
Solvents and Hansen Space in the MCP, something new and useful

by Chris Stavroudis with Juliana Ly and Donna Williams

My father had an odd sense of humor. Being a mathematician working in geometrical optics he was surrounded by physicists. When a colleague would ask him “what’s new”, he would reply as if they asked, “what’s nu”. He would, unfailingly retort “c over lambda.”

Those with less of a sense of humor would defensively retort “I didn’t ask what’s nu but what’s new.” For those whose encounters with physics is a distant memory, remembered fondly or not, the equation is

$$n = c/\lambda$$

(frequency of electromagnetic radiation equals the speed of light divided by the wavelength of the light).

And so nearly ends our physics lesson for today. Nearly.

The Dull Stuff (Theory)

Solubility theory has a tenuous underpinning in thermodynamics -- the 19th-century holdout of modern physics.

Solubility theory is confounding. To tell if a solute dissolves in a solvent we look at the properties of the solvent and the properties of the solute, but counterintuitively, we don’t consider the interaction between the two, just whether the properties are similar.

All liquids and solids are held together by some intermolecular force. Our first thermodynamic task is to quantify that force. The measurement of the total force is

$$-U = \Delta H_v - RT \text{ (at room temperature)}$$

where ΔH_v is the molar enthalpy of vaporization at room temperature.

Solvent	-U (kJ/mole)	$\Delta H_v @ 25^\circ$ (kJ/mole)
ethanol	39.84	42.32
acetone	28.51	30.99
toluene	35.62	38.10
n-heptane	34.09	36.57

Examining the numbers above and knowing what we know about solvents, we notice that the numbers make no intuitive sense. Strong, weak or high number, low number – there’s no correlation.

Remember these are scientific numbers and, in a way have no relation to the real world. We don’t work with moles of a material; we work with grams or milliliters. So, let’s convert these abstract values to something non-physicists care about.

Enter molar volume, a correction if you will, to convert moles into volume, a property we understand.

$$V_M = MW/\text{density}$$

Where V_M is the molar volume, MW is the molecular weight and density is, well, the density (weight divided by volume).

And just to show that the units work out: [MW (grams/mole) / density (g/ml) = ml/mole].

Solvent	V_M (ml/mole)
ethanol	58.5
acetone	74.0
toluene	106.8
n-heptane	147.4

Suddenly, these numbers start looking sensible. Weak solvent – held together with less energy, strong solvent, held together with stronger intermolecular force. Note, too, that acetone, a strong solvent is out of place – kind of too high a value.

Let’s apply the molar volume correction to the molar enthalpy of vaporization.

This calculation yields the cohesive energy density (CED). And, again, with the exception of acetone, the higher number corresponds with the stronger solvent.

For physics-y reasons, we actually want the square root of the CED, and this is the Hildebrand solubility parameter, δ .

Solvent	δ	
ethanol	681	26.5
acetone	385	20.0
toluene	333	18.3
n-heptane	231	15.3

Again, with the exception of acetone, we have numbers that reflect the strength of the solvent.

Problems. If we compare the Hildebrand solubility parameter of n-propanol ($\delta=24.5$) and dimethylformamide, DMF ($\delta=24.8$) we note that solubility parameters of these vastly different solvents have nearly identical solubility parameters.

Dr. Charles M. Hansen’s solution to this problem was to deconstruct the Hildebrand solubility parameter into component parameters based on the types of intermolecular force. And this is where we lose the thermodynamics underpinning of solubility theory.

Thus the Hildebrand solubility parameter will be parsed into three component intermolecular forces: dispersion (δ_d), dipolar (δ_p), and hydrogen bonding (δ_h), such that:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

Dispersion forces, δ_d , are present between all molecules, are the weakest of the intermolecular forces, are also referred to

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as London or van de Waals forces, and are based on quantum mechanics. They exemplify “like is attracted to like.”

Dipolar forces, δ_p , are based on electrostatic attraction between molecules whose structure caused some parts of the molecule to be partially negatively charged leaving the rest of the molecule with a partial positive charge. The partial negative charge on one molecule will be attracted to the partial positive charge on an adjacent molecule.

