Article

HSP-Based Dispersants Selection Method for Instant Match

Sander van Loon – Apr 20, 2016

The selection of a suitable <u>dispersant</u> for a filler or a pigment (solid particle) can be difficult and time-consuming (variety & amount of <u>dispersants</u>, nature & surface treatment of the solid particle...).

Discover an effective method, tested & validated by VLCI, based in Amsterdam. It will help you to turn this complex selection task into an immediate prediction of the best <u>dispersant</u> by applying Hansen Solubility Parameters (HSP) in your paint, coating or ink development.

The validity of this new screening process has been proven using a the more conventional optimum <u>dispersant</u> concentration (ODC) test methodology.

Another reason to explore this screening method is the fact that the more you use it, the less effort you need to find perfect pigment / <u>dispersant</u> pairs...

Selection of Dispersants: How Is it Done in the Industry?

The most used but the least efficient method:

When a suitable <u>dispersant</u> is introduced into a pigment dispersion, there is a dramatic reduction in the viscosity of the paste or slurry, as the particles become more mobilized in the solvent. This can be easily illustrated when mixing slurry of particles in a solvent – often water. As the <u>dispersant</u> is added gradually into the slurry, there can be a fairly rapid decrease in the viscosity of the slurry, which is seen to develop a larger vortex than before.

So, one <u>dispersant</u> at a time, you just add it to your solid slurry and see if they have a positive effect. And you move to your next <u>dispersant</u>. With so many <u>dispersants</u> to choose from, and adding them drop wise to the slurry, lot of time and materials are wasted.

An improved method available to all
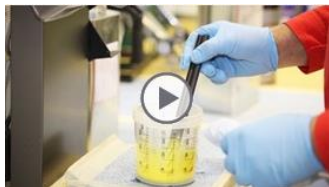
In a tutorial by Jochum Beetsma, we show how to rationalize your <u>dispersant</u> selection process by starting with looking at Technical Datasheets. Basically, you limit your compatibility study to candidates having matching characteristics.

This method, which is available to all, will allow you to work with fewer candidates, and also have a starting estimation of the loading you need.

Watch tutorial now!

A tremendously more efficient method, requiring less & less efforts over time

This selection method is based on the use of Hansen Solubility Parameters (HSP) to get accurate predictions between solid particles & <u>dispersants</u>, as well as between <u>dispersants</u> and solvents. The goal is to better take into consideration the chemical and physical characteristics of each of a range of particles and of <u>dispersants</u> and to predict the relative compatibilities of particle-<u>dispersant</u> combinations.

## The HSP-based Dispersant Screening

Hansen solubility parameters (HSPs) are used to define the attractive forces Hydrogen bonding, Polar forces and Dispersion forces within materials (solvents, polymers, actives, etc.), or to map the interactions of those with other materials.

The three HSP parameters (D, P & H) give numerical values for the forces of cohesion within solvents and so they can be usefully visualized using a 3D diagram, as shown on the picture. The key finding of HSP theory is that solvents with more similar HSP values will tend to be comparable in their affinities to other materials.

To quantify this 'likeness', we calculate HSP distances:

$$Dist = \sqrt{4(D_2 - D_1)^2 + (P_2 - P_1)^2 + (H_2 - H_1)^2}$$

But before you can make these calculations, you must first gather the HSP data of the materials.
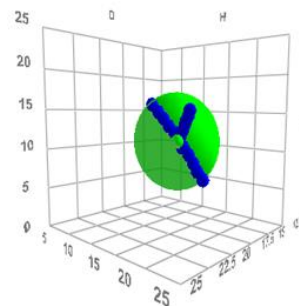
Determining HSP of Pigments, Fillers & Dispersants

Although the determination of HSP can be done manually, it is recommended to use High-Throughput equipment, which allows you to have data in one or two days, in comparison to more than a week otherwise.

HSP for Pigments & Fillers

The measurement of the HSP of particles is achieved by comparing the sedimentation rate of the particles within different solvents. This is done in sample tubes like the one shown. Fixed distances are set out with markers, which give a fixed height over which the particle descent can be timed.
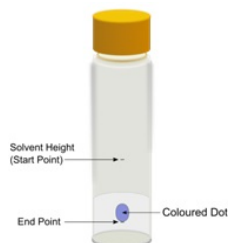
The velocity of these particles is subject to the viscosity and density of the solvent medium in which it is suspended and so a correction is made, to determine a Relative Sedimentation Time (RST) for each solvent. Differences in the RST values for the solvents inform us about their relative affinities for the surface of the particles.

