Development and Significance of the Phosphorus Emission Index of Engine Oils

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Summary: This paper reports the author's effort to verify some of the present assumptions regarding causes and relationships in the volatility of engine oil phosphorus. Using Selby-Noack volatility data from 1300 engine oils collected by the Institute of Materials in three areas of the world, volatilized phosphorus showed very low statistical dependence on either oil volatility or phosphorus concentration in the fresh oil. Rather the data seemed to indicate that the chemistries of the phosphorus-containing additives and their formulation with other additives were the controlling cause of phosphorus volatility and, by extension, emission level.

The study permitted the development of a Phosphorus Emission Index that predicts the emission potential of a formulated oil based on the amount of phosphorus found in the volatilized oil collected in the Selby-Noack test.

1. Background

Engine Oil and Phosphorus

Early Work on Volatility – Engine oil volatility has been a concern for a number of years. K. Noack, in the 1930s developed a technique and apparatus to measure mineral oil volatility **[1]**. The technique required the use of molten Woods Metal as a stable means of heat transfer at the test temperature of 250°C. In time, this technique became a general bench test method for engine oil volatility determination (DIN 51-581 **[2]**, CEC L-40-T-87 **[3]**, and ASTM D 5800 **[4]**).

An Alternative Procedure - In 1993, the author's laboratory was requested to run the Noack test but found it could not risk exposure of its personnel to the fumes of Woods Metal, a toxic and carcinogenic mixture of bismuth, cadmium, lead and tin. The decision was made to develop an alternative heating procedure **[5]** while retaining the principles and practice of the Noack test. In the process, it became apparent that the test could be made more informative by also collecting all the volatilized oil and making this oil available for comparative analyses **[6 - 10]**. The resulting instrument is shown in Figure 1 and has been made a part of ASTM D 5800 **[4]** as a result of close correlation with the original Noack.

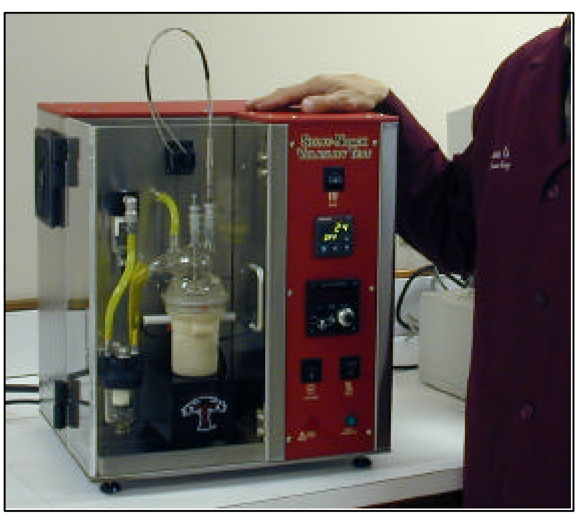

Fig. 1 The Selby-Noack volatility test instrument

During this period of developing an alternative form of the Noack test, another problem associated with engine oil volatility came to the fore and became more and more of an issue.

The Phosphorus Issue - For decades, phosphorus, has been an effective antiwear/antioxidation agent in engine oils in the form of zinc di-organo di-thio phosphates (ZDDPs). However, over the last twenty years it has been shown **[Ref.: 11, 12, 13, 14, 15, 16]** that phosphorus also reduces the effectiveness of the exhaust gas catalyst used in emission reduction. This dual nature of ZDDPs led to a high level of debate concerning the issue of reducing or eliminating phosphorus in the engine oil.

Subsequently, in an effort to control phosphorus effects on the catalyst, engine oil volatility -- which appeared to be involved in transferring phosphorus -- was reduced. Phosphorus concentration in the oil was similarly reduced for some SAE passenger car engine oil classifications. With introduction of ILSAC GF-1 phosphorus levels were limited to no more than 1200 parts per million (PPM) **[17]** and with GF-3 to 1000 PPM **[18]**.

Considerations and Questions - With phosphorus having both positive and negative importance for the manufacturers of vehicles and engines **[16]**, it seemed wise to verify the assumptions made under the duress of high technical concern about engine emission control.

The questions are simple:

1) Is phosphorus emission correlated with engine oil volatility?

2) Overall, are phosphorus emissions generally correlated with the amount of phosphorus present in fresh oils?

3) Are phosphorus emissions dependent on the particular chemistries of the ZDDPs and/or their admixtures with other additives?

An appropriate direction for resolving these questions would seem to be to emulate the phosphorus emissions from the engine using a bench test and a broad selection of engine oils. It was the author's hope that analysis of such data would provide meaningful answers.

