

Present Noack Techniques – Applications, Limitations, and Use in Specifications

A Report by the Savant Laboratories

Background¹

The objective of this paper is to bring better understanding to what seems to be a simple procedure generating a measure of oil volatility – the Noack test. This test depends on proper and simple transmission of heat to an oil sample. Factors such as oxidation, deposition, viscosity, and oil additives all have influence on oil volatility. Consequently the Noack test -- used over the years to establish specifications -- produces a unique response which should not be lost in recent efforts to emulate its results with modern technology. This paper will at bring technical facts to the table to permit good judgment in designing and operating instruments to meet volatility specifications.

Instrumental Approach

For many years the technique developed by K. Noack [1] in the 1930s has been applied to the determination of volatility. The technique used molten Woods Metal -- a low-melting combination of bismuth, cadmium, tin and lead -- as a heat transfer fluid. Relatively recently, Woods Metal was recognized as being potentially toxic [2,4] and new instruments were developed to eliminate its use.

Basic Method - The heart of various Noack devices is a cup filled with 65 grams of oil that is subjected to a temperature of 250°C under a small vacuum (20 mm H₂O) for an hour. The vacuum draws a stream of air through the cup and carries out the volatile products.

Designed Non-Woods Metal Noack - In the early 1990s, a new Noack design was developed which did not require Woods Metal. In the development process this instrument was further designed to collect all of the volatile material for subsequent analysis. Technical papers on this instrument, its correlation with the Woods Metal Noack, and information from the collected volatiles were published [2-7]. The temperature sensor/control was placed against the inner wall of the heated cup.

Modified Non-Woods Metal Noacks - Subsequently, several companies which previously had made Woods Metal Noacks also rose to the challenge by redeveloping their own instruments without using Woods Metal. Most manufacturers continued to place the temperature-controlling sensor in the heating block. One used a temperature-controlling sensor immersed in the center of the oil.

The three approaches are simply sketched in Figure 1. The most important difference among the three methods is the placement of the thermal control device. What seems to be a simple heat transfer process is actually complex and subject to several factors. These factors have led to differences in results that have been of concern to both the CEC and the ASTM -- and led to this paper.

Considerable effort has gone into bringing the facts presented in this paper together in a cohesive view of Noack volatility and the instruments used.

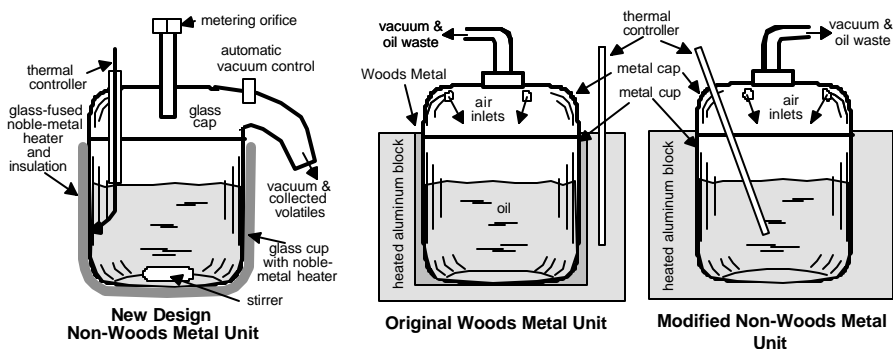


Figure 1 - Simple schematic comparison of three Noack Units

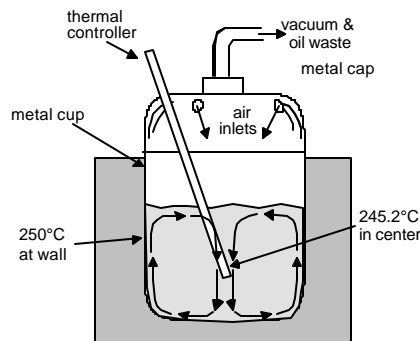
¹ The author of this white paper, Theodore Selby, has long experience with oil volatility and heat transfer. This background was applied in the development of the new design of Noack. Information gained during that development work is the basis for some of the observations made in this publication. Comments and other viewpoints regarding this white paper are welcomed. Please contact him by E-mail at tselby@savantgroup.com

