Using a Mageleka *M*agno*M*eter XRS™ *R*elaxo*M*eter to Analyze and Characterize a Series of Non-aqueous Carbon Black Dispersions

Introduction

Carbon blacks are used extensively in a wide variety of applications, often at high solids concentrations, and in both aqueous and non-aqueous media. Examples of applications utilizing carbon black include a model for "soot" created in engine oils in the development of suspending and dispersing agents. Another example is the use of carbon black as a conductive additive in Li-ion batteries to improve the fast-charging ability of anodes. Indeed, improvements in energy and power densities, charge and discharge times, cost, lifetime, and safety are all critical to the success of next generation batteries.

A major use is in the production of tires, where it is known that the particle size/surface area of carbon black used directly affects performance properties such as abrasion resistance and heat build-up. Additionally, the surface activity of carbon black is considered to have a great influence on its reinforcing properties. Thus, accurate and repeatable evaluation of the size, morphology, and surface characteristics of carbon black particles is important for production of the carbon black itself, as well as any products that depend on it as a raw material (see Mageleka Technical Note #4 at www.mageleka.com).

One method of producing carbon blacks is by thermal dehydrogenation of hydrocarbons. The surface chemical properties are determined to a large extent by the presence of functional groups – hydrogen, oxygen, nitrogen and sulphur, etc. – that arise because of different sources of the raw feed material and subsequent processing conditions. Further, the ability to predict the most appropriate liquid(s) to use for wetting/dispersing a given carbon black is of considerable interest to the formulator. However, in addition to being opaque, many real-world suspensions of carbon blacks can also be pasty/thick and/or viscous. This makes analysis of these suspensions by traditional particle characterization instrumentation difficult, if not impossible.

Thus, in any application – and especially those involving carbon blacks – accurate, quantitative, and reliable characterisation and analysis methods are needed from the initial stage of checking incoming raw materials, to development of new formulations, and through to quality control within high volume manufacturing. To be truly versatile, such a method would allow any sample to be measured quickly, easily, and without special preparation.

NMR relaxation time provides this versatility and it can be measured directly using an NMR spectrometer, such as the *M*ageleka *M*agno*M*eter XRS *R*elaxo*M*eter. The NMR relaxation time is a fundamental *intrinsic* property of solids and liquids NMR relaxation is sensitive to both the extent of wetted surface in a suspension as well as the chemical nature of a particle surface and so measurements will reflect the contribution of

> "Nuclear magnetic resonance (NMR) relaxation is an ideal technique for measuring suspensions at high solids loadings."

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both features. NMR relaxation is quantifiable and fast, without the need for dilution or other sample preparation and so offers practical advantages. The total amount of sample needed is typically ca 0.1 mL and can be as little as 250 µL. Further, the technique is noninvasive/nondestructive, so repeatability measurements can be made conveniently.

The *M*agno*M*eter *R*elaxo*M*eter is a small benchtop device that is easy to employ, requires limited input data, and provides rapid measurement. The instrument can work with any industrially relevant solids concentration and with virtually any liquid. Moreover, it has easy-to-use software, so it has the additional benefit of being able to be operated by a non-NMR specialist.

The *R*elaxo*M*eter can be used at every stage of manufacture to help improve efficiency and to reduce costs – from quality control (QC) of incoming materials, through formulation R&D and process monitoring, to quality assurance (QA) of final commercial products (see the series of *M*ageleka Technical Notes at www.mageleka.com).

This Application Note uses two studies to demonstrate the use of NMR relaxation time measurements from the *R*elaxo*M*eter for routine interrogation of carbon blacks dispersed in non-aqueous media. Both studies investigate the effect of solvents and reveal how useful NMR relaxation time measurements can be in characterizing carbon blacks to compare materials from different manufacturers and revealing, for example, variations in batches of the same material.

STUDY 1.

