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The correct division of friction reducers is given and a clear distinction between them and AW/EP additives drawn. The factors affecting frictional properties in lubricants are examined and weighed. The chemistry and dynamics of friction reducers are analyzed and expressed in easily understood patterns. The application of friction reducers, in fuel economy lubricant formulations, interactions with other additives, and useful concentration for cost effectiveness are discussed. It is shown that oil-soluble friction reducers improve boundary lubrication, oil film retention even after draining, and reduce frictional losses in a wide range of speed and load conditions. Their use is a positive means for improving fuel efficiency in a wide variety of lubricants including engine oils, gear oils and industrial lubricants.

HISTORY

Oil-soluble friction modifiers—as friction reducers were known until recently—have been used for many years by the lubricant industry. Types of products that made use of friction modifiers include the following:

- Way lubricants (which eliminate stick-slip phenomena from slide-ways)
- Automatic transmission fluids (those designed for a smooth clutch engagement
- Limited slip gear oils
- Multipurpose tractor fluids for wet brakes
- Some factory fill engine oils containing a significant dosage of sulfurized sperm oil (a natural friction modifier-reducer) or recently products containing jojoba oil.

There were many other, lesser known products, also containing friction modifiers/reducers in the form of animal or vegetable fats and oils, sulfurized or not.

Such products made use of friction modifications as a way to meet performance requirements calling for smooth transition from static to dynamic conditions and vice versa, as well as for reduced squawk, chatter, noise, frictional heat and start-up torque.

In the early seventies, some gear oil additives were found to reduce frictional heat and gear operating temperatures under extreme load conditions while eliminating chatter in limited slip differentials. The connection was made in an ASLE paper presentation and energy savings were postulated from the use of such gear oil additives. However, fuel economy was not at the time considered an important factor and the concept was shelved for later use.

Today, fuel economy and hence friction-reducing methods serve an important national goal and will continue to do so for the foreseeable future. Therefore, research into such phenomena has now assumed prime importance in most lubricant and petroleum additive companies.
INTRODUCTION

Terminology: FM versus AW/EP

The ability to reduce friction and sometimes wear, over and above that which is predicted by the oil viscosity, has been called “oiliness” or “lubricity”. Both terms, however, are ill defined and intensely disliked by the purists.

Early experimenters noticed the ability of vegetable or animal fats and oils, as well as fatty acids, to strengthen the tenacity of the oil films when incorporated in lubricating oils. Their effectiveness was often rated in terms of “film strength,” an expression that still remains in use. However, the above terms are imprecise and lead sometimes to confusion. One of the most easily confused things is the relationship between friction modification (FM) and antiwear (AW) or extreme pressure (EP) properties. Since such confusion leads to serious errors, we will now clarify the meaning of these two different quantities.

Friction modification (FM) is a part of the so-called boundary lubrication. The latter occurs when mating metal surfaces under very high loads, extreme temperature, or in extremely low-viscosity oil; squeeze most of the lubricating film from between them and come dangerously close to metal-to-metal contact. At that time, a thin coat of adsorbed, chemisorbed, or otherwise deposited molecules is the major component that keeps the two surfaces and their asperities from plowing into each other. That is called boundary lubrication.

Antiwear (AW) EP additives are among the type of compounds that provide good boundary lubrication. Such materials as zinc dialkyldithiophosphates, sulfurized fat, or low concentrations of second-generation gear oil additives have shown their capacity to build and maintain strong boundary lubrication films under severe load conditions. However, with the possible exception of second-generation gear oil packages, conventional antiwear additives have little friction-modification capabilities.

The critical difference between antiwear/EP additive films and friction-modification films is mainly in their mechanical properties. Antiwear/EP films are semiplastic deposits which are hard to shear off. Thus, under shearing conditions, their coefficient of friction is generally moderate to high. Conversely, friction-modification films consist of orderly, closely packed arrays of multimolecular “whiskers,” loosely adhering to each other and with the polar head of the lowest ones on the totem pole anchored on the metal surface. The outer layers of that film can be sheared off easily, allowing for low coefficient of friction. The phenomenon resembles the sliding of a deck of cards laying on a table, a task which is easier to do than moving a book stuck on the table.

