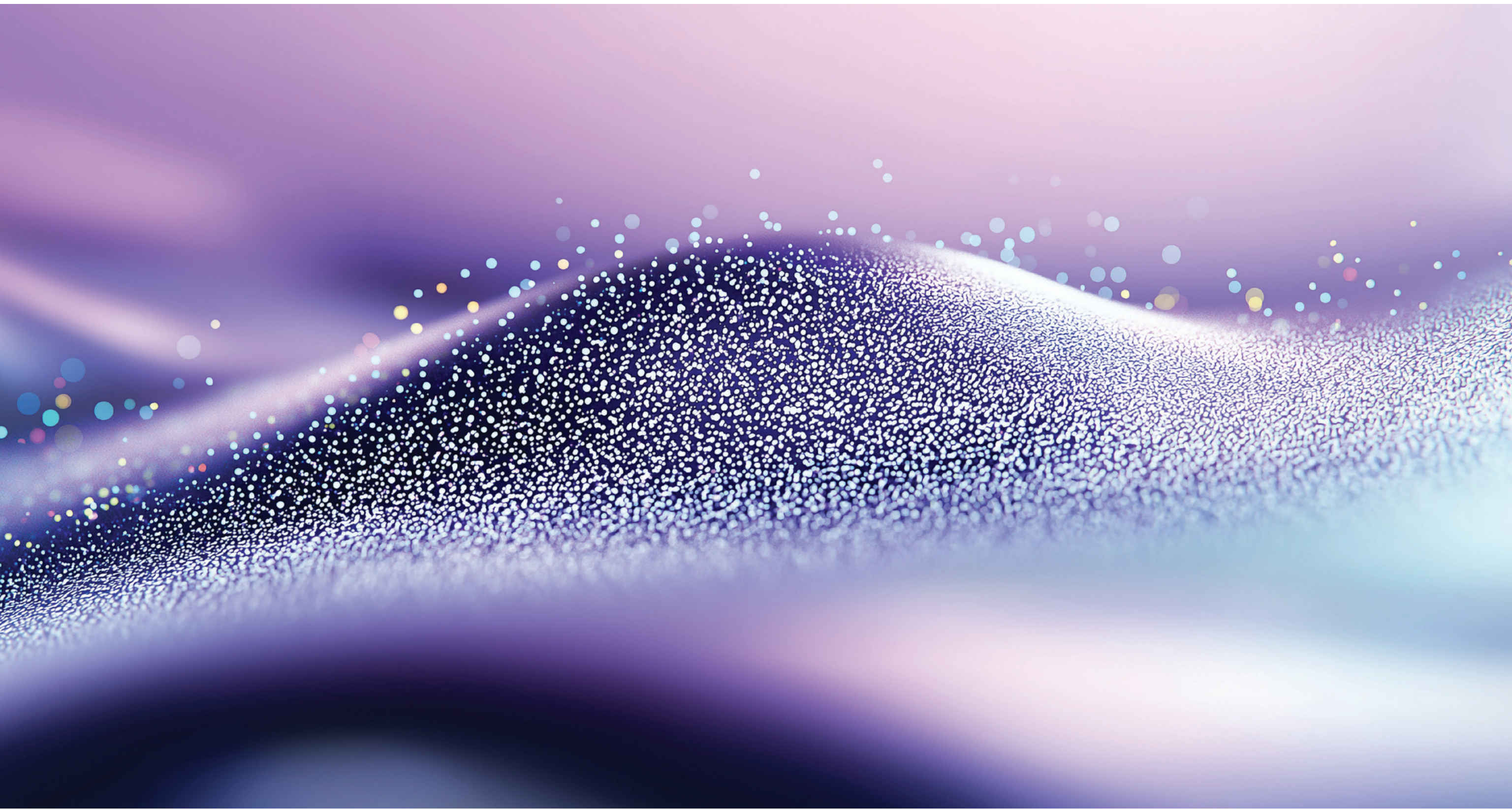
Low-Field (LF)-NMR Liquid Relaxation: A Useful Technique for QC and to Determine the Equivalency of Materials for Coatings Formulations

By David Fairhurst, Colloid Consultants Ltd.;
R. Sharma, Mageleka, Inc.;
and R. Wörheide, Metromation Inc.



Having a metric that represents a specific material quality and developing quality numbers is the key to implementing an appropriate QC protocol.

Paints and coatings in their final composition are complex; their formulation entails a multitude of system details that influence the final outcome. Hence, it is difficult to attribute the root cause when deviations are found via testing or performance quality control (QC). Further, a major concern in the industry is the question of material "equivalency." Having a metric that represents a specific material quality and developing quality numbers is the key to implementing an appropriate QC protocol. Low-field nuclear magnetic resonance (LF-NMR) liquid relaxation is shown to provide such a test, and we explore its application as a powerful, fast, and nondestructive analytical tool to improve QC and assess material equivalency in coatings formulations. Traditional methods often fall short in evaluating raw materials, particle dispersions, or complex formulations without extensive sample preparation or dilution. LF-NMR relaxation, using a small benchtop spectrometer, overcomes these limitations by enabling direct measurements on opaque, high-solid suspensions under real-use conditions and affords a cost-effective methodology to identify the replacement of both powder and solvent raw materials. Measurements are also shown to be sensitive to solvent-particle intermolecular forces, making it a useful technique to easily determine the Hansen solubility parameters (HSP) for both polymers and pigments.

Introduction

The importance of the process of dispersion[1] and its profound effect on the economics and quality of the subsequent product has long been recognized.[2] Thorough characterization and quality control (QC) of particulate suspensions is, therefore, paramount in obtaining optimum performance features and cost-effective benefits from such systems.

QC is a process through which a business seeks to ensure that product quality is maintained or improved. High quality products are much more efficient and effective, benefiting both the manufacturer and the consumer. A major function in QC is to verify the product quality against some predefined standard(s), to ensure the quality of all the batches of products manufactured at every stage of production. In their final composition, paint and coating formulations are complex, and it is difficult to attribute the root cause when deviations are found via testing or performance QC.

Important factors in the consistency of final products are the raw and semi-finished materials used in formulation.[3,4] Maintaining their quality is critical; having a metric that represents a specific material quality and developing quality numbers is the key for implementing an appropriate QC protocol. This, in turn, can minimize waste since these materials can be rejected before formulation, or the production process can be adjusted at an earlier stage. Analysis of less complex mixtures is also much simpler.

Further, a major concern is the question of material "equivalency"—for example, when dictated by regulatory obligations to replace components of a paint system. Many actions to show equivalence address the final dried film with less focus on the application sensitivity of the paint system, which is highly related to the dispersion characteristics of the matrix. Unfortunately, supply houses and distributors are not usually the primary manufacturer of raw materials. However, it is critical to verify the technical specification of all materials, as this can directly influence their behavior at every stage in the manufacturing process—from basic formulation to final end-use product. Indeed, potential variable chemical and physical characteristics can have profound effects on the behavior of paint and coating suspensions, for example, a change in rheology owing to shear stress.[5,6] Also, with incomplete dispersion of pigments, shear stress in the paint line can result in a "post-dispersion" with the effect of color shifts. Thus, an exact specification is needed for all materials used in formulations because, without these, comparisons (e.g., between batches, lots, or just concentrations) can often be meaningless.

Any QC test must be objective, easy to run, and predictive; that is, it should measure fundamental characteristics of any system and is neither a function of the instrument, nor of the operator. However, studying these systems in situ is not straightforward, as the formulations are opaque and are often highly concentrated dispersions in a variety of aqueous and nonaqueous liquids. There are few tools available with which to *directly* measure the suspension characteristics. LF-NMR liquid relaxation provides such a test. Further, the ability to store, and reanalyze, samples is a very useful, convenient advantage of the technique. It is quantifiable, fast, and noninvasive, and offers practical and economic benefits as a QC tool.

Liquid Relaxation NMR

NMR spectroscopy is one of the most powerful analytical tools used to probe details

for a Resilient Future

of molecular structure and dynamics.[7] Such devices require very high magnetic fields and hence very large magnets. However, the advent of small powerful permanent magnets has allowed *low-field* instruments to be designed that have small footprints and so are suited to normal, routine laboratory analysis.[8] Further, it is apparent that NMR liquid relaxation measurements can provide valuable information about the strength and interaction between a liquid and the particle surface functional groups.[9-13] Such measurements can be grouped as particulate and molecular analyses. An important feature of the former is the direct measurement of the *wetted* surface area of suspensions, but the technique also permits observation of the influence of morphology, the impact of surface chemistry (and its modification), as well as the wetting and the dispersion of powders in liquids.[14,15] As such, NMR relaxation complements the classical techniques of particle sizing and zeta potential measurements used to characterize particulate suspensions by providing information that these latter techniques cannot. In molecular analysis, NMR liquid relaxation can be used to determine not just the adsorption of surfactants and polymers onto particle surfaces but also the inter-reaction of these moieties with each other.[11,12] Indeed, the technique of NMR "relaxometry" has become an active area of research.[16-20] It is known that values for the critical adsorption energy of polymers adsorbed from solvents onto particles can be estimated from relaxation measurements.[21] LF-NMR relaxation has been shown to correlate directly with inverse gas chromatography (IGC).[22] The authors suggest that, since measurements are fast, it can be used to quickly prioritize the need, if required, for quantitative testing and analysis using IGC. Relaxation measurements can correlate with those from photon correlation spectroscopy (PCS).[23]

> **LF-NMR liquid relaxation offers several important practical advantages to the formulator.**

The rheology of coatings is crucial to their behavior during film formation such as adhesion, leveling, and texture. The viscous (flow) and elastic (deformation) characteristics arise from the structure of the dispersed particles in the concentrated state.[5] Intuitively, it would seem that LF-NMR relaxation—which can be made on the same sample material—should correlate with such measurements.[24] This might be an interesting subject for future study.

