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Applications of dielectric thermal analysis and X-ray photoelectron spectroscopy: properties of dialkyl hydrogen phosphites and iron

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Abstract

Solution properties of several different phosphorus compounds prepared in hydrocarbons of various polarities were studied by dielectric thermal analysis and yielded data as to conductivity and surface reactivity. X-ray photoelectron spectroscopy was performed on steel gear teeth and provided elemental composition as well as thickness of the reacted surface layer. This data was correlated with ASTM test results. A mechanism is proposed that explains the relative phosphorus content and thickness of the protection films on the steel surface. The mechanism is based on correlating the organophosphorus molecular mass and hydrocarbon polarity as it relates to ASTM test results.

The same phosphorus compound was blended into several hydrocarbons of differing polarities and was observed to give varying ASTM test results. Several different phosphorus compounds of various molecular masses were blended into the same base fluid and were observed to also give varying ASTM test results.

Keywords: Organophosphorus; ASTM standard tests; Gear steel; Wear; DETA; XPS; Molecular weight; Polarity; Mobility; Surface reactivity; Surface layer

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1. Introduction

Gear sets and vane pumps need to be protected from wear and gear distress by the addition of extreme pressure and anti-wear (EP/AW) additives. Dialkyl hydrogen phosphites are important examples of such EP/AW additives. However, all dialkyl hydrogen phosphites do not function equally as EP/AW additives. Data collected to date demonstrated that lower molecular weight phosphites had a basic performance advantage over higher molecular weight phosphites.

A blend matrix was constructed that included five hydrocarbons of different polarity and seven phosphites with varying molecular weight. Mixtures of seven dialkyl phosphites (see Table 1) were also prepared in a conventional base oil for dielectric thermal analysis (DETA). The blends and mixtures were formulated at equivalent phosphorus level and at relative constant viscosity. The blends were evaluated in the FZG gear test apparatus (ASTM D5182) to determine extreme pressure performance (Fig. 1). Selected formulations were evaluated before and after

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Table 1
Dialkyl hydrogen phosphites: DETA properties and FZG results

Dialkyl phosphite	Code	DETA log conductivity (pS/m)	DETA log polarization time (ms)	FZG load stage pass
Dilauryl	DLPH	4.3	2.50	8
DLPH + Di-4-methyl-2-pentyl	DLPH + DMPPH	3.8	2.30	9
Diisooctyl	DIOPH	4.0	1.75	9
Dicyclohexyl	DCHPH	4.4	1.50	9
Di-4-methyl-2-Pentyl	DMPPH	6.8	1.50	10
Di-2-ethyl-1-Hexyl	DEHPH	6.3	1.25	11
Dibutyl	DBPH	8.8	−0.75	12

the FZG test for relative phosphorus levels. FZG test parts were cut and prepared for surface examinations.

X-ray photoelectron spectroscopy (XPS) was performed upon selected gear teeth to support the proposed hypothesis. Gear teeth from several test specimens were sectioned and mounted for XPS examination. Depth profiles, elemental distributions with respect to the depth of reacted surface layers, were obtained on several specimens. The results revealed striking differences in the amount and thickness of the reacted surface chemistries depending on the base stock/additive combination. Overall, the