On the other hand, antiwear/EP performance does not work by lowering friction but by protecting the mating metal surfaces from asperities physically gouging the opposite surface. Early experimenters of boundary lubrication thought that EP performance was just lowering of the friction. This is not believed anymore since the confusion between the two mechanisms has been dispelled.

Frictional Regimes

To understand better the coefficient of friction relationship with the different types of lubrication regimes, some relevant figures are cited:

The coefficient of friction of unlubricated surfaces is 0.5 and higher, reaching as high as 7. In physical simulation, the process resembles the resistance of dragging an irregular rock over irregular rocky ground.

The coefficient of friction of antiwear/EP films is about 0.1 to 0.2. In simulation it would resemble dragging a more or less flat stone over a flat rock.
The coefficient of friction for a friction modified film is about 0.01 to 0.02. It could be compared to ice skating.

The coefficient of friction of fully fluid films or hydrodynamic lubrication is about 0.001 to 0.006. It can be compared to hydroplaning.

From these figures, it is obvious that the preferred or ideal regime is that of hydrodynamic lubrication. This is closely followed by a friction-modified mode of operation and that, in turn, followed by an antiwear/EP regime. When high speeds and low loads exist, it is easy to maintain the hydrodynamic regime. When the speed falls, however, or the load rises above a critical point, the hydrodynamic regime breaks down and then it would be very desirable to be able to slide smoothly into a friction modification mode of operation, as seen in Fig. 1. If no friction modification has been provided, the system will fall by default into the antiwear/EP regime which will cause an order of magnitude higher friction. In this light, friction modification is a logical addition to a lubricant in order to wider the range of effectiveness of the lubricating film.

THEORY OF FRICTION MODIFICATION

What is Friction Modifier/Reducer?

A friction modifier is an additive or combination of additives that has the ability to change the frictional profile of a lubricant/machine system. Usually, the frictional forces between moving lubricated parts are controlled by the viscosity and chemistry of the existing oil film between them. With a straight mineral oil, that static coefficient of friction is higher than the dynamic coefficient of friction. If polar additives are added to the oil, they will coat the metal surfaces and establish an equilibrium between the amounts dissolved in the oil and the ones adsorbed or chemisorbed on the metal. The new (coated) metal surfaces will now rub against each other, not only through a thin oil film, but also through their coatings. Therefore, the frictional forces will be different under both breakaway and dynamic conditions. How much they differ will depend, among other factors, on the additives, especially on their molecular configuration and type, as well as on the overall geometry of the rubbing surfaces.

Thus, in transmission clutches with frictional facing material, especially the one of resin-treated paper, friction modification shows frequently as a lower static than dynamic coefficient of friction. In plain metal surfaces, friction modification will show as a sharp drop in the static coefficient of friction and a moderate drop in the dynamic. The curtailing of the usually high static coefficient of friction is referred to in the transmission manufacturers' trade as cutting off the "rooster tail".

Factors Affecting Frictional Properties

Experimental work by both automotive manufacturers and lubricant additive suppliers has shown that there are several factors affecting the measured frictional properties of lubricated systems.
The following are among the major factors applying specifically to automatic transmission clutches. Most of them would also apply to other situations.

**Pressure**
The dynamic coefficient of friction, and, to a lesser degree, the static coefficient decrease with increasing pressure.

**Speed**
Increased speed lowers the whole frictional profile, i.e., lowers both static and dynamic coefficients.

**Surface Finish**
The surface finish of the mating surfaces affects the coefficient of friction. Within certain limits, the finer the finish, the higher the coefficient of friction.

**Facing Material**
In automotive and industrial transmission clutches, different facing materials exhibit different frictional profiles. On this fact is based the continued progress of the highly advance clutch facing industry.

