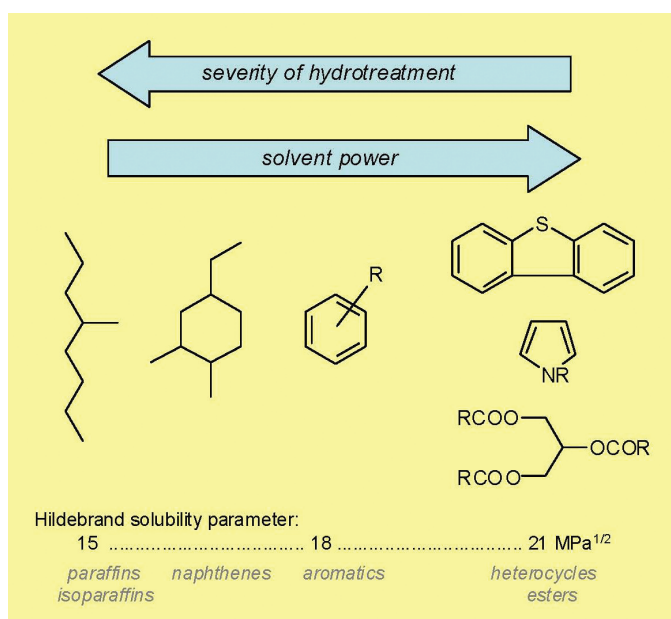# New base oils pose a challenge for solubility and lubricity

Broad commercialisation of hydrocracking, catalytic dewaxing and hydrofinishing technologies in the past two decades have created an abundant supply of API Group II and Group III base oils. However, despite the many undisputed advantages over the Group I in terms of viscosity index (VI), sulphur content, volatility, pour point and antioxidant response, the new base oils are winning the market much slower than many analysts predicted at the rise of the hydrotreatment technology.

Why is it that difficult? Serious formulators are skillful in property -blending, preparing "cocktails" with desired specs being a daily routine for them. There must be something that accounts for formulators' reluctance to interchanging their base oils.

It appears that, when discussing technical implications of the base oil interchange, very little attention is normally given to solubility and lubricity issues. However, the fact remains that, the greater the degree of hydrotreatment, the lower the solubility:

Scheme 1

severity of hydrotreatment

solvent power

Hildebrand solubility parameter:
15 .... 18 .... 21 MPa$^{1/2}$

paraffins   naphthenes   aromatics   heterocycles
isoparaffins   esters

Severely hydrotreated base oils, as well as GTL (gas-to-liquid) base stocks and PAO (polyalphaolefins), are often regarded as "dry" base oils because they only contain fully saturated non-polar hydrocarbon (isoparaffin) molecules.

This trend can be easily seen if aniline point values are compared. Lower aniline point means higher solvent power. For high-aromatic products, such as aromatic extracts, the aniline point is around 20-40°C; for naphthenic base oils, 70-100°C depending on the degree of refining and viscosity; for Group I paraffinic base oil, 90 to 110°C; and for Group II-IV base oils, 100-130°C or higher. It is interesting to note that the aniline point steadily increases with the increasing viscosity of the oil for oils with identical polarity. For instance, in the series PAO 2, 4, 5, 6, 8, 10, 40, it raises from ca 100°C for the lightest to ca 160°C for the heaviest homologue. This is because, as can be shown by thermodynamic arguments based on the Hildebrand solubility theory, aniline point depends upon the product $V_M(\delta_{anil}-\delta_{oil})^2$ where V_M is the average molecular volume, and δ_{anil} and δ_{oil} are the Hildebrand solubility parameters for the aniline and for the oil, respectively. Increasing the average molecular volume raises the aniline point.

Low solubility not only makes it difficult to dissolve some essential additives, but it also compromises some essential quality parameters, such as dispersancy and seal compatibility. For instance, PAOs are unbeatable in terms of pour point and volatility, and at the same time, have the lowest lubricity and solubility ranking.

This is normally compensated by using solubility improvers in finished lubricant formulations. Theoretically, any chemical

compound addition of which causes a drop in aniline point or an increase in the seal compatibility index in the base oil may be regarded as a solubility improver. However, in practice, many other requirements have to be met, such as flash point, pour point, viscosity index, etc. This limits formulators to one of the following strategies:

(i) Blend with naphthenic basestocks or alkylaromates. Improvement in solvency comes at a price of a loss in viscosity index. Naphthenics have no effect on lubricity.