Lower RST values reflect more rapid sedimentation, and indicate poorer affinities between solvents and particles, so that higher RST values suggest solvents that are better suited to the preparation of stable dispersions with that particular particle.

These scores can be used as inputs into the HSPiP software, to determine the HSP that characterizes the surface of the particle. See how to do it in practice in the tutorial below:

HSP for dispersants

HSP of several dispersants were measured by observing their differences of miscibility in known HSP solvents.

This can be done relatively, using ranks from 1 to 6, or in a binary fashion (1 or 0) depending on whether the dispersant is perfectly or imperfectly dissolved or mixed with the reference solvent. As with the particle HSP measurement, these solubility scores are then inputted into the HSPiP software for analysis.

The most important parameters in the HSP output are the D, P, H and R. These represent the δD, δP, δH and the radius parameters, which together describe the solubility sphere – its position and its size.
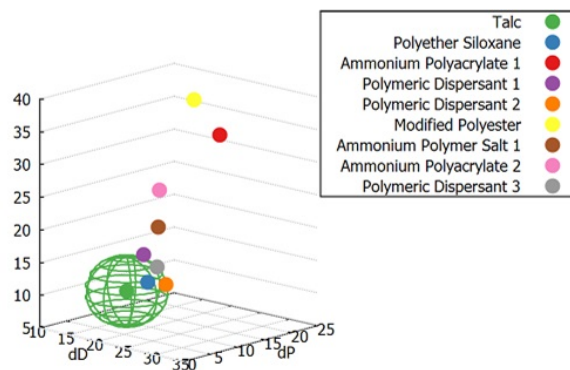
Calculation of Particle-Dispersant Distances

Particle-dispersant Distances

Once the HSPs have been measured for a particle and a range of dispersants, it is then possible to calculate the HSP distances between each dispersant and the test particle. Again, this is computed using the HSP Distance equation:

$$Dist_{HSP} = \left(\sqrt{4(\delta D_1 - \delta D_2)^2 + (\delta P_1 - \delta P_2)^2 + (\delta H_1 - \delta H_2)^2} \right)$$

HSP distance

It tends to be the case that shorter HSP distances are found between materials that have greater affinities for one another. The closeness of HSPs can be visualized by the plot below:

HSP plot for talc along with dispersants

Particle-dispersant Sphere Separation Distances

However, the HSP distance value does not take into consideration the radii of the HSP spheres, which show the breadth of compatibility of two materials. By one simple modification to the HSP distance

equation we can improve its predictive power.

$$Dist_{Sep} = \left(\sqrt{4(\delta D_1 - \delta D_2)^2 + (\delta P_1 - \delta P_2)^2 + (\delta H_1 - \delta H_2)^2}\right) - (R_1 + R_2)$$

HSP distance including radii (Sphere Separation Distance)

By introducing the values of the two HSP radii, we arrive at an updated equation, which effectively quantifies the distance between the surfaces of the two spheres.
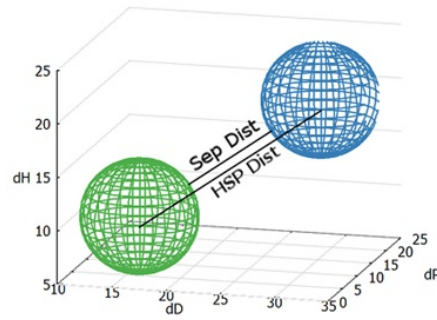
Negative values signify that the spheres are overlapping – the more negative the value, the higher the degree of overlap. It has been found that greater sphere overlap correlates with better compatibility of materials.