2. Engine Oil Effect on Phosphorus Volatility

Source of Engine Oil Volatility/Phosphorus Data

The Institute of Materials Engine Oil Database - As previously mentioned, once a comparison technique was in hand, a next need was to find a broad mass of engine oil data for analysis. The Institute of Materials (IOM) Engine Oil Database has been the source of a world wide collection and analysis of engine oils since 1984 and has amassed over 5000 oils in its database. To accomplish its purpose, IOM has utilized several laboratories over the years for analysis of the physical, chemical, and performance of the oils collected. In 1993, IOM began including Noack analysis and in 1996 began use of the Selby-Noack test to obtain phosphorus volatility data as well for the interests of subscribers to the Engine Oil Database.

All data presented in this paper was with the permission of The Institute of Materials.

First Bench Studies of Phosphorus Emissions

Assumptions – As previously noted, resolution of the three questions posed earlier required a massive body of data from which to abstract the relationships sought. To do this with full-scale engine tests is not reasonable. Consequently, the primary assumption in this work is that the volatility obtained in the Selby version of the Noack instrument reflects the volatility conditions of the engine sufficiently well to draw meaningful conclusions.

The author believes that the use of this volatiles-collecting bench test is reasonable considering

a. the temperature of test, 250°C, is near the upper ring-belt temperature,

b. the slight vacuum of 20 mm water applied to the sample encourages air flow over the test sample and the capture of volatile products, and

c. the length of time that the 65 g sample of engine oil is exposed to these temperature and vacuum conditions (60 minutes) should be adequate to strip the sample of its more volatile material.

Earlier Work - The author's initial results from using the Selby-Noack to collect the volatilized oil was reported in an early paper **[8]**. This paper studied the relationship of the physical and chemical composition of the volatilized oil compared to those of the fresh and remnant oils. The study suggested that the amount of phosphorus volatilized might be independent of the amount of oil volatilized. A second paper **[10]**, amplified this finding and raised questions regarding differences in additive phosphorus composition and formulation.

Repeatability of Phosphorus Volatilization - An important factor regarding the data to be presented is the level of repeatability of both the Selby-Noack test and the collection of volatile phosphorus. Fortunately, the Institute of Materials sends a set of reference oils out with every few samples to determine how well their selected laboratories are meeting predicted levels of precision. At the request of the author, some information on an SAE 5W-30 engine oil was made available for the years 1999 and 2000. Figure 2 shows results from the Selby-Noack test.

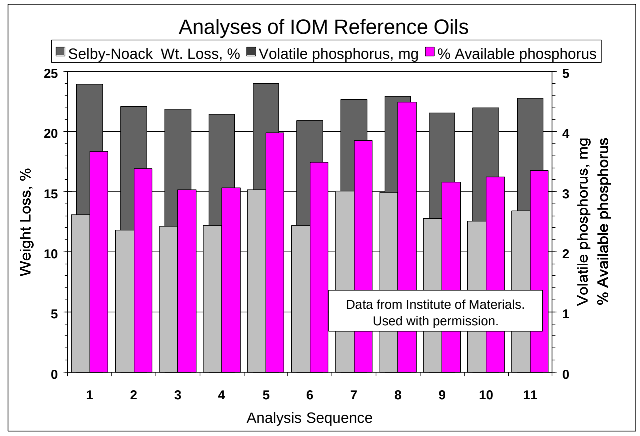

Fig. 2 Repeatability of analyses of IOM reference oil

Statistically analyzing the data: Standard Deviation (SD) of percent volatility loss run periodically on this particular reference oil was 0.99%. SDs on the volatilized phosphorus weight and the percent of the available phosphorus volatilized were 0.25mg and 0.44%, respectively.

It was also interesting to apply the Selby-Noack technique to appraise field-collected engine oils. The North American IOM database was searched for recent samples of SAE 5W-30 oils made by a blender known to exercises good quality-control practices with a consistent additive package. Results are shown in Figure 3.

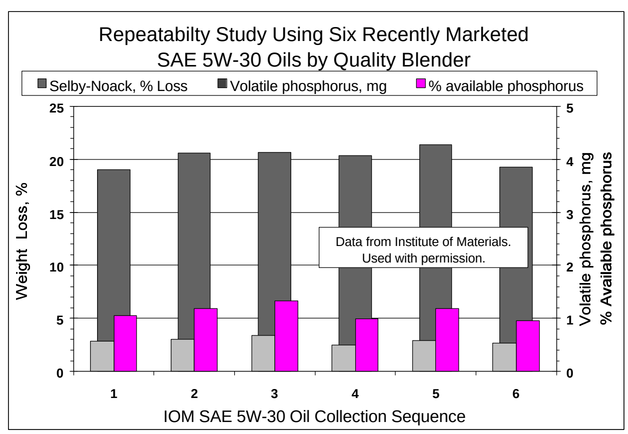

Fig. 3 Repeatability of analyses of field-marketed samples from well-controlled sequential blending

Variation in percent volatility loss is indicated by a Standard Deviation (SD) of 0.89. Variation in weight of phosphorus volatilized has a SD of 0.06mg and variation in the percent available phosphorus volatilized is SD = 0.14%/%.

