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Richard J. Bosch and Darrell C. Fee
Phosphorus Derivatives Inc.

Theodore W. Selby
Savant Inc.

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ABSTRACT

Previous studies have shown that there is a lack of correlation between engine oil phosphorus volatility with both oil volatility and the initial level of phosphorus in the engine oil. On the other hand, these and more recent studies have illustrated that phosphorus volatility is related to temperature, other additives in the oil, and the chemical composition of the zinc di-organo di-thio phosphate (ZDDP) used. This paper reports the results of continued studies associated with engine oil phosphorus volatility, with the ultimate goal of reducing the amount of phosphorus that deposits on catalytic converters adversely affecting catalyst function.

INTRODUCTION AND BACKGROUND

Zinc Di(organo) Di(thio) Phosphates, commonly referred to as ZDDPs, are the most widely used and effective anti-wear/anti-oxidation additives in engine oil. Phosphorus contained in the ZDDP molecules has been shown to partially volatilize during engine operation [1]. However, volatile phosphorus in the exhaust stream degrades the function of the exhaust catalytic converter and, as a consequence, there have been decisions to reduce both the volatility of the engine oil and the initial amount of ZDDP in engine oil.

In response to the growing importance of engine oil volatility [2-4], the Selby-Noack instrument – a new approach to the earlier protocol developed by Noack [2] – was developed during the 1990s [5]. The Selby-Noack instrument also measures the volatility of motor oil. However, in addition, it collects all of the volatile material generated in the test. During the development and early use of the Selby-Noack test, it was reported that phosphorus-containing compounds were present in the volatiles obtained from the procedure [6]. With the growing interest in the subject of volatile engine oil and phosphorus, in 1993 the Institute of Materials (IOM) incorporated the Selby-Noack test as part of the database they publish on worldwide oil analyses [7] and, with the information showing that volatile phosphorus was produced in the Selby-Noack test [6], also began inclusion of the concentration of phosphorus in the volatile material

generated in 1996 (initial phosphorus concentration of the fresh oil was always a part of the IOM database).

Subsequently, in 2002, a paper was published on the phosphorus volatility results that appeared in the IOM database from 1999-2001 [8]. Contrary to expectations, it was found that phosphorus volatility was neither related to engine oil volatility nor to the phosphorus content in the unused engine oil. It was speculated that this lack of correlation with initial phosphorus additive concentration might be reasonably explained by either or both 1) the effects of the other engine oil additives and 2) the variations in the chemistry of the phosphorus additives.

In this same paper [8], a parameter called the Phosphorus Emission Index (PEI) was introduced which compares the phosphorus volatilization tendency of engine oils on the basis of milligrams of volatile phosphorus produced per liter of engine oil during the Selby-Noack test protocol.

A 2002 field study conducted by Ford Motor Company of catalyst degradation by phosphorus-containing oils [9] was subsequently shown to correlate with the PEI data generated from the Selby-Noack bench test. However, after the correlation data had been reported, it was later shown that the phosphorus present in these oils was identical in composition and content. Thus, the correlation interestingly was primarily related to the other oil additives [10] and confirmed the prior speculation about the importance of the effects of other engine oil additives.

In 2005, two papers [11,12] were published on work that demonstrated the feasibility of using the Selby-Noack method to measure reproducibly the amount of phosphorus that volatilizes from a variety of engine oils at 250°C. These investigations also included the use of ³¹P NMR to further study the phosphorus-containing components in both the Volatiles and the Residues remaining after the Selby-Noack experiment. These results showed that the phosphorus components in both the volatiles and the residue are very reproducibly produced and dependent on the specific ZDDP used to formulate the engine oils. The volatile components were shown to consist of the ZDDP itself (or the corresponding dithioacid), trace impurities in the ZDDP, and ZDDP thermal decomposition products.

One of the objectives of these studies was to examine the premise concerning whether variation in the chemistry of phosphorus-containing ZDDP additives also affects phosphorus volatility from the formulated engine oil. Further studies were performed with ZDDPs generated in our labs from 2-ethylhexanol and 2-methyl-4-pentanol and formulated into a 'basestock' consisting of fully formulated GF-3 oil – except for ZDDP. The latter 'basestock' material was provided to us by Chevron Oronite LLC and was of significant assistance in performing these studies.

When subjected to Selby-Noack testing at 250°C, the studies showed that the Secondary ZDDP (synthesized from 2-methyl-4-pentanol) decomposed much faster than the Primary ZDDP (synthesized from 2-ethylhexanol). In fact the Secondary ZDDP had completely decomposed to inorganic phosphate after 10 minutes at 250°C – much sooner than we had anticipated.

In October 2005, an oral presentation was given at the SAE Fall Powertrain and Fluid Systems [13]. The presentation included work on extending our studies to GF-4 oils and also the initiation of explorations of temperatures besides 250°C, particularly 165°C. The highlights from this previous talk are incorporated in the present paper.

EXPERIMENTAL

General Protocol for Selby-Noack PEI Tests

In all Noack-protocol tests, 65 grams of oil are heated in air in a metal or glass cup for one hour at 250°C under a slight vacuum of 20mm_{water} and the percent loss of sample mass measured.

A sketch identifying the important test components of the Tannas Selby-Noack is shown in Figure 1. To prepare for test, the masses of the empty volatilization vessel (Volatilizer) and the volatiles collection vessel (Collector) are obtained. Sixty-five grams of the oil to be examined (the normal amount for a Noack test) are weighed into the Volatilizer. If desired or required for adequate

collection volume, 10 grams of a co-volatile hydrocarbon fluid is added and the total mass of Volatilizer, test oil, and co-volatile recorded.

The Volatilizer and Collector are then reassembled into the instrument, a correct vacuum (20mm_{water}) established, and whatever Volatilizer heating and timing program desired is selected from those set up on the temperature controller. The absolute pressure of the vacuum is recorded during the test to assure that proper operation is maintained. This is of considerable importance during longer running test protocols.