Hydrogen bonding, δ_h , is the strongest of the intermolecular forces and the most complicated. It can be as strong as one-tenth the value of a typical covalent bond. To have hydrogen bonding there must be a hydrogen bond donor and a hydrogen bond acceptor. The interaction between the donor portion of one molecule and the acceptor portion of another molecule causes this strong interaction.

For more about solubility parameters I refer you to either of these excellent articles:

John Burke. 1984. “Solubility Parameters: Theory and Application.” *The Book and Paper Annual*, 3. AIC. pp 13-58. (Also online: cool.conservation-us.org/byauth/burke/solpar/.)

or

Alan Phenix. 1998. Solubility Parameters and the Cleaning of Paintings: an update and review. *Kunsttechnologie Konservierung*. Heft 2, Jargang 12. pp 387-409.

So, I hear you asking, what’s nu in the MCP.

The Good Stuff (Application)

Well, I’ve added a new button “Play with Hansen Solubility Space.” In Hansen solubility space, solvents are points in the three-dimension space and solutes are spheres. Any solvent inside the sphere will dissolve the solute. Any solvent outside the sphere will not be a solvent. The center of the sphere is the point of greatest solubility.

The sphere is defined by its center, that point of greatest solubility, and the radius of the sphere. A solute with a very narrow solubility will have a small radius while one that dissolves in almost everything will have a large radius.

How are these numbers determined? Trial and error. A solute is placed into various solvents and its solubility in each solvent is noted. With a little mathematics, that data allows one to calculate the best fitting sphere and then calculate the center of the sphere and the radius. (In practice, the math is done with HSPiP, Hansen Solubility Parameters in Practice.)

But none of this is nu. What I’ve done with the new version of the MCP is to allow the conservator to mix up to five solvents and see how the solvent or solvent blend should

interact with a coating. And, since we care more about the substrate than the coating, how that mixture will interact with the substrate. This follows the logic in the MCP where we always think about what we are trying to remove and what we are trying to remove it from.

The MCP calculates the RED, Relative Energy Difference, of the solvent or solvent mixture and the coating we are trying to remove (as well as that of the substrate). The RED is the ratio of the distance between the center of the solute sphere and the solvent or solvent mixture and the radius of the sphere.

A RED of 1 means that the solvent sits on the edge of the solubility sphere. A RED of less than one means the solute is soluble in the solvent mixture; the lower the value, the closer to the point of maximum solubility. A RED of greater than 1 means that the solute will not dissolve in the solvent mixture.

See where we’re going? We want to find a solvent mixture where the RED is as small as possible for what we are trying to remove and as large as possible for what we are trying not to affect.

As conservators, we know that this is pretty much an academic exercise. No two coatings are alike. Age, light exposure, formulation, conservation history all conspire to make our jobs more difficult. If there was an accurate solubility sphere for each material, were it that simple, we would have a bottle of the perfect solvent for cleaning paintings with a natural resin varnish over oil paint. Another bottle for removing a different coating. But it’s a start and sometimes we can find interesting solutions (pun intended) to solubility problems.

Where do these numbers come from? The initial solute sphere coordinates in the MCP come from the HSPiP program which has data on an impressive 626 solutes, a few of which are of interest to conservators. But we can do better.

Dr. Gregory D. Smith, now at the Indianapolis Museum, had his Buffalo conservation students measure and plot the solubility of common materials used in conservation. The data was plotted onto Teas diagrams and appear in Velson Horie’s *Materials for Conservation*.

Not only are the Teas diagrams published, but the solvents that were and were not solvents for the material are published. And these values can be input into the HSPiP program which can calculate the coordinates of the solubility sphere. These values should be included in the next version of the MCP, I hope by the time you read this.

