Dye and Pigment Dispersions: Using NMR Relaxation Measurements as an Aid in Their Formulation

Introduction

The particle size distribution (PSD) – and, hence, the wetted surface area - of a colored organic pigment or dye determines the tone and hue. Additional attributes, such as brightness, gloss, and coating, are paramount properties in applications like decorative cosmetics and high quality automotive paints. Correct dispersion of the pigment material is critical to producing the desired characteristics of a final product and so aggregation must be kept to a minimum. For example, in concentrated suspensions, dispersion of the pigment dramatically impacts the rheological behavior (flow and deformation). In any application using pigment, the final PSD depends very specifically on how the pigment material is dispersed.

Unfortunately, direct, precise physical characterization of dye and pigment dispersions is difficult owing to the high solids concentrations normally used and the resulting suspension opacity. Further, a challenge in, for example, water-borne coatings is efficient wetting of the pigment.

So, what technique can make fast, reliable, direct measurements of wetted surface area and other physical characteristics for any suspension, and especially at the high solids concentrations typically needed for dye and pigment dispersions? Nuclear magnetic resonance (NMR) relaxation, which is the basis for Mageleka's *M*agno*M*eter XRS™, provides direct measurement of such attributes for any type of particulate suspension.

This application note will explore the use of nuclear magnetic resonance (NMR) spectroscopy to aid in the formulation of a product containing a dispersed blue carboxy dye. NMR relaxation measurements that trend with desired characteristics of the final product are compared across formulations containing a variety of surfactants. NMR measurements such as these can be readily made using the *M*agno*M*eter XRS™ (see Mageleka Application Note 4).

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 Mageleka's *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 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).

The *M*agno*M*eter's measurement technique is non-invasive and non-destructive and the *M*agno*M*eter can work with suspensions at any

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MAGELEKA, Inc.
1319 N. New York Avenue
Winter Park, FL 32789 USA

Worldwide: +1 617 331 1130
Europe: +44 (0)1744 325005

www.magnometer.com

industrially-relevant concentration. This is especially important when working with dye and pigment dispersions, and the *M*agno*M*eter eliminates the dilution issues inherent in making measurements using, for example, dynamic light scattering. 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?)

What does the *M*agno*M*eter 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 (see Mageleka White Paper 1). 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, 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 the value depends critically upon the exact composition of the dispersion fluid. The surface area value calculated from NMR relaxation is based on a calibration using a dispersion of the same type of particles where the surface area is already known (see Mageleka White Paper 1).

Effect of surfactant type on final characteristics of a suspension containing a dye

The data in this case study are reported as a wetted surface area and Table 1 presents the results of measurements of a 20 wt% aqueous suspension of a blue carboxy dye prepared using a group of well-known, water-soluble anionic surfactants that are widely used as dispersing aids throughout many different industries. There are literally hundreds of surfactants and dispersants on the market. The structure of a surfactant determines its functionality (see Mageleka Technical Note 3), and all dispersants work (see Mageleka Application Note 4), but which one works best to disperse a particular dye or pigment?

Here we can see clear differences in efficacy within this test group. The choice of surfactant affected the wetted surface area (Table 1), which ultimately influenced two desired characteristics of the final

Table 1. Comparison of 20 wt% aqueous suspensions of a blue carboxy dye that differed only in the surfactant used.

Surfactant (trade name)	Surface Area (m^2g^{-1})
None	15.4
Fluorad	16.0
Natrol 42	18.5
Lomar D	35.5
Aerosol AOT	42.0
Ultravon W	46.2

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product: opacity and color intensity. The most efficient surfactant was Ultravon W, which resulted in a suspension with wetted surface area values three times greater than one with no surfactant at all. This is, undoubtedly, because of the molecular structure of Ultravon W. It is an anionic benzimidazolene disulphonate surfactant and can adsorb strongly onto the dye surface and impart a high zeta potential (or surface charge; see Table 2). This not only promotes better dispersibilty but also inhibits any re-aggregation, as it is generally accepted that, for electrostatically stabilized suspensions, a higher zeta potential will lower the probability that particles will re-aggregate.

It is worth noting that the raw relaxation time data could have been used just as effectively in this case study because we were comparing data from the same material-liquid combination that differed only in dispersant type. Another example would be comparisons of the effect of milling time, where the dispersion is otherwise identical across differently-

Table 2. Comparison of zeta potential values of identical blue dye suspensions differing only in the surfactant used.

Surfactant (trade name)	Type	Average Zeta Potential (mV)
None	-----	-25
Fluorad	fluorocarbon-based surfactant	-33
Natrol 42	lignin sulphonate	-37
Lomar D	naphthalene sulphonate	-40
Aerosol AOT	alkyl sulphosuccinate	-44
Ultravon W	imidazolium compound	-51

milled samples. However, when different materials are compared it is better to use wetted surface area or the relaxation number, which is a dimensionless parameter directly proportional surface area (see Application Note #4). Not all techniques for measuring wetted surface area are ideal. For example, measurements from dynamic light scattering make an assumption that the particles in the sample are spherical, and such measurements require significant dilution from the original concentration. Dilution is not always an innocuous process and, therefore, can introduce errors (see Mageleka White Paper #2: Particles in Liquids). By contrast, surface area measurements based on NMR relaxation, such as those from the *M*agno*M*eter , do not require dilution – any industrially relevant concentration can be measured – and do not make assumptions about particle shape. As a result, surface area measurements from NMR techniques are significantly less subject to error and, thus, less likely to lead to erroneous conclusions (Table 3).

The data in Table 3 reveal how sample dilution and assumption of particle shape can bias results. In all cases the surface area values computed from a mean dynamic light scattering particle size are smaller than those determined directly from NMR relaxation time.

Table 3. Comparison of surface area values calculated from NMR relaxation with those from dynamic light scattering.

Surfactant (trade name)	Calculated Surface Area (m^2g^{-1})	
	NMR	DLS
None	15.4	11.5
Fluorad	16.0	13.2
Natrol 42	18.5	15.4
Lomar D	35.5	25.6
Aerosol AOT	42.0	33.8
Ultravon W	46.2	42.0

This case study demonstrates the utility of the *M*agno*M*eter's NMR-based technology in determining which surfactant is the most effective for a given dye material and liquid combination. Determining this will result in a suspension with superior performance attributes. Moreover, measurements using NMR relaxation avoid assumptions and limitations inherent in other traditional particle characterization techniques.

Thus, the *M*agno*M*eter can help formulators optimize the dispersion process and so improve the economics and quality of products in any industry that utilizes suspensions or emulsions.

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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