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## Analysis of the Volatiles Generated during the Selby-Noack Test by <sup>31</sup>P NMR Spectroscopy

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### **ABSTRACT**

A series of engine oil samples collected during a study of their Phosphorus Emission Index values were analyzed by <sup>31</sup>P Nuclear Magnetic Resonance Spectroscopy. (The PEI analyses themselves were presented in an associated paper [1]). NMR spectra were generated to obtain and explain the mode of formation and identity of the phosphorus-containing species in the volatiles generated during the Selby-Noack volatility test and compare these species to those found in both the fresh oil and the residual oil remaining after the volatility test.

### **KEY WORDS**

Phosphorus volatility, exhaust catalyst, exhaust emissions, ZDDP, zinc dithiophosphates, Phosphorus Emission Index, PEI, <sup>31</sup>P NMR, NMR spectroscopy

### **ABBREVIATIONS**

ZDDP	Zinc Di(organo) Di(thio) Phosphate
PEI	Phosphorus Emission Index
NMR	Nuclear Magnetic Resonance

### **INTRODUCTION**

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[2]. Unfortunately, volatile phosphorus in the exhaust stream degrades the function of the exhaust catalytic converter and, as a consequence, there has been pressure to reduce the amount of ZDDP in engine oil.

One of the new analytical test procedures developed during the 1990s is the Selby-Noack instrument [3]. This instrument uses the earlier protocol developed by Noack [4-6] to measure the volatility of motor oil but, in addition, collects all of the volatile material generated in the test. In 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 20 mm<sub>water</sub> and the percent loss of sample mass measured.

During the development and early use of the Selby-Noack test, it was found that phosphorus-containing compounds were present in the volatiles obtained from the procedure [7]. With the growing interest in the subject of volatile phosphorus, the Institute of Materials incorporated the Selby-Noack test as part of the database they maintain on worldwide oil analyses[8] and also determined the concentration of phosphorus in the volatile material generated (initial phosphorus concentration of the fresh oil was already a part of the database).

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In 2002, a paper was published on the phosphorus volatility results that appeared in the IOM database from 1999-2001[9]. 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 could be explained by either or both 1) effects of other engine oil additives and 2) variations in the chemistry of the phosphorus additives. A 2002 field study conducted by Ford Motor Company of catalyst degradation by phosphorus-containing oils [10] was subsequently shown to correlate with the PEI data generated from the Selby-Noack bench test and, further, showed that phosphorus volatilization was strongly affected by other oil additives [11].

One of the objectives of the present studies is to examine the second premise concerning whether variation in the chemistry of phosphorus-containing ZDDP additives also affect phosphorus volatility from the formulated engine oil.

## ***EXPERIMENTAL***

Small samples of the original oils and the volatile materials and residues obtained during the Selby-Noack tests in the associated paper [1] were analyzed by  $^{31}\text{P}$  NMR 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 phosphorus-31 peak because of the different chemical environment around the phosphorus atom in phosphorus-containing oil components (or decomposition fragments) compared to the phosphorus atom in phosphoric acid ( $\text{H}_3\text{PO}_4$ ). This shift is reported in units of ppm (which term has no relation to concentration). By definition, the shift for the phosphoric acid standard is zero ppm. Average data accumulation time for these spectra was one hour.

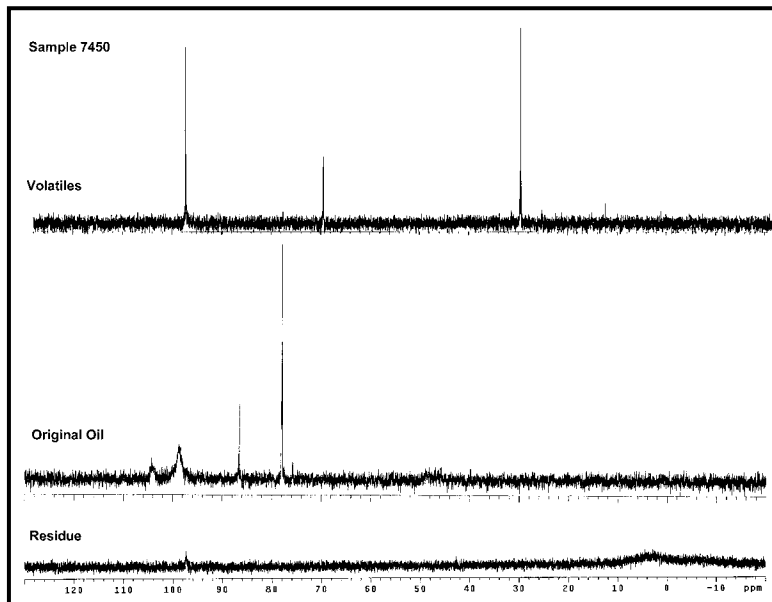
## ***RESULTS***

### ***First Study – Comparison of Formulated Oils with Different PEIs***

A series of five motor oil samples, four from the Institute of Materials database (samples EO-7450, EO-7459, EO-7538, and EO-7551) and one of a typical GF-3 motor oil supplied by Chevron Oronite Co., L.L.C (Sample RO-780) were subjected to the Selby-Noack test. The first four engine oils were chosen from the database because of similar volatilities but dissimilar phosphorus contents in the volatilized oil. The fifth oil was matched to a second sample of oil that contained no ZDDP (Sample RO-779).

A series of  $^{31}\text{P}$  NMR spectra were taken of each of the fresh oils and of their volatiles and residue generated by the Selby-Noack test (see Figures 1-5 and Summary Tables 1-5). Also included in the Summary Tables were the Selby-Noack oil volatility results and the PEI values for each of the starting oils.

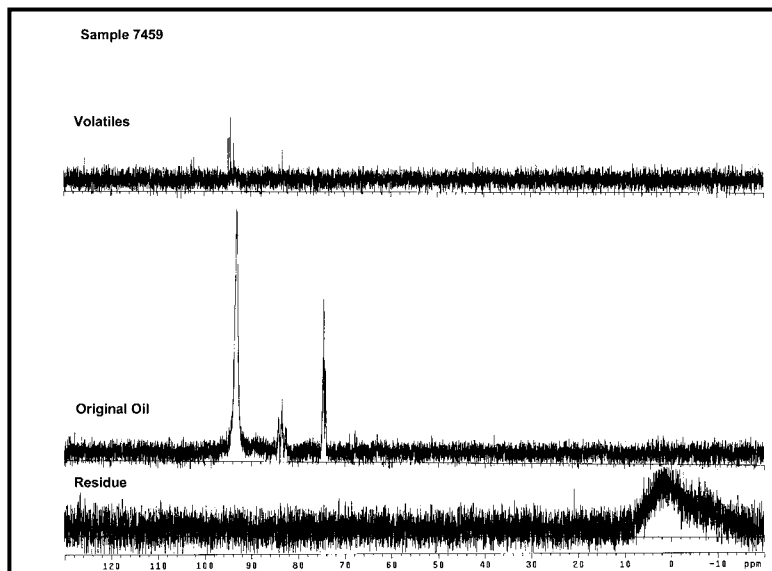
**Figure 1 - EO-7450, Oil**



**Table 1 - Summary of <sup>31</sup>P NMR Results for EO-7450**

Sample: EO-7450	Selby - Noack Volatility	PEI, mg/L	Chemical shifts (ppm)
EO-7450 Fresh Oil	19.4%	46	104.3, 99.5, 86.4, 77.8, 75.6
EO-7450 Volatiles			97.1, 69.4, 69.3, 29.6, 29.4, 29.3, 12.4
EO-7450 Residue			97.3, 3(broad)