When the test protocol is completed, the Volatiles cup and Collector are reweighed. All of the volatilized material and the residual oil are collected in vials and small samples taken for various analyses including elemental analysis and nuclear magnetic resonance (NMR) spectroscopy. The unused oil is also sampled for similar analyses to provide comparative analytical information, particularly important for NMR studies.

For purposes of calculating the PEI value, the phosphorus concentration in the volatilized material is obtained. From this information, milligrams of phosphorus are calculated per liter of the unused oil.

In the work of in this paper, the PEI notation will include both temperature and time. For example, the notation for the protocol of exposing the test oil for one hour at 250°C is 'PEI₂₅₀₋₁' while that for exposing the test oil for 16 hours at 165°C is 'PEI₁₆₅₋₁₆', etc.

Elemental Analysis

For the elemental analyses reported in this paper, the Leeman Model CP-1000 inductively-coupled plasma (ICP) sequential spectrometer was used. Sample size required for the analysis was only a few tenths of a gram for most of the work reported, although higher concentrations were sometimes used where greater sensitivity and precision was desired.

NMR Analysis

Small samples of the original oils, the volatiles, and the residuals obtained from the Selby-Noack tests were analyzed by phosphorus-31 (³¹P) NMR spectrometry at Washington University (St. Louis, MO). The spectra were obtained either on a 500 MHz Varian NMR equipped with a 10-mm probe or on a 600 MHz Varian NMR equipped with a 5-mm probe. Samples were diluted with 10-15% chloroform-d (CDC13), which also served as an internal reference for establishing spectral positions.

The individual phosphorus-containing species are identified by a "chemical shift" in the ³¹P peak because of the different chemical environment around the phosphorus atom in phosphorus-containing oil components and decomposition fragments compared to the phosphorus atom in phosphoric acid (H₃PO₄). This shift is reported in units of 'ppm' (a term that in NMR has no relation to concentration). By definition, the chemical shift for the phosphoric acid standard is zero ppm. The average data accumulation time to obtain these NMR spectra was one hour.

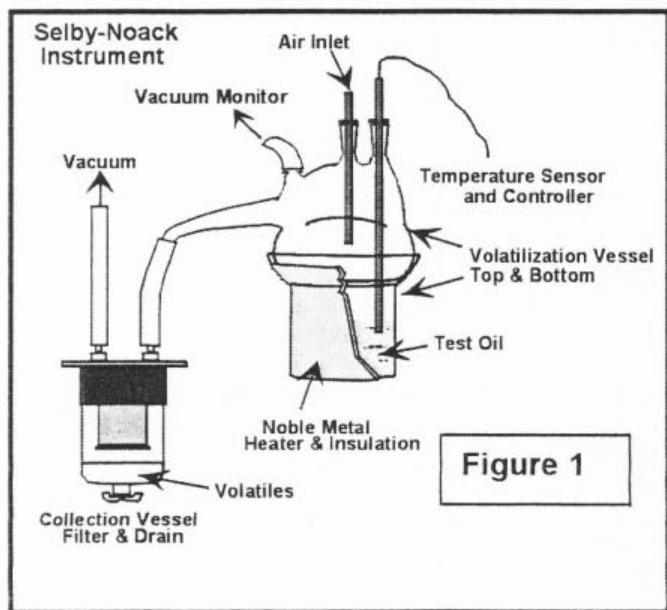


Figure 1

RESULTS AND DISCUSSION

PEI₂₅₀₋₁ and PEI₁₆₅₋₁ of Five Formulated Oils

To further investigate the volatilization of phosphorus, a study was made to determine the effect of temperature on PEI values using both PEI₂₅₀₋₁ and PEI₁₆₅₋₁ protocols on commercial engine oils. These were chosen to have high PEI₂₅₀₋₁ values so that differences in phosphorus volatility would be clearly evident. The two temperatures represent 1) ring-belt and 2) circulating oil temperature under severe engine operation.

Five motor oil samples with high PEI₂₅₀₋₁ values were selected from the IOM database and were subjected to the Selby-Noack PEI₁₆₅₋₁ protocol. Results are shown in Figure 2.

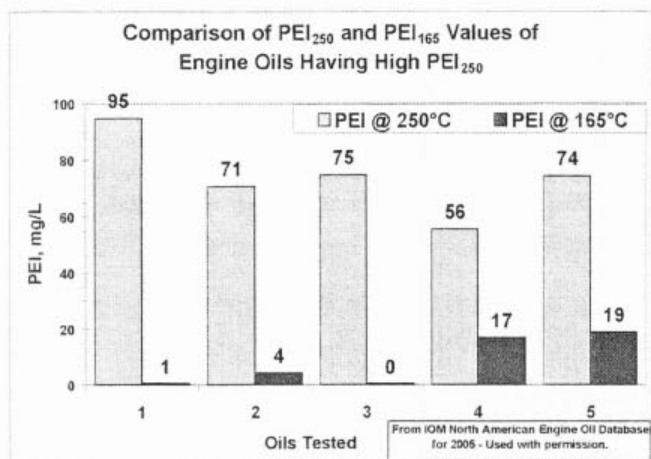


Fig. 2: Comparison of PEI₂₅₀₋₁ and PEI₁₆₅₋₁ values of engine oils having high PEI₂₅₀₋₁ values.

It is evident that PEI₁₆₅₋₁ values obtained have no general correlation with the PEI₂₅₀₋₁ values given in the IOM database. As is well known, thermal decomposition of ZDDPs in engine oils is temperature dependent, and this study shows that the effect of such temperature dependence may vary widely with the formulation of the oil and the choice and chemistry of the ZDDP.

Study of Four ILSAC GF-4 Engine Oils

Since the previous five oils were selected by their atypically high PEI₂₅₀₋₁ values, the same experiments were repeated on four oils meeting ILSAC GF-4 specifications as well as having considerably lower PEI₂₅₀₋₁ values. Results are shown in Figure 3.