**Temperature**
The higher the temperature, the lower the static coefficient of friction and, in most cases, the lower the dynamic coefficient of friction. This affects the engagement time and it is a prime design parameter in the industry. Higher operating temperatures necessitate the use of higher apply pressures to maintain torque output.

**Energy**
Generally, the dynamic coefficient of friction affects the torque output. An overly "slippery" fluid decreases output torque and, in clutches, this is undesirable. A slippery clutch consumes energy (and fuel) by "spinning its wheels" in meaningless friction which soon raises the temperature to a dangerous level for the durability of both clutch and fluid. As a rule, higher energy inputs require longer engagement times or higher pressures to avoid slipping.

**Chemistry**
The frictional characteristics of a lubricant and especially of the additive in it are of paramount importance to the frictional behavior of a system. The effect of the chemical composition and structure on friction is a continuing major project of the additive and lubricant suppliers. It will be dealt with in more detail later on in this paper.
Degradation
Oxidation or thermal breakdown of a lubricant can change considerably its original desirable frictional characteristics. Sometimes it can also cause deterioration of the clutch surfaces by glazing, erosion, or other attack. That is why additive suppliers insist on screening their additives for durability.

Chemistry of Friction Modifiers/Reducers
Friction modifiers are usually compounds comprised of long, slender molecules with a straight chain of 10 or more carbon atoms and a polar group at one end. The magnitude of their polarity is an important factor in their performance.

Chemically friction modifiers belong usually to one of the following categories:

- Long-chain carboxylic acids or their derivatives, including salts
- Long-chain phosphoric or phosphonic acids and their derivatives
- Long-chain amines, amides, imides, and derivatives

Long-chain alcohols or mercaptans are not serious friction modifiers because they are weak adsorbers.

Acids can be chemisorbed on a metal surface as an anion. Amines, phosphates, and phosphates use coordination. Salts can form an ionic pair. Whatever the mechanism, the result is a multi-decked film of friction modifier on the metal surface affecting its frictional properties.

The thickness and hence the effectiveness of the adsorbed film is a function of several variables

Let’s examine each variable:

- (a) Polar Group
- (b) Chain length
- (c) Configuration of the molecule
- (d) Solvent or carrier (base stock)
- (e) Concentration
- (f) Temperature
- (g) Metallurgy of the surface
- (h) Contaminants or competitors

The stronger the polarity, the greater the thickness and tenacity of the adsorbed film. In alcohol, the film is very weak. In stearic acid, on the other hand, the film is thick and stiff enough to increase the viscosity near the surface to five times that of the oil. Hydrogen bonding helps produce thick stable films of stearic acid. The molecular length of stearic acid is 25 Å (Angstroms). Though hydrogen bonding, two molecules form a dimer of 50 Å length. These molecules align themselves parallel to each other. The orienting force (the one that directs the polar head on the metal and the long chain out into the oil) is mainly the dipole field.

The longer the chain length, the thicker the adsorbed film. Akhmatov estimates that the resistance of the –CH₂ chain to compression and bending is quite significant. Shear can cause some thinning out of the adsorbed film but later on it reforms itself by reorientation of the molecules.

The configuration of the molecule is a factor affecting the number of them that can be adsorbed per unit surface. The slimmer molecules make stronger films because they allow closer packing. As the molecules are oriented with their hydrocarbon chains normal to the surface, their lateral interactions between adjacent chains are attractive. This is consistent with a minimum energy state resulting in a cohesive arrangement of the molecules.

The solvent or base oil chain length affects the strength of the adsorbed film in a roundabout way. When the chain length of the adsorbed molecule and the solvent or base oil are similar, the residual film is stiffer or stronger if all other things are equal. However, the effect of the base oil molecular size is not as strong as the effect of the adsorbed molecule size. One explanation is
that under such conditions some oil molecules are trapped into the adsorbed layer making for a stagnant film of both oil and adsorbant that is ready and in place to carry the load. This could account for the easier staring of engines with oil containing certain friction modifiers.