(ii) Retro-blend with Group I basestocks. Improvements in solvency and lubricity come at a price of deteriorating viscosity index, Noack volatility, pour point, antioxidant response, and health safety and environmental (HSE) profile.

(iii) Blend with synthetic esters. Improvement in solvency comes at a price of downgrading high-temperature stability. Saturated branched-chain fatty esters themselves often lack lubricity. Even more dangerous is that some linear-chain esters passivate the surface against reaction with extreme pressure (EP) additives, undermining anti-wear protection at high loads.

(iv) Blend with vegetable oils. This technology existed before synthetic esters. Vegetable oils have their own advantages and disadvantages. The chief advantages are the use of a renewable resource, excellent lubricity and anti-wear properties, excellent thermal stability, high specific heat, high flash, and completely benign HSE profile. The chief disadvantage is low oxidation stability.

(v) Blend with ionised vegetable oils. These products have rather unique properties, inheriting their positive features such as high lubricity and anti-wear efficiency from vegetable oil, and at the same time adding oxidation stability and anti-sludge capability.

As base oils are concerned, solvent power is chiefly determined by polarity of oil molecules. PAOs are non-polar, so they have low solvent power. Esters are polar, so they have high solvent power. Differences in polarity between various basestocks can be illustrated using the Teas diagram (Figure 1).

Figure 1
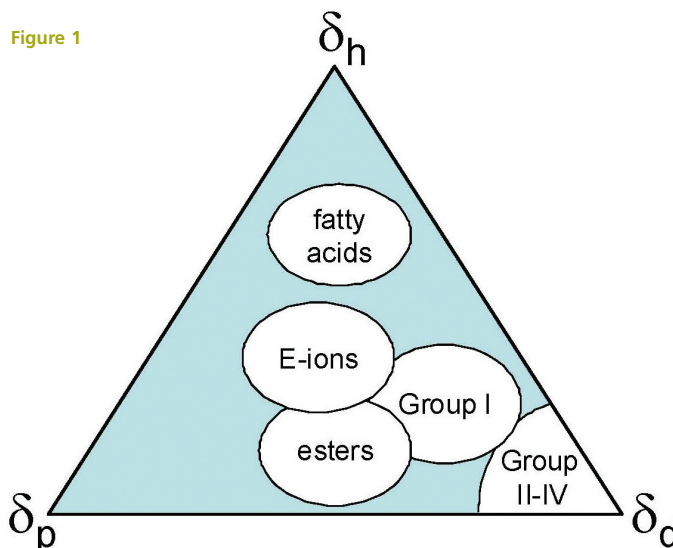
Teas diagram showing relative contributions of various types of intermolecular interactions to the intermolecular cohesive energy. d - dispersion interaction, p - polar interaction, and h - hydrogen bonding interaction. Group II-IV base oil contain fully saturated hydrocarbon molecules, hence polar and hydrogen bonding interactions are negligible. Esters reveal more significant polar interactions. Ionised vegetable oils have both polar interactions and hydrogen-bonding interactions.

What has lubricity to do with that? Solvent power and lubricity are inter-related properties. This fact can be proven, both experimentally and theoretically, by studying the adhesion of lubricant films to metal surfaces. Talking about lubricity, one refers to the slipperiness of lubricant films separating the rubbing surfaces from each other. As long as the lubricant film is thick and resilient enough to prevent direct asperity-asperity contact, the coefficient of friction tends to be very low. In this case, one talks about the film lubrication regime. However, solvent power alone does not guarantee good lubricity. Lubricity requires that polar and non-polar molecules be present simultaneously. Since metal surfaces are highly polar, polar oil molecules dissolved in non-polar ambient tend to adsorb to the metal surface, forming a protective surface film. Strength of the film and solvent power are linked to the same cohesion parameters.

Group I base oils have sufficiently high content of polar species (heterocycles, aromatics) and demonstrate superior lubricity as compared to Group II-IV base oils. Correspondingly, Group II-IV base oils will benefit the greatest in terms of lubricity from using lubricity additives, also known as friction modifiers in the automotive field. Many amphiphilic molecules, such as fatty amides, esters and ionised vegetable oils, can be used as lubricity additives, but performance varies broadly. Unlike conventional anti-wear and extreme pressure additives, such as tricresylphosphate (TCP) and zinc dialkyldithiophosphate (ZnDTP), which act when a direct asperity-asperity contact occurs in the boundary lubrication regime, lubricity additives function by postponing the beginning of the boundary lubrication regime (see Figure 2).

