

## Phosphorus Additive Chemistry and Its Effects on the Phosphorus Volatility of Engine Oils

**ABSTRACT:** The most widely used and effective anti-wear/anti-oxidation additives in engine oil contain phosphorus that can partially volatilize during engine operation. Unfortunately, volatile phosphorus in the exhaust stream degrades the function of the exhaust catalyst in reducing air pollution. Earlier studies in a special volatility bench test using the Phosphorus Emission Index have shown that phosphorus volatility is not related to engine oil volatility or to phosphorus content in the unused engine oil. At the time, it had been speculated that this unexpected lack of correlation with initial phosphorus concentration could be explained by 1) the effects of other engine oil additives and/or 2) variations in the phosphorus additive chemistry. The first speculation was relatively recently confirmed by taxi fleet studies of catalyst degradation by phosphorus-containing oils by the Ford Motor Company. It remained to determine if differences in phosphorus additive chemistry were also a factor and this is the subject of the present study.

**KEY WORDS:** phosphorus volatility, Phosphorus Emission Index, PEI, ZDDP, zinc dithiophosphates, exhaust catalyst, exhaust emissions

### List of Notations

#### Abbreviations

ZDDP	zinc di(organo) di(thio) phosphate
PEI	Phosphorus Emission Index
API	American Petroleum Institute
ILSAC	International Lubricant Standards and Certification
EGR	exhaust gas recirculation system

## Introduction and Background

### *Importance of ZDDPs*

The class of anti-wear, anti-oxidation additives commonly known as ZDDPs have been a mainstay of engine oil formulation and performance for more than 60 years [1]. Engine designers and metallurgical engineers have found significant help in overcoming problems by utilizing the protection brought by the chemists and lubrication engineers forming and formulating with these additives. Concentrations of ZDDP phosphorus in the formulated engine oil have often been above 0.1% to be sure of obtaining the level of protection desired even though somewhat lesser amounts have been shown to suffice. More recently, with emphasis on smaller, more powerful engines (carrying ever longer warranties), the circumstances would seem ideal for increasing use of ZDDPs.

### *Phosphorus and Catalyst Interaction*

However, a problem demanding creative solutions arose over the last score years. Automotive exhaust pollution control requires expensive exhaust catalysts and today – as a result of government mandates – these catalysts must remain highly effective for up to 100,000 miles of service. The problem was that it became evident that these catalysts were degraded by phosphorus in the exhaust stream [1-8].

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*Association of Phosphorus Emission with Oil Consumption and Volatility* - Oil consumption caused by oil volatility has always been a concern for automotive engineers because of the associated deposits often formed on piston rings and combustion chambers. Concern that oil volatility could cause phosphorus in the exhaust stream, added to the desire to reduce oil volatility. Consequently, progressively lower formulated engine oil volatility (as measured by the classic Noack volatility test [9-12]) was required for oils meeting API and ILSAC GF-2 (22% loss) and GF-3 (15% loss) specifications.

*Phosphorus Concentration Reduction and Concerns* - A more challenging and debated direction in limiting phosphorus volatility was to limit the concentration of ZDDPs in the engine oil. Understandably, this brought intense discussion among automotive and lubrication engineers about

1. lowering levels of ZDDP in engine oils without considerable field experience in modern high-performance engine durability, at a time when
2. engine oil operating viscosities and levels of hydrodynamic lubrication were being reduced to gain fuel efficiency, as well as concern about
3. the impact of such changes on older, used, and presumably more vulnerable automobiles.

Despite these concerns, phosphorus levels were reduced first to a maximum of 0.10% in lower viscosity grades passenger car engine oils designated API SJ and ILSAC GF-2 in 1995 and then, in 2004, to a level of 0.08% for API SM and ILSAC GF-4.

#### ***A New Noack Test for Determining Phosphorus Volatility***

*Selby-Noack Volatility Test* - The toxic nature of the Woods Metal used for heat transfer in the classic Noack volatility test [9-12] led to the development of a new approach [13-17]. This approach, while retaining all Noack test conditions\*, was designed to heat the test oil safely using noble metal resistive heating and to collect 99+% of all the material volatilized. Figures 1a and b respectively show a picture of the Selby-Noack instrument and a sketch of the arrangement of the essential components.



