Phosphorus Volatility of Lubricants --
Use of the Phosphorus Emission Index of Engine Oils

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Abstract: During 2002 the concept and principles of the Phosphorus Emission Index (PEI) was introduced. This paper first reviews the background of the benefits and concerns regarding phosphorus additives. In particular, the paper focuses on the two factors until recently assumed important in phosphorus volatility and catalyst contamination -- oil volatility and initial phosphorus concentration.

Studies of Selby-Noack data on 1300 oils collected in 1999 and 2000 by the Institute of Materials showed the invalidity of the two assumptions and this led to the concept of the PEI. Further studies in conjuction with a field taxi study by the Ford Motor Company to determine correlation of the PEI with catalyst contamination shows not only correlation but also proved that phosphorus volatility was independent of either oil volatility or fresh oil phosphorus levels. Rather, phosphorus volatility was, as earlier predicted, found to be highly dependent on its chemistry and the chemistry of other additives. Engine oil formulation using the PEI technique should markedly reduce phosphorus volatility and resultant catalyst

1. Background

a. Volatility of Engine Oil Components

Overall Oil Consumption -- Through many years of use of the reciprocating engine, oil consumption has been a strong indicator of engine condition and engine design. Long mileage intervals between need to add oil was a sign of an engine in good shape -- just as short mileage and a plume of burned oil from the exhaust was an indication of poor condition.

Oil Volatility - Engine oil volatility was an important aspect of oil consumption and an early focus of technical improvement of lubricating oils starting in the earlier 1900s. K. Noack, in the 1930s developed a technique and apparatus to measure mineral oil volatility **[1]**. In the absence of readily controlled sources of heat, the technique required the use of molten Woods Metal as a stable means of heat transfer at the test temperature of 250°C. Engine oil volatility has continued as a concern and Noack's approach stood the test of time. His technique was adopted as a bench test method for engine oil volatility determination (DIN 51-581 **[2]**, CEC L-40-T-87 **[3]**, and ASTM D 5800 **[4]**).

Reduction of Oil Consumption - Automotive engineers have been no less concerned with oil volatility and consumption. A particular concern was with the effects of oil consumption on combustion chamber deposits and the additional engine stress of knock caused by these deposits. Over the many years, and with the assistance of computer design, automotive engineers have been able to improve engine design to the point where oil consumption is much less a problem in modern engines.

b. The Phosphorus Issue

However, as is often the case, resolution of one problem reveals another. In this case, another form of volatility concern has become more visible over the last 20 years. The issue has to do with recognition of the effect of volatile phosphorus on reducing the effectiveness of the exhaust catalyst and the recently determined significant role of the other additives present in the engine lubricant.

Phosphorus Additive Benefits - Phosphorus additives in the form of zinc-diorgano-dithio phosphates (ZDDP) have been a critically important part of engine oil formulation for more than a half century. The intimate interdependence of the engine oil and engine permitted automotive engineers to capitalize on the effectiveness of these phosphorus additives. Using ZDDP, more efficient engines could be designed that had greater resistance to wear and engine oil oxidation even at higher power.

Phosphorus Impact on Emissions - Unfortunately, as mentioned, volatilization and other avenues of loss of ZDDP also adversely affects exhaust emissions by progressively inactivating the exhaust catalyst.

Efforts to Control Phosphorus Effects on the Catalyst -- As concern increased with increasing demanding governmental regulations, two steps were taken to reduce phosphorus volatility effects:

Engine Oil Volatility Reduction - One of the early actions was to place limits on the volatility of passenger car engine oils based on the reasonable assumption that oil volatility influenced phosphorus volatility.

Limits on Phosphorus Concentration - A further effort was to limit the amount of the phosphorus additives used in automotive engine oils. In this case the assumption was that phosphorus volatility was directly related to the phosphorus content in the engine oil -- again, a very reasonable assumption. However, limiting the phosphorus concentration in the engine oil would have a quickly apparent negative aspect. That is, since the use of phosphorus had for years been an important aspect of engine wear protection, how susceptible would engines be to loss of such benefits from the engine oil.

Better metallurgy and better engine design are positive answers for modern engines but no answer for older engines whose designs were founded on the premise of the availability of ZDDP additives. Introduction of any replacement technology always carries the burden of no harm to the consumer. It also carries the cost of proving its equivalency or superiority to past technology. This is the nub of ongoing discussions in the industries involved.

2. Studies of Phosphorus Volatility

a. Early Work - Instrument Design

In 1993, the author's laboratory was requested to run the Noack test. Rejecting the use of Noack's Woods Metal heating approach because of potentially toxic fumes from the Woods Metal, an alternative approach was developed and patented **[5,6]**.

Upon initiating this developmental process, it was recognized that the instrument and test should be made more informative by collecting all the volatiles thus permitting analysis of the separate but interrelated properties of the volatiles, the residue, and the original oil.

The Instrument - Accordingly, the new design also also collects 99% of the volatilized oil **[9]** and makes this oil available for such comparative analyses **[7-11]**. The resulting instrument called the Selby-Noack is shown in Figure 1 as manufactured by its licensee, the Tannas Co.

A schematic drawing of the important elements of the instrument is shown in Figure 2. Essentially these are 1) the volatilizing chamber heated by the resistance of a surrounding noble-metal coating and 2) the volatiles coalescing collector. The slight vacuum used in the Noack technique of 20 mm of water is maintained by an adjustable regulator designed for this use. For tests of engine oil volatility, temperature is held at 250°C (but can be any desired temperature) by a programmed controller.

The instrument has been made a part of ASTM D 5800 **[4]** as a result of acceptable correlation with the original Noack but with somewhat higher precision as shown in Figures 3 and 4.

