

Sulfur Emissions from Engine Oil - Information from the Sulfur Emission Index

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Summary: Data published by the Institute of Materials (IOM) included information on the volatility, sulfur content, and sulfur volatility of 913 engine oils were compiled. These engine oils were collected in three geographic areas – North America, Europe, and Asia. The volatility data were generated on the Selby-Noack in which all volatilized material is collected for the further analysis of phosphorus and sulfur content. It was found that under the normal Noack test exposure conditions of 250°C for one hour, the Sulfur Emission Index (a measure of sulfur volatility in mg/L) varied markedly among the engine oils. In a correlation study, minor correlation up to $\%R^2 = 15$ was found between sulfur volatility compared to oil volatility while greater correlation of up to $\%R^2 = 39$ was found between sulfur volatility and sulfur content of the formulated engine oils. A new concept and application of the Sulfur Volatility Ratio may be useful in explaining observations concerning sulfur volatility dependence.

1. INTRODUCTION

1.1 The Sulfur Issue

Sulfur in engine exhaust emissions has been an endemic form of pollution since the reciprocating engine has existed. Only in modern times has there been a sufficient growth in world understanding concerning the deleterious effects of such pollution to cause corrective efforts.

Until relatively recently, the presence and amount of sulfur in emissions was dominated by the sulfur in the fuel. However, over the last score years this source has been severely reduced by government mandate and attention has consequently been turning to the sulfur levels in engine oils.

Sulfur in emissions is not only a direct pollutant but has been shown [1,2] to be an indirect source of pollution by its effects on catalysts effective in reducing nitrous oxides in the exhaust - the latter being the original and continuing prime target of pollution control.

Thus, sulfur is both a direct and indirect cause of pollution and a prime target for corrective action. Moreover, in regard to engine oils, sulfur is often present in both base stocks and additives. With the advent of more highly hydrotreated base stocks and the growing use of synthetic oils, attention is increasingly focused on the additive content of engine oils as a source of sulfur emissions.

1.2 Measurement of Elemental Volatility

Approach Using ASTM Method D 5800c – In the early 1990's, a bench test was developed by the author to obtain both

1. Noack volatility – a widely-used test [3-6] of engine oil volatility at a temperature similar to that of the passenger car piston (250°C), as well as
2. Collection of all volatile matter produced during the test which enabled further laboratory study [7-9].

This version of the Noack bench test is shown in Fig. 1. The test was later incorporated into the Noack methods of ASTM as D 5800c.

The Sulfur Emission Index – Earlier studies on phosphorus volatility [10-13] using the Selby-Noack instrument were encouraging (see Appendix 7.1). With this success, it seemed reasonable to apply the same techniques to measure the sulfur in the volatiles which was also generated during the test. Subsequently, in 2002 the author extended the Selby-Noack test to quantifying the sulfur volatilized in the test by a measure called the Sulfur Emission Index or SEI:

$$SEI = \text{mg S/L} = \text{mg sulfur/liter engine oil}$$

Information for the following analyses and observations came from the Institute of Materials (IOM) Engine Oil Database (see Appendix 7.2) and is used with their permission. Over 900 oils constituted the data available.

Figs. 1a and b – Complete picture of Selby-Noack instrument and closeup of noble-metal resistance heated cup for volatilizing oil on the right, and the smaller volatiles collector on the left (see arrows).

Essentially all (99+%) volatile material [10] is trapped in the volatiles receiver using a special coalescing filter. (Total recovery makes it possible to analyze the recovered volatiles as representative of all the material generated.)



Fig. 1a – Complete Selby-Noack instrument.

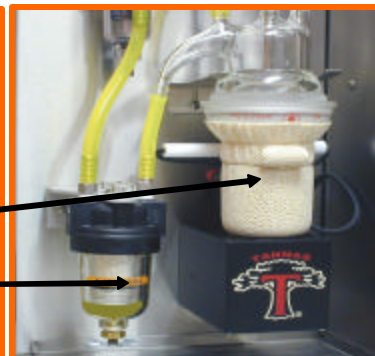


Fig. 1b – Close-up of noble-metal-heated volatilizing cup (right) and collector (left).