**Figure 2 - EO-7459, Oil**



**Table 2 - Summary of <sup>31</sup>P NMR Results for EO-7459**

Sample: EO-7459	Selby - Noack Volatility	PEI, mg/L	Chemical shifts (ppm)
EO-7459 Fresh Oil	18.05%	1	93.2, 83.9, 83.5, 81.2, 74.6, 74.2
EO-7459 Volatiles	-	-	125.6, 94.8, 94.6, 94.3, 94.0, 93.6, 83.2, 48.2
EO 7459 Residue	-	-	2 (broad)

Figure 3 – EO-7538, Oil

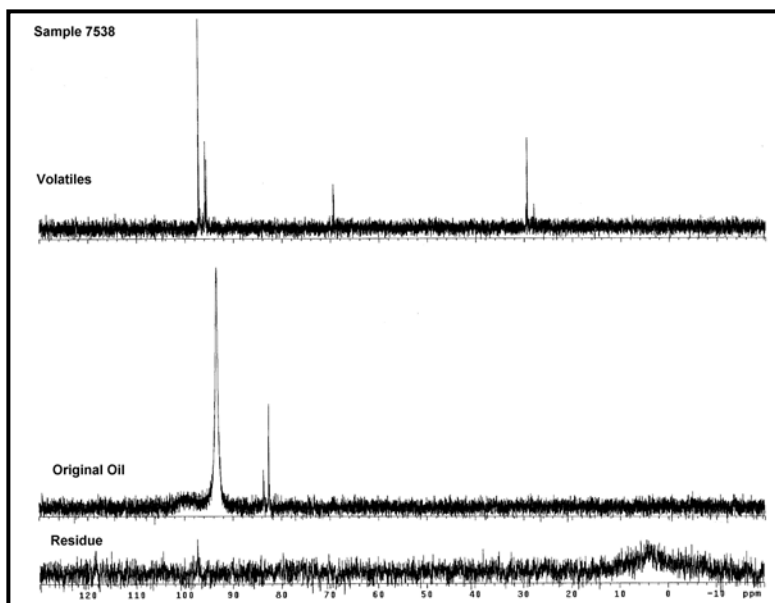


Table 3 – Summary of <sup>31</sup>P NMR Results for EO-7538

Sample: EO-7538	Selby - Noack Volatility	PEI, mg/L	Chemical shifts (ppm)
EO-7538 Fresh Oil	22.55%	31	93.3, 83.7, 82.6, 82.5
EO-7538 Volatiles	-	-	97.1, 96.9, 96.3, 95.8, 95.7, 95.5, 69.3, 69.2, 29.5, 29.4, 29.3, 28.0
EO-7538 Residue	-	-	4 (broad)

Figure 4 – EO-7551, Oil

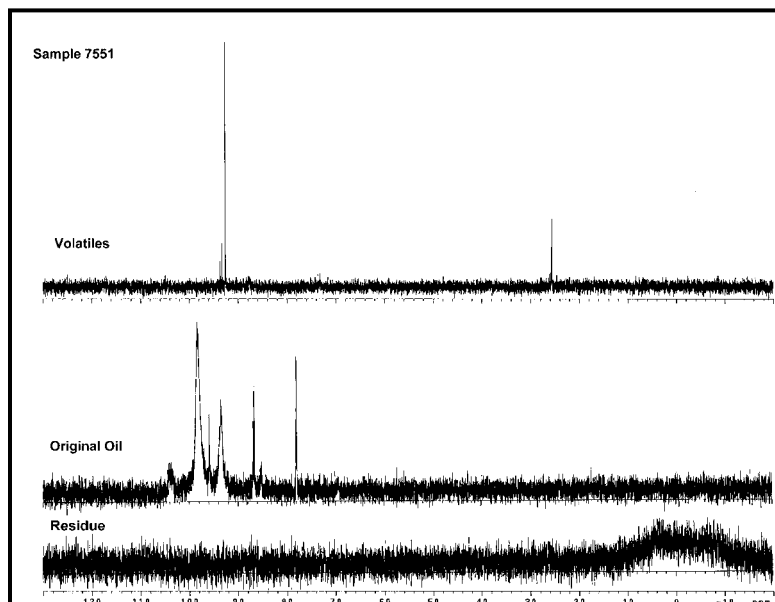
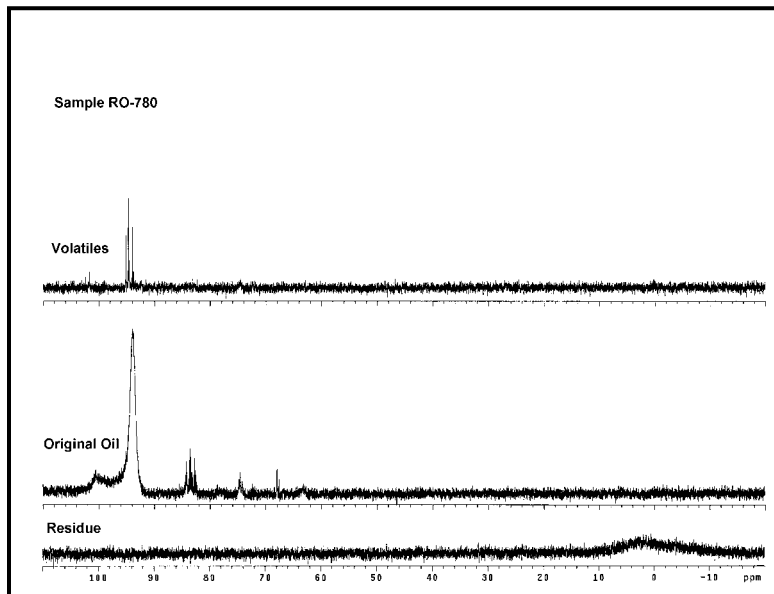


Table 4 – Summary of <sup>31</sup>P NMR Results for EO-7551

Sample: EO-7551	Selby - Noack Volatility	PEI, mg/L	Chemical shifts (ppm)
EO-7551 Fresh Oil	17.34	8	103.6, 98.1, 95.8, 93.3, 86.7, 86.6, 78.0, 77.8
EO-7551 Volatiles	-	-	93.7, 93.3, 92.6, 25.7, 25.6
EO-7551 Residue	-	-	0 (broad)