Example Data

As part of a case study, we compared the HSPs of 7 dispersants and then calculated their HSP Distances and Separation Distances from the talc product of interest. These data are presented below

dispersant	dD	dP	dH	Radius	Dist$_{sep}$
Polyether Siloxane	18.1	11.48	11.14	15.6	-14.55
Ammonium Polyacrylate dispersant 1	22.8	19.83	32.81	18.6	6.35
Polymeric dispersant 1	12.2	17.04	12.99	14.9	-3.75
Polymeric dispersant 2	19.3	13.56	10.58	8.1	-4.11
Modified Polyester 1	17.9	20.31	37.05	19.9	6.81
Ammonium Polymer Salt 1	18.0	13.54	19.11	12.1	-4.38
Ammonium Polyacrylate dispersant 2	18.7	12.95	25.07	6.1	6.99

HSP data for a selection of the dispersants tested

Based upon the HSP data the following dispersants are predicted to be more suitable for the particle in question:

     Polyether Siloxane (Considered the best)

     Polymeric dispersant 1 & 2

     Ammonium Polymer Salt 1

For the same materials (talc & dispersants), ODC & viscosity reduction were measured, allowing to check HSP predictions:
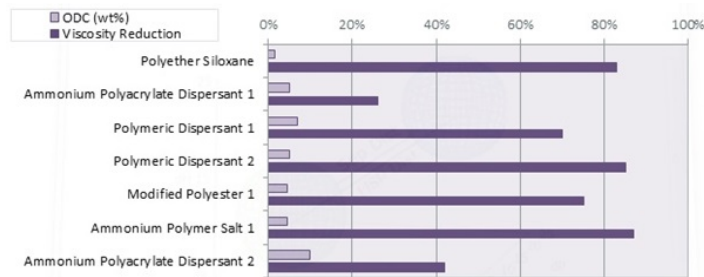

Figure 1: ODC results overview for talc

dispersant	ODC (wt%)	Viscosity Reduction	Performance
Polyether Siloxane	1.5%	83%	++
Ammonium Polyacrylate dispersant 1	5.0%	26%	--
Polymeric dispersant 1	7.0%	70%	+
Polymeric dispersant 2	5.0%	85%	++
Modified Polyester 1	4.5%	75%	+
Ammonium Polymer Salt 1	4.5%	87%	++
Ammonium Polyacrylate dispersant 2	9.9%	42%	-

ODC results overview for talc

Validation of HSP with ODC

Agreement between ODC and HSP

Agreement between ODC and HSP

If we now go back to the HSP prediction table we can add the results from the ODC test.

dispersant	Dist$_{sep}$	ODC Performance
Polyether Siloxane	-14.55	++
Ammonium Polyacrylate dispersant 1	6.35	--
Polymeric dispersant 1	-3.75	+
Polymeric dispersant 2	-4.11	++
Modified Polyester 1	6.8	+
Ammonium Polymer Salt 1	-4.38	++
Ammonium Polyacrylate dispersant 2	6.99	-

dispersants with negative HSP Separation Distances (i.e. overlapping spheres) tend to offer better performance in ODC tests. In particular, Polyether Siloxane gives the most suitable ODC profile, as well as the highest degree of overlap, in this case.

Savings with HSP-based Dispersant Selection method

Determining HSP for both solid particles & dispersants is an investment at start. But the good news is, the more data you have, the less cost.

With 4 dispersants and 4 Particles we get 16 sets of distance values.

So, with 8 HSPs you get 16 predictions, to help you with your screening process. That's 8 fewer experiments that you have to run to test for the best dispersant via ODC. Furthermore, HSP of mixtures can be calculated too, which allows for blending dispersants if you haven't find the right HSP to match the HSP of the particle or particle mixture.

Knowledge increases with HSPs Tested!
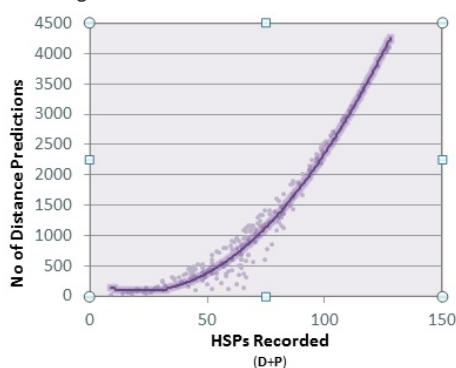
In general:
As you measure more and more HSPs the predictive power rapidly increases. This means:

- More knowledge
- Fewer experiments
- More savings – in time and money!

Conclusion

The use of HSP value to predict the best dispersant to use with a particular pigment or filler matches compatibility results obtained with more traditional screening...and **once you have a HSP database available, you can match your raw materials almost instantaneously!**

Imagine if your raw material supplier provided you with HSP data when delivering its additives… You could formulate faster and with more precision, probably saving you from negative side-effects that are so frequent in non-optimal systems. Yes, it's a dream right now but a very accessible dream for tomorrow!