The concentration of the friction modifier/reducer also affects performance. The higher the concentration, the higher the friction reduction. However, this is true up to a point above which the improvement is small. Thus the contribution of the friction modifier is large enough at, <1 percent treat, sometimes at, <0.5 percent, so that an increase in dosage would be only moderately rewarding and maybe not economically attractive.

The temperature influences the thickness and tenacity of the adsorbed film. Too high a temperature might provide enough energy to desorbs the adsorbed molecules and thus weaken the film. This happens extensively when the critical temperature is reached.

Metallurgy seriously affects the adsorbed film thickness. The higher the heat of adsorption on the particular metal surface, the stronger the film. Conversely, the film thickness decreases with degreasing surface energy of the metal. To be more precise the oxide film always found on a metal surface affects the adsorption. For example, if the oxide is compact and nonporous and, hence, quite thin, the adsorbed friction-modifier film will be thin, too. Stainless steel and titanium are two metals that are difficult to lubricate because of that reason. Anodizing increases oxide thickness and, therefore, improves lubrication and friction-modification capability.

The type of the steel alloy used also affects the adsorption. Thus, nickel in steel has been found to increase slightly the heat of adsorption (and the adsorption) whereas tungsten sharply increases adsorption. Chromium increases up to a point then decreases adsorption. Therefore, different types of steel in engine parts or gears are bound to have different response not only to EP but also to frictional properties.

Contaminants will affect the film thickness of friction modifiers/reducers. The oxidation byproducts of aromatic molecules have been found to lower the response of friction modifiers because of competition for the metal surface. This is one explanation of why many experimenters find aromatic base stocks or additives to be detrimental to frictional modification. Short-chain acids resulting from oxidative degradation of lubricants and additive also compete for the metal surface to the detriment of friction modification. Thus, durability of friction modification is another important consideration in formulation technology.

Conversely, antiwear and EP agents as well as antirust, detergent, and other polar materials will find in a strong friction modifier a true competitor. This fact indicates that lubricant formulations must always be carefully balanced in order to achieve all-around satisfactory performance.

Table 1 illustrates the effect of the chain lengths on the adsorbed film thickness of a friction modifier. The longer chain in carboxylic acid is associated with the greatest film thickness. Stearic acid being stereochemically somewhat straighter than oleic acid is also somewhat stronger in film building. Sebacic acid resembling a two-headed worm in molecular shape is clearly weaker than short-chained heptanoic acid and much weaker than stearic acid. This fact is consistent with the view of film building through dipole orientation. A two-headed polar molecule could be internally self-defeating to a large extent with respect to building multilayer films.

The type of polar group is also important to achieve maximum effect. Thus, thioheptanoic acid identical to the heptanoic acid in chain length is much weaker in film building because of the sulfur atom in place of oxygen in the polar group. This is shown in Table 2.
A classicist might have thought that sulfur, because of its inherent antiwear/EP properties, would be a plus here. Also, he would have picked the halogenated heptanoic acid as the one to make a thicker film. He would be wrong on both counts because the mechanism that produces friction-modification film is fundamentally different from the antiwear/EP mechanism. In the case of the halogenated heptanoic acid, the chlorine or fluorine atoms are hindrances rather than helps in building up a multimolecular adsorbed film. This is due to the distorting influence of the extra polarity introduced into the molecule by the halogen atoms.