**Figure 5 - RO-780, Oil**



**Table 5 – Summary of <sup>31</sup>P NMR Results for RO-780**

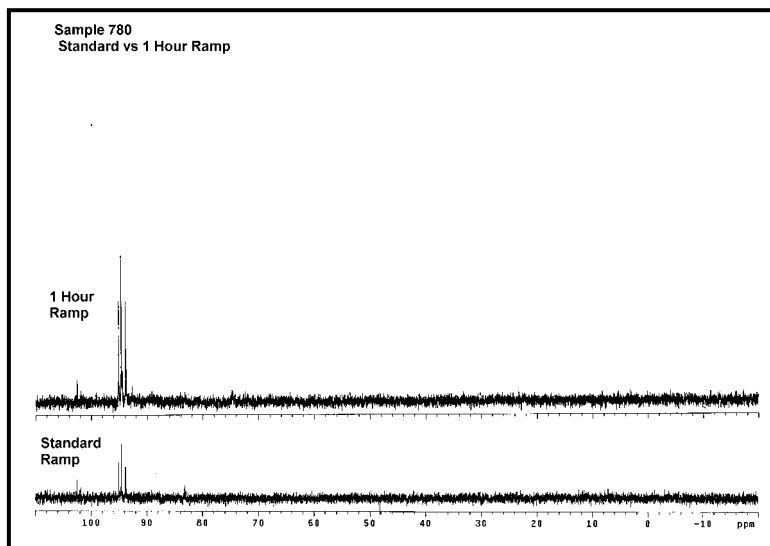
Sample: Typical GF-3 oil (RO-780)	Selby - Noack Volatility	PEI, mg/L	Chemical shifts (ppm)
RO-780 Fresh Oil	14.23%	4	100 (broad), 93.8, 84.3, 83.7, 83.6, 83.5, 82.8, 74.6, 67.9
RO-780 Volatiles	-	-	101.7, 95.1, 94.6, 94.5, 93.9, 72.4
RO-780 Residue	-	-	2 (broad)

***Second Study – Rate of Heating Dependence***

As a preliminary test to determine when phosphorus volatiles were generated during the Selby-Noack test, RO 780 was given a one-hour ramping time to the temperature of 250°C followed by the normal hour duration at that temperature. The volatiles generated during this study were subjected to <sup>31</sup>P NMR analysis. The results of this study are presented in Figure 6 and are summarized in Table 6. The <sup>31</sup>P NMR analysis of the volatiles generated during a typical Selby-Noack test (normal ramp time of about nine minutes to 250°C followed by a 60 minute hold) are also presented in Figure 6 and are also summarized in Table 6.

Both residue samples were also analyzed by <sup>31</sup>P NMR and were found to consist of a large broad peak centered at approximately 2 ppm.

**Figure 6 - RO-780, 1 Hr. Ramp vs. Normal Ramp, Volatiles**



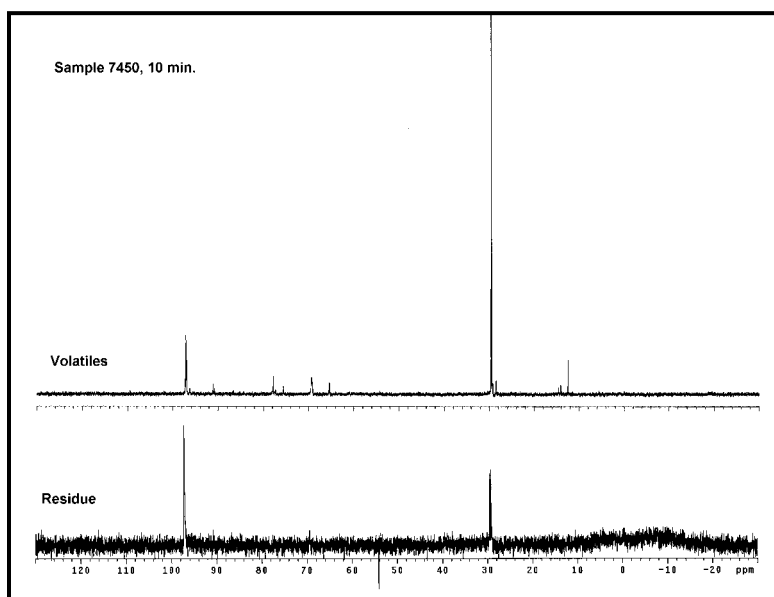
**Table 6 - Summary of the  $^{31}\text{P}$  NMR results of a 1 Hour Ramp vs. the Standard Ramp in the Selby-Noack Test.**

Sample: Typical GF-3 oil (RO-780)	Selby - Noack Volatility	PEI, mg/L	Chemical shifts (ppm)
1Hr Ramp volatiles	16.03%	9	102.5, 95.0, 94.5, 93.8, 93.7, 92.7
Standard Ramp-volatiles	14.23%	4	102.5, 95.0, 94.5, 93.8, 83.2

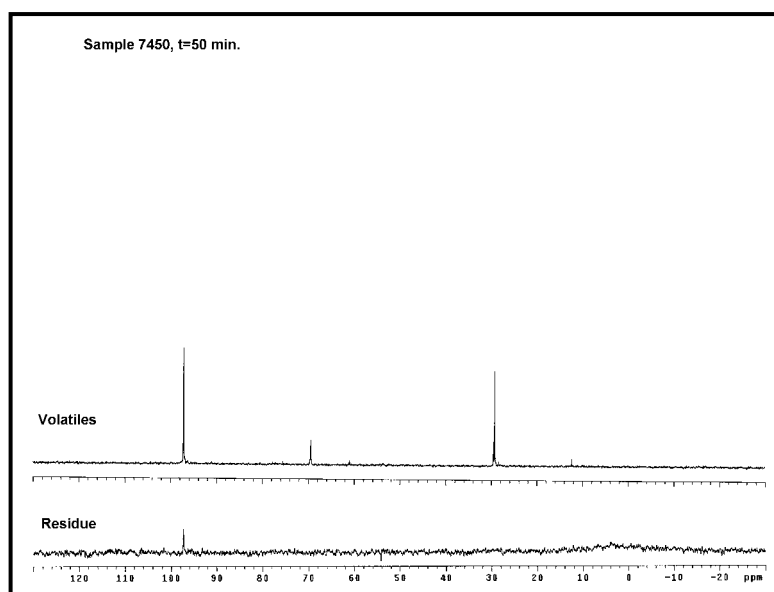
***Third Study – Time Dependence***

Modified Selby-Noack tests were performed on EO-7450 and RO-780. These experiments were performed using a normal ramp heat-up time of about nine minutes to 250°C followed by a variable hold of 10, 20, 30, or 50 minutes for each progressive test. The volatiles and residues were all subjected to  $^{31}\text{P}$  NMR analyses, however only the results of the 10 minute and 50 minute runs were included in this paper. They are presented in Figures 7 and 8 and are summarized in Table 7 for EO-7450 and Figure 9 and are summarized in Table 8 for RO-780.

