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Using the Physicochemical Properties and the Thermo-oxidation Degradation Products of ZDDP to Justify its Functions as an Additive of Choice for Automotive Crankcase Oil Formulation

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ABSTRACT

Additives are used as lubricant fortifiers against thermal and thermooxidative degradation under tribological conditions. However some additives can decompose at very high engine temperature regimes into products that may pose serious threats to the environment, if unchecked. For instance ZDDP in spite of its tribological importance as a powerful antioxidant and anti wear additive in automotive crankcase oils, has been suspected as a precursor of environmental hazards due to its perceived tendency to cause electrolytic corrosion and poisoning of the catalysts in the exhaust gas converter. It is against this backdrop that the automobile manufacturers have called for a change from ZDDP to some other antiwear additive or at least reduce its concentration from the present 0.08 to 0.05%. This review is therefore aimed at allaying the fears of exhaust catalyst poisoning which could result in emission of toxic exhaust fumes into the environment. The mechanism of thermooxidative degradation showing the expected products has been proposed to address this apprehension. The study also collaborates the views of the lube oil producers that 0.08% of ZDDP in lube oils is ideal for optimum performance of the automotive crankcase engines and that this concentration has no adverse environmental implications to warrant a call for reduction or an outright ban.

***KEYWORDS**: Antiwear Additive, ZDDP, Degradation Products, Environmental Concern*

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I. INTRODUCTION

The quality of oils used in the automotive crankcase engine is determined by the type of hydrocarbons present in the base oil and the physicochemical properties of the additives incorporated. A combination of these factors is a measure of the thermal and thermooxidative stabilities of lubricants. At high temperature regimes most additives are vulnerable to thermal degradation which brings about major changes in their physicochemical properties and decline in the performance characteristics of lubricating oils. Consequently aging [1] of lube oil sets in with increases in temperature till the oil completely loses its lubricity or tribological value. Thus the lubricating properties or performance characteristics of lube oils used in the spark ignition internal combustion engines according to [2] depends largely on the thermal stabilities of the base oil and the additives incorporated. Therefore to ensure optimum performance premium must be placed on the quality as well as the quantity of additive used. The quantity of additives usually varies from less than 0.01 to greater than or equal to 30%[3]. High quality additives of tribological significance include hindered phenol (fig.1) used asanti-oxidants to prevent deterioration associated with oxygen attack on the base fluid by interacting with hydroperoxide radicals to form inactive compounds thereby inhibiting the formation of varnish and sludge [4]; antiwears such as ZDDP (fig. 2)which are film forming compounds that prevent metal-to-metal contact thereby reducing the activities of abrasive particulate matter responsible for corrosion and wears. Others are pour point depressant such as alkylated naphthalene; dispersants and viscosity improver which are long chain high molecular weight polymers such as styrene- butadiene copolymers which act by counteracting the temperature effect on the hydrocarbon matrix[5]. However at certain temperature regimes some additives break down[Korcek ,1980] and lose their fortifying properties. The products of this breakdown may generate a serious environmental concern if not checked. This however forms the main thrust of this review and the focus is on Zinc dialkyldithiophosphates being among the most widely used anti-wear additives in lube oil formulation. Those with film forming properties for specific materials whose details are not captured in this study include olefins for aluminium [6] and iodine for high temperature alloys.

1.1 The Tribological Characteristics of ZDDP

Zinc dialkyldithiophosphates are oil soluble compounds which are used as additives in lubricating oils for spark ignition internal combustion engines and transmissions. They are a key component of modern synthetic and mineral based lube oils. Although they represent only a small percentage of the total engine oil, they play a crucial role in improviding wear protection of key metal-metal contact points in the crankcase engines and transmissions thereby boosting the lifespan of the engine. The presence of Sulphur and Phosphorus as reducing agents prevents the attack of hydrocarbons by oxygen di-radicals formed at high temperature regimes. This in effect provides oxidation protection which extends the lifespan of the lubricant. Perhaps its capacity to perform the dual function explains why Zincdialkyldithiphosphate is sometimes referred to multifunctional additive. Zincthiophosphates as they are generally called are prepared by reacting various types of alkanols especially aromatic alcohols with Phosphorus (v) oxide followed by the addition of Zinc oxide to the resultant intermediate. The physicochemical properties of Zincdialkyldithiphosphates as antiwear additives derive from the sulphur-zinc linkage interactions with metal surfaces in relative motion.

1.1.2 Stuctural Representation of Some Additives in Lube Oils

Below are the structures of some lube oil additives of interest mentioned in this review work. The products are usually synthetic in origin and are meant to achieve the desired functions in lube oils.