Two of the oils, Oil C and Oil D, carried the same brand name and other technical property identification (viscosity grade, API quality designation, and ILSAC number, etc.) but were marketed in two widely separated locations in North America.

As with the previous five oils, PEI₁₆₅₋₁ values are low when compared to PEI₂₅₀₋₁. Replicate analyses for oils A and B were run at 165°C and illustrate the repeatability of the PEI test protocol at this temperature. However, the most interesting information was the magnitude of change in the decrease of volatilized phosphorus shown

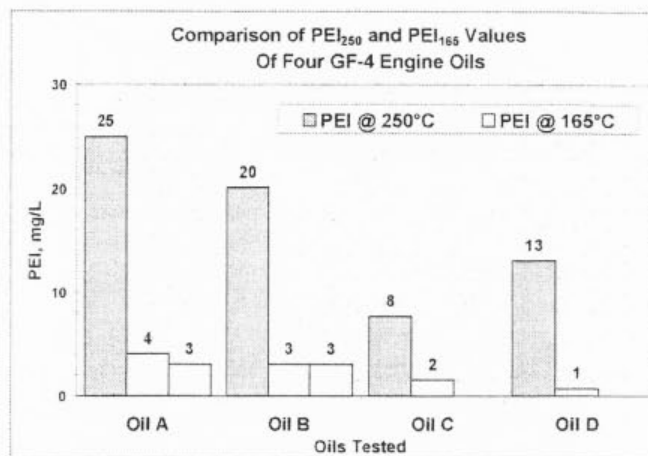


Fig. 3: PEI₂₅₀₋₁ and PEI₁₆₅₋₁ analyses of four ILSAC GF-4 engine oils.

by the PEI analyses at these two temperatures. Obviously, a significant transition in ZDDP decomposition occurred between these two temperatures and NMR was considered a strong tool to use for investigation of these differences.

NMR ³¹P Results on Oils from PEI Analyses

Preliminary Comparison Using GF-4 Oil B – A series of ³¹P NMR experiments were run on GF-4 Oil B (Figure 3) to appraise the differences between the spectra of samples obtained from the PEI protocols at 250°C and 165°C. These spectra were taken of the original oil, the volatiles, and the residuals obtained from the Selby-Noack PEI analyses. Results of these NMR studies are shown in Figures 4 (PEI₁₆₅₋₁ data) and 5 (PEI₂₅₀₋₁ data).

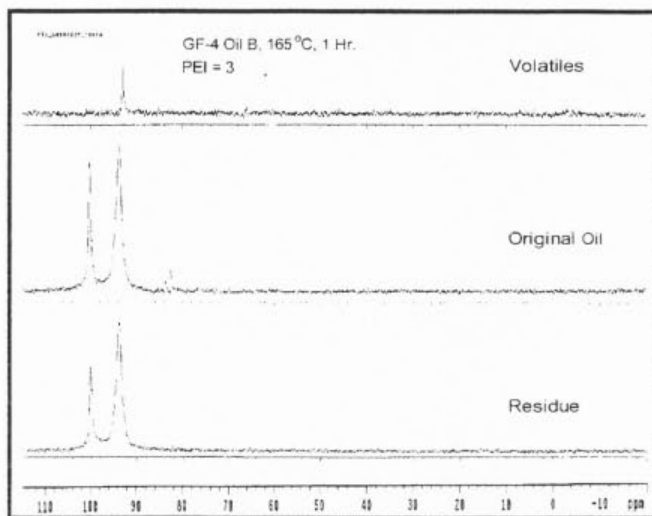


Fig. 4 – NMR ³¹P spectra of original oil, Volatiles and Residue generated in PEI₁₆₅₋₁ analysis of GF-4 Oil B.

In Figure 4, the NMR spectrum of the residue is very similar to the original oil sample and the volatiles appear as one peak at approximately 93 ppm. This peak occurs at the same place in the spectrum as one of the peaks in the original oil. All of this is indicative that the ZDDP had not changed much over the course of a one-hour exposure. This is also supported by the relatively low PEI₁₆₅₋₁ value of 3.

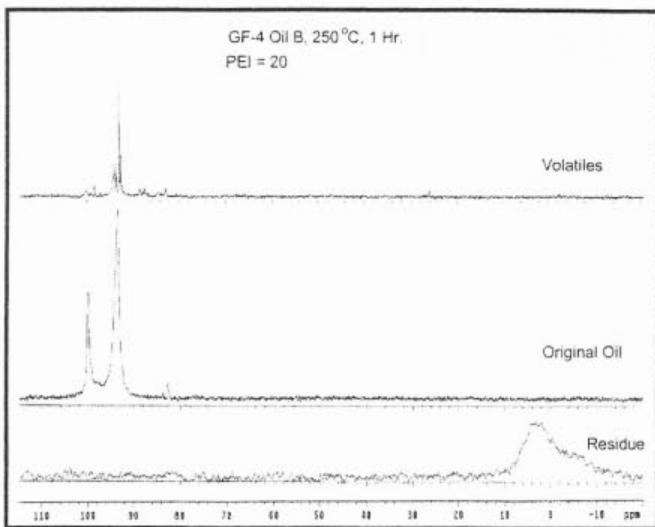


Fig. 5: NMR ^{31}P spectra of original oil, volatiles and residuals generated in PEI_{250-1} analysis of GF-4 Oil B.

In Figure 5, for PEI_{250-1} , the appearance of both the volatiles and residual spectra are quite different than that shown using the PEI_{165-1} protocol. Regarding the volatiles spectra, there are several additional peaks in the 85 to 105 ppm range, which, when combined, give the considerably larger PEI value of 20.