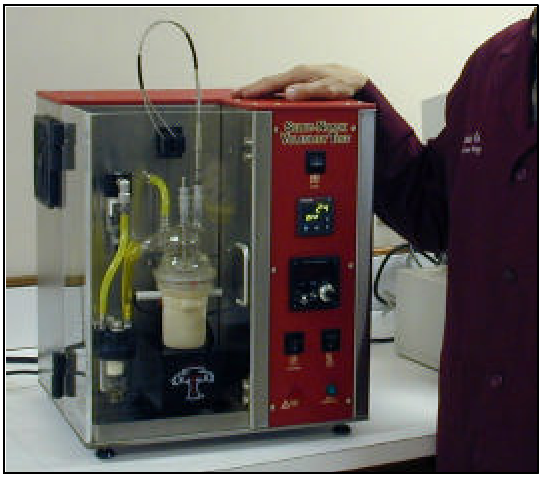

Fig. 1 - Picture of Selby-Noack instrument

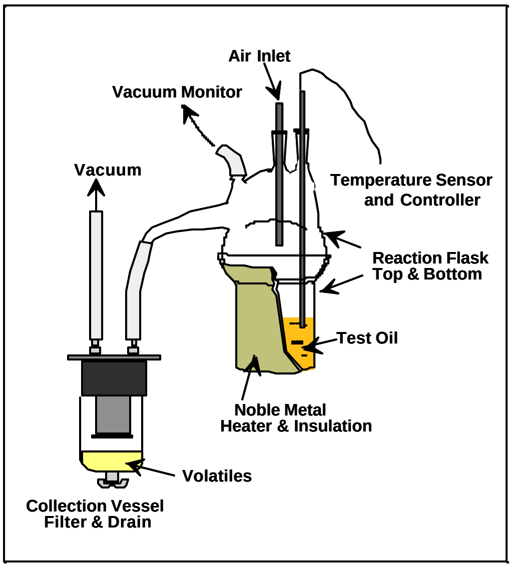

Fig. 2 - Schematic drawing of Selby-Noack

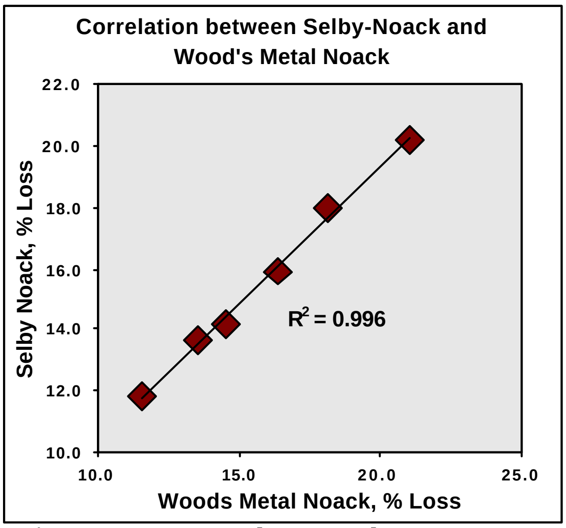

Fig. 3 - ASTM correlation study

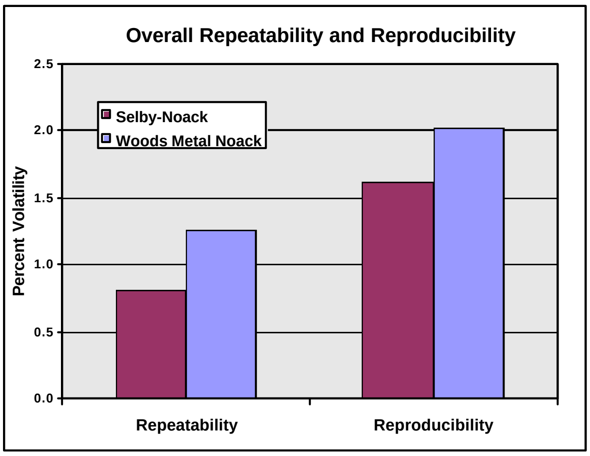

Fig. 4 - Precision of Selby-Noack compared to Noack

b. Later Work -Testing the Assumptions

Two principle assumptions have been indicated concerning the manner by which phosphorus reaches the exhaust catalyst. One is related to engine oil volatility and the other is related to the amount of phosphorus in the engine oil. Both assumptions were generated through reasonable considerations of the need to correct the phosphorus problem. However, the validity of such assumptions have been untested up until this paper and one preceding **[12]**.

Dependence on Engine Oil Volatility? - This assumption was first tested in earlier papers by the author and his associates **[9,10,11]** using the Selby-Noack instrument.

Limited data showed 1) that phosphorus was one of two volatile elements (boron was another) found in significant quantity using inductively coupled plasma (ICP) spectroscopy (sensitive to a few parts per million) and 2) that there might not be an engine oil, phosphorus volatility dependence. However, the number of samples was not considered sufficient for firm conclusions.

In a following paper given in early 2002 **[12]**, information from 1300 engine oils was obtained from the Institute of Materials (IOM) engine oil database for the years 1999 and 2000. (In this database, engine oils are collected by the Institute from the market around the world and are analyzed thoroughly.) Tests include the Selby-Noack volatility test and, thus, data was available on the phosphorus levels of volatilized and fresh oils.

Analysis of IOM Data - The data for oil volatility in percent volatility loss was plotted against milligrams of phosphorus found in the volatiles. Figures 5, 6, and 7, show the correlation study.

Error of the First Assumption -- Statistical values of the Coefficient of Determination, R^2 (a measure of degree of correlation -- 1.0 is perfect correlation), are very low (ranging from 0.006 to 0.067) and indicate that phosphorus volatility is not dependent on

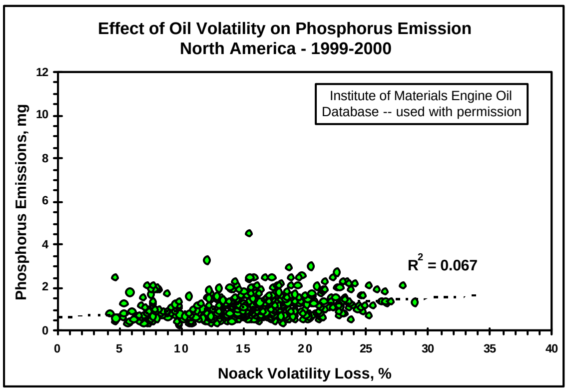

Fig. 5 Comparison of oil and phosphorus volatilities for North American engine oils

