NMR Relaxation Measurements and Powder Wettability

Introduction

When starting with a dry powder, the formulation of any suspension or slurry involves three distinct steps – wetting, dispersing, and stabilizing (see Mageleka White Paper #3). The initial step, wetting, is described as the affinity of a liquid for a surface, and this is an important characteristic of solid-liquid dispersions. Moreover, it is crucial to understanding how dispersibility impacts industrial processes and applications. The physical interaction between a liquid and a solid can vary enormously from case-to-case; different situations often require different wetting behavior, and some common examples are listed in Table 1.

Table 1: Common examples of commercial and industrial products and processes and the desired wetting behavior associated with each.

Non-Wetting desired	Partial Wetting or Wetting Differences desired	Good Wetting desired
Anti-soil surfaces Anti-stick surfaces Release coatings Water-proofing Adhesives (pressure sensitive; removeable)	Ore flotation Printing plates Two-in-one shampoo/conditioners	Absorbency (wicking) Coating Washing (detergency) Personal Care Adhesion Inks Printing/Painting

Liquids are affected to different extents by the chemical and morphological nature of particle surfaces (e.g., surface chemistry and roughness). The smaller the contact angle of a liquid for a solid surface, the greater the wetting. A knowledge of powder wetting is important to good dispersibility. Hence, it is often instructive to simply measure the characteristics of particles suspended in an homologous series of liquids (such as alkanols or alkanes) that have different contact angles for a given material surface. By doing this, one can determine which liquid provides the desired wetting (e.g., maximizing paint hue while minimizing suspension viscosity).

The wettability is also a function of the interfacial tension between a liquid and a solid. This can be lowered by adding surfactants into the liquid, liquids. As such, wettability impacts the resulting dispersed surface area. Hence, it is important to know, or recognize, if the dispersion liquid is a “pure” liquid, or if it is one that contains additives such as polyelectrolytes or surfactants. This is especially relevant when comparing suspensions from different sources (see Mageleka Application Note #1).

Despite the importance of understanding powder wettability, and the implications this has for the performance of industrial products and processes, there are few reliable measurement techniques to determine the wettability of

“Accurate assessment of powder wetting is crucial to understanding how dispersibility impacts industrial processes and applications.”

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powders. Contact angle measurements are only useful for flat, planar surfaces, and interfacial tension measurements are generally only applicable only to liquids. Although the heat of immersion method can provide some fundamental measure of powder wettability, such instrumentation is very expensive, has significant experimental complexities, and requires a long measurement time – characteristics that make it unsuitable for quick, routine laboratory analysis.

By contrast, nuclear magnetic resonance (NMR) relaxation is a fast and easy method to assess wettability for almost any type of solid-liquid combination – and this includes not only materials such as powders but also fibers (e.g. textiles), sheets (plastics), and other forms. Further, NMR relaxation can be used not only to monitor the wetting efficiency of pure solvents, but also liquid mixtures (see Mageleka Application Note # 11) as well as to follow the adsorption of surfactants and polymers onto surfaces (see Mageleka Application Notes #14 and #15) and, therefore, potentially can help in optimising industrially relevant formulations.

This Application Note will explore NMR relaxation measurements as a simple means of determining the wetting efficiency of powders directly, and introduce the Mageleka *M*agno*M*eter XRS™ Relaxometer as a compact and powerful instrument for routine analysis of this kind. More information as to how such measurements can be of use is available at www.mageleka.com

About NMR Relaxation

NMR spectroscopy is one of the most powerful analytical tools used to probe details of molecular structure and dynamics. Devices employing NMR technology require very high magnetic fields and, hence, very large magnets. However, the advent of small powerful magnets has allowed instruments, such as the *M*agno*M*eter XRS™, to be designed that have small footprints and simple operation, making them well-suited to normal, routine laboratory analysis.

NMR relaxation time is a fundamental intrinsic property of solids and liquids. What the *M*agno*M*eter measures is the extent of molecular motion as protons react when perturbed by a magnetic field. The liquid in contact with the particle surface relaxes much more rapidly than does the rest of the liquid, which is free (i.e., “bulk” liquid). This is typically of the order of microseconds, compared with the NMR relaxation time for the bulk liquid (i.e., in the absence of particles), which can be of the order of seconds. Generally, what we measure is an exchange average of these two states. Thus, the measurement of relaxation time provides direct information about the extent and nature of any particle-liquid interface, (see Mageleka Technical Note 1: Physical Characterization of Suspensions and Slurries using NMR Relaxation) and it is this basic technique that is used in the *M*agno*M*eter.