It is interesting and significant that at 250°C the NMR spectrum of the residue no longer has any evidence of peaks similar to the original oil particularly evident in the range of 90 to 105 ppm. Instead the residual spectrum shows only a single broad peak from 10 to -10 ppm. This broad, single peak is believed to indicate inorganic phosphates formed by the complete thermal decomposition of the ZDDP used in the formulation. In contrast, Figure 4 shows none of these presumed inorganic phosphates.

It may reasonably be inferred from these tests that the ZDDP is virtually completely decomposed at 250°C. Contrasted to the PEI_{165-1} value of 3, the PEI_{250-1} value of 20 confirms much more ZDDP decomposition. In contrast, Figure 4 shows none of the inorganic phosphates of Figure 5.

The PEI portion of this study raised the question of what PEI values would result with experimental conditions more severe than PEI_{165-1} and less severe than PEI_{250-1} . It was reasonable that PEI values should increase in some manner between these two test limits but the form that the transitions might take was important information regarding ZDDP decomposition.

PEI Temperature Study

Four oils, including Oils 1 and 3 from Figure 2 and Oils C and D from Figure 3, were subjected to a PEI temperature-effect study at temperatures ranging from 165° to 250°C. All PEI tests were run for one hour in this study. The results of these experiments are shown in Figure 6.

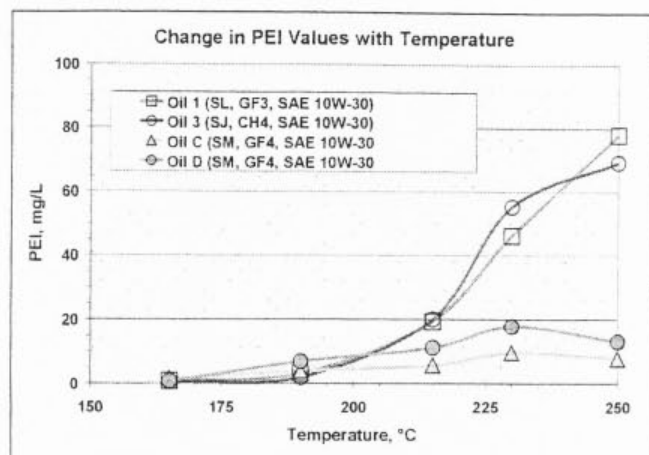


Fig. 6 – Change in one-hour PEI values with changes in temperature for four oils.

For Oils 1 and 3, which were chosen to have high values of PEI_{250-1} , the PEI values across the temperature range from 165° to 250°C increased significantly, but not linearly, with temperature. In contrast, the GF-4 Oils C and D, showed much lower change with temperature and actually showed a somewhat surprising maximum in PEI values at about 230°C. These results show that variation of phosphorus volatility may or may not be strongly temperature dependent at least up to 250°C.

PEI Exposure Time Study

The foregoing temperature-effect study led to the question of the effect of increasing time of exposure at a given temperature.

The PEIs of Oils 1 and 3 were measured at 165°C at various exposure times ranging from 1 hour up to 48 hours. These results are given in Figure 7.

Not unexpectedly, the PEI values increased with longer exposures through the entire range studied. However, it was of interest to find that the phosphorus volatilized at 165°C for 48 hours was higher than that found at 250°C for one hour. This suggested that the phosphorus decomposition path was different at this lower

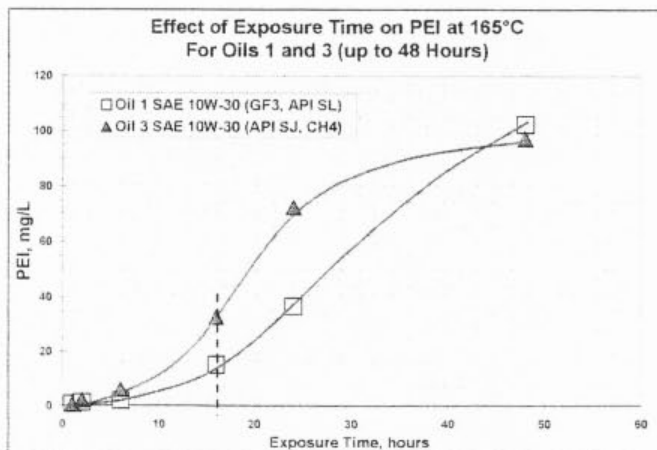


Fig. 7: Effect of exposure time on PEI at 165 C for Oils 1 and 3.

temperature of exposure. Moreover, the rate of phosphorus decomposition was not linear but accelerated with increased exposure time (but at different rates) for both Oils 1 and 3. NMR ^{31}P spectra in the temperature range where significant changes in phosphorus volatility were occurring were obtained from samples of Oil 3 from PEI analyses at 6, 16, and 24 hours (PEI_{165-6} , PEI_{165-16} , and PEI_{165-24}). These results are shown in Figures 8 to 10 respectively.

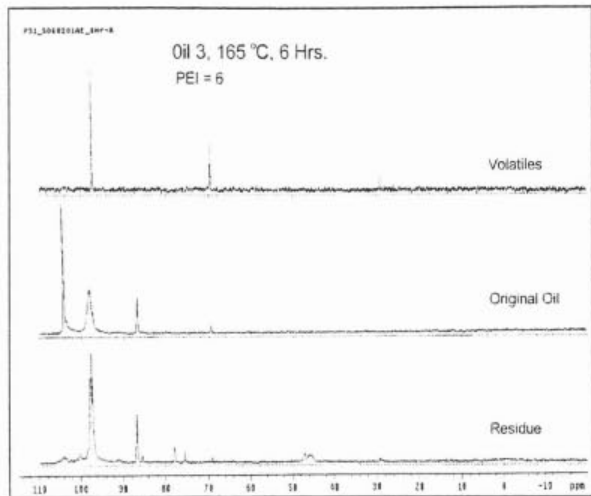


Fig. 8: ^{31}P NMR spectra of original oil, Volatiles and Residue generated during the PEI_{165-6} test of Oil 3 after 6 hours exposure.