**Figure 7 - EO-7450, t=10 min. Volatiles and Residue**

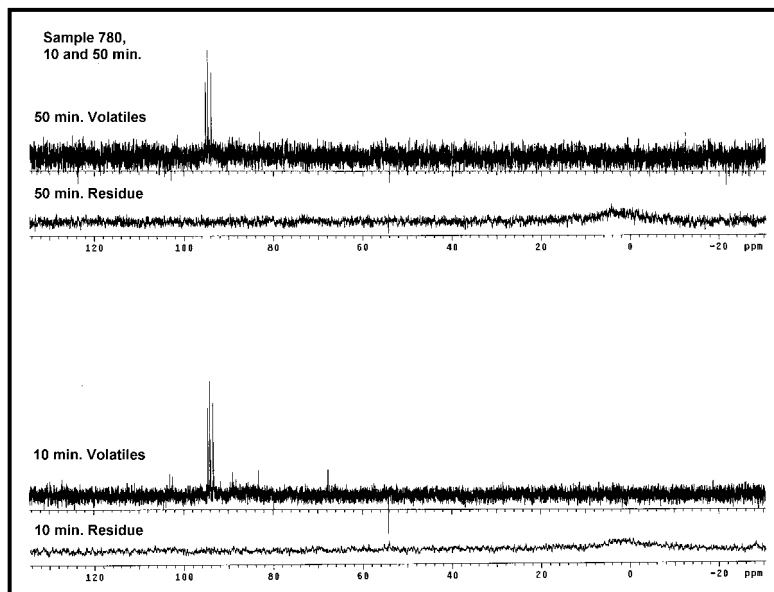


**Figure 8 - EO-7450, t=50 min. Volatiles and Residue**



**Table 7 - Summary of 31 P NMR Results for EO-7450, 10 and 50 Min. Runs**

Sample: EO-7450	Selby - Noack Volatility	PEI, mg/L	Chemical shifts (ppm)
Original oil (from Table 1)	19.4%	46	104.3, 99.5, 86.4, 77.8, 75.6
Volatiles, T=10min	6.12%	39	97.0, 91.1, 77.8, 75.6, 69.3, 65.3, 29.6, 29.4, 29.3, 28.4, 14.5, 14.1, 12.5, 12.4,
Residue T=10 min.			97.1, 29.4, 29. 2, 0 (broad)
Volatiles, T=50min	12.97%	53	97.2 91.1, 75.5, 69.5, 69.4, 61.0, 29.5, 29.3, 28.4, 12.4
Residue T=50 min.			97.3, 4 (broad)



**Figure 9 - RO-780, t=10 Volatiles and Residue and t=50 min Volatiles and Residue**

**Table 8 - Summary of 31 P NMR Results for RO-780, 10 and 50 Min. Runs**

Sample: RO-780 oil	Selby - Noack Volatility	PEI, mg/L	Chemical shifts (ppm)
Original oil (from Table 5)			100 (broad), 93.8, 84.3, 83.7, 83.6, 83.5, 82.8, 74.6, 67.9
Volatiles, T=10 min	4.03%	9	103.0, 102.4, 94.4, 94.0, 93.8, 93.3, 88.9, 83.2, 67.6, 54.1
Residue, T=10 min.			54.1, 0 (broad)
Volatiles, T=50 min.	13.62%	5	95.1, 94.6, 93.9, 83.0, 54.1
Residue, T=50 min.			4 (broad)

***Fourth Study – Effects of ZDDP Chemistry and Formation***

Four ZDDP samples were prepared in the Astaris labs. The alcohols employed were 2-Ethylhexanol, a primary alcohol, and 4-Methyl-2-pentanol, a secondary alcohol. Two P<sub>2</sub>S<sub>5</sub> samples were employed, one with a phosphorus content of 27.77% (Low Phos. P<sub>2</sub>S<sub>5</sub>) and the second with a phosphorus content of 28.07% (High Phos. P<sub>2</sub>S<sub>5</sub>). These four ZDDPs were blended into a typical GF-3 oil at Savant using a non-ZDDP-containing version of RO 780 provided by Chevron Oronite Company LLC.

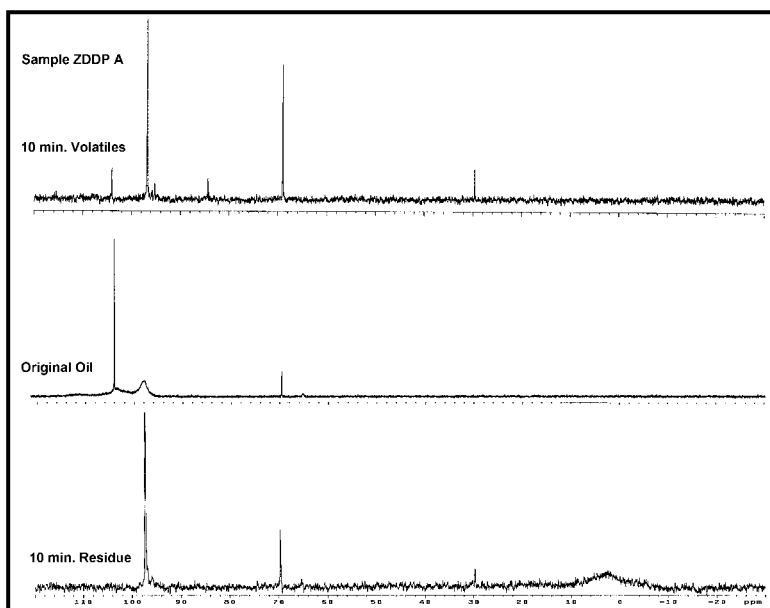
ZDDP A	2-Ethylhexanol	Low Phos. P <sub>2</sub> S <sub>5</sub>
ZDDP B	2-Ethylhexanol	High Phos. P <sub>2</sub> S <sub>5</sub>
ZDDP C	4-Methyl-2-pentanol	Low Phos. P <sub>2</sub> S <sub>5</sub>
ZDDP D	4-Methyl-2-pentanol	High Phos. P <sub>2</sub> S <sub>5</sub>

These samples were subjected to a series of Selby-Noack tests in which the runs were terminated at 10, 20, 30 and 50 minutes progressively. The resulting volatiles and residues, along with the starting oil samples, were subjected to  $^{31}\text{P}$  NMR analyses.

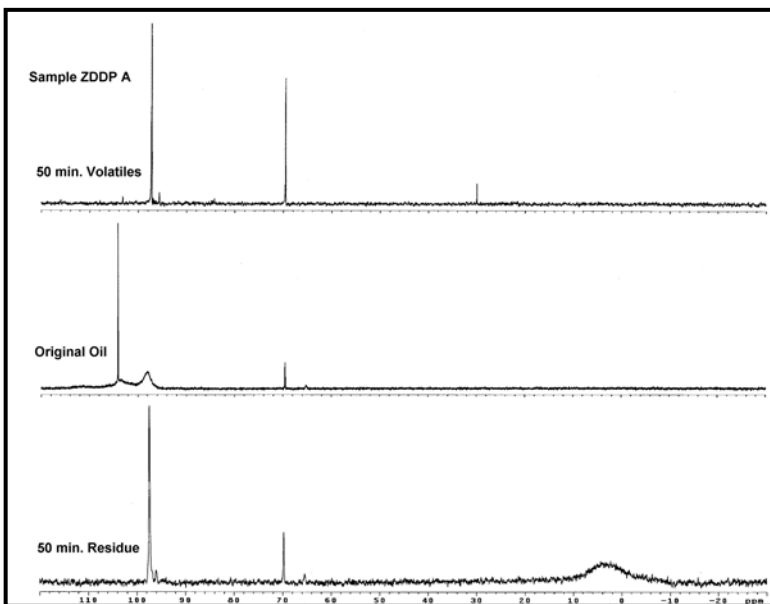
Figures 10-14 contain the most relevant  $^{31}\text{P}$  NMR spectra, however Tables 9-12 contain summaries of the results of all of the NMR spectra.

