Using NMR Relaxation for Rapid Screening of the Rheological Characteristics of Cosmetic Emulsions

Rheology is the science of the deformation and flow of matter under the influence of externally imposed mechanical forces (see Mageleka White Paper 6 at www.mageleka.com). It is a subject of tremendous technological importance because in many industries the quality and suitability of products is, to a large extent, judged in terms of their mechanical nature and properties. For example, the pliability of rubber, rigidity of plastics, mouthfeel and texture of food, leveling and sagging of paint, aesthetics of cosmetics, and fiber processability of textiles are all rheological characteristics of fundamental importance to those products. Not surprisingly, then, understanding and measuring such characteristics are of economic interest to the industries that rely on them.

In this Application Note we will explore the use of nuclear magnetic resonance (NMR) relaxation as a tool to rapidly screen the rheological characteristics of emulsions.

Two limiting types of rheological behavior are possible: deformation and flow. The deformation may reverse (relax) spontaneously when the external force is removed and is characteristic of what are termed Hookean *elastic* solids. The energy used in causing the deformation is stored and then recovered when the solid relaxes. A typical example is a simple rubber band. At the other extreme, matter flows under an external stimulus and the flow ceases (but is not reversed) when the force is removed; this is characteristic of what are termed Newtonian *viscous* liquids. Commonly encountered examples are honey and pure liquids like mineral oil and some silicone fluids.

However, emulsions (and semisolid formulations), which are mixtures of two otherwise immiscible liquids, exhibit mechanical behavior that is intermediate between these two extremes. When both viscous and elastic characteristics are evident, such materials are termed *viscoelastic*. There is a strong relationship between the structure of emulsions and their flow and deformation characteristics.

Emulsions are widely used in the cosmetic industry as the base for many formulations for skin creams and lotions because they offer almost unlimited versatility in meeting the primary market objectives of efficacy, aesthetics, and cost parameters.

Sensory features of cosmetic products are one of their most important characteristics for consumer acceptance. Consumers preferably choose one product among many based on their perceptions: first of its packaging, and then of its smell, appearance, and texture (e.g., the ease of rubbing on the skin and overall skin feeling after application). For example, *consistency* (viscosity) plays an important role in the *feel* of a product. The consumer expects a higher consistency for a hand-cream as compared to a body-lotion, whereas, the latter has to present a better spreadability over larger areas of the skin.

To obtain products with desired properties for the consumer's satisfaction, additives are often used in formulation to manipulate and control the rheological (viscoelastic) characteristics – and, thereby, the structure – of an emulsion.

> *"The Magnometer can be used to rapidly screen cosmetic emulsions to prioritize the need for thorough, quantitative, viscoelastic analysis."*

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When optimizing a product, in order to adapt it to the needs and desires of consumers, cosmetic companies use sensory evaluation methods. Unfortunately, these require trained panels making them time-consuming and expensive. In addition, such tests are, of course, subjective. Almost all sensory properties are directly associated with the rheological behavior of the systems and so rheological measurements, which are objective and more repeatable, are used in the evaluation of cosmetics properties prior to sensory evaluation.

A rheometer is a device that can measure absolute values of both viscosity and elasticity under well-defined conditions. These instruments are designed for exacting, precise, measurements, as are often needed in R&D studies. However, such devices require a skilled operator with extensive training on both hardware and software; precise measurements on these instruments also can take considerable time. Overall, such devices are not well-suited for use in a quality control (QC) environment, where rapid assessments are key.

Thus, a methodology that requires minimal training, is easy to employ, produces rapid results, and requires limited input data offers practical and economic advantages as a QC tool. NMR relaxation measurements using the Mageleka *M*agno*M*eter XRS™ have been shown to be valuable for QC of incoming raw materials used in the formulation of products (see Mageleka Application Note 1) as well as comparison of commercial finished cosmetic lotions (see Mageleka Application Note 2). In this Application Note, we will apply the NMR technique to rapidly screen the rheological characteristics of emulsions.

About NMR Relaxation

NMR spectroscopy is one of the most powerful analytical tools used to probe details of molecular structure and dynamics. Traditional devices employing NMR technology require extremely high magnetic fields and, hence, very large magnets with related complex instrumentation. However, the advent of small powerful magnets has allowed relaxometers such as the *M*agno*M*eter to be designed that have small footprints and are suited to normal, routine laboratory analysis. Moreover, measurement takes only minutes (see Mageleka Technical Note 2: The Mageleka *M*agno*M*eter: What is it and why use it?).

The basic technique used in the *M*agno*M*eter is NMR liquid relaxation. Importantly, the relaxation time is a fundamental intrinsic property of liquids. As such, its measurement is neither a function of the instrument nor of the operator; it provides direct information about the extent and nature of any liquid-liquid interface (i.e., emulsions).

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

The *M*agno*M*eter measures the extent of molecular motion as protons interact when perturbed by local magnetic fields and the resulting relaxation time obtained for a bulk liquid is an average value that is dependent upon the exact composition of the liquid – whether it is pure, mixed, or contains dissolved moieties.

Regular emulsions are two-phase systems and so there will be two major intrinsic relaxations (a short time and a long time) characteristic for the total oil phase and for the total water phase, respectively.

Critically, the *M*agno*M*eter's measurement technique is non-invasive, non-destructive, and it can work any type of emulsion (whether oil-in-water or water-in-oil) and, importantly, irrespective of the internal phase concentration.

