

**Analysis of Engine Oil
and Phosphorus
Volatility -
Development and Use of
the Selby-Noack Apparatus
to Recover and Study
Phosphorus Volatiles**

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Presented at
11th International Colloquium Tribology
Technische Akademie Esslingen
Stuttgart/Ostfildern, Germany
January 13-15, 1998

And
Published in
Tribotest Journal 6-4
June 2000

Analysis of Engine Oil and Phosphorus Volatility - Development and Use of the Selby-Noack Apparatus to Recover and Study Phosphorus Volatiles

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Summary

Work is presented showing that engine oil volatility and phosphorus volatility are not interdependent. On the basis of the data generated, it would seem reasonable to reduce the level of phosphorus emissions from the engine oil in the operating engine by choice and design of the phosphorus-containing additives. The work done thus far suggests the direction that new studies of phosphorus generation by volatilization might take.

1. INTRODUCTION

Early Concerns with Volatility

The volatility of engine oil has been a concern to engine manufacturers since two- and four-cycle engines were first commercialized in the early 1900's. Early motorists were often required to carry spare containers of oil to replace that which was lost either through leakage or, most usually, through passage into the combustion chamber and being burned or volatilized.

Leakage past the piston rings and down the valve guides was more of a problem than simple loss of lubricating oil. If the oil had a tendency not only to leak but to also readily form deposits, the engine owner was liable for a severe penalty in the form of a vicious cycle of leakage, deposits, stuck rings, cylinder wall scoring, and more leakage, spiraling down into a destroyed engine. Since some of the base oils used during the period up until the 1930's and '40's were relatively high in naphthenic composition -- and commensurably low in Viscosity Index (VI) -- their viscosities fell more rapidly with increasing temperature. Thus, they not only leaked more readily past the piston rings and valve guides but, once there, were much more likely to form piston and combustion chamber deposits.

In contrast, paraffinic base oils with higher VI leaked less readily into areas where they might burn or volatilize. For this reason as well as easier startability, they became premium base stocks. Ultimately, in the late '40's and early '50's other ways of accomplishing good viscosity control through the development of Viscosity Index improvers became available and, with other additive advances, the age of designed lubricants came into being.

Modern Concerns with Volatility

Design of modern engines has drastically reduced oil consumption. However, by this very fact, the engine oil had to be much more sturdy in its service since partial restitution of its additive by replacement of volatilized oil is considerably reduced. This, in turn, has progressively led to the development of additives which individually or collectively serve as oxidation inhibitors, anti-wear agents, detergents, dispersants and VI improvers. Some of the more important of

these additives were based on zinc-phosphorus chemistry and were very effective both as anti-oxidants and, even more important, as anti-wear agents.

Emission effects - With the more recent effort to control emissions from the automotive engine, oil volatility was seen as not only affecting engine deposits but was also linked with emission catalyst poisoning because of the phosphorus content of the volatile product [1].

Noack test application - Regarding the prior issue of controlling oil volatility, Dr. Noack's apparatus and test of the early 1930's [2] had been further developed into a CEC volatility test in the early '80's [3]. To those who became additionally concerned about phosphorus volatility, it seemed appropriate to relate engine oil volatility and phosphorus volatility in an effort to control the latter problem area as well.

Further developments - The information and engine simulation character given by Noack's test was easily appreciated. The approach seemed superior to other methods such as gas chromatography (which, while informative, tended to reflect a volatility associated with the separation dynamics of the packed columns and capillaries associated with the latter method). However, wishing to avoid the associated use of Woods Metal because of its toxic components and, in addition, collect the volatiles for subsequent analysis, in 1993, the author and his associates initiated work to develop a considerably modified approach to Noack's test.

It was thought that such an approach could shed light on the relationship of oil volatility and phosphorus volatility. Three papers were published [4,5,6] on aspects of the work.

