



Impact of ethanol on the formation of antiwear tribofilms from engine lubricants



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ABSTRACT

This paper investigates the impact of contamination of engine lubricants with ethanol fuel on the growth and stability of anti-wear tribofilms from ZDDP-containing lubricants. The MTM-SLIM technique was used to monitor the effects of blending 5 wt% of both anhydrous and hydrated ethanol on tribofilm thickness in a fully-formulated Group I oil and in a solution of ZDDP anti-wear additive dissolved in Group I base oil. Tribofilm thickness was significantly reduced by the addition of ethanol for both oils, and the reduction was more severe for hydrated than for anhydrous ethanol. When a tribofilm was allowed to form during rubbing using an ethanol-free oil, the subsequent addition of hydrated ethanol showed both the destruction of the pre-formed antiwear tribofilm and damage to the rubbed surfaces.

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1. Introduction

The use of renewable fuels, in particular ethanol, has increased worldwide as an alternative to petroleum-based gasoline and diesel derivatives [1].

In Brazil, the development of flex-fuel engines, which can run on any proportion of ethanol and gasoline, means that ethanol fuel is in widespread use [2] and this has helped the country to reduce carbon emissions [3], particulate mass concentration in vehicle exhausts [3,4] and dependence on fossil fuels. Today, half of the fuel used in Brazilian automobiles is renewable [5] and according to the national association of automotive vehicle manufacturers (Anfavea), over 85% of the vehicles produced in Brazil since 2006 have been flex-fuel.

In other countries, the use of ethanol fuel has also increased in recent years. In the United States most vehicles now use 10–15% ethanol (E10) but 11 million vehicles with so called “bi-fuel” engines capable of using 85% ethanol, 15% gasoline (E85) [6] were sold in 2013. In 2007 the Energy Independence and Security Act established a target of 36 billion US gallons of renewable fuel use by 2022 [7] and, according to the US Energy Information Administration (EIA), the production of ethanol in the US in 2014 was over 14 billion US gallons, which is more than twice the production in Brazil.

Sweden [8] and Belgium [9] have also adopted policies to increase the use of biofuels, in particular of ethanol. This has encouraged considerable research to produce ethanol from non-food sources such as cellulose.

However, the use of ethanol as fuel poses some tribological issues due to the possibility of contamination of the lubricant with ethanol. Since ethanol has a much higher latent heat of evaporation than gasoline, accumulation of ethanol in the lubricant can be significant [10]. Considerable amounts of ethanol (between 6% and 25%) have been measured in the sump after bench sequence tests [11,12] and field tests [13]. Ethanol accumulation is expected to influence lubrication and friction and has been suggested as the main cause for severe wear that has been frequently reported by users of various sizes and models of flex-fuel engines [14,15].

A few studies have investigated the impact of ethanol in engine oil on friction. For a fully formulated lubricant, although the presence of ethanol did not affect friction measurements significantly, the combined presence of water and ethanol in the lubricant reduced friction [10,16].

In a previous paper [17], we reported the effects of ethanol on film formation and friction. Elastohydrodynamic (EHL) film thicknesses were measured for lubricants contaminated with ethanol over a wide range of speeds, to span lubrication regimes ranging from boundary to EHL. These results were complemented with measurement of Stribeck friction curves, to help understand the mechanisms by which the presence of ethanol could affect friction. In order to separate the interaction of ethanol with the base oil from that with other additives, both base oils and formulated oils without friction modifiers were investigated.

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It was shown that the addition of quite small proportions of ethanol decreased the viscosity of both the base and formulated oils. This had the effect of slightly reducing EHD film thickness and friction and causing the shift from full film to mixed lubrication to occur at lower entrainment speeds. However, in slow speed, boundary lubrication conditions, the effect of ethanol in the base oil was very different from that of ethanol in the formulated oil. A boundary layer, which was not present in the ethanol-free base oils, was found when the base oil was contaminated with ethanol. This boundary layer may originate from oxidation of ethanol when in contact with a hot, rubbing metal surface. In a formulated engine oil, the presence of ethanol interfered with the formation of a thick boundary film by additives, reducing its thickness. Consecutive Stribeck friction curves obtained for the non-contaminated formulated oil showed a progressive shift to higher entrainment speeds, indicative of the growth of a thick, rough boundary film, but this was suppressed by the addition of ethanol [17]. These results suggested that ethanol may have a strong influence on the formation of tribofilms.

When metal surfaces move against each other under low entrainment speeds so that EHD films are very thin, significant rubbing contact of their asperities can occur. For lubricants containing ZDDP antiwear additives, such rubbing has been shown to induce the formation of thick tribofilms that protect the moving surfaces against wear [18,19]. Zinc dialkyldithiophosphates (ZDDPs) are still used in the vast majority of commercial lubricants, despite considerable efforts in the last two decades to replace them with alternative antiwear additives since the presence of sulphur and phosphorus oxides and metal salts in ZDDP is harmful to engine exhaust after-treatment devices [20].