In this first study, seven commercial carbon blacks, from five different manufacturers, were dispersed (at approximately 9%w/w) in two solvents – isopropanol (IPA) and hexane – as typical examples of polar and non-polar media. An additional study (see below) was later made using acetone. The surface tensions of IPA and acetone are similar but IPA has a greater potential for hydrogen bonding compared with acetone: IPA can H-bond as both a donor and acceptor, while acetone is capable of H-bonding only as an acceptor (1).

The carbon blacks were all of the type and grade used in tire manufacture. Surface area data (measured independently by gas adsorption) for the carbon blacks are in agreement with values provided in the manufacturer's literature and are presented in Table 1. Note that the two samples of the CABOT Regal 300 were different batches obtained from two suppliers.

Table 1. N_2/BET gas adsorption surface area values for commercial carbon blacks.

Carbon Black	Surface area (m^2g^{-1})
DEUTSCHE GRW	130.4
CABOT VULCAN 1391	122.1
CABOT REGAL 300 (1)	57.5
CABOT REGAL 300 (2)	57.5
SID RICHARDSON N326	60.6
ORION	58.3
BIRLA CD2125X7	88.4

Results and Discussion

*R*elaxo*M*eter measurements were made directly on the suspensions without any further sample preparation. No problems were experienced in making the relaxation time measurements and the results are summarized in Table 2. For reference, average T_2 relaxation times were also measured for pure hexane (1956 ms) and IPA (1047 ms).

Table 2. Average T_2 relaxation times for suspensions (9.09% w/w) of Carbon Blacks dispersed in Hexane and Isopropanol

Carbon Black	Average T_2 relaxation time (ms)	
	HEXANE	ISOPROPANOL
ORION	130.4	915.6
CABOT REGAL 300 (1)	122.1	955.2
CABOT REGAL 300 (2)	57.5	967.4
SIDRICH N326	57.5	893.9
CABOT VULCAN 1391	60.6	853.9
DEUTSCHE GRW	58.3	767.4
BIRLA CD2125X7	88.4	673.3

From these results in Table 2, we can see that the relaxation times for the two CABOT REGAL 300 samples differ in both hexane and isopropanol, even though their surface areas are identical. This should not be surprising since N_2/BET gas adsorption is measured on samples of the *dry* material. It illustrates why such measurements can have limited use when dealing with *wetted* suspensions, and why the NMR relaxation technique used by the *R*elaxo*M*eter can be more accurate and reliable in such instances.

It may be preferable to normalize out the effect of solvent (which could include dispersants, additives, etc) and assess the strength of solvent-surface interaction. To do this, the relaxation time can be presented as a relaxation number, which is a useful, *dimensionless parameter*, R_{no}, defined as:

$$R_{no} = [R_{suspension}/R_{solvent}] - 1$$

Where, R = 1/T

Table 3 shows the same data as above, but coverted to relaxation number and ranked.

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Table 3. Relaxation numbers, R_{no}, for carbon black suspensions calculated using T_2 data from Table 2).

Carbon Black	RELAXATION NUMBER, R_{no}	RANKING
HEXANE		
DEUTSCHE GRW	1.01	1 (best dispersed)
CABOT VULCAN 1391	0.78	2
SIDRICH N326	.060	3
ORION	0.56	4
BIRLA CD2125X7	0.37	5
CABOT REGAL 300 (2)	0.29	6
CABOT REGAL 300 (1)	0.21	7 (least dispersed)
ISOPROPANOL		
BIRLA CD2125X7	0.56	1 (best dispersed)
DEUTSCHE GRW	0.36	2
CABOT VULCAN 1391	0.23	3
SIDRICH N326	0.17	4
ORION	0.14	5
CABOT REGAL 300 (1)	0.10	6
CABOT REGAL 300 (2)	0.08	7 (least dispersed)

The relaxation numbers clearly differentiate the interaction of each of the solvents with the individual carbon blacks. This is a consequence of not only true variations in geometric surface area (because of both the size and surface roughness of the carbon black particles) but also the wettability (determined in large part by surface chemistry) between the carbon black particles and the solvents.