Figure 1a – Selby-Noack instrument

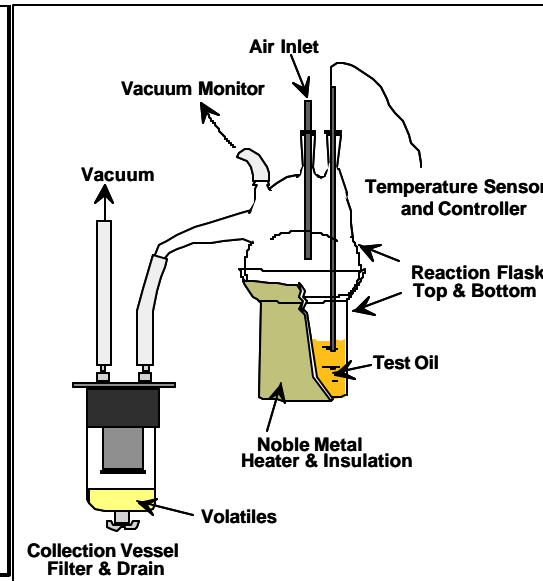
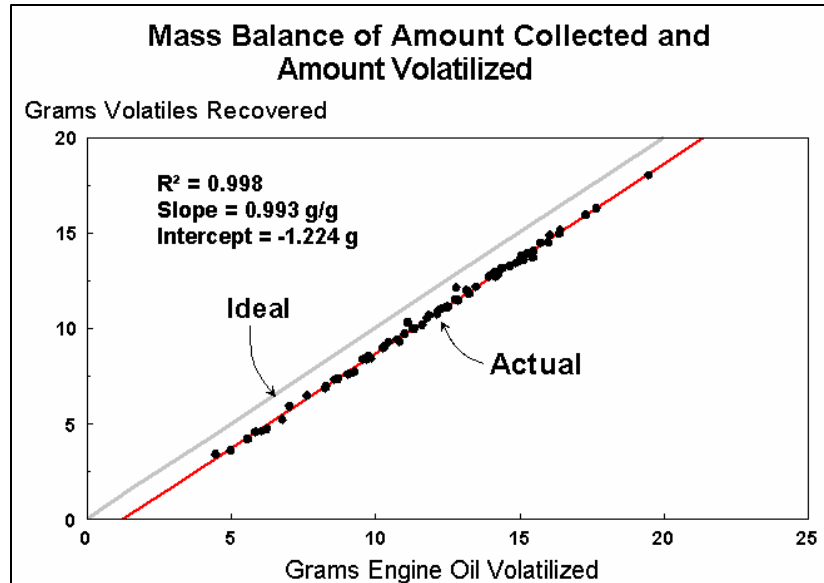


Figure 1b – Essential components of Selby-Noack

\* The Noack volatility test determines percent loss of volatile material from 65 grams of the test oil when exposed to a small vacuum of 20mm water at 250°C for one hour.

As indicated in Figure 2, early studies with the Selby-Noack showed that more than 99% of the oil mass lost from the volatilization chamber was accounted for either in the collector or the ~1 g on the walls of the tubing leading to the collector [16]. Such efficiency is important to be sure that the volatilized material collected is essentially identical to all material volatilized rather than forming a questionable composition.

Figure 2 - Mass balance of loss and collection of volatilized material



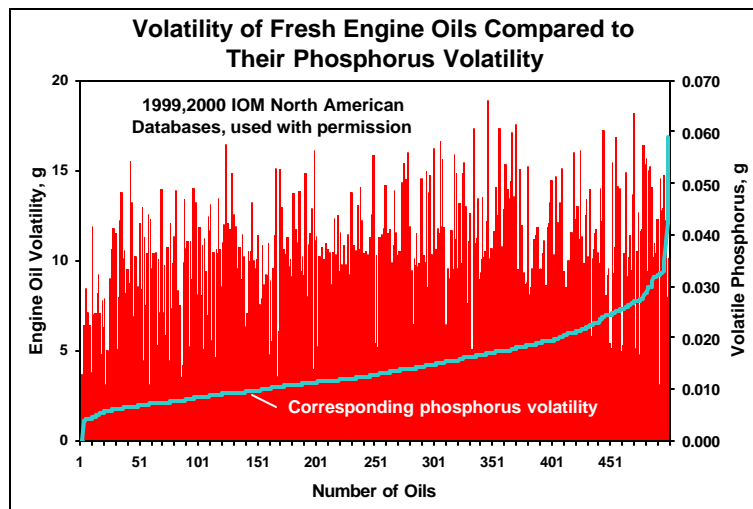
Analyses of phosphorus in the collected volatiles from the Selby-Noack in these early studies [13-17] showed that phosphorus was present. Moreover, the limited data also suggested that phosphorus volatility was not closely related to oil volatility.

***Effects of Oil Volatility and Concentration on Phosphorus Volatility***

This new Selby-Noack approach – permitting collection of all volatiles – was opportune. Among other applications, it presented the ability to evaluate the relationship of phosphorus volatility to oil volatility and/or phosphorus concentration in the fresh oil.

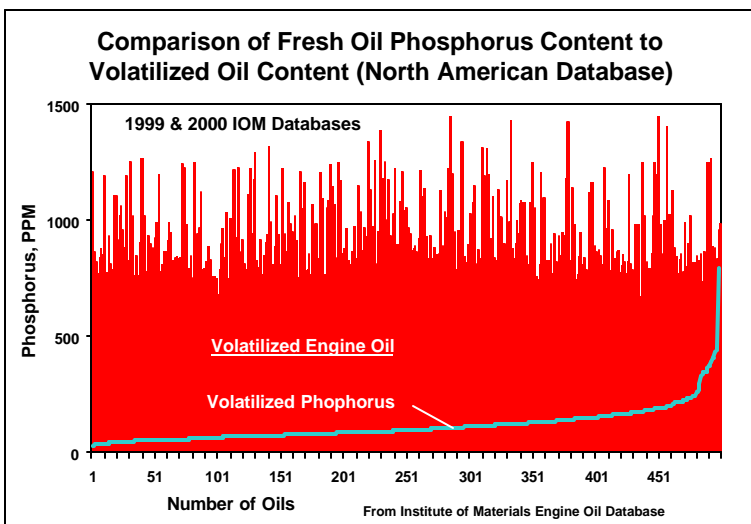
A further comprehensive study compared the phosphorus in volatilized engine oils from over 1,200 oils to both their oil volatilities and initial phosphorus concentrations in the fresh oils, respectively. (Data were supplied to the authors by the Institute of Materials (IOM) [18] for the years 1999 and 2000). Phosphorus volatility was first shown not to be dependent on engine oil volatility. This is evident in Figure 3 where variation in engine oil volatility varies independently of the associated phosphorus volatility.