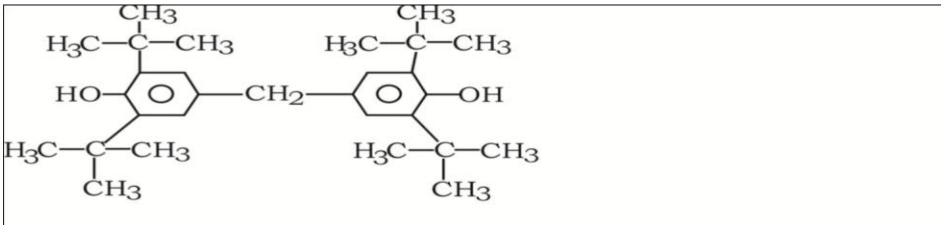

Figure 1: Structure of 4,4-Methylene-bis(2,6-di-tertbutyl)phenol (An example of Hindered phenol)

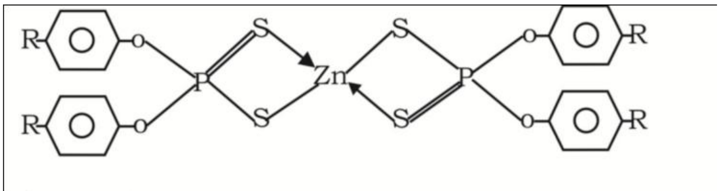

Figure 2: Structure of Zinc dithiophosphate

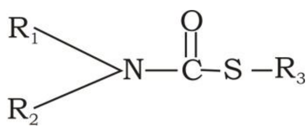

Figure 3: Structure of Thiocarbamate

It is pertinent to note that figures 2 and 3 above both contain sulphur which is widely known as a precursor of contaminants such as SO_2 and H_2S. But figure 2 contains four sulphur atoms compared with structure 3 with only one atom of sulphur. This obviously explains why ZDDP (fig.2) is seen as an environmental threat in lube oils, a misconception meant to be addressed in this review.

II. RESEARCH REVIEW

2.1 Comparison of Synergistic Lubricating Effect Between ZDDP and BSD

Based on the synergistic lubricating effects of ZDDP with a heterocyclic compound such as dialkyldithiocarbamate (Fig.3) derived from benzothiazole, four oil samples were prepared from the mineral based lubricants. The base oil was obtained by stripping each mineral lubricant of its additive components using chromatographic columns stacked with Florisel (100-200) and Silica Gel (90-230) mesh arranged in alternate positions (Ekot and Ofunne, 2001). For each oil sample, the total concentration of both BSD and ZDDP in base oil is fixed at 0.5 per cent and the concentrations of BSD and ZDDP were changed accordingly at different ratios. The antiwear properties of four samples were evaluated by using a four-ball machine at the load of 490N ($50kg \times 9.8m/s^2$) and sliding time of 15 min [7]

Table 1: Performance Comparison Between ZDDP and BSD

Additive	Concentration (%)	Pb Value (Kg)	WSD (mm) 30Kg	50Kg
Base oil	Nil	40	0.58	Seizure
ZDDP	0.5	75	0.38	0.49
BSD	0.5	70	0.46	0.87

The synergistic effect between ZDDP and BSD is quite considerable as shown above . However, using BSD to partially replace Zinc dialkyldithiophosphate will certainly lower the performance characteristics of the lube oil although the antiwear properties of the former are comparable. For instance a novel borate ester derivative(simply coded BDDP) containing dialkylthiophosphate groups was prepared and on evaluating its tribological significance it was observed that BDDP as an additive in synthetic ester (Esterex A51) showed a better load-carrying and friction-reducing property and can therefore improve the antiwear performance of the base oil to a large extent but its degradation products adsorbed on worn surface and the elemental Phosphorus and Sulphur produced reacted with metal and generated FePO4, Fex(SO4)y, both of which contributed to the formation of boundary lubricating film [8]. . Thus BDDP despite its high thermal stability and efficiency in controlling the oxidation of Esterex A51 cannot compare favourably with ZDDP in terms of the antioxidative property. Hence ZDDP is a better additive than BDDP.

In the same vein another investigation has shown that ZDDP possesses a very good anti wear capabilities. The study revealed that addition of 0.25% (v/v) of ZDDP increased the antiwear properties (i.e load carrying capacity) of OIL by thirteen times as shown in column 2:row 3 (Table 2). The presence of same amount of ZDDP increases the load carrying capacity of sand-contaminated lube oil by five times(column2:row4). ZDDP also helps in reducing wear, particularly when abrasive contaminants are present in the lubricants [9]. The summary of the results is given in Table 2.