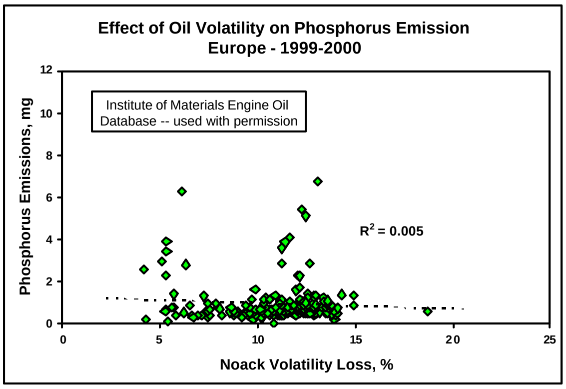

Fig. 6 Comparison of oil and phosphorus volatilities for European engine oils

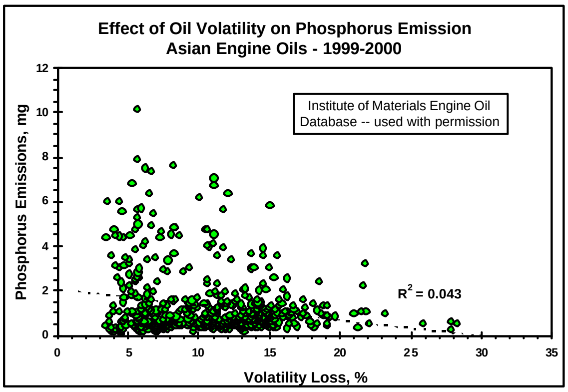

Fig. 7 Comparison of oil and phosphorus volatilities for Asian engine oils.

engine oil volatility. Consequently, modifying engine oil volatility to control phosphorus volatility is an ineffective approach. Another piece of information found in the data presented in these plots is that the level of phosphorus volatility varies over a wide range, from 0 to 10 mg, particularly in Asia.

Dependence on Phosphorus Level? - The second assumption was that reducing phosphorus concentration in the formulated engine oil will reduce the phosphorus levels reaching the exhaust catalyst.

Again, the 1300 oil analyses for the years 1999 and 2000 from the Institute of Materials database were used with the results shown in Figures 8 through 10 which generated by plotting the concentration of phosphorus in the fresh sample against the so-called Phosphorus Ratio. (The author previously defined Phosphorus Ratio as the ratio of the concentration of phosphorus in the volatile material to the phosphorus concentration in the fresh oil, both in parts per million **[12]**.)

Phosphorus Ratio Analysis - When appraising the relationship between the phosphorus concentration in the fresh oil to that in the volatiles, it is necessary to eliminate the variable levels of oil volatility since no comparison of absolute amounts of phosphorus in the volatiles would be valid. The Phosphorus Ratio does this and, in addition, tests any relationship between the phosphorus present in the volatiles and that in the fresh oils.

Phosphorus Ratio = 1 - If, for all oils, the concentration of phosphorus in the volatiles is equivalent to the concentration in the fresh oils, all values of the Phosphorus Ratio will, of course, be unity.

Phosphorus Ratio < 1 - If the Phosphorus Ratio for all oils is constant but less than unity, it suggests that some uniform constraint is controlling the rate of release of the phosphorus.

Phosphorus Ratio > 1 - If, however, the Phosphorus Ratio of all oils is constant and above unity, it indicates that some form of selective decomposition or volatilization is occurring which is directly associated with the phosphorus additives.

Variable Phosphorus Ratio - Lastly, if the Phosphorus Ratio of oils is variable, the second assumption that lowering phosphorus levels to control phosphorus volatility is not a meaningful approach except where phosphorus volatility is not the primary source of catalytic degradation by phosphorus.

Surprising Failure of Second Assumption - Appraising Figures 8, 9, and 10, the answer is clear but surprising -- the Phosphorus Ratio varies significantly from oil to oil. In some cases, the Phosphorus Ratio indicates that the phosphorus concentration in the volatiles may exceed that of the fresh oil by as much as 400%. Phosphorus concentration in itself is not found closely related to phosphorus volatility even though the presence of the former provides the expression of the latter.

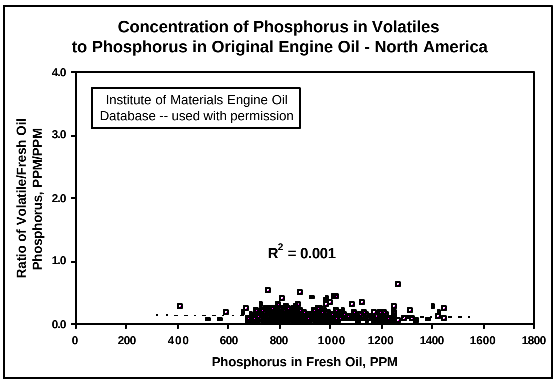

Fig. 8 Comparison of Phosphorus Ratio of fresh and volatilized North American engine oils

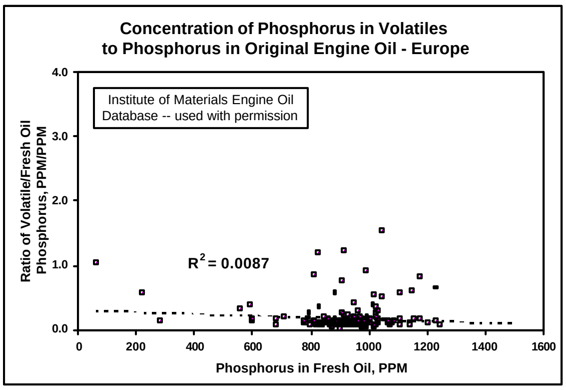

Fig. 9 Comparison of Phosphorus Ratio of fresh and volatilized European engine oils

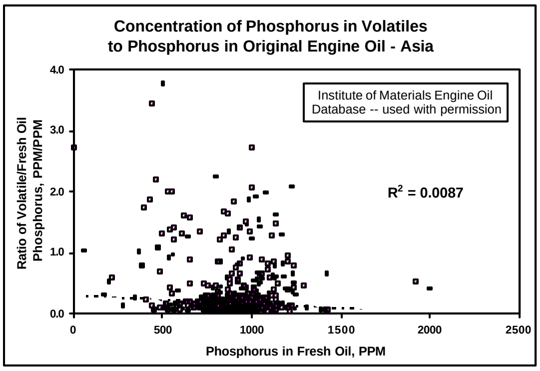

Fig. 10 Comparison of Phosphorus Ratio of fresh and volatilized Asian engine oils

It is of interest to see how the Phosphorus Ratio varies among the oils of the three regions of the world sampled by the Institute of Materials. Cumulative plots are shown in Figures 11, 12, and 13.

