Using Mageleka *M*agno*M*eter XRS™ *R*elaxo*M*eter Measurements to Optimize Processing Procedures

Introduction

Milling is an important tool available to both the R&D formulator and process engineer. There are several different basic milling processes, and a variety of machinery is available. No matter which method is used, it is necessary to monitor the milling process over time to avoid costly and wasteful "over-milling" (i.e., particle re-aggregation). Moreover, any process of attrition or comminution impacts the overall dispersion process.

In the preparation of slurries, a batch "premix" is initially prepared, and this slurry is then transferred to a high shear milling device. However, measurement of industrial suspensions *in situ* is not straightforward, as the formulations are opaque and are often highly concentrated dispersions in a variety of aqueous and non-aqueous liquids. There are few tools available with which to *directly* measure the suspension characteristics.

Nuclear magnetic resonance (NMR) relaxation is an ideal technique for measuring suspensions at high solids loadings because it does not make any assumptions about the size, shape, or concentration of particles, or the liquid in which they are suspended. NMR relaxation is easy to employ, produces rapid results, and requires limited input data.

About NMR Relaxation

NMR spectroscopy is one of the most powerful analytical tools used to probe details of molecular structure and dynamics. Traditional devices employing NMR technology require high magnetic fields and, hence, large magnets and related instrumentation. However, the advent of small powerful magnets has allowed instruments such as the Mageleka *M*agno*M*eter XRS™ *R*elaxo*M*eter to be designed that have small footprints and are suited to normal, routine laboratory analysis.

The *R*elaxo*M*eter has harnessed the power of NMR spectroscopy to measure liquid relaxation. Importantly, the relaxation time is a fundamental intrinsic property of liquids and its measurement provides direct information about the extent and nature of any liquid-particle interface (i.e., slurries, suspensions, and dispersions). The *R*elaxo*M*eter measures the extent of molecular motion as protons interact when perturbed by local magnetic fields, and the resulting relaxation time obtained for a bulk liquid is an average value that is dependent upon the exact composition of the liquid – whether it is pure, mixed, or contains dissolved moieties.

What does the *R*elaxo*M*eter do?

The *R*elaxo*M*eter's measurement technique is noninvasive and nondestructive, and it can work with any type of slurry, suspension, or dispersion and, importantly, at industrially relevant solids concentrations. Of practical utility, the *R*elaxo*M*eter eliminates the dilution issues inherent in making measurements using, for example, traditional light scattering

> "Measurement of industrial suspensions *in situ* is not straightforward, as the formulations can be opaque and are often highly concentrated dispersions. Both cases can be analysed using NMR relaxation."

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techniques. The simple measurement technique takes only minutes. Importantly, samples can be stored under thermally controlled conditions (e.g., ICH guidelines) and reanalyzed to understand, for example, thermodynamic stability. Thus, the *R*elaxo*M*eter provides complementary information to traditional particle characterization devices. But it also provides additional interfacial insight not possible with those devices.

Using the *R*elaxo*M*eter to optimize processing procedures

Because of its unique optical, thermal, electronic, and chemical properties, zinc oxide is utilized in an extremely broad and diverse range of industrial, medical, pharmaceutical, agricultural, and cosmetic applications.

In this Application Note we will explore using the *R*elaxo*M*eter to optimize the processing of a "microfine" grade of zinc oxide (ZnO). This specific grade of ZnO is different from regular USP (pharmaceutical) grade material and industrial pigmentary grade material in that its particle size is much smaller (<200nm). At this size, visible light scattering is minimized to the extent that the particles appear transparent in thin films, such as those created when a sunscreen product – typically formulated as a water-in-oil (W/O) emulsion for beach use – is rubbed on the skin, making these products aesthetically acceptable.