Original Woods Metal Method – As mentioned, the Woods Metal Noack (around which most oil volatility standards have been generated) maintains the cup inner surface temperature contacting the test oil at 250°C by a thermal control device inserted in the heated aluminum block surrounding the cup as shown in center sketch of Figure 1. Sample heating by this method sequentially establishes the temperature of 1) the block, 2) the Woods Metal, and 3) the cup wall by conductivity of these metals. The oil in the cup is left to respond to the cup wall temperature of 250°C by the convection pattern developed and consequent heat transfer throughout the cup. It should be kept in mind that in comparison to metal, oil is a relatively poor conductor of heat. Volatilized oil is swept out of the cup chamber as air is drawn through the cup under a slight vacuum of 20 mm H₂O.

In essence, it is important to recognize that in the original Noack technique; the cup’s metal walls conduct heat to the boundary layers of test oil in contact with the wall (or to any wall deposits generated during the test). Since the test oil temperature is being controlled by a device conducting heat steadily through the wall at 250°C, the conditions of test fluid heating are constant no matter what convective path the particular test oil may follow within the cup.

The New Design Non-Woods Metal Noack – In the development of the new design Noack, it was experimentally found that placement of the temperature sensor/controller within the oil gave variable results depending on distance from the wall. Three primary causes were identified: 1) oil conductivity, 2) oil viscosity, and 3) deposits on the temperature sensor/controller as well as various interaction of these three factors. Information gained showed that, to simulate the Woods Metal Noack, it was imperative to have the temperature sensor/controller in direct contact with the cup wall – a condition which closely simulated the original control and heat path of the Noack test. Heat transfer has also been assisted by stirring the test oil for good oil homogeneity during test.

The Modified Original Noack Using No Woods Metal – As noted previously, one of the non-Woods Metal redesigns placed the temperature sensor/controller in the center of the oil (third sketch in Figure 1). This location was found (during the author’s work on the aforementioned new design non-Woods Metal instrument) to be a poor location for simulating the Woods Metal instrument. Such a position also calls for higher cup wall temperatures as a result of the cooling taking place across the volatilizing surface as the fluid circulates in a toroidal fashion first up the cup walls and then to the center of the cup as shown in Figure 2. (In this figure the circulation of the oil in the cup is indicated by the thickness of the lines indicating the toroidal pattern of flow determined in the author’s experiments).



Modified Noack (non-Woods Metal)

Figure 2 - Oil Circulation and Impact on Thermal Sensor/Controller

Thus, operating temperature necessary at the sensor in this configuration (later called Procedure B) had to be lower than the original Woods Metal Noack value of 250.0°C. Not surprisingly, it was found by the developers of this instrument that 245.2 ± 0.5°C was needed in order to approach Woods Metal Noack results. Unfortunately, this approach has other side effects on the volatility of oils which became evident in ensuing round robins.

First ASTM Round Robin Results

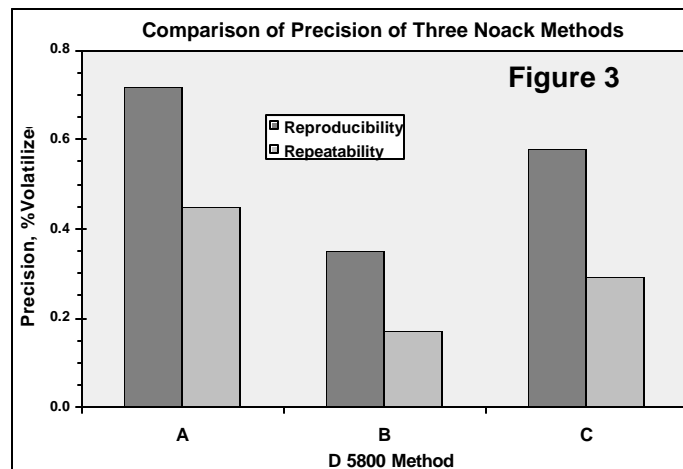
Until 2000, the only technique included in ASTM D 5800, *Evaporation Loss of Lubricating Oils by the Noack Method*, was the original Woods Metal Noack. With the development of the two non-Woods Metal instruments included in Figure 1, a new round robin was formed and produced data in 1998 and 1999 for comparison and expansion of D 5800. Emulating the original Woods Metal results was considered to be the prime need in considering a method to be included in D 5800.