The  $^{31}\text{P}$  NMR spectra for the experiments involving the two 2-Ethylhexyl ZDDPs were integrated, which are summarized in Tables 13 and 14.

**Figure 10 - ZDDP A, Original Oil and t=10 Volatiles and Residue**



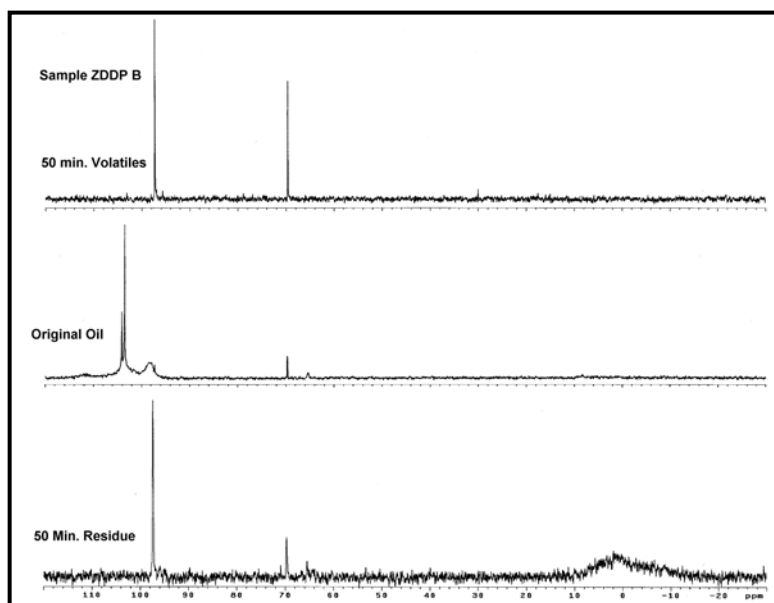
**Figure 11 - ZDDP A, Original Oil and t=50 Volatiles and Residue**





**Table 9 - Summary of <sup>31</sup>P NMR Results for ZDDP A (2-Ethylhexanol + Low Phos. P<sub>2</sub>S<sub>5</sub>)**

Sample: ZDDP A	Selby – Noack Volatility	PEI, mg/L	Chemical shifts (ppm)
Oil			104, 98.1, 69.5, 65
Volatiles, T=10 min.	3.31%	6	104, 96.7, 84.4, 69.0, 29.6
Volatiles, T=20 min.	7.09%	13	103.3, 97.2, 84.2, 69.5, 29.9
Volatiles, T=30 min.	8.43%	14	103.2, 97.2, 69.6, 30.0
Volatiles, T=50 min.	11.82%	19	103.5, 97.2, 69.6, 30.0
Residue, T=10 min.	-	-	97.3, 69.6, 29.7, 2
Residue, T=20 min.	-	-	97.2, 69.6, 29.7, 2
Residue, T=30 min.	-	-	97.3, 69.7, 29.7, 2
Residue, T=50 min.	-	-	97.3, 69.7, 65, 2

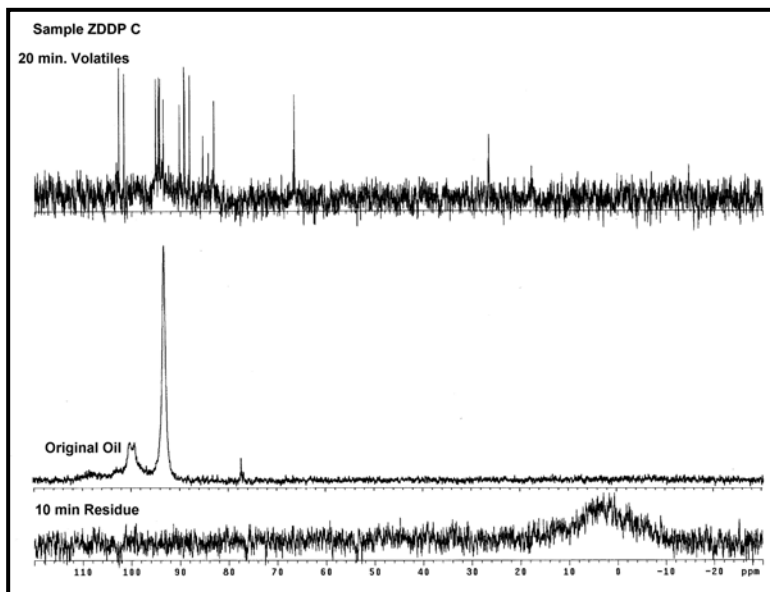


**Figure 12 - ZDDP B, Original Oil and t=50 Volatiles and Residue**

**Table 10 - Summary of <sup>31</sup>P NMR Results for ZDDP B (2-Ethylhexanol + High Phos. P<sub>2</sub>S<sub>5</sub>)**

Sample: ZDDP - B	Selby - Noack Volatility	PEI, mg/L	Chemical shifts (ppm)
Oil			104.1, 103.5, 98.5, 69.7, 65
Volatiles, T=10 min.	3.59%	6	103.9, 96.8, 84.3, 69, 29.6
Volatiles, T=20 min.	5.97%	10	103.3, 97.2, 84.2, 70, 29.9
Volatiles, T=30 min.	8.55%	13	103.5, 97.1, 69.4, 29.8
Volatiles, T=50 min.	13.72%	18	103, 97.3, 69.6, 30.0
Residue, T=10 min.			97.2, 69.6, 65.3, 29.6, 2
Residue, T=20 min.			97.3, 69.7, 65.2, 29.7, 3
Residue, T=30 min.			97.2, 69.6, 65.3, 1
Residue, T=50 min.			97.3, 69.7, 65.4, 2

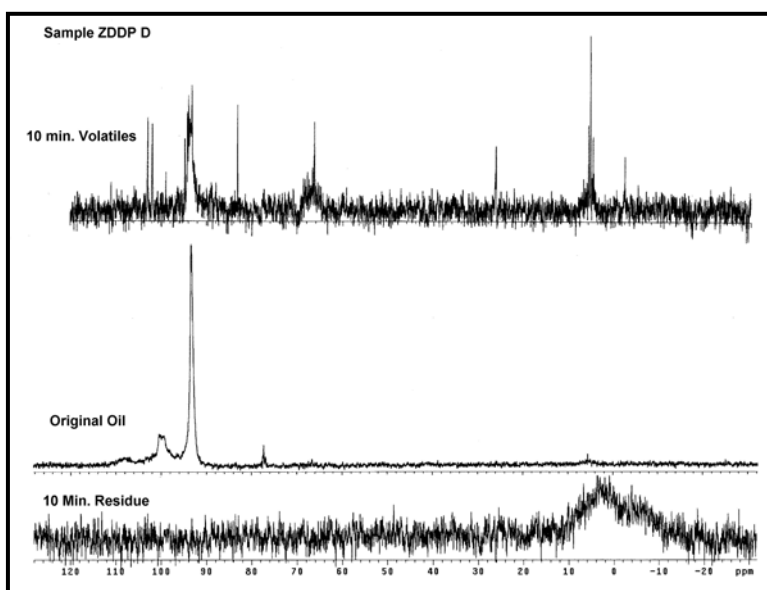
**Figure 13 - ZDDP C Original Oil and t=20 Volatiles and t=10 Residue**