2. RESULTS: SEI AND OIL VOLATILITY

2.1 First Analyses of Engine Oils Sulfur Volatility

In determining the source(s) of sulfur volatility, the first logical question was whether sulfur was simply carried over with the oil volatilized. Fortunately, the data were available to answer this question since SEI has been a part of the IOM Engine Oil Databases for N. America, Europe and Asia from 2002. From this database, SEI analyses of over 900 oils were available as well extensive other measurements on these oils. Fig. 2 shows sulfur volatility in mg/L by SEI plotted against oil volatility in % mass loss.

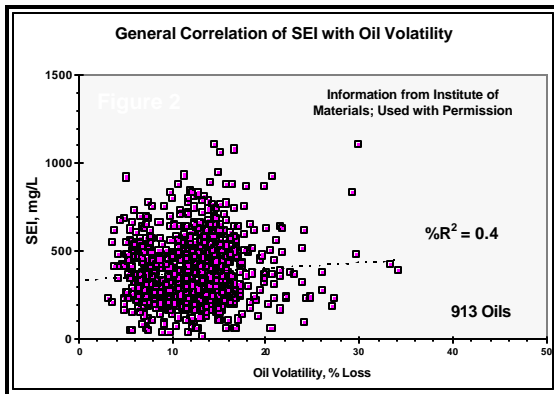


Fig. 2 – Overall correlation between oil volatility in % mass loss and sulfur volatility in mg/L using the Sulfur Emission Index.

Very limited correlation is shown as indicated by the Coefficient of Determination, $\%R^2 = 0.4$ (see Appendix 7.3 for further explanation of $\%R^2$). Recognizing that formulation practices vary considerably in different parts of the world, this finding of low correlation between sulfur and oil volatilities posed a further question of whether stronger correlations would be found by similarly analyzing each area independently.

More important, the data of Fig. 2 shows that SEI values vary widely – from 15mg/L to over 1100mg/L. This latter information underscores the importance of determining the cause(s) of high sulfur volatility.

2.2 North American Database

Analysis of SEI and engine oil volatility data from the IOM North American Database is shown in Fig. 3. Correlation, although relatively low, is found to

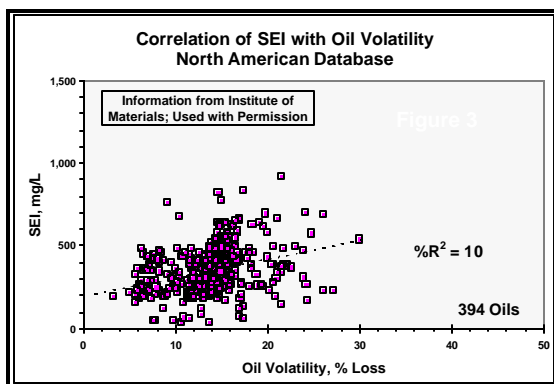


Fig. 3 – N. American data: correlation of oil volatility in % loss in mass and sulfur volatility in mg/L using the Sulfur Emission Index.

improve to the value $\%R^2 = 10$ compared to the value of $\%R^2 = 0.4$ shown by the overall data in Fig. 2. This stronger correlation indicates that there is some dependence of sulfur volatility on oil volatility.

The SEI range of the oils collected in North America was from 35 to 919mg/L with an average SEI sulfur volatility value of approximately 350mg/L.

2.3 European Database

Analysis of oils in the European IOM Engine Oil Database is shown in Figure 4. Correlation of SEI with engine oil volatility, although still relatively low, was even more pronounced at $\%R^2 = 16$. The volatility data varied from 8 to 930mg/L SEI sulfur with an average value of about 450mg/L

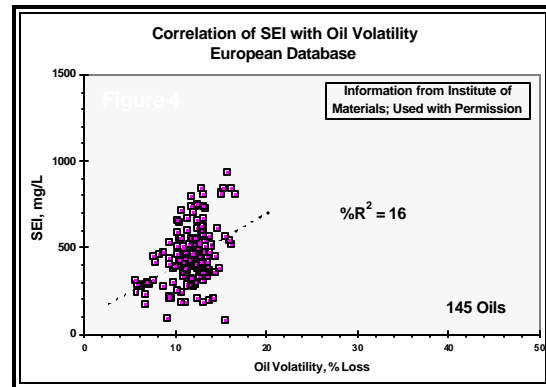


Fig. 4 – European data: correlation of oil volatility in % loss in mass and sulfur volatility in mg/L using the Sulfur Emission Index.

