Report to
Exhaust System Compatibility Improvement Team (ESCIT)
On
Study of Extended-Time Phosphorus Emission Index (PEI) Values at 165°C

A Report by the ESCIT Task Group

Summary: The study indicates that extending the time for collecting PEI data does not add to the usefulness of the technique. An ancillary study compared ICP methods for determination of phosphorus. No difference was shown.

Background of Task Group Formation

At the previous ESCIT meeting in Arlington, Virginia, on June 14th, 2007, the Task Group was appointed by Hannah Murray, Chair of ESCIT. The purpose of the Task Group was to investigate any improvement that might be made by longer exposure intervals on Phosphorus Emission Index (PEI) at 165°C which, when run at 16 hours, had previously shown good correlation with engine results.

Composition of Task Group

At the formation of the Task Group, eight members of ESCIT volunteered to become members in addition to Ted Selby who, because of background in the PEI methodology, agreed to chair the group. These individuals and their affiliations are shown in Table 1.

Table 1 -- Composition of Task Group on Extended Time Study of PEI

Name	Company	Industry Segment
Brad Cosgrove	Chrysler	Automobiles
Joe Franklin	Intertek	Laboratory
Greg Guinther	Afton	Additives
Wangkan Lin	Infineum	Additives
Jim Linden	GM	Automobiles
Ron Romano	Ford	Automobiles
Ted Selby	Savant	Laboratory
Jerry Wang	Oronite	Additives
Lew Williams	Lubrizol	Additives

Almost all of the members had some degree of familiarity with the development of both the concept and the application of the Phosphorus Emission Index

Background and Importance of the Task Group Work

Studies Using the Phosphorus Emission Index – In papers and reports over the last several years, the Phosphorus Emission Index has strongly indicated that the practice of trying to control phosphorus emissions from engine oils on the basis of phosphorus concentration in the fresh oil is seriously questionable. Rather, it was indicated that the chemistry of the ZDDP used and the influence of other engine oil additives seem to be the dominant factors in phosphorus emission. Actually, the PEI data indicated that setting a phosphorus concentration limit on fresh oil might be counterproductive since some ZDDPs, at lower concentrations, are more prone to produce volatile phosphorus-containing material in the PEI test.

Formation of ESCIT - With this indication that there were better ways to control phosphorus emission, ILSAC formed the Exhaust System Compatibility Improvement Team (ESCIT). ESCIT's responsibility was to bring a test method measuring the phosphorus emission tendencies of engine oils to ILSAC's balloting procedure for GF-5 by early 2008 after choosing and establishing a method and the method's precision.

Exit Ballot on PEI(165-16) - On the basis of PEI data correlating with engine and fleet tests, the PEI bench test was one of two approaches chosen by an ESCIT exit ballot to meet this timeline. In addition, it was the only bench test. For those choosing it, the PEI bench test offered simplicity, precision, adaptability, and freedom from the much greater cost and always challenging logistical problems of a long-term engine specification test.

Round Robin and ASTM Method Timeline – Prior to the meeting of ESCIT on June 14th, the Chair requested a timeline from the sponsor of the PEI test for completing its round robin and method. This was presented at the meeting as shown in Figure 1.

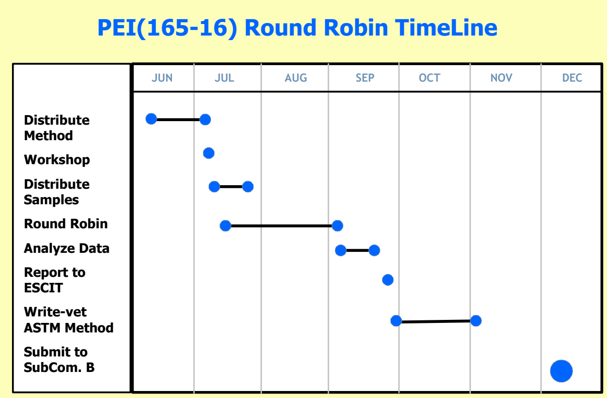


Figure 1

However, despite evidence of good correlation with engine and field tests, question was raised as to whether the correlation could be improved with longer running time. Moreover, there was a desire to run such tests with different industrial sources of ZDDP.

It was obvious that such a study would have evident consequences on the timing of the PEI round robin. Nonetheless, the information to be gained would be technically interesting and might produce an even more correlative test although it was well recognize that the major limiting factor in generating correlation is usually the degree of reproducibility of the engine test.

Task Group Formation and Organization - Accordingly, the ESCIT set up a Task Group which was joined by the nine members of ESCIT listed in Table 1. This Task Group took up the challenge of selecting and producing extended PEI data at 165°C on a number of oils which were to be chosen, delivered, and analyzed by the time of the next ESCIT meeting set for August 9th. Appendix 1 presents the Scope and Objectives established by the Task Group.

PEI analyses would all be done by the Savant Laboratories because of their expertise. Major funding of the effort was offered by the Alliance of Automobile Manufacturers with any additional needs funded by industrial sources of ZDDP.

Matrix Oils - The first critical need was to establish the matrix of oils to be run. In a telephone conference meeting of the Task Group on July 2nd, eight oils were selected that, first of all, involved at least one of each ZDDP manufacturer's product and second, of these eight oils, seven had some amount of engine performance data. The one oil selected had no direct engine information but used a ZDDP additive content widely applied in the field. Table 2 shows this matrix and sources.