In Figure 8 using protocol PEI_{165-6} , (which produces a PEI value of 6), the NMR spectra reveal that much is happening regarding ZDDP transformation. The original oil shows three significant peaks at 105, 97, and 87 ppm. One of these peaks (at 105 ppm) is almost gone in the Residue but the peaks at 98 and 87 have increased and several new peaks have appeared at 78, 76, 69, 47, 46 (broad), and 29 ppm. There is also a slight lifting in the spectra at approximately 0 ppm. The Volatiles spectrum is interesting in that there are three significant peaks at approximately 97, 69, and 29 ppm. These peaks correspond to three of the peaks in the Residue sample, (which has, as noted above, multiple other peaks).

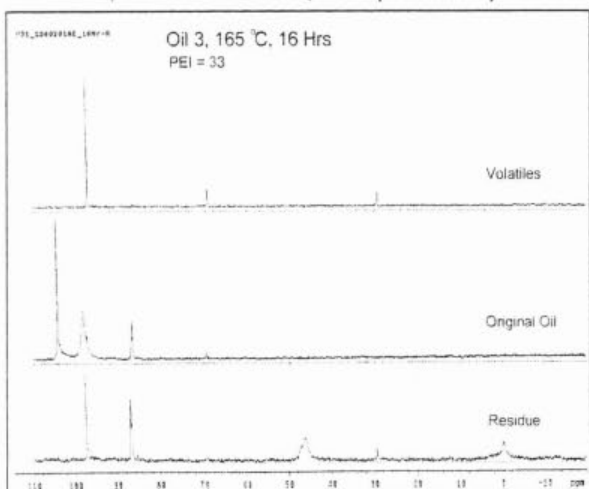


Fig. 9: ^{31}P NMR spectra of original oil, Volatiles and Residue generated during the PEI_{165-16} test of Oil 3 after 16 hours exposure.

In Figure 9 using protocol PEI_{165-16} , the PEI increases significantly to 33 and significant changes begin to appear in the Residue and Volatiles spectra. In regard to the Residue, peaks at 98, 87, and 78 ppm – all in the original spectrum – are still present. However, the 46/47 ppm peak has broadened and grown as has the smaller peak at 29 ppm. A peak at 0 ppm is now clearly manifest. For the Volatiles spectrum, the peaks shown remain the same in location but the peak at 69 ppm has grown smaller and that at 29 ppm increased.

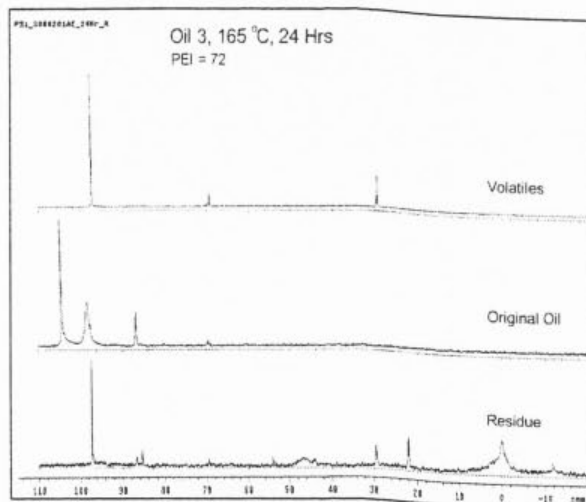


Fig. 10: ^{31}P NMR spectra of original oil, Volatiles and Residue generated during the PEI_{165-24} test of Oil 3 after 24 hours exposure.

In Figure 10 protocol PEI_{165-24} was used and produced a value of 72. The Residue peaks have again increased in number – 98, 87, 85, 54, 44-49, 29, 22, and 0 (broad) ppm. The latter has grown considerably. In the Volatiles spectrum, the peak at 29 ppm has increased and that at 69 ppm has diminished.

Additional study of these changes by extending the length of the time of the PEI experiments and careful integration of the various peaks in the NMR could be enlightening and potentially a subject for future work.

With the information gained in this portion of the study, it seemed as though gathering information at 16 hours was an appropriate time period in which both significant volatility and ZDDP transformation was occurring yet the time of running the test was not onerous. This choice is shown in Figure 7 by the vertical dashed line.

Lower Temperature 16-Hour PEI Study

With the information brought by the increased time study on PEI, it was thought to be valuable to look at the effect of temperatures of 165°C and lower using the 16-hour protocol. GF-4 Engine oils C and D were used to study to determine the results of PEI_{165-16} , PEI_{140-16} , and PEI_{120-16} . These results are compared with the results of Selby-Noack runs performed earlier at 250°C for one hour and are shown in Figure 11.

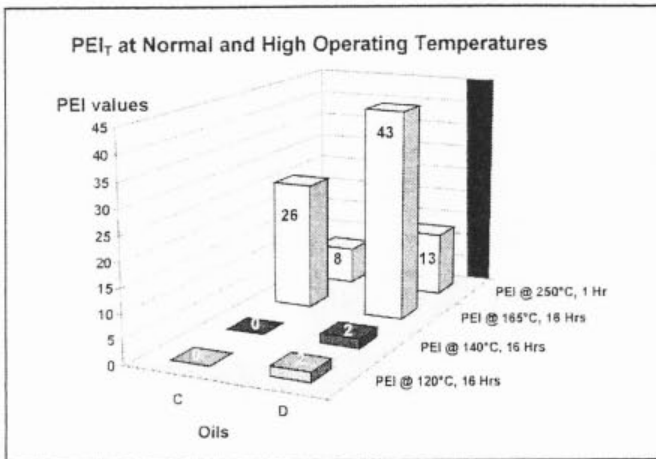


Fig. 11: Comparison of PEI levels at 16 hours and lower temperatures to that at 250°C for two GF-4 oils of similar composition.

The PEIs measured at 120°C and 140°C were very low. However, a large increase in PEIs was observed at 165°C, considerably higher than those at 250°C for 1 hour as shown in this figure.

