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Article

Optimizing Coating Performance via Predictive Compatibility Parameters of Carbon Blacks and Dispersants

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TAGS:

In the coating industry, **achieving optimum dispersions of carbon black pigments** is a challenging task with a crucial outcome. Carbon black suppliers are investing a lot of time and effort in developing specific surface treatments to improve the aesthetic performance and stabilization of their products.

In the particular field of automotive applications, jetness is a key factor, where the darkest and most bluish undertones must be achieved. Jetness values are a result of stabilized primary particles. These values include:

- My (degree of blackness)
- Mc/dM (jetness/undertone)

Different post-treatments on the same core pigment particles will have a drastic influence on their **compatibility with wetting and dispersing additives**, impacting their final stabilization.

Firstly, you should be aware that for the coatings market, there is a wide range of carbon black grades available. To understand how carbon black properties influence the final applications and to know which carbon black is used in which category, **take a quick tour to our exclusive guide for tips to find the right grade for your formulation**.

As part of the formulation process, selecting the right dispersant for a pigment is essential. A poorly chosen dispersant can have a very detrimental effect on a coating's final properties, such as:

- **Stability**
- **Rheology**
- Pigment loading, and
- Color intensity (jetness in the case of black pigments)

Therefore, knowing how to select the best dispersant is vital to optimizing the final coating performance.

Here, we will showcase how Hansen Solubility Parameters (HSP) can be used to quickly predict the most compatible dispersant/pigment pairing out of a selected set of dispersants, leading to optimized performance of the pigments in the coating. After determining the HSP of 2 carbon black grades (**Raven 5000 Ultra II** and **Raven 5100 Ultra**) and 2 dispersants (**Tego® Dispers 761 W** and **CLiQSPERSE® 149**), compatibility predictions were made and validated via practical experiments.

	NSA (Nitrogen Surface Area) [m^2/g]	STSA (Statistical Thickness Surface Area) [m^2/g]	OAN (Oil Absorption Number) [$cm^3/100g$]	Particle Size [nm]	Volatile Content at 950°C [%]
Raven 5100 Ultra	583	350	95	10	-
Raven 5000 Ultra II	583	350	95	10	10.5
Note: *In these pigments, the basic properties like surface area, structure, primary particle size are the same; the main difference is the surface treatment and functionalities on the pigment surface area.*					

The Carbon Black Pigments Studied

Before determining the values of these pigments & dispersants, let us brief you on the basics of HSP.

Practical Determination of Hansen Solubility Parameters

In 1967, **Charles Hansen** submitted his doctoral thesis "*The three-dimensional solubility parameter and solvent diffusion coefficient*" introducing the theory which has since become known as the **Hansen Solubility Parameters (HSP)**. These parameters have removed the trial-and-error process and given practical solutions to countless problems across a wide variety of formulation-based industries (Hansen, 2017).

Today, the term "solubility parameters" is considered to be quite restrictive, as the use of HSP goes beyond solubility challenges. These parameters can predict the compatibility for various types of chemicals/ingredients, even insoluble ones, allowing for **smart and predictive**

ingredient matching. Therefore, HSP should be interpreted as “Hansen Similarity Parameters”, as recognized by Dr. Hansen.

The Hansen Solubility Parameters are made up of:

- δD (Dispersion forces)
- δP (Polar forces), and
- δH (Hydrogen bond forces)

By plotting these in a 3D space in the HSPiP software, it is **easy to obtain the HSP of unknown ingredients** by entering their ranking in different solvents with known HSP, and also to visualize and interpret the results. When the HSP has been practically determined, the Compatibility Radius is also provided. All solvents/ingredients within this radius are compatible with the test product.

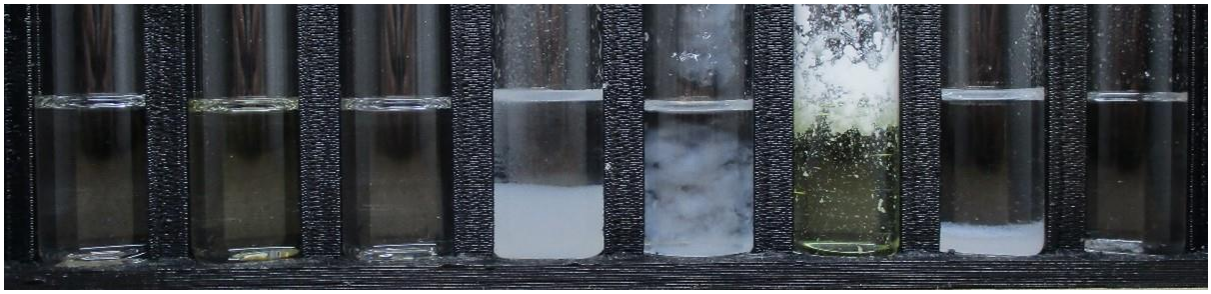
The radius is concentration-dependent: the higher the concentration of the product, the smaller the radius.