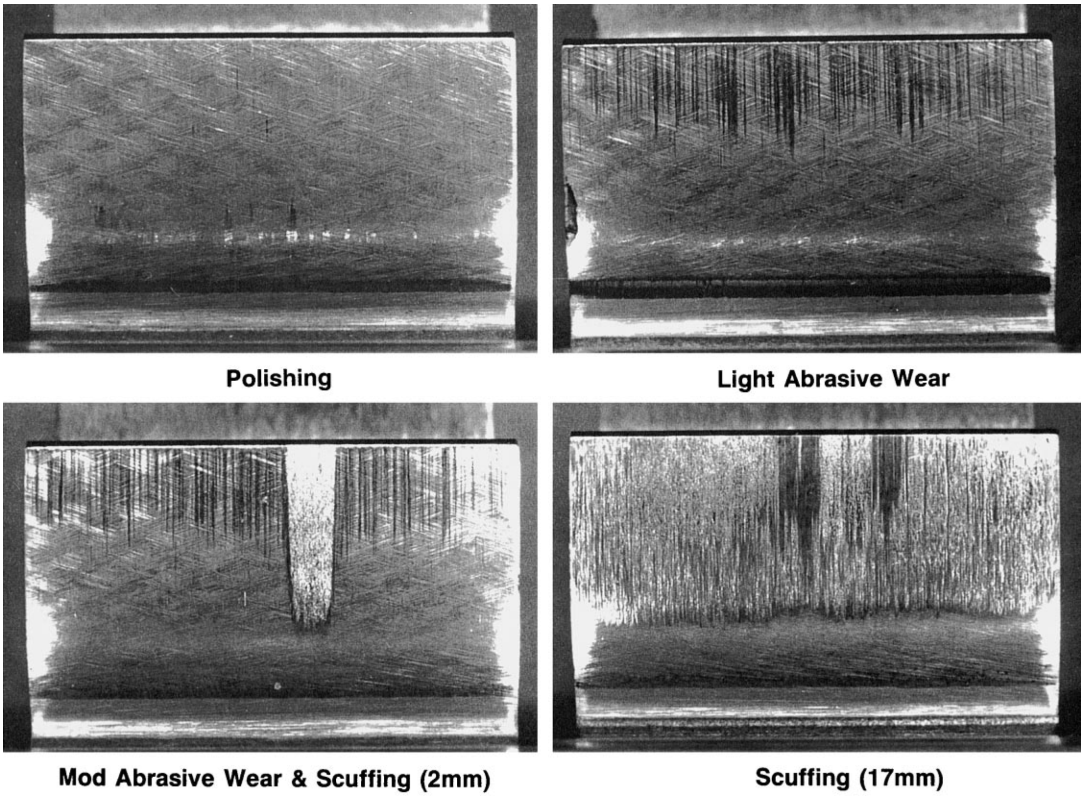


Fig. 1. Examples of gear damage in the FZG test.

analytical data support the original hypothesis that the mechanism is based on surface/additive interactions.

DETA measures a materials response to a time-varying voltage signal, and provides an excellent means to characterize molecular polarization in a complex fluid. The high sensitivity of DETA allows the technique to detect subtle differences in the organic phase that have not been detected by more traditional techniques, such as differential scanning calorimetry.

DETA measures two fundamental electrical characteristics of a material or fluid, capacitance and conductance, as a function of time, temperature and frequency. The capacitive nature is the ability of the material to store an electrical charge and dominates the electrical response at low temperatures. The conductive nature is the ability to transfer an electrical charge and this component becomes important when the material is heated above its melting temperature or at higher temperatures. The capacitance or conductance are important electrical properties that have been correlated to changes in molecular and/or structural state of the material or chemical [1–8]. The actual parameters monitored using DETA are e' or permittivity, which is a measure of the degree of alignment of the molecular dipoles to the applied electric field; and e'' (loss factor), which is proportional to the ac conductivity and reflects the energy required to align the dipoles or to move ions. The ratio of e''/e' is the tangent delta. A plot of tan delta versus log frequency (Debye plot) at constant temperature at a variety of frequencies reveals the relative degree of molecular polarization for a given material or fluid and is inversely related to molecular mobility [9]. The molecular polarization time (tau) is based on the critical peak frequency in a tan delta plot.

2. Experimental

2.1. Chemicals and base oils

The dialkyl hydrogen phosphites used in this study were: dilauryl, dilauryl mixed with di-4-methyl-2-pentyl, di-*iso*-octyl, dicyclohexyl, di-4-methyl-2-pentyl, di-2-ethyl-1-hexyl and dibutyl (see Table 1 for the identifications codes used). The base oils blended with dibutyl hydrogen phosphite and dilauryl hydrogen phosphite were poly-alpha-olefin, hydrorefined, naphthenic, alkylaromatic and an ester base oil (see Table 2 for details).

2.2. FZG test procedure

The FZG visual test method assesses the load-carrying capacity of additive treated oils [1]. The procedure uses a standard four-square gear tester that has torsion bars to provide successively higher levels of torque to a pair of test gears. The FZG gear test machine is operated at a constant speed, e.g. 1450 rpm, in a fixed period (15 min) with successively increasing loads until failure. The failure criteria is reached when the summed total width of scuffing, scoring or adhesive wear damage from all teeth is equal to one gear tooth width or 20 mm. Examples of gear damage in the FZG test are described in Fig. 1.

2.3. X-ray photon spectroscopy (XPS)

Selected gear teeth specimens were sectioned at the base from the ring and transversely through the tooth by electrical discharge machining (EDM). Residual fluids and oils were rinsed from the samples with petroleum ether. Any further removal of surface

Table 2
FZG results of base stock polarity with phosphite variations

Base oil	Dielectric constant	FZG: no additive	FZG: DBPH[a]	FZG: DLPH[b]
Poly-α-olefin	2.12	5	11	8
Hydrorefined	2.18	5	12	8
20–75% Napththenic	2.17	4	12, 11	10, 9
Alkylaromatic	2.32	9	10	7
Ester	3.37	7	8	9

[a] DBPH — dibutyl hydrogen phosphite.

