Dispersing Agents: Determining Effectiveness Using NMR Relaxation Measurements

Introduction

An important step in the process of dispersing particles in liquids is deagglomeration, where particles are separated from each other. Unlike surfactants, true dispersing agents are not "surface active" – that is, they do not reduce the surface tension of liquids. Instead, their role is to chemically aid separation of agglomerated particles by increasing the electrostatic repulsive forces between the particles. This allows liquid penetration into the inter-particle spaces which, in turn, enhances the separation process, thereby creating a better dispersion. In addition to improving the quality of formulations, the use of dispersing agents can also improve the economics of production because they reduce the need for expensive and labor-intensive mechanical energy (i.e., milling).

There are literally hundreds of dispersants on the market and they all work. So, which one is the most effective for a given material and liquid combination? Determining this will result in a suspension with superior performance attributes. This application note will explore nuclear magnetic resonance (NMR) relaxation measurements as a means of quantifying the efficiency of dispersant action simply and quickly.

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 Mageleka *M*agno*M*eter XRS™ to be designed that are suited to normal, routine laboratory analysis.

The basic technique used in the *M*agno*M*eter is NMR relaxation. The relaxation time is a fundamental intrinsic property of solids and liquids. What the *M*agno*M*eter measures is how protons react, through their molecular motion, in a magnetic field. Liquid in contact with a particle surface relaxes much more rapidly than does the rest of the liquid (i.e., "bulk" liquid), so measurement of relaxation time provides direct information about the extent and nature of any particle-liquid interface (i.e., suspensions and emulsions; see Mageleka Technical Note 1).

The *M*agno*M*eter's measurement technique is both non-invasive and non-destructive. The *M*agno*M*eter can work with suspensions at any industrially-relevant concentration, and the inherently simple measurements technique takes only minutes (see Mageleka Technical Note 2).

What Does The *MagnoMeter* Do?

The *M*agno*M*eter provides complementary information and intelligence to traditional particle characterization devices. As mentioned above, the basic measurement is a relaxation time which is directly proportional to the wetted surface area of the suspension or slurry. The calculation of a surface area value is quite straightforward. This is in contrast to the measurement of particle size by light scattering where the raw intensity data has to be deconvoluted by means of complex algorithms,

> *"Determining which dispersant is most effective will result in a suspension with superior performance attributes."*

and the assumption of particle sphericity must be made (see below).

The actual relaxation value obtained by NMR is an average, and is dependent upon the exact composition of the suspension. This is somewhat analogous to the zeta potential of a material where its value depends critically upon the exact composition of the dispersion fluid.

The Relaxation Number

Although the fundamental measurement is a relaxation time, a very useful practical metric, in any application, is the relaxation number, R_{no}. The relaxation number 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 relaxation time.

The relaxation number can be used to follow kinetic processes such as adsorption and desorption, and even competitive adsorption.

In addition, R_{no} is directly, and linearly, proportional to the wetted surface area of a suspension, viz:

$$R_{no} = S\, k_A\, R_b\, \phi_p$$

Where S is the surface area and ϕ_p is the volume of particles.

The k_A parameter is a constant termed the *specific surface relaxivity*. It can be considered analogous to the Refractive Index required in a laser scattering device to calculate the correct particle size distribution, in the sense that it depends on the specific combination of the material and liquid (see Mageleka White Paper 1).

Comparing Dispersant Efficacy Using NMR Relaxation Measurements

In the following example we show NMR relaxation data from a series of suspensions, each created with a different dispersant (Fig. 1). A 60 wt% suspension of metallic silver flake in Texanol was prepared using 2 wt% of each dispersant, and the relaxation time

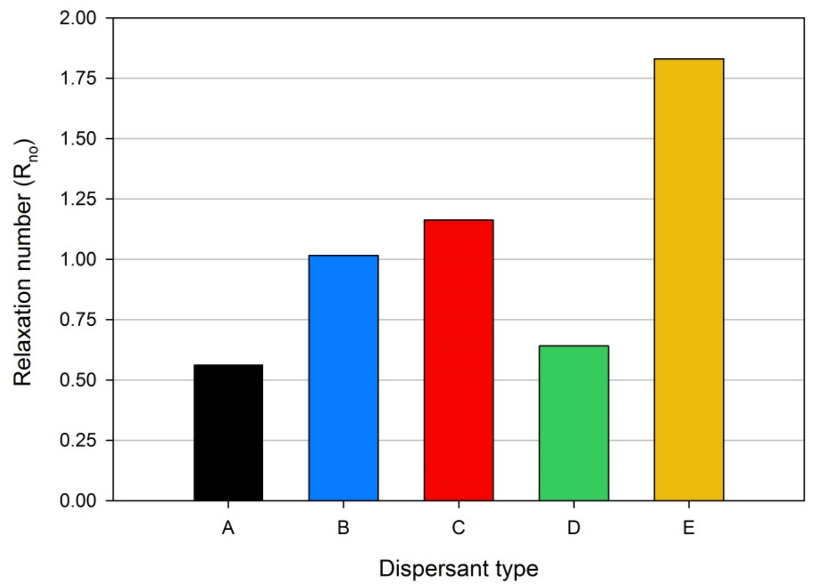

Figure 1. NMR relaxation measurements for identical suspensions prepared using a variety of dispersants. Average repeatability of relaxation time was <1.0%.

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of each suspension was measured. Texanol is an alcohol ester is used in paints and inks, and metallic silver flake is used to impart decorative properties.

The data in Figure 1 show that the largest relaxation number, reflecting the largest wetted surface area, was found for the suspension prepared using the Hypermer KD1 dispersant (type E in Fig. 1). The smallest relaxation number was found using the Crodafos M915A dispersant (type D), which performs only marginally better than a suspension prepared without any dispersant (type A). Thus, the Hypermer KD-1 was demonstrably the most effective of this group of dispersing agents.

These results can be explained by considering the chemical nature of the dispersants examined. The Crodafos M915A is an alkylphosphate anionic dispersant more suited to the preparation of aqueous dispersions. In contrast, the Hypermer KD1 is a polyester/polyamine co-polymer that is well-recognized as an efficient dispersant for use with non-aqueous liquids. The Zephrym PD 2206 (type B) and the Hypermer B210 (type C) are both poly-hydroxystearic acid/PEG-type copolymers and their dispersant performance is intermediate, with the Hypermer B210 being marginally the better of the two: its relaxation number is slightly larger than that of the Zephrym PD 2206.

These data demonstrate the utility of the *M*agno*M*eter for determining which dispersant is the most effective for a given material and liquid combination. Determining this will result in a suspension with superior performance attributes. Thus, *M*agno*M*eter measurements can be used to rapidly fingerprint preparations of suspensions using different dispersant types and so aid in formulation development and optimization resulting in improved economics and quality of products.

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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