**SCRIPT for UK COLLOIDS 2021**

**SLIDE 1: Intro**

Hello, my name is Ravi Sharma, Principal Research Fellow at Mageleka, Inc.

Today I will present a few highlights of our recent work on the application of Low Field NMR relaxation measurements to determine the HSP of Particles. The results, as we shall see, are helpful to formulators dealing with particle dispersions including polymerics and carbon black.

**SLIDE 2: Particle dispersions are important….**

The dispersion and wetting of powder into liquids is a critical process step in the manufacturing of dispersions of inks, paints, cosmetics, and pharmaceuticals. There is practical and economic benefit in reducing the time spent in identifying the appropriate solvent or solvents.

The HSP is a very useful method to select solvents and solvent mixtures. In the HSP approach, the particle of interest is dispersed into variety of solvents (usually between 10-20), and then rank ordered in terms of their stability. This is time-consuming (Days).

**We can use NMR solvent relaxation measurements which are fast – typically only minutes.**

**SLIDE 3: NMR Solvent relaxation……..**

Upon application of a magnetic field of a sample containing any liquids that contain at least one proton, the spin state of the protons is in a higher energy state. They relax back to equilibrium at a rate depending on the local magnetic coupling.

Solvent molecules in contact with an interface are not free to rotates and translate as in the bulk. Hence relaxation times are shorter.

A single relaxation rate is measured that is a weighted average of bound and free solvent.

**The relaxation rate is enhanced** when a solvent is in contact with an interface, (for example particle-solvent interfaces). It is sensitive to **dispersion quality** and to the **interaction strength between solvent and additives (relates to compatibility/solubility of additive).**

**A useful advantage is that the technique is non-invasive/non-destruction so samples can be saved for future re-analysis.**

**SLIDE 4: ……..can rank order compatibility of solvents with powder……..**

All the measurements were made using a small, bench-top Low Field NMR spectrometer – a Mageleka *M*agno*M*eter.

Normalized relaxation rate constants were calculated from the basic relaxation time(s). The Relative Relaxation Rate, Rno, is a dimensionless parameter.

We see that Rno depends on the solvent, and that its value depends on the magnitude of the interaction of the solvent with a surface.

**Rno values are 5-10 x larger for the same solvents in contact with hydrophilic particles (the silica-coated ZnO) than with hydrophobic particles (the silane-coated ZnO).** This is not unexpected because the latter powder is poorly wetted by high surface tension liquids (e.g., water).

**SLIDE 5: …..and determine the HSP of particles**

Rank-ordered solvents can be used to generate a Hansen sphere using the three co-ordinates of interaction energy, *viz* Dispersion, polar and H-bonding that contribute to the total cohesive energy – as shown on the left. We used custom HSPiP software.

**Thus, once the HSP of a particle is known then any combination of solvents (even poor ones) having the same average HSP value will provide good wettability.**

The Figure on the right show the results presented as a 2-D TEAS plot.

As expected, (from the primary relaxation results in the previous slide), there is a large difference between the silane- and silica-coated ZnO powders. The dispersion component (D) is higher, and the hydrogen-bonding (H) component is lower for the hydrophobized powder

Uncoated ZnO and Al2O3 have similar polar energy. **While ZnO and Al2O3 are clearly different chemical materials, the HSP data suggest that the interaction of solvents having strong affinity with the surface of these materials is comparable.** This can be rationalized by considering that both are hydrophilic, cationic in water, (and we measured similar zeta potentials) and is likely related to the acid-base (electron acceptor-donor) properties of the surface(s) in relation to the solvent(s)

**The silane-coated Al2O3 has significantly less hydrogen bonding than the silane-coated ZnO.**

**Thus, the type of silane coating of these two oxides must be quite different, in chemical nature and/or coating density.** Such a marked difference affects the choice not only of the solvent used but also any other moiety – such as a surfactant, dispersant, or stabilizer - that might subsequently be used in the formulation of a suspension, since it will impact the interaction (e.g., adsorption) with the surface.

**Hence, the HSP can be used to probe and discriminate the surface chemical nature of materials. Understanding this allows a formulator to more efficiently, and better, optimize the preparation of a suspension**.

**SLIDE 6: Surface properties of Carbon Blacks**

A main challenge in advancing battery technology is to optimize the composition of the carbon slurry mixture used to make the electrodes.

The surface chemistry of Carbon Black is complex and depends critically on its manufacture.

Here we compare the Relative Relaxation Rate(s), Rno, for a series of commercial carbon blacks dispersed directly in hexane and isopropanol.

**The Carbon Blacks cluster in three areas of HSP space. The 353 BIRLA material is clearly atypical of all the other carbon blacks.**

**Hence, NMR relaxation can differentiate the interaction of each of the solvents with the individual carbon blacks**. The differences are a consequence of manufacturing variability - not only true variations in geometric surface area (because of both the size and surface roughness of the carbon black particles) but also the wettability (determined in large part by surface chemistry) between the carbon black particles and the solvents.

Based on the known HSP values for hexane and IPA, we can conclude that hexane-CB interaction strength arises solely from the Dispersive contribution to the total cohesive energy; in contrast, the IPA-CB interaction is dominated by the hydrogen bonding contributions.

The data trends with Inverse Gas Chromatography data for the Carbon Blacks in the same solvents.

**SLIDE 7: Solubility of Polymeric Dispersants**

Two hypersdispersants were obtained from LUBRIZIOL. The determination of polymer solubility is tedious and subjective – **especially when all the solutions are visually clear.**

Here we demonstrate, by comparison of the Relative Relaxation Rate (Rno), that it is possible to rank order polymeric dispersant compatibility with solvents, **and importantly, we can identify that the Solsperse B had a stronger interaction with all the solvents used than Solsperse A,** and which we conclude as being overall more soluble.

The NMR solubility ranking correlates with published LUBRIZOL sales literature.

Time does not permit but we have additional data that suggests an Rno > 0.2 represents strong solvent-hyperdispersant interaction.

**SLIDE 8: Comparison of Dispersant Efficiency**

Here we show a comparison of solvent relaxation rate for aqueous suspensions of a phthalocyanine pigment prepared under identical mixing conditions using two different dispersants (added at ca 6wt%) over a wide range of solids concentration.

The graphs are linear over the concentration range studied – up to ca 35wt%.

JOB-1 Dispersant C (blue), JOB-2 Dispersant D (red).

**The NMR relaxation data indicates that the dispersion quality of JOB-1 is much better than JOB-2**.

Thus, the “structure” of the two particulate suspensions is clearly not the same. Since the pigments used are identical, this can only be a result of differences in the structure/conformation of adsorbed dispersant. In slurries, at high solids loading, this will impact the flow and processing characteristics.

This conclusion was confirmed by other independent observations. For example, at 35wt% the JOB-1 suspension was quite fluid; in comparison the JOB-2 suspension was thick and pasty.

**The data also demonstrates that the technique can work at industrially relevant solids concentration without any sample preparation or manipulation.**

**Indeed, we have made measurements up to 90wt% (a silver paste used in the production of solar panels).**

**SLIDE 9: Conclusion**

In conclusion: Solvent relaxation NMR is a useful complementary technique for characterizing solvent-particle and solvent-solute interactions.

The technique is fast, and a simple way to characterize the surface properties of the particle for dispersion purposes.

**SLIDE 10: Thank you**

If any have any questions, please contact me.