The results in Figures 2 and 3 show the degree of precision of collection and analysis of volatilized oil in the Selby-Noack test. Particularly, the data in Figure 3 shows the value of such analysis in appraising consistency in formulation and blending engine oils.

Complete Transfer of Any Volatile Phosphorus- To draw conclusions from the amount of phosphorus transferred to the collected oil during the test, it is necessary that all oil and phosphorus volatilized be collected in the receiver section of the Selby-Noack. Past work [11] has shown that a patented technique [12] for coalescing the hot oil aerosol will collect over 99% of the volatile oil and phosphorus.

Determination of Phosphorus Concentration – After the Selby-Noack test, both the collected, volatilized oil and the fresh oil are subjected to inductively-coupled plasma (ICP) spectroscopy to determine the phosphorus concentration. This analytical technique is both sensitive and linear in calibration over a several-decade range of phosphorus concentration.

3. Results of the Study

Relationship of Phosphorus Volatility to Engine Oil Volatility Using IOM Engine Oil Database

General – Several views of the IOM data are presented in order to answer the three questions posed by the author at the beginning of this paper. One of these views is aimed at the question of the relationship between engine oil volatility and phosphorus volatility. Another is the relationship between phosphorus presence in the volatilized oil and that in the fresh oil.

The Degree of Phosphorus Emission Dependence on Engine Oil Volatility? – Shown in the next three figures are general comparisons of and correlation between engine oil volatility and phosphorus volatility for three areas of the world: North America, Europe, and Asia. The value for phosphorus is the actual number of milligrams of phosphorus volatilized from the 65g of the test oil used in Noack tests.

North American Engine Oils - Figure 4 shows the comparison of oil volatility and phosphorus volatility information for North American engine oils of all SAE classifications.

It is evident in Figure 4 that there is very little overall relationship between the volatility of the oils and that of the phosphorus – the Coefficient of Determination, R^2, is only 0.067.

Briefly, oils with very similar levels of both volatility and initial phosphorus concentration can show both low and high levels of phosphorus in the collected oil. The above findings agree with limited reported data from engine tests **[11]**.

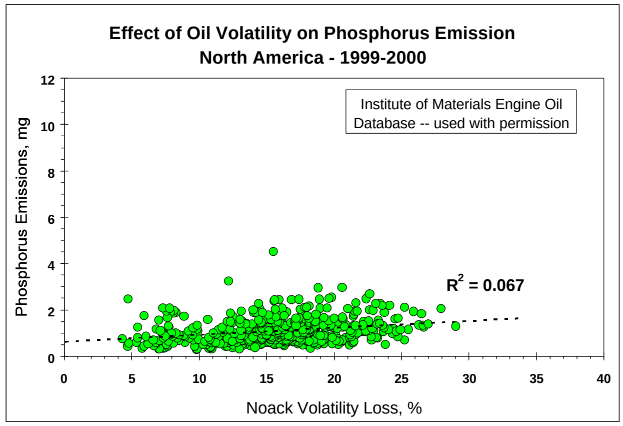

Fig. 4 Comparison of oil and phosphorus volatilities for North American engine oils

For the 500 North American oils collected in 1999 and 2000, the average volatilized phosphorus level was about 2% of the phosphorus in the engine oils. However, as will be shown, this ranged from less than 1% to more than 5%. Also of interest, the spread of oil volatilities is from about 4% to 29% loss with the average value of 15.7%. In the ensuing reports, engine oil volatilities less than about 4% were generally not included if it produced an inadequate sample of collected oil.

European Engine Oils – Data obtained on 200 oils collected from Europe during 1999 and 2000 show that the bulk of the data in Figure 5 also show lack of correlation between the oil volatility and the phosphorus volatilized (the slope of the best line through the data actually shows a slightly negative correlation.) However, this is not thought to be meaningful since R^2 = 0.005.

Figure 5 also shows that there were several oils of higher phosphorus volatility clustered vertically at about 5% and 11-13% volatility loss of oil that did not fall into the general pattern and these may reflect some particular form of additive chemistry or formulation practice. The range of oil volatility is considerably narrower than the North American oils with an average value of 10.8% loss.