The software HSPiP is now led by **Professor Steven Abbott** with **Dr. Hiroshi Yamamoto**. Since 2010, the HSPiP team recognizes VLCI as a certified center for practically determining HSP, for all areas of the formulation industries and all over the world.

HSP Determination of Dispersants

A **dispersant’s HSP can be determined** by the classic test method which involves the test material being added to a **range of solvents** that cover the HSP space. The samples are shaken and left to dissolve. After this, they are visually assessed with a qualitative rank from 1 to 6, where a 1 means that the product is completely dissolved, 6 means that there has been no interaction between the solvent and the product; the other scores indicating various stages of dissolution. VLCI uses an automated process for HSP sample preparation via the **High Throughput system FORMAX (Chemspeed technologies)**.

Some of the test samples can be seen in the image below.



Tego® Dispers 761 W Samples

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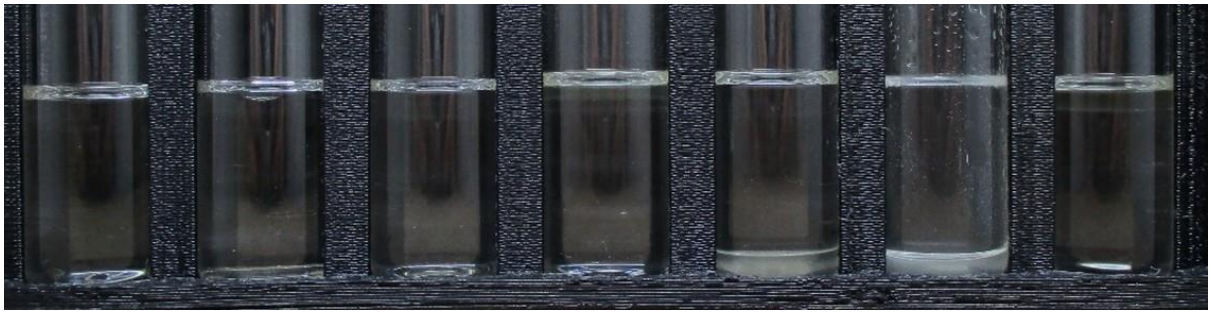
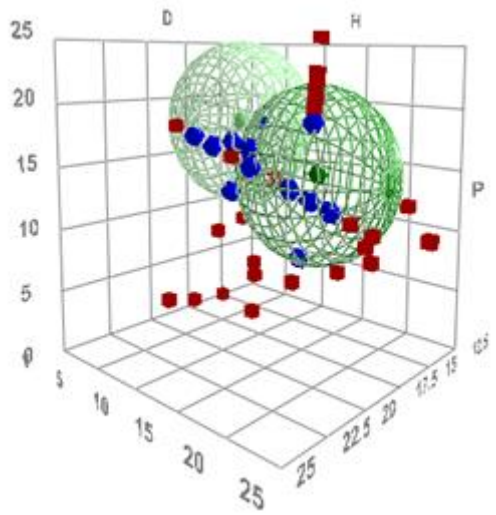
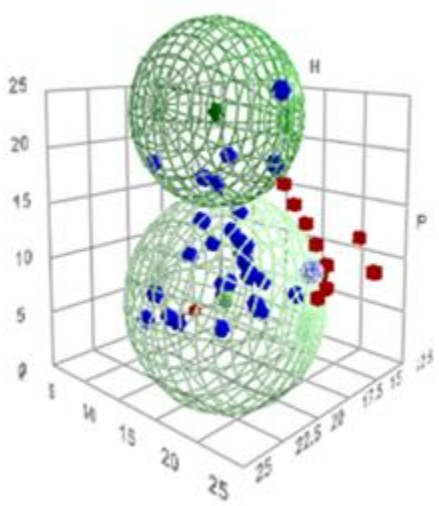


CLiQSPERSE® 149 HSP Samples

The HSP results of the 2 tested dispersants are shown in the following table.