So, how do we play with Hansen spheres in Hansen solubility space? After clicking on the button “Play with

Play with Solvents and Hansen Space

Solvent 1 acetone change

Solvent 2 xylenes change

Solvent 3 ethanol change

Solvent 4 n-methyl-2-pyrilidone change

Solvent 5 change

Hansen Spheres

shellac

RED=.58
distance=6.2
 $\partial d=19.7, \partial p=10.1,$
 $\partial h=15.1,$
radius=10.7

dried linseed oil

RED=1.52
distance=7.6
 $\partial d=16, \partial p=6, \partial h=7,$
radius=5

parts	mLs		
1	.7	14%	acetone
1	.7	14%	xylenes
3	2.1	43%	ethanol
2	1.4	29%	n-methyl-2-pyrilidor
0	0	0%	

Total volume: 5 mL

Solubility Parameters

Hildebrand $\partial=23.56$
Hansen parameters: $\partial d=16.68; \partial p=9.59; \partial h=13.58$
Teas $f d=47.71; f p=22.14; f h=30.14$
Aromatic Index = 11.45 (Aliphatic Index = 29.65)
Teas from Hansen space: $f d=42; f p=24; f h=34$

86.1 V% ethanol
13.9 V% xylenes

Done

YES: Clean

NO: Stop

Test it

View Test Results

Hansen Solubility Space” the MCP user is presented with the screen above.

We are shown that pure heptane has equally poor solvent effects on both shellac (RED=1.89) and dried linseed oil (RED=1.90).

To select the solutes, click on the solvent name or empty yellow box if none has been selected.

As of this writing one can select from: shellac, dammar, dammar dark aged, dammar dewaxed, mastic aged, dried linseed oil, BEVA 371, Paraloid B-72, poly(methyl methacrylate), Laropal A-81; Ketone Resin N, Paraloid B-67 and B-72, Regalrez 1094, cellulose nitrate, Butvar B-76, natural rubber, cellulose acetate, lignin, bitumen, and tar from the La Brea tar pits. Admittedly a short list.

Case Study 1

Julianna Ly (WUDPAC) was recently confronted with the treatment of a 17th-century (est.) Baltic oak panel painting. Privately owned, the panel painting entered the Winterthur Museum painting conservation studio with extensive areas of restoration.

Her treatment included analyzing and reducing a thick, shiny varnish which was not soluble in traditional solvents commonly used in conservation. She took small samples from areas of the varnish and overpaint materials for organic analysis. FTIR spectra confirmed that the varnish layers were comprised of both cellulose nitrate and an alkyd coating.

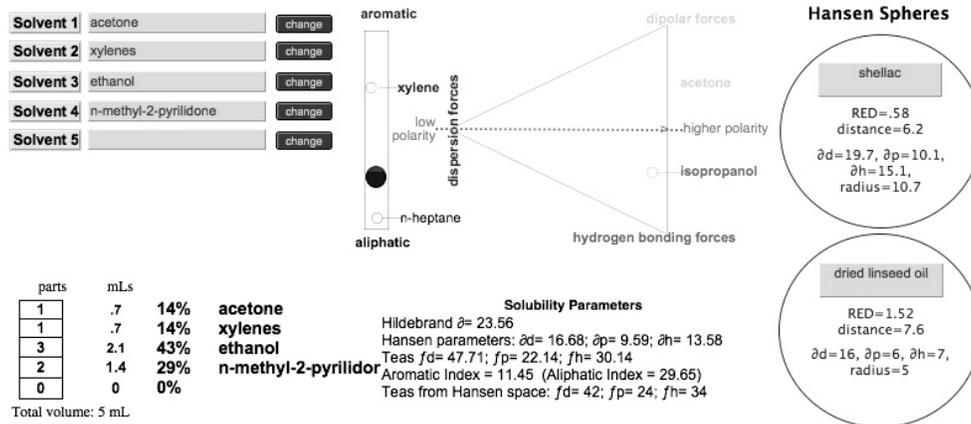
The cellulose nitrate layer was reduced with a xylene-Carbopol solvent gel with 20% benzyl alcohol (v/v). After extensive testing, she reduced the remaining alkyd coating with quick passes of neat acetone which effectively targeted the narrow solubility range of the material.

Weaker solvent mixtures would have significantly blanched the surface; the neat solvent was chosen over an acetone Carbopol gel in order to avoid the need for additional passes with a polar solvent to clear the gelled solution.