It will also be noted that the range of European engine oil volatility do not exceed values of about 18% mass loss in contrast to analyses shown in Figs. 2 and 3 where some volatilities exceed mass losses of 30%.

2.4 Asian Database

Data from the IOM Asian Database are shown in Figure 5. Correlation was found similar to that of the North American oils with a $\%R^2$ value of 8. The average value of SEI was about 380mg/L.

Range of SEI values was from 15mg/L to 1110mg/L

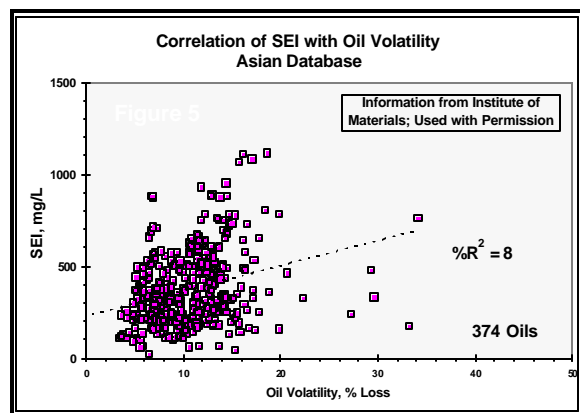


Fig. 5 – Asian data: correlation of oil volatility in % loss in mass and sulfur volatility in mg/L using the Sulfur Emission Index.

2.5 Consideration of the Oil Volatility Study

The values of $\%R^2$, 10, 16, and 8 for North America, Europe, and Asia respectively, may have some significance beyond limited correlation between sulfur and oil volatilities. On the basis of the meaning of $\%R^2$ (Section 7.3), this data can be interpreted to mean that there is a somewhat higher order of relatedness between the volatilities of sulfur and oil in the European oils than in either the Asian oils or the North American engine oils. If so, there may be value in determining the basis of this difference despite the tenuous nature of the data,

Perhaps both the $\%R^2$ values and the differences found in the average values of SEI for each geographical area are related as shown in Fig. 6 and this might be a guide to determining the relationship between sulfur volatility and blending practices.

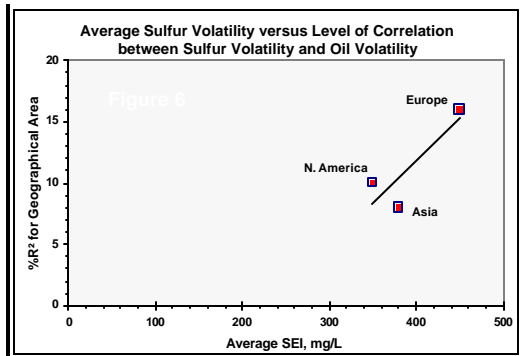


Fig. 6 – Possible relationship between average sulfur volatility in a geographic region and the degree of correlation between sulfur volatility and oil volatility.

3. RESULTS: SEI AND SULFUR CONTENT

One of the more basic questions is whether or not the sulfur content of the unused oil – sulfur either in the base oil and/or the additives – is an important factor regarding sulfur volatility.

Since sulfur content of the engine oil is also one of the pieces of information provided by the IOM Engine Oil Databases, this information was used to determine the degree to which sulfur concentration in the original oil influenced sulfur volatility.

3.1 North American Database

Fig. 7 shows the correlation between initial sulfur content of the engine oil and the sulfur volatility using SEI. The value of $\%R^2$ of 33 indicated that the initial sulfur concentration was a significantly higher contributor to sulfur volatility than engine oil volatility given in Fig. 3 which showed a correlation of 10%.

3.2 European Database

Similarly, Fig. 8 shows the correlation between sulfur content of the engine oils in the European geographic area and the sulfur volatility expressed by SEI. The correlation of 38 was even higher than that shown by the North American data.

3.3 Asian Database

Information on correlation between sulfur content and the SEI in Asian engine oils is shown in Fig. 9. The data indicate correlation of $\%R^2 = 39$, highest of the three geographical areas.