Figure 3 – Showing lack of relationship between the grams of an engine oil volatilized in the Selby-Noack test (from an initial charge of 65 grams for the test) and the grams of phosphorus volatilized during the same test.



In a further analysis of the IOM data, it was unexpectedly found that phosphorus volatility also unrelated to phosphorus concentration in the fresh oil [19, 20] as is shown in Figure 4.

Figure 4 – Showing lack of relationship between the concentration of phosphorus in a fresh engine oil and the concentration of phosphorus volatilized from the particular engine oil in the Selby-Noack test



### ***Phosphorus Emission Index***

Considering the lack of relationship of volatilized phosphorus with either oil volatility or initial phosphorus concentration in the oil, it seemed important to have a measure of the comparative phosphorus volatility of engine oils. This led to a concept of ranking engine oils based on the volatility of their phosphorus-containing additive(s) [20]. The ranking method was called the Phosphorus Emission Index or PEI.

PEI is defined as milligrams of phosphorus volatilized per liter of fresh oil based on results obtained in the Selby-Noack test. Repeatability was tested and shown in past papers [20, 21].

Considering the surprising lack of correlation with phosphorus concentration in the fresh oil, it was thought likely that phosphorus volatility might be dependent on

1. ZDDP variations of chemistry and/or
2. effects of other additives in the formulation.

However, at the time, there was no evidence whether the Phosphorus Emission Index and the volatile phosphorus to which it was related had any correlation with the degeneration of exhaust stream catalysts.

### ***Correlation of PEI with Field Study***

Further work testing the significance of the PEI concept was undertaken as a consequence of a taxi fleet tests of phosphorus volatility and catalyst degradation conducted by Ford Motor Company [22, 23]. Interest in the PEI concept led Ford engineers to submit three blind-coded, fresh engine oils of the several that had been used in the taxi fleet tests.

On completion and submission of this blind-sample PEI study to Ford, it was revealed that the ZDDP, concentration of ZDDP, and the base oil used in each engine oil were the same. Moreover, one of the oils had no additives present other than the ZDDP

Results are shown in Table 1 and Figures 5 and 6 in which four of the Ford test oils are listed. (Oil X, which contained no phosphorus, was not submitted for PEI evaluation by Ford but has value in the comparisons made.) The figures show the additives present as well as the level of phosphorus deposits and the NO<sub>x</sub> emissions for each oil.

Table 1 – Comparison of PEI to phosphorus found on exhaust catalyst and NOx emitted at end of Ford Motor field taxi tests.

Table 1 - Information from Taxi Fleet Test and Phosphorus Emission Index Tests on Fresh Oils					
Test Oil	Additive	Fresh Oil, Phosphorus, mg/L	Volatilized Oil (PEI)	End of Test	
				Phosphorus on Catalyst, grams	NO <sub>x</sub> /Mile
				Grams	
A	Ca	761.1	15.9	14.6	0.76
B	none	758.5	42.5	24.6	1.20
C	Ca/Mg	759.8	15.6	14.6	0.85
X	Ca/Mg	0.0	0	-	0.41

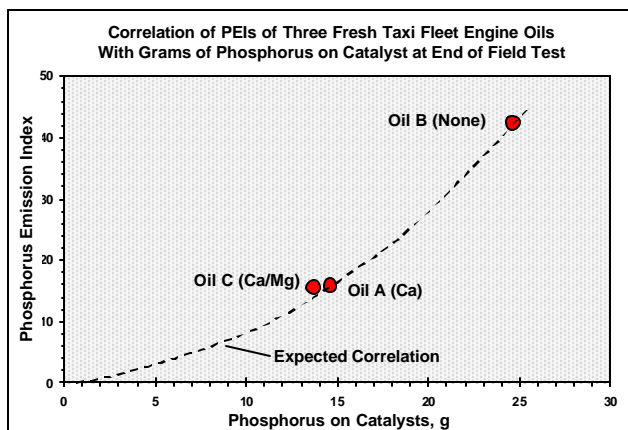


Figure 5 - Correlation of PEI and catalyst phosphorus

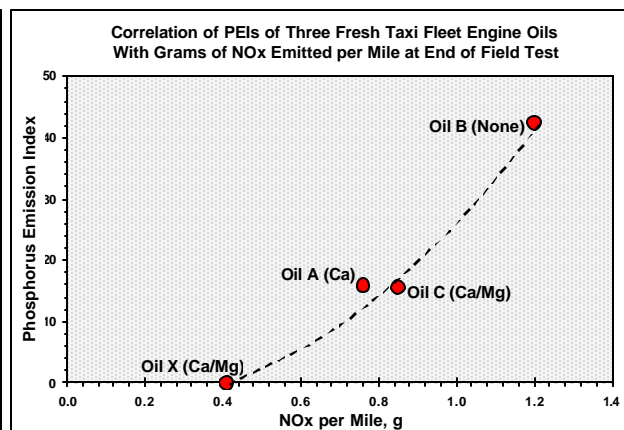


Figure 6 - Correlation of PEI and NO<sub>x</sub> emissions

This study of field test oils resulted in three important findings regarding the questions raised in the earlier work [19, 20, 21] regarding the significance of PEI and the effects of other oil additives. That is:

1. PEI level was found to correlate with the phosphorus found on the catalyst,
2. presence of other additives reduced the PEI value considerably, and,
3. PEI also correlated with the grams/mile of NO<sub>x</sub> emitted.