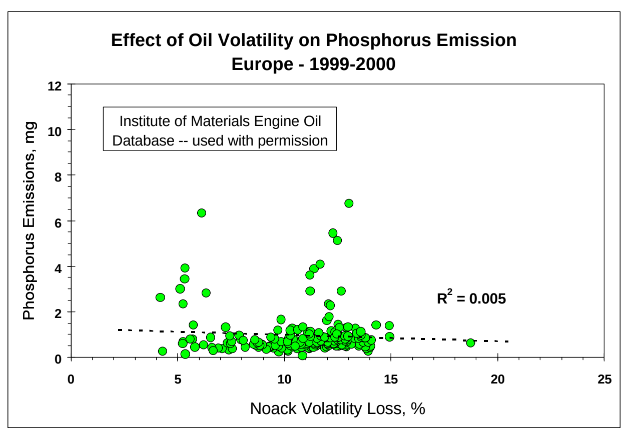

Fig. 5 Comparison of oil and phosphorus volatilities for European engine oils

Asian Oils – The Institute of Materials collects oils from a number of Asian countries. The overall data from 600 engine oils comparing the oil volatility to the phosphorus volatility are shown in Figure 6.

Asian data show a core of horizontal data and many scattered data points. Again, the correlation is poor with a value of R^2 = 0.04 and a negative slope. Engine oil volatility ranged from about 1% to 28% loss with the average percent volatility loss being 10.4%. In one case the amount of phosphorus in the volatilized oil was more than three times the phosphorus in the fresh oil. Scatter in the values for Asian engine oils is considerably greater than North American or European.

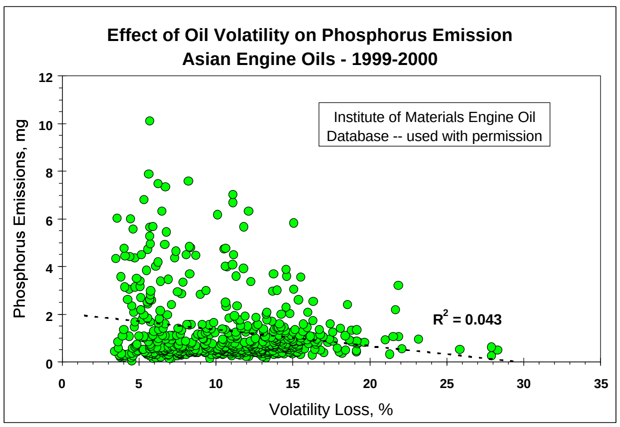

Fig. 6 Comparison of oil and phosphorus volatilities for Asian engine oils.

Overall Independence of Phosphorus Volatility and Engine Oil Volatility - Summing the extensive data gathered from the IOM Engine Oil Database: generally, phosphorus volatility seem independent of engine oil volatility. Although the mass of data may hide limited volatility relationships, broadly, the data indicate that <u>efforts to control phosphorus emissions by controlling engine oil volatility have not apparently been successful nor are likely to be so</u>.

If engine oil volatility is not a significant cause of phosphorus emissions, attention is necessarily drawn to the question of the vulnerability of the phosphorus additives in the engine oil to volatilization. This relationship of the phosphorus available compared to the phosphorus volatilized is presented next.

Relationship of Phosphorus Volatility to Available Phosphorus Levels Using IOM Engine Oil Database

North American Engine Oil Data - Phosphorus concentration in the volatilized oil was compared to that in the fresh engine oil in Figure 7. The data indicates that there is a broad range of relationship between the amount of phosphorus available and that volatilized. The result is an overall poor correlation with R^2 = 0.0002.

Differences in Collective and Individual Volatilization Results - To thoroughly understand the foregoing information, it is important to note that, for a given

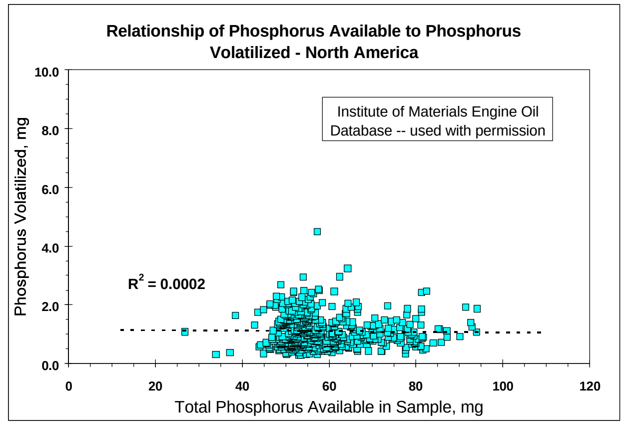

Fig. 7 Comparison of phosphorus levels in the fresh and volatilized North American engine oils

phosphorus additive in a particular formulation, increasing concentration very likely will produce increasing levels of phosphorus volatility. The relative independence of the phosphorus volatilized from the initial phosphorus concentration as shown in Figure 7 points to other factors such as

1) variation in the nature of engine oil additive packages containing ZDDP and

2) variations of the ZDDP itself.