Tego® Dispers 761 W	CLiQSPERSE® 149
	
GA Fit	GA Fit
In=12, Out=27, Total=39	In=30, Out=15, Total=45
D1=14.91, P1=13.74, H1=12.81	D1=17.75, P1=22.94, H1=8.91
Tot=24.0, R1=7.9	Tot=30.3, R1=8.9
D2=16.24, P2=17.99, H2=5.33	D2=18.12, P2=5.46, H2=10.70
Tot=24.8, R2=7.1	Tot =21.7, R2=10.3
Fit=0.975	Fit=0.978
Wrong In=1	Wrong In=0
Wrong Out=0	Wrong Out=1
Dimethyl Formamide (Dmf)	Cis-2-Butene-1,4-Diol

The HSP Results for the Dispersents

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Both products display **double sphere behavior**; this occurs when a compound has 2 distinct regions of functionality, which is common in surfactants, dispersants, and block co-polymers.

How to Quickly Find the Dispersant You Need – Watch This Free Tutorial Now

HSP Determination of Pigments

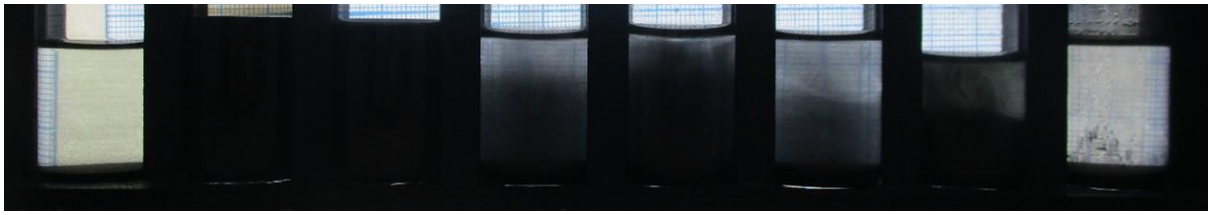
To determine the HSP of insoluble pigments, a test method called the **Sedimentation Method** is used. As in a traditional HSP, the pigment is added to a range of solvents that covers the HSP space. In our case, this is done in an automated manner. Then, instead of waiting for the samples to dissolve, all tubes are thoroughly shaken to disperse the pigment in each of the solvents simultaneously. Then, the time taken for the pigment to sediment out of the liquid is measured. From this time, the **relative sedimentation time (RST)** is calculated (Equation 1), which corrects for differences in sedimentation due to **density** and **viscosity**, meaning that the resulting times are purely indicative of their interactions.

$$\text{Equation 1: } RST = t_s \frac{(\rho_p - \rho_s)}{\eta}$$

where:

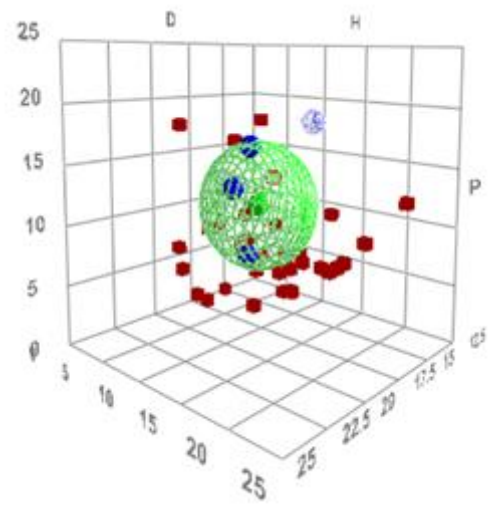
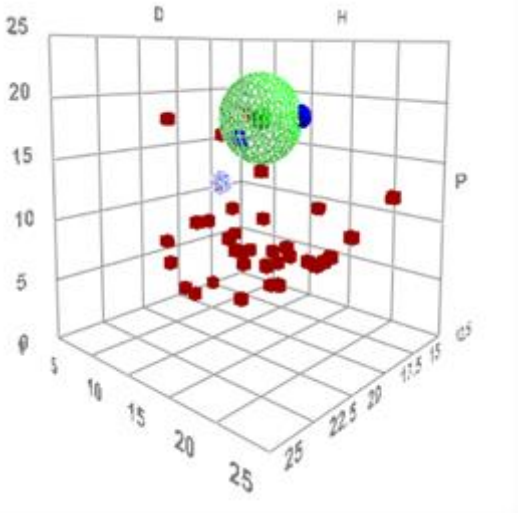
→ t_s is the actual sedimentation time
→ ρ_p and ρ_s are the densities of the particles and solvent respectively
→ η is the viscosity of the solvent

These times are then the basis for the ranking used in the HSP determination. Some of the samples can be seen in the image below.