This fourth paper gathers the critical information of the previous work, particularly in regard to phosphorus volatility, and presents new precision information obtained with the use of automatic vacuum control.

2. APPARATUS AND OPERATION

The Selby-Noack is pictured in Figure 1a and the essential components are sketched in Figure 1b. There are three critical elements.



Fig. 1a - Picture of Selby-Noack Volatility Testing apparatus.

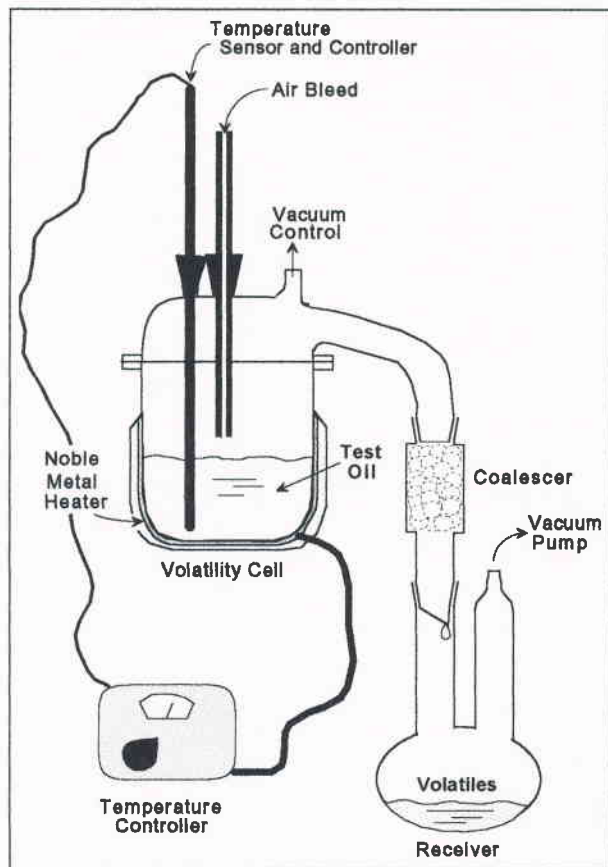


Fig. 1b - Sketch of Selby-Noack Volatility Testing apparatus indicating critical elements.

The first is the volatilizing cell (volatilizer) which is a specially designed glass vessel heated by a thin film of noble metal fused to the outer surface of the glass. The resistivity of this thin film provides the heat necessary to raise the temperature of the oil from room temperature to 250°C within six minutes. The temperature is reasonably precisely held within $\pm 1^\circ\text{C}$ during the test by an on-board controller monitoring a temperature probe extending down into the test fluid.

The second important element is a specially designed coalescer which both regulates the rate of air flow into the volatilizer and establishes the level of vacuum required. It also coalesces the volatilized oil very efficiently (as will be discussed).

The third important element is the automatic vacuum control. This is a built-in electronic device which is sensitive to, and can modulate, vacuum within a tenth of a centimeter absolute pressure of water or less.

All three of these elements are desirable for best response of the apparatus although the automatic vacuum control can be done by careful, but tedious, manual control during the duration of the hour test.

Test Protocol

Setup - Sixty-five grams of sample oil are weighed into the volatilizer to the nearest 0.01 gram. The volatilizer is then coupled with its cap, the coalescer, and the receiver and set into place behind the clear plastic door on the apparatus cabinet.

When the three glass components are firmly clamped the air inlet tube is inserted through the center ground glass joint to the proper depth. Similarly, the thermocouple tube and thermocouple are put in place. The vacuum control is set to the proper value and both vacuum lines are attached, one to the cap for vacuum control and the other to the receiver vessel.

If desired, the temperature of the oil in the volatilizer and the vacuum in the cap can be monitored by either a computer or a strip chart.

Operation - When the vacuum lines are attached, the test is begun by simultaneously switching on the vacuum pump and the heater. At some point the receiver will begin to collect volatile product.