**Table 11 - Summary of  $^{31}\text{P}$  NMR Results for ZDDP C (4-Methyl-2-pentanol + Low Phos.  $\text{P}_2\text{S}_5$ )**

Sample: ZDDP-C	Selby - Noack Volatility	PEI, mg/L	Chemical shifts (ppm)
Oil			99.2, 93.1, 77.3
Volatiles, T=10 min.	4.28%	5	103, 97, 94.1, 89.1, 83.2, 66.4
Volatiles, T=20 min.	6.23%	5	102.7, 101.6, 95.0, 94.5, 94.2, 93.5, 90.2, 89.2, 89.1, 88.1, 85.3, 83.1, 66.6, 26.5
Volatiles, T=30 min.	9.80%	5	102.5, 101.5, 94.3, 93.5, 89.3, 88.1, 83.1, 66.7,
Volatiles, T=50 min.	15.29%	4	102.3, 101.2, 95.3, 94.7, 94.4, 93.7, 93.5, 83.1, 66.8, 26.8
Residue, T=10 min.	-	-	3 (broad)
Residue, T=20 min.	-	-	4 (broad)
Residue, T=30 min.	-	-	3 (broad)
Residue, T=50 min.	-	-	3 (broad)

**Figure 14 - ZDDP D - Original Oil and t=10 Volatiles and Residue**



**Table 12 - Summary of <sup>31</sup>P NMR Results for ZDDP D(4-Methyl-2-pentanol + High Phos. P<sub>2</sub>S<sub>5</sub>)**

Sample: ZDDP D	Selby - Noack Volatility	PEI, mg/L	Chemical shifts (ppm)
Oil			100.4, 93.1, 77.3, 5.5
Volatiles, T=10 min.	3.98%	9	102.9, 101.9, 94.2, 93.9, 83.2, 66, 26.5, 5.9, 5.5
Volatiles, T=20 min.	5.83%	9	102.4, 101.3, 83.1, 67.5, 66.7, 26.6, 5.9, 5.4, 4.8
Volatiles, T=30 min.	8.65%	8	102.6, 94.5, 83.1, 67.8, 66.7, 5.5, 4.8,
Volatiles, T=50 min.	13.99%	9	102.2, 95.4, 94.5, 83.1, 66.8, 5.9, 5.4, 4.8
Residue, T=10 min.	-	-	4 (broad)
Residue, T=20 min.	-	-	4 (broad)
Residue, T=30 min.	-	-	3 (broad)
Residue, T=50 min.	-	-	6 (broad)

**Table 13 - Integrals of the <sup>31</sup>P NMR Results for ZDDP A (2-Ethylhexanol + Low Phos. P<sub>2</sub>S<sub>5</sub>) Reported as Relative Mole%**

ZDDP A	104 ppm	97 ppm	84 ppm	69 ppm	30 ppm	2 ppm
Sample						
V, t=10	7	54	6	28	5	
V, t=20	5	57	3	30	5	
V, t=30	5	64		27	4	
V, t=50		70		28	3	
R, t=10	trace	38		6	2	55
R, t=20		26		4	1	69
R, t=30		28		5	1	67
R, t=50		25		5	1	69

**Table 14 - Integrals of the <sup>31</sup>P NMR Results for ZDDP B (2-Ethylhexanol + High Phos. P<sub>2</sub>S<sub>5</sub>) Reported as Relative Mole%**

ZDDP B	104 ppm	97 ppm	84 ppm	69 ppm	65 ppm	30 ppm	2 ppm
Sample							
V, t=10	9	53	6	26		6	
V, t=20	4	62	2	28		5	
V, t=30	3	67		25		5	
V, t=50	2	67		27		5	
R, t=10		32		5	2	2	59
R, t=20		24		4	2	1	69
R, t=30		23		4	2		71
R, t=50		19		7	1		73

## DISCUSSION

### General

From the foregoing studies it is evident that the ZDDPs in all the engine oils and simulated engine oils decompose during the Selby-Noack test and are converted to different phosphate species, some portion of which are volatile. Similarly, it has been shown in other studies [2] that ZDDPs also break down under analogous conditions of temperature, time, and oxygen exposure in an engine.

### ***First Study***

The NMR analyses shown in Figures 1-5 and Tables 1-5 indicated that the various samples of volatiles from these Selby-Noack volatilization tests contain multiple phosphorus species and that most of these species are different from those present in the original motor oil. Perhaps more interesting, the first study gave clear evidence that different formulations of engine oils with different values of PEI gave considerably different phosphorus breakdown products. The residue oil left in the heated cup after completion of the Selby-Noack volatility test also contains totally different phosphorus species than those in the original motor oil. More specifically, all of the residue samples were observed to consist of a broad peak centered at 0 – 4 ppm, which is indicative of inorganic and/or simpler organophosphate compounds than ZDDP. In these typical GF-3 oils, a PEI of 8 corresponds to approximately 1% of the phosphorus volatilizing from the engine oil sample.

In three of the five motor oils tested, the ZDDPs completely decomposed under test conditions. In samples 7450 and 7538, small amounts of ZDDP remained in the residual oil at the end of the test.

### ***Second Study***

In the experiments on RO-780 (typical GF-3 oil) in which the effect of extending the time of the heat up ramp from 9 minutes to 60 minutes was examined, it was found that although the PEI increased when the time to operating temperature was considerably extended, the NMR spectra did not change significantly. That is, the same species were volatilized from the oil. This is illustrated Figure 6 and summarized in Table 6.

### ***Third Study***

The experiments performed on samples EO-7450 and RO-780, (see Figures 7-9 and Tables 7 and 8) were, as noted, run to determine what and when different volatile phosphorus species were generated. The tests were run in 10-, 20-, 30-, 50-, and 60-minute (from the first and second studies) exposure times to the Selby-Noack operating condition. From these samples the NMR analyses of the residue and volatile samples collected from the samples at 10 and 50 minutes were compared

Unexpectedly, in the RO-780, the decomposition of the motor oil was essentially complete after 10 minutes. In addition, it was noted that the PEI of the 50 minute sample was lower than that of the 10 minute sample. Although this might be associated with repeatability of the PEI at low values, it may also indicate that some of the phosphorus-containing species in the collected volatiles could be lost because of even further volatilization from the collection vessel during the Selby-Noack test. This requires further investigation. The NMR spectra of the volatiles obtained in these two runs were compared with Figures 5, 6, and 9. Qualitatively, the respective spectra were found to be very similar, which illustrates the repeatability of the volatilization and collection technique as an analytical method.