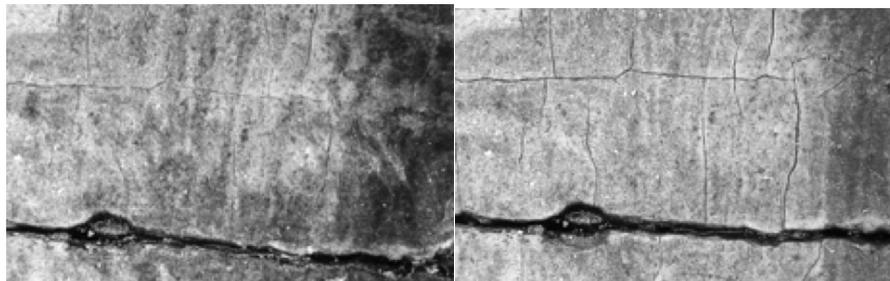
After the reduction of these two layers, she found a localized yellow coating remained along the edges of previously joined splits. Due to the thick, insoluble nature of this coating, she took an additional sample for FTIR and the coating was determined to be shellac. Julianna was unable to reduce this coating using traditional solvents and/or gelled emulsions, so I played with solvents suggested by a number of conservators for shellac with the MCP.

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The calculations (made by the computer) suggested that a mixture of 1:1:3:2 acetone: xylene: ethanol: NMP might work well on the layer and not affect the oil paint substrate.

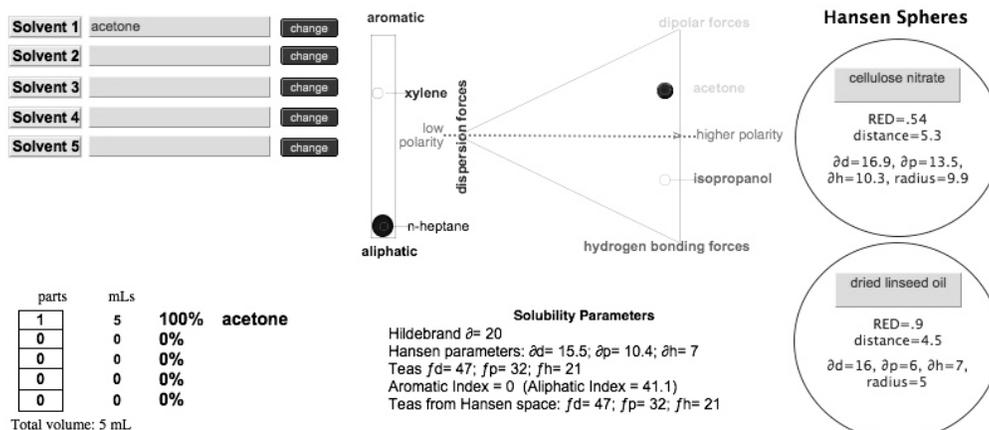


Julianna used the solvent mixture suggested by the MCP by first masking the areas with cyclomethicone D5 and applying the solvent mixture by brush under the microscope. Often, multiple applications were needed in order to swell the thick shellac layer. Once swollen, she used delicate mechanical action, and the coating began to break up and almost sugar off. Once the coating was disrupted enough, neat acetone was effective in quickly picking up the remaining bulk on the surface. In areas that exhibited sensitivity, the shellac was only thinned and not completely removed.