The data show the continuously variable nature of the Phosphorus Ratio again emphasizing the lack of correlation between the fresh level of phosphorus and that of the volatiles. This evidence points to another cause of phosphorus volatility. As previously stated **[12]**, "the influence of phosphorus content in the fresh oil is apparently modified by both the chemistry of the phosphorus compounds ... as well as the overall formulation".

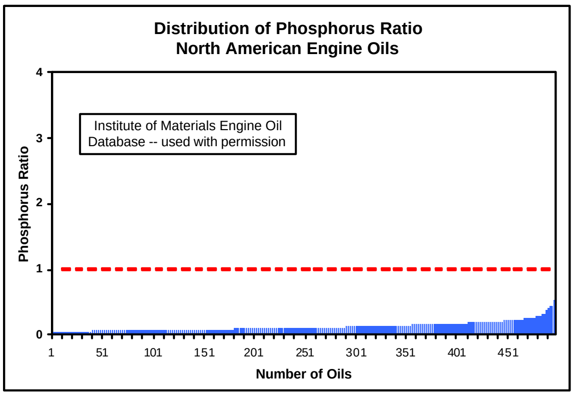

Fig. 11 Phosphorus Ratio distribution of fresh North American engine oils

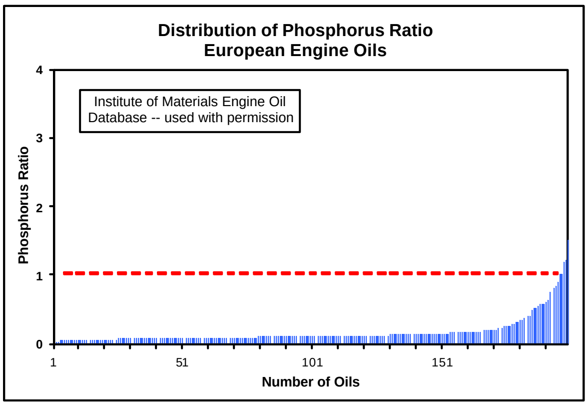

Fig. 12 Phosphorus Ratio distribution of fresh European engine oils

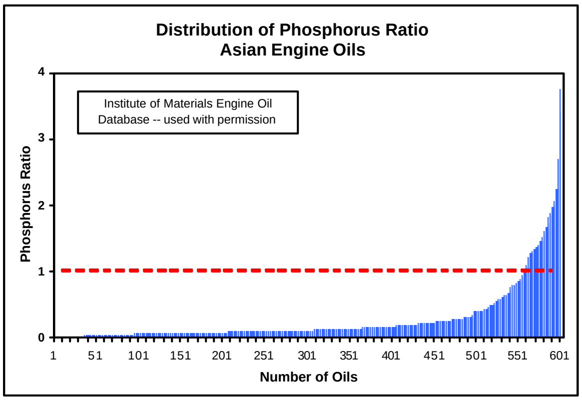

Fig. 13 Phosphorus Ratio distribution of fresh Asian engine oils

3. The Phosphorus Emission Index

a. Rationale

In considering the results from testing two reasonable but invalid assumptions regarding phosphorus volatility, the question became one of finding a technique of measuring the proclivity of an engine oil to produce volatile phosphorus. Preferably, the technique would be simple, inexpensive, and reasonably repeatable.

The Noack form of volatility testing seemed to be a good approach as a relatively simple bench test requiring only 65g of sample and an hour at 250°C. Coupling this with the volatiles-collecting ability of the Selby-Noack, measuring amounts of both the original phosphorus and the phosphorus volatilized during the test would provide the necessary data.

b. Calculation Phosphorus Emission Index

Since the primary information of interest was determing the amount of phosphorus that would volatilize from a given quantity of engine oil, the Phosphorus Emission Index (PEI) was developed and previously presented **[12]** as:

milligrams of phosphorus volatilized in the Selby-Noack test per liter of engine oil

As an equation:

$$\mathbf{PEI = mg\,P_{SN} \cdot 850g/L \div 65g \;=\; mg\,P/L}$$

This met the criteria of being both a simple and inexpensive approach but still required the further step of determining of repeatability.

c. Phosphorus Emission Index Repeatability

Repeatability was measured by taking an oil collected several times over the two year period by the IOM database. The manufacturer of the oil was know to be scrupulous in formulation and blending. Data from the database for six samples of this oil are shown in Figure 14.

Despite batch-to-batch variations, repeatability of both oil volatility and the Phosphorus Emission Index seem acceptable. Standard deviation of oil volatility and the Phosphorus Emission Index was 4% and 11%, respectively.

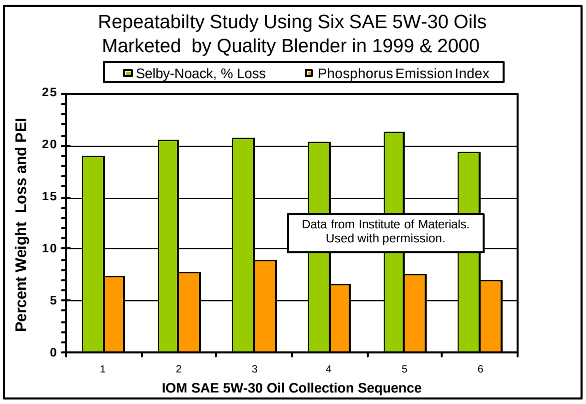

Fig. 14 - Repeatability of oil volatility and Phosphorus Emission Index

d. PEI Analysis of IOM Engine Oil Database

Application of the Phosphorus Emission Index to the phosphorus volatility values in the IOM Engine Oil Database for 1999 and 2000 produced the results shown in Figures 15, 16, and 17.

The similarities and differences in the three areas of the world are evident. Asia, in particular has a 10% of its oils above a PEI level of 40 mg/L and some PEI values that are over 100 mg/L. The questions these observations raise is 1) how well do these values correlate with the engine and 2) if they do correlate, what is a reasonable value of PEI?

