Using NMR Relaxation as an Aid in Understanding Formulation of Pigment Dispersions

Introduction

In general, the composition of commercial pigment dispersions – to produce, for example, paints and inks – is complex and typically comprises a fluid, a dispersant, a polymeric resin and the pigment material. In the preparation of aqueous dispersions, a wetting agent may additionally be needed if the pigment materials are hydrophobic.

Determining the individual effects of different components at the different stages in the creation of the formulation is crucial to understanding not only how the end-product was produced but also how the process might be optimized to provide better end-use performance characteristics. For example, a formulator may want to compare and contrast the efficacy and behavior of similar raw materials from different suppliers (see Mageleka Application Note 1).

Nuclear Magnetic Resonance (NMR) relaxation measurements provide considerable benefits over traditional analytical techniques for characterizing dispersions and improving formulations, for example in the quality control of ink-jet pigments (see Mageleka Application Note 9). In this application note we will demonstrate the importance of understanding all components of a pigment formulation, and introduce a compact next-generation NMR relaxometer that provides fast, easy, and reliable measurements of dispersion characteristics.

NMR Relaxation

NMR spectroscopy is one of the most powerful analytical tools used to probe details of the structure and dynamics of molecules. Traditional devices employing NMR technology require very high magnetic fields and, hence, very large magnets and related instrumentation. However, the advent of small powerful magnets has allowed instruments – such as the Mageleka *M*agno*M*eter XRS™ – to be designed that have small footprints and 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, and its measurement provides direct information about the extent and nature of any particle-liquid interface (i.e., suspensions and emulsions; see Mageleka Technical Note 1: Physical Characterization of Suspensions and Slurries using NMR Relaxation).

What the *M*agno*M*eter measures is the extent of molecular motion as protons interact when perturbed by local magnetic fields. The liquid in contact with a particle surface relaxes much more rapidly than does the rest of the liquid, which is free (i.e.,

> *"The speed and simplicity of the NMR technique make it an ideal tool in the development of paints and inks."*

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"bulk" liquid). This surface relaxation 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. For many dispersions of interest we can assume that there is a fast dynamic exchange between the liquid associated with the particle surface and the bulk liquid. We measure a dynamic average which reflects the properties of the interface.

What does the *M*agno*M*eter do?

The *M*agno*M*eter provides complementary information to traditional particle characterization devices, but it also provides additional interfacial insight not possible with those devices.

Because the actual relaxation value obtained by NMR for the bulk liquid is an average, it is dependent upon the exact composition of the suspension and is therefore affected by each of its components. This is somewhat analogous to the zeta potential of a material where the value depends critically upon the exact composition of the dispersion fluid. For aqueous systems in which the water phase is multicomponent, there may be preferential adsorption of one component which will affect the average of all the components. However, this can be disentangled through selective deuteration (using D_2O).

The *M*agno*M*eter's measurement technique is non-invasive and non-destructive and it can work with suspensions at any industrially-relevant concentration. This is especially important with industrial slurries that can be highly concentrated.

From a practical perspective, the *M*agno*M*eter eliminates the dilution issues inherent in making measurements using, for example, traditional light scattering techniques. Moreover, the simple measurement technique takes only minutes (see Mageleka Technical Note 2: The Mageleka *M*agno*M*eter: What is it, and Why use it?).

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In the example below (Figure 1) we show the results of one type of relaxation measurements (called "T_2") made using various combinations of the main components used to create a dispersion of a pigment:

(1) Solvent alone
(2) Solvent + Dispersant
(3) Solvent + Dispersant + Polymer Resin
(4) Solvent + Dispersant + Pigment
(5) Solvent + Dispersant + Pigment + Polymer Resin

In this study we simply illustrate the potential effect of adding additional components on a final pigment formulation; the concentrations of dispersant, polymer resin, and pigment were chosen arbitrarily and so are not necessarily comparable to those used in commercial formulations (for a deeper exploration of commercial pigment dispersions, see Mageleka Application Note 5). Mixing of the components was achieved initially using a paddle stirrer then followed by sonication in an ultrasonic bath.