Combining methods of analysis can be extremely useful in all aspects of formulation of suspensions. LF-NMR liquid relaxation offers several important practical advantages to the formulator. For example, any particle, of any size or shape can, in principle, be studied.[8] Since the technique utilizes proton (^{1}H) NMR, the dispersing liquid must contain at least one NMR active nucleus such as the hydrogen atom (proton). In principle, any NMR active nucleus would work. Hence, it would be suitable for methylene chloride (CH_3Cl), but it would not be appropriate for a solvent such as carbon tetrachloride (CCl_4); mixtures of any miscible liquids such as ethanol/toluene and cyclohexanone/methylethylketone can be used. The solids concentration can be very high; the limit is simply dictated by whether the sample can be transferred into an NMR tube.[9] Importantly, no dilution is necessary, which permits the analysis of samples as they are intended to be used. The measurement time is dependent upon the precision required but can be very fast, typically between 1 and 5 min. From a quality control/quality assurance (QC/QA) perspective, the method is also attractive because only a small amount of sample is necessary (*ca* 0.1 mL), and, importantly, the technique is noninvasive and nondestructive. This means that samples can be stored in the NMR tube, under, say, International Conference on Harmonization (ICH) guidelines, and can be reanalyzed at any later date.

NMR Relaxation Time

Relaxation is a fundamental *intrinsic* property of solids and liquids.[7] What is measured is the extent of molecular motion as protons react when perturbed by a magnetic field. In a suspension, liquid that is in contact with a particle surface (i.e., "bound" liquid) relaxes much more rapidly than does the rest of the liquid, which is free (i.e., "bulk" liquid). This surface relaxation is typically of the order of microseconds, compared with the relaxation time for the bulk liquid (i.e., in the absence of particles), which can be of the order of seconds.[25]

For many dispersions of interest, we can assume that the dynamic exchange between the bound liquid associated with the particle surface and the highly mobile free state of the bulk liquid is very rapid (i.e., a "fast exchange"). Thus, the measurement of relaxation time provides direct information about the affinity of a liquid for a specific particle surface and so can characterize the extent and nature of any particle-liquid interface.

If the surface and bulk liquids are in fast exchange, a single relaxation time, $T_{nd(av)}$, is determined from the *reciprocal* of the spin relaxation rate, $R_{nd(av)}$. The relaxation rate is an *average* of the relaxation rates of the bound surface liquid, R_{ns}, and the free bulk liquid, R_{nb}, weighted by their relative populations:

$$R_{nd(av)} = p_s R_{ns} + p_b R_{nb}$$

where n = 1 for spin–lattice relaxation (T_1 method); n = 2 for spin–spin relaxation (T_2 method); p_b is the fraction of liquid in the bulk phase, and p_s is the fraction of liquid at the surface. Both methods of relaxation time measurement can be used. The NMR spectrometer used in the studies presented in this article (a *M*agno*M*eter, from Mageleka Inc.) provides both methods to measure relaxation rates: T_1 using inversion recovery or progressive saturation pulse sequencing[26] and T_2 using a Carr–Purcell–Meiboom–Gill pulse sequence.[27,28]

Experimentally, the average relaxation value obtained by NMR is thus dependent upon the *exact* composition of the suspension (i.e., particle concentration, plus liquid plus additives, etc.). This is somewhat analogous to the zeta potential of a material, where the measured value depends critically upon the exact composition of the dispersion fluid.[29]

T_1 and T_2 each depend on the rotation and translation motions of molecules,[30] but the magnitude of the shift is not necessarily the same.[9] Experimentally, each approach has advantages and disadvantages; the choice is based upon sample characteristics such as suspension solids concentration, particle surface chemistry, and the chemical makeup of the dispersed phase.

Furthermore, the frequency dependence of the surface (bound) liquid relaxation is different from the bulk (free) fluid relaxation frequency dependence.[31] Surface liquid relaxation times are typically shorter at the low frequencies that are characteristic of a benchtop NMR than at the higher frequencies of high field analytical instruments, although bulk liquid values are largely unchanged.[9] This can result in an enhanced sensitivity at low fields because it is the difference between the bulk and surface liquid relaxation rates that is the key parameter.

The Relaxation Number, R_{no}

Although the fundamental measurement is a relaxation rate, a useful practical metric in any application is the relaxation number, R_{no}, which is a dimensionless parameter defined as:

$$R_{no} = (R_{susp} - R_{solv})/R_{solv}$$

where R_{susp} and R_{solv} are the relaxation rates of the suspension and its (bulk) dispersion solvent, respectively.

The relaxation number, which is, essentially, a relative relaxation rate enhancement, can be used to follow kinetic processes such as adsorption and desorption, and even competitive adsorption.[9,11,12] Rearranging the above equation gives:

$$R_{no} = [R_{susp}/R_{solv}] - 1$$

R_{no} is, thus, a useful parameter in which the effect of solvent (which could include dispersants, additives, etc.) is normalized out and it allows us (as we will show later) to rank the strength of solvent-surface interaction. Solvents with strong interaction with a powder result in a larger R_{no} value for the suspension of that powder. Since relaxation time is a function of the affinity of the adsorbing solvent molecules for a surface, such values are a measure of particle wettability.

Experimental

Materials

All materials (powders and polymers) were obtained from a variety of sources, and used as received: Cabot Corporation, Chemours, BASF, Dynamic Cosmetics Inc., Inolytix, Kronos, Auginish, Sumitomo Chemical Company, Sherwin Williams, Tronox, and Lubrizol, UK.

Similarly, solvents were obtained and used as received from the following sources: Lab Alley, Sigma-Aldrich, Tokyo Chemical Industry Company, and Wako Pure Chemical Corporation. Aqueous samples were prepared with deionized water having a resistivity of 18MΩ cm^{-1}.

HSP Analysis

For a specific material (polymer or powder), the choice of solvents is somewhat arbitrary; however, the solvents must encompass a range of behavior characteristics from highly polar to highly nonpolar and Hansen recommends that a minimum of 12 probe solvents be used to ensure maximum interrogation of a material and, hence, the most precise construction of the 3-D sphere.[32,33]

For the studies presented in this article, between 14 and 18 of the following solvents were used: acetone (>99.9%), acetonitrile (99.8%), benzyl alcohol (99.8%), benzyl benzoate (>99.0%), butanol (>99%), caprolactone (97%), chloroform (>99.5%), cyclohexane (99.5%), cyclohexanone (99.5%), cyclopentanone(>99%), decyl alcohol (>98%), dichloromethane (>99.8%), diacetone alcohol (>98%), dimethylformamide (99.8%), dimethyl sulfoxide (>99%), 1,4-dioxane (>99%), dodecane (>99%), ethanol (>99.5%), ethyl acetate (99.8%), ethylene glycol (>99%), ethyl lactate (>98%), ethyl oleate (98%), heptane (99%), hexane (>98%), isopropanol (>99.7%), methanol (>99.9%), methyl cellosolve (99.8%), methyl ethyl ketone (>99.0%), methylene chloride (>99.8%), N-methyl formamide (>99%), N-methyl pyrrolidone (>99.7%), monoethanolamine (>99%), n-pentane (99.7%), propylene carbonate (99.7%), tetrahydrofuran (>99.9%), trichloro ethylene (>99.9%), toluene (99.8%), and xylene (98%).

It is cautioned that the NMR relaxation time of any liquid is sensitive to both the water content and the presence of any dissolved oxygen (which is paramagnetic).[34,35] The relaxation time of water is long—typically of the order of 2 to 3 sec—while that for many solvents/fluids can be much shorter, for example, glycerol (*ca* 50 ms) and ethyl oleate (*ca* 450 ms). The presence of trace amounts of water will result in an increase in the relaxation time, and this contributes to the variation of values found in the literature for solvents. Further, trace water in nonpolar solvents (e.g., dodecane) will also dramatically affect wetting/dispersibility of hydrophilic materials such as metal oxides and hydroxides. Unfortunately, it is neither practical nor economical to remove trace moisture. The effects can only be monitored and a note made when differences are found, so that the cause of any future deleterious behavior can potentially be so attributed.