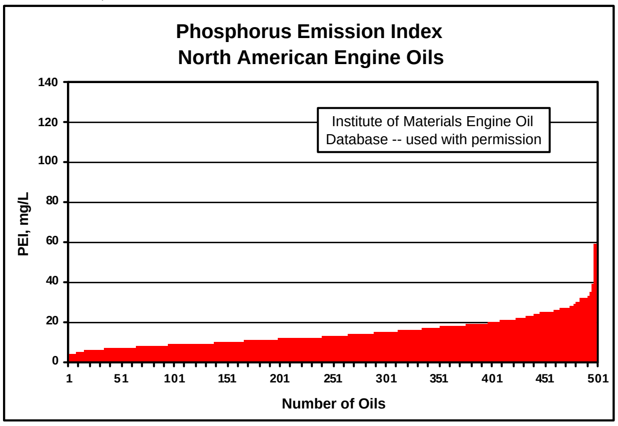

Fig. 14 - Distribution of Phosphorus Emission Index for oils collected in North America during 1999 and 2000

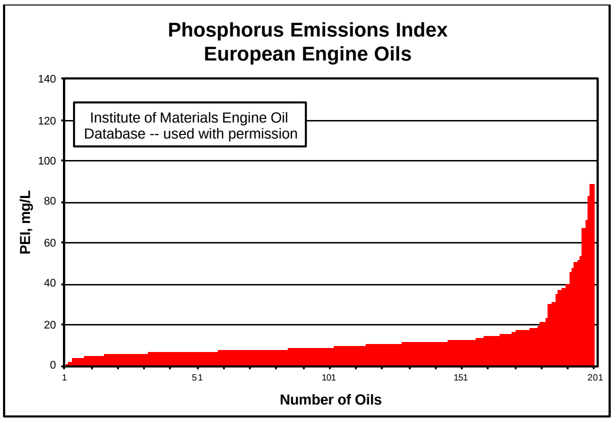

Fig. 15 - Distribution of Phosphorus Emission Index for oils collected in Europe during 1999 and 2000

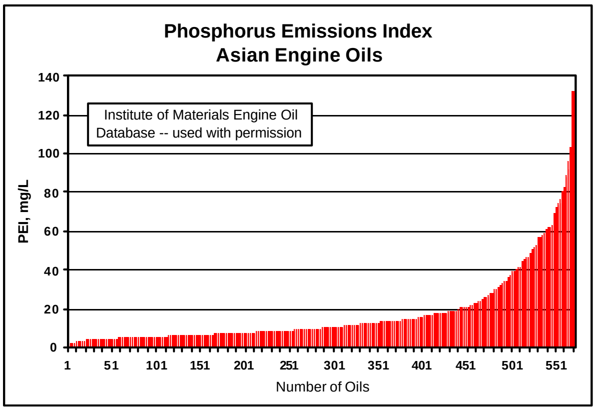

Fig. 16 - Distribution of Phosphorus Emission Index for oils collected in Asia during 1999 and 2000

4. Initial Studies of Field Correlation

a. PEI Correlation with Field Catalyst Studies

Source of Test Samples -- Three unknown samples from a taxi fleet study already completed by the Ford Motor Company were made available to the author's company in a preliminary investigation of the applicability of the PEI concept. The objective was to test the Phosphorus Emission Index against data already obtained regarding the level of phosphorus deposition on the catalyst and resultant emissions.

Oil Volatility and Phosphorus Levels -- Two Selby-Noack analyses were made of each oil to also get a feeling for repeatability with these oils. Samples of the fresh oils and of the volatilized material were analyzed elementally for phosphorus. Results on fresh engine oil volatility and the amount of phosphorus in 65g of these fresh oils are shown in Figures 17 and 18.

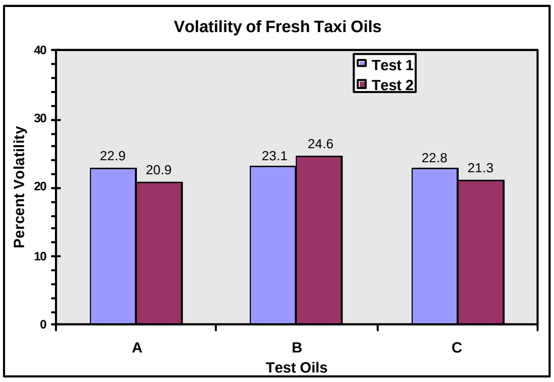

Fig. 17 - Fresh engine oil volatility from taxi fleet test

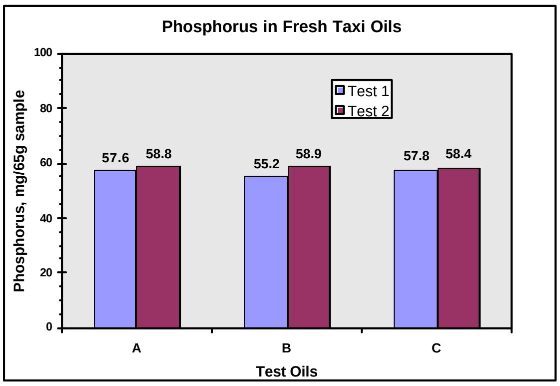

Fig. 18 - Mass of phosphorus in 65g sample of fresh engine oil from taxi fleet test

Both pieces of taken together were quite interesting because of the similar oil volatilities and phosphorus content. This combined information suggested that the concept of the Phosphorus Emission Index would be thoroughly and interestingly tested.

Phosphorus Emission Indices -- The Selby-Noack test information was subsequently analyzed by elemental spectroscopy for phosphorus and produced the Phosphorus Emission Index data shown in Figure 19.