[b] DLPH — dilauryl hydrogen phosphite.

contamination would be done during the argon ion beam sputtering process.

All samples were examined by the surface analytical technique of XPS which yielded wide and narrow scan data [10]. 1 mm spot size with the sample at 45° with respect to the detector and pass energy of 89.50 eV were utilized to collect wide or survey scans. High resolution multiplexes were obtained on all selected elements with a reduced pass energy of 37.5 eV. Spectral peaks were referenced to the adventitious carbon peak at 284.6 eV. Each sample was analyzed in a depth profile mode whereby, successive elemental data was obtained after each sputtering cycle of approximately 2 nm. All individual elemental spectral data was compiled in a montage, a 3D plot of elemental intensity and binding energy versus sputtering cycle (depth). Representative depth profiles and spectral montages are reported (see Figs. 2–5).

2.4. Dielectric thermal analysis (DETA)

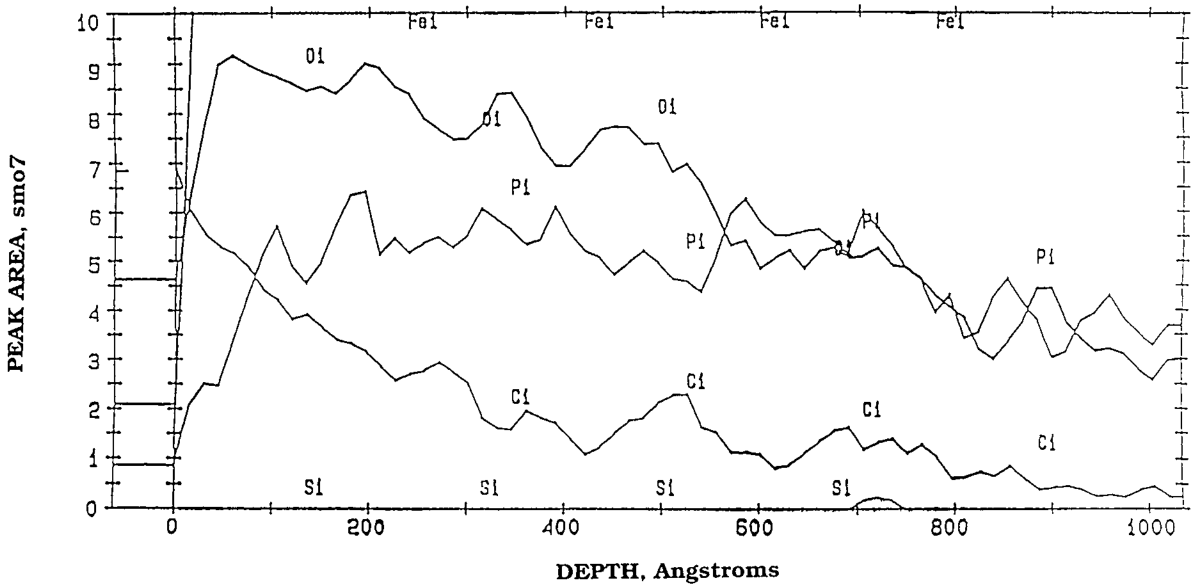
In DETA, the sample is placed in contact with an interdigitated electrode [2]. The electrodes transmit an applied oscillating voltage signal, at a frequency range from 0.1 to 1000 Hz, to the sample and measure the response of the complex fluid to the applied voltage. An isothermal system was used that employs an aluminum chip sensor electrode, 2 mm × 3 mm in size. The dielectrometer operates at a variable temperature, e.g. 40 and 80°C. The chip sensor utilizes 3–4 ml of fluid in air.

Mixtures of dialkyl phosphites, from dibutyl to dilauryl, were prepared at ten times the normal-use concentration in the blends to enhance detection by DETA. The mixtures were also formulated at equivalent phosphorus level.

3. Results and discussion

A number of dialkyl hydrogen phosphites were examined by DETA at 10 times their normal level in a fully formulated oil to enhance detectability. The following phosphites were tested at 80°C by DETA: dibutyl, dicyclohexyl, di-4-methyl-2-pentyl, di-*iso*-octyl, di-2-ethyl-1-hexyl and dilauryl (or di-dodecyl).