Thus, the purity and source of a solvent is critical when making comparisons. Indeed, it is well accepted that traces of polar impurities and, especially, water play a key role in any nonaqueous application.[36-39] Hence, this sensitivity of NMR relaxation suggests that the measurement can also be used as a fast QC tool to fingerprint solvents for industrial coatings applications.

Instrumentation

All relaxation time measurements were made using a small, benchtop low-field NMR spectrometer—a *M*agno*M*eterXRS™ *R*elaxo*M*eter, operating at 12.6 MHz (Mageleka Inc., Naples, FL, USA). A Carr-Purcell-Meybohm-Gill pulse sequence was used to measure the spin–spin relaxation time; a 180° pulse spacing of 1000 µs and up to 20,000 echoes were recorded with a 90° pulse length of 4.5 µs. Typically, a series of five replicate scans were averaged to produce the CPMG trace which, unless noted below, was then fitted with a single exponential to extract the relaxation rate coefficient. A recycling delay between scans of at least 5xT_1 was used.

Results and Discussion

Wetting of Powder Surfaces

It is well known that the knowledge and understanding of wetting behavior of fluids/liquids/solvents on surfaces is important,[40] not just from basic physics but also because it impacts a whole array of industrial processes and applications such as coatings. Particle dispersion is also crucial for many end-use product properties such as color and opacity of paints and inks. In formulation, for the purposes of solvent selection, the formulator will frequently talk of *dispersibility;* however, there is no generally agreed upon definition for this term[41] and its common usage varies widely across different fields and applications. Notwithstanding, the key phenomenon underpinning dispersibility is how a liquid wets a particle surface.

Liquids are affected to different extents by the chemical and morphological nature of particle surfaces (in other words, surface chemistry and surface roughness). The smaller the contact angle of a liquid for a solid surface, the greater the wettability will be. Conversely, different liquids are affected by the same particle surface to differing extents. Hence, how powders are "wetted" is crucial to dispersibility; a knowledge of powder wetting is a critical metric in formulation. However, 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 powders. Contact angle measurements are only useful for flat, planar surfaces, and interfacial tension measurements are strictly only suitable for liquids. Flow calorimetry and IGC have been used for such characterizations,[42,43] and these methods determine thermodynamic surface energetics of the interactions. However, 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, we can demonstrate that LF-NMR relaxation is a fast and easy method to assess wettability (and, thereby, bed permeability) for almost any type of solid-liquid combination.

Pigments are ubiquitous as colorants in printing inks of all types. Comprehensive characterization of their surface physical and chemical properties is key to their formulation for high-performance ink-jet printing. **Figure 1** shows a comparison between the relaxation numbers, R_{no} determined for two organic colored (blue and yellow) pigments (used in the preparation of ink-jet dispersions) each dispersed (at 10 wt%) in the same six solvents, as part of a preliminary investigation into determination of their Hansen solubility parameter (HSP).

Here it can be seen that the relaxation numbers have a significant dynamic range across the selection of solvents, and that the magnitude of the R_{no} itself is markedly higher for the blue pigment (**Figure 1A**) compared with the yellow pigment (by approximately a factor of 20) (**Figure 1B**). Indeed, this data suggests that it might not be possible to prepare a well-dispersed stable suspension of the yellow pigment using any of the nonpolar solvents tested unless a wetting agent is used.

These LF-NMR data demonstrate two points. First, the solvents clearly differ in their ability to separate and disperse the particles. Second, the solvent-surface interaction is an important determinant of dispersibility. 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.

Efficacy of Surface Coating and Modification

Surface coatings are used to obtain more uniform surface chemical properties of a material, or to provide different surface chemical functionality/behavior.[44]

In this study, the powder was a hydrophobically modified micronized zinc

FIGURE 1A
Relaxation number, R_{no} for a blue organic pigment dispersed (at 10 wt%) in various solvents.

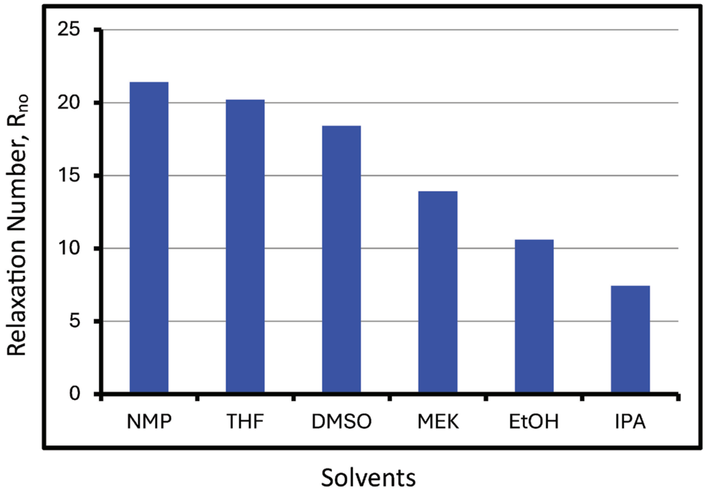
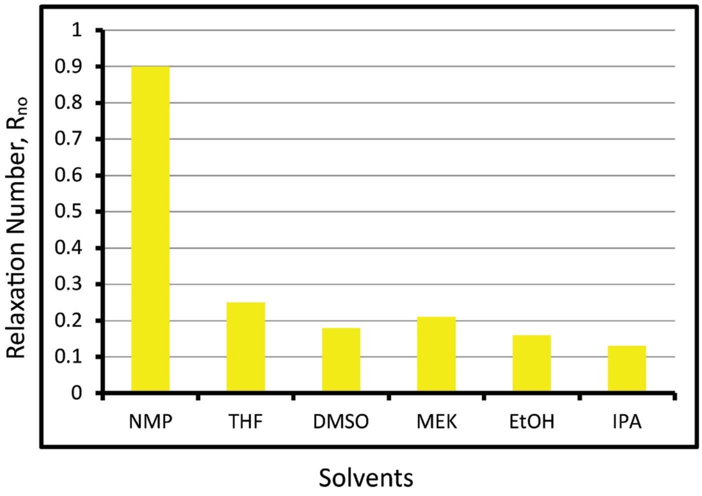


FIGURE 1B
Relaxation number, R_{no} for a yellow organic pigment dispersed (at 10 wt%) in various solvents.



oxide (ZnO) marketed by three different manufacturers (USA, EU, and Japan). They were claimed to be equivalent products, i.e., they had the same nominal particle size (*ca* 120 nm) and the same silane-based coating (specifically, a triethoxycaprylsilane). The silane coating makes the ZnO completely nonwetting in water and so enables it to be readily incorporated, for example, into an oil phase.

We have already seen (**Figure 1**) that different nonaqueous fluids will wet the surface to a different extent. **Figure 2** compares the relaxation time for three samples of ZnO materials, each dispersed (at 8 wt%) in two dissimilar fluids: **Figure 2A**: 100 centistoke silicone fluid (an inorganic fluid)—a polydimethylsiloxane ("dimethicone") and **Figure 2B**: hexane (an organic aliphatic hydrocarbon).

Each of the powder samples are wet to almost the same extent in the silicone fluid. Indeed, the relaxation times for materials B and C are virtually identical. This is likely because the surface (silane) coating is of a type which is very compatible with linear silicone fluids such as dimethicone.[45]

However, what happens if the dispersing fluid is not silicone fluid? When challenged with a noncompatible solvent, such as hexane, we see not unexpectedly that there is a far lower wetting efficiency for all three materials, and large differences can be seen in the relaxation time for each of the three dispersions. This is undoubtedly because, notwithstanding the manufacturer's claims, the "silane coating" for each ZnO surface cannot be the same.

This data demonstrates well how LF-NMR relaxation data can be used to discriminate materials based (via coatings) on their surface chemistry and, by extension, how such measurements can be used to determine material "equivalency" and to select an appropriate dispersal fluid.

QC of Incoming Raw Materials

The preparation of any suspension or slurry typically begins with dry powder material. Too often this aspect of formulation is a forgotten factor. Raw materials are never 100% pure; in all cases, the type and level of impurities depends on the source of the material and any subsequent processing.

Alumina is a widely used chemical that is produced from bauxite ore mined in different parts of the world. The four samples measured here were raw material sourced from Australia, Brazil, West Africa, and Russia **(Figure 3)**. High solids slurries were prepared at 37.5 wt% in 200 proof undenatured ethanol and the relaxation measurements are displayed, in **Figure 3A**, as a relaxation number, R_{no}.

The bauxite from Sources 2 and 4 are quite similar, which is not surprising since they are from West Africa and Brazil. Overall, the data demonstrates how nominally identical raw materials can vary when sourced from different locations. The difference between the four materials is likely a consequence of real variations in their geometric surface area (because of both the size and roughness of the slurry material particles) as well as, potentially, the surface chemistry. Determining which would require additional physical characterization using, for example, traditional particle sizing and zeta potential instrumentation.