**The Mechanics of Friction Modification/Reduction**

A friction modifier dissolved in oil is attracted to the metal surface by strong adsorption forces. Actually, the polar head is attracted by the metal while the long hydrocarbon chain is preferentially attracted by the base oil which is also composed mainly of hydrocarbons. The result is anchoring of the molecule with the polar end on the metal surface and the long chain sticking out into the oil, perpendicular or normal to the metal surface. Consequently, according to the Ordered Liquid theory, other friction-modifier molecules through hydrogen bonding and Debye orientation forces get their polar groups attracted with a force of about 15K cal/mole in dimer fashion. Due to van der Waal forces, the molecules tend to align themselves parallel to each other in multimolecular clusters. At the same time, the orienting field of the adsorbed layer induces the positioning of the clusters with their methyl groups stacking up on the methyl groups of the tails of the adsorbed monolayer. As a result, they all line up straight up, normal to the metal surface. That is repeated many times, depending on the strength of the orienting polar group, creating a multistoried construction of friction-modifier molecules. Some researchers compare these structures to liquid crystals or ordered domains in the liquid state. Others explain them in terms similar to the cooperative phenomenon seen in ferromagnetism. Whatever their true nature, they are hard to compress out but easy to shear at any layer.

Figure 2 shows the mechanics of this phenomenon. The example used in this case is stearic acid but it adequately represents any chemisorbed friction modifier. The bond between polar group and metal is called adhesion and it is estimated to be about 13 K cal/mole. The forces between the hydrocarbon tails are cohesive ones and help pack the molecules closely together. Interactions between carbon atoms of methylene chains are about 0.84 K cal/mole. Interaction between methyl radicals through London dispersion forces is about 0.1 K cal/mole. That is why if a slip is to occur, it should take place at the nonpolar methyl ends of the fatty acid molecules, at the methyl-methyl midplane location.
Figure 3 shows the stratigraphy of lubricated metal surfaces in the presence of a friction modifier according to one theory. Thus, on top of the regular metal crystal layers is a thin “worked” layer and on it is an oxide/metal zone. The oxide rich layer is next and on it is the adsorbed FM film immersed in the oil.

Figure 4 shows the multistoried friction-modifier construction being sheared at a low-resistance plane by a metal asperity. The plane could be any one where methyl groups are laying on top of methyl groups according to the same theory. This occurs because it is easier to slide the
molecules over each other than to extrude them. The result of this mechanism is lower shear resistance with friction modifier layers than with an antiwear on EP film which is not layered but semiplastic.

The sheared-off friction modifier layers and molecules are not staying away from the metal for too long. The strong orienting forces mentioned before continue to act and they rebuild the thick layer as it was before. This allows the same surface area to be ready for another shearing encounter.

Fig. 4—Asperity shearing off layers of friction modifier (reducer)
APPLICATION

Measuring Friction Reducing Properties

There are many methods of measuring the friction-reducing properties. They cover bench, full-scale, and field tests. As reported earlier, in other papers, they can be divided into three broad and sometimes overlapping categories:

- Tests for measuring coefficient of friction
- Tests for measuring temperature rise
- Tests for measuring fuel economy

Fuel Economy Formulations

Since friction reducers cut down on friction losses and thereby save fuel and energy in general, it makes good commercial sense to include them in lubricant formulations. Such formulations exist today in gasoline engine and automotive gear oils. Highly promising work is being conducted on developing fuel economy formulations for diesel engine oils as well as other lubricants. However, all friction reducers are not created equal since they are chemically different molecules. They vary considerably in composition, effect on friction reduction, as well as a host of other arrears.

Following is a list of properties for screening friction reducers before selecting the one to use in a fuel-saving formulation.

- Friction-reducing properties
- Dosage needed for practical effect (efficiency)
- Chemistry (chlorine, phosphorus, nitrogen, boron, etc.)
- Toxicity
- Safety in handling (flash point etc.)
- Oil Solubility
- Effect on metals, seals and other materials
- Possibility of synergism or extra benefits
- Acidity or alkalinity
- Compatibility with other additives in the formulation
- Effect on engine or gear performance (antagonism against other useful properties including antiwear, cleanliness, etc.)
- Raw materials availability
- Ease of manufacturing
- Cost
- Patent coverage

Oil-soluble friction modifiers/reducers can be employed in different forms in an additive package for a specific lubricant. It can be in the form of an added clear-cut friction modifier without any other function. It can be part of a molecule in a detergent, like a sulfonate, or it can be a part of any other additive from antioxidant to VI improvers.

