Maximising dispersion stability

High throughput testing optimises additive selection

Contact:
Sander Van Loon
VLCI
T: +31 6 50874415
s.vanloon@vlci.biz

Veli Kilpeläinen
Alejandro Gutierrez
Sander van Loon
Sam Peel

Optimising the choice and addition rate of a pigment dispersant can be difficult and time-consuming. A method has been developed to achieve this by using also high throughput screening. This is used to establish the Hansen solubility parameters and optimum addition rates of dispersants. Those with solubility parameters closest to that of the pigment can be expected to perform best.

Selecting a suitable dispersant for a filler or a pigment (solid particle) is not an easy task, when one has to take into account:

- » The variety and amount of dispersants available.
- » The surface modification and/or the nature of the particle, both of which can vary greatly.

An effective dispersant performs the role of a protective buffer – with one portion specifically attracted to the particle (e.g. a hydrophobic tail adhering to the surface of the particle) and another portion specifically attracted to the solvent medium (e.g. a hydrophilic head for water compatibility).
To match the dispersant with the particle in order to develop a stable dispersion in the solvent, much needs to be known about the nature of the dispersant, the particle and the solvent.

Figure 1: Overview of the HT system

Solubility parameters provide the key to analysis

The information needed can be obtained by using the Hansen Solubility Parameter (HSP) of the products, with sample preparation via high throughput screening. Hansen solubility parameters (HSPs) are used to define the attractive forces Hydrogen bonding, Polar forces and Dispersion forces[1] within solvents or solvent blends, or to map the interactions of those with other materials.
By the principle of like-seeks-like, solvents and solutes with similar solubility parameters are more likely to form stable solutions than those with significantly different parameters. The net difference between the parameters of two materials can be quantified using the HSP distance, which is given by the following equation, based on the three parameters mentioned above:

$$Dist = \sqrt{((4(\delta D_1 - \delta D_2)^2) + (\delta P_1 - \delta P_2)^2 + (\delta H_1 - \delta H_2)^2)} \quad \text{Equation 1}$$

Thus, the smaller the HSP distance between two materials, the more likely it is that the two will be favourably associated. Ultimately it is possible to determine a solubility sphere or solubility radius: if this is determined for a resin, then a solvent (or mixture) whose parameters fall within this radius will dissolve it, while those with further distant will not.
Initially this concept was applied to determine the most suitable solvent or blend of solvents to dissolve polymers; but subsequently it has been developed to allow the calculation of ‘solubility parameters’ for insoluble materials such as pigments and substrates. Applying this concept to interactions between dispersants and particles, once the HSPs of these match, a stable dispersion can be formed.
In this work, the HSP method was verified by the Optimal Dispersant Content (ODC) method [2], a classical method to determine the right dispersant in a trial-and-error manner. These methods will be described and compared in this article to provide the selection of the best water-based dispersant to disperse the hydrophobic talc product “Finntalc M15” in a water-based coating.

High throughput formulation simplifies selection

“Finntalc M15” and a broad selection of dispersants with different chemistries were studied in relation to HSP and ODC. In order to speed up the process and make it more precise, samples were produced via the “Formax” High Throughput (HT) equipment from Chemspeed technologies.
A sedimentation time method in different solvents with different HSPs was used to establish the HSPs of the talc

product. Fast sedimentation means no compatibility with the solvents and slower sedimentation means better to good solvents. Good solvents are rated as 1, bad solvents as 6 and the rest are in between. Based on this rating, a distinction can be made in the HSP space.

The HSP can then be calculated via the dedicated "HSPiP" software (version 4.0.05, www.hansensolubility.com), by introducing this rating. All ratings are relative for each of the products.

For the surfactants, the normal HSP method was applied, meaning solvents were rated for good and bad solubility, again with rankings between 1 and 6. Samples of the products with the different solvents are made via the HT system, as it requires quite a large amount of samples for each product.

Optimising the dispersant concentration

An effective dispersant for waterbased applications performs the role of a protective buffer – with its hydrophobic 'tail' adhering to the surface of the particle and its hydrophilic 'head' associating favourably with the solvent medium.

In addition to ionic repulsions between the particles, the dispersant-rich region that forms whenever two particles happen to come close together is subject to osmotic pressure from the surrounding solvent, which tends to force the particles apart again.