The Relaxation Number

Although the fundamental measurement from the *M*agno*M*eter is a relaxation time, a very useful practical metric, in any application, is the relaxation number, R_{no}, which is a dimensionless parameter defined as:

$$R_{no} = (R_{av} - R_b)/R_b$$

Where, R_{av} and R_b are the relaxation rates of the suspension and its (bulk) dispersion fluid, respectively. Note that the relaxation rate is the reciprocal of the measured relaxation time. The relaxation number can be used to follow kinetic processes such as adsorption and desorption, and even competitive adsorption.

What Does The *M*agno*M*eter Do?

The *M*agno*M*eter provides complementary information and intelligence to traditional particle characterization devices. The actual relaxation value obtained from NMR is an average (see above) which is dependent upon the exact composition of the suspension. This is somewhat analogous to the zeta potential of a material where the value depends critically upon the exact composition of the dispersion fluid.

Importantly, the *M*agno*M*eter’s measurement technique is both non-invasive and non-destructive so

samples can be stored for future re-analysis. Hence, the *M*agno*M*eter is particularly useful for measuring properties such as accelerated aging or shelf storage. Further, the instrument will work with suspensions at any industrially-relevant concentration or opacity, and the inherently simple measurements technique takes only minutes (see Mageleka Technical Note 2: The Mageleka *M*agno*M*eter Relaxometer).

Comparing Powder Wettability Using NMR Relaxation Measurements

Here we demonstrate the usefulness of *M*agno*M*eter XRS™ measurements in determining the wetting efficiency of powders. The basic powder material used was a hydrophobically-modified micronized zinc oxide (ZnO) obtained from three different manufacturers (in the USA, EU, and Japan). They were claimed to be equivalent products: they had the same nominal particle size and the same silane-based coating (specifically, a triethoxycaprylsilane). The basic silane is an inorganic compound, silicon hydride (SiH_4). Silanes are compounds with up to four substituents on the silicon (e.g., organosilicon compounds) that are structural analogues of the saturated hydrocarbons (alkanes).

The material in question, ZnO, is used in the formulation of sunscreen products because it is an efficient absorber of UVA and UVB radiation but, in its natural state, is hydrophilic (i.e., it can readily be wetted by water). The silane coating makes the ZnO completely non-wetting in water and so enables it to be incorporated into the oil phase of a sunscreen formulation. For beach use, such formulations are typically water-in-oil emulsions.

However, different non-aqueous fluids – what we would call “oils” – will wet a surface differently. In this case study we show a comparison of the three ZnO samples each dispersed at 8 wt% in two completely different fluids: octyl dodecyl neopentanoate (an organic aliphatic hydrocarbon), sold under the trade name “Elefac I-205”, and 100 centistoke silicone fluid (an inorganic fluid). This latter chemical is a polydimethylsiloxane fluid (“dimethicone”) often erroneously (and confusingly) referred to as “silicone oil”.

In the first example (Fig. 1) – the silicone fluid (repeatability of the relaxation time measurement was ~1%) – it can be seen that each of the powder samples are wetted to almost the same extent. Indeed, the relaxation numbers, R_{no} for materials B and C are virtually identical. This is likely because the surface coating is a silane which is very compatible with linear silicone fluids such as dimethicone. Material A is, however, slightly different as is evident from the lower R_{no} value, which indicates less efficient wetting compared with Materials B and C.