The DETA results of the phosphites in a conventional base oil are given in Fig. 6 and Table 1. The



LEGEND: O1 = Oxygen, C1 = Carbon, P1 = Phosphorus, S1 = Sulfur

Fig. 2. Depth profile of gear surface for blend containing dibutyl hydrogen phosphite in hydrorefined base oil.

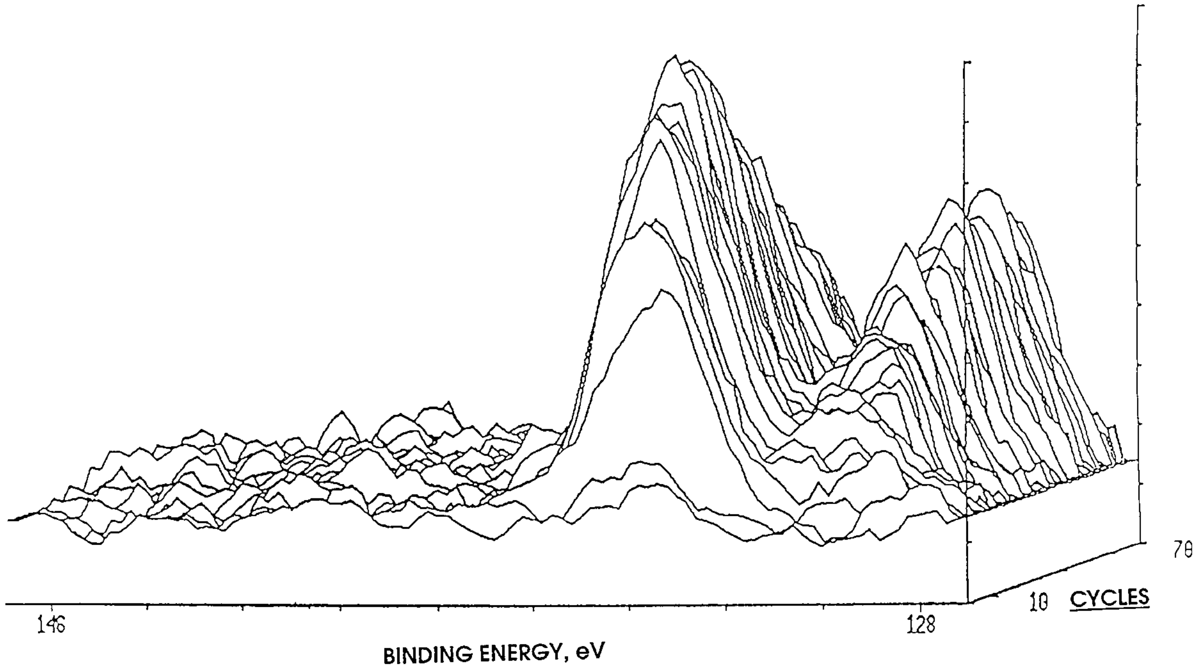
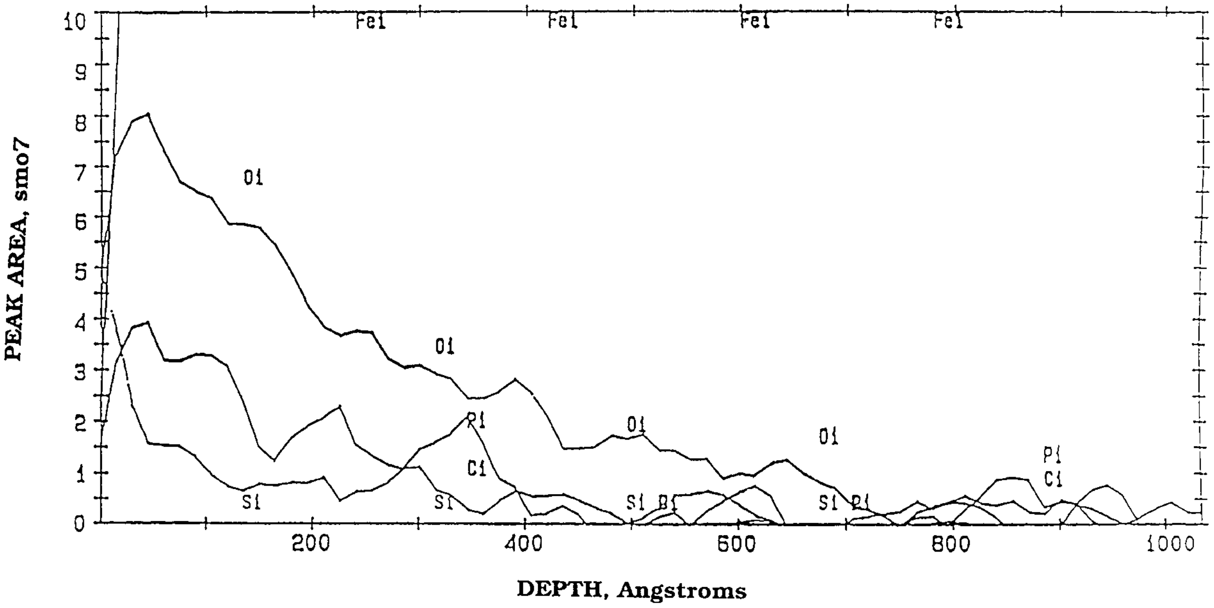