As observed before, in sample 7450, the decomposition of the phosphorus containing species is not complete after 50 minutes. It is very interesting to note that both the 10 minute and 50 minute residue spectra are significantly different from that of the original oil sample. It appears that this oil first decomposes to an intermediate state, which then undergoes further reaction to generate additional phosphorus volatile species. It is also noted that the NMR spectra obtained on the 10- and 50-minute volatile samples qualitatively consisted of the same peaks. However the proportionate size of the peaks varied between the two samples.

#### ***Fourth Study – ZDDP Composition Effects***

Evolution of volatile components was found to depend strongly on the alcohol used in ZDDP manufacture, as illustrated in Figures 10-14 and Tables 9-12. ZDDPs C and D made from the secondary alcohols, 4-methyl-2-pentanol, appear to break down readily under the conditions of the Selby-Noack test. Within the first 10 minutes, whatever volatile species were formed were given off and the only phosphorus-containing species in the residual oil were fully oxidized phosphates. Interestingly, the PEI values were comparatively low and constant.

In contrast, ZDDPs A and B made from the primary alcohols, 2-ethylhexanol, have a longer life. Volatile phosphorus-containing species were given off for up to 60 minutes. Concomitantly, the residual oil contained some of the original ZDDPs, but consisted primarily of other phosphorus-containing components in addition to fully oxidized phosphates.

However, in contrast to aforementioned results with the primary alcohol, the PEI values increased with time and became comparatively high. These differences in rate and degree of breakdown between ZDDPs made with primary and secondary alcohols reflect other findings in the literature[2].

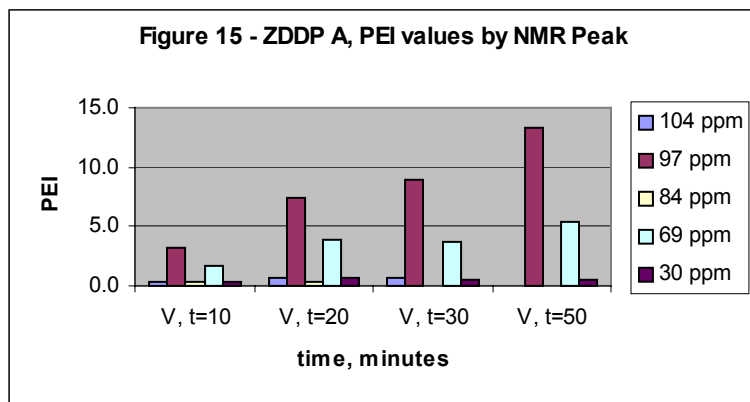
#### ***Fourth Study – Stoichiometric Effects***

*Results with ZDDPs A, B, C, and D* – In the limited testing described in this paper, the phosphorus/sulfur molar ratio of the  $P_2S_5$  does not appear to have a very significant effect on the composition of the volatile species generated from the ZDDP made from 2-ethylhexanol. Similar results were obtained from ZDDP made from both High and Low Phos  $P_2S_5$ . However the PEI values obtained on the ZDDPs manufactured from High and Low Phos  $P_2S_5$  and 4-methyl-2-pentanol differed significantly. Close examination indicates that some of the unique impurities in ZDDP D are most likely volatilizing and thereby increasing the PEI value of this oil. These impurities are observed in both the original oil and the volatiles at 3-8 and from 65-70 ppm.

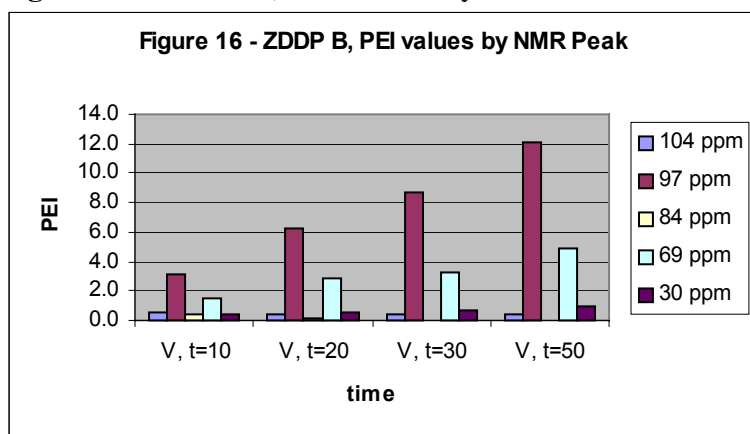
Unpublished studies at Astaris have found that typical yields of dithioacids (the ZDDP precursor prepared from the reaction of  $P_2S_5$  and alcohol) are generally between 85-95%. These reactions are typically run with an excess of alcohol to drive the reaction to completion. The phosphorus/sulfur molar ratio in the  $P_2S_5$  has been found to affect the trace components generated during the reaction of  $P_2S_5$  and alcohols. Use of  $P_2S_5$  of a slightly lower-than-stoichiometric phosphorus level generates some impurities that are rich in sulfur, while some of the impurities generated in reactions performed with  $P_2S_5$  at a slightly higher-than-stoichiometric level of phosphorus consist of  $P^{+3}$  compounds but do not include sulfur-rich impurities. Similarly, the  $P^{+3}$  impurities of higher than stoichiometric reactions are not generally found in the products generated from  $P_2S_5$  with a lower than stoichiometric level of phosphorus. This was one of the primary points of interest in performing the stoichiometric experiments with  $P_2S_5$ . That is, to see if these different impurity mixtures lead to ZDDPs with different PEIs – which, in fact, appears to be the case.

To generate more detailed information regarding the composition of the volatile products from the PEI studies, the relative ratios of the various peaks found in Tables 13 and 14, which were taken over the time interval of 10 to 50 minutes of the Selby-Noack test, were multiplied by the PEI values of these samples to calculate the PEIs of the individual peaks. That is, the total PEI value for the sample was separated into the individual PEI components in the same relative ratio as the  $^{31}P$  NMR peaks. The results of this comparison are presented in Figures 15 and 16 and show interesting trends.

**Figure 15 - ZDDP A, PEI values by NMR Peak**



**Figure 16 - ZDDP B, PEI values by NMR Peak**



Some peaks grow while some stay the same or slightly shrink during the duration of the test. Two peaks, those at 104 and 84 ppm remain the same or shrink. The peaks, at 97 and 69 ppm clearly grow, and the peak at 30 ppm appears to grow somewhat, but not dramatically. Before the test, Oil A has peaks at 104, 98.1, 69.5, and 65 ppm and Oil B has peaks at 104.1, 103.5, 98.5, 69.7, and 65 ppm. Therefore it is possible that the peak at 104 ppm is an impurity that volatilizes and the small peak at 69 ppm in the before-test oils is generated during the thermal decomposition of the oils during the PEI test and subsequently is volatilized. The large peak at approximately 98 ppm in the before-test oil is perhaps represented as the dithioacid in the volatilized oil samples. Further study is required.

**General Observations**

Volatile components from ZDDPs may arise from the manufacturing process. Zinc dithiophosphates are typically a mixture of phosphorus containing species. In addition to the desired ZDDP,  $[(RO)_2P(S)S]_2Zn$  and basic ZDP salt, there are a number of other trace components containing phosphorus, as shown in Table 15. Some of the trace components in the unused oil were also observed in the volatiles.