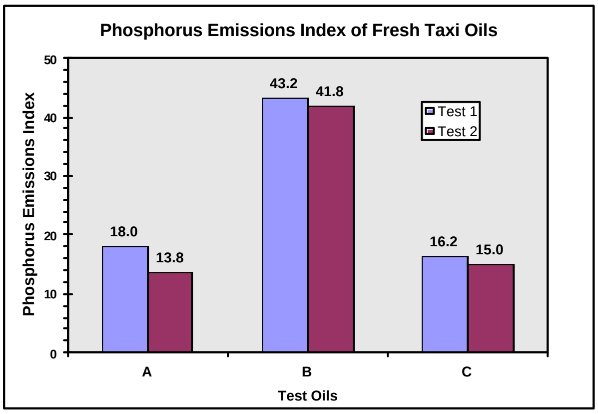

Fig. 19 - Phosphorus Emission Indices of three fresh engine oils used in taxi fleet test

It is obvious from Figure 19 that even though the volatility of the oil and the concentration of the phosphorus in the fresh oils were the same, there were marked differences in the phosphorus volatility and the related Phosphorus Emission Index.

Comparison of Field Results to the PEI -- The data of Figures 17, 18, and 19 were presented to Ford Motor Co. who then made data available regarding the phosphorus deposits on the catalyst with the three oils. This data is shown in Table 1 and Figure 20.

Table 1 - Information from Taxi Fleet Test and from PEI Tests on Fresh Oils		
Test Oil	Phosphorus Emission Index	Phosphorus on Catalyst, g
A	15.9	14.6
B	42.5	24.6
C	15.6	14.6

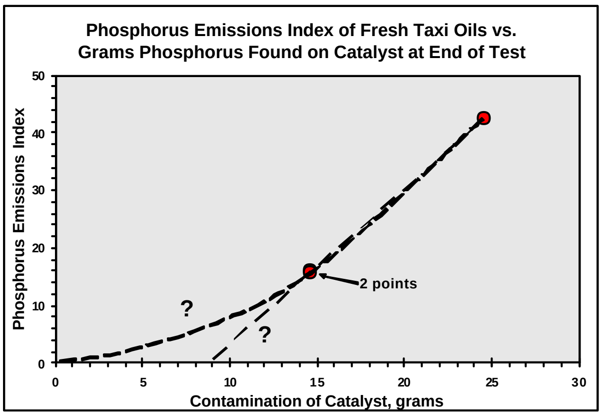

Fig. 20 - Cross plot of PEI data and Ford catalyst phosphorus deposit tests

The data of Table 1 and Figure 20 show clear correlation between the Phosphorus Emission Index and catalyst deposits. Dashed lines on Figure 20 indicate that with essentially two pieces of data, it is not possible to know whether the relationship is linear (with some other nonvolatile mechanism involved in phosphorus contamination of the catalyst) or if the relationship is continuous to zero PEI and zero deposits on the catalyst. More data is being sought.

<u>Further Information Regarding the Ford Field Data - Effects of Other Additives on Phosphorus</u>

The study conducted by Ford using Oils A, B, and C contained further interesting information explaining the relationships found in Figures 17 and 18.

It turned out that all three oils had the same base oil, the same phosphorus chemistry at the same level. The three oils varied only in the other additives used to make up a formulated engine oil. Oil A had a calcium-magnesium "package" while Oil C had an all calcium additive package. Most interestingly, Oil B had no additives other than the phosphorus.

These results, then, confirmed the previous findings and deductions regarding the development of the Phosphorus Emission Index. That is, it was now clearly evident from the phosphorus deposit and PEI data gathered, that phosphorus volatility is independent of both oil volatility and phosphorus content of the fresh oil. In this case, however, the independence was profound since the base oils and phosphorus additive were the same and the phosphorus was at the same concentration. Most important, one of the causes of phosphorus volatility was clearly revealed -- the critical effect of other additives or their lack.

By collecting emission information, the Ford study also permitted a relative answer to the question of relationship of PEI, and the associated phosphorus catalyst deposits, to such emissions. Data gathered on one gas, NO_X, of the three emissions gases documented, is shown in Table 2.

Table 2 - Information from Taxi Fleet Test Regarding NO_x Emissions

Test Oil	Phosphorus Level, mg/L	NO_x/Mile grams
A	**761.1**	**0.76**
B	**758.5**	**1.20**
C	**759.8**	**0.85**
5	**0.0**	**0.41**

Although the study was conducted on same model and age vehicles, the data also permit a view of how PEI relates to emissions resulting from phosphorus deposition on the catalyst

Oil 5 in Table 2 -- which was used as comparator in the Ford taxi fleet study -- was indicated to contain no phosphorus. As further shown in Table 2, this oil gave a value of 0.41 grams NO_X/mile which was about half of that shown by Oils A and C and about one-third that shown by Oil B.

With this information it is possible correlate Phosphorus Emission Index to the NO_X emissions resulting from phosphorus degradation of the catalyst in the vehicles comprising the Ford taxi fleet. This is shown in Figure 21.

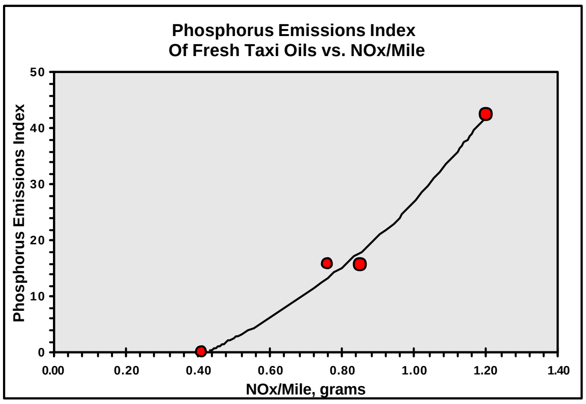

Fig. 21 - Relationship of the PEI and the emission of NOx obtained from the Ford taxi fleet study

The data of Figures 18 and 21, and Table 2 indicate that, for these particular vehicles, a PEI of about 42 gives an NO_X value of about 0.8 g/mile above the reference Oil 5, while a PEI of about 16 gives an NO_X value of about 0.4 g/mile more than Oil 5. Figure 22 shows this latter relationship for the Ford taxi fleet study with PEI plotted against the relative NO_X generated at this level of phosphorus volatility.