Figure 2
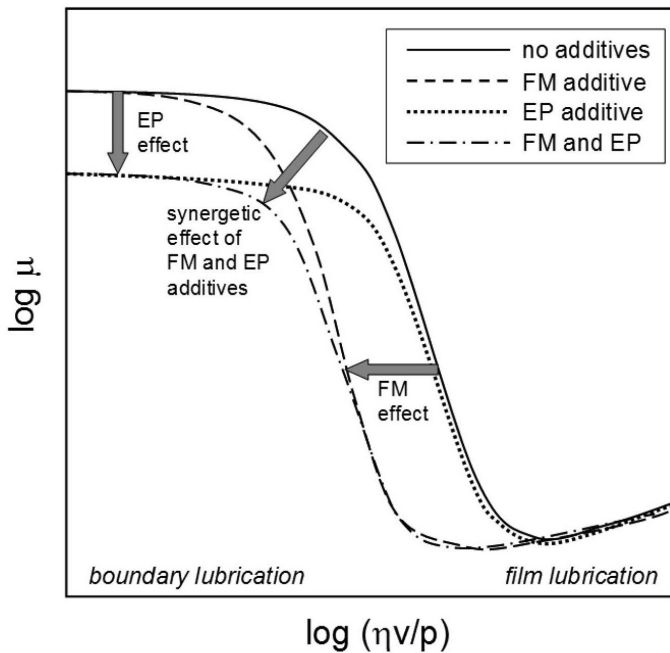
Stribeck diagram showing the tribological effects of EP additives and lubricity additives. μ - the coefficient of friction, η - viscosity, v - sliding velocity, and p - applied pressure. High pressure and low sliding velocities force the tribosystem into the boundary lubrication regime in which most intense friction and wear occur. EP additives shift the Stribeck curve down, reducing friction in the boundary lubrication regime. Lubricity additives shift the Stribeck curve to the left, maintaining the film lubrication regime over a broader range of tribological conditions.

It should be realised that commonly used "lubricity" standards, such as BOCLE (ASTM D 6078) and HFRR (ASTM D 6079), overestimate the effect of EP additives and underestimate the effect of friction modifiers. This often leads to misunder-standings, terminological muddle, and endless debates regarding correlations between laboratory tests and field. For instance, in HFRR, 200 g load is applied to a 6 mm steel ball reciprocating on a steel flat (AISI52100, 650HV). In this case, the Hertzian contact pressure in the beginning of the experiment is around 1 GPa, corresponding to a point in the top left end of the Stribeck diagram. Under such a pressure, the soft adsorbed film of friction modifier gets punctured and the measured coefficient of friction is dominated by the local coefficient of friction in the high-pressure zone (Figure 3).

Figure 3
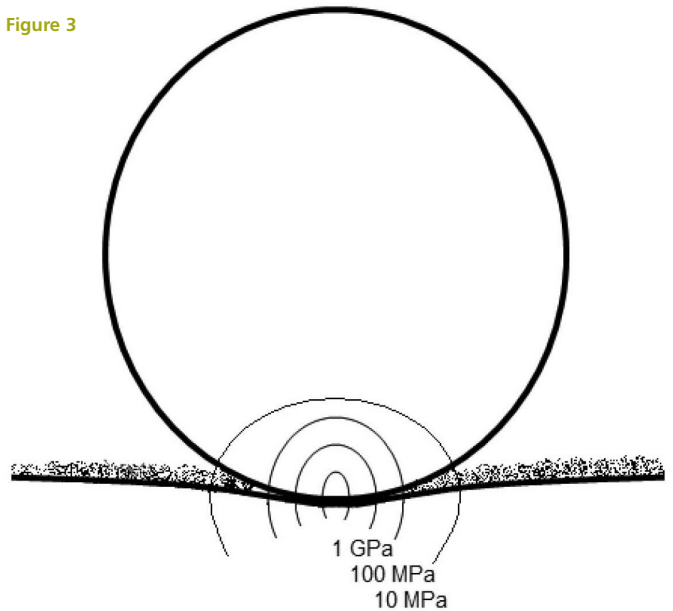
Pressure map for a steel ball/steel substrate tribocontact in the presence of an adsorbed visco-elastic film of friction modifier under the conditions of ASTM D6079 lubricity test. The Hertzian contact pressure in the central point is around 1 GPa, decaying to zero on the periphery of the contact zone. The local coefficient of friction in the 0.1 to 1 GPa pressure zone is ca 0.1 (boundary lubrication), while the local coefficient of friction in the 0 to 10 MPa pressure zone is ca 0.001 (film lubrication). The coefficient of friction measured experimentally is dominated by the greatest term and thus is close to 0.1.