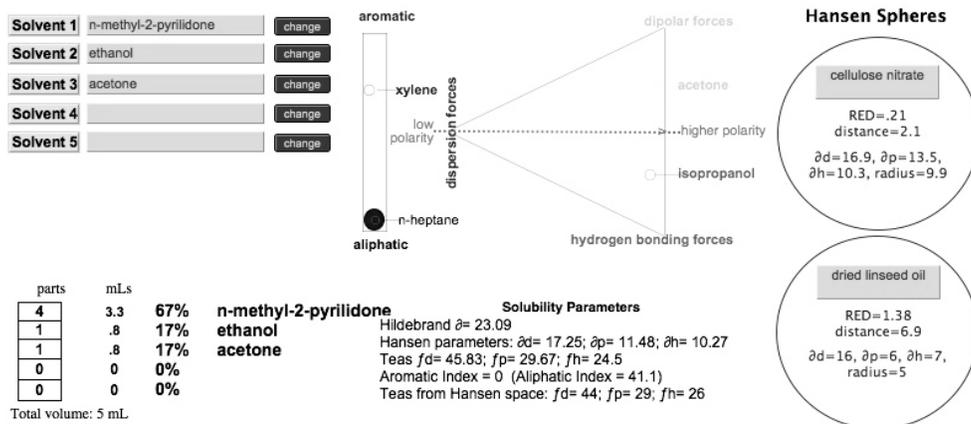
Case Study 2

Donna Williams needed to remove a cellulose nitrate coating from an outdoor bronze (in the summer). Acetone worked but evaporated so quickly on the warm/hot bronze that she needed to find a different solution. Playing with different solvents in the program we came upon the following mixture:

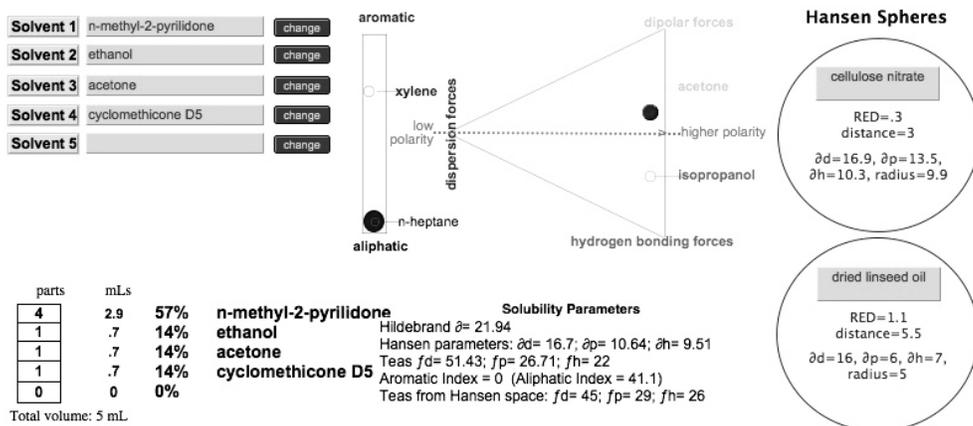


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Ignoring the dried linseed oil, the substrate was bronze, we see that the mixture of 4 parts n-methyl-2-pyrilidone; 1-part ethanol; 1-part acetone had a RED of 0.21, very close to the optimum solubility of cellulose nitrate which would have a RED of 0.0. And, we note that acetone alone has a RED of 0.54, so not as good as our new mixture, ignoring the health effects of the pyrrolidone. And, significantly to the cleaning problem, the evaporation rate of the mixture is much less than that of acetone alone.



In practice, Donna found that the following mixture worked even better, even though it shouldn't have. The mixture with one-part cyclomethicone D5 added has a RED of 0.3 so it shouldn't have worked better than the mixture without the D5. Perhaps it worked better by slowing the evaporation rate further.



Commercial lacquer thinners are all proprietary mixtures, but some information on their composition is given in their Safety Data Sheets (SDS). One is a mixture of methyl ethyl ketone (MEK), butyl acetate and butanol and playing with different proportions of the three components the best RED was 0.63 (4:1:2). According to the CAMEO database, Agateen thinner is a mixture of methyl isobutyl ketone (MIBK), toluene, butanol, and amyl acetate. Playing with these four components the best RED was 0.84 (4:1:4:1). Note that other concerns go into formulating a solvent mixture for a coating. The component solvents must evaporate in such a way as to leave a uniform and cohesive film behind. Optimum solubility is not the highest priority in a coating formulation.

While the problem was to remove the cellulose nitrate from bronze, imagine we were removing it from a painted surface (oil paint). We would then be paying attention to the RED values for dried linseed oil in the lower sphere. Remember, we would want the highest RED value to pose the least risk of solubilizing the paint layer. Comparing these three solutions we would clearly choose the solvent mixture without the cyclomethicone that has a RED for dried linseed oil of 1.2 compared to that of 1.1 for the mixture with cyclomethicone and 0.9 for acetone alone. Note that the suspected Agateen recipe gave a RED of 0.7 for oil paint so it should dissolve (or at least swell) oil paint more effectively than it dissolves lacquer.