Fig. 3. XPS spectra of gear surface for blend containing dibutyl hydrogen phosphite in hydrorefined base oil.



LEGEND: O1 = Oxygen, C1 = Carbon, P1 = Phosphorus, S1 = Sulfur

Fig. 4. Depth profile of gear surface for blend containing dilauryl hydrogen phosphite in hydrorefined base oil.

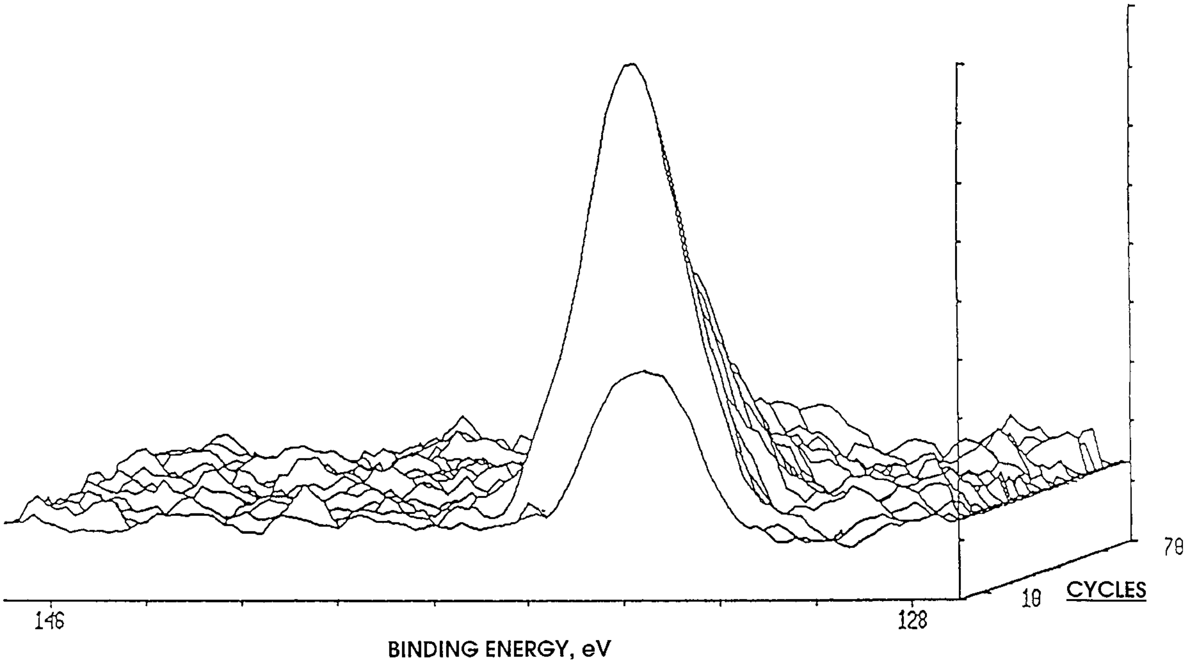


Fig. 5. XPS spectra of gear surface for blend containing dilauryl hydrogen phosphite in hydrorefined base oil.

