mixing. Hildebrand and Scott coined the term “solubility parameter” to account for the enthalpy of mixing effect on solubility.³ They define the Hildebrand solubility parameter (δ_T in Eq. 3) as the square root of the cohesive energy density in $(\text{J/mL})^{1/2}$, which is the enthalpy of vaporization (ΔH_{vap}) for a solvent divided by that solvent’s molar volume (V_m). (Many tables list the units of the solubility parameter as the equivalent $\text{MPa}^{1/2}$.) A solvent’s molar volume is easily calculated by dividing the solvent’s molar mass (M in g/mol) by its density (ρ in g/mL):

$$\delta_T \equiv \sqrt{\frac{\Delta H_{vap}}{V_m}} = \sqrt{\frac{\Delta H_{vap}}{(M/\rho)}}$$

Each solvent will have a Hildebrand solubility parameter and these may be compared to yield the enthalpy of mixing via Eq. 4:

$$\Delta H_{mix} = x_1 x_2 V_T (\delta_{T,1} - \delta_{T,2})^2$$

Therefore, one may predict that mixing will occur if two substances have similar Hildebrand solubility parameters. Hildebrand, however, used non-polar hydrocarbons in the development of his solubility parameters. Later, Hansen refined the solubility parameter approach to account for three types of intermolecular forces—dispersion (δ_D), polarity (δ_P), and hydrogen-bonding (δ_H)—thus creating the Hansen solubility parameters (HSPs).⁴ They are related to δ_T via the geometric mean (Eq. 5):

$$\delta_T^2 \equiv \delta_D^2 + \delta_P^2 + \delta_H^2$$

This has proven to be a very useful system for understanding the interactions of solvents with soils, substrates, and other solvents because the δ_D -, δ_P -, and δ_H -terms can be displayed as three Cartesian axes (Fig. 1). The HSPs of solvents and soils can be plotted in this three-dimensional Hansen solubility coordinate space. This sounds complicated, but it is not! Rather, it leads to a very easy and intuitive way to select solvents and solvent blends:

The solvent abbreviations in Fig. 1 represent Asahiklin (AK225) from Asahi Glass Co. Ltd.; HFE-7100 (HFE71), HFE-7500 (HFE75), HFE-7300 (HFE73) from 3M Company; Solstice LBA (Sols) from Honeywell International Inc.; the cyclic dimethylsiloxane tetramer (D4) from Dow Corning; d-limonene (dLIM), toluene (TOL), perchloroethene (Perc), n-Propyl bromide (nPB), isopropyl alcohol (IPA), acetone (ACE), and trans-dichloroethene (tDCE). The soil in this example is a high-vacuum grease (HVG). The color coding of the data points follows the coloration of the δ_P (red), δ_H (green), and δ_D (blue) axes. Similarly colored solvents and soils interact strongly—like dissolves like.

Determining the HSPs of the soil may be as easy as an Internet search if the soil is a commercial oil or grease. But sometimes, a small series of solvent exposure lab tests are required. This procedure—detailed in Hansen’s handbook⁴ and online⁵—consists of exposing soiled parts to approximately 30 solvents that cover a large range of DPH-space. The strongly interacting solvents will be clustered within a sphere (with radius R_0) centered on the HSPs of the soil. A numerical fitting routine is used to select the interaction sphere parameters (δ_D , δ_P , δ_H , and R_0) that contain all the good solvents while excluding all of the bad solvents.⁶ Once these HSPs are known, solvent substitution and blend prediction may begin.

Solvent and blend evaluation, prediction, and selection

The HSPs of a blend are simply the volume fraction weighted sum of the HSPs of the blend components (Eq. 6):

$$\delta_{D,blend} = \sum_i x_i \delta_{D,i}$$

In Eq. 6, the $\delta_{D,i}$ represents the dispersion Hansen solubility parameter for the i -th component of the blend. The same treatment is used for the $\delta_{P,blend}$ and $\delta_{H,blend}$ parameters.

