

Friction and Film-Formation Properties of Oil-Soluble Inorganic Nanoparticles

Mark T. Devlin, Allen A. Aradi, Jeffrey M. Guevremont and Tze-Chi Jao

Afton Chemical Company

Victor Abdelsayed and M. Samy El-Shall

Virginia Commonwealth University

Copyright © 2008 SAE International

ABSTRACT

Many vehicle and engine test studies have shown that the fuel efficiency of automobiles can be improved by reducing friction between moving parts. Typically, organic friction modifiers such as glycerol monooleate (GMO) or metal containing friction modifiers such as molybdenum dithiocarbamate (MoDTC) have been added to engine oils to reduce boundary friction and improve fuel efficiency. These traditional friction modifiers act by forming either a self-assembled organic film (in the case of GMO) or a Mo-disulfide chemical film (in the case of MoDTC). More recently, the ability of inorganic tungsten disulfide (WS_2) nanoparticles to reduce boundary friction has been described. Martin has proposed that WS_2 nanoparticles are transported into a contact zone where they are compressed and peel open like an onion to form a film. In this study, oil-soluble inorganic nanoparticles containing cerium (Ce) and zinc (Zn) have been synthesized. These nanoparticles reduce friction when solubilized in base oil or fully-formulated engine oil. In addition, boundary films formed in or around the contact zone by oils containing the nanoparticles contain the metal in the nanoparticle.

INTRODUCTION

The ability of crankcase oils to improve fuel economy is critical in vehicles worldwide. As a result several fuel economy engine tests exist in the industry. In Europe, the M111E fuel economy engine test is used to quantify the fuel economy performance of oils with Association des Constructeurs Européens d'Automobiles (ACEA) claims [1, 2]. In North America and other regions, the Sequence VIB fuel economy engine test is used to quantify the fuel economy performance of oils with International Lubricant Standardization Approval Committee (ILSAC) claims [1, 2]. Furthermore, ILSAC is undertaking a new initiative to measure the fuel economy benefits of engine oils in vehicles operating under US EPA corporate average fuel economy test conditions. This initiative will lead to the development of

a new fuel economy engine test (Sequence VID) for the ILSAC GF-5 performance category.

It is generally agreed that fuel consumption is reduced when an oil's viscosity, boundary frictional properties and thin-film or mixed lubrication frictional properties are reduced [1-9]. However, due to the operating conditions of different engines, an oil's viscosity and ability to reduce either boundary friction or thin-film friction or both have different relative importance in different tests [1-9]. For example fuel consumption measured in the M111E engine test is most influenced by an oil's boundary friction reducing properties, while fuel consumption measured in the Sequence VIB engine test is most influenced by an oil's viscosity and thin-film friction reducing properties [1, 2, 4, 8, 9]. The effect of boundary friction on fuel consumption can be observed in the Sequence VIB, but only in Stages 1, 2 and 3, which are the high temperature stages of the test [1, 2, 4, 8, 9].

Typically, organic friction modifiers such as glycerol monooleate (GMO) or metal containing friction modifiers such as molybdenum dithiocarbamate (MoDTC) have been added to engine oils to reduce boundary friction and improve fuel efficiency [3, 10-12]. These traditional friction modifiers act by forming either a self-assembled organic film (in the case of GMO) or a Mo-disulfide chemical film (in the case of MoDTC) [10-14]. More recently, the ability of inorganic tungsten disulfide (WS_2) nanoparticles to reduce friction has been described [14-16]. Martin has proposed that WS_2 nanoparticles are transported into a contact zone where they are compressed and peel open like an onion to form a film [14-16].

This paper reports the synthesis of oil-soluble inorganic nanoparticles containing cerium (Ce) or zinc (Zn), as well as nanoalloys containing both Ce and Zn. Using bench test models which have been developed in our laboratory [1-3], the effect of the Ce and Zn nanoparticles on the frictional properties of engine oils

determined. In addition the film formation properties of the Ce and Zn nanoparticles are analyzed to elucidate the mechanism by which these nanoparticles reduce friction.

EXPERIMENTAL

NANOPARTICLES

Oil soluble inorganic nanoparticles containing cerium (Ce) and zinc (Zn) were synthesized. The detailed synthesis of these nanoparticles has been described previously [17-19]. Specifically, Ce-acetate or Zn-xanthate are combined with oleylamine and oleic acid and then heated and microwaved. In the case of nanoalloys containing Ce and Zn, Ce-acetate and Zn-xanthate are combined in ratios of 4:1, 1:1 and 1:2, respectively to form mixed metal nanoparticles. The nanoparticles which are formed consist of a Ce oxide or Zn sulfide core coated with enough oleylamine and oleic acid to allow them to be oil soluble. The nanoparticles are then washed with ethanol to remove excess oleylamine and oleic acid.