As a dispersant is introduced into a pigment dispersion, there is a dramatic reduction in the viscosity of the paste or slurry, as the particles become more mobile in the solvent. The extent of the viscosity reduction is dependent on the amount of dispersant added.

However, the amount must often be minimised in order to reduce costs or to prevent other harmful effects which might arise from using high proportions. If the amount of dispersant used is too small, the full benefits will not be obtained. Clearly, for each system studied there is an optimum dispersant concentration (ODC).

Results at a glance

- ››› The selection of the optimum dispersant for a pigment or extender and the optimum addition rate can be a difficult and time-consuming task.
- ››› A composite method has been developed which provides an efficient route to achieving this; HSP, ODC and highthroughput formulation.
- ››› The optimized process consists of first establishing the Hansen Solubility Parameters (HSP) of a particle, select dispersants based on HSP and then obtain the optimum dispersant concentration.
- ››› Those dispersants whose solubility parameters are closest to that of the pigment can be expected to give the best performance.
- ››› This procedure was applied to find the best dispersants for a hydrophobic talc in waterborne systems.

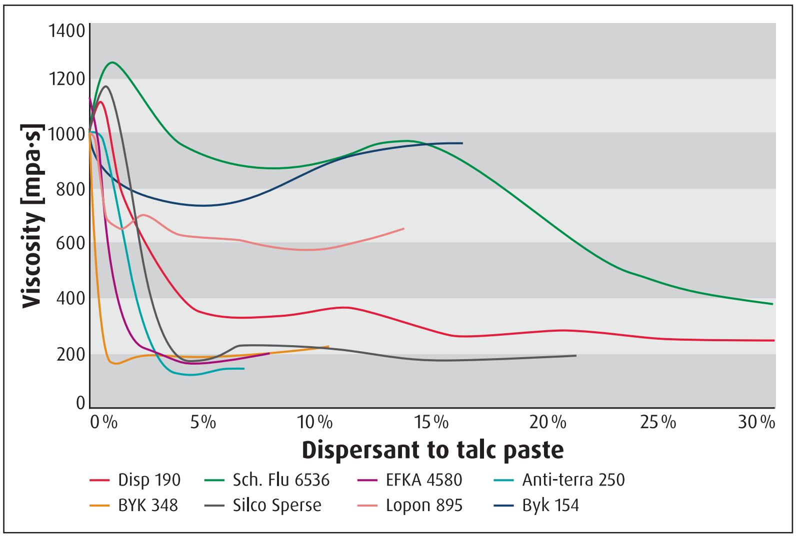

Figure 2: ODC analysis for the talc

Many factors affect the ODC, including the chemistries of the dispersant, solvent and pigment, and especially the surface area of the pigment to be tested. The ODC is the concentration of dispersant at which a plateau is reached in the pigment/solvent viscosity curve and this can be tested in order to adjust the final formulation. This experiment can be performed easily with HT screening on a wide range of pigments and dispersants.

Principles of high throughput screening

High Throughput (HT) is a valuable tool to automatically prepare formulations in parallel with high precision. In order to be flexible in various formulation preparations as in this project, an HT system was used that can add liquids, viscous and solid materials on a weight basis whilst processing, which is a unique feature.

On the HT platform, different processing methods can be operated, including mixing by horizontal shaking of glass tubes in a rack and dispersing with a Cowles dissolver disc in a temperature-controlled reactor.

In this HT system, the raw materials are thus brought to the glass tubes and reactors, in order to not disturb the processing, as required to make proper formulations. For this project, the HT system prepared the dispersions of talc in water via the HT reactors and the HSP and ODC samples in glass tubes present in the HT stirring rack. *Figure 1* provides an overview of the HT system used.

How optimum dispersant concentration is determined

In a first step, the ODC analysis on the talc paste was performed with respect to a selection of waterbased dispersants. The method for each dispersant was to prepare tubes containing 30 % of talc in distilled water, which was then thoroughly mixed to a paste. The viscosity of the paste was then recorded.