Essentially, binary blends are represented in DPH-space by a straight line between the two components, and if this line goes near the targeted soil, then this is a promising blend recipe. Likewise, a three-component blend is represented by a triangle in DPH-space, and a four-component blend creates a four-sided pyramid-like polygon. If the soil lies close to the triangle or within the polygon, then these blend components will produce a promising blend. Programs are available that will search for the optimum blend recipe given that the HSPs of the soil are known.

All processes are subject to “garbage in – garbage out,” therefore it saves time to eliminate all unacceptable solvents from consideration before predicting blend recipes. If the process may only use VOC-exempt solvents, then only VOC-exempt solvents will be entered into the blend prediction model. An excellent overview of cleaning agents, solvents, and cleaning systems is available for the SME who wants to improve their knowledge in this area.⁷

Even after this down-selection, there may be hundreds of suitable blend recipes for a given soil. Therefore, one must determine an overall desirability function for ranking the many possible blend recipes. The common criteria are flammability (F), toxicity (H), volatility (Y), and effectiveness (E). For the purposes of optimization, each criterion will be transformed into a 0 (bad) to 1 (good) scale.

The flammability term (F) uses the Hazardous Material Identification System (HMIS) flammability number that is found on the MSDS for the solvent.⁸ The flammability number ranges from 0 (low) to 4 (high) flammability, and Eq. 7 converts this to the necessary 0 to 1 range:

$$F_i = 1 - \frac{HMIS(F)}{4}$$

A similar treatment is used for the health rating (H) from the HMIS(H) term as seen in Eq. 8.

$$H_i = 1 - \frac{HMIS(H)}{4}$$

The volatility term (Y) is based upon the solvent evaporation rate (RER) relative to n-butylacetate.⁵ Because the magnitude of RER may vary from near-zero to several thousand, the inverted percentile rank of the RER relative to the full set of solvents under consideration is used. In English, the most volatile solvent will have a near-zero rank and the least volatile solvent will have a rank near one. However, the non-inverted percentile rank may be used if the SME desires fast-evaporating solvents in the blend. This percentile rank is based upon a normal distribution function which is standard in Excel (Eq. 9):

$$Y_i = 1 - Norm.Dist(RER_i, average(RER), stdev.p(RER), true)$$

A similar treatment is used to rank the predicted effectiveness of the solvent against a particular soil. A small Hansen distance (R_a , Eq. 10), indicates that a solvent is effective⁵:

$$R_a = \sqrt{(2\delta_{D,solvent} - 2\delta_{D,soil})^2 + (\delta_{P,solvent} - \delta_{P,soil})^2 + (\delta_{H,solvent} - \delta_{H,soil})^2}$$

The inverted percentile rank (Eq. 11) is used on R_a to bring the effectiveness rating to a range of 0 (bad) to 1 (good):

$$E_i = 1 - Norm.Dist(R_{a,i}, average(R_a), stdev.p(R_a), true)$$

The individual rankings are averaged (Eq. 12) to give a desirability rating for each solvent:

$$D_i = \frac{F_i + H_i + Y_i + E_i}{4}$$

The desirability ratings of the blend components are averaged along with the blend effectiveness rating (E_{blend}) to determine the overall blend desirability rating (Eq. 13):

$$D_{blend} = \frac{1}{N+1} \left(E_{blend} + \sum_i^N D_i \right)$$

The N in Eq. 13 represents the number of blend components and D_i is the desirability rating for each component solvent. The effectiveness of the blend (E_{blend}) is calculated using the Hansen distance of the blend to the soil using Eq. 11.

Example

To illustrate this process, a silicone-based high vacuum grease (HVG) was used as the soil. The Hansen solubility parameters were determined to be (16.0, 2.3, 1.4) using the solvent interaction method.⁶ Fourteen solvents that are commonly used or proposed in cleaning applications are shown in Table 1. The Hansen distance from the solvent to HVG is shown as well as the other figures of merit used in ranking the desirability of each solvent against HVG.

One can see in Table 1 that dLIM is the most desirable solvent based upon its low volatility. But this analysis has shown that AK225 has superior flammability and health ratings, and it evaporates much quicker. The HFE75 solvent has similar volatility to dLIM with less flame and health risk. If fast-evaporating non-flammable solvents are desired, then the HFE71 and Sols solvents are expected to perform well against this particular soil. This treatment allows the SME to balance risk and requirements in solvent substitution decisions.