In the order of submission of round robin results to the ASTM, the three techniques were identified as Method A (original Woods Metal Noack and non-Woods Metal, block temperature controlled instruments), Method B (test fluid immersed sensor non-Woods Metal Noack), and Method C (new design non-Woods Metal Noack with immersed sensor at the cup wall). The reference oils used in the round robin were all formulated oils. Table 1 presents the results.

For these six formulated oils, it may be noted that Method B was systematically higher than Method A. In contrast, Method C had both higher and lower results than Method A. Correlation between Methods A and B and C gave R² values of A vs. B of 0.999 and A vs. C of 0.996.

Precision of the three methods is shown in Figure 3 and it is evident that both Methods B and C show more precision than Method A with Method B showing the best precision of the three but, from Table 1, also showing greatest difference from Method A.

# Labs:	24	22	14	Difference	
Reference	Method A	Method B	Method C	A-B	A-C
Oil	% Vol.				
51	18.17	18.69	17.96	-0.52	0.21
52	13.50	13.73	13.61	-0.23	-0.11
55	16.35	16.76	15.88	-0.41	0.47
56	21.05	21.56	20.18	-0.51	0.87
57	11.53	11.83	11.84	-0.30	-0.31
58	14.51	14.59	14.18	-0.08	0.33
Average:				-0.34	0.24



CEC SG-L-040 Round Robins

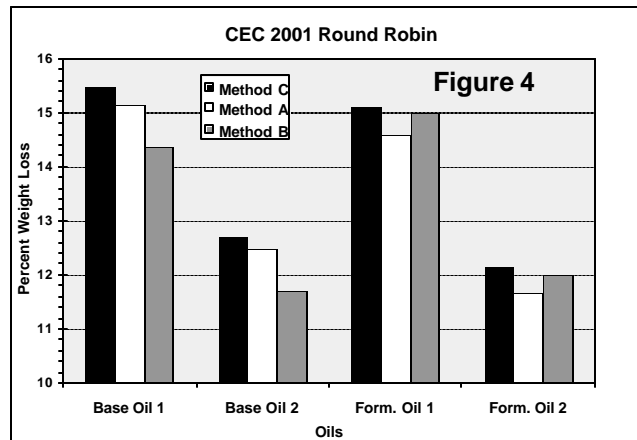
From its beginnings, the Noack volatility test has a long history in Europe. Coordinating European Council (CEC) SG-L-040 is responsible for surveillance of methods of determining volatility of base oils and formulated oils. Each year SG-L-040 runs a Noack round robin and in 2001 and 2002, as a member of the committee, the author was able to attend the reports of these round robins.

Round Robin of 2001 – In this CEC round robin, three different forms of Noack instruments were run: 1) Woods Metal Noacks (Procedure A), 2) modified non-Woods Metal Noacks with oil-immersed temperature sensor/controllers (Procedure B), and 3) a few Procedure C Noacks with oil-immersed temperature sensor/controllers contacting the inside of the cup wall.

Results Using Procedures A, B and C - Review of the round robin data at the meeting of 2001 May 10, brought renewed concerns that had been noted at previous meetings. Procedure B gave variably different results compared to Procedure A and this difference was shown to be dependent on whether the oil analyzed was a base oil or a formulated oil.

A plot of the accumulated data from the three instruments using the four round robin oils is shown in Figure 4. Fifteen laboratories used Method A, twenty-one used Method B, and five used Method C. The data show that Method B is lower than Method A by 0.7 volatile-% for the two base oils and higher by 0.4 volatile-% for the two formulated oils. In contrast, Method C shows overall values consistently about 0.4 volatile-% higher than Method A.

