Lubricant Aging: Characterization using NMR

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Lubricants (lubricating oils and greases) are an essential part of mechanical processes, in which friction and heating occur. Lubricants, i.e. oils with additives, prevent damage to bearing components thus maximizing life time. Lubricants age due to multiple stress factors, and require replacement from time to time. Complementing established analytics, NMR with its various facets is a powerful tool to quantitatively characterize this class of materials.

Lubricants are multicomponent systems consisting of base oil (80 % - 99.9 %), additives (0.1-10 %), and thickeners in case of greases (10-20 %) [1, 2]. Additives provide functionalities in form of protecting metallic components (e.g. corrosion inhibitors), protecting the base oil from aging (e.g. oxidation inhibitors, dispersants) or specifying tribological properties (e.g. viscosity index improvers). Translational mobility, measured in form of D, the diffusion coefficient, of the additives hereby is a decisive criterion. D depends on the lubricant's chemical composition and influences the concentration required to ensure a sufficient tribologically active layer. Spectrally resolved NMR diffusion measurements allow to identify additives and measure their diffusion properties. Fig. 1 illustrates the difference in mobility on the example of amine phosphate in a mineral base oil.

Figure 1

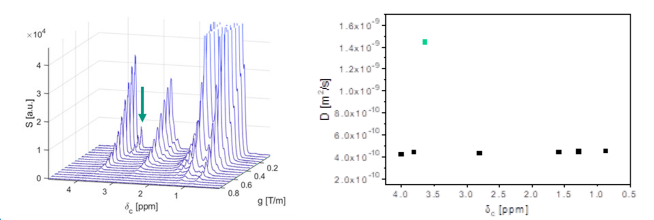

Figure 1: Translational mobility of additives in lubricants measured by pulsed field gradient (PFG) NMR. Left: Spectrally resolved signal decay as a function of gradient. The example shows the diffusion measurement of a mineral base oil with amine phosphate as one additive. Right: The diffusion coefficients of amine phosphate (3.6 ppm) and base oil components (signals in the range 0.9 - 4 ppm) differ significantly. This fact is essential for lubricant's functionality, but also spans an additional dimension in NMR ^{1}H peak assignment.

Not only chemical composition fingerprints in PFG-NMR, but also aging as translational mobility often decreases with increasing running time t_m, which is also reflected by higher viscosities, among other facts. Data modeling needs to be adapted to the complexity of lubricants. Modeling according to Stejskal-Tanner usually is sufficient for low concentrations of an analyte in a low viscous solvent [3, 4]. Lubricants are multicomponent systems with high viscosity, therefore, a distribution of D is likely a more appropriate way of modeling [5, 6]. Modeling with a gamma distribution function results in two parameters: a mean diffusion coefficient $<D>$ and a mean distribution width σ_D (γ: gyromagnetic ratio, δ: gradient duration, g: gradient, Δ: diffusion time).

$$\frac{S}{S_0} = \left(1 + \frac{k\sigma_D^2}{<D>}\right)^{-\frac{<D>^2}{\sigma_D^2}}$$

$$k = (\gamma\delta g)^2\left(\Delta - \frac{\delta}{3}\right)$$

Multimodal distribution functions are also conceivable. A sample series from an engine test bench clearly shows the sensitivity of $<D>$ on t_m. The example also illustrates the effect of an engine oil change.

Figure 2

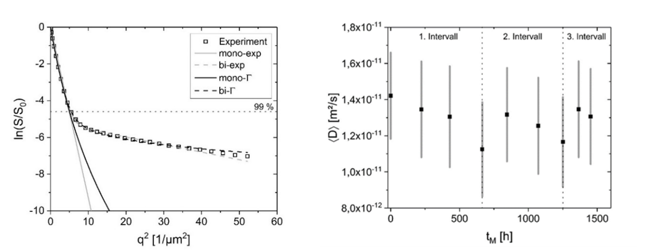

Figure 2: Left: The properties of the multicomponent system lubricant with chain lengths distribution of base oil molecules must be considered when modeling magnetization decays. The gamma distribution function accurately describes the magnetization decay due to diffusion with an average diffusion coefficient $<D>$ and a distribution width σ_D. Engine oils from a test rig show decreasing $<D>$ with increasing engine run time t_M, while σ_D is depicted in form of error bars and is approximately constant. Two oil changes are evident and are indicated by the dotted lines [6].