Thus, the PEI analysis of the Ford Motor Company field study resolved the previous posed question [20] of whether other additives in the oil formulation can influence the volatility of phosphorus. More specifically and importantly, it seems apparent that engine oil formulation can be tailored to control phosphorus volatility.

Interestingly, Ueda and his associates found much earlier [8] that both calcium and magnesium diminished phosphorus effects on the catalyst. (Were these two types of additives capable of forming volatiles they might curtail adverse phosphorus effects.)

The major remaining question was whether the various chemistries of ZDDPs also affect the volatility of phosphorus and answering this question was the focus of the present paper.

## Studies of the Chemistry and PEI of ZDDPs

### Instruments and Techniques

#### Noack Test Procedures

The Selby-Noack is the only instrument capable of generating the Phosphorus Emission Index and was consequently used to obtain the PEI data of this study. Volatile and residual materials were also used to provide samples for the associated NMR determinations to be presented in a second paper.

As briefly described in the previous section, the routine Selby-Noack technique applies the same conditions as the original Noack procedure. (For greater detail, this procedure

is fully described in ASTM Method D 5800c [12].) However, in generating data for this study, in some experiments the technique was modified to be run either for longer temperature ramps to the operating temperature of 250°C or for shorter intervals than one hour at 250°C. In these modified tests, other than collecting volatiles for longer or shorter time periods, the overall technique was identical to the routine Selby-Noack test.

**Elemental Analyses**

A Leeman Model PS 1000 inductively coupled plasma (ICP) spectrometer was used to determine all elemental concentrations of phosphorus required in these studies. ASTM Method D 4951 [24] was followed using cobalt at 200 PPM as an internal standard.

**Nuclear Magnetic Resonance Procedure**

Small samples of the original oils and the volatile materials and residues obtained during the Selby-Noack tests were analyzed by <sup>31</sup>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. Average data accumulation time for these spectra was one hour. As mentioned, a second paper covers this aspect of the study.

**Initial Studies**

**Reference Oils**

**Formulated and Reference Oils** – The fully formulated oil, RO 780, was classified as SAE 5W-30 engine oil known to be in API/ILSAC categories SL/GF-3. This oil – but minus any ZDDP – was the primary Reference Oil, RO 779 providing blending stock for specially prepared ZDDPs.

**PEIs of the Comparator and Reference Oils** – Volatilities and PEIs using the Selby-Noack were obtained on these two oils and results are shown in Table 2. As expected, the formulation without ZDDP, RO 779, shows no phosphorus in either the formulation or the volatiles. In comparison, RO 780 has a PEI of 4.0 – considered relatively low among the engines oils collected around the world by the International Engine Oil Database of the Institute of Materials [18].

Table 2 – Oil and phosphorus volatilities of fully formulated Oil RO 780 and ZDDP-deficient Reference Oil 779

Description	Selby-Noack Volatility		Phosphorus			PEI mg/L
	Grams	%	Fresh	Volatiles		
			PPM	mg		
RO-780	9.25	14.23	966	30.0	0.28	4
RO-779	8.92	13.72	0	0	0	0

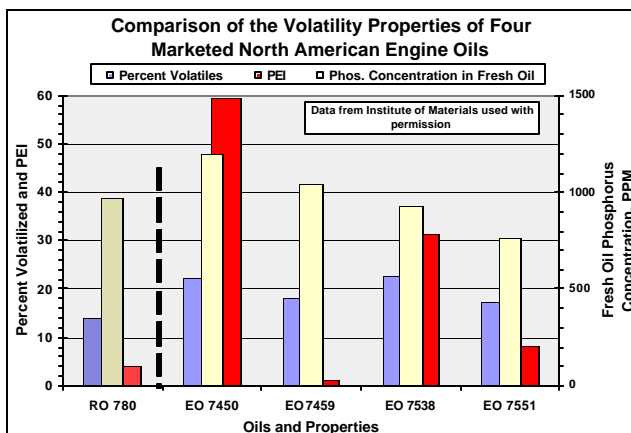
**PEI Analysis of Engine Oils Selected from the Market**

For purposes of determining the effect of large differences in PEI on the NMR signature of the volatile and residue material, four oils having similar oil volatilities but widely different phosphorus volatilities were selected from the IOM International Engine Oil Database for North America and samples obtained. The analyses of these four oils – as well as RO 780 for comparison – are shown in Table 3 and Figure 7.

Table 3 – Comparative oil and phosphorus volatilities of four marketed engine oils of considerably different PEIs.