The Carbon Black Samples on Test

Based upon their RST's, the samples are then grouped into ranking from 1 to 6, used as input for HSPiP.

Raven 5000 Ultra II	Raven 5100 Ultra
	
GA Fit In=4, Out=33, Total=37 D=18.08, P=11.45, H=10.54 Tot=23.9, R=5.0 Fit=0.946 Wrong In=1 Dimethyl Formamide (DMF) Wrong Out=1 N-Methyl Formamide	GA Fit In=3, Out=34, Total=37 D= 18.16, P=17.87, H=13.02 Tot=28.6, R=4.2 Fit=0.973 Wrong In=0 Wrong Out=1 n-Methyl-2-Pyrrolidone (Nmp)

The HSP Results for the Carbon Blacks

Due to the different treatments of the carbon blacks, the two products clearly exhibit different HSP's, even though they are both carbon black pigments at their core.

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Compatibility Predictions – Selecting Optimum Dispersant for Pigments

From these HSP's, the optimum dispersant for the pigments can be selected via compatibility calculations. These calculations allow the parameters to be easily implemented in formulations.

The equation to calculate distance is:

$$\text{Equation 2: } Ra^2 = 4(\delta D_1 - \delta D_2)^2 + (\delta P_1 - \delta P_2)^2 + (\delta H_1 - \delta H_2)^2$$

Using Equation 2, the smaller the distance, the more compatible the products are.

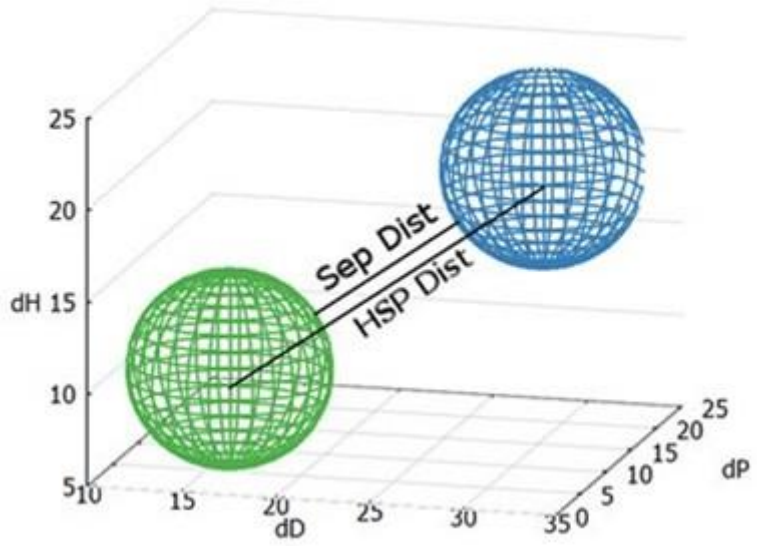
To calculate this distance relative to both product spheres, the Sphere Separation distance is used:

$$\text{Equation 3: } Dist_{Sep} = \left(\sqrt{4(\delta D_1 - \delta D_2)^2 + (\delta P_1 - \delta P_2)^2 + (\delta H_1 - \delta H_2)^2}\right) - \left(R_1 + R_2\right)$$

Equation 3 introduces the two HSP radii to the distance equation, and now 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.

A larger amount of sphere overlap predicts better compatibility of materials.

The below figure demonstrates the difference between Equation 2 and Equation 3.