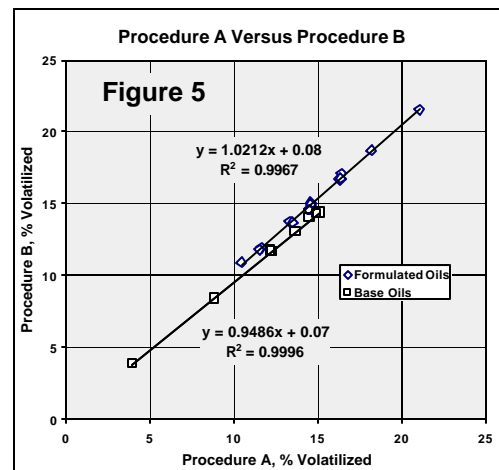
Concerns about different base oil/formulated oil results of A and B Procedures was not resolved at this meeting but further work was planned to try to determine the cause of these differences.



Round Robin of 2002 – Data gathered in this later round robin again showed the same systematic differences between Procedures A and B. That is, in comparison to Procedure A, Procedure B gave systematically lower values for base oils and higher values for formulated oils. This is shown in Figure 5 taken from two of the slides exhibited at the CEC SG-L-040 meeting of 2002 April 18 in Salzbergen, Germany. Precision for each of the two sets individually is good.

Effects of Locating Temperature Sensor in the Oil - At this same meeting, a presentation was made by Theo Kweekel, one of the members of CEC SG-L-040 who had made a study of the cause or causes of the differences during the year following discussions of the causes for such differences at the round robin of 2001. His report using differential scanning calorimetry (DSC) is attached as Appendix 1.

In his report, he pointed out that heating the oil sample using the heated walls of the cup (as in Procedure A) is an endothermic process of volatilization – an external source of heat provides the energy and the sensor is not affected by other conditions within the cup. Measuring the temperature inside of the cup subjects the sensor to both endothermic (volatilization) and exothermic (oxidation) processes. The latter processes would be more likely with those products having lower oxidation stability such as base oils and his data from the DSC underscored this reasoning.



Redesign - Theo Kweekel then went on to show that the first few minutes of exposure to higher temperatures were particularly different for base oils in comparison to oils formulated to be resistant to oxidation. Summing up his concluding remarks, he made the point that, based on the dependence of the instrument and technique on factors of oxidation stability, Apparatus B is dependant on thermal stability of test oil and accordingly “Apparatus B cannot be a base for correlation testing”. Moreover, he suggested that the instrument be modified to obtain temperature control from the block heater to eliminate the differences shown in the round robins.

Corrective Equations – In view of the distinct differences shown by results from the use of Procedure B on base oils on one hand and formulated oils on the other, the linearity of the two relationships shown in Figure 5 led to the proposal that two corrective equations be used to calculate Procedure A values from Procedure B values, one for base oils and one for formulated oils. However, it was noted that the laboratories receiving oils for analysis would not necessarily know whether the oil was base oil or formulated oil and, thus, not know which equation to apply.

On 2002 July 25, the value of the two equations in eliminating differences between Methods A and B led to the recommendation to Subcommittee 6 of ASTM Committee D02 by the Chair of SG-L-040 for using these equations in ASTM Procedure D 5800 which included Methods A and B.

Further ASTM Round Robin on Methods A, B, and C

The ASTM Test Monitoring Center oversees the volatility tests required for the Bench Test Surveillance Panels of Subcommittee B on Automotive Lubricants. In its 2001 December report on volatility test results under D 5800, there were evident severity trends primarily using Method B (CEC Procedure B). As a consequence, it was decided to hold a workshop for operators followed in time by a round robin including Methods A and B. The workshop was held 2002 March 13/14 with the round robin run over the following few months. Round robin results from Method C are not yet complete but results from eight participating laboratories have been collected and can be used for comparison.