Using the *M*agno*M*eter for rapid screening of the rheological characteristics of cosmetic emulsions

In this Application Note, three "pairs" of different cosmetic lotion are compared. Each pair comprised a product from an established brand-name manufacturer (Aveeno*, Jergens* and GoldBond*) with its suggested, less expensive, generic equivalent (manufactured by

Walgreens* and sold under the Studio 35* label) – for example, Aveeno Active Naturals Daily Moisturizing Lotion and Walgreen's Studio 35 Daily Moisturizing Lotion (see Figure 1).

Although the three brand-name products (and their generic siblings) are all lotions, they have each been formulated differently (ingredient composition, etc.) and are marketed to customers as providing distinctive tactile sensory attributes.

Figure 1. Two 'similar' Daily Moisturizing Lotions. Note the label for the generic Studio 35 product asks the customer to "Compare to Aveeno" brand-name product.

Four aliquots of each lotion were analyzed to ensure sampling reproducibility. The T_2 relaxation time was then measured five times for each sample aliquot and the entire data set averaged. No issues were experienced and the total measurement time per sample was less than 10 minutes.

The raw relaxation data was fitted to a double exponential to obtain the two intrinsic relaxation times (short and long). The reproducibility (coefficient of variation) was typically 1.25% or better; the results are, therefore, statistically robust and the differences found are reliable.

The rheological characteristics (viscosity and yield stress) for all six cosmetic lotions were then measured using a TA Rheometer Model AR1000 – a representative plot is shown in Figure 2 for the Jergens brand-name product and Walgreen's Studio 35 generic equivalent product.

By plotting the data from the rheometer (Figure 2), we obtain values for the two (viscous and elastic) parameters of the emulsion. The first is the (zero shear) viscosity and the second is the yield stress. This latter parameter is an important material property corresponding to the point at which the material will begin to flow. Prior to the yield point, a material will deform elastically but, after, a

* Note: The trade names are owned by the companies. The measurement and analysis of the products herein are an independent assessment and no endorsement or criticism is implied.

fraction of the deformation will be permanent and non-reversible. Further discussion of this topic is beyond the scope of this Application Note (but see Mageleka White Paper 6).

Nevertheless, it should be obvious that viscosity and yield will directly impact sensory features such as consistency, spreading, and rubbability. The yield value will also dictate the orifice dimensions if a tube is to be used as packaging for the emulsion.

Table 1 summarizes the results of the relaxation and rheology measurements.

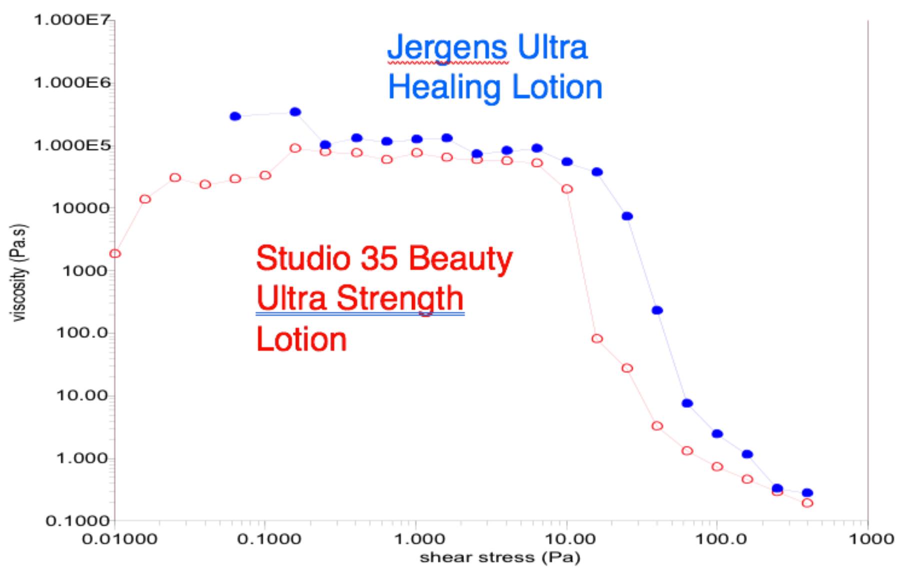

Figure 2.Rheology data for two Daily Moisturizing Lotions

Table 1. Comparison of the relaxation times of "similar" brand name and generic commercial lotions and the estimated percentage composition of their final oil and water phases (%).

Sample Lotion	Viscosity (Pa.s)	Long T_2 (ms)	Short T_2 (ms)	Yield Stress (Pa)
Jergens	93,640	302	80	20
Generic	66,790	541	278	10
Aveeno	280,170	497	256	100
Generic	450,040	337	148	170
Gold Bond	233,700	251	77	60
Generic	280,400	244	48	110

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The absolute values of viscosity and elasticity are, as expected, not the same for each of the brand-name products because they have been formulated differently.

However, for each individual brand-name/generic "pair", even though the list of ingredients appears the same, the rheology data shows that they are not truly "equivalent" which, in turn, would suggest that the tactile sensory behavior for each product will be different.

It is also clear that the NMR relaxation times are associated with emulsion viscoelastic characteristics: as the viscosity increases the value for the **long** T_2 relaxation time decreases, and as the yield stress increases the **short** T_2 relaxation time also decreases.

This does not imply that NMR relaxation should be used to replace rheological characterization; simply that the *M*agno*M*eter can be used to rapidly screen cosmetic emulsions in order to prioritize the need for thorough, quantitative, viscoelastic analysis. As such NMR relaxation should be thought of as a useful complementary tool.

In Conclusion

These data demonstrate that NMR relaxation offers a quantifiable, fast, and non-invasive method for routine screening of the rheological characteristics of emulsions in any application. NMR relaxation measurements using a *M*agno*M*eter are well-suited to any context where emulsions are formulated. Importantly, measurements with the *M*agno*M*eter were made directly on the commercial products without any further sample preparation.

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