Identity	Conditions of Test	Selby-Noack Volatility		Phosphorus			PEI mg/L
		Grams	%	Fresh	Volatiles		
				PPM	mg		
RO 780	routine	9.25	14.23	966	30	0.28	4
EO 7450	routine	14.40	22.15	1198	316	4.55	59
EO 7459	routine	11.73	18.05	1038	9	0.11	1
EO 7538	routine	14.66	22.55	933	164	2.40	31
EO 7551	routine	11.27	17.34	763	56	0.63	8

Figure 7 – Variation of PEI among four marketed North American engine oils of different formulations with somewhat similar overall volatility loss and initial phosphorus concentrations



Compared to phosphorus concentrations of the fresh engine oils, Table 3 and Figure 7 show that the volatilized material of the four oils have widely different concentrations of phosphorus and, thus, considerably different levels of associated PEIs. It was considered reasonable that these oils would provide good opportunity in later NMR studies to determine the cause(s) of differences in phosphorus volatility and the related PEI.

**Preliminary Study of Temperature Ramping on Phosphorus Volatility**

As a preliminary test to determine when phosphorus volatiles were generated during the Selby-Noack test, the ZDDP-containing RO 780 was given a one-hour ramping time to the temperature of 250°C followed by the normal hour duration at that temperature. Results are shown in Table 4 contrasted with the normal ramp time of about nine minutes to 250°C.

The data show that although the total volatile material increased by about 13% because of the longer test time, the phosphorus volatilized increased by slightly more than 100%. From these results, it would seem that

1. the longer test encouraged the volatilization of more phosphorus, and/or
2. the slower, longer ramping interval affected the nature of the phosphorus being volatilized

Table 4 – Effects on phosphorus volatilization using one-hour ramp versus normal, 9-minute ramp

Description	Conditions of Test	Selby-Noack Volatility		Phosphorus Fresh Volatiles		PEI mg/L	
		Grams	%	PPM	mg		
		RO 780	normal test	9.25	14.23		966
	1-hour ramp	10.42	16.03		63	0.70	9

The questions raised by these considerations led to further tests reported in the next section of the paper.

**Second Stage of Studies**

**General Considerations**

The question of when phosphorus volatilizes as well as what volatile compounds are produced and what compounds are left in the residual oil during the Selby-Noack test was of considerable interest. It was recognized by the authors that the study of these various relationships would constitute a sizable effort and it was decided to resolve the questions progressively. Some of these efforts are reported in this paper, others in a second paper.

### Dependence of PEI on Residence Time in the Selby-Noack Test

One of the first studies was a modified Selby-Noack test on RO 780 (having a PEI of 4) and a formulated engine oil having much higher PEI. Modified Selby-Noack tests were run in four progressive time intervals of 10, 20, 30, and 50 minutes exposure after the normal nine-minute ramp to volatility-inducing conditions. A special vial-filling drain for collecting small amounts of the volatilized oil was attached to the bottom of the collection vessel. Normal 65-gram samples were used for the test. Following the test, the collected samples were analyzed by ICP to determine their phosphorus content and the related PEI. Table 5 and Figures 8 and 9 show the data obtained (including the 60-minute data given earlier in Table 2).

Table 5 - Progression of Phosphorus Volatility and PEI of Reference Oils in Time-Modified, Selby-Noack Tests							
Oil	NOACK Run Time, minutes	Selby-Noack Volatility		Phosphorus (ASTM D4951)		PEI	
		Grams	%	Fresh ppm	mg Volatiles		
Reference Oil 780	10	2.62	4.03	966	272	0.71	9
	20	4.20	6.46		151	0.63	8
	30	6.12	9.42		111	0.68	9
	50	8.85	13.62		46	0.41	5
	60	9.25	14.23		30	0.28	4
EO 7450	10	3.98	6.12	1198	749	2.98	39
	20	5.45	8.38		684	3.73	49
	30	7.89	12.12		522	4.12	54
	50	12.97	19.95		314	4.07	53
	60	14.40	22.15		316	4.55	60

Table 5 – First sequence of exposure-modified Selby-Noack results on the low-PEI formulated Reference Oil 780 compared to the results from a marketed oil having a relatively high value of PEI