It was apparent from this work that conditions of the PEI_{165-16} protocol should yield significant amounts of volatile phosphorus compounds resulting in informative PEI values. However the conditions were not so onerous as to lead to complete decomposition of the ZDDPs in the engine oil samples to inorganic phosphates.

Temperature Effects on Primary and Secondary ZDDP Decomposition

As noted under the previous section on Background, part of earlier studies involved the synthesis of ZDDP samples from 2-ethylhexanol, one of the primary alcohols (used in forming a so-called Primary ZDDP), and 4-methyl-2-pentanol, one of the secondary alcohols (forming a Secondary ZDDP). Again as noted, these ZDDPs were added to an otherwise fully formulated ILSAC GF-3 type engine oil lacking only ZDDP.

In considering previous studies at 250°C reported by us, the results were unexpected. ZDDPs made with primary alcohols were known to be more thermally stable than ZDDPs made with secondary alcohols [1]. However, the PEI_{250-1} values were higher for the ZDDPs made from the primary alcohol.

NMR work gave the answer in that the Secondary ZDDP was quickly converted to inorganic phosphate. Thus, it is reasonable that the low PEI value of this oil sample was caused by rapid decomposition of the Secondary ZDDP to inorganic and, thus, non-volatile phosphates.

With this in mind, it seemed appropriate to measure the PEI_{165-16} values for these two oils (Oils A and C from earlier work [11,12] but indicated here as Oils E and F to avoid confusion).

Results of these experiments are presented in Table 1. PEI experiments were run on both oils under the protocols of PEI_{165-1} , PEI_{165-16} , and PEI_{250-1} – the latter a repeat of work reported in an earlier 2005 paper.

Table 1 -- PEI results on GF-3 Oils E and F

Sample	Oil E	Temp, °C	Time Hours	PEI mg/L
Primary ZDDP		165	1	0
Primary ZDDP		165	16	6
Primary ZDDP		250	1	14
Primary ZDDP (2004 paper)		250	1	16
Oil F				
Secondary ZDDP		165	1	1
Secondary ZDDP		165	16	13
Secondary ZDDP		250	1	4
Secondary ZDDP (2004 paper)		250	1	2

It is evident from Table 1 that there are significant differences in phosphorus volatility for the Primary and Secondary ZDDPs of Oils E and F, respectively, as a consequence of the temperature of exposure.

In the PEI_{165-1} protocol studies of the Primary ZDDP Oil E, both PEI and ^{31}P NMR data show that no phosphorus-containing compounds were evolved. Under protocol PEI_{165-16} some phosphorus volatiles were detected and much more of these volatiles were produced during the PEI_{250-1} protocol (which PEI value agreed with that of the study of Oil E reported in 2005).

PEI_{165-1} studies of the Secondary ZDDP Oil F, showed a very small amount of phosphorus-containing compounds evolved as measured by PEI and ^{31}P NMR. Considerably more phosphorus-containing compounds were detected after using the PEI_{165-16} protocol but relatively little using the PEI_{250-1} protocol (which value agreed with that of the 2004 study of this Oil F).

Thus, there is a complete reversal in their respective responses to the two temperatures regarding PEI values as shown more clearly in Figure 12.

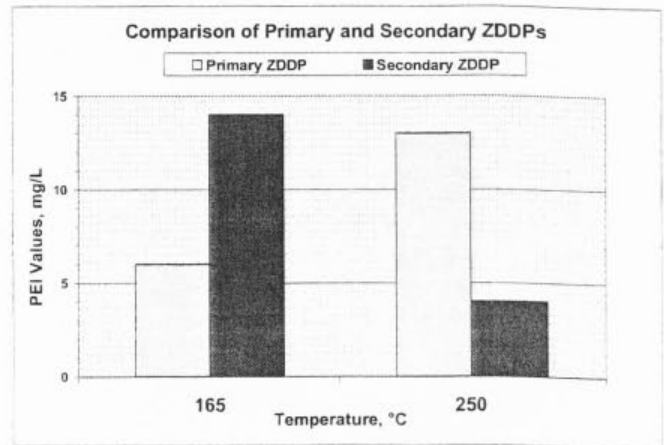


Fig. 12: Comparison of the phosphorus volatilities of a Primary ZDDP and a Secondary ZDDP in the same formulation at 165° and 250°C.

In summation of this comparison of Oils E and F, Table 1 and Figure 12 show that the phosphorus decomposition and volatilizing behavior of a particular engine oil may change significantly when exposed to ring-belt temperatures (~250°C) as compared to its response at rigorous operating temperatures (~150°C). There are many forms of ZDDP manufactured and many more that actually result from the manufacturing processes or can be designed. Whether all or only some ZDDPs respond

in this manner is not presently known but the PEI technique is evidently capable of showing clear distinctions and is versatile in its application to measuring the phosphorus volatility of engine oils.

NMR Studies of ZDDP Behavior – A series of ^{31}P NMR studies were generated on the Primary and Secondary ZDDP studies just presented. Spectra from the studies of Secondary ZDDP Oil F are shown in Figures 13-15.

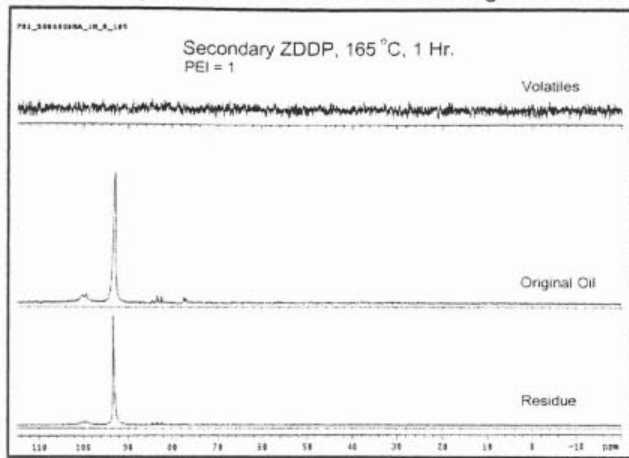


Fig. 13: ^{31}P NMR Spectra of samples of original oil, Volatiles and Residue generated during the PEI_{165-1} analysis of Oil F in Table 1.