After the viscosity had been measured, a small amount of a dispersant was weighed into the tube, which was then thoroughly mixed. Again the viscosity was measured and

Table 1: Summary of ODC results obtained

Dispersant	Performance	ODC (wt%)	Viscosity reduction (%)
"BYK 154"	--	5.0 %	26 %
"Disperbyk 190"	+	7.0 %	70 %
"Schwego Fluor 6536"	--	9.0 %	30 %
"Efka 4580"	++	5.0 %	85 %
"Anti-Terra 250"	++	4.5 %	87 %
"BYK 348"	++	1.5 %	83 %
"Silco Sperse HLD-5"	+	4.5 %	75 %
"Lopon 895"	-	9.9 %	42 %

Table 2: HSP data for a selection of the dispersants tested

Dispersant	dD	dP	dH	Radius	Talc distance	Dist$_{sep}$
"Byk 348"	18.1	11.48	11.14	15.6	3.65	-17.25
"BYK 154"	22.8	19.83	32.81	18.6	25.79	3.19
"Disperbyk 190"	12.16	17.04	12.99	14.9	13.70	-6.60
"Efka 4580"	19.6	13.26	10.73	8	6.56	-6.84
"Silco Sperse HLD-5"	17.07	20.35	37.12	11	5.10	-3.10
"Anti-terra 250"	20.36	13.4	25.86	19.35	16.83	-7.37
"Lopon 895"	23.08	13.23	35.62	17.75	25.59	4.49

Table 3: Summary of results with best dispersants shown at the top of the listing

Dispersant	Talc distance	Particle-dispersant separation	ODC (wt%)	Viscosity reduction (%)
"Anti-terra 250"	4.25	-7.37	4.5 %	87 %
"Efka 4580"	6.77	-6.84	5.0 %	85 %
"BYK 348"	3.65	-17.25	1.5 %	83 %
"Silco Sperse HLD-5"	29.37	-3.10	4.5 %	75 %
"Disperbyk 190"	13.77	-6.60	7.0 %	70 %
"BYK 154"	17.11	3.19	5.0 %	26 %
"Lopon 895"	15.92	4.49	9.9 %	42 %
"Schwego Fluor 6536"	-		9.0 %	30 %

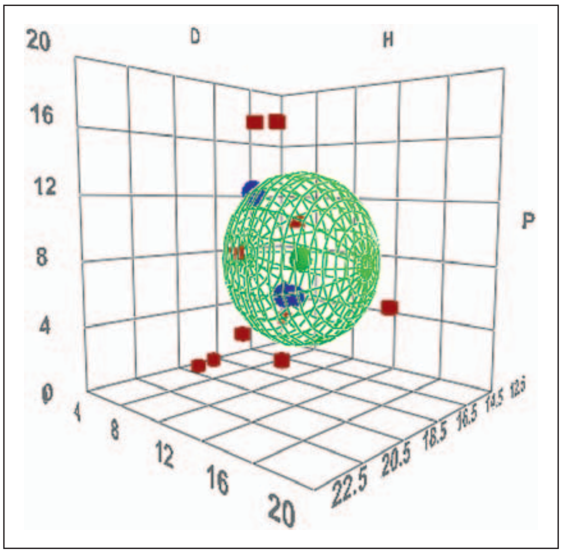

Figure 3: HSP data for the talc

this process was repeated over and over until the viscosity values had plateaued, and then a little further.

The viscosity of the paste with every dispersant and its concentration can be seen in *Figure 2*. The results of this ODC study are shown in *Table 1*. The profiles of the dispersants showed some interesting characteristics: the best of the dispersants displayed clear and large reductions in viscosity that remained even at low dispersant concentrations.

These 'step-changes' in viscosity varied in their slopes and in the mass-efficiency of each dispersant, but they all showed approximately the same relative viscosity changes of around 80 % reduction relative to the original talc-water paste. The dispersants which showed this behaviour most clearly were "BYK 348" "Anti-terra 250" and "EFKA 4580". Besides these, "Silco Sperse HLD-5" can also be considered good, but slightly less so than the others mentioned above.

Sedimentation tests to measure HSP values

Because talc does not show solubility but dispersion characteristics in a solvent, resulting in sedimentation, the sedimentation time of talc in the different solvents with known HSPs was measured. The rating of each solvent was entered in the software, resulting in the HSP data and solubility sphere for the talc as shown in *Figure 3*.

In order to match the HSP of the talc with a dispersant, the HSP of the dispersants was determined. The conventional HSP tests can also be extended to calculating the parameters of surfactants and dispersants. In this case, the solubility in the different solvents is rated.

Table 2 shows the experimental HSP parameters for the dispersants tested previously in the ODC studies, including the distance from the talc calculated in accordance with *Equation 1*. Although the HSP distance between two materials is useful in itself, more understanding can be gained when the radii of the solubility spheres are also employed in the analysis.

