

## MOLECULAR BASIS OF LUBRICATION

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Rapid advancements in analytical instrumentations and techniques in the last several decades offer an unprecedented opportunity to analyze the complex chemistry and probe the surfaces for chemical evidence. Recent developments in nanotechnology provide further ability to examine phenomena and mechanisms at the nanometer level. As a result of these advances, our understanding of the complex lubrication system has improved significantly. This paper will attempt to provide a molecular basis of how lubricant and additives function in lubrication.

**Keywords:** boundary lubrication, additives, molecular structures, alkyl chain length, monomolecular film design, shear strength of surface films

### 1. INTRODUCTION

Lubrication is an art that has been practiced for thousands of years. Rapid advancements in analytical instrumentations and techniques in the last several decades offer an unprecedented opportunity to analyze the complex chemistry and probe the surfaces for chemical evidence. Recent developments in nanotechnology provide further ability to examine phenomena and mechanisms at the nanometer level. As a result of these advances, our understanding of the complex lubrication system has improved significantly. Monomolecular thin films have been developed to investigate the fundamental mechanism of boundary lubricating films. Results provide additional insights of how antiwear films work in the lubrication system. This paper will attempt to provide a molecular basis of how lubricant and additives function in lubrication.

Lubricants consist of base oils and additive. The base oil also contains heteroatoms of three major types: sulfur-containing compounds, nitrogen-containing compounds, and oxygen-containing compounds. The sulfur-containing compounds typically are alkyl, cyclic & aromatic thiols, alkyl sulfides, alkyl-cyclo alkyl sulfides, and cyclic sulfides. The nitrogen compounds are typically quinolines & pyridine alkyl substituents (basic nitrogens) and pyrroles, indoles, carbozoles (non-basic nitrogens). The oxygen compounds are normal & branched acids, acids containing a cyclic group (acidic oxygens) and 1-, 2- or 3-, and 4-methyldibenzofurans (neutral oxygens). Some of these compounds possess anti-oxidant and anti-wear functions and some of them are pro-oxidants and corrosive. They tend to interfere with the chemical additives either physically or chemically. Specific compound types often are determined by crude source and the method of refining in producing the base oils.

### 2. BOUNDARY LUBRICATING FILM

Under boundary lubrication regime, lubrication is achieved primarily by the formation of a chemical film. This film is easily sheared to protect the surface. The chemical film can be organic, inorganic, and mixture of inorganic/organic in nature. Analyses performed on these films using ESCA, Auger, SIMS, EDAX, and XPS suggest a mixture of organic polymeric materials, oxides, wear particles, and inorganic reaction products from phosphorus- and sulfur-containing additives ( $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{FePO}_4$ ,  $\text{FeS}$ ,  $\text{Fe}_x\text{O}_y\text{S}_z$ , etc.). The

lubricant oxidizes forming surface-active carboxylic acids (or the surface-active additives added to the lubricant). The polar molecules then react with the iron surface forming an iron-organocompound, which polymerizes through condensation reactions to form high molecular weight products. This high molecular weight product (3000-5000) is critical in providing lubrication for typical bearing surfaces (0.05-0.1  $\Phi\text{m}$  Ra). When the molecular weight reaches 100,000, it becomes insoluble in the liquid lubricant phase, producing what is generally referred to as "sludge." If the reaction rate with the surface is too rapid, chemical corrosion would result and wear would increase. An insufficient reaction rate, of course, does not form a film quickly enough to protect the surface. When chemical antiwear additives (phosphorus, sulfur, nitrogen, and chlorine containing compounds) are used, inorganic "glassy" films are formed (structures such as  $\text{FePO}_4$  and  $\text{FeP}_4$  have been identified). Oftentimes, the organo-metallic polymers work synergistically with the inorganic reaction products forming a reinforced film with stronger mechanical properties. The thickness of the films is typically between 0.1 to 0.3  $\Phi\text{m}$  (or 100 to 300 nm) depending on the contact pressures.

### 3. SOLUTION STATE OF ADDITIVES

The solution state of a mixture of base oil molecules and additive molecules is important. Many of the additives have polar functional groups and these molecules behave similarly as surfactants in water. They aggregate together to form micelles. There is a critical micelle concentration (CMC) below which, the molecules exist in an individually solvated state. Similarly, the additives tend to form aggregates in the base oil solution (reversed micelle, i.e., polar groups in the inside and the hydrocarbon tails on the outside). However, the CMC generally is not as distinct as those in surfactant-water systems. The typical CMC for most petroleum additives in base oils tends to be in the range of  $10^{-7}$  to  $10^{-4}$  molar concentration depending on the molecular structure, molecular weight, and molecular configuration (packing density). Also, in a complex lubricant mixture, mixed molecule aggregations tend to form. Since different molecules have different functional groups and polarity, the bonding mechanism among different molecules in a micelle tends to be much more complex than the surfactant-water systems. Not only Van der Waals forces are involved, hydrogen bonding, dipole-dipole

interaction, and sometimes even chemical bonds are formed between different additives. This gives rise to additive-additive interactions. This is illustrated in Fig. 1.