If foreign matter such as (bio-)fuel contaminates the oil, diffusion changes. Detection by FT-IR (Fourier Transform – Infrared Spectroscopy), as performed in routine oil quality control, or by NMR can be explored. $<D>$ and viscosity $\nu_{40°C}$ correlate as does $<D>$ and biofuel content c_{biofuel}. These parameters help to differentiate fuel ingress and other aging processes. Correlations between analytical parameters allow for drawing a more comprehensive picture.

The example shows the multidimensionality of lubricant oil aging, which requires different analytical parameters to be considered.

Figure 3

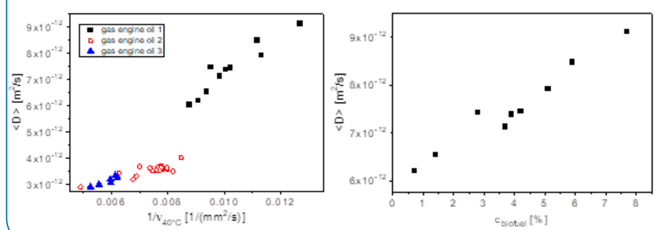

Figure 3: Different analytical tools are established to analyse lubricants. Left: Diffusion coefficients correlate with oil viscosity for three types of biogas engine oils. For biogas engine oil #1 a correlation between $<D>$ and $1/\nu_{40°C}$ leads to a different slope compared to oil #2 and #3. Another aging factor must be present. Right: diffusion is significantly influenced by foreign matter ingress in form of biofuels which is evidenced by the correlation with the concentration of biofuels in the oil.

An important aspect, especially for gear oils, is particulate abrasion as a result of wear. These particles can be detected indirectly by PFG-NMR. Diffusion measurements under variation of the diffusion time Δ are sensitive to geometric obstructions, as it is the case for particulate abrasion - independent of its origin or composition.

Figure 4

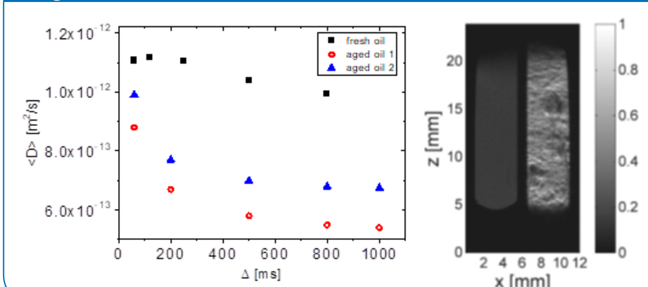

Figure 4: Abrasion is an important aging mechanism. Diffusion measurements as a function of diffusion time Δ allow particle input to be detected - independent of origin and chemical composition. D of lubricating oils with considerable particle loadings decreases with Δ, therefore indicating geometric hindrance of diffusing molecules by particles (Measurements: A. Simon 2017). Right: Particle abrasion in aged oil (right image) is also evident from susceptibility artifacts in MRI compared to fresh oil (left image).

In addition to oil aging and fatigue of bearing or engine components, aging of seals leads also to machine failures. Diffusion of lubricating oils into seals - usually elastomers – is one cause of seal aging. The elastomer becomes brittle and no longer fulfils its function as a sealing material. Oil diffusion into the seal can be detected by MRI. Characterizing seals in terms of their resistance to swelling due to penetration of different types of oils is possible, too.

Figure 5

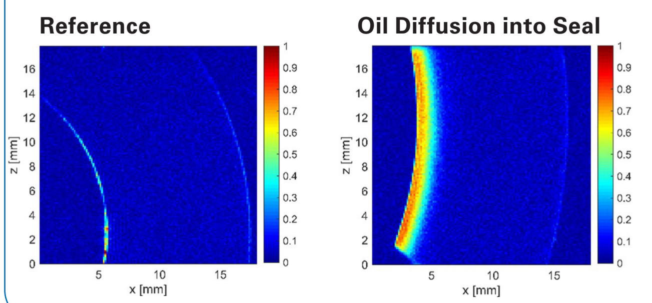

Figure 5: Oil in an elastomeric seal was detected and quantified by MRI. The state of stressed elastomer seals was compared with new materials with regard to swelling and oil ingress (Samples: MEGT University of Kaiserslautern).

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