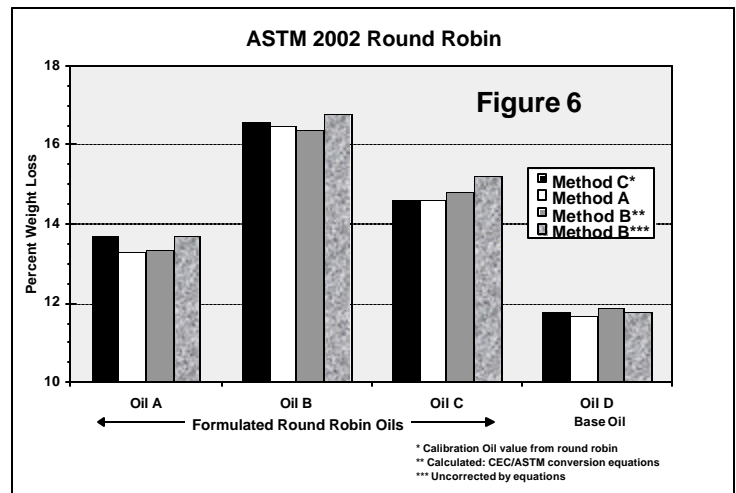
Round Robin Results –

Good Results with Correction of Method B - ASTM round robin results are shown in Figure 6 for all three methods. Method B values are shown both corrected and uncorrected by the CEC/ASTM equations developed to emulate Procedure A. Method C values reflect the corrected values for the calibration oil obtained from the round robin results of Methods A and B on this calibration oil as intended.

It is evident that the three methods are in good agreement with one another when Method B is corrected by the equations.

Poor TMC Trending if Method B is Uncorrected - If Method B is not corrected by the CEC/ASTM equations, Test Monitoring Center (TMC) information is not encouraging as shown in the attached TMC conclusions (Appendix 2) reported in December 2002 at the semi-annual ASTM meeting.

Seventy percent of the instruments reporting were using Method B and 25.7% of the tests failed to meet the TMC target precision in the last quarter (5% failure or less is expected). Moreover, the combined Noack A and B Methods (70% Method B) were trending even more severe than before – the degree of difference between the established target value and the Method B results is growing.





Discussion

Variable Bias with Procedure B

The data generated in round robins over the last two years conclusively show that, when correlated with Procedure A, Procedure B produces a bias. Evident need to operate the Procedure B instrument at a significantly different temperature than Procedure A in order to obtain relatively similar results is a first sign that operating conditions are different. Moreover, the bias is not a simple displacement of the data but varies depending whether the test fluid is base oil or formulated oil. The consistency of this bias shows that the cause of the bias is fundamental to the test instrument used.

Causes of Procedure B's Bias

Analysis of the reasonable causes of this oil-source bias indicated that the oxidation stability of test oils plays an important roll in affecting the temperature sensor/controller which in this instrument is placed in the midst of the oil in the cup.

In oxidation studies, the author has found that if some of the additives in formulated oil deposit on the temperature sensor/controller, even a very thin layer of these deposits significantly change the heat flow kinetics to the sensor. With such a heat step barrier, the controller would call for slightly higher temperatures to compensate for the heat loss up the sensor's stem. This would have the effect of increasing the volatility of formulated oils. In contrast, any heat generated by oxidation of base oils noted by Kweekel would increase the temperature sensed by the controller surrounded by the oil -- which is a relatively poor heat conductor. The result would be a decrease in the external heat called for by the sensor and lower volatility of base oils.

Other Factors

Viscosity Effects - Beyond the two aforementioned effects likely producing the bias of Procedure B, there are three more which must be considered. One is the viscosity of the oil at the temperature of exposure. As shown in Figure 2, the toroidal path taken by the oil is influenced in speed and shape by the viscosity of the oil. This would provide another unwanted effect influencing the kinetics of heat exchange at the boundary of the temperature sensor/controller which would produce even greater variability when comparing oils.

Relationship of Base Oil and Finished Oil Volatility - Another consideration is the relationship between base oil volatility and formulated oil volatility. If Procedure B already produces a bias between base oils and formulated oils, any correlation between the volatility of a base oil alone and the formulation from this base oil might be lost.