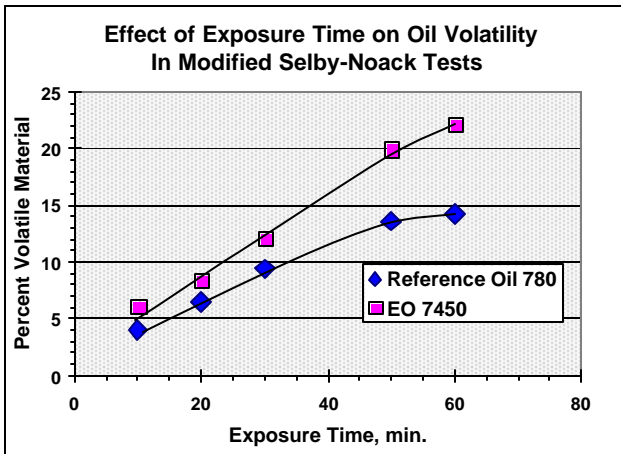


Figure 8 – Dependency of oil volatility on exposure

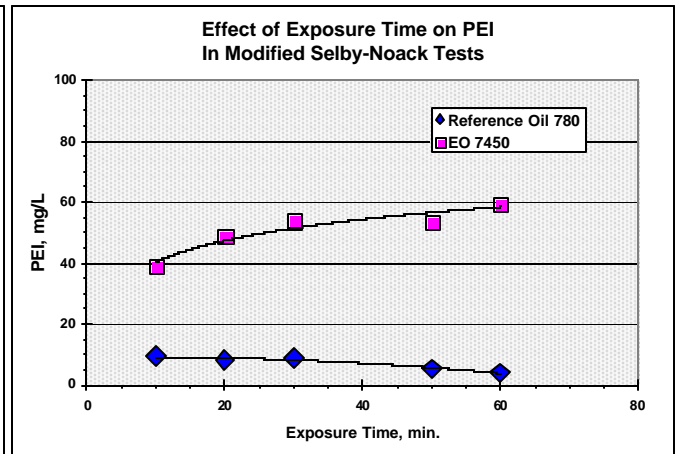


Figure 9 – Dependency of PEI on exposure

As would be expected, the oil volatilities rise with increasing time of exposure as shown in Figure 8. Oil 780 may be coming to equilibrium in about 50 to 60 minutes while the volatility of EO 7450 is still rising, although slowing.

Effects of the forgoing study on the Phosphorus Emissions Index is shown in Figure 9. With Reference Oil 780, the PEI remains essentially constant and may even be interpreted as falling somewhat. In contrast, the ZDDP producing the much higher volatilizing Oil 7450 increases exponentially during the exposure. These dissimilar results raise further questions regarding the nature of the chemical composition of the phosphorus additives as well as effects of the other additives in the two oils – questions appropriate for the NMR study in the paper to follow.

### Modification of the Chemistry of ZDDPs on PEI

**Chemistry and Test Setup** - 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 that consists of slightly lower (at 27.77%) and the other of slightly higher (at 28.07%) levels of phosphorus than the stoichiometric value of 27.87% phosphorus theoretically calculated for P<sub>2</sub>S<sub>5</sub>. These four ZDDPs were blended into a typical GF-3 oil at Savant using the non-ZDDP-containing RO-779. These blends, identified as Test Oils A through D, were again exposed to the time-interval approach.

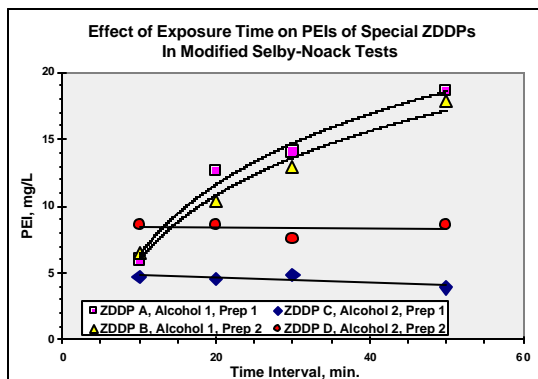
In this portion of the work; exposure times of 10, 20, 30, and 50 minutes in the Selby-Noack instrument were used with the routine 9-minute ramp to an operating temperature of 250°C.

**Test Results** - Results are shown Table 6 and in Figure 10.

Table 6 - Effect of ZDDP chemistry and reaction stoichiometry on the level of phosphorus volatility in exposure-modified Selby-Noack tests.

Forms of ZDDP and Alcohol	NOACK Run Time	Noack Volatility		Phosphorus by ASTM D4951			PEI
		Grams	%	ppm			
				Fresh	Volatiles	Volatiles	
ZDDP A 2-Ethyl Hexanol (P <sub>2</sub> S <sub>5</sub> Less than stoichiometric)	10	2.15	3.31	1062	213	0.46	6
	20	4.61	7.09		210	0.97	13
	30	5.48	8.43		196	1.07	14
	50	7.68	11.82		185	1.42	19
	60	9.85	15.15		127	1.25	16
ZDDP B 2-Ethyl Hexanol (P <sub>2</sub> S <sub>5</sub> Greater than stoichiometric)	10	2.32	3.57	981	214	0.50	6
	20	3.88	5.97		205	0.80	10
	30	5.56	8.55		177	0.98	13
	50	8.92	13.72		153	1.36	18
	60	10.76	16.55		117	1.26	16
ZDDP C 2-Methyl-4-Pentanol (P <sub>2</sub> S <sub>5</sub> Less than stoichiometric)	10	2.78	4.28	991	129	0.36	5
	20	4.05	6.23		86	0.35	5
	30	6.37	9.80		58	0.37	5
	50	9.94	15.29		30	0.30	4
	60	10.22	15.72		15	0.15	2
ZDDP D 2-Methyl-4-Pentanol (P <sub>2</sub> S <sub>5</sub> Greater than stoichiometric)	10	2.59	3.98	1064	254	0.66	9
	20	3.79	5.83		174	0.66	9
	30	5.62	8.65		103	0.58	8
	50	9.09	13.99		72	0.65	9
	60	9.49	14.6		35	0.33	4

Figure 10 - Plot of PEI data from Table 6 showing the clear differences of type of alcohol chosen and the chemistry of preparation of ZDDP.



As evident from Figure 10, PEI values of each of the Test Oils A through D show major differences between the primary and secondary ZDDPs when added in similar concentrations to the Stock Oil RO 779. That is, primary ZDDPs A and B increase in PEI with increasing exposure time in the test while secondary ZDDPs C and D show little change in their PEIs. The latter response indicates that ZDDPs C and D emit all of their volatilizable phosphorus components in less than 10 minutes exposure in the Selby-Noack test. More important is the fact that the one-hour PEI values of the secondary ZDDP-containing oils are comparatively low and do not increase whereas the primary forms of ZDDP investigated in this study are considerably higher and increase further in PEI values with exposure time. For reasons offered earlier, increase in PEI implies continuing generation of phosphorus volatiles during the test.