Taking the above a step further, virtually all the aluminum hydroxide, $Al(OH)_3$, used commercially is manufactured by the Bayer process which involves dissolving crude bauxite in sodium hydroxide. However, as seen in **Figure 3A,** there are material variations (chemical and/or physical) in bauxite that can influence the quality of the final hydroxide product.

The relaxation time was measured for seven batches of $Al(OH)_3$—randomly obtained over time—dispersed at 15 wt% in 200 proof undenatured ethanol. Again, the results are displayed, in **Figure 3B**, as a relaxation number, R_{no}. The significant difference between some of the sample batches might also have been a result of different processing conditions.

FIGURE 2A
Relaxation time (ms) for surface-modified ZnO dispersed (at 8 wt%) in 100 cSt silicone fluid.

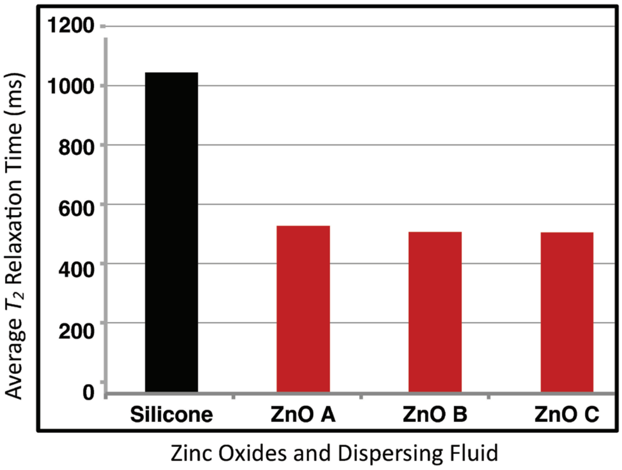


FIGURE 2B
Relaxation time (ms) for surface-modified ZnO dispersed (at 8 wt%) in hexane.

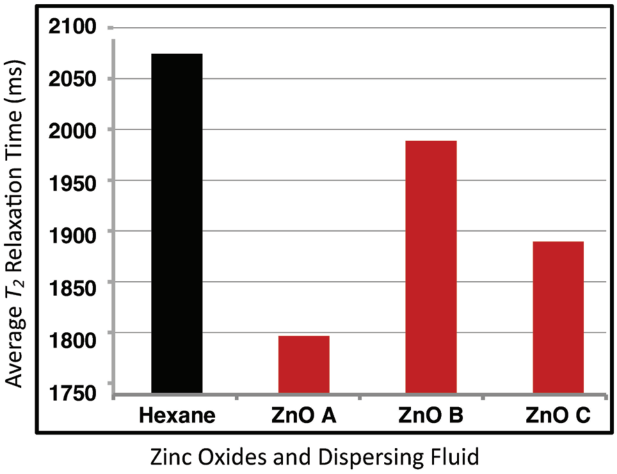


FIGURE 3A

Comparison of the relaxation number, R_{no}, for bauxite ore samples from different sources dispersed at 37.5 wt% in ethanol.

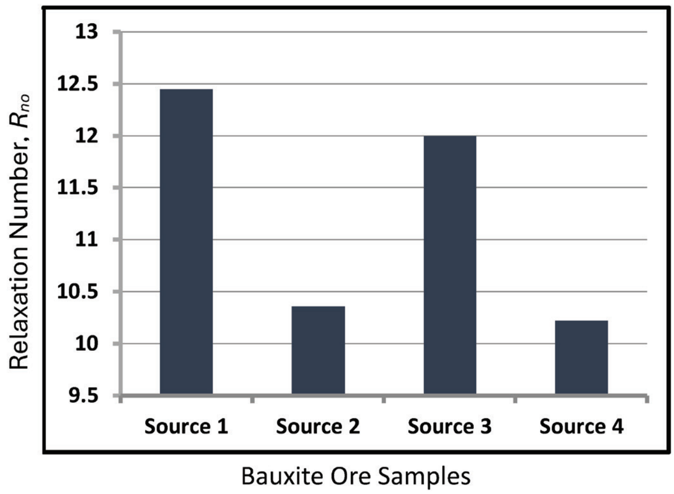
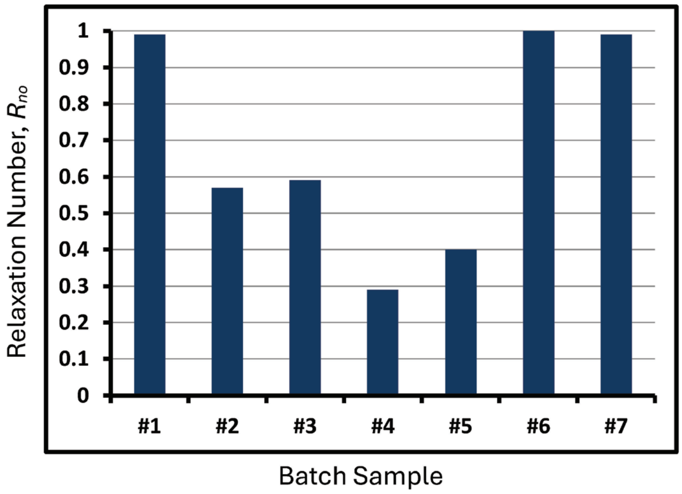


FIGURE 3B

Comparison of the relaxation number, R_{no}, for random batches of aluminum hydroxide dispersed at 15 wt% in ethanol.



Had this been batch-to-batch or lot-to-lot samples of the same $Al(OH)_3$, it would permit setting upper and lower control limits to provide a rigorous QC quantification.

These two sets of data show how LF-NMR relaxation can be used as a fast, simple tool for QC and easy comparison of raw materials and that, for both types of chemicals investigated, nominally identical materials were clearly not the same. In addition to influencing the performance of any subsequent procedures that use them, the potential economic impact of variation in these raw materials must also be considered.

Comparison of Pigmentary TiO_2

Titanium dioxide is the whitest and brightest of commercial white pigments. The pigment particles are often modified by being coated with layers of other chemicals to reduce undesirable chemical activity (such as photoreactivity) and to improve dispersion in both aqueous and nonaqueous vehicles.[44]

Figure 4 shows relaxation time data obtained for 15 wt% aqueous dispersions of six samples of pigmentary grade Titania obtained from three different major global manufacturers (Chemours, Kronos, and Tronox); all are used in paint formulation.

A decrease in an average T_2 value arises, for example, because of an increase in the available (wetted) surface area (through better dispersibility and particle deaggregation), i.e., a decrease in particle size. Further, for a homogeneous suspension of particles having a uniform surface chemistry, the T_1 and T_2 values are often similar (but with T_1>T_2). However, if the material, under examination, comprises particles that are ferromagnetic, paramagnetic, or quadrupolar in nature, the values can differ considerably.[46] This is clearly the case here (**Table 1**). The MSDS supplied with the materials indicates they all contain silica and alumina. Further, titanium dioxide is manufactured

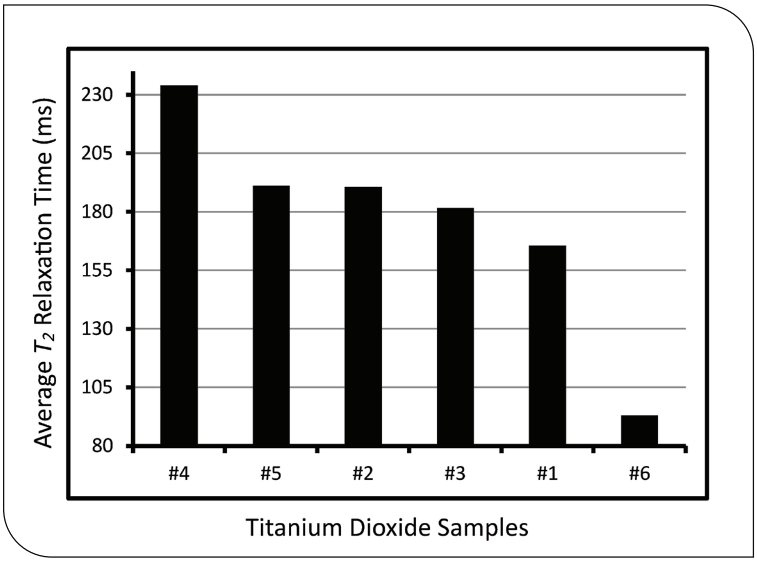
TABLE 1

Ratio of T_1:T_2 Relaxation Times for 15 wt% Aqueous Dispersions of Pigmentary Grade TiO_2 from Different Global Manufacturers

TiO_2 I.D.	T_1:T_2 Ratio
#1	6.6
#2	8.1
#3	7.38
#4	6.4
#5	6.7
#6	10.2

FIGURE 4

Comparison of the relaxation time (ms) for 15 wt% aqueous dispersions of pigmentary grade TiO_2 from different global manufacturers.



synthetically by two processes and the crystal structure contains lattice defects associated with ions such as Fe^{3+}, Al^{3+}, and Cr^{3+} from impurities in the initial crude raw ilmenite or rutile ores used. And, to put the above values into perspective, the T_1:T_2 ratio for a pure colloidal silica is typically 1.10. Further, the T_1:T_2 ratio will vary depending upon the nature of the interfacial bound layer of liquid at the material surface—as well as the presence of adsorbed moieties (deliberate or unwanted). Essentially, the ratio depends on the strength of the interaction of the liquid (here, water) with the interface. Hence it is clear that the surface chemical nature of the pigments is a critical factor.