Relationships between the base oil and the formulated product are important to establish and maintain clear understanding. Such understanding should not be affected by the vagaries of the instrument and method of measurement. At this time it would seem to be an unfortunate choice to change the significance of established specifications because of factors related to instrument design.

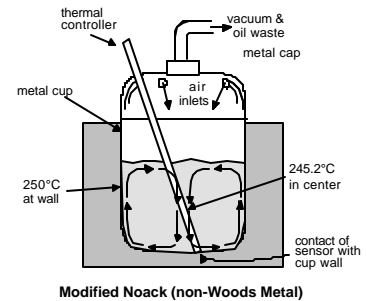
Procedure A and Its Simulation - There are still many Woods Metal Noacks used and there are also a growing number of non-Woods Metal Noacks, such as the instrument used in Method C, which correspond correctly to Procedure A. These instruments maintain support for the many specifications built around the principles of K. Noack's work and its later applications. In contrast, Procedure B arbitrarily disrupts the historical relationships as a consequence of sensor placement.

Simple Redesign of the Non-Woods Metal Noack

In the final slide of his attached presentation in Appendix 1, Theo Kweekel suggested that the non-Woods Metal Noack should be modified to measure and control the block temperature surrounding the cup. However, this would require a considerable redesign for the many instruments in the field and a much simpler approach is suggested based on the author's experience.

The author suggests the more direct approach of simply extending the temperature sensor/controller to any heated wall of the cup as shown in the simple sketch of Figure 7. The sensor/controller could be spring-loaded to maintain contact between the sensor and the wall. Measuring the wall temperature avoids all of the effects convoluting the measurements resulting from Method B.

Following redesign, based on his experience, the author would expect that the appropriate operating temperature would reasonably be expected to be 250°C and it is further anticipated that reasonable correlation with Procedure A would very likely be reestablished.



Modified Noack (non-Woods Metal)
Figure 7 - Simple correction of design to emulate Procedure A

Conclusions

The instrument used in Procedure B (ASTM Method B) does not meet the criterion of systematic, linear correlation with Procedure A with all oils. That is, Procedure B does not reflect the results from Procedure A nor does it vary in a regular way which would permit simple mathematical correction. Rather, it gives a variable bias when compared to Procedure A depending on whether the test oil is a base oil or a formulated oil. This bias is believed responsible for the continued and growing severity trend in the TMC monitoring efforts reported over the last two years.

It has been strongly suggested in a past meetings of the CEC and in this paper -- based on data from both CEC and ASTM as well as the authors experience in factors affecting volatility -- that the cause of the variable bias of Procedure B is a design problem which locates the temperature sensor/controller in the test oil. In this position, the sensor is subject to several influences other than block temperature in controlling volatility. This location affects the sensor's ability to give results reliably simulating Procedure A. On the other hand, a relatively simple and inexpensive correction of the design would most likely bring the instrument used in Procedure B back into close agreement with Procedure A around which many specifications in the world are established.

It seems technically inappropriate to modify specifications to fit the requirements of an instrument -- especially one that has evident bias caused by temperature sensor placement. Moreover, with its dual bias on base oils and formulated oils, it would be expected that further difficulties would be caused in matching base stocks and resultant formulated oils to specifications using more modern base oil sources such as Group 2, 3, and 4 oils.

Until the instrument used in Procedure B is corrected, it is clearly the most proper technical direction to continue to use the equations matching it to Procedure A results which gives acceptable correlation to Procedure A as shown in the last ASTM round robin (Figure 7).

Recommendations

Rather than alter the values from a long established method and the application of these results to volatility decisions in specifications, a simple change in the instrument of Method B would seem much more technically prudent and acceptable. It is recommended that the conversion equations applied by the CEC and recommended to the ASTM be applied until the instrument used in Method B be modified to correspond to results of Method A.



Bibliography

- [1] K. Noack, *Angewandte Chemie*, **49** (1936) 385.
- [2] 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).
- [3] Selby, T.W., Cluff, B.J., **Selective Volatilization and Collection**, Patent Number 5,667,302; issued 1997.
- [4] 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 Akademie 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.
- [5] 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).
- [6] 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.
- [7] 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).