Figure 4 describes how the HSP distance between the centres of two spheres is related to the radii of those two solubility spheres and the minimum distance that separates their surfaces, taking into account the values obtained in *Equation 1*. In *Table 2* these separation distances are also given (Dist$_{sep}$), where of course the lower the value the better.

This data can be depicted nicely by plotting it on a 3D grid, along with the positions and radii of the sphere for the talc, as in *Figure 5*.

Based on the HSPs and distance data, it can be seen that the dispersants found to have the best performance from the ODC study are indeed inside the HSP sphere of the talc and the poor ones are far away. In this case, "Silco Sperse HLD-5" is very far away from the HSP of talc, but is much closer to that of water than the other dispersants. This might be one reason why this product is a good dispersant for water-based systems and therefore shows a good result from the ODC study.

HSP and ODC results combined

As shown, both the HSP and ODC study result in the same selection of good and bad dispersants for the talc. As a couple of dispersant HSPs are now known, next time it is a

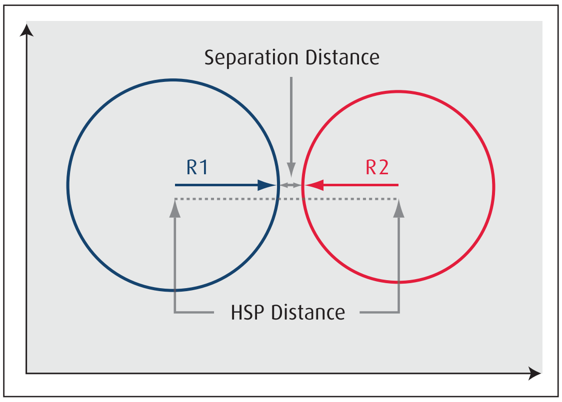

Figure 4: The concept of HSP distance including radii

matter of measuring the HSP of a particle and plotting the dispersants in HSP space to see if there is a match or not. The best dispersants can then be selected and tested via ODC in order to obtain the right amount of the dispersant for the particle. HSP can reveal the best matching dispersant, so this one should have in principle the best interaction, thus the lowest amount required with the highest viscosity reduction, but the ODC method is needed to obtain the data.

The strong point of using this HSP method in the first place is that it requires less effort than performing a full dispersant study for a particle via ODC.

An effective selection procedure in summary

Table 3 summarises the data for Finntalc M15, obtained from ODC test and HSP experiments, with the dispersants having the best performance shown first. The data collected for the ODC and the HSP study both show the same best-suited dispersants.

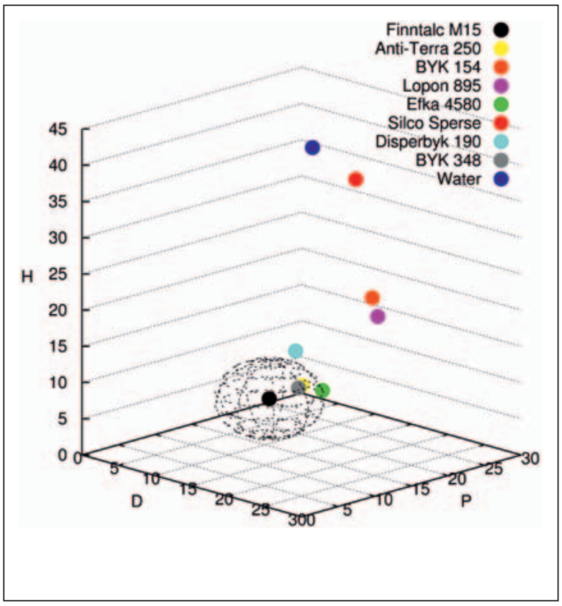

Figure 5: HSP plot for talc and dispersants

In terms of the minimisation of their addition levels and the efficiency of viscosity reduction obtained from ODC, low HSP distances from Finntalc M15 are also exhibited. This leads to a useful method to select the right type and amount of dispersant to use with a solid particle:

- Use the HSP method to obtain the HSP of the particle and then select dispersants with matching HSPs.
- Use the ODC study with these best dispersants to obtain the optimal amount of dispersant for the particle.

REFERENCES

[1] *Abbott S., Hansen C., Yamamoto H.*, Hansen Solubility Parameters in Practice – software, eBook and datasets, www.hansen-solubility.com

[2] *Bieleman J.*, in Additives for Coatings, 2000, p 65, Wiley-VCH.