It will also be noticed in Table 6 that the primary and secondary alcohol preparations are made with two samples of P<sub>2</sub>S<sub>5</sub> that contain different levels of phosphorus. Of these two pairs of ZDDPs, little difference is shown between the primary ZDDPs A and B. However, significant differences are shown between the secondary ZDDPs C and D. That is, at closely similar concentrations (991 versus 1064 PPM, respectively), ZDDP C has about half the value of PEI shown by ZDDP D.

Table 7, obtained from the Institute of Materials Engine Oil Database show that both of these secondary ZDDPs are at relatively low levels of PEI compared to other oils around the world.

Table 7 – Comparison of PEI of specially prepared primary and secondary alcohol ZDDPs to marketed oils from around the world.  
(Data from IOM Engine Oil Databases – used with permission)

<b>Table 7 - PEI Values for Special ZDDPs Compared to Values of Oils in the International</b>					
ZDDP in Stock Oil 779	NOACK Run Time	PEI	Percentile of Oils Better Than Test Oil *		
			N. Amer.	Europe	Asia
ZDDP A	10	6	5	17	26
	20	13	51	77	64
	30	14	56	80	69
	50	19	78	90	79
ZDDP B	10	6	5	17	26
	20	10	31	59	53
	30	13	51	77	64
	50	18	74	88	77
ZDDP C	10	5	3	8	18
	20	5	3	8	18
	30	5	3	8	18
	50	4	0	4	12
ZDDP D	10	9	23	52	48
	20	9	23	52	48
	30	8	18	43	43
	50	9	23	52	48
* IOM Database for 1999-2000					

## Discussion

### *Relevance of the PEI to Observed Field Catalyst Deterioration*

On the basis of the Ford Motor Company field studies, correlation of the PEI generated using the Selby-Noack shown in Table 1 and Figures 5 and 6 is evident. The degree of correlation suggests that the volatility of phosphorus is perhaps the most important source of such catalyst contamination whether or not it is generated from the crankcase and passed to the exhaust stream through the EGR valve or from oil leaking directly into the combustion zone from piston ring bypass or down the valve stems.

Moreover, the work clearly shows that engine oil formulation is a critical aspect of controlling phosphorus volatility and raises the question of whether certain additives are more effective than others or whether some of the other additives actually enhance phosphorus volatility.

### *General Comments on PEI Technique Used in These Studies*

In this work a special technique was used to drain the contents of the collection cup of the Selby-Noack instrument into a small vial after a shortened run where it was desirable to catch small amounts of volatile material. This was successful in obtaining PEIs over the series of time intervals. Considering the results obtained on those samples continuing to generate phosphorus to the end of the 60-minute test, it is evident that longer exposure periods should be even more revealing

### ***Comparison of Two Special Reference Oils***

As previously noted, two special reference oils, RO 779 and RO 780 were provided by Chevron Oronite Company LLC. RO 779 had no ZDDP added but otherwise was identical in base stock and additive content to RO 780. Table 1 showed that the responses of the two reference oils were as expected with RO 779 evidencing no volatile phosphorus and RO 780 showing a PEI of 4 – a comparatively low value. RO 779 was thus considered to be acceptable as a stock for the subsequent blending studies of specially made ZDDPs.

### ***Comparison of Four Marketed Engine Oils***

In an effort to determine the differences between engine oils having similar oil volatilities and fresh oil phosphorus concentrations but markedly different phosphorus volatilities shown by the PEI, four oils were chosen from the IOM Engine Oil Database. Sufficient samples were received through the courtesy of IOM to run comparative Selby-Noack tests from which were collected the volatile material as well as the residual oil for NMR studies. This data, shown in Table 3 and Figure 7, show both the similarities of oil volatilities and fresh oil phosphorus concentrations and are in clear contrast to the different levels of PEI, which are as great as 3700%.

### ***Effect of Different Temperature Ramps***

A preliminary effort was made to determine if ramping time from ambient to 250°C for the Selby-Noack test would show differences in the phosphorus volatiles collected. Data presented in Table 4 using RO 780 indicates that significant differences in ramping time does have an effect and raised the questions of whether the effect is related to

1. a difference in phosphorus decomposition products or
2. merely the extended time of exposure of the sample.

In view of the later experiments shown in Table 5 and Figure 9 conducted by varying exposure time for Oil 780 (in which the full content of volatilizable phosphorus was delivered to the Selby-Noack collector in less than 10 minutes), it is more likely that there is a difference in the path of phosphorus decomposition. That is, for Oil 780, the difference in oil volatility increase with and without extended ramping time – about 13% – for the longer ramping test is considerably less than the 125% increase in volatilized phosphorus. This preliminary finding emphasized the value of further investigation using the NMR spectrometer to determine what differences were present.

### ***Effects of Exposure Time in Otherwise Normal Test Technique***

*First Evaluation of Technique* - Desire to determine the progression of the breakdown and volatilization of ZDDP in the fresh oil led to the technique of varying the length of exposure of the oil to 10, 20, 30, 50, and 60 minutes in the Selby-Noack test. In this initial study, RO 780 was compared to IOM's EO 7450, a formulated oil from the market having relatively high PEI.