All 91 pairwise combinations of these solvents were computed and Table 2 shows the optimized blend recipes for the top 16 binary blends sorted by desirability. Both of the top blends contain AK225, and if this solvent is being phased-out the next best blend is a mixture of 47% HFE-7100 and 53% toluene.

All 364 three-component blends and 1,001 four-component blends were optimized, but none of them had desirability

ratings above the promising binary blend recipes.

The most promising blends may now be prepared in small vials as a test of miscibility. Godfrey's M-numbers may be used to screen out blends that are unlikely to mix, but at this point it is best to test the miscibility of the blend components directly.^{9,10} This is an active area of research. Research is currently being conducted into an HSP-based model of the Godfrey M-number

to serve as a screening test for blend miscibility.¹¹

Now that the most-desirable blends or substitute solvents have been selected, it is time to perform cleaning effectiveness testing. There are many ways to do this from high-fidelity parts cleaning to metal coupon dip testing.¹² Whatever the method, one can be confident that the process outlined in this article will save solvent, time, and money by eliminating the wasteful and random trial-and-error testing of the past.

Solvent	δ_D	δ_P	δ_H	RER	HMIS(H)	HMIS(F)	R_a	F_i	H_i	Y_i	E_i	D_i
dLIM	17.2	1.8	4.3	12	2	2	3.8	0.50	0.50	0.77	0.77	0.64
AK225	14.1	3.2	1.0	1415	1	1	3.9	0.75	0.75	0.26	0.73	0.62
HFE71	13.7	2.2	1.0	1501	0	1	4.6	0.75	1.00	0.23	0.49	0.62
HFE75	13.3	2.0	1.0	151	1	1	5.4	0.75	0.75	0.73	0.23	0.61
Sols	15.1	4.1	2.8	3933	2	0	2.9	1.00	0.50	0.00	0.94	0.61
HFE73	13.8	0.2	0.0	499	1	1	5.1	0.75	0.75	0.60	0.33	0.61
D4	12.8	1.3	1.0	15	0	2	6.5	0.50	1.00	0.77	0.04	0.58
TOL	18.0	1.4	2.0	139	2	3	4.1	0.25	0.50	0.73	0.66	0.54
Perc	18.3	5.7	0.0	87	3	0	5.9	1.00	0.25	0.75	0.12	0.53
nPB	16.4	7.9	4.8	582	2	0	6.6	1.00	0.50	0.57	0.04	0.53
IPA	15.8	6.1	16.4	153	1	3	15.4	0.25	0.75	0.73	0.00	0.43
ACE	15.5	10.4	7.0	786	1	3	9.9	0.25	0.75	0.49	0.00	0.37
ACN	15.3	18.0	6.1	211	2	3	16.4	0.25	0.50	0.71	0.00	0.36
tDCE	16.7	7.8	3.3	1186	2	3	6.0	0.25	0.50	0.34	0.11	0.30

Table 1: A selection of solvents ranked according to their ability to clean a high-vacuum silicone grease with the (δ_D , δ_P , and δ_H) values of (16.0, 2.3, 1.4). The components of the desirability rating are color-coded green and red for good and bad, respectively.