Interestingly, Titanias #1 and #2 are marketed as providing similar performance, as are Titanias #4 and #5. LF-NMR analysis clearly demonstrates that this is not so.

Solubility of Polymerics

Polymeric materials are widely used in coatings formulations. Their solubility in solvents is determined by a delicate interplay of entropic and enthalpic forces[47]; the measurement of polymer solubility can be tedious and subjective—especially when all the solutions are visually clear.

Hyperdispersants, sold commercially under the trade name Solsperse™, have well-defined chemical composition and molecular architecture. Analogous to normal surfactants, they are comprised of two parts: polymeric stabilizing chains and anchor groups. The former is for solubility in a solvent and/or resin combination, and the latter is for strong adsorption to the pigment particle surface. The dosage is determined by the particle's surface area. Compared with traditional lower molecular weight dispersants or surfactants, they can result in (sterically stabilized) dispersions with higher solids content, lower viscosity, and improved viscosity and particle size stability.

The solvent medium used during dispersion is an important criterion used in hyperdispersant selection. There are dozens of hyperdispersants to select from, with many of them apparently soluble in a variety of different solvents. So, how to quantitatively differentiate them? This can be determined quickly using LF-NMR relaxation as is demonstrated in **Figure 5** where we compare two Solsperse™ hyperdispersants—24000 and 39000—dissolved in "good" solvents; photomicrographs **Figure 6A** and **6B** show that, for both hyperdispersants, all the solutions are visibly completely clear. However, relaxation measurements distinctly reveal that the 39K is more compatible (a larger relaxation number, R_{no}) than the 24K in all the solvents.

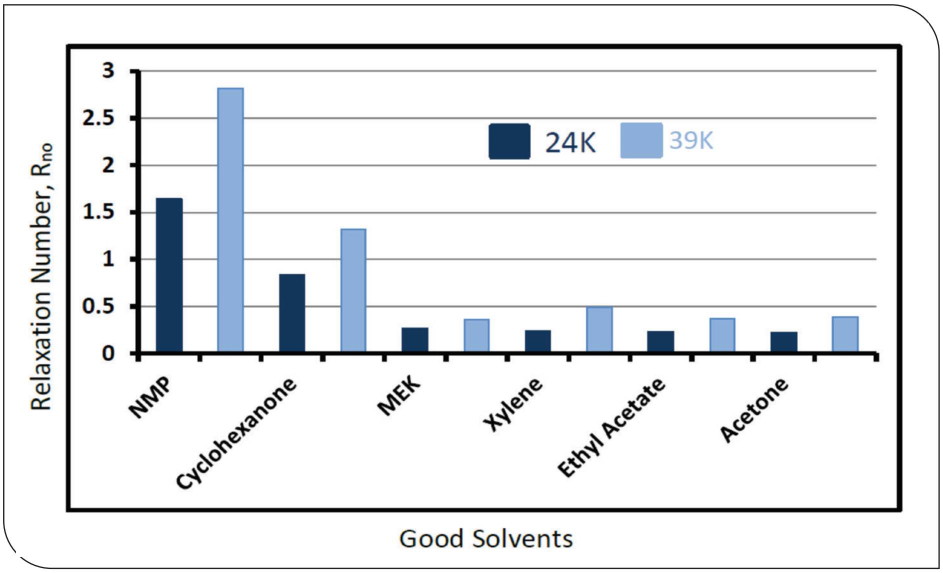
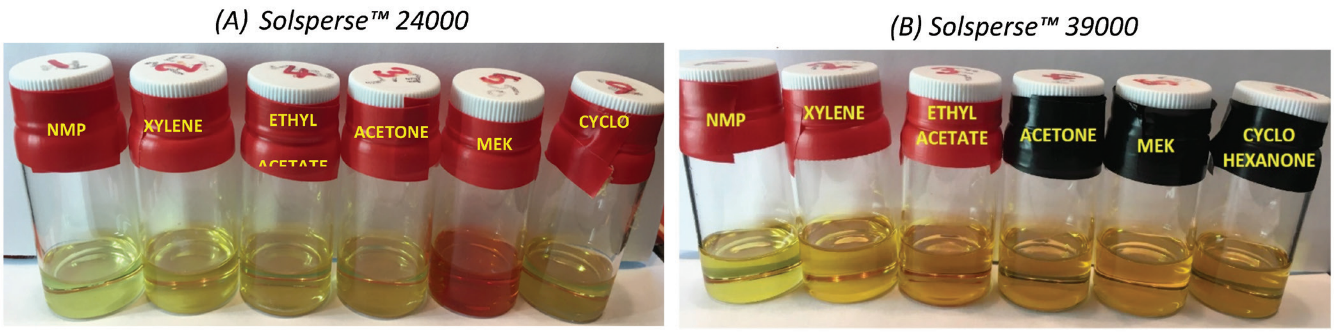


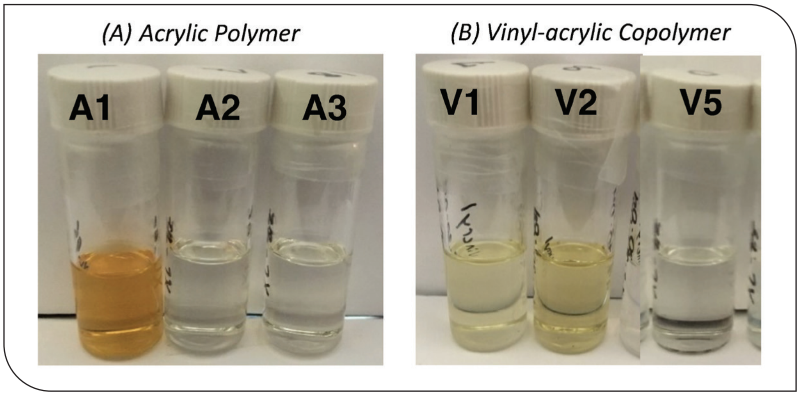
FIGURE 5
Comparison of the R_{no} for solutions of two hyperdispersants in "good" solvents.

FIGURE 6
Solutions of two hyperdispersants in "good" solvents.


(A) Solsperse™ 24000

(B) Solsperse™ 39000

FIGURE 7
Solutions of two industrial grade polymers in “good” solvents.



In the following second example, we compare samples of an acrylic polymer and a vinyl-acrylic copolymer that were obtained from a major U.S. paint manufacturer. However, since the materials were proprietary, no information was provided as to their chemical composition, such as the exact architecture (whether random, alternating, or blocks), and the segment distribution and molecular weights. Again, for “good” solvents, the solutions are clear (**Figure 7A** and **7B**. Nevertheless, the relaxation data show that there is an apparent clear trend in polymer-solvent affinity for both polymers, with measurable differences seen between the various solvents (**Figure 8A** and **8B)**. As with the hyperdispersants, such comprehensive discrimination cannot be achieved with visual inspection alone, which highlights a drawback of the latter technique.

A significant practical advantage of the LF-NMR technique is that relaxation data can be obtained in a very short time. Thus, reliable data from multiple runs can be obtained in a few minutes, which is important in QC where many samples may need to be analyzed.

Even though these polymers are not pure, a quantitative analysis is possible with solvent relaxation since the relaxation time is an average of all the components present. This makes it possible to routinely and economically track the different nature of commercial polymers used in paints, from manufacturer to manufacturer, to determine their interfacial “equivalency,” and even from the same manufacturer to verify if significant batch-to-batch variations exist.

The magnitude of R_{no} is larger for the acrylic polymer compared with the vinyl-acrylic copolymer; for example, with the same solvent (DMF), it is approximately a factor of 2.5.

A more rigorous approach is to derive the specific HSP for a given polymer. This is relatively straightforward using LF-NMR relaxation. A solvent with known energy characteristics can be considered as being either a good solvent or a poor solvent. In the calculation of HSP, the user is required to input this solvent quality information. R_{no} values provide a direct, reliable, and quantitative means to obtain this. The procedure for calculating HSP values is iterative and is described in detail elsewhere.[15] The results of HSP analysis for the two polymers are shown in **Table 2**.

Interestingly, comparison of the HSP values suggests that the acrylic polymer is significantly less polar than the vinyl-acrylic copolymer (P=7.7 and P=12.3, respectively). Further, the two polymers apparently contain the same number of acrylic acid groups *available* for hydrogen bonding (H=10.1). However, owing to the unknown nature/characteristics of both polymerics, no further inferences can be drawn. The importance of knowing the HSP value is that solvent blends—even mixtures of individually poor solvents—having volume average HSP values like that for the specific polymeric will be effective. This can provide the formulator with greater flexibility to improve paint performance.