First results were shown in Table 5 and Figures 8 and 9. Not surprisingly, increasing exposure showed progressive increase in oil volatilization. The technique, however, showed dissimilar results in progressive values of the PEI since RO 780 gave results indicating that all volatile forms of phosphorus from the ZDDP additive in this oil were generated within the first 10 minutes of exposure at 250°C.

*Volatile Phosphorus a Small Part of Available Phosphorus* - As noted previously, the PEI data of RO 780 showed no further generation of phosphorus with more lengthy exposures (and, in fact indicated some decrease in PEI at 50 and 60 minutes exposure). Thus, whatever volatile decomposition products were produced before 10 minutes exposure comprised only a small fraction of the phosphorus-containing additive(s) present in the fresh oil. That is, 850 grams of the fresh RO 780 contains 966 PPM phosphorus or approximately 820 mg/L whereas the PEI is 9 mg/L - about 1% of the phosphorus in the fresh RO 780 is volatilized in this test.

In contrast, the IOM EO 7450 contains 1198 PPM or approximately 1020 mg/L. In this case, the PEI rises to 60 at 60 minutes of exposure and, thus, about 4% of the phosphorus material in the fresh oil is capable of being volatilized at this length of exposure. Greater length of exposure might increase this level of phosphorus volatility of IOM EO 7450 although it does seem to be reaching a plateau.

*Application of Progressive Exposure Technique to Special ZDDPs* - The four special ZDDPs made by Astaris to generate further understanding of the causes and forms of phosphorus volatilization were added to the stock oil, RO 779, at levels of about 1000 PPM. Using the technique of progressive time exposure, the results are shown in Table 6 and Figure 10.

The PEI values obtained demonstrate obvious differences in phosphorus volatility between the particular primary- and secondary-alcohol ZDDPs. Specifically, both higher and lower stoichiometric variants of this primary alcohol's ZDDPs show continuing release of volatile phosphorus during the one-hour Selby-Noack test with the rate of release decreasing with increasing time of exposure. At 50 minutes about 2% of the original phosphorus in the oil has been volatilized. Both preparations of the primary ZDDP at slightly higher and lower  $P_2S_5$  stoichiometries are closely similar in their PEI response to increasing exposure.

In contrast, the particular secondary alcohol ZDDPs show little or no change in PEI with exposure time indicating that all the volatile phosphorus entities that will be formed are volatilized early in the test. However, in this case there is a difference in whether the ZDDP is formed from  $P_2S_5$  that contains a higher or lower than stoichiometric level of phosphorus. The higher-than-stoichiometric ZDDP C gives phosphorus release of about 1% of the original phosphorus in the oil. In contrast, the lower-than-stoichiometric ZDDP D gives phosphorus release of about 0.6% of the original phosphorus – a considerable difference in phosphorus release.

*Resolution of the Question of the Volatility Role Played by ZDDP Formation* – Most important, this latter data answers the question of whether the chemical form of ZDDP can markedly affect its tendency to volatilize. As to how well this statement applies to other forms of ZDDP, this is a matter of further study. Certainly, from the viewpoint of controlling phosphorus volatility, there is a strong need for much more information regarding the relationship of the chemical form of ZDDP and its dependence on the other additives used in formulating engine oils.

## Conclusions

This series of studies of the variation of the Phosphorus Emission Index generated from several applications of the Selby-Noack instrument has been effective in revealing some of the characteristics of the phosphorus volatilization from ZDDPs made from a primary and a secondary alcohol. Thus, the primary objective of this study has been met. That is, it has been shown that phosphorus volatilization and the associated PEI are affected strongly by the chemistry of the ZDDP. Whether or not these differences are caused by thermodynamic effects and/or some form of steric interference remains to be determined as well as the range of differences that may exist among the different alcohols.

Moreover, using the PEI as an investigative tool for this initial study, differences between the primary and the secondary alcohols chosen are also found in the immediacy and ultimate levels of forming volatile forms of phosphorus species. Variation in PEI of four marketed engine oils in North America have shown marked differences of 3700%. Even comparing the two alcohols used in this study, the differences in PEI were about 400%. To be sure, at this point, the latter observations are limited to the two alcohols used to make the ZDDPs for this study but the technique is obviously readily applicable to all other variations of ZDDPs.

The study also generated sufficient volatilized samples to permit the generation of NMR spectra and this work will compose a second paper in this set.

One area of question that was not part of this study but should be considered is the impact of phosphorus volatilization on the residual oil from the Selby-Noack test. That is, to what extent is the anti-wear and anti-oxidation performance of a ZDDP compromised by phosphorus volatilization. This information is of obviously high interest and importance given the primary purpose of ZDDPs in engine oils.

## Acknowledgments

The authors would like to thank those who dedicated their efforts in preparing, blending and analyzing the various oils used in this study. Among these were Skip Ramsey of Astaris for his assistance in preparing the ZDDPs, George Schaller of Savant Labs for running the Selby-Noack tests and both he and Mike Habitz of Savant Labs for blending the test samples and analyzing the results. For the marshalling of samples and data, the help of Amy Parker and Joyce Gee were indispensable. Special thanks are extended to Chevron Oronite Company LLC for providing typical GF-3 oil samples with and without ZDDP.

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