#### 4. MONOLAYER FILM STUDY

Monolayer films have been organized to study the molecular origin of the lubrication action in terms of adhesive bonding strength and shear resistance. Molecular size (molecular weight) also influences the shear strength of the film when the size of the molecule is larger than the asperity contact radius. The durability of the film under light loads increases due to the ease of the molecules to move about (to diffuse back to the wear track for another contact, this ability can be defined as the self-repairing ability) to accommodate stresses but the load-bearing ability of the film will decrease. This mobility implies that the molecules cannot be chemically bonded to the surface, hence low bonding strength. This diametrically opposite requirement of strong adhesive strength and self-repairability poses an interesting challenge. To meet this dual requirement, one way will be to design a mixed molecular system where one species will bond to the surface and another specie will be allowed to move freely on the surface. Another approach will be to have a solid-liquid mixed system where the solid (such as the phosphate glass produced by ZDDP) and the liquid (soft organo-metallic compounds) combined to provide long lasting protection. Ultimately, a carefully designed molecular assembly consisting of different molecules arranged at a monolayer level with each molecule having a specific function or characteristics will give the best combination of tribological properties.

Different monolayer films were deposited on metal films with silicon as the substrate. A technique was developed to measure the film rupture strength of the monolayer. The films are deposited using a dip-coating technique and the film thickness is measured using FTIR and XPS calibrated with Langmuir-Blgett films. Basically a diamond tip was used to scratch the surface under controlled loading. The sample is inclined at 0.01 degrees so the loading increases linearly as the scratching progresses. Fig. 2 shows the typical data for a series of model compounds. Results suggest that the adhesive strength of the films is directly related to the "polarity" of the functional groups. This is intuitive and therefore validates the test instrumentation and test method. Based on this, different films are organized and measured for optimum shear resistance.

We have succeeded to organizing molecular assemblies at one nanometer scale incorporating various concepts. These films have shown superior strengths as well as good durability. The durability is measured in a similar test setup as the film strength test except that the normal loading is much lower so that one pass scratch will not induce failure. The number of cycles then determines the tenacity of the film as well as the self-repairing property of the molecular assembly.

#### 5. SUMMARY

The paper presents the origin of boundary lubricating films and examines the various processes occurring in a lubricant. Monolayer films were deposited and measured for shear rupture strength. The data were then compared with the film structure of ZDDP to see how an ideal film should and can be designed. A test technique was developed to measure the

durability of films. Concepts of how ZDDP films can be improved were examined.

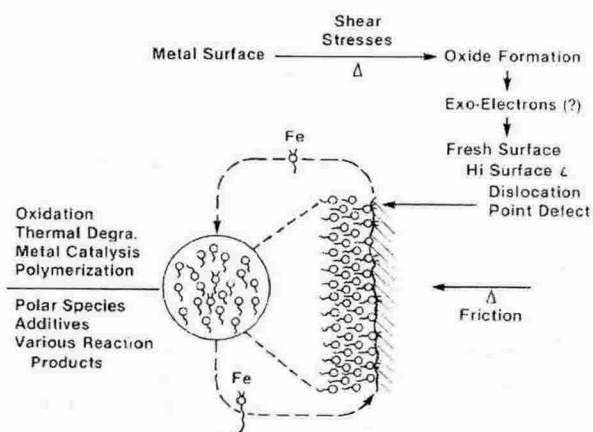


Fig. 1 Solution model of a rubbing surface in a lubricant solution showing the influence of competitive adsorption, oxidation, friction, and aggregation.

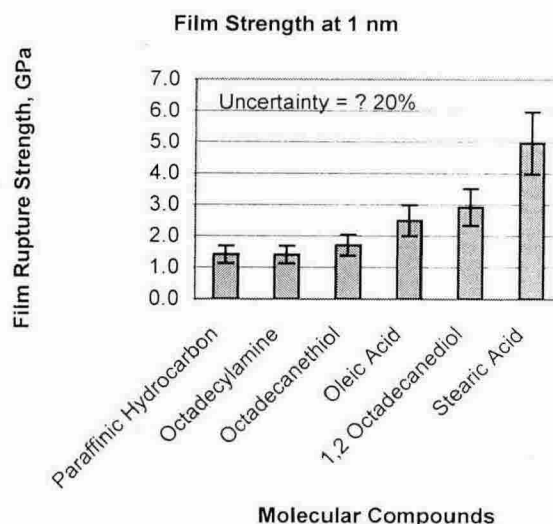


Fig. 2 monolayer film shear strength measured by diamond tip scratching on iron film on silicon showing the influence of functional groups as well as the way the molecules arranged themselves.