FIGURE 8
Comparison of the affinity ranking (using the R_{no}), for solutions of two industrial grade polymers in “good” solvents.

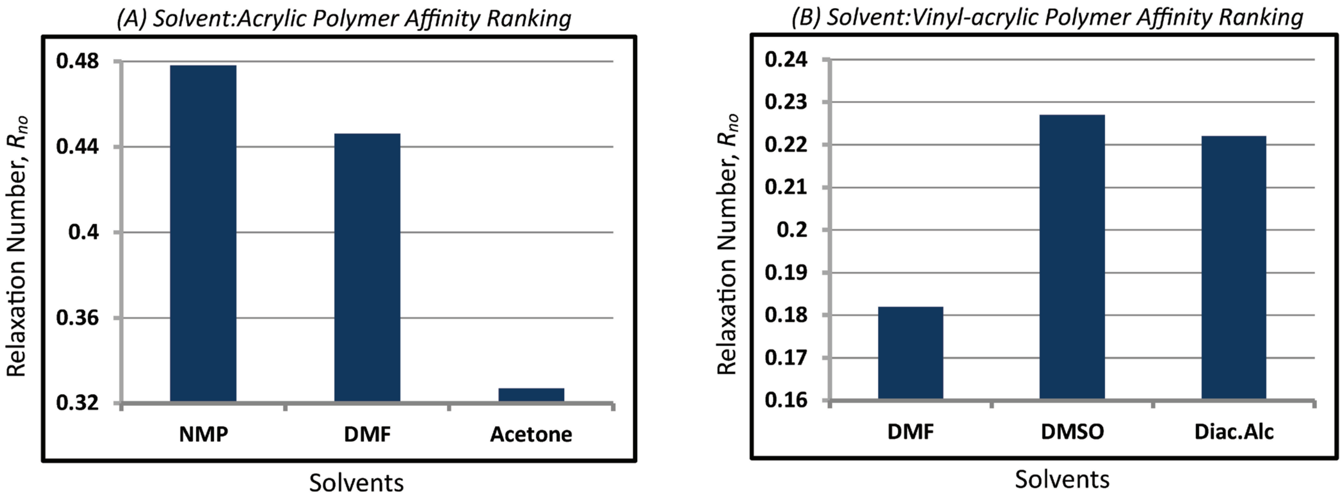


TABLE 2
Average HSP Values for Two Industrial Grade Polymers

Polymer	δD	δP	δH
Acrylic	17.4	7.7	10.1
Vinyl-acrylic	17.1	12.3	10.1

TABLE 3
Average HSP Values for Five Different Samples of Titanium Dioxide

TiO_2 I.D.	δD	δP	δH
-001	17.3	6.4	8.1
-002	16.3	11.0	3.8
-003	17.3	6.6	8.3
-004	16.7	7.5	8.2
-005	18.2	13.6	4.6

Hansen Solubility Parameters of Particles: Titanium Dioxide

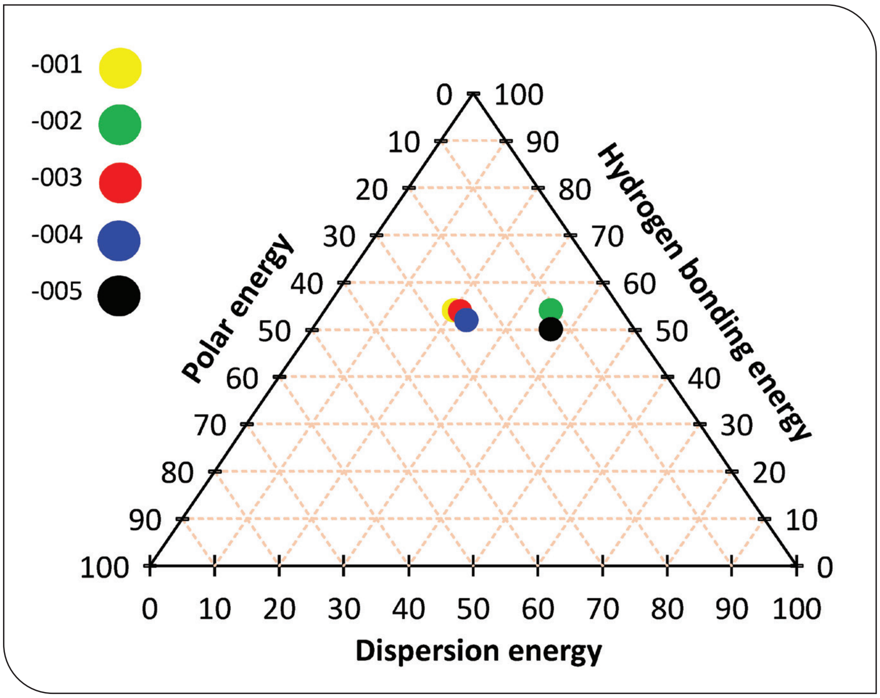
HSP can be used to select the most appropriate solvents for wetting and dispersing nanoparticulate powder materials. We can apply the same fast and robust methodology that is used to determine the HSP of polymers to accomplish the same for powders. A series of five titanias were supplied blind by KRONOS but they are known to be used in a variety of different applications. The materials were part of a study presented at a Workshop on the Current State of HSP for Particles, at the University of Duisberg-Essen in December 2023. The results are summarized in **Table 3.**

TiO_2 samples -001 and -003 are quite similar possibly because they have comparable surface coatings. The largest differences are seen in the values of the polar and hydrogen bonding components to the total interaction energy highlighting that the solvent-surface interaction is an important determinant of dispersibility. As with polymer, solvent blends—even mixtures of individually poor solvents—having volume average HSP values like that for the specific powder material will be effective at wetting and dispersing it.

Using the percentage of the interaction forces (based on the data in **Table 2**), we can construct a TEAS plot (**Figure 9**) which provides a convenient way to discriminate the particle surfaces and the efficacy of surface modification. Inspection shows that the five titanias cluster into two separate areas, namely Samples #1, #3, and #4 and Samples #2 and #5, that are defined by the different contributions of the polar and dispersion energies. These are related to the specific nature of the various surface coatings (which were not disclosed).

For each set of materials, the data suggests that the interaction of solvents having strong affinity with their surfaces is comparable. Understanding such fundamentals is critical not just to helping improve current paint formulations (by allowing a formulator to more efficiently optimize the preparation of a suspension), but also to design and prepare new advanced products.

FIGURE 9
TEAS plot for KRONOS titanias using data from Table 2.



Milling and Grinding

The importance of adequate dispersion to application properties and color is significant because the dispersion of colored organic/inorganic pigments and dyes affects brightness and gloss.

Further, the state of dispersion of any solid material directly affects suspension properties. For example, as particulate material is added to any liquid medium its flow becomes increasingly non-Newtonian and, with high particle concentrations, can become thixotropic.[5,6]

Milling is an important tool available to both the R&D formulator and process engineer.[48] Regardless of the milling technique or device used, monitoring the process can reveal important insights relevant to the state of suspension dispersion. LF-NMR relaxation measurements are especially useful in this regard because they can be made on particulate suspensions at virtually any industrially relevant solids concentration without dilution. Hence, samples can be taken directly from the mill. Such measurements provide formulators and process engineers with a fast, simple tool to monitor milling in real time and so can be used to improve both the quality of materials and final product, as well as the economics of the process.

In addition to coatings, carbon blacks are used extensively in a wide range of applications.[49] Their particle morphology and physical surface properties directly affect performance behavior,[50] and so an accurate and repeatable evaluation of those characteristics is important. The surface chemical properties of carbon blacks are equally important, and they can vary considerably.[51] This can make finding equivalent materials problematic since even batches of the same material can differ.[22] Milling impacts both and LF-NMR relaxation is sensitive to both.

In **Figure 10,** we compare the relaxation time as a function of the milling of a 10 wt% suspension of a carbon black dispersed (using a Netzsch media mill) in toluene; the type and concentration of dispersing agent used was not disclosed.

A shorter relaxation time reflects an increase in particle-solvent affinity and an increase in available surface area (a decrease in particle size). As expected, the smaller 0.1 mm grinding media produces a finer grind. However, there can be practical (separation and cleanup) and economic issues (cost) when using the smaller beads. Hence, the relatively small increase (an average of *ca* 13%) found here in milling efficiency might not be sufficient justification. Having quick comparative quantitative data allows optimization decisions to be made and to prioritize the need, if required, for additional quantitative testing and analysis using traditional characterization techniques.

As we have previously mentioned, a practical advantage of NMR relaxation is that its measurement is noninvasive/nondestructive and so samples can be stored for reanalysis at any future date. The NMR tubes were sealed and the carbon black samples stored at RT for one week and then the relaxation time(s) remeasured. The results are shown for the 0.2 mm grinding media in **Figure 11**.

The relaxation times have increased (by an average of *ca* 13%) suggesting that aggregation of the carbon black has occurred (and which could not be detected by visual inspection of the opaque samples). This suggests that the dispersant is not providing sufficient long-term stabilization—likely because the initial concentration has not been optimized (too low).