These two factors are critical in determining the ten-fold variation in phosphorus mass volatilized.

Briefly stated, the IOM data shown here emphasize the importance of engine oil formulation in controlling phosphorus emission.

Another view of the North American data is to compare the concentration of phosphorus in parts per million (PPM) in the volatilized material and compare this to the concentration in PPM in fresh oil. A ratio of these two values provides a measure of how much of the phosphorus compounds in the original engine oil are degradable and/or volatile. The lower the Phosphorus Ratio, the less the phosphorus in the fresh oil is volatilizing at 250°C.

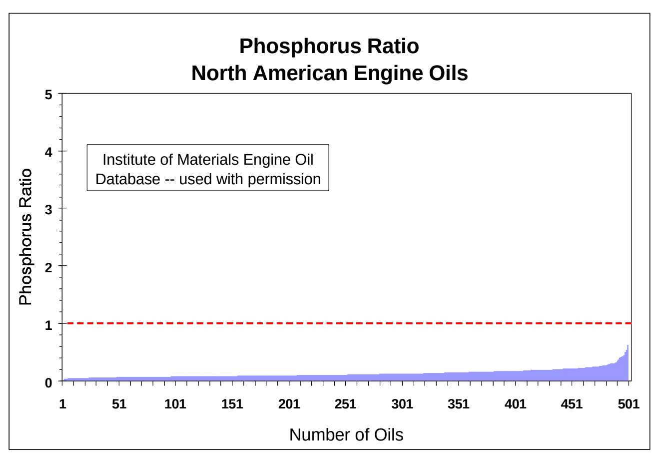

Fig. 8 Distribution of the Phosphorus Ratio for North American engine oils

Figure 8 shows the distribution of the author-termed Phosphorus Ratio across the North American group of engine oils analyzed during the years 1999 and 2000. The Phosphorus Ratio varies from about 0.03 to 0.63 (3% to 63% of the phosphorus level in the fresh oil).

European Engine Oil Data - Figures 9 and 10 show data similar to Figures 7 and 8 from the European Engine Oil Database for 1999 and 2000

Figures 9 and Figure 7 are similar in showing generally little correlation between initial and volatilized phosphorus. Volatilized phosphorus mass varies by over 100-fold.

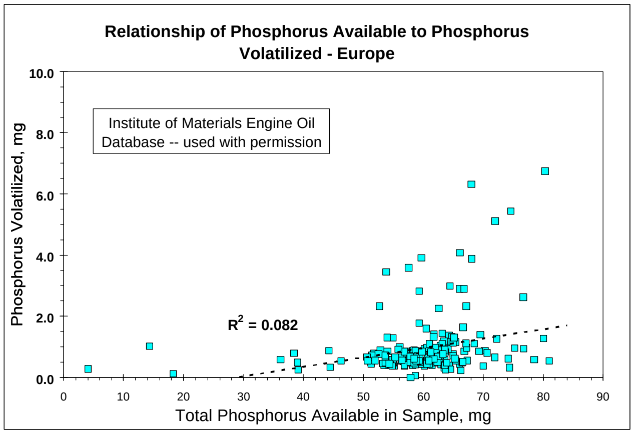

Fig. 9 Comparison of phosphorus levels in the fresh and volatilized European engine oils

However, there are several datum values above the mass of data. As mentioned previously, these few values suggest that some of the oils have essentially similar overall formulations with different concentrations of the same phosphorus chemistry. Further study of the IOM database will be helpful and will be reported in another paper.

Among other information, Figure 10 shows for the first time in this study that the concentration of phosphorus in the volatilized oil may exceed the concentration in the fresh oil by as much as 50%. First of all, this behavior supports the conclusion that oil volatility is not the cause of phosphorus volatility. Secondly, to produce this effect such response would seem to require some form of additive degradation or selective volatilization of phosphorus-containing material.

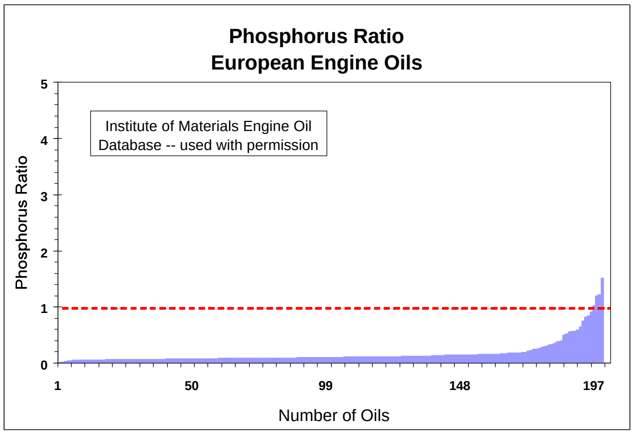

Fig. 10 Distribution of the Phosphorus Ratio for European engine oils

Asian Engine Oil Data - Figures 11 and 12 complete the portion of the study related to the effects of available phosphorus on the volatilized phosphorus and the Phosphorus Ratio.