This explains why common EP additives, such as molybdenum, phosphate esters and polysulfides, always excel in those tests. In other words, the standard "lubricity" tests do not really test lubricity - they test the EP functionality. If the rubbing parts in an engine were continuously exposed to such a stress, the engine lifetime would have been limited to few days! In reality, the majority of tribosystems in cars are exposed to repeated loading-unloading cycles, with the typical stress range of 1 to 10 MPa. The lubricity-enhancing effect of friction modifiers is circumscribed to a Hersey number range in which transition from the EHD to the boundary lubrication occurs, and this is outside of the scope of BOCLE and HFRR in their standard setup.

Due to their greatly reduced volatility and good low-temperature performance, new base oils of API Group II-IV allow the formulation of lighter automotive viscosity grade oils, such as SAE 5W-40, 0W-30 and even 0W-20, to achieve better fuel economy. However, as explained in Figure 4, the use of thinner base oils increases the risk of engine wear unless appropriate friction modifiers are simultaneously deployed in the formulations. By shifting the Stribeck curve to the left in Figure 2, friction modifiers cause an equivalent shift of the wear and the frictional losses curves in Figure 4. The result is that the "optimal viscosity" point corresponding to the greatest fuel economy also is shifted to the left, towards lower viscosities. In

practice, however, it is wise to prefer a somewhat heavier oil to a somewhat lighter one to further minimise wear. After all, changing the oil is more economical than changing the engine!

Figure 4

HTHS visc 2.0   2.2   2.4   2.6   2.8   3.0   3.2 mPa s
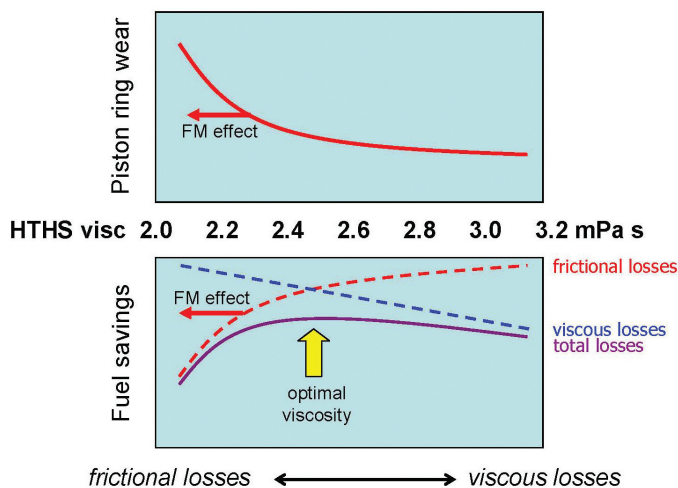
Relationship between engine oil viscosity, engine wear and fuel economy. Thinner base oils reduce viscous losses but simultaneously increase frictional losses and engine wear. Use of friction modifiers allow one to reduce frictional losses and to maintain good protection against wear while using thinner base oils for better fuel economy.

While solubility and lubricity improvers help formulators address certain challenges brought by a changeover to "dry" base stocks, their use requires some experience and understanding of chemical differences. For instance, the antioxidant response of vegetable-based solubility improvers is different from that of hydrocarbon bases, and therefore, the antioxidant package may need to be redesigned accordingly. Phosphites and some conjugated dual antioxidant systems, such as tocopherol-disulfide, are known to be efficient antioxidants for vegetable oils.

In combination with synthetic and severely hydro-processed VHVI and XHVI mineral base oils, as well as with emerging Group III+, or "Super-Group III" base stocks produced by the Fischer-Tropsch process, lubricity and solubility improvers serve a solid foundation for formulating top-quality lubricants.

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