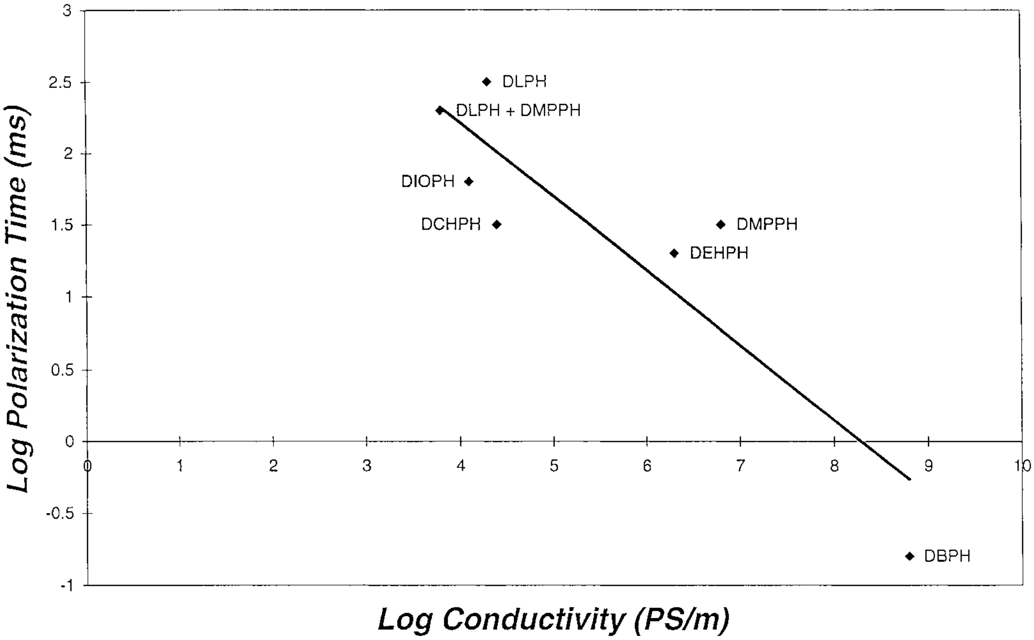


Fig. 6. Dialkyl hydrogen phosphites: log polarization time vs. log conductivity ($R^2 = 0.79$).

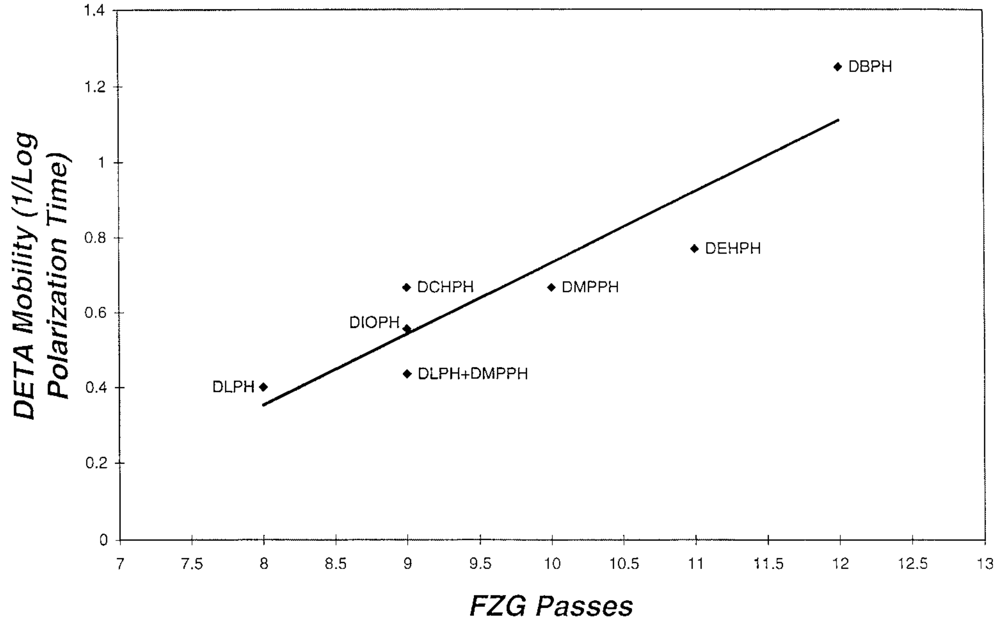


Fig. 7. Dialkyl hydrogen phosphites: DETA mobility vs. FZG gear stage passes ($R^2 = 0.84$).

faster polarization times [inversely related to tan delta peak frequency] and higher conductivity are associated with the dibutyl hydrogen phosphite structure. The dielectric mobility (inverse polarization times) and conductivity decreased as the molecular weight of the alkyl group increased up to dilauryl hydrogen phosphite (a dodecyl phosphite). In Fig. 7 the dielectric mobility of the phosphite mixtures is directly related to the pass stage of the fully formulated blends in the FZG test and inversely related to the molecular weight of the phosphite. The precision of the log of the polarization time (ms) is ±0.04 and ±8% for the polarization time. The precision of the log of the conductivity (pS/m) is ±0.03 and ±6% for the conductivity.