The NMRs spectra in Figure 13 indicate that no volatile phosphate-containing species were observed generated by the PEI_{165-1} protocol – which itself showed a very low value of 1. This Residue spectrum also indicates that no inorganic phosphate was generated in this PEI analysis. In Figure 14, the NMR spectra generated from samples from the longer 16-hour exposure of the PEI_{165-16}

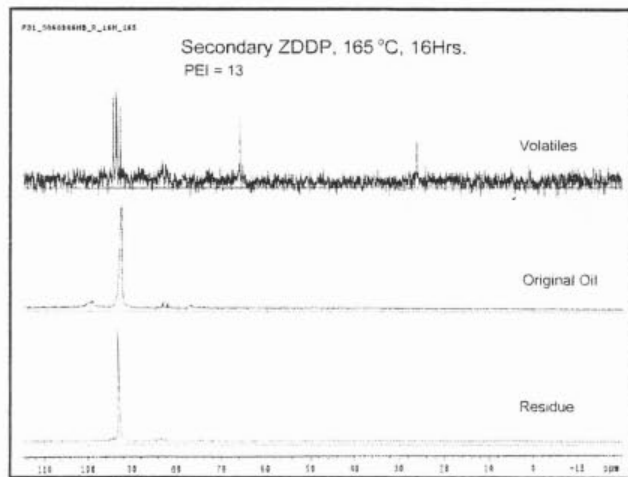


Fig. 14: ^{31}P NMR Spectra of samples of original oil, Volatiles and Residue generated during the PEI_{165-16} analysis of Oil F in Table 1.

protocol, multiple peaks were observed in the Volatiles and some inorganic phosphate in the Residue. However the NMR spectrum of the latter also showed significant amounts of unreacted ZDDPs remain in the oil.

As in our earlier studies, in Figure 15 it was observed, that the conditions of PEI_{250-1} generate some Volatiles

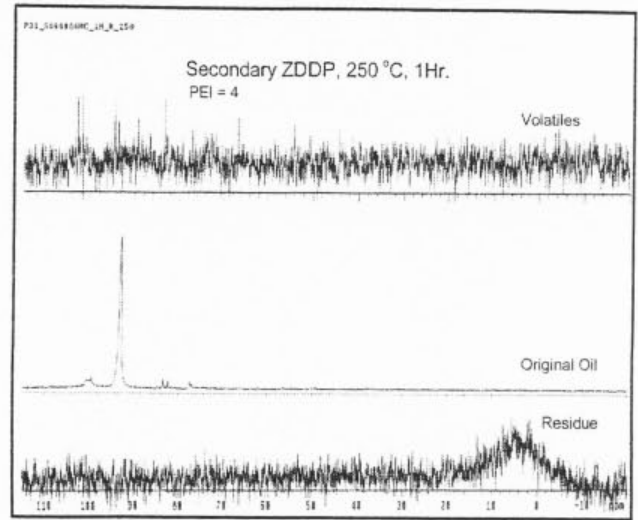


Fig. 15: ^{31}P NMR Spectra of samples of original oil, Volatiles and Residue generated during the PEI_{250-1} analysis of Oil F in Table 1.

(multiple peaks), however only inorganic phosphate (no ZDDP) is observed in the Residue.

Summarizing this portion of the PEI-NMR study using the Secondary ZDDP containing Oil F, it is evident that the two techniques give complementary views of the decomposition and volatilization phenomenon of these interesting engine oil additives.

Use of Co-Volatiles in PEI Analyses

Some engine oils have low volatilities in the Noack-type of volatility tests and little volatiles are available for PEI analysis. To assure that sufficient volatile material is available for subsequent analysis, it has been found effective to add a pure hydrocarbon co-volatile to the original oil sample. At different temperatures of producing the PEI information, hydrocarbons of different volatilities can be chosen.

Very early work in developing the PEI technique had shown that volatility of the basestock does not influence the amount of phosphorus volatilizing from the engine oil through the ZDDP decomposition process. Figure 16 demonstrates this.

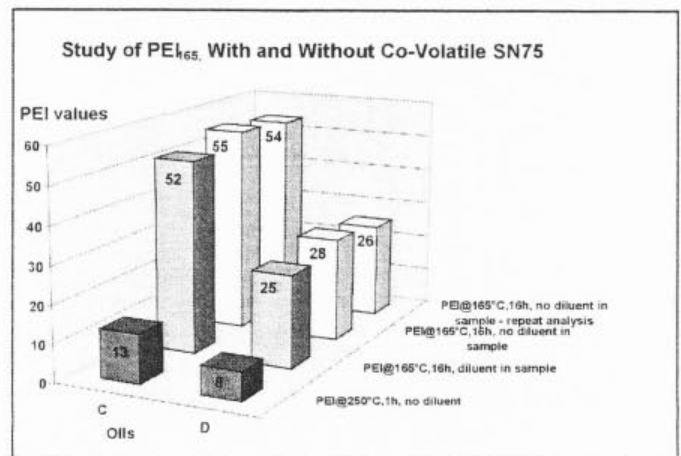


Fig. 16: Study of PEI_{165} with and without Co-Volatile SN75 base oil.

Addition of 10g of a relatively high volatility, phosphorus-free, base oil shows no effect on the results of the Selby-Noack PEI test results.

The work was performed using GF-4 Oils C and D discussed earlier (see Figures 3 and 6). Experiments were run using the PEI₁₆₅₋₁₆ protocol both with and without 10 grams of co-volatile added to facilitate recovery of the phosphorous containing species. A comparative experiment was performed on these oils without using any co-volatile since each oil would provide sufficient volatile material even without a co-volatile using the PEI₁₆₅₋₁₆ protocol.