The shapes and sizes of the nanoparticles were determined using Transmission Electron Microscopy (TEM). The amount of Ce or Zn in the nanoparticles was determined by inductively coupled plasma atomic emission spectroscopy (ICP).

OILS EXAMINED

The nanoparticles containing only Ce or Zn and the Ce/Zn nanoalloys were solublized into a Group II base oil with a 100°C kinematic viscosity of ~4.0 cSt. Samples containing oleylamine and oleic acid blended into the same Group II base oil were also prepared along with samples containing glycerol monooleate (GMO), a common friction modifier used in engine oils. The nanoparticles, nanoalloys and GMO were also blended into a fully-formulated SAE 5W-30 engine oil which did not contain additional friction modifiers. All fully-formulated engine oil samples contained the dispersants, detergents, antioxidants and polymers needed to pass all of the ILSAC GF-4 engine tests.

FRICTION MEASUREMENTS

Boundary lubrication regime friction coefficients were measured using a PCS Instruments High Frequency Reciprocating Rig (HFRR). In these tests a 4N load was applied between an ANSI 52100 steel ball and an ANSI 52100 steel disk. The average roughness (Ra) of the HFRR balls and disks were 30 nm. The ball was oscillated over a 1 mm path at a frequency of 20 Hz so the maximum sliding speed of the ball is ~30 mm/s. Friction coefficients were measured at 130°C. The test conditions employed here have been used previously to relate the boundary frictional properties of oils to fuel efficiency in engine and vehicle tests [1-3].

Thin-film friction coefficients were measured using a PCS Instruments Mini-Traction Machine (MTM). These friction coefficients were measured at 100°C with an applied load of 35N between an ANSI 52100 steel disk and an ANSI 52100 steel ball as oil was being pulled through the contact zone at entrainment speeds between 30 and 2000 mm/s. (Entrainment speed is the speed at which fluid is drawn into the contact zone.) The average roughness (Ra) of the MTM balls and disks were 8 and 15 nm, respectively. A slide-to-roll ratio of 20% between the ball and disk was maintained during the measurements. The test conditions employed here have been used previously to relate the frictional properties of oils to fuel efficiency in engine and vehicle tests [1, 13].

EHD FILM FORMATION MEASUREMENTS

Elastohydrodynamic (EHD) film thicknesses of the base oil and fully-formulated engine oil were measured using a PCS Optical Interferometer [3, 7, 20]. Film thicknesses as a function of entrainment speed at 100°C were measured. The film thicknesses of the base oil and fully-formulated engine oil are compared to the surface roughness of MTM balls and disks to ensure that the frictional properties of thin-oil films are measured at high entrainment speeds in the MTM.

TRIBOFILM FORMATION MEASUREMENTS

Tribofilm formation was measured in a PCS Mini-Traction Machine with a Spacer-Layer Imaging Method attachment (MTM-SLIM) [21-24]. In the MTM-SLIM, a rolling-sliding contact is generated between an ANSI 52100 steel ball and an ANSI 52100 steel disk operating at a mean rolling speed of 100 mm/s and a slide-roll-ratio of 50%. Tests were performed at 100°C with an applied load of 31N between the ball and disk. The average roughness (Ra) of the MTM balls and disks were 8 and 15 nm, respectively. The test conditions employed here have been used previously by Spikes et al. to ensure that boundary lubrication conditions are present while observing the formation of tribofilms by anti-wear additives [21-24]. Tests were run for a total of one hour but were stopped periodically so that the SLIM technique could be applied to measure the film thickness of the tribofilm formed on the ball.

After selected MTM-SLIM tests, the MTM balls were rinsed with heptane to remove any excess oil. The area of the ball that made contact with the disc was examined with a JEOL JSM-5800LV Scanning Electron Microscope (SEM). This microscope was also equipped with a ThermoElectron Nanotrace Detector for performing Energy Dispersive X-ray Spectroscopy (EDX) to allow chemical analysis of the tribofilm. SEM images and EDX spectra were recorded at 7 keV incident beam energy.

FUEL CONSUMPTION MEASUREMENTS IN ENGINE TEST

Fuel consumption was measured using Stages 1, 2 and 3 of the Sequence VIB Engine Test since these stages respond to oils' boundary and thin-film frictional properties [1, 2, 4, 8, 9]. The test conditions used in the high temperature stages of the Sequence VIB are shown in Table I. Stage 1 is most responsive to oils' boundary frictional properties and Stage 3 the least responsive, while Stage 3 is most responsive to oils' thin-film frictional properties and Stage 1 the least responsive [1, 2]. In the Sequence VIB engine test the fuel consumed while running the test with a candidate oil is compared to the fuel consumed while running the test with an industry standard reference oil. The percent fuel economy improvement (%FEI) for the candidate oil versus the reference oil is calculated for each stage. The Sequence VIB engine test measures the effect of fresh and aged engine oils on fuel consumption. The fuel consumption properties of only fresh oils were measured in this study.

