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ZDDP-ADDITIVE-CATALYST INTERACTIONS IN ENGINE OIL

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ABSTRACT

The phosphorous content in engine oil is found to be the major cause of the poisoning of Catalytic converters in automobiles, hence environmental regulations limiting the phosphorous level in GF4 and GF5 oils have been introduced. Zinc dialkyl dithiophosphate (ZDDP) being the only major source of phosphorous in current engine oils, is also an indispensable component of the additive package in these oils for it has been the primary anti wear – as well as anti oxidant – additive for over fifty years. Efforts are made to replace the ZDDP with other materials with the same properties which would not be harmful to the environment and also an economically feasible substitute. Another solution to this problem is to reduce the amount of ZDDP used while improving its antiwear performance. Anti-wear action of ZDDP, involves its break down reaction with the steel surface by Zn □ Fe ion exchange and subsequent formation of an amorphous chemisorbed film containing zinc, phosphorus, oxygen and sulfur and also iron in the form of polyphosphates and sulfates of zinc and iron. The efficiency of this mechanism is reduced by parallel reactions between ZDDP and other additives as well as their antagonistic effects. Introduction of a material with catalytic properties which would reduce the negative effects of the presence of the other additives on the anti wear properties of ZDDP is an option that was explored in this paper. Both triboligical wear tests (Ball on cylinder lubricity evaluation tests) as well as mechanism studies (DSC, FT-IR and NMR) were used to evaluate the performance of ZDDP in the presence of the most common additives (i.e. Anti-oxidants, Detergents and Dispersant). Iron Fluoride is also introduced as a potential additive to improve the efficiency of wear protection mechanism of ZDDP. The improvements observed in the presence of the Iron Fluoride will allow further reducing the amount of ZDDP in engine oils containing this material as an additive [1].

INTRODUCTION

Substantial amount of wear in engines occurs under boundary lubrication conditions. In order to evaluate the lubricity of oil samples, boundary condition lubrication can be simulated using a Ball on Cylinder Boundary Lubrication Evaluator testing unit (BOCLE). A BOCLE unit that was designed and built at UTA [2] was used to conduct wear tests in order to evaluate different chemistries of oils. Wear test results were coupled and correlated with analytical methods and, using DSC, FT-IR and NMR (^{31}P) to study and characterize the structure-performance relationship.

The study focuses on using a fluorinated compound with catalytic properties to enhance the anti wear properties of ZDDP. The study has also been conducted in presence and absence of selected additives, in order to study the possible synergistic and antagonistic effects between the ZDDP, the additives and the catalyst (FeF_3).

RESULTS AND DISCUSSION

Boundary condition ball on cylinder wear tests were performed on oil samples containing commercially obtained ZDDP, selected additives (Calcium Sulfonate detergent, commercially available dispersant, Aminic Anti oxidant and Olephinic Co-polymer VI Improver), each in presence and absence of the catalyst. A significant reduction in wear volume was observed when catalyst was used in each case (Figure 1). It was necessary to understand the basis for the improvement observed in anti wear performance of ZDDP when catalyst is present.

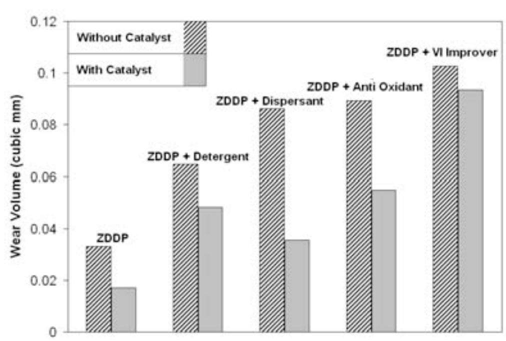

Figure 1. Wear Volume Data for the oil samples tested

It is possible that the fluorinated catalyst could be providing lubricity by itself in conjunction with the iron surface during the boundary lubrication tests. However the DSC data of ZDDP with and without catalyst suggest the fact that energy changes are involved between ZDDP and catalyst even in absence of iron surface.

The decomposition temperature of ZDDP was lowered in presence of catalyst (Table 1). While most engine oil additives are known to increase the break-down temperature of ZDDP, deteriorating its anti wear properties, the same decrease was observed when catalyst was added to ZDDP-additive formulations in most cases.