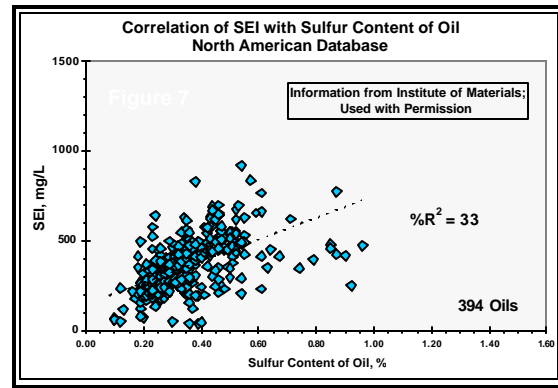


Fig. 7 – N. American IOM database: Correlation between sulfur content of the formulated engine oil in % mass and sulfur volatility in mg/L.

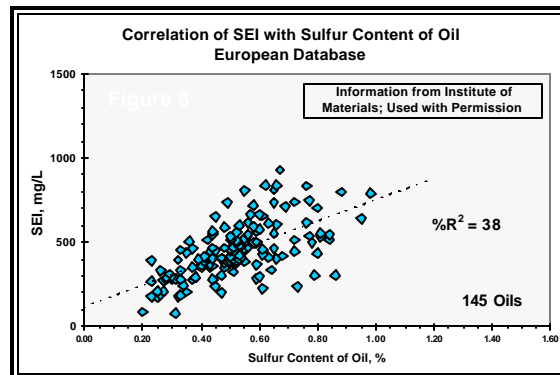


Fig. 8 – European IOM database: Correlation between sulfur content of the formulated engine oil in % mass and sulfur volatility in mg/L.

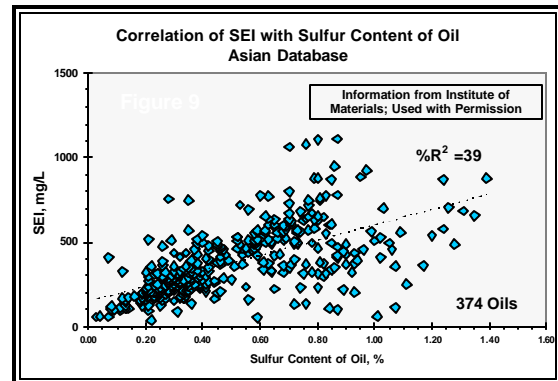


Fig. 9 – Asian IOM database: Correlation between sulfur content of the formulated engine oil in % mass and sulfur volatility in mg/L.

3.4 Variation in SEI/Sulfur Correlation

In each of the geographical areas, many of the engine oils analyzed fall well off the best regression line through the data. These are the oils which may give much more information regarding the dependencies of sulfur volatility. It is to be noted that many of these oils have lower – and in some cases, much lower – sulfur volatilities than would be expected from the sulfur content of these particular formulated engine oils.

4. RESULTS: SULFUR AND SEI DISTRIBUTION CURVES

The distribution curves for the sulfur content of the unused engine oils in all three geographical regions are shown in Fig. 10. Significant differences are evident as shown by both the distribution curves and the average concentration of sulfur in the formulated engine oils from each geographical region.

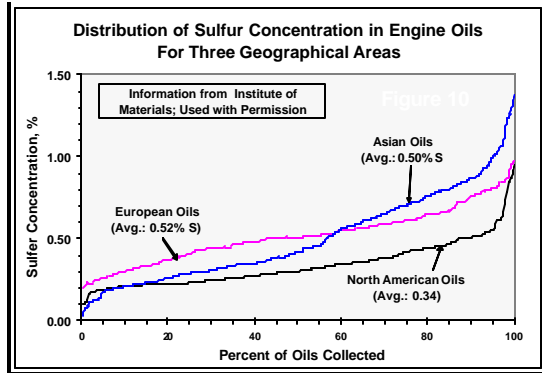


Fig. 10 – Distributions and averages of sulfur concentration in engine oils from three geographical regions

In Fig. 11, distribution curves of sulfur volatility values in mg/L SEI are plotted and averages of the SEI values are given as well as the sulfur concentration in the volatilized oil.