Termination of test and measurements - The test terminates in one hour and vacuum and heat to the sample are immediately shut off.

After the volatilizer is allowed to cool, it is weighed and the tare subtracted to obtain the percent of oil volatilized. In the same manner, the receiver is weighed and the tare subtracted to get the amount of recovered volatile product.

Recovery level for volatiles - Early development work with the Selby-Noack approach showed relatively low levels of recovery of volatiles. Such a low level of recovery could not permit conclusions based on the total volatiles. Consequently, much effort was made to markedly increase the percentage of recovered volatiles.

The work was successful: the amount of oil accounted for is approximately 99% or more if the

amount of oil clinging to the glassware is taken into account -- about 1.25 grams. A small amount of oil is passed through -- about 0.02 grams -- in each test. This oil is trapped by a downstream zero-pressure-drop absorber to protect the vacuum pump.

Such recovery of volatiles at all levels of volatility is demonstrated by the consistency of recovery in a random selection of 67 tests on engine oils whose volatilities ranged from less than 5% to almost 20% and included both straight and multigraded engine oils. Results are shown in Figure 2.

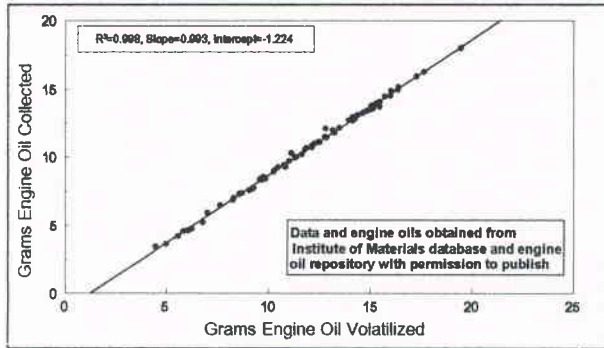


Fig. 2 - Cross-correlation of weight of engine oil volatilized and the weight of volatiles recovered.

The correlation between the amount volatilized and the amount collected is high (R^2 : 0.998) and slope very near unity (slope: 0.992). However, interestingly, the best line does not pass through the origin but intersects the Y-axis at -1.224 grams. Investigation showed that the amount of oil still retained in the coalescer and on the glassware is very close to this amount indicating that all except for about 0.02 grams are collected either in or before the receiver. That is, about 99.9% of the volatiles are prevented from reaching the last stage oil absorber before the vacuum pump and, so, essentially no oil reaches the pump itself.

This level of recovery permits confidence in examining the volatiles for their properties as representative of all volatiles produced.

Precision Using Automatic Vacuum Control

Very recent studies using the automatic vacuum control technique with the Selby-Noack apparatus gives an understanding of the precision of the technique.

Table 1 presents repeatability tests on the reference volatility oil and another reference oil of higher volatility.

Results show good repeatability at both levels.

3. PHOSPHORUS VOLATILIZATION STUDY

The aforementioned concern with the effect of volatilized phosphorus and the question of the relationship between such volatilization and overall engine oil volatilization led to a preliminary study.

The sixty-seven oils used to study volatile recovery were also used to determine the level of correlation between the amount of phosphorus volatilized and

Reference Oil		Higher Volatility Oil	
Test #	% Lost	Test #	% Lost
1	15.41	1	24.33
2	15.01	2	24.84
3	15.11	3	24.39
4	15.22	4	24.82
5	15.14	5	24.67
Average	15.178	Average	24.61
Std. Dev.	0.150	Std. Dev.	0.238
%SD	0.99	%SD	0.97

the amount of engine oil volatilized. This investigation was thought to be helpful in determining the best way to reduce phosphorus contamination of the emission catalyst.

Both the percent of oil volatilized (data from IOM Database on engine oils) and the phosphorus present by weight in grams of these same oils were cross-plotted. The results are shown in Figure 3.