The interaction of a liquid with a surface is dictated, in large part, by its cohesive energy. This has three components – dispersive energy, polar-dipolar energy, and hydrogen bonding energy – that are memorialized as the Hansen Solubility Parameters (HSP). It is known that HSP can help in the selection of the most suitable solvent for initial wetting and dispersing of powders.

NMR solvent relaxation measurements are sensitive to the same intermolecular forces (as well as the dynamics) between solvent and surfaces with which HSP are concerned and so is a very useful technique for determining HSP of materials (2.) However, determination of the HSP requires using a minimum of 12 solvents for each individual carbon black, which is beyond the remit of this study but is the subject of a separate Application Note (#17).

Nevertheless, we can plot the correlation of the Relaxation Numbers for the two solvents used in this first study (Figure 1).

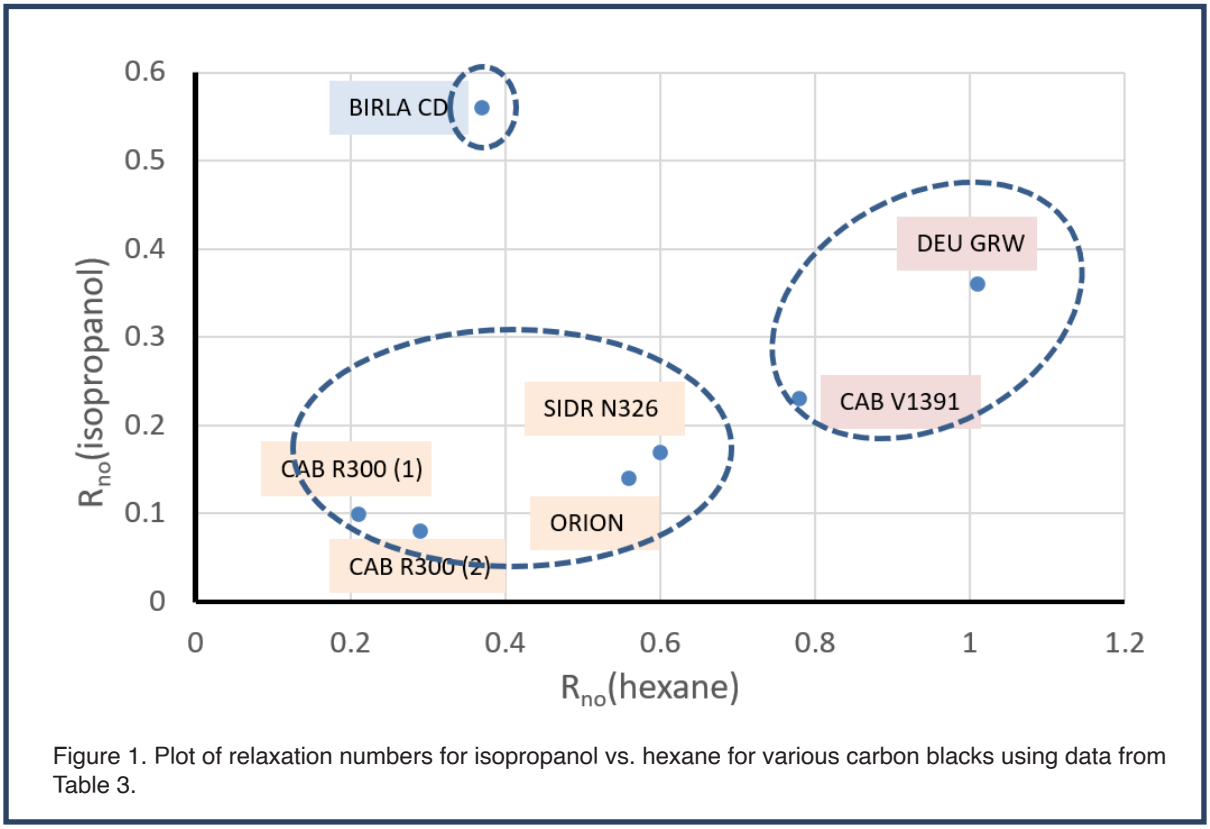

Figure 1. Plot of relaxation numbers for isopropanol vs. hexane for various carbon blacks using data from Table 3.