The data obtained from the analysis of the IOM Asian collection of engine oils completes the gathering of data related to the first two questions regarding source of phosphorus volatility.

Figure 11 shows a mixed pattern with a core of data similar to the North American and European accompanied by a diffuse scatter of datum points with no evident pattern for the dependency of volatile phosphorus on initial phosphorus.

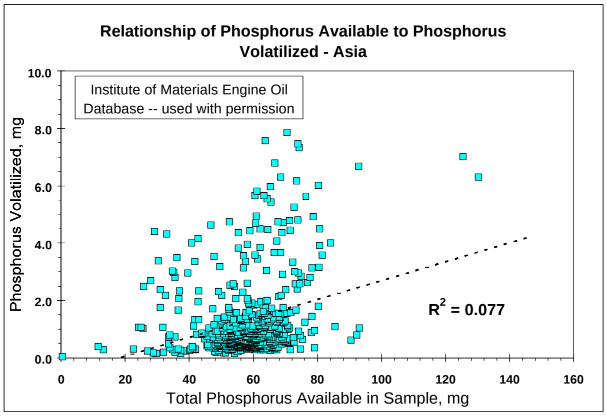

Fig. 11 Comparison of phosphorus levels in the fresh and volatilized Asian engine oils

The Asian database information in Figure 12 shows much greater range of variation and scatter. About 10% of the 600 oils tested had a higher concentration of phosphorus than the initial concentration in the fresh oil. Of even more importance, PPM of phosphorus concentration in the volatilized oils ranged up to almost 300% greater than the fresh oil. Volatilized phosphorus mass varied 250-fold.

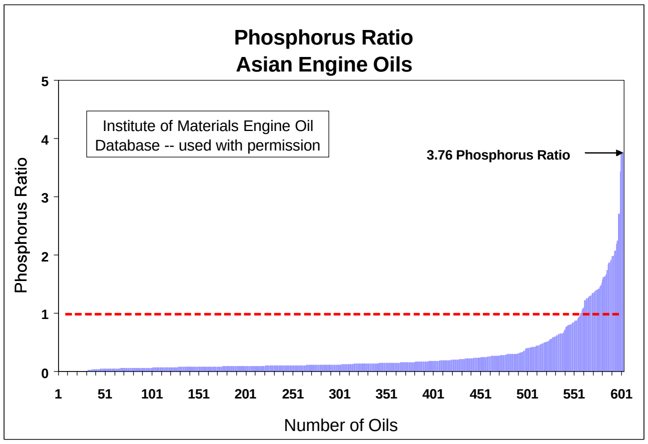

Fig. 12 Distribution of the Phosphorus Ratio for Asian engine oils

Obviously, this greater presence of phosphorus in the volatilized oil could not be caused by simple carry-over with the volatilized oil. Just as evidently, the phosphorus level in the fresh engine oil could not produce higher levels in the volatilized oil except by some process in which the phosphorus compounds were degraded or volatilized selectively at the temperature of Noack-type tests.

4. Implications of the Data - Chemistry and Challenge

The mass of information from the IOM Engine Oil Database Analysis seems to provide an understanding of the variation and source of volatile phosphorus from the engine oil.

In particular, the data have shown several specific paths to reduction of the level of volatile phosphorus without necessarily reducing the amount of phosphorus in the engine oil. This is considered one of the important issues facing the automotive industry as well as those supplying additives and formulated engine oils **[16]**.

With proper understanding and attention to the choice of ZDDP chemistry (and any other phosphorus additives) as well other components of the additive package and the formulation of the engine oil, it may be possible to significantly restrict phosphorus volatilization and thus gain greater freedom in applying the advantages of phosphorus additives in the engine oil.

In essence, the data presented above lead to five conclusions:

1. The chemistry of the phosphorus-containing additives control the rate of decomposition and release of phosphorus at the 250°C temperature of the Noack-type tests -- not the volatility of the engine oil.

2. There are wide differences in the susceptibility of these phosphorus-containing additives to the process of degradation and/or volatilization at the 250°C temperature of test.

3. On the basis of the data available for this study, there are formulated engine oils on the market that are quite stable regarding phosphorus volatilization that also have substantial levels of phosphorus in the formulation.

4. At the same time there are presently a number of marketed engine oils with high phosphorus volatility even at lower initial phosphorus levels in the fresh oil.

5. Considering the foregoing conclusions, there seems to be major opportunities for a number of creative solutions to preserve both the engine and the catalyst by advanced engine oil formulation.