Depending on material properties, conditions of manufacture and storage, all powders contain aggregates and agglomerates. Dispersing any dry inorganic powder material in a non-aqueous vehicle is not trivial, but correct processing to remove agglomerates is essential in any formulation and, in particular, the preparation of ZnO-based sunscreen products, because the presence of agglomerates critically impacts both performance and aesthetics that have a profound effect on the economics and quality of the product.

High solids suspensions of microfine ZnO dispersed in a variety of non-aqueous vehicles – including mineral oils, fatty esters (e.g., isopropyl myristate), capric/caprylic triglycerides, and silicone fluids – are available from a variety of commercial suppliers. These "prepared" suspensions spare formulators the time and effort to disperse dry powder ZnO and can be readily incorporated into the "oil phase" of the specific W/O emulsion system.

Here, we present data obtained on materials supplied by a manufacturer of ZnO suspensions to demonstrate both the utility and simplicity of the *R*elaxo*M*eter. We will explore how relaxation time measurements can be used to detect changes in processing conditions – conditions that affect both the performance and economics of emulsions. Results of relaxation time measurements are presented for two high solids suspensions of the same microfine grade of ZnO. The data are plotted as a dimensionless parameter, the Relaxation Number, R_{no}, a very useful practical metric. The value of R_{no} increases with increase in internal phase (such as particle concentration) in a suspension or emulsion, such as occurs in the former when massive particles or aggregates are broken down by milling. R_{no} is directly and linearly proportional to the available wetted surface area of a suspension (see Mageleka Application Note 4 at www.mageleka.com).

Using a simple calculation to convert the raw relaxation time data into wetted surface area measurements (see Mageleka White Paper 1), the initial wetted surface area of the zinc oxide pre-mix dispersion was determined to be 50 m^2g^{-1}. The pre-mix batch was then further processed using a cavitation device run at increasing processing pressures. Resulting samples from various levels of pressure were analyzed for relaxation time - relaxation measurements were made on samples taken directly from the device with no further sample preparation. Results are presented in Figure 1.