The plot shows that the NMR results cluster into three "areas of 2-D HSP space" – defined by IPA and hexane data – in which reside different groupings of the seven carbon black materials:

Group 1: CABOT REGAL 300 (1), CABOT REGAL 300 (2), ORION, SID RICHARDSON N326
Group 2: CABOT VULCAN 1391, DEUTSCHE GRW
Group 3: BIRLA CD2125X7

The BIRLA CD2125X7 material is clearly atypical compared with all the other carbon blacks.

Inverse Gas Chromatography (IGC) is a useful powder characterization technique that, in principle, could be used to determine the HSP of solid materials – because it provides fundamental measurements of, for example, the dispersive component of the surface energy of materials – but it requires the time consuming step of packing the solid material into a column. Further, such instrumentation is expensive, has significant experimental complexities, and requires a long measurement time – characteristics that make it unsuitable for quick, routine, laboratory analysis. Importantly, because IGC relies on gas(vapor)-solid interaction analysis, it cannot provide *wetted* surface area information, which is an important metric in the *dispersion* of carbon blacks in solvents.

Ageing of a material, and any surface modification will result in a change in its surface energy. Hence, IGC has been used to identify differences between treated and non-treated surfaces, or even significant variations between materials from different providers or different batches.

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The carbon black samples presented above were all analysed by IGC using the same solvents and the results are summarized in Table 4 and shown graphically in Figure 2.

Table 4. Summary of inverse gas chromatography data for a series of carbon black samples from different manufacturers.

Carbon Black	ΣI_{SP}	γ_{sd} (mJm^2)
ORION	57.5	231
CABOT REGAL 300 (1)	55.0	257
CABOT REGAL 300 (2)	64.6	171
CABOT VULCAN 1391	35.2	484
SIDRICH N326	35.5	197
DEUTSCHE GRW	28.1	485
BIRLA CD2125X7	78.5	391

I_{sp} is a specific interaction parameter that is related to known acceptor (A_N) and donor (D_N) numbers of solvents, which, in turn, arise from the semi-empirical acid/base scale of V. Gutmann. Hence, I_{sp} is a measure of the relationship between the acid/base properties of both solvent and surface (i.e., it is a measure of the polar contributions to any interaction).

The plot shows that the seven carbon blacks cluster into three different groups in “IGC space”, as defined by donor-acceptor numbers and dispersive interaction, in a similar manner to those obtained by NMR relaxation. Again, the BIRLA CD2125X7 material is clearly atypical compared with all the other carbon blacks. The IGC data for the two Cabot Regal 300 materials is different which indicates that the surface chemistry clearly cannot be the same even though the particle sizes (and surface areas) are the same.

Note that the members in each of the clusters defined using IGC remain the same as those in Figure 1. However, the NMR data can be obtained in a fraction of the time. For example, when considering NMR relaxation time measurements on the Mageleka *R*elaxo*M*eter, the longest measurement time – for 348 CABOT REGAL in hexane – took approximately 35 seconds per run and the shortest time – for 353 BIRLA CD2125X7 in isopropanol – was only 14 seconds per run. 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 analysed. Comparative data from IGC takes many hours for a single sample.