Visual Representation of Equation 2 & 3

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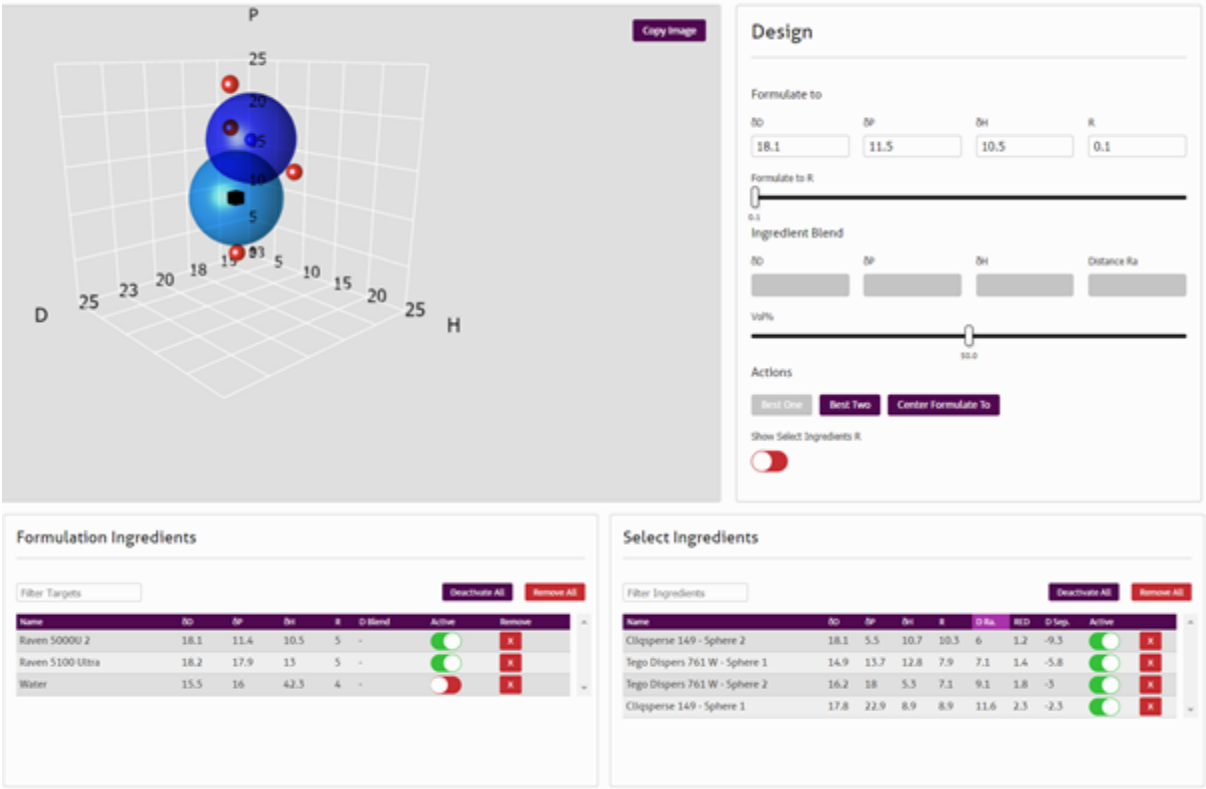
Product Name	Tego® Dispers 761 W Sphere 1	Tego® Dispers 761 W Sphere 2	CLiQSPERSE® 149 Sphere 1	CLiQSPERSE® 149 Sphere 2
Raven 5000 Ultra II	-5.79	-2.96	-2.28	-9.31
Raven 5100 Ultra	-4.40	-2.70	-6.52	-1.87

Sphere Separation Distances Between the Products

From the sphere separation distances, it is seen that both pigment samples are predicted to have better compatibility with **CLiQSPERSE® 149** than with Tego® Dispers 761 W, based on a higher overlap with one of the spheres (more negative). Between the pigments, Raven 5000 Ultra II will have better compatibility with CLiQSPERSE® 149 (-9.31) than Raven 5100 Ultra (-6.52). Tego® Dispers 761 W still shows some overlap and therefore some compatibility with both pigments (-5.79 and -4.40).

The HSP of these ingredients was then loaded as a dataset into VLCI's web-app, to map and visualize them, together with both distance calculations.