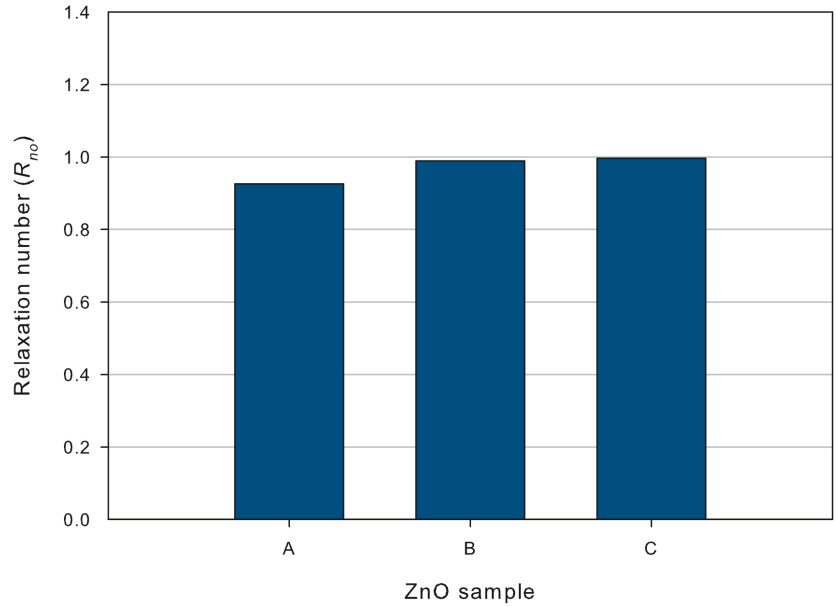

FIGURE 1: Variation in relaxation number of hydrophobically-modified micronized zinc oxide (ZnO) samples obtained from three different manufacturers. All samples were dispersed at 8 wt% in a polydimethylsiloxane (dimethicone) fluid.

However, what happens if the dispersing fluid is not a silicone (which is an inorganic fluid)?

A diverse variety of different organic oils – such as isopropyl myristate, capric/caprylic triglyceride and C_{12}-C_{14} alkyl benzoate – are used in the preparation of suncare products; Elefac I-205, for example, is used as an emollient and sun protection factor (SPF) booster.

In the second example (Fig. 2) – octyl dodecyl neopentanoate – the measurement repeatability was, again, <1%. However, this change to an *organic* dispersing fluid results in a far lower wetting efficiency for all three materials and large differences can be seen in the relaxation number for each of the three dispersions. This is undoubtedly because, notwithstanding the manufacturer's claims, the "silane coating" for each ZnO surface is not exactly the same and, hence, differences in wetting by any non-compatible organic fluid should be expected. From the results in Figure 2, it can be seen that the dispersion of the ZnO sample A has the largest value for R_{no} and so was by far the most efficiently wetted by octyl dodecyl neopentanoate.

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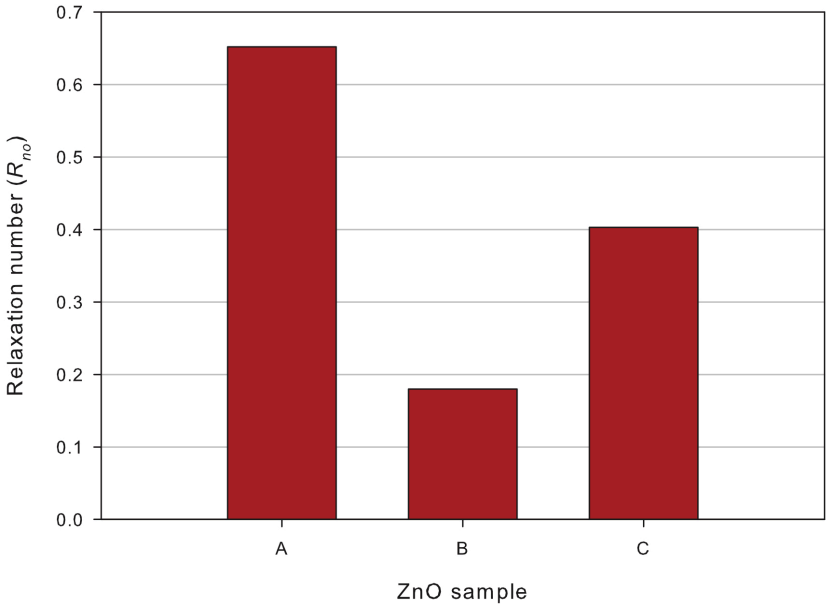

FIGURE 2: Variation in relaxation number of hydrophobically-modified micronized zinc oxide (ZnO) samples obtained from three different manufacturers. All samples were dispersed at 8 wt% in octyl dodecyl neopentanoate.

This case study demonstrates well how NMR relaxation data can be used not only for fast determination of powder wettability by liquids, but also to discriminate materials based (via coatings) on their surface chemistry and, by extension, how the *M*agno*M*eter XRS™ can be used to select an appropriate dispersal fluid. This can aid in understanding how to develop and create improved suspensions which, in turn, can result in better and more efficient product performance, thereby providing an economic benefit in terms of product formulation. This case study also highlights the need for quality control of any incoming raw materials (see Mageleka Application Note #1) and to verify manufacturer's claims regarding product specifications and performance.

For more information, to send samples, to arrange a demonstration of the MagnoMeter at your facility, or to talk to one of Mageleka's technical applications specialists, please email roger@mageleka.com

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