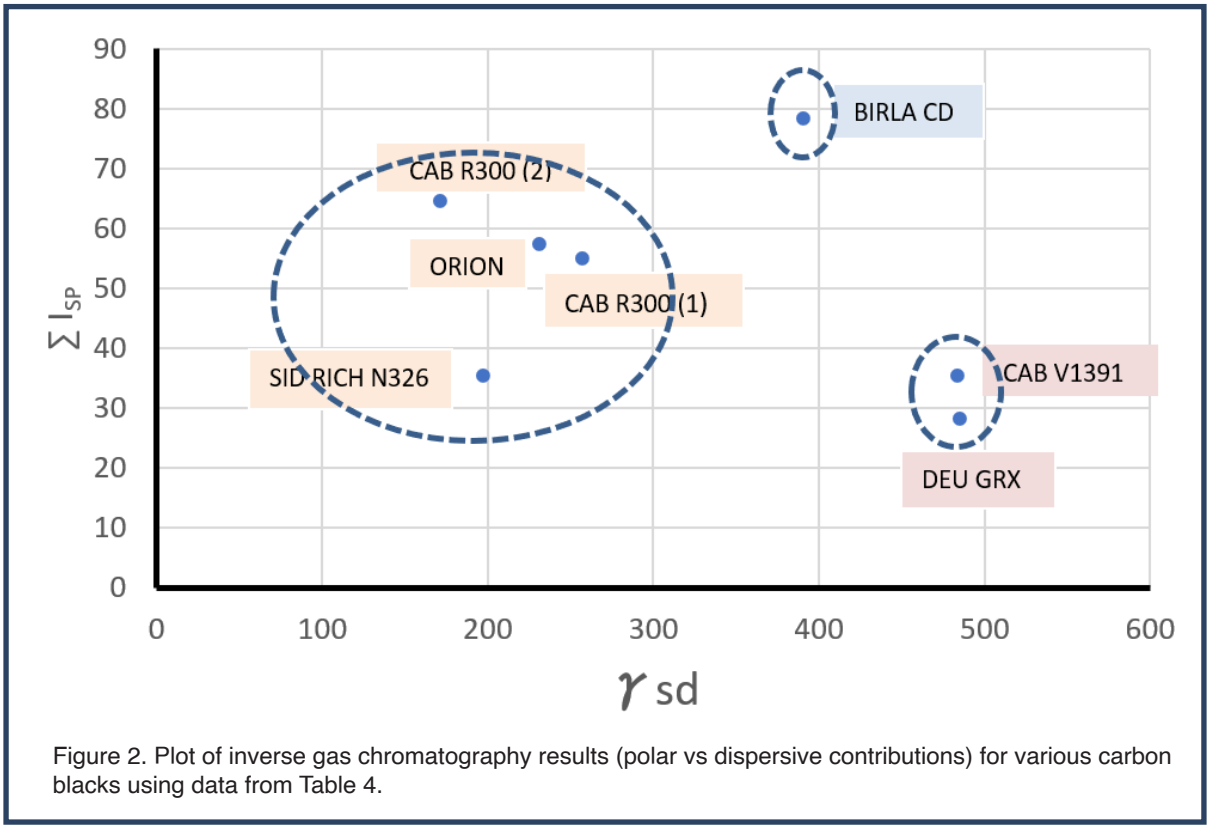

Figure 2. Plot of inverse gas chromatography results (polar vs dispersive contributions) for various carbon blacks using data from Table 4.

These results demonstrate that NMR relaxation provides a complimentary technique that can directly – and quickly – characterize the interaction of solvents with carbon blacks in order to prioritize the need, if required, for thorough, quantitative testing and analysis using IGC.

STUDY 2.

Suspensions of the carbon blacks in acetone were prepared in the same manner and conditions as in the study above. A comparison of the relaxation times of acetone and IPA carbon black suspensions is useful because it further sheds light on the differences that can exist in carbon black surface chemistry, in particular for the two CABOT Regal 300 samples. This, in turn, will impact any subsequent choice of, for example, dispersing agents. The results of the NMR relaxation measurements are summarized in Table 5.

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Table 5. Summary of NMR relaxation data for suspensions of carbon blacks dispersed in acetone.