x_1	Solvent ₁	x_2	Solvent ₂	R_a	E_{blend}	D_1	D_2	D_{blend}
0.51	AK225	0.49	TOL	0.06	0.96	0.62	0.54	0.71
0.49	AK225	0.51	dLIM	1.42	0.86	0.62	0.64	0.71
0.47	HFE71	0.53	TOL	0.54	0.94	0.62	0.54	0.70
0.56	dLIM	0.44	HFE71	1.61	0.83	0.64	0.62	0.70
0.43	HFE75	0.57	TOL	0.67	0.93	0.61	0.54	0.69
0.59	dLIM	0.41	HFE73	1.65	0.83	0.64	0.61	0.69
0.61	dLIM	0.39	HFE75	1.76	0.81	0.64	0.61	0.69
0.39	D4	0.61	TOL	0.97	0.90	0.58	0.54	0.67
0.61	Sols	0.39	TOL	1.37	0.86	0.61	0.54	0.67
0.38	dLIM	0.62	Sols	2.16	0.75	0.64	0.61	0.67
0.34	D4	0.66	dLIM	1.97	0.78	0.58	0.64	0.67
0.44	HFE73	0.56	TOL	1.50	0.85	0.61	0.54	0.66
0.54	HFE73	0.46	Perc	1.51	0.85	0.61	0.53	0.66
0.57	HFE71	0.43	Perc	1.76	0.81	0.62	0.53	0.65
0.52	HFE75	0.48	Perc	1.83	0.80	0.61	0.53	0.65
0.47	D4	0.53	Perc	1.73	0.82	0.58	0.53	0.64
0.62	AK225	0.38	Perc	2.10	0.76	0.62	0.53	0.64
0.21	HFE73	0.79	Sols	2.66	0.66	0.61	0.61	0.63
0.24	Perc	0.76	Sols	2.30	0.73	0.53	0.61	0.62
0.06	AK225	0.94	Sols	2.88	0.62	0.62	0.61	0.62
0.06	HFE71	0.94	Sols	2.88	0.62	0.62	0.61	0.62

Table 2: A selection of binary blend recipes that have been optimized to target the HVG soil. The blends are sorted by the overall desirability rating (D_{blend}).

Acknowledgements

This work has been developed over the years with funding from SHSU, US-DOE, NASA-WSTF, and the Welch Foundation. Meaningful conversations with Charles Hansen and his colleagues Steven Abbott and Hiroshi Yamamoto are gratefully acknowledged. The actual lab testing and procedure development could not have reached the current state of utility without the meticulous efforts of my research students Karl Kuklenz (M.S. 2009) and James Huskey.

References

1. United States Environmental Protection Agency. *Significant New Alternatives Policy (SNAP) Program*. Available at: <http://www.epa.gov/ozone/snap/>. Accessed June 12, 2013.
2. University of Massachusetts - Lowell. *Toxics Use Reduction Institute*. Available at: <http://www.turi.org/>. Accessed June 13, 2013.
3. Hildebrand JH, Scott RL. *The Solubility of Nonelectrolytes*. 3rd ed. New York: Reinhold; 1950.
4. Hansen CM. *Hansen Solubility Parameters: A User's Handbook*. Boca Raton, Fla.: CRC Press LLC; 2000.
5. Hansen CM. *Hansen Solubility Parameters in Practice*. Available at: <http://www.hansen-solubility.com/>. Accessed June 24, 2013.
6. HSPiP: The Software. *Hansen Solubility Parameters Web Site*. <http://hansen-solubility.com/index.php?id=13>. Accessed June 26, 2013.
7. Kanegsberg B, Kanegsberg E. *Handbook for Critical Cleaning - Cleaning Agents and Systems*. 2nd ed. Boca Raton, FL: CRC Press; 2011.
8. American Coatings Association. *HMIS III - Hazardous Materials Identification System*. Available at: <http://www.paint.org/programs/hmis.html>. Accessed June 24, 2012.
9. Godfrey NB. Solvent Selection via Miscibility Number. *CHEMTECH*. June 1972:359-363.
10. Perry RH, Green DW. Section 15. *Perry's Chemical Engineer's Handbook*. 8th ed. New York: McGraw Hill; 2008:34-39.
11. Huskey JE, Williams DL. Predicting Solvent Blend Miscibility. Paper presented at: Texas Academy of Science 2013, 2013; Schreiner University, Kerrville, Texas.
12. Durkee JB. Description of Analytical Procedures for Cleanliness Testing. *Management of Industrial Cleaning Technology and Processes*. New York, N.Y.: Elsevier; 2006:455-460.

Darren L. Williams, Ph.D. is an associate professor in the chemistry department at Sam Houston State University in Huntsville, Texas. He has over a decade of experience in cleaning verification, solvent substitution, and blend prediction in addition to his work in spectroscopy (Raman, IR, and UVVIS) and computational chemistry (color prediction and spectroscopic modeling). He can be reached at williams@shsu.edu; http://www.shsu.edu/~chm_dlw 