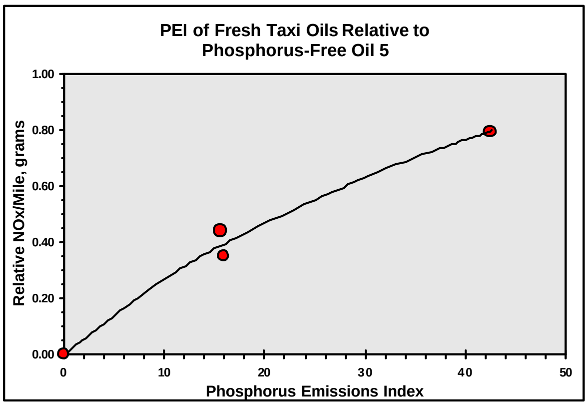

Fig. 22 - Relative relationship of the PEI to the emission of NOx obtained from the Ford taxi fleet study

Essentially, Figure 22 shows how the NO_X values change with increasing phosphorus volatility as represented by the values of PEI generated by the Selby-Noack test. The shape of the curve suggests that NO_X increases more rapidly for these vehicles and engines as PEI and phosphorus emissions increase.

<u>General Comments</u> -- Considering that the above relationships are developed from four oils in the Ford study, there is opportunity and need to expand the collection of data in order to determine the influence of engines, driving patterns, phosphorus chemistry, and the chemistry and interactions of other additives in the engine oil.

The data obtained in the Ford taxi fleet study has shown direct support for the prior conclusions from the study of oils in the IOM database and has given definition of the meaning of Phosphorus Emission Index values in regard to both phosphorus volatility and emissions of NO_X.

4. PEI and Engine Oil Formulation

a. Formulation and Phosphorus Volatility

The data resulting from these studies of phosphorus volatility, phosphorus deposits, effects on emissions, influence of other additives and the Phosphorus Emission Index are challenging in regard to engine oil formulation. The data have shown that reducing oil volatility and/or phosphorus content in the oil is not necessarily helpful to catalyst protection.

In fact, as a result of the ILSAC specification change from GF-1 to GF-2 (API SH to SJ), maximum phosphorus content was lowered from 1200 to 1000 PPM. Using the aforementioned information from the IOM Engine Oil Database for North America indicates that average change in maximum phosphorus concentration levels went from about 1050 PPM to about 900. However, the Phosphorus Emission Index remained the same. This is shown in Figure 23.

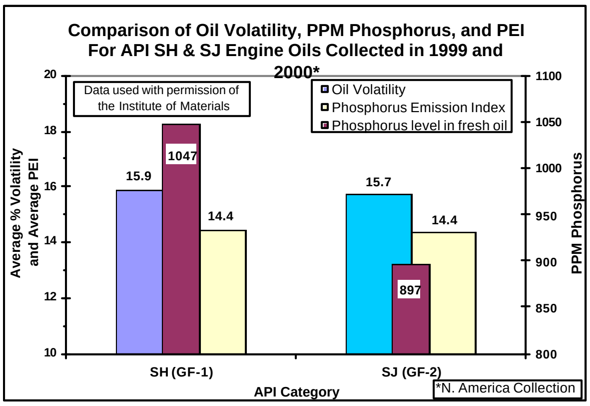

Fig. 23 - Reduction in phosphorus concentration did not result in change in Phosphorus Emission Index

Apparently, reformulating some oils led to higher phosphorus volatility even though the average phosphorus concentration dropped by 15%.

b. Phosphorus Content Compared to Volatility

If phosphorus volatility is dependent on both choices of phosphorus chemistry as well as other engine oil additives, it is of interest to look at the actual levels of phosphorus in fresh oils compared to the Phosphorus Emission Index values shown earlier as Figures 14, 15, and 16. These overlays are shown in Figures 24, 25, and 26.

All three collections of marketed oils indicate that

1. Phosphorus levels in the oil are independent of phosphorus volatility,
2. Low phosphorus volatilities can be formulated with relatively high levels of phosphorus levels,
3. High phosphorus volatilities can be unknowingly formulated with relatively low levels of phosphorus,

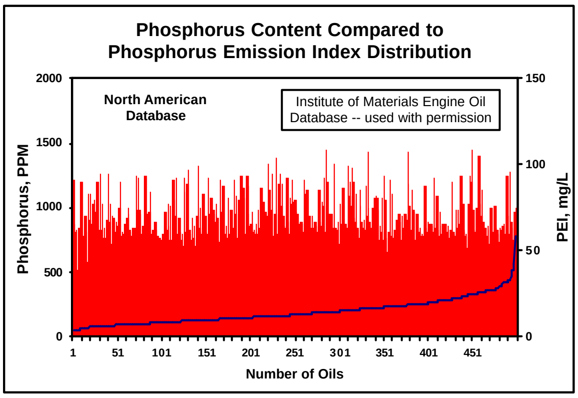

Fig. 24 - Overlay of phosphorus content of North American oils on distribution of PEI shows no inter-dependence - high phosphorus oil can give low Phosphorus Emission Indices

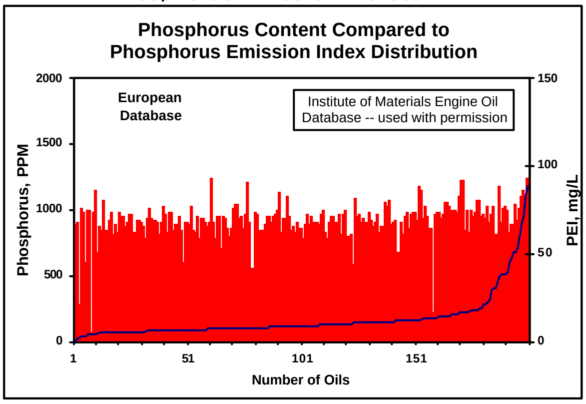

Fig. 25 - Overlay of phosphorus content of European oils on distribution of PEI shows same pattern as North American oils

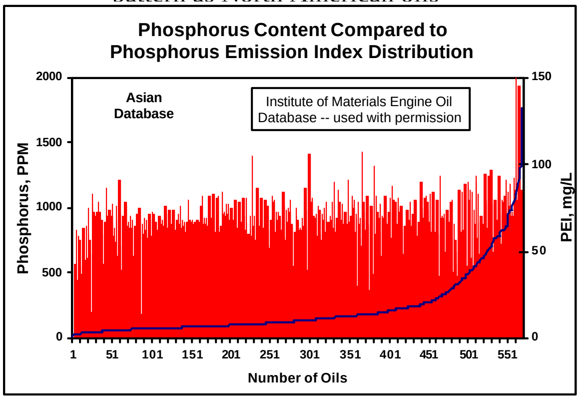

Fig. 26 - Overlay of phosphorus content of Asian oils on distribution of PEI shows same pattern as North American oils

4. The role of other additives in controlling phosphorus volatility requires dedicated study to capitalize on this relationship.
5. In the range of 500 to 1500 PPM, there seems to be little or no value in attempting to control phosphorus volatility by specifying a given level of phosphorus for reasons given under previous Points 1, 2, and 3.
6. Direct measurement of the phosphorus volatility of proposed and resulting formulations seems effective and the Phosphorus Emission Index seems to be a correlative and useful technique.