The design and choice of milling equipment must be handled with care for both the initial wetting of a powder (and sometimes de-aeration)—often called the premix stage—and for final dispersion. The choice of equipment also depends on factors such as the nature of the mill base, and the quality and volume required.[49] Two well-known mixing devices are the three-roller mill and the rotor-stator mill. Each provides a different degree of processing shear. In this next example, three high solids (*ca* 40 wt%) carbon black slurries were prepared, in the same solvent mixture containing a proprietary polymeric dispersant, using a roller mill, a rotor-stator, and a roller mill followed by a rotor-stator. T_2 relaxation time measurement results are summarized in **Table 4.**

TABLE 4
Comparison of Efficiency of Different Milling Techniques Using T_2 Relaxation Time (ms) Measurements for a Non-aqueous 40 wt% Carbon Black Slurry

Slurry Batch I.D.	Milling Device	Average T_2 Relaxation Time (ms)
CB-1	Three Roller Mill	75.8
CB-2	Rotor-Stator	22.0
CB-3	Roller Mill + Rotor-Stator	60.4

FIGURE 10
Milling of a carbon black in a media mill using two different sizes of grinding media.

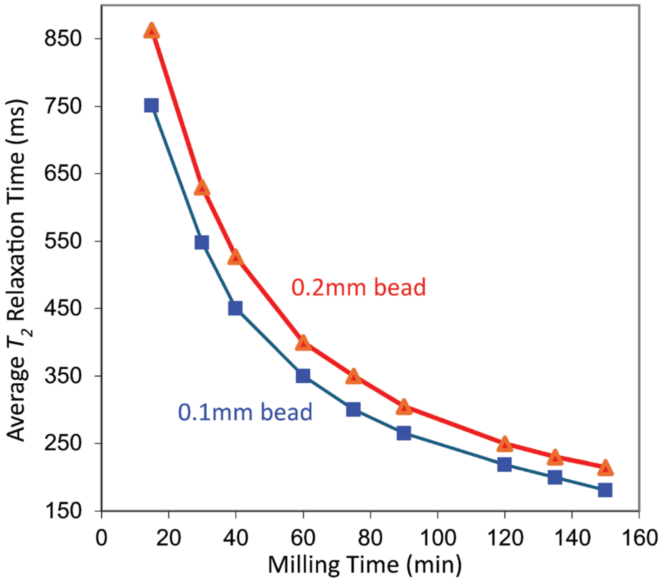
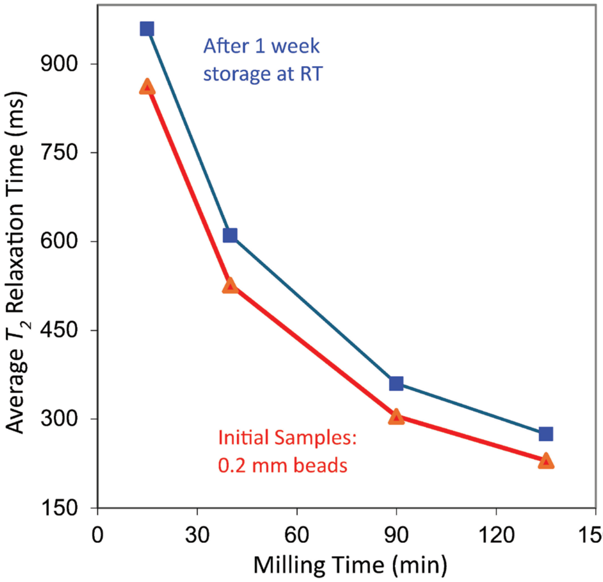


FIGURE 11
T_2 relaxation time (ms) of carbon black milled using 0.2 mm beads after storage at RT for one week.



The data suggests that the most efficient comminution arises from using the rotor-stator mill and the least efficient is using a basic roller mill. However, the combination does not provide any advantage; indeed, it suggests that it results in over-milling.

The total solids concentration for the two carbon black studies was sufficiently high (10% and 50%, respectively) that, together with the fact that they were also opaque (black), it would be impossible to obtain a precise characteristic analysis from microscopy or light scattering instrumentation. Additionally, for the latter devices, the product must be diluted extensively.

Determining the Effectiveness of Dispersing Agents

The act of dispersing a powder into a liquid is a complex process; a comprehensive review has been given elsewhere.[52] It entails overcoming the various binding forces between particles by using physicochemical, mechanical, and thermal means and an important step in the process of dispersing particles in liquids is deagglomeration, where particles are separated from each other.

Dispersing agents are essential components in a formulator's toolbox. However, unlike surfactants, true dispersants 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 interparticle 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.[53] 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.

Here we explore how LF-NMR relaxation measurements can, simply and quickly, quantify the efficiency of dispersant action. This is because solutions of free dispersant molecules have little effect on the relaxation time of the bulk liquid, but with a suspension of particles in a liquid any dispersant molecule adsorbed at the particle-liquid interface will change the relaxation time of the suspension (because it will displace bound liquid). This effect can also be used to determine the adsorption of solutes (surfactants, polymer, and polyelectrolytes) onto the surface of materials.[9,11-13]

In this study, a 60 wt% suspension of metallic silver flake in Texanol was prepared using 2 wt% of different commercial dispersants, and the relaxation time of each suspension was measured (**Figure 12**). Texanol is an alcohol ester that is used in paints and inks, and metallic silver flake is used to impart decorative properties. The data (plotted as the R_{no}) show that the largest value, reflecting the best dispersibility (and the largest *wetted* surface area), was found for the suspension prepared using the Hypermer KD1 dispersant (type E in **Figure 12**). The smallest value was found using the Crodafos M915A dispersant (type D), which performed 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.

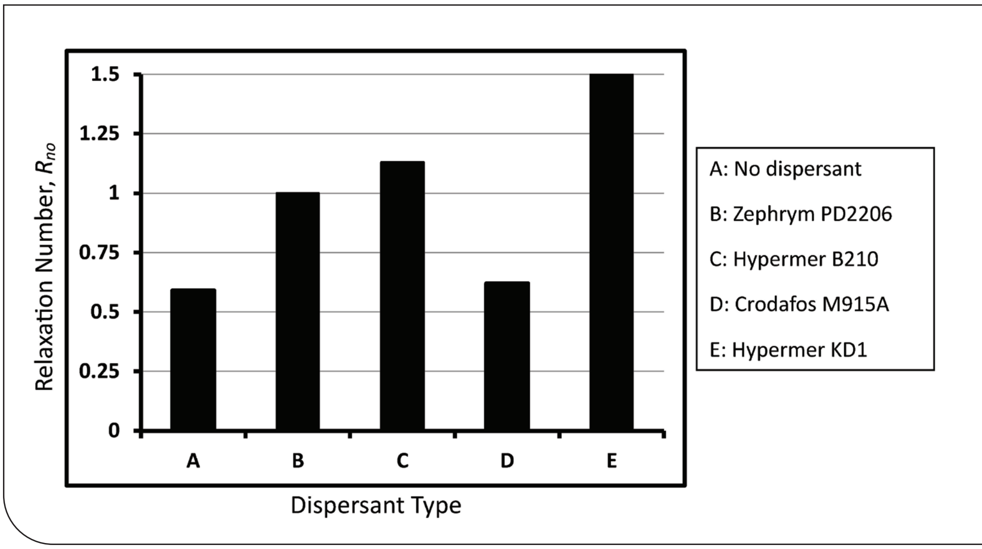
These results can be understood by considering the chemical nature of the dispersants examined. The Crodafos M915A is an alkylphosphate anionic dispersant more suited to the preparation of aqueous dispersions. In contrast, the Hypermer KD1 is a polyester/polyamine copolymer that is well recognized as an efficient dispersant for use with nonaqueous 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.

Hence, such measures 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. Further, dispersants are expensive, hence optimizing their concentration in a formulation is important to producing the best product possible at the lowest cost; solvent relaxation measurements can be used to determine optimal use concentrations.[9]

Comparison of Two Finished Paint Formulations

Being complex, multicomponent formulations, paints cannot be diluted without consequence. For example, the (dilution) process not only destroys any structural characteristics but also can induce instability.

FIGURE 12
LF-NMR relaxation measurements for identical silver flake suspensions prepared using a variety of dispersants.



Formulators must routinely assess multiple metrics as part of necessary quality assurance (QA) in production. Many industries establish product specifications to ensure product consistency during manufacture, but all too often they are not sufficient to guarantee that a truly high quality product has been manufactured. How, then, can formulators ensure that their paints are, in fact, always of the same high quality?

LF-NMR relaxation does not make any assumptions about the composition of the formulation, and this makes it an ideal technique for measuring finished commercial products.

The relaxation time obtained for any paint formulation is an average value that is dependent upon its exact composition. Hence, batches of paint manufactured with the same components and using the same processing should, within experimental error, have the same relaxation time. Any changes will impact on the measured relaxation time. This makes LF-NMR an ideal tool for QA.