Table 1. ZDDP decomposition temperature (DSC)

Additives Present	ZDDP Decomposition Temperature [°C]
ZDDP	199.59
ZDDP + Catalyst	190.34
ZDDP + Detergent (Ca-sulfonate)	217.97
ZDDP+Detergent (Ca-sulfonate) + Catalyst	206.93
ZDDP + Anti Oxidant (Aminic)	204.65
ZDDP + Anti Oxidant (Aminic) + Catalyst	226.18

FT-IR and ^{31}P NMR results were obtained for ZDDP and ZDDP-catalyst at room temperature and also for thermally treated samples (20 min, 150C in Nitrogen). ^{31}P NMR at 121.65MHz, relaxation delay of 6 seconds, 300 scans, decoupled with respect to proton and with phosphoric acid as the reference. The chemical shifts are defined as positive in the low-field direction.

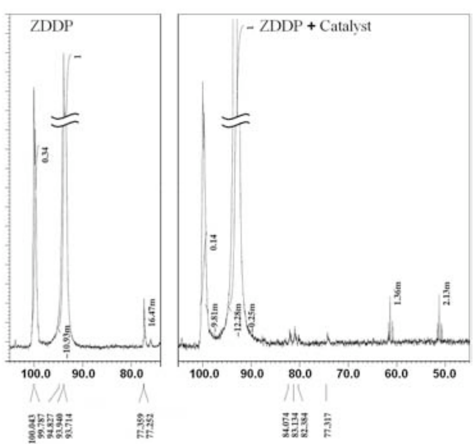

Figure 2. NMR Spectra of ZDDP and ZDDP + Catalyst

The ^{31}P NMR offers some interesting features worth noting (Figure 2). Note that the range shown for each spectra in Figure 2, is the range where peaks were observed. The observed peak at 100 ppm attributed to basic secondary ZDDP and 76-77 ppm attributed possibly to (RO)(RS)POSZn^{-}[3,4] diminishes markedly in intensity along with the appearance of numerous peaks in case of ZDDP-catalyst suggesting chemical interactions set off in early stages between basic ZDDP and catalyst (Lewis acid) .

This suggests that decomposition of ZDDP is accelerated in presence of catalyst supporting the DSC results. Whether the catalyst reacts with the parent ZDDP and/or side products (impurities) present in it or just catalyze the reaction by favorable energy kinetics is currently being studied. In the case of former, this could trigger series of reactions with new products that have antiwear properties, responsible for early protection in boundary lubrication. New Peaks indicative of new structural product/s (~ 68, ~57) are definitely observed in ^{31}P NMR. Wear tests on the same baked samples have shown better antiwear performance than the case where only ZDDP is present. More thermal degradation tests are currently in progress to give better understanding of underlying mechanisms.

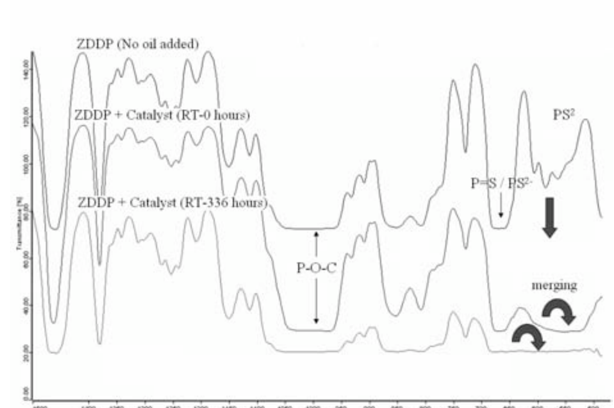

Figure 3. FT-IR Spectra of ZDDP and ZDDP-Catalyst.

FT-IR results for ZDDP-catalyst mark a significant merging of the ZDDP peaks in the region around 550-600 cm^{-1} (Figure 3). The peak for the catalyst is known to be around ~ 720 cm^{-1} in the solid state [5]. This merging of the peaks increases with time (spectra 0 hours and 2 weeks). It could be possible that complexation occurs between the PS^{2}ions/P=S and the fluorinated catalyst that prevents the unwanted complexation between ZDDP and other additives at ambient temperatures. This complexation however is seen to break up as observed in FT-IR of baked samples, releasing ZDDP upon heating. This might possibly explain the DSC results of ZDDP-catalyst and additives where the ZDDP is available for the antiwear action much earlier than it would when complexed with additives.

ACKNOWLEDGMENTS

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