Table 2: Tabulation of Results

Oil Sample	Timken Ok Load (Pound)	Weight of Bullet before Test (gm)	Weight of Bullet after Test (gm)	Wear Weight Loss (gm)	Percentage Wear Wight Loss (%)	Scar Diameter (Major) (mm)	Scar Diameter (Minor) (mm)
(A) Raw Base Oil	40	29.3549	29.3035	0.514	0.1750	10.00	6.076
(B) Base oil+0.25% ZDDP	520	29.3300	29.3100	0.200	0.0681	7.00	4.076
(C) 0.1% Sand Particles in base oil +0.25%ZDDP	200	29.3408	29.3054	0.354	0.1206	8.028	5.0008

2.2 Mechanism of High Temperature Degradation of ZDDP

Another important aspect of this research review is the environmental implication of using Zinc thiophosphate, a compound containing Zinc as the central atom to which as many as four Sulphur atoms are attached (Fig.2) as additive in lube oil formulation. The environmental concern probably stems from the perceived fear that given the huge Sulphur content in the compound the thermo-oxidation degradation products of ZDDP may likely have the potentials to poison the catalyst in the exhaust converter which can result in emissions of environmentally unfriendly substances. To debunk this stereotyping the mechanism of high temperature degradation of a typical thiophosphate compound most commonly used as lube oil additive (ZDDP) has been proposed to give an insight into the type of products expected when ZDDP is thermo-oxidatively decomposed (Fig.4). It is pertinent to note that the breakdown of additives is a free radical process and occurs at very high temperatures. The products of this high temperature process are the organic fragments which are predominantly resinous in texture as opposed to products arising from the breakdown of hydrocarbons in the base oil which are mainly volatiles[10]. The reason is that most additives are aromatic compounds of higher molecular weight (HMW) which are more heat resistant than long- chained hydrocarbons that make up the base oil. Thus when aromatic systems break down under the influence of heat their degradation products such as biphenyls are very thermodynamically stable species and can still protect the degraded hydrocarbon matrix of the base oil to some extent. It follows therefore that the compounds coming into the exhaust chamber may be largely a product of base oil degradation with only a little input such as molecular oxygen (as seen in the mechanism) from the degradation of ZDDP.

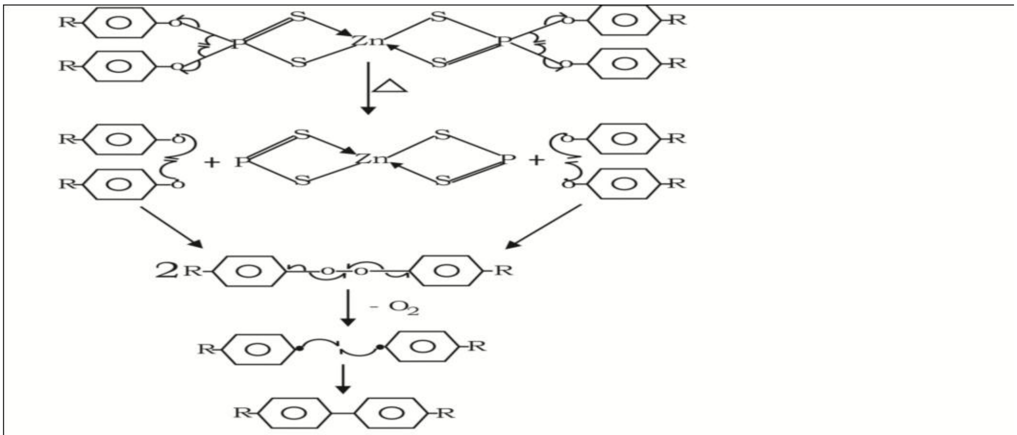

Figure 3: Mechanism of degradation of Zinc dithiophosphate

III. DISCUSSION AND CONCLUSION

The review has examined the synergistic effect of ZDDT with other related compounds such as BSD and BDDP and the evaluation reveals that none of them has the anti-wear capacity as high as that of ZDDP. Besides, ZDDP show an exceptionally high ability to suppress and contain the effect of contaminants present in the lube oils. This is another physicochemical property that gives ZDDP an edge over its rivaling counterparts. Again the proposed mechanism clearly shows that thermo-oxidative degradation is purely a free radical process which in most cases results in the formation of short or long-chained, branched or even cross-linked polymeric materials depending on functionality or the number of bonding sides [11] of the free radical monomer generated. Although the proposed mechanism only shows biphenyls and oxygen as degradation products, there is a vast array of low molecular weight(LMW) polymeric products generally referred to as sludge formed as a result of copolymerization between phenoxy radicals and long-chained radical species from the degraded base oil. These are all light resinous materials which deactivate or suppress the reactivity of the sulphur-bearing species (mainly from the degraded ZDDP) thereby dimming the chances of the formation of gaseous substances like Sulphur(IV)oxide and Hydrogen sulphide, which are strong catalyst poisons. Thus the fear of exhaust catalyst poisoning has been allayed based on the above mechanism which is however subjuct to further evaluation. In the light of the foregoing, ZDDP has all it takes to outclass every other compound evaluated in this study and should therefore be used for now as antiwear additive of choice for the formulation of the automotive cankcase oils.

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