Here we simply compare two nonaqueous finished magenta paint formulations. The MSDS (supplied with them) disclosed that the dispersing fluid was a mixture of three solvents: no further information was given. The data in **Table 5** shows that both the T_2 relaxation time and T_1:T_2 ratio are not the same and so the two paints are clearly different. We would therefore expect that some characteristics of their application behavior would differ.

TABLE 5
Comparison of Relaxation Data for Two Finished Magenta Paint Formulations

Formulation I.D.	Average T_2 Relaxation Time (ms)	T_1:T_2 Ratio
#1	94.1	1.75
#2	75.2	2.43

The instrument (*M*agno*M*eter) software automatically uses a single exponential fit to the raw data to obtain the relaxation time(s). However, close inspection of the T_2 relaxation plots suggests that a single exponential fit (red line) to the raw data (black dots) is not good, as can be seen in **Figure 13** for Formulation #1.

Such results are typically found in suspensions where there are defined fractions of larger (aggregated) particles and/or smaller particles ("fines"), or if the material is porous (the "porosity" could arise from inter-particle or intra-particle penetration of liquid). It also occurs with suspensions containing more than one solid component, and with emulsions where there are two distinct liquid phases.

The data can be reanalyzed using CONTIN, a well-established, powerful regularization method[54] frequently used, for example, to obtain the size distribution of colloidal suspensions from dynamic light scattering data. Using this fitting routine (also available as part of the operational software of the Mageleka instrument), we can obtain a distribution of relaxation times for the two formulations, as shown in **Figure 14**.

This robust reanalysis shows that the distributions are similar in form—each with three "fractions"—but the height(s) and width(s) vary. The average relaxation time(s) and the percentage(s), in parenthesis, are summarized in **Table 6**.

TABLE 6
T_2 Relaxation Time (ms) Distribution Data for Two Finished Magenta Paint Formulations Extracted from Figure 13

Formulation #1			Formulation #2		
140 (42)	30 (49)	8 (9)	100 (60)	20 (29)	10 (11)

The MSDS also discloses that the paints contain barium sulphate which is likely one of the fractions. We cannot speculate further without more detailed information about the exact composition of each formulation.

Conclusions

The application of LF-NMR liquid relaxation to the study of suspensions and slurries offers a new and versatile technique for probing events and interactions at almost any particle-liquid interface. We have illustrated how LF-NMR liquid relaxation can be used to study and optimize formulations of a variety of materials used in coating applications over a wide concentration range. The technique is a useful, rapid complimentary technique to traditional characterization methods, and it can provide information that cannot readily be obtained by them. A major advantage is to be able to make measurements using industrially relevant concentrations with no dilution, virtually no sample preparation, and no necessity for optical transparency. Furthermore, the technique is nondestructive, so samples can be stored and remeasured at any future time permitting later reanalysis of reference samples, or long-term aging studies to be undertaken quite easily.

FIGURE 13
Single exponential fit to the raw relaxation data for magenta paint formulation #1.

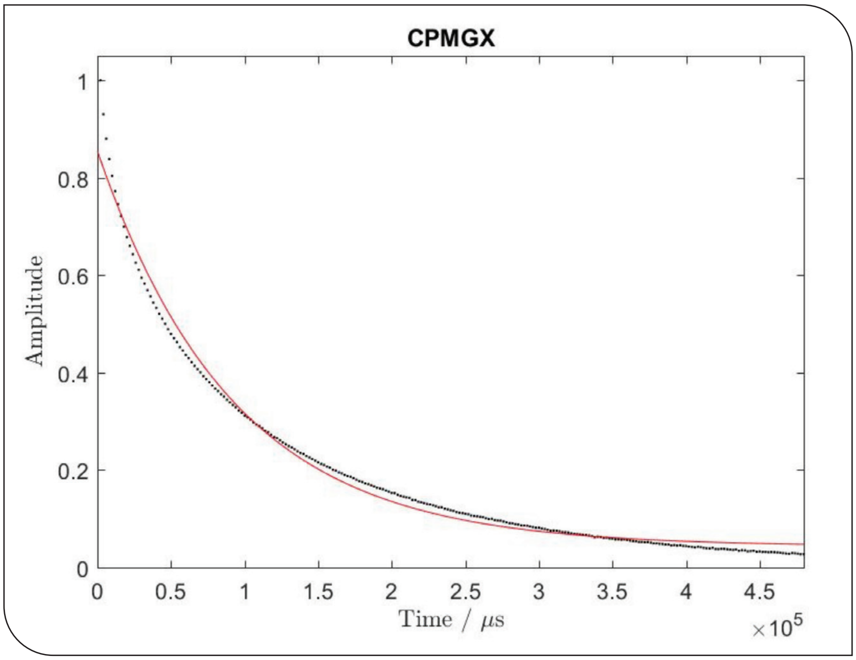
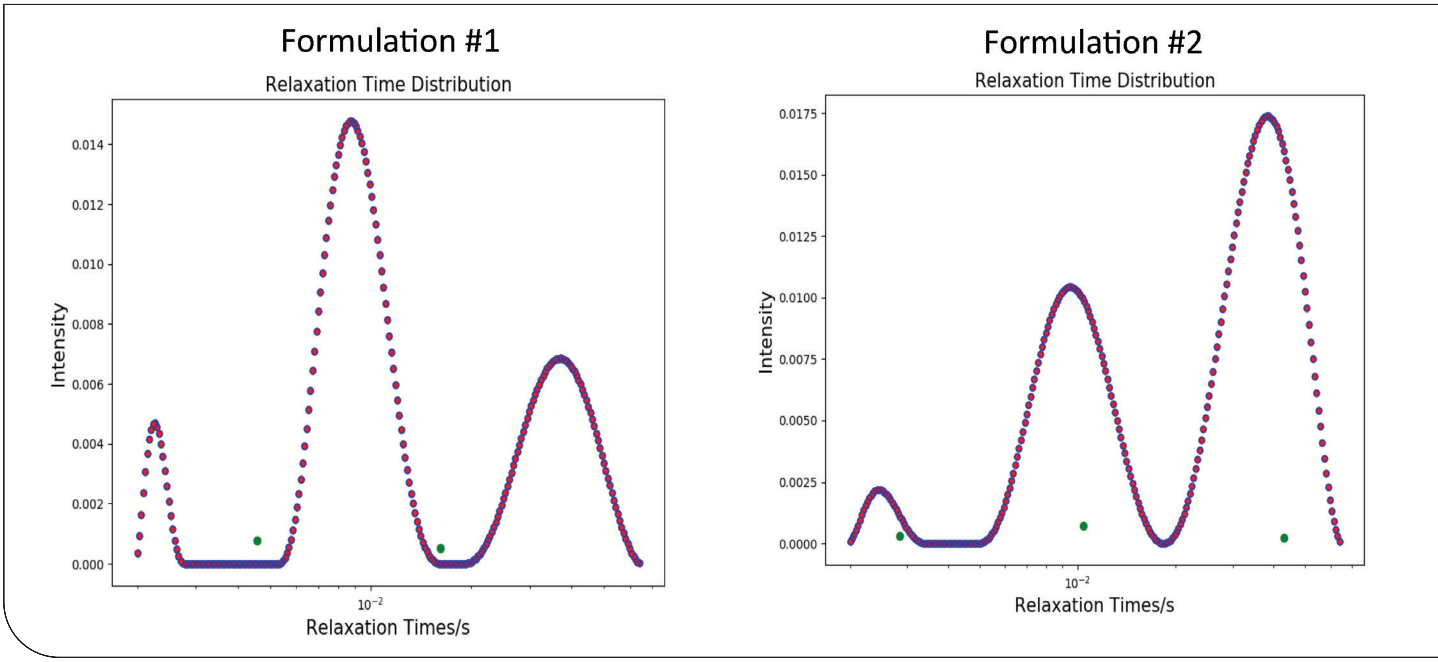


FIGURE 14
Distribution of relaxation times using CONTIN for magenta paint formulations.



The studies suggest that LF-NMR relaxation measurements can be used to (1) quickly and easily QC incoming raw materials (solids and liquids), (2) determine the "equivalency" of those materials, (3) discriminate surface coatings and modification, (4) monitor milling processes in real time, (5) accelerate the whole process of HSP determination of polymers and particulate materials, (6) quantitively determine the efficacy of dispersants, and (7) rapidly screen batches and lots of finished paint formulations for QA purposes.

At the simplest level, LF-NMR relaxation information can help maintain a more consistent product, enhancing end-use value and profitability. At the more complex level, LF-NMR relaxation information can help reduce in-process modifications, and reworking, and so make products more competitive. ❊

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Mageleka Inc. manufactures bench-top NMRs.

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David Fairhurst, Ph.D., *is president at Colloid Consultants Ltd. Email: 1colloidman@gmail.com*

R. Sharma, Ph.D., *is principal research fellow at Mageleka, Inc. Email: ravi@mageleka.com*

R. Wörheide *is president at Metromation Inc. Email: ralph@metromation.co*

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