To meet these opportunities, two tools seem to be needed. One is a bench test capable of emulating the operating engine repeatably regarding the generation of phosphorus. The second is a need for a criterion of phosphorus emission tendencies.

While there may be other approaches, as already shown in this paper and others **[8, 10]** a bench test is already in hand with the Selby-Noack protocol used in these studies. The second tool, a criterion of phosphorus-emission tendencies of a formulated engine oil is proposed in the following section of the paper.

5. The Phosphorus Emission Index -- A Criterion of Phosphorus Emission Potential

Application of the IOM Data to Generate the Phosphorus Emissions Index (PEI)

Rationale - The foregoing analysis of field-marketed engine oils from around the world showed a number of regional differences and similarities as well as the overall information leading to the immediately preceding conclusions.

Considering, then,

1. that a method of repeatably measuring the phosphorus volatility of engine oils is available, and

2. the need for some simple criterion of formulated engine oil phosphorus emission performance,

a value was generated that was directly related to the phosphorus volatilized, collected, and analyzed in the Selby-Noack test.

It is important to note that the criterion proposed and used in this paper is related to phosphorus emission tendency alone. Other factors such as adsorption on the catalyst surface, etc. only become critical if sufficient phosphorus is emitted to the exhaust.

The Criterion of the Phosphorus Emission Index (PEI) - The most critical need to be met by such a criterion is that each oil formulation should be fairly and reproducibly compared to other oil formulations.

On this basis, the Phosphorus Emission Index is based on the amount of phosphorus found in the volatilized oil in milligrams per 850g (~ one liter) of the fresh oil. Since 65g of oil are required in all versions of the Noack test, the equation is:

$$PEI = \text{volatile } P(\text{mg}) \cdot 850/65$$

The value is simple to calculate and is based on the foremost concern -- the amount of phosphorus capable of emitting into the engine exhaust by a liter of engine oil.

From the assumptions given at the beginning of the paper (cf. Section 2), each liter of engine oil in a crankcase refill will generate approximately the number of milligrams of phosphorus indicated by the Phosphorus Emission Index. For an engine oil having an Index value of 10, and assuming 20 refills of engine oil of 5 liters each in 100,000 miles, the number of milligrams of phosphorus passing into the exhaust would be 1000mg or one gram. To what degree one gram of phosphorus would contaminate the catalyst would be dependent on the efficiency with which the phosphorus would coat the active catalyst surface as well as other factors mentioned by Korcek, Nakada, and others **[16]**.

Applying the collected IOM data to determine the range of PEI values was of considerable interest and the following section presents some preliminary data.

Analysis of the IOM Engine Oil Data - The three IOM databases previously used in this paper were once more applied. Distribution plots for the PEI of North America, Europe, and Asia are given in Figures 13, 14, and 15.

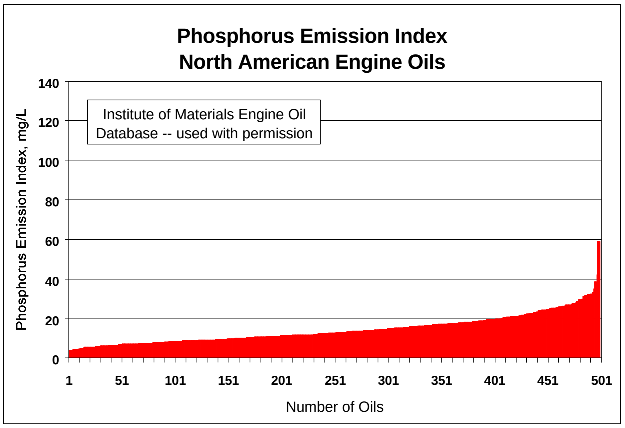

Fig. 13 Phosphorus Emission Index distribution curve for North American engine oils

