Comparison of Commercial Cosmetic Products Using NMR Relaxation Measurements

Formulators working in the cosmetics and personal care industries have numerous delivery vehicles from which to choose when formulating skin-care products: emulsions, gels, sticks, mousses, aerosols, and ointments all have specific benefits. However, the emulsion is by far the most popular because it offers almost unlimited versatility in meeting the primary market objectives of efficacy, aesthetics, and cost parameters.

Emulsions are most simply defined as a stable mixture of two otherwise immiscible liquids. The individual liquid components are called phases, and the basic "varieties" of emulsions are oil-in-water (O/W) and water-in-oil (W/O). The former is more common in the majority of commercial uses, for example in daily-wear products such as moisturizers, and the latter tends to be used for formulations where substantivity (the ability to remain on the skin) is required, such as in beach-wear sunscreen products. Substantivity is of enormous importance where products are used outdoors and in settings where abundant sweating or repeated immersion in water is common.

There are two basic "styles" of emulsions: lotions and creams. Lotions are more popular than creams owing to their easier spreadability on the skin and dispensability (from tubes, bottles, etc). An emulsion is termed a cream or lotion based on its viscosity (resistance to flow) but the exact point at which a lotion becomes a cream is quite arbitrary.

The design of a cosmetic emulsion is quite complex – it can typically comprise 15 or more components (surfactants, emollients, humectants, thickeners, etc.). Thus, it often requires several iterations to produce a stable, efficacious, safe, cost effective, and elegant product. With so many components, it represents a challenge in scale-up to reproduce a consistent commercial product.

Being multi-component, cosmetic emulsions cannot be diluted without consequence. The (dilution) process not only destroys any structural characteristics but also can induce instability leading to creaming and, often, breaking/coalescence. This explains the common difficulty of correlating droplet size and zeta potential measurements with flow properties, freeze-thaw activity, and shelf-storage behavior.

In addition to cosmetics, formulators of foods, paints, pharmaceuticals, and agrochemicals all must routinely assess multiple metrics of emulsions 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 emulsions are, in fact, high-quality? Irrespective of the application, a methodology that is quantifiable, fast, and non-invasive – without the need to dilute emulsions – offers practical advantages. However, the test must be objective, easy to run, and be predictive – that is, a test that measures *fundamental* characteristics and is neither a function of the instrument nor of the operator. Until recently, the ability to quickly and accurately characterize emulsions has been limited.

> *"Measurements from the MagnoMeter help answer the question, 'Would two products that purportedly contain the same ingredients perform the same?'"*

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As we will explore in this Application Note, nuclear magnetic resonance (NMR) relaxation is a technique that is easy to employ, produces rapid results, and requires limited input data. Importantly, because it does not make any assumptions about the composition of the formulation and requires little, or no, sample preparation this makes it an ideal technique for measuring finished commercial products.

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 Mageleka *M*agno*M*eter XRS™ to be designed that have small footprints and are suited to normal, routine laboratory analysis.

The *M*agno*M*eter has harnessed the power of NMR spectroscopy to measure liquid relaxation. Importantly, the relaxation time is a *fundamental* intrinsic property of liquids and its measurement 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 and non-destructive and it can work any type – whether O/W or W/O – and, importantly, irrespective of the internal phase concentration. Indeed, in principle it can determine which phase is the internal one.

Of practical utility, the *M*agno*M*eter eliminates the dilution issues inherent in making measurements using, for example, traditional light scattering techniques. Moreover, the simple measurement technique takes only minutes (see Mageleka Technical Note 2: The Mageleka *M*agno*M*eter: What is it and why use it?). Thus, the MagnoMeter provides complementary information to traditional particle characterization devices, but additionally provides interfacial and structural insight not possible with those devices.

Using NMR relaxation to compare a variety of brand-name and generic cosmetic lotions

Brand recognition, brand awareness, and brand loyalty are different concepts, but they are equally important in the marketing of products to consumers and this is nowhere more crucial than with cosmetics. However, perusing the aisles of the drugstore, just about every brand-name beauty product has a generic version produced to mimic the original. They appear to contain the same ingredients and in the exact same order. The only difference? The price.

So, what is it about the brand-name version that always makes it more expensive?

Unfortunately, starting with the basics of formulation, all ingredients are not created equal – no matter what a supplier's literature may claim. Raw materials can be sourced from different countries and may be extracted from natural sources or synthesized in the laboratory (see Mageleka Application Note 1). In addition, different, more costly, processing technologies can be used in the creation of brand name products (see Mageleka White Paper 5 and Application Note 12).

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.

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. Table 1 summarizes the results of the relaxation measurements.

The absolute values of the relaxation times (short/long) are, as might be expected, not the same for each of the brand-name products because they have been formulated differently.

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

* 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.

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	Cost ($/kg)	Short T_2 (ms)	%	Long T_2 (ms)	%
Jergens	57	278.1	30.0	540.7	70.0
Generic	16	80.2	21.3	301.7	78.7
Aveeno	51	147.7	53.1	337.1	46.9
Generic	38	255.7	43.3	497.0	56.7
Gold Bond	26	47.1	24.0	244.1	76.0
Generic	21	76.9	47.6	251.0	52.4

However, for each individual brand-name/generic "pair", even though the list of ingredients appears the same, the difference between relaxation times (short/long) shows that they are not truly "equivalent". Further, the estimated percentage composition of the final oil and water phases in the emulsion is different which suggests that the partitioning of the surfactants and the various adjuncts/excipients, etc., into those phases is not the same. Thus, it is likely that some of the raw ingredients used must also differ.

Measurements from the *M*agno*M*eter allow a formulator to answer the question "Would two products that purportedly contain the same ingredients perform the same?" Not necessarily. As the current results suggest, each brand-name product and its generic counterpart product would perform differently when applied to the skin. This conclusion was confirmed in subsequent measurements of the rheological characteristics of the lotions (see Mageleka Application Note 8).

Further, this study suggests that the *M*agno*M*eter can be used for quality assurance purposes. Characteristic T_1 and T_2 relaxation times for the lotions provide a use fingerprint for comparison purposes. It also provides a tool for a generic manufacturer to compare and contrast competitive products and a means to improve equivalency – and the economics – of formulations.

In Conclusion

NMR relaxation measurements made by the *M*agno*M*eter are well-suited to any context where emulsions are formulated. Considering that the internal phase concentrations analyzed in the present study reached 53%, these data also demonstrate that NMR relaxation offers a quantifiable, fast and non-invasive method for routine screening of emulsions for any application. 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

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