Sample	Average T_2 Relaxation time (ms)	Average Relaxation rate, R_2 (sec)	Relaxation Number, R_{no}	Ranking
Acetone	2964.0	0.337	---	---
ORION	1240.8	0.806	1.39	5
CABOT REGAL 300 (1)	1977.3	0.501	0.49	7 (at least)
CABOT REGAL 300 (2)	1268.2	0.789	1.34	6
SIDRICH N326	1050.3	0.952	1.83	3
CABOT VULCAN 1391	1203.6	0.831	1.47	4
DEUTSCHE GRW	835.9	1.196	2.55	2
BIRLA CD2125X7	770.5	1.298	2.85	1 (best)

The relaxation numbers (R_{no}) for acetone are significantly larger than those for IPA and hexane which indicates a stronger solvent-surface interaction (and, hence, wetting). This is likely a consequence of a stronger interaction of the more polarized acetone molecule with a carbon surface, which can contain a heteroatom such as oxygen that can produce a δ^+ charge on neighboring carbon atoms. The surface of carbon black is known to contain a variety of oxygenated species (e.g., carboxylic acid, ethers, lactones, phenols, ketones), all of which are capable of interacting with a polarized molecule such as acetone and IPA, but the interaction will be stronger for acetone owing to to its higher polarizability – the dipole moment of acetone is significantly larger (2.69D) than that for IPA (1.66D). The solvent ranking efficiencies for acetone and IPA are compared in Table 6.

Table 6. Comparison of NMR relaxation data for suspensions (9.09% w/w) of carbon blacks dispersed in Acetone and IPA

Carbon Black	Acetone	Isopropanol
ORION	5	5
CABOT REGAL 300 (1)	7	6
CABOT REGAL 300 (2)	6	7
SIDRICH N326	3	4
CABOT VULCAN 1391	4	3
DEUTSCHE GRW	2	2
BIRLA CD2125X7	1	1

The difference in ranking of any carbon black-solvent interaction is always attributable to the difference in one or more of the three Hansen Solubility Parameters (HSP; dispersive energy, δd; polar-dipolar energy, δp; and hydrogen bonding energy, δd) between solvents, and this can be readily probed using NMR relaxation.

In acetone, the relative order of interaction for the Regal 300 (1) and Regal 300 (2) is reversed, potentially indicating a reduced H-bonding surface for Regal 300 (2) compared with Regal 300 (1). This finding is important since it will impact not just the choice of wetting liquid but also any subsequent dispersing or stabilizing agent(s) that will be used in preparing formulations of the carbon black. This reversal is also observed by IGC, confirming the IGC results that the surface chemistry of the two carbon blacks must be different.

It may be useful to generate HSP numbers routinely as a way to economically track the surface quality of carbon blacks from manufacturers, and even from the same manufacturer to determine if significant batch-to-batch variations exist.

Although the data here were obtained on carbon blacks typically used in tire manufacture, the methodology and analysis employed using the *R*elaxo*M*eter is not limited to these and can be applied to any applications involving non-aqueous dispersions of carbon blacks of any type/grade. In fact, the *R*elaxo*M*eter can measure virtually any solid-liquid or liquid-liquid dispersion without the need for dilution.

For example, improvement in storage capacity, charge rate, and lifetime are common goals in battery development. A main challenge in advancing battery technology is to optimize the complex composition of the different types of slurry mixtures used. Small particles provide a large surface area (and, more specifically the *wetted* surface area) for better power production; large particles provide better electrolyte mobility for energy storage. In both cases, thorough characterization of all the materials/components is essential. Using the *M*agno*M*eter *R*elaxo*M*eter, NMR solvent relaxation measurements can provide characterization of materials in the wetted state that is more appropriate for such applications. Moreover, the characterization is low-cost and economical in time.

Literature Cited

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2.D. Fairhurst, R. Sharma *et al*, “Fast NMR relaxation, powder wettability and Hansen Solubility Parameter analyses applied to particle dispersibility”, *Powder Technology*, 377 (2021) 545-552.

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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