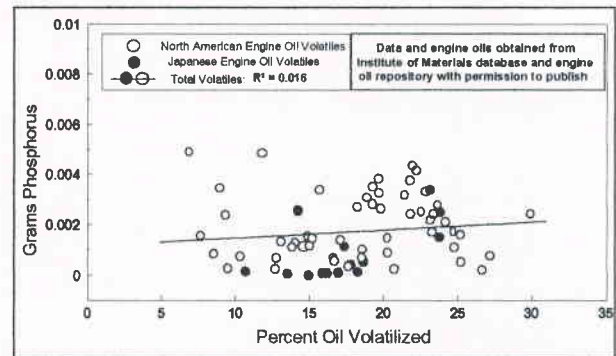


Fig. 3 - Comparison of phosphorus content of volatiles versus amount of oil volatilized for Japanese and North American engine oils.

Low engine oil/phosphorus volatility correlation - If there were close interdependence between the percent volatility of the engine oil the percent of engine oil lost and the amount of phosphorus volatilized, would show a high value of the Coefficient of Determination, R^2 . Instead, the data obtained on oils from two sectors of the world, show that there appears to be no correlation between the volatility of engine oil and that of the phosphorus in the oil.

Phosphorus availability and volatility - If the amount of volatile phosphorus was not generated by the amount of oil volatilized, what, then, was the cause? This question led to the next question of whether the amount of phosphorus in the original oil dictated the amount of phosphorus volatilized.

Accordingly, the fresh oils producing the results in Figure 3 were analyzed for phosphorus levels. Results are shown in Figure 4.

Two observations may be made. One, in regard to North American Oils which form the majority of the data, there is no correlation between the amount of phosphorus available and the amount volatilized.

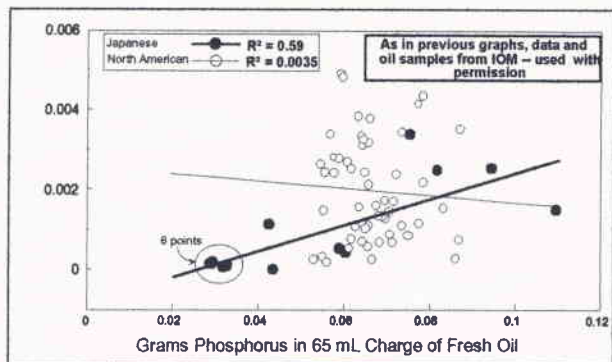


Fig. 4 - Comparison of phosphorus content in the volatiles versus initial content of phosphorus in fresh Japanese and North American engine oils.

The slope is actually negative showing that, if anything, the two concentrations are opposed.

The second observation shows a fair level of correlation in the Japanese oils evaluated (R^2 : 0.56). The apparent contradiction can be removed if it is the case that the Japanese oils are more alike in the type and amount of phosphorus containing additives they use.

Designed phosphorus-containing additives? - Both pieces of information suggest that phosphorus-containing additive can, perhaps, be designed to reduce phosphorus volatility.

4. CONCLUSIONS

This paper has discussed the results from analysis of engine oil phosphorus volatility using the Selby-Noack apparatus. Several conclusions are suggested from the data.

1. Engine oil phosphorus volatility is likely not influenced by engine oil volatility.
2. Engine oil phosphorus volatility may not be influenced by phosphorus concentrations in the engine oil -- unless the relationship is founded upon use of the same phosphorus-containing additive.
3. Further studies should be made of the relationship of phosphorus composition and concentration to its volatility.
4. Similar studies should be directed at the time of volatilization of the phosphorus compounds from the test oil and how this is related to composition and concentration.

5. ACKNOWLEDGMENTS

The author would like to acknowledge with great appreciation the contributions, insights, and dedication of

Richard Hall
 Brian Cluff
 Andrew Stephenson
 Ellie Reichenbach
 Dan McMahon
 and
 Larry Schember

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