5. Discussion and Conclusions

a. The Phosphorus Problem - New Paths

Phosphorus in engine oils, a considerable advantage to development of higher powered engines over a half century or more, has in the last 20 years become the epitome of a mixed blessing. Its dual nature expressed in protecting the engine from wear and the engine oil from oxidation but also in being volatilized to coat the exhaust catalyst has brought a number of views toward this ubiquitous additive. Views have ranged from total replacement of phosphorus in the oil by yet to be strongly proven alternative additives imparting equivalent wear and oxidation resistance, to chemically modifying the catalyst or changing its composition.

Understandably, these views reflect the technical and commercial interests of those expressing them and most of these views are more or less reasonable. However, until recently, all of the views have been founded on the twin conceptions that phosphorus' impact on the catalyst could be mitigated by either or both oil volatility and/or phosphorus concentration in the engine oil. Neither assumption has been found valid.

After finding that

1. phosphorus volatilization is not dependent on either oil volatility or phosphorus concentration in the engine oil, and that
2. phosphorus volatilization was dependent on the choice of phosphorus chemistry and the strong influence of accompanying additives,

the door has been opened to new focus and new opportunities to advance engine oil lubrication.

The better path today is to find and expand on those formulations that have shown low phosphorus volatility even at older, higher concentrations.

The most critical aspects of the issue are that the owner of any automotive vehicle should have reasonable expectation of service from one of his or hers more expensive investments of civilized life and, yet, that the operation of the vehicle not be a source of pollution to the civilized environment. With the findings in this and a previous paper on the character of phosphorus and the evidence that appropriate formulation already shows evidence of controlling its volatility, time is now available to resolve the issues with thought rather than urgency.

The use of the Phosphorus Emission Index has been shown to be a key to understanding and predicting phosphorus volatility effects on the catalyst. Much more work remains to be done and, with hope, others will participate in these new studies of the chemistry of phosphorus additives and other engine oil additives controlling phosphorus volatility.

Present emphasis should clearly be on appropriate and creative formulation of engine oils using the chemistry of the phosphorus and other additives in an effective combination to reduce phosphorus volatilization and to retain its presence in the oil for greater service in preventing engine wear and resisting engine oil oxidation. In this effort, the Phosphorus Emission Index should prove its worth.

b. Conclusions

The conclusions are:

1. Phosphorus volatility is dependent essentially on its molecular chemistry coupled with the physical chemistry of the other additives present.
2. Engine oil formulation should be directed toward those combinations of additives which have shown most effectiveness in reducing phosphorus volatility while still serving their primary roles in the engine oil.
3. The Phosphorus Emission Index information produced using the conditions of volatilization and collection of volatiles by the Selby-Noack will be a key to help resolve the phosphorus problem regarding automotive catalyst deposits.

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6. Bibliography

[1] K. Noack, *Angewandt Chemie*, **49** (1936) 385.

[2] Determination of Evaporation Loss of Lubricating Oils, (Noack Method), DIN 51-581 (1981).

[3] Evaporation Loss of Lubricating Oils, CEC L-40-T-87 (1987).

[4] Evaporation Loss of Lubricating Oils by the Noack Method, *ASTM Standards, 2001* **Vol. 5.03** published by the ASTM (2001) 839-853.

[5] Selby, T.W.; Hall, R.W.; Reichenbach, E.A.; **A new approach to the Noack test for volatility measurement**, *Ninth International Conference on the Characterization of Lubricants and Lubrication*, Savant, Inc., Dearborn, MI, USA, (1993); *SAE International Fuels & Lubricants Meeting and Exposition*, Philadelphia, PA, USA (1993).

[6] Selby, T.W., Cluff, B.J., **Selective Volatilization and Collection**, Patent Number 5,667,302; issued 1997.

[7] Reichenbach, E.A.; Hall, R.W.; Selby, T.W., **A new approach to the Noack volatility test**, *Proceedings of the 9th International Colloquium, Ecological and Economic Aspects of Tribology*, Technische Academie Esslingen, Stuttgart/Ostfildern, Germany (1994) 5.5-1 to 5.5-15; also published in *Tribotest Journal*, Leaf Coppin Publishing Ltd. England, **1 No. 1** (1994) 3-31.

[8] Selby, T.W.; Reichenbach, E.A.; Hall, R.H., **Base oil characterization techniques using a new approach to the Noack volatility test**, *Symposium on The Processing, Characterization and Application of Lubricant Base Oils, Part II*, American Chemical Society Meeting, San Diego, CA, USA (1994).

[9] Selby, T.W. and Reichenbach, E.A., **Engine oil volatility studies - generation of phosphorus**, *Proceedings of the International Tribology Conference*, Yokohama, Japan (1995) 813-816.

[10] Cluff, B.J.; McMahon, D; Selby, T.W., **A laboratory method for measuring bulk volatility of engine oils**, *SAE International Spring Fuels and Lubricants Meeting*, Paper #961227, Dearborn, MI, USA, (1996).

[11] Selby, T.W., **Analysis of engine oil and phosphorus volatility - development and use of the Selby-Noack apparatus to recover and study phosphorus volatiles**, *11th International Colloquium, Ecological and Economic Aspects of Tribology*, Technische Academie Esslingen (1998).

[12] Selby, T.W., **Development and Significance of the Phosphorus Emission Index of Engine Oils**, *Supplement to Proceedings of 13th International Colloquium - Lubricants, Materials, and Lubrication Engineering*, Technische Academie Esslingen,, pp. 93-102, (Jan. 15-17, 2002).