Selected sectioned FZG gear teeth were examined by XPS to determine the composition and thickness of wear protection layers formed in situ. The goal of this portion of the study was to correlate the XPS data of the surface to the FZG test results as presented in Table 2.

The XPS analyses entailed depth profiling the specimens until the substrate is the only detectable signal. Depth profiles began by collecting data, peak intensities and areas, for: C, O, P, S and Fe. The sample is then bombarded by an argon ion beam (sputtering) to remove a portion of the surface layer, 2 nm at a time, and then the same elemental regions, as previously denoted, are re-run. This ion bombardment process is referred to as "sputtering". The process takes several hours, but at the end the only detectable remaining signal is due to the iron substrate. Therefore, the analysis has worked its way through the entire surface layer(s). The collected data reveals the layer thickness and composition at any point in time. Quantification can be performed with results stated in terms of atomic concentration. Representative depth profile plots are reported for the first pair of samples. The figure is an expansion of the data along the abscissa by forcing iron to the upper axis.

3.1. Hydrorefined base oil blend

Without additive package, the hydrorefined base oil achieved only a five pass in the FZG test, this is an unacceptable result for any practical fluid (Figs. 1–5). The first three base oils without additives had similar unacceptable FZG test results (Table 2). They all had similar values for the dielectric constant at 25 or 80°C. The FZG and dielectric results indicate that these oils were apolar and afforded minimal wear protection without additives. When the formulated blends, containing additives, were tested the results improved dramatically.

The blend containing dibutyl hydrogen phosphite had a 12-stage pass result which was a more acceptable FZG result indicating greater wear protection. The thickness of the surface layer measured in excess of 100 nm (see Fig. 2). Quantification after five cycles yielded a 3.3% phosphorus content. The most interesting event for this analysis was the detection of two phosphorus peaks in the XPS spectrum. One peak at approximately 134 eV was due to surface phosphate formation [8,11,12]. The second peak at about 130 eV can be explained best as an iron phosphide [10,11]. All of the other blends showed traces of phosphide formation, however, it was most prominent in this instance. Some sulfide formation was observed, for the blend contained 0.02–0.03% sulfur, even though no sulfur containing additives were used in this blend.

An eight-pass result was observed when dilauryl hydrogen phosphite was added to a base oil. This is considered an unacceptable FZG fluid result. The depth profile of the gear surface was completed and indicated a surface layer of approximately 75 nm (Figs. 6 and 7). After five sputtering cycles the amount of phosphorus was 6.0%. This was greater than obtained with the blend containing dibutyl hydrogen phosphite.

A diminished phosphorus surface layer resulted from the use of a dilauryl hydrogen phosphite blend and was due to steric hindrance of the larger alkyl group compared to the dibutyl hydrogen phosphite alkyl group. Significantly less lauryl phosphite molecules can be packed onto a given surface than butyl phosphite molecules. The result was less phosphorus content and a thinner reacted layer. The combined effect produced the noted lower number for FZG pass rating and an unacceptable FZG test with the dilauryl hydrogen phosphite blend.

3.2. Naphthenics base oil blend

This base oil (with 20–75% naphthenics) had a dielectric constant similar to the hydrorefined oil and exhibited analogous unacceptable FZG wear results in the absence of additive treatment.

The dibutyl hydrogen phosphite package in this oil yielded a 12-stage pass on the first run and 11-stage pass on the second run, an acceptable and repeatable wear test result. The surface layer of the gear after five cycles was approximately 90 nm with a phosphorus content of 6.7%. The main component was identified as a phosphate with a trace of the phosphide. Sulfidation was noted again in the spectra. The blend contained 0.26% sulfur, as determined by inductively coupled plasma (ICP) analysis, which was derived from the base oil. The end-of-test (EOT) oil contained 0.16% sulfur which indicated either surface consumption of sulfur, blend contamination or a questionable ICP result. The phosphorus content was measured in all blends and EOT oils. Very little difference in phosphorus level was noted; it appeared that it does not require much phosphorus to react with the surface in the 0.1 nm regime. Therefore, it is felt that the questionable sulfur level was not attributable to the surface reactions.

A duplicate surface examination was performed on another gear tooth specimen and yielded a similar layer thickness. The repeatability of the XPS results was verified. It can be used to discriminate among the various FZG gear samples. It can also be used to show a correlation with the FZG pass results. The reverse side of this gear tooth, the non-contact surface, was analyzed and found to contain no measurable phosphorus throughout the depth profile. Examining both sides of the gear tooth highlights differences observed on the wear loaded side.