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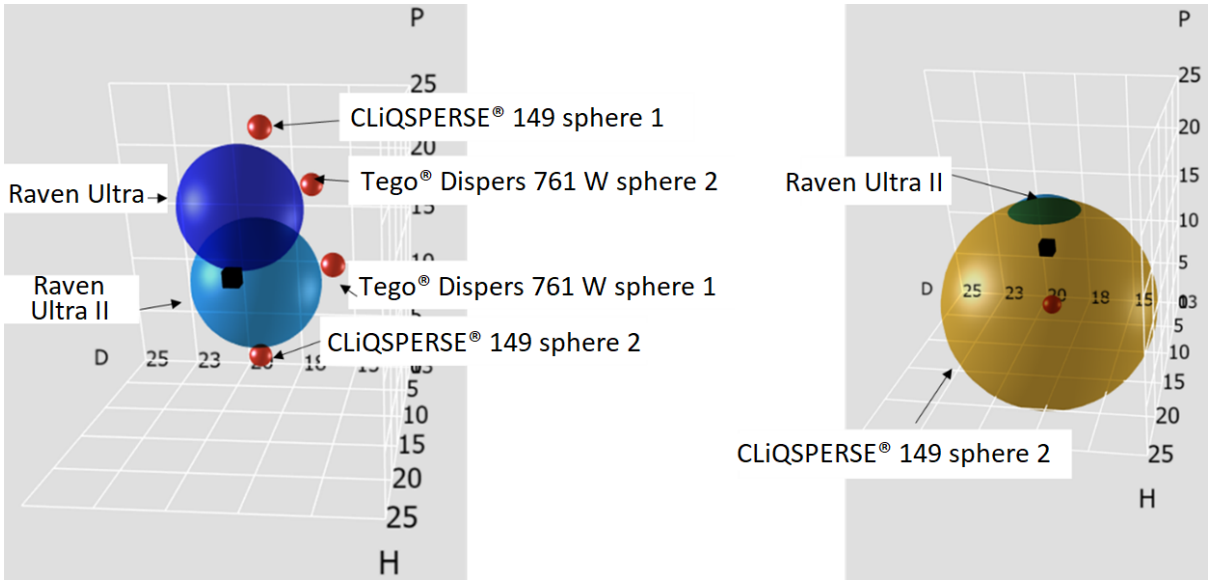

Overview of VLCI's App and the Loaded Ingredients from the Database

From these HSP results, it is expected that the performance of the pigments is better with CLiQSPERSE® 149 than with Tego® Dispers 761 W. Furthermore, it is believed that **CLiQSPERSE® 149 will give the best viscosity and post post-application results with Raven 5000 Ultra II**. These HSP predictions were then compared with the attributes of the pigments after applications.

Comparison of HSP Compatibility with Performance

TMC GmbH provides **formulation simplification and R&D services** to manufacturers of recipe-based production methods. Their main area is the stabilization of pigments in intermediates, providing a 360° view of raw materials supplied to the ink, coatings, and adhesives industry. TMC studied the performance of the **Carbon Blacks** during milling and after application.

From the Optimal Dispersant Concentration (ODC) study performed by TMC, it was found that:

- **Raven 5000 Ultra II** has the best viscosity reduction with CLiQSPERSE® 149 (20 mPas) and the least viscosity reduction with **Tego® Dispers 761 W** (567 mPas) (measurements with Viscosity Haake MARS III at $10s^{-1}$).
- **Raven 5100 Ultra** also has the best viscosity reduction with CLiQSPERSE® 149 (40 mPas) and the least viscosity reduction with Tego® Dispers 761 W (1226 mPas).

This is in line with the HSP matching of Raven 5000 Ultra II and CLiQSPERSE® 149, having the largest amount of overlap (most negative sphere separation value) and Raven 5100 Ultra having the least overlap (least negative sphere separation value).

For evaluating the jetness, the **dispersions were added into a water-borne refinish base coat**, which was recoated with a solvent-borne HS 2K Clear. Afterwards the jetness values My, Mc and dM were measured. Various water-borne dispersants were used in this study and then compared to the HSP results.

Product Name	Raven 5000 Ultra II			Raven 5100 Ultra		
	My	Mc	dM	My	Mc	dM
Tego® Dispers 761 W	282	290	8	275	281	6
CLiQSPERSE® 149	291	295	4	275	281	6

Jetness Measurements of the Pigments with Each Dispersant

Also, here the results of the jetness study are in line with the results in HSP predictions.

Conclusion

The HSP of 2 pigments and 2 dispersants was successfully determined. These values were then used to predict the compatibility between the products, and consequently, to define which combination within this set would lead to **optimized performance of the coating**. These predictions were then validated against traditional application test methods, such as ODC and Jetness, which confirmed the predictions.

This case study validates the use of HSP as a predictive compatibility tool for the matching of optimum dispersants with specific pigments. Consequently, this leads to improved coating performance. Overall, the HSP approach results in rational ingredient selection, saving a significant amount of time, samples and costs.

Note: *Raven is a trademark of Birla Carbon*