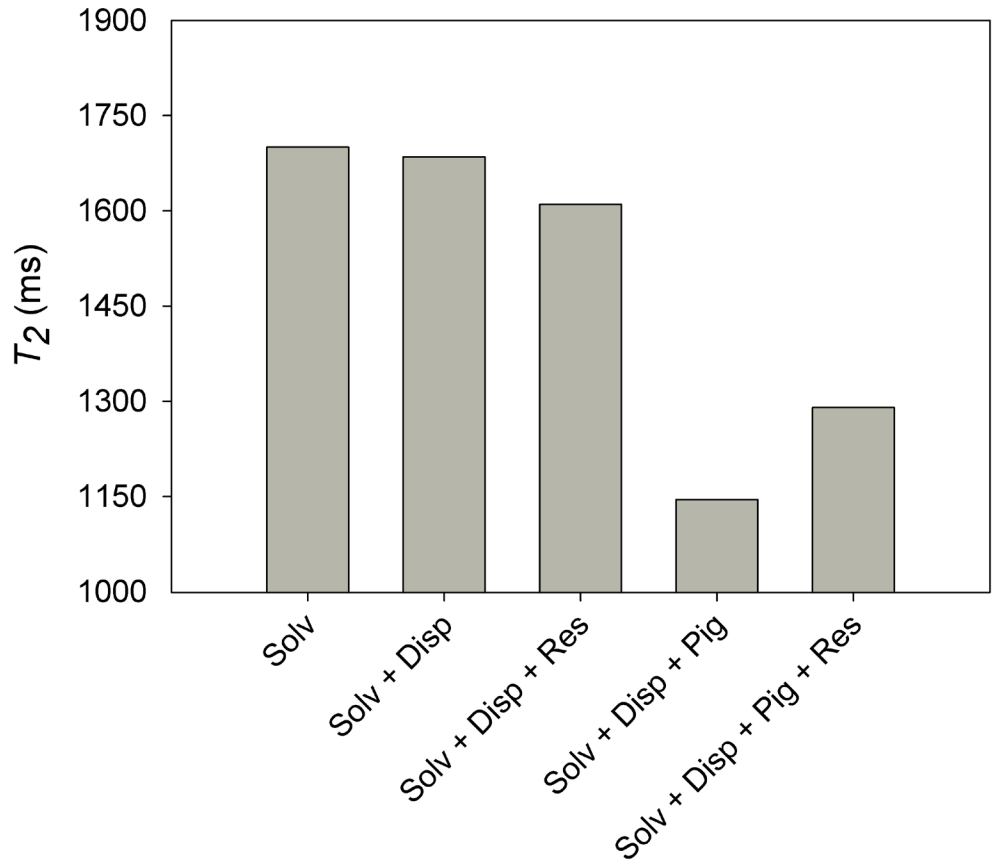

Figure 1. The Relaxation time of components of pigment dispersions. The reproducibility (coefficient of variance) of the T_2 relaxation time measurements was <1%; thus, the data are statistically robust and the differences among samples are reliable.Solv = solvent, Disp = dispersant, Res = polymer resin, Pig = pigment.

The data in Figure 1 show that the addition of the dispersing agent has only a very small effect on the T_2 relaxation time of the solvent. This result is not unexpected because the molecular weight of simple dispersants tends to be only a few hundred Daltons and the typical use concentration is low (10% based on the solids). Likewise, the subsequent addition of the polymer resin causes a further small decrease in solvent relaxation time. These materials, called binders, are used to form a matrix holding the pigment in place and modify the viscoelastic behavior of the pigment suspension.

As can be seen from the data, even the small effect of this binder was readily detected using the *M*agno*M*eter. However, binders can have a much larger molecular weight (tens to hundreds of kiloDaltons) and their use concentration can be quite high (ca 30%). In such circumstances, the effect on relaxation can be far more marked. Thus it is important to note that any measured solvent relaxation time will depend upon both these characteristics of a polymer (see Mageleka Technical Note 1).

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By far the biggest difference is seen for the pigment suspension. Here there is a dramatic decrease in the T_2 time. This is a consequence of the dispersing agent adsorbing at the particle surface. The measured value reflects the subsequent degree of wetting and dispersibility of the pigment material under the processing conditions used (see Mageleka Application Notes 3, 4 and 12). Although a more detailed discussion is beyond the scope of this application note, the greater the amount of available wetted surface area, the larger will be the decrease in relaxation time. The relaxation time also decreases as the concentration of particles increases and so, when carrying out comparison studies, it is important to keep the solids concentration fixed. For a detailed discussion of the relevance of NMR relaxation to the measurement of wetted surface area of particulate suspensions, see Mageleka White Paper 1.

The final measurement in Figure 1 shows that the addition of the polymer resin to the pigment dispersion results in an increase in the T_2 time. This implies a loss in wetted surface area through some aggregation of the pigment particles by the polymer resin, which will also impact the subsequent viscoelastic behavior of the suspension. In this example, it appeared that the pigment particles were flocculated as evidenced by the fact that they could be re-dispersed by sonication. Hence, it would be possible to investigate several formulation approaches to mitigate such particle aggregation. For example, the amount of surfactant may be increased (see Mageleka Application Note 6), a different surfactant showing better pigment affinity may be used (see Mageleka Application Note 4), or one might select a resin binder that does not displace the surfactant from the pigment surface. Using NMR relaxation as a diagnostic tool allows the formulator to narrow down and quickly test fixes to formulation problems.

In Conclusion

NMR relaxation measurements, using the Mageleka *M*agno*M*eter, can be used to great effect by a formulator. The speed and simplicity of the NMR technique make it an ideal tool to study and quantify the different stages in the development of paints and inks.

The advantage of NMR relaxation measurements is that important characteristics of component materials can be quantified quickly and easily – and at virtually any industrially relevant solids concentration – resulting in not only better performance characteristics but also a potential reduction in costs. Importantly, NMR is a non-invasive, non-destructive technique and so samples can be saved and, if necessary, re-measured at some later date to explore possible time-dependent behavior.

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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