The anti-wear performance of ZDDP appears to rely on the formation of thick anti-wear films that act as mechanically protective barriers. Such films can be generated thermally by immersion in heated solution (thermal films) at high temperatures (generally above 150 °C), but they can also form at much lower temperatures within a rubbing contact (tribofilms). Actual sliding contact is necessary for the formation of tribofilms, *i.e.*, they do not develop in rolling contacts or when the hydrodynamic film thickness is significantly greater than the surface roughness [21]. Comparison between the chemistry of ZDDP thermal and tribofilms has shown that they have similar characteristics [22], although tribofilms are mechanically stronger [23].

Various studies have investigated the thermal decomposition of ZDDP. In an influential study, a wide range of species formed during ZDDP thermal decomposition were identified, including several thionyl species, where the alkyl groups of ZDDP had been linked to P by S atoms. This led to a proposed oxygen/sulphur (O/S) exchange mechanism for ZDDP reaction and film formation [24]. However the relevance of this is questionable since it has been recently shown that zinc dialkylphosphates, that have no S atoms in their molecules, form tribofilms very similar to those formed by ZDDP [25].

The process of tribofilm formation is believed to be similar to the thermal degradation process that occurs in thermal films, but driven to take place at much lower temperatures. The drive mechanism is controversial, but the main candidates are frictional heating due to sliding and/or pressure in the rubbing contact and mechanisms involved in rubbing process itself (e.g., molecular strain, exoelectron or other particle emission, free surface catalysis or molecular strain) [21,26].

A study in 1993 [27] showed a negative impact of methanol on ZDDP tribofilms and wear during ball-on-flat sliding tests, in particular at low temperatures. To explain the higher wear rates for lubricants containing methanol, Olsson [28] proposed a mechanism by which methanolysis acts directly on the ZDDP molecule, affecting the reactions that would otherwise occur in

the normal decomposition of ZDDP to suppress the formation of higher sulphides.

The current work aims to investigate the extent to which the tribological problems frequently reported for flex-fuel engines may result from the effects of ethanol on the formation and stability of protective ZDDP tribofilms. To do this, the effects on tribofilm thickness and friction of blending 5 wt% of both anhydrous and hydrated ethanol in a fully-formulated Group I oil and in a solution of ZDDP anti-wear additive dissolved in Group I base oil were monitored during prolonged rubbing tests.

2. Methodology

2.1. Materials

One fully formulated oil was used in this work. The classification of this according to the American Petroleum Institute (API) was SL and it is denoted as SLB in this paper. This lubricant is representative of a wide range of lubricants used today in Brazil but did not contain a friction modifier additive so as to preclude the latter's possible interactions with ethanol. As well as containing a secondary ZDPP additive, chemical analysis of the oil also suggested the presence of a calcium sulphonate-based detergent. In order to separate the effects of ethanol from its interactions with other additives present in the fully formulated oil, the corresponding base oil (Group I), to which only ZDDP was added at a concentration of 0.08 wt% P, was also studied and it is denoted as Base ZDDP in this paper.

Small amounts of ethanol (5 wt%) were added to both lubricants to investigate the effects of ethanol contamination on the formation of tribofilms. In Brazil, hydrated ethanol (6.2–7.4 wt% water) is used in flex-fuel engines, whereas in bi-fuel engines in the US anhydrous ethanol is employed, since water is not soluble in gasoline. In this study, the effects of the contamination of the lubricant with both hydrated (HE) and anhydrous ethanol (AE) were investigated.

By heating samples of the blends on a hot plate at different temperatures, it was found that 5 wt% AE was fully soluble in the lubricants at temperatures of 40 °C and above, but 5 wt% HE did not fully dissolve and tiny dispersed droplets were observed even when the blends were heated at 100 °C. These were presumably due to the water content. Viscosities and densities were measured for the oils and their blends with ethanol using a SVM3000 Stabinger viscometer at 40 °C, 70 °C and 100 °C. Table 1 shows that the addition of ethanol reduced the viscosity of all the oils at 40 °C and 70 °C, but at 100 °C it was not possible to measure the viscosity of the mixtures containing ethanol due to the formation of a large number of bubbles in the measurement tube, resulting from rapid evaporation of ethanol. The reduction in viscosity caused by AE was larger than that caused by HE, as observed in a previous study [17].

2.2. Experimental methods

The growth of ZDDP tribofilms and the influence of the presence of ethanol on this growth was monitored using optical interferometry. However standard spacer layer interferometry [29] cannot be employed to study ZDDP tribofilm formation because such films are generated only when direct rubbing and solid contact occurs and this process rapidly abrades the optical coatings used for interferometry [21,30]. Spacer layer interferometry also produces a single, averaged film thickness of a selected region of the contact, while to study ZDDPs it is advantageous to produce a map of film thickness so as to identify the rubbed track region. Such maps can be produced by the technique of spacer layer

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