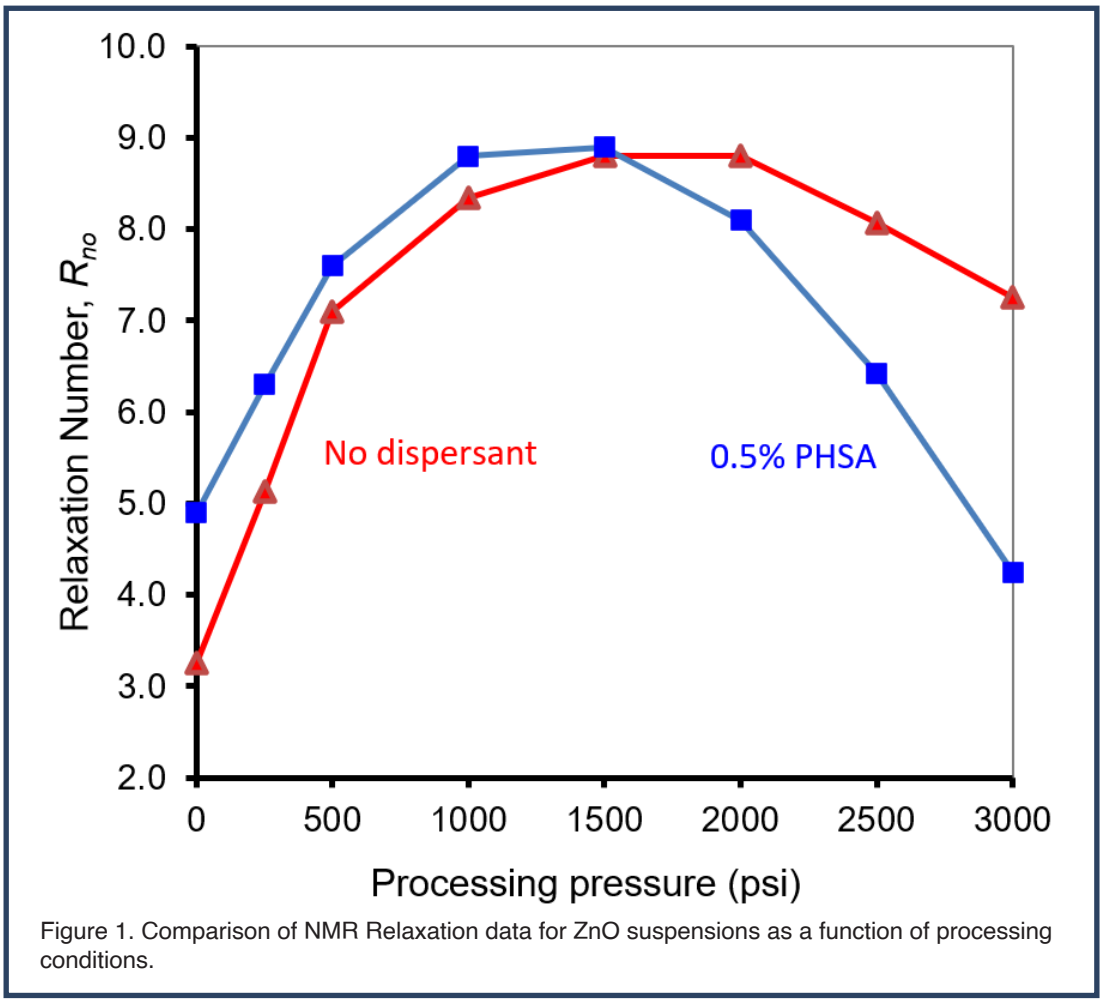

Figure 1. Comparison of NMR Relaxation data for ZnO suspensions as a function of processing conditions.

In the first experiment – seen as the red curve – the ZnO was initially simply dispersed directly in a C_{12}-C_{15} alkyl benzoate (which is widely used as an emollient in cosmetic formulations for the skin such as sunscreens and facial moisturizers) under high shear (rotor/stator) mixing. It was possible to obtain a solids loading at approximately 52% wt/wt.

With no dispersant, subsequent cavitation milling results in a rapid increase in R_{no}, but a pressure over 2000psi is clearly counterproductive because R_{no} then decreases due to "overmilling" (the wetted surface area peaks at around 350 m^2g^{-1}).

In the second experiment – seen as the blue curve –the same rotor/stator was used, (to produce the pre-mix) but samples now contained a dispersing agent (a polyhydroxystearic acid) added at a concentration of only 0.5%. As a result, the ZnO concentration was able to be appreciably increased to 60% wt/wt without any detrimental change in pre-mix viscosity. Importantly, the addition of a dispersing agent significantly increased the initial wetted surface area from 50m^2g^{-1} to 180m^2g^{-1}. Again, the pre-mix batch was then further processed using the same cavitation device but note that optimum milling was now achieved at a much lower pressure – around 1500psi – which represents a significant energy (and cost) savings. However, any further increase in operating pressure again resulted in overmilling. This data also demonstrates the dramatic effect of the addition of a suitable dispersing agent, suggesting that the *R*elaxo*M*eter could be used to optimize the amount of dispersant used (see Mageleka Application Note 6).

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In summary, the results are but two examples of information that can be directly obtained from magnetic resonance relaxation measurements using the *R*elaxo*M*eter. Such analysis is not possible with traditional laboratory particle characterization instrumentation. Given the effect of milling (and dispersants) on performance features, together with the economic implication of over-milling, a direct measurement of processing conditions at industrially relevant conditions would be beneficial in production quality control. This is now possible with the Mageleka *R*elaxo*M*eter. Measurements can be made in minutes, so any milling process can be monitored virtually in real-time to obtain optimum conditions thus saving time and money, and the *R*elaxo*M*eter's small footprint allows it fit easily into production, research, and QA/QC environments.

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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