Table 15 - Literature Survey of <sup>31</sup> P NMR Analyses of ZDDPs												
		Species Observed										
		$((RO)_2P(S)S)_2Zn_4O$	$((RO)_2P(S)S)_2Zn$	$(RO)_2P(S)S_nR$	$(RO)_2P(S)SH$	$(RO)_2P(S)OR$	$(RO)_2P(S)O^-$	$[(RO)_2P(O)S]_2$	$(RO)_2P(O)SR$	$(RO)_3P(O)$	$(OR)P(S)(SR)_2$	$(S)P-(SR)_3$
		basic ZDDP	neutral ZDDP	sulfide n = 1,2,3	thio acid	thiophosphate	thiophosphoric salt		thiophosphate	phosphate		
Ref.	Experiment	[shift, ppm]										
12	15000 km engine field test	$((RO)_2P(S)S)_2Zn_4O$ [102 to 110]	$((RO)_2P(S)S)_2Zn$ [93 to 102]	$(RO)_2P(S)SR$ [85 to 93]		$(RO)_2P(S)OR$ [60 to 72]	$(RO)_2P(S)O^-$ [37 to 55]		$(RO)_2P(O)SR$ [24 to 30]	$(RO)_3P(O)$ [13 to -13]		
13	lab oven 180°C, in air			$(RO)_2P(S)SR$							$(OR)P(S)(SR)_2$	$(S)P-(SR)_3$
14	lab 4-ball rigs in air	$((RO)_2P(S)S)_2Zn_4O$	$((RO)_2P(S)S)_2Zn$	$(RO)_2P(S)SR$			$(RO)_2P(S)O^-$		$(RO)_2P(O)SR$			
15	lab; 150° to 200°C, in air *	$((RO)_2P(S)S)_2Zn_4O$	$((RO)_2P(S)S)_2Zn$	$(RO)_2P(S)SR$								
16	lab; 200° to 260°C, in air **									$(RO)_3P(O)$ [0.5 to -12]		
17	ZDDP + cumene hydroperoxide 40°C	$((RO)_2P(S)S)_2Zn_4O$ [103]	$((RO)_2P(S)S)_2Zn$ [99]	$(RO)_2P(S)SR$ [79 to 85]			$(RO)_2P(S)O^-$ [49]	$[(RO)_2P(O)S]_2$ [22]				
18	ZDDP synthesis	$((RO)_2P(S)S)_2Zn_4O$ [101 to 103]	$((RO)_2P(S)S)_2Zn$ [96 to 100]	$(RO)_2P(S)SR$ [78 to 80]	$(RO)_2P(S)SH$ [70]	$(RO)_2P(S)OR$ [69]	$(RO)_2P(S)O^-$ [40 TO 45]		$(RO)_2P(O)SR$ [20 to 26]	$(RO)_3P(O)$ [13 to -13]		
19	ZDDP synthesis		$((RO)_2P(S)S)_2Zn$				$(RO)_2P(S)O^-$			$(RO)_3P(O)$		

\*ZDDP gone in 1 hr at 200°C or 24 hr at 150°C; \*\* all ZDDP gone in 4 hr at 200° and 260°C

The volatile components from ZDDPs may also arise from thermal degradation and/or oxidation. The mechanisms proposed for ZDDP anti-wear and anti-oxidation performance in motor oil have included both the effects of ZDDP degradation and oxidation [2]. In addition, <sup>31</sup>P NMR studies at other laboratories have identified ZDDP breakdown fragments in the used motor oil [12], as shown in Table 15.

Moreover, ZDDP breakdown fragments have been observed using <sup>31</sup>P NMR in lab tests elsewhere[13-16]. These lab tests were also done in the presence of air. So the relative contribution of thermal degradation versus oxidation is not clear. The direct oxidation of a ZDDP with hydroperoxide [17], as observed by <sup>31</sup>P NMR, also gives fragments that may be volatile.

The evolution of volatile components has been found to depend strongly on the alcohol used in ZDDP manufacture. ZDDPs made from the secondary alcohol 4-methyl-2-pentanol appear to break down readily under the conditions of the Selby-Noack test, but only a small percentage of the phosphorus break-down products were volatile. Within the first 10 minutes, all the volatile species were given off and the only phosphorus-containing species in the residual oil were fully oxidized phosphates. In contrast, ZDDPs made from the primary alcohol 2-ethylhexanol appear to have a longer life but produce more volatile phosphorus over their break-down life. Volatile phosphorus-containing species were generated for at least 60 minutes. In concert, the residual oil contained ZDDPs and other phosphorus-containing components in addition to fully oxidized phosphates.

The rapid break down of ZDDPs has also been observed elsewhere: Lab tests in air using <sup>31</sup>P NMR show that all the ZDDP is gone in 1 hour at 200°C [15], 24 hours at 150°C [15], 4 hours at 200°C[16], or 4 hours at 260°C[16]. In the latter two tests, the only phosphorus containing species was a fully oxidized phosphate.

A recently published study by scientists at MIT[20] has indicated how to quantify the amount of oil lost by three possible mechanisms. These include thermal decomposition of the oil in the engine, aerosol generation, and oil volatilization. The information gathered in the present paper using the Selby-Noack and the related NMR spectroscopy testing methods can be used to quantify phosphorus volatility in the same manner. Measurement of zinc in the volatiles can be used to determine the amount of phosphorus generated via aerosol generation. In addition, it appears that careful <sup>31</sup>P NMR analyses of the volatiles

could be used to measure the phosphorus generated by volatilization of the components of the motor oil versus the phosphorus homologs generated by thermal decomposition.

Earlier studies by Savant showed that there were trace levels of zinc in the phosphorus volatiles obtained from the Selby-Noack test. The combination of varying the length of the Selby-Noack test, followed by  $^{31}\text{P}$  NMR analysis of the volatiles and residues, has the potential to be a very useful tool to further understand the mechanism of phosphorus volatility of motor oil.

## **CONCLUSIONS**

The  $^{31}\text{P}$  NMR data are reproducible using the Selby-Noack procedure. For the same conditions of time and temperature, the information, though limited, shows that the composition data are consistent when the experiments were repeated.

Different oils formulated with different ZDDPs and other additives have different volatile components. Moreover, the composition of the volatile phosphorus containing components depends on the specific ZDDP.

In most cases, the phosphorus forms found in the volatiles appeared to contain some of the ZDDP additive. But the  $^{31}\text{P}$  NMR spectrum also indicated the presence of more species in the volatiles than in the untested oil. That is, the volatile components appear to be generated primarily by the decomposition of ZDDP. However, volatile phosphorus containing trace components arising from the ZDDP manufacturing process may be significant in some cases.

It appears possible to meet engine oil performance standards using additives having low phosphorus volatility. Although all the oils in the IOM Database for North America are presumed to have met minimal standards for engine wear and oil oxidation, there is a large difference in Phosphorus Emission Index (PEI) among these oils. By using PEI as an additional criterion for additive selection, it would seem reasonable to provide protection for both the engine and the emissions control system. Certainly, approaching the control of phosphorus volatility by actual measurement is highly preferable to attempting to control phosphorus volatility by limiting the phosphorus content of fresh engine oil.

## **ACKNOWLEDGEMENTS**

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