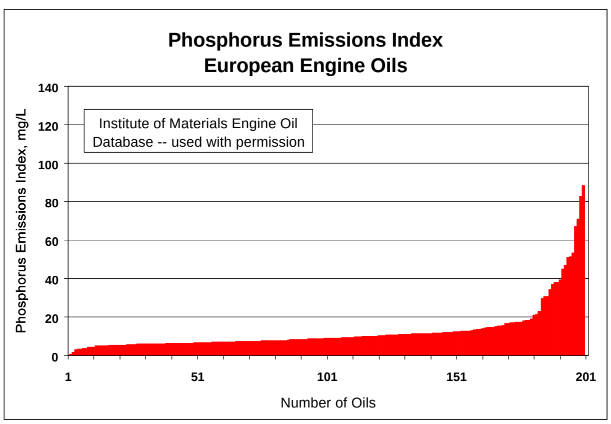

Fig. 14 Phosphorus Emission Index distribution curve for European engine oils

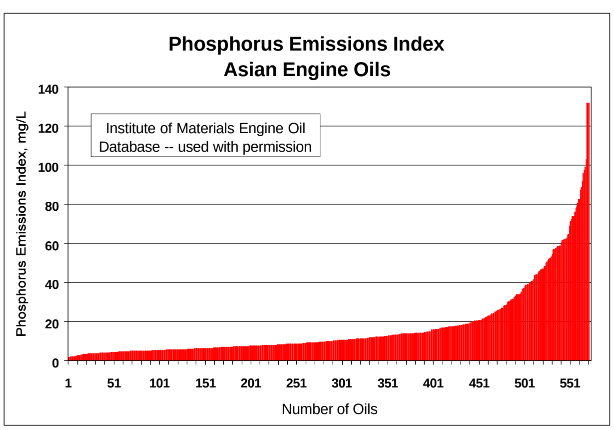

Fig. 15 Phosphorus Emission Index distribution curve for Asian engine oils

The data reveal several aspects of phosphorus volatilization and its relationship to engine oil formulation practices in different parts of the world.

North America presently has the most rigorous standards regarding emissions and the PEI of its engine oils are comparatively low across the range. The average PEI across the range of 500 oils composing the IOM database for 1999-2000, is 14.4.

In Europe, however, where emission standards are rapidly rising has an even lower average PEI of 12.6 although in the last portion of the distribution curve of Figure 14, there is a sharp rise extending to higher values than those shown in North America.

Asian engine oils have an average PEI of 17.0 which is decidedly highest of the three world areas. One oil showed the highest Index thus far seen at PEI = 131. However, it will also be noted that for more than 50% of the oils analyzed the PEI values were as low as those in Europe and lower than those in North America. This could be a reflection of lower levels of phosphorus-containing additives over the first 50% of the range.

These relationships will be further analyzed in a future paper.

6. Discussions and Conclusions

Reliability of the Instrument and Approach to Measuring Phosphorus Volatility on the Bench

Past papers and present data show that the Selby modification of the Noack volatility test apparatus is both consistent and repeatable. This consistency applies to both volatilizing the oil and the phosphorus. The repeatability of the Selby-Noack test was shown to be good using multiple samples of two commercial engine oils.

Conditions of test in the Noack-type instruments are considered by the author to be similar to the conditions producing volatility in the engine. With the unique ability of the Selby-Noack to collect essentially all (99+%) of the volatile products of the test, this permits direct comparisons of volatile and fresh oils regarding their content of phosphorus (as well as sulfur and other volatile elements).

Source of Data

The Institute of Materials Engine Oil Database was the source of all data presented. Since the IOM database is available in several spreadsheet forms, the data presented represents many oils from three major areas of the world involved in automotive production and use. The availability of such data and its analysis will lead to further, more specific, comparisons in future publications by the author and others.

Influences on Phosphorus Volatility

Effect of Oil Volatility - The studies in this paper have shown that, generally, oil volatility is not a factor in controlling phosphorus volatility. While it is obviously desirable to control oil volatility in the automotive engine for other reasons, such control should not be expected to modify exhaust emissions of phosphorus.

Effect of Phosphorus Content in the Fresh Oil - Essentially, the data indicated that the influence of phosphorus content in the fresh oil is apparently modified by both the chemistry of the phosphorus compounds in the additive package used as well as the overall formulation practices.

It was apparent from the data that high phosphorus volatility could be obtained from low initial levels of phosphorous in the oil and vice-versa. Such results can only be explained by differences in the vulnerability of different phosphorus chemistries since even formulation differences would not explain such results.

The Primary Conclusion of the Study

Considering the wide range of phosphorus volatility compared to the initial concentration in the fresh oil, the basic conclusion from this study is that the choice of phosphorus chemistry and formulation should be able to produce low phosphorus emissions. If so, engine oils having sufficient phosphorus additive content to serve the engine in preventing wear could have minor effects on the ability of the exhaust stream catalyst to process emissions.

The Phosphorus Emission Index

Significance and Application - The Phosphorus Emission Index's significance is based on the assumption that the Noack-type tests of volatility are reasonably imitative of the engine-induced volatility. However, this assumption is already the basis of the acceptance of Noack-type tests' by the automotive, additive, and petroleum products industries.

On this basis, application of the PE Index makes the comparison of potential phosphorus emissions from engine oils a simple matter of extending the information already gained in a Noack-type volatility test. . Moreover, the PE Index is derived from data that is reasonably repeatable. In that regard, the Index can be used to develop, screen, and exercise quality control practices in the effort to produce better engine lubricants with phosphorus additives chosen for low-emissions.

7. Acknowledgments

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