DISCUSSION

General

This paper has presented part of an ongoing effort to develop a bench test of phosphorus emissions from engine oil.

The value in developing a bench test is that dynamometer engine tests are difficult to develop, standardize, and maintain as a dependable and reasonably precise test capable of being part of a numerical specification. They are also very expensive to run and to replace with new engine configurations.

Fleet tests are more reflective of the 'real world' of engine operation but much more difficult to control and virtually impossible to standardize to generate a numerical specification.

The bench test, however, requires engine or fleet tests to provide the acceptable degree of correlation needed to be relevant. Bench test strength is in relative ease of generating precision and – if strong correlation with the chemistry and physics of the engine is obtained – the bench test can be productive of the knowledge and understanding to bring about lubricant- and catalyst-system improvement.

Temperature and Phosphorus Volatility

It has been shown in this paper that the two sources of such emissions – the piston-ring belt and the circulating oil – may have different effects on a given ZDDP. In the GF-3 type oil formulated without ZDDP, adding a Primary ZDDP to one blend with the 'basestock', and a Secondary ZDDP to another produced very evident variations in response in PEI values at 250°C in comparison to those at 165°C (see Figure 12).

As noted earlier, this is not to say that all Primary or Secondary ZDDPs – or aryl alcohol-containing or mixed alcohol ZDDPs – would show this same degree of variation in response to these temperatures but only that these two oils demonstrate that significant variation can occur. Applying this information to the operating engine, the studies have also shown that phosphorus volatility under strenuous engine operating conditions may produce relatively large phosphorus emission and that this emission may increase in rate of release with longer exposure at the operating temperature.

Another method has been developed to measure phosphorus volatility in engine oil [14]. This method indirectly determines volatilized phosphorus by measuring phosphorus retention in the residual motor oil. This is an engine approach that may show correlation with the Selby-Noack test procedure in which the phosphorus in the residual oil is measured after the PEI protocol is applied.

This Residual Oil approach has been given the tentative name of Phosphorus Retention Index or PRI and is also measured in mg/L.

CONCLUSIONS

The objectives of this overall study of phosphorus volatilization, its causes, and its reliable prediction are being fulfilled.

The studies presented in this paper have indicated that analyzing engine oil samples at 250°C for one hour may not be appropriate temperature to compare potential phosphorus volatility. The temperature was found too high for some oils and caused rapid decomposition of the ZDDP. Significant phosphorus is volatilized after 16 hours at 165°C, and decomposition of the ZDDP is more in keeping with high engine oil temperatures.

We have shown that there are substantial differences between some Primary and some Secondary ZDDPs. NMR studies have demarcated those differences as attributable to the rapid formation of inorganic phosphates at ring-belt temperatures of 250°C and the associated curtailment of further organic phosphorus volatilization.

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REFERENCES

- [1] Spikes, H., "The History and Mechanisms of ZDDP", *Tribology Letters*, (2004), 17(3), 469-489.
- [2] K. Noack, *Angewandte Chemie*, Vol 49, p. 385, 1936
- [3] **Evaporation Loss of Lubricating Oils by the Noack Method**, ASTM D 5800, *ASTM Standards, 2004* Vol. 5.03 published by the ASTM, pp. 352-366, 2004.

- [4] **Determination of Evaporation Loss of Lubricating Oils**, (Noack Method), DIN 51-581, 1981.
- [5] Selby, T.W., et. al., **"A New Approach to the Noack Test for Volatility Measurement"**, *SAE International Fuels & Lubricants Meeting and Exposition*, Philadelphia, PA, USA, 1993
- [6] Selby, T.W. and Reichenbach, E.A., **"Engine Oil Volatility Studies - Generation of Phosphorus"**, *Proceedings of the International Tribology Conference*, Yokohama, Japan, pp. 813-816, 1995.
- [7] **Institute of Materials Engine Oil Database**, *Published by the Institute of Materials*, Midland, Michigan, Issued yearly from 1984.
- [8] Selby, T.W., **"Development and Significance of the Phosphorus Emission Index of Engine Oils"**, *Proceedings of 13th International Colloquium - Lubricants, Materials, and Lubrication Engineering*, Esslingen, Germany, pp. 93-102, 2002.
- [9] Johnson, M.D., McCabe, R.W., Hubbard, C.P., Riley, M.E., Kirby, C.W., Ball, D.J., Tripp, G., McDonnell, T.F., and Lam, W. Y., **"Effects of Engine Oil Formulation Variables on Exhaust Emissions in Taxi Fleet Service"**, *SAE Paper #2002-01-2680*, SAE Powertrain Meeting, 2002.
- [10] Selby, T.W., **"Phosphorus Volatility of Lubricants – Use of the Phosphorus Emission Index of Engine Oils"**, *9th F&L Asia Conference*, Singapore, January 21-24, 2003.
- [11] Selby, T.W., Bosch, R.J., Fee, D.C. **"Phosphorus Additive Chemistry and Its Effects on the Phosphorus Volatilization of Engine Oils"**. *Elemental Analysis of Fuels and Lubricants*, Ed. Nadkarni, ASTM STP 1468, pp. 239-254, 2005.
- [12] Bosch, R.J., Selby, T.W., and Fee, D.C., **"Analysis of the Volatiles Generated During the Selby-Noack Test by ³¹P NMR Spectroscopy"**, *Elemental Analysis of Fuels and Lubricants*, Ed. Nadkarni, ASTM STP 1468, pp. 255-273, 2005.
- [13] Bosch, R.J., Selby, T. W., Fee, D. C., **"Continued Studies of the Causes of Engine Oil Phosphorus Volatility"**, SAE Powertrain Meeting, San Antonio, Oct., 2005
- [14] Chamberlin, W.B., Kelley, J.C., and Wilk, M.A., **"Impact of Passenger Motor Oil on Emission Performance"**, SAE Paper #2003-01-1988.