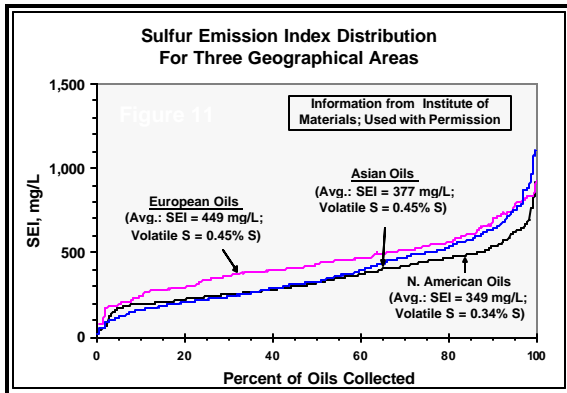


Fig. 11 – Distributions and averages of the sulfur volatility in mg/L SEI and sulfur concentration in the volatilized material from three geographical regions.

Again, the differences are apparent. Volatile sulfur, on the average, is about 30% less in the N. American oil than in the European oils and about 8% less than the Asian oils.

4.1 Direct Comparison of Sulfur Concentrations in Unused and Volatilized Oils

With these distribution curves, a relationship can now be more clearly shown regarding the degree of dependency of volatile sulfur on sulfur concentration in the engine oil.

Plots of the distribution curves of Fig. 11 are given a backdrop of a bar chart of the concentration of sulfur in each unused oil to indicate how it matches the SEI curve. Plots for the three geographic regions are presented in Figs. 12, 13, and 14.

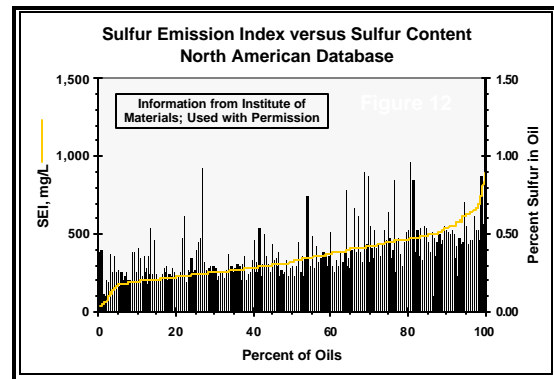


Fig. 12 – N. American engine oil distribution curve for sulfur volatility in mg/L by SEI from Fig. 11 versus bar graph of individual oil sulfur concentrations.

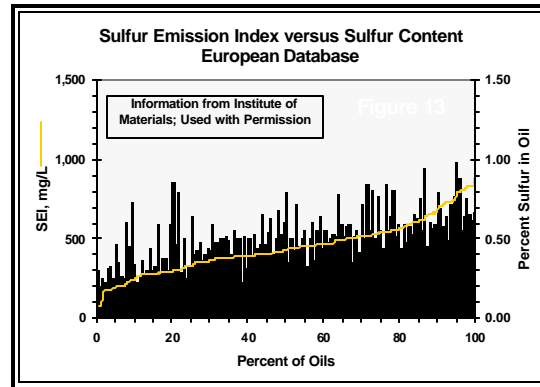


Fig. 13 – European engine oil distribution curve for sulfur volatility in mg/L by SEI from Fig. 11 versus bar graph of individual oil sulfur concentrations.

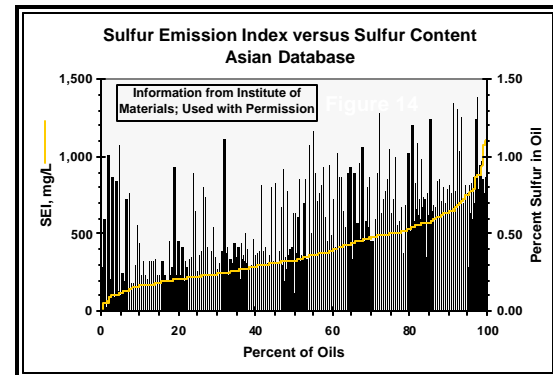


Fig. 14 – Asian engine oil distribution curve for sulfur volatility in mg/L by SEI from Fig. 11 versus bar graph of individual oil sulfur concentrations.

The foregoing Figs. 12, 13, and 14 clearly show the relatively poor predictability of sulfur volatility of a given oil by means of the sulfur concentration of the unused, formulated engine oil. A better approach seems needed.