Table I: Sequence VIB Engine Operating Conditions

Stage	Engine Speed (RPM)	Power (kW)	Oil Temperature (°C)
1	1500	15.39	125
2	800	2.18	105
3	800	2.18	70

RESULTS

CHARACTERIZATION OF NANOPARTICLES

Figure 1 shows TEM images of four types of nanoparticles examined here, Ce1, Ce2, Zn1 and Zn2. The only metal in Ce1 and Ce2 is Ce and the only metal in Zn1 and Zn2 is Zn. The shapes and sizes of the nanoparticles can be determined from the TEM images and are shown in Table II. Ce1 and Zn1 are spheres, Ce2 are plates and Zn2 are rods. The diameters of Ce1 and Zn1 nanoparticles are between 1 and 5 nm and 1 and 10 nm, respectively. The length from one corner to the opposite corner (diameter) of the Ce2 and Zn2 nanoparticles are between 1 and 15 nm. TEM images for the nanoalloys, Ce/Zn1, Ce/Zn2 and Ce/Zn3, are not shown but these nanoparticles are spheres with diameters of between 1 and 10nm. Ce/Zn1, Ce/Zn2 and Ce/Zn3 contain both Ce and Zn and were synthesized with Ce acetate to Zn xanthate ratios of 4:1, 1:1 and 1:2, respectively.

The surfactants that coat the nanoparticles possess friction reducing capabilities (see below), so the amount of surfactant coating the nanoparticles needs to be determined in order to see whether friction reduction is due to the surfactants or the nanoparticle cores. An estimate of the maximum amount of surfactant on the nanoparticles can be calculated by subtracting the amount of metal in the nanoparticles from 100%. ICP

analyses indicate that Ce1 and Ce2 contain 14% and 9% Ce, respectively and that Zn1 and Zn2 contain 55% and 18% Zn, respectively. Therefore, for example, Ce1 can contain as much as 86% surfactant. Keep in mind that the nanoparticle cores are either oxides of Ce or sulfides of Zn, so the total metal in the nanoparticles represents only a portion of the core.

Figure 1: TEM Images of Nanoparticles

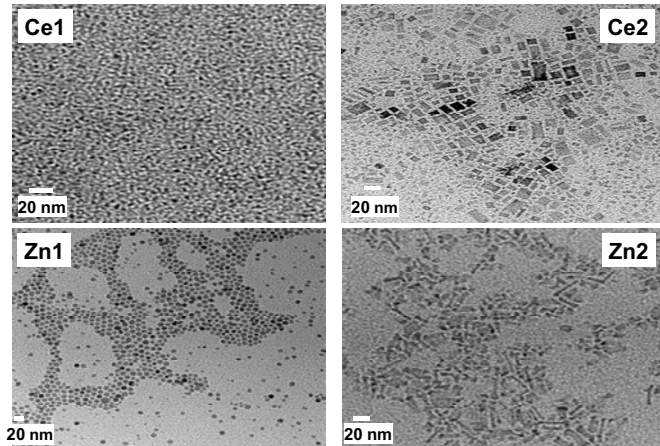


Table II: Nanoparticle Characteristics

Nano-Particle	Shape	Diameter (nm)
Ce1	Spheres	1-5
Ce2	Plates	1-15
Zn1	Spheres	1-10
Zn2	Rods	1-15
Ce/Zn1	Spheres	1-10
Ce/Zn2	Spheres	1-10
Ce/Zn3	Spheres	1-10

FRICITIONAL PROPERTIES OF NANOPARTICLES IN BASE OIL

Figure 2: Boundary Friction of Surfactants in Base Oil

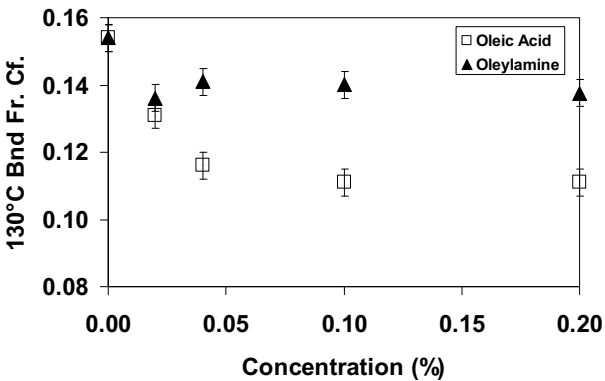


Figure 2 shows that the 130°C boundary friction coefficient for the Group II base oil is 0.154 (value at 0% surfactants in base oil). (Boundary friction coefficients are measured at 130°C, since boundary friction