Example of a clear-cut friction modifier/reducer to be added on top of a balanced package is FM-1 or FM-2. Both have good oil solubility and package compatibility and excellent rating in reducing frictional losses in a wide front of conditions. Table 3 presents relevant data with respect to fuel economy and engine performance. Example of a detergent/friction reducer is a long-chain calcium, magnesium or sodium sulfonate, preferably with one long chain on the benzene ring.
Succinimide-type ashless dispersants have some capability for improving the static coefficient of friction, but not for the dynamic coefficient. In an experiment, 1 to 3 percent succinimide dispersant increased the adsorption heat and the critical temperature significantly. The latter went up from 140°C to 190°C.

VI improvers could be a source for serious friction reduction. Thus, in experiments with long-side chain homopolymer methacrylate, and copolymer acrylates, it was found that the coefficient of friction decreased rapidly with concentration. Further increases in concentration decreased the coefficient of friction even more but not as rapidly. It was calculated that the thickness of the friction-reducing film was in the area of 3700 to 4110Å. Of the three VI improvers tested, the octadecyl methacrylate homopolymer was superior in film durability to the methyl hexadecyl acrylate copolymer, and to the methyl octadecyl acrylate copolymer, even though the latter had just as many carbons in the side chain. However, the homopolymer had more long side chains. It has been suggested that the side chain and not the polymer backbone is the friction reducer. The effect of the long-alkyl-side chain on the coefficient of friction and film durability is related to its flexibility and capability of orientation during rubbing. However, visco-elastic properties (temporary shear loss, etc.) in VI improvers heavily influence friction measurements and it is difficult to assess the exact frictional contribution of the side-chain group.

Useful Concentration of Friction Reducers

Many soluble friction modifiers/reducers have been evaluated for concentration effect on fuel economy of lubricants. As predicted by theory, their effect invariably increases with concentration but the rate of increase soon slows down. The economy improvement reaches a near maximum after which very little further improvement is realized with subsequent increases to concentration. Different friction reducers could have a different concentration/effect response. Figure 5 shows two friction reducers: one highly effective, the other moderately effective. The former reaches a 9 percent economy improvement at 0.3 percent concentration and a near plateau of 11½ percent improvement at 0.5 per cent. The latter reaches only a 2.5 percent improvement at 0.3 percent concentration and a near plateau of 5 percent improvement at 1.0 percent concentration.

This concentration/effect profile is used as guidance in formulating cost effective fuel efficient engine and gear oils. Other effects of the friction reducer on the properties of the lubricant are also taken into account in deciding the proper concentration. Ideally, each lubricant property
should have its own concentration/effect response curve before either choosing a friction reducer or its concentration.

CONCLUSIONS AND RECOMMENDATIONS

-Oil soluble friction reducers are long-chain polar molecules that through intermolecular forces establish and maintain tenacious but easily sheared films on the lubricated metal surfaces.

-These films improve boundary lubrications, oil-film retention even after draining, and reduce frictional losses in a wide range of speed and load conditions.

-The use of oil-soluble friction reducers is a positive means to improve fuel efficiency in a wide variety of lubricants including engine oils, automotive gear oils, and industrial lubricants.

It is recommended that oil-soluble friction modifiers/reducers be incorporated in any lubricant that could conceivably benefit from their presence in terms of lowering operating temperatures and reduced frictional losses. Since friction modifiers/reducers are surface-active materials and, as such, compete for the metal surface with other useful additives (detergents, antitrust, AW/EP, etc.) care should be exercised in their selection and incorporation into finished formulations. A friction reducer should be operating in harmony with the other components in all areas of applications. Extensive testing is required to ascertain the suitability of a given friction reducer in a given lubricant-machine system and, therefore, added-on “mouse milks” for a lubricant should not be attempted lightly.