4.2 The Sulfur Volatility Ratio

Since sulfur volatility is more important than unused oil sulfur content to the performance of the emission system, the ratio of the concentration of sulfur in the volatilized oil per liter to the sulfur concentration of the unused oil per liter, S_v/S_u would seem to be of value to establish the

acceptability of an oil regarding sulfur emissions. The lower the ratio, termed herein as the Sulfur Volatility Ratio or SVR, the better the oil in regard to obtaining lower sulfur volatility effects. Sv is identical to SEI and Su can be readily calculated from the sulfur concentration of the unused oil in the IOM databases.

Using this criterion of the Sulfur Volatility Ratio, Fig. 15 show the cumulative distribution curves for the three geographical areas and the SVR averages.

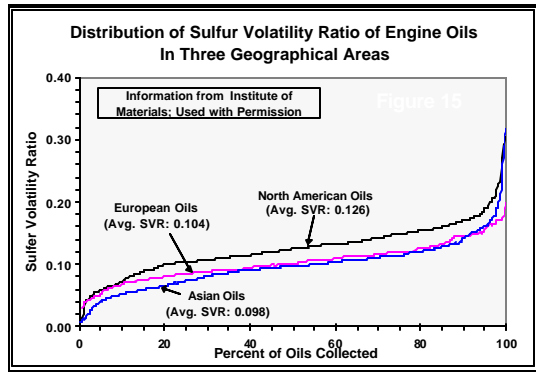


Fig. 15 – Sulfur Volatility Ratio distribution curves for N. America, Europe, and Asia.

The data of Fig. 15 are quite interesting and reveal another aspect of sulfur volatility. The data indicate that even though the Sulfur Emission Indices of the North American oil is lower than the other two geographical areas as shown in Fig. 11, the Sulfur Volatility Ratio is higher. Moreover, the Asian oils produced the best overall Sulfur Volatility Ratio with the European oils having similar values.

The answer lies in the nature of the Sulfur Volatility Ratio which compares the amount of sulfur available in the formulated oil to the amount of that sulfur volatilized. If larger amounts of sulfur are present in the formulated oil but only some given amount of sulfur is volatilized, then the Sulfur Volatility Ratio will be less than in the case where a same amount of sulfur is volatilized from a smaller initial concentration in the engine oil.

Thus, while the Sulfur Emission Index directly relates to the amount of sulfur volatilized from a given volume of engine oil, the Sulfur Volatility Ratio is related to how the different sulfur-containing oil components respond and/or interact to produce sulfur volatiles. In this aspect, the length of time and temperature of exposure to test conditions may certainly play a strong role and this, in turn, may explain some of the wide range of response shown by the SEI.

4.3 Sulfur Volatility and Engine Oil Sources

Base Oils – Considering the composition of the engine oil’s base stock, it would be reasonable to expect that if an oil contained significant sulfur across the molecular weight range of its base stock, volatility of these molecules would produce proportional presence of sulfur in the volatilized material.

This reasoning presumes (but not too rigorously) that the sulfur-containing molecules are as volatile as non-sulfur-containing molecules of equivalent molecular weight. Again, it also presumes that the sulfur-

containing molecules are distributed proportionately by molecular weight among the non-sulfur-containing molecules.

Additives – The sulfur content of the additives composing engine oil formulations vary widely. These additives include sulfonates and zinc dithiophosphates. The direct volatility of these additives and/or the sulfur volatility produced by their decomposition is an obvious source of sulfur emission as was indicated by the work of Asunuma, et.al. [2] in bench tests of oils and additives associated with their engine studies of sulfur emissions and effects.

5. DISCUSSION AND CONCLUSIONS

5.1 General

The study reported in this paper has been based on the conditions of the Noack test method: a one hour time exposure of 65 grams of engine oil under a slight vacuum of 20mm water at a temperature of 250°C. As such, the conditions represent one test environment. Although this environment is realistic from the viewpoint of engine piston and wall temperatures, other test temperatures and exposure times can be envisaged and these could generate different correlations than those presented herein. However, as a first study, the present test conditions – using the Selby-Noack to collect all volatile materials – seem to be a reasonable choice.