The dilauryl hydrogen phosphite additive system gave a 10-stage pass with a 9-stage pass repeat in this base oil. This FZG result is evaluated as unacceptable by most original equipment manufacturers (OEMs). The surface layer measured about 90 nm, but with a phosphorus content of 0.5%. This is significantly lower than the phosphorus content measured for the dibutyl hydrogen phosphite blend. Absolute quantification of the phosphorus content is difficult. However, based on peak areas and signal to noise ratios there was less phosphorus present throughout the surface film with dilauryl hydrogen phosphite than dibutyl hydrogen phosphite. It appears that steric considerations dictated the surface phosphorus content. Sulfate/sulfonate and sulfidation were also observed at approximately the same level as in the other blends. A 0.19% sulfur level was measured in the dilauryl hydrogen phosphite blend and 0.16% in the EOT oil. There was a 0.07% sulfur difference between the two blends although their EOT oil data was identical.

3.3. Ester base oil blends

This base oil had the highest dielectric constant, 3.37 at 25 and 80°C, of all the blends in the matrix. This fluid is more polar than any of the other base oils. The pure base oil without additives gave a seven-stage pass in the FZG test, with added dibutyl hydrogen phosphite an eight-stage pass and with added dilauryl hydrogen phosphite a nine-stage pass. These test results are considered statistically the same with the repeatability of plus or minus one-stage pass being the accepted norm.

What occurred in the ester base oil system was competing surface reactions between the ester and phosphorus additive. The ferrous gear surface is amphoteric, capable of reacting either as an acid or base, and can interact with adsorbates. The ester, a weak base, is the major solution component. The solvent was able to mostly preclude the phosphorus additive which is acidic (and present at only 0.05% by weight) from reacting with the surface. The surface layer in both the dibutyl hydrogen phosphite and dilauryl hydrogen phosphite blends measured 60 nm; the thinnest layers observed in this study. The effect was the lowest stage passes in the matrix due to the thin reacted layer not affording sufficient wear protection. After the phosphorus signal became undetectable there remained a considerable amount of carbon and oxygen, probably the ester, on the surface. The presence of Oxygen was attributable to the additive, the oil and the surface oxide. However, in all of the other base oil blends, when the phosphorus level goes to zero so does the oxygen and carbon.

The phosphorus content in the surface layer when dibutyl hydrogen phosphite was used was 3% and for the dilauryl hydrogen phosphite blend it was 4%. Even though these blends contained 0.004% sulfur, evidence of sulfate and sulfide were evident. Measurements on the EOT oils revealed no sulfur. It was apparent throughout this study that even minute amounts of sulfur compounds in the base oils will react synergistically with the phosphorus compounds in the formation of surface wear protection layers. The amount and thickness of the reacted surface layers were the determining factors in FZG stage pass results.

4. Conclusions

Higher dielectric conductivity and surfactancy differentiated dibutyl hydrogen phosphite from dilauryl hydrogen phosphite in the hydrocarbon test fluid. A linear relationship exists between the molecular mass of the alkyl phosphite chemicals, their dielectric characteristics and the ASTM D5182 wear test results. Dibutyl hydrogen phosphite delivered more phosphorus to the gear steel surface. The surface phosphorus content (as detected by XPS) was more uniform and at a greater depth for the butyl than the dodecyl phosphite.

Dibutyl hydrogen phosphite was the most surface active phosphite and formed a reaction film on the gear tooth surface to a greater depth than any of the other dialkyl phosphites studied, including dilauryl hydrogen phosphite. Good wear performance was observed for dibutyl hydrogen phosphite. The dielectric conductivity (mobility) of the other hexyl to dodecyl dialkyl phosphites varied directly with ASTM test acceptability, i.e. the number of stage passes decreased with increasing molecular mass and steric size.

Small dialkyl chain length phosphites provide higher surface loading due to minimal steric hindrance factors and result in covalently bound films. The phosphorus content and thickness of reacted thin film ($\sim 10^{-7}$ m) provide the necessary wear protection to achieve an ASTM stage 12 pass. Both phosphate and phosphide surface chemistries were identified and led to enhanced ASTM D5182 performance.

Competing surface reactions take place when higher polarity hydrocarbons (ester) were used. This interaction with the polar oxide surface is an acid/base interaction and precludes much of the phosphorus surface chemistry reactions.

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