5.2 Critical Observations from the Study

Control of engine oil sulfur volatility with its negative impact on methods of reducing oxides of nitrogen emission is an undeniably important technical problem. However, recognizing a problem and resolving it require different viewpoints. The most important hurdle in resolving the problem of sulfur volatility is to find the cause(s) using a wide range of engine oil compositions and subsequently testing their sulfur levels and response in generating sulfur volatility.

Moreover, the sulfur volatility problem is shown not to be a matter of sulfur concentration in the engine oil but, rather, the degree of sulfur volatility from the engine oil. Particularly, with modern engine designs having much reduced oil consumption, volatility from the cylinder walls during the power and exhaust strokes are an important source of catalyst contamination by both sulfur and phosphorus. That is, volatility rather than oil consumption is the more likely source of these volatile elements in modern engines.

As mentioned, the data presented in this paper have shown a wide range of sulfur volatility. This seems to be a strong indication that much can be done to reduce sulfur volatility by the “rapier” of formulation chemistry and choice of base oils rather than by the “axe” of simplistically reducing sulfur concentration in the engine oil.

As evident in the data presented, the “axe” approach does not correct the problem in any case since the study has also shown that higher levels of sulfur volatility may be generated by lower levels of sulfur concentration in the engine oil. Regulation of sulfur volatility is the key to reduction of its adverse effects and the Sulfur Emission Index and Sulfur Volatility Index may be effective tools to accomplish this purpose.

It will be of interest and the source of further papers to observe the change, if any, in values of SEI and to

calculate values of SVR from the published data of the Institute of Materials Engine Oil Databases as efforts are made to contend with sulfur volatility. Further studies have been initiated by the author to use the IOM databases to more particularly search for the source(s) of highest contributors to sulfur volatility.

6. REFERENCES

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7. APPENDICES

7.1 Phosphorus Emission Index

One of the first applications of the volatile collecting ability of the Selby-Noack instrument was to learn more about the source of phosphorus volatility. As is well known, phosphorus is a critical element in engine oil because of

1. its presence in the oil as a long-established and desirable anti-wear, anti-oxidation additive, and
2. phosphorus' negative effect in coating and reducing the benefit of exhaust catalysts.

To quantify phosphorus volatility, the author developed a measure called the Phosphorus Emission Index (PEI) defined as the number of milligrams of phosphorus volatilized in the Selby -Noack test per liter of engine oil. PEI was shown to correlate with limited field studies of catalyst poisoning.

Using Selby-Noack data on 1300 engine oils in the Institute of Materials Engine oil data base, PEI was first compared to the volatility of the engine oil and it was found that there was essentially no correlation. That is, phosphorus volatility was essentially independent of oil volatility. Surprisingly, it was also shown that PEI also did not correlate well with the concentration of phosphorus in the engine oil. It was reasoned that the only way this could be possible was if phosphorus volatility was highly dependent on the chemistry of the phosphorus additive and/or on the other additives present in the oil formulation.

It was later shown that the additives present in the oil formulation were quite influential and studies of phosphorus chemistry and its effect on volatility are presently underway.

7.2 Institute of Materials

The Institute of Materials (IOM) has provided published data on engine oils collected from the market since 1984. The data are presented in 26 different tests and 72 data values. IOM engine oils are presently collected in North America, Europe, and Asia. Data from all three areas were used in this study.

As a consequence of the author's development of a means to quantify sulfur volatility, SEI data was added to the IOM database in 2002 and approximately 913 oils compose the basis for the presently reported study.

7.3 Correlation of Data Using R² and %R²

The Coefficient of Determination, R², is defined as "the proportion of total variance which has been explained" by the statistical analysis of the relation between two variables producing the value [14]. It is used by the author and others as a measure of the degree of dependency or "relatedness" of one variable to another. A value of 1.0 is taken as perfect correlation or complete interdependency – that is, one variable being the complete

cause of the other. The lower the value of R^2 in any given comparison, the more likely that factors other than the two being correlated are influential or even dominant.

If a percent value rather than a decimal value is used to indicate the value of R^2 – that is, $\%R^2$ rather than R^2 – it is often easier to understand the significance of Coefficient of Determination information as well as to more easily estimate the degree to which one variable is dependent upon the other.