After establishing the test oil matrix, the next most important and initially somewhat difficult task was to obtain these oils quickly. However, the hurdles were overcome and by July 18th, all test matrix oils were in hand leaving somewhat less than three weeks to complete the study and this report.

Table 2 - Oils Selected for Test Matrix

Oil Source	Oil Code
JAMA	Oil 2
	Oil 4
	Oil 5
Lubrizol	'Low Impact'
	'Conventional'
Afton	FT-33
	RBR-10443-L-02
Oronite	Low PEI

Engine test data available on these matrix oils were quite varied and did not allow overall correlation with PEI(165-T). Moreover, any correlation requires knowledge of the precision of the tests being compared and no work had been done in this regard with longer running PEI tests.

However, such overall correlation was not necessary since the work of the Task Group was to determine if longer test PEI test periods would add to the level of correlation already reported at past meetings and this could be done by ranking and comparing the PEI values of the oils.

Ancillary Second Study of ICP Methods - A further question was raised during the intensive Task Group phone conferences (of which there were three: July 2nd, July 16th, and August 1st). This question concerned the choice of ASTM ICP Method D 4951 used by the Savant Laboratories for elemental analysis of phosphorus when the general industry was using the later Method D 5185. The question led to a small comparison study of samples from the PEI(165) tests as well as sample of the fresh oils. Two laboratories cooperated in this, Afton and Intertek. This first report uses the former data.

Later communication in the Task Group established that Method D 4951 was the most accurate for fresh oil while D 5185 was most applicable to used fluid.

Test Protocol – The choice of time intervals for the Task Group's study were 16, 32, 48, and 64 hours. Several of the oils had already been run at 16 hours by the Savant Laboratories – in some cases on earlier samples of the same oil – and so it was not considered necessary to rerun these tests. Moreover, in regard to the very long 64-hour tests, it was thought to be expedient to first run the 32- and 48-hour tests and then to decide whether there was value in obtaining the 64-hour data.

Four Selby-Noack instruments were available for use in this study. Two of these were older models and two were of more recent vintage. A calibration volatility test on a standard for the Noack test was run at the beginning of the day in which any PEI or other test sequences were to be run to assure both proper vacuum of 20 mm_{water} and air flow rate at this vacuum.

Using the PEI protocol, the practice at 16 hours has been to run SN75 oil as a co-volatile to be sure of sufficient volatilized product in the collection vessel. This approach was continued for consistency even in the case of the longer tests run with the PEI protocol which were certain to produce sufficient sample for ICP analyses without the use of the co-volatile.

Considering the very tight schedule to obtain all of the required PEI(165-T) data, no effort was made to establish the precision of the extended-time test protocol

Results

Table 3 shows the results of the study to this point. There are several interrelated pieces of information in the table. The first of these is that the blue highlighted information of rows 4, 5, 8, 9, 11, and 13 shows the identity and PEI(165-T) values for oils sent to the Savant Laboratories earlier.

The oils identified as 'Low Impact', 'Conventional'(Rows 4 and 5) as well as the sample of FT-33 (Row 8) listed in the table, were all received in 2006 or earlier. Each played a significant part of the development of PEI correlation with taxi-fleet studies.

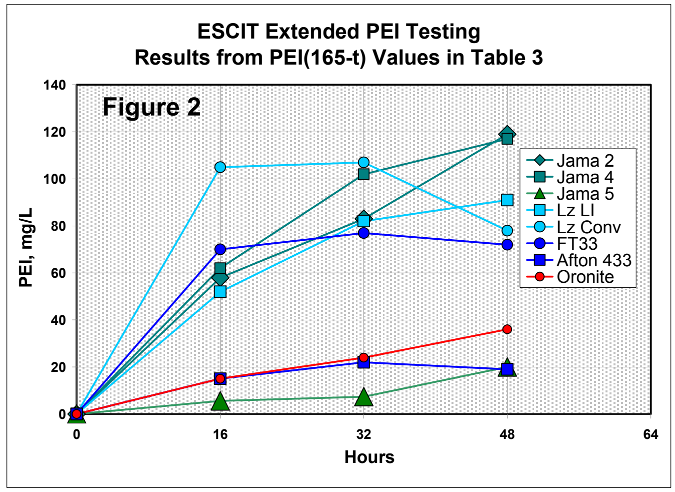
The sample of FT-33 listed in Row 9 had been received earlier this year. In the pace of developing test data it was selected in error to generate the 32- and 48-hour data for this study. Although it was necessary to rerun the tests with the latest sample of FT-33 (Row 10) for the present study, the earlier and later data do provide some indication of the repeatability that can be obtained. In some contrast however, the PEI(165-T) values on the 'Low Impact' and 'Conventional' oils in Rows 4 and 5 had been obtained in 2006 in extended time analyses associated with special correlation studies. The present sample of the 'Conventional' oil in Row 7 gave much lower PEI results and the sample is to be reanalyzed.

Table 3 -- ESCIT Extended PEI Testing Matrix

Oil Source		Oil Code	PEI @ 165ºC				
			16 hrs.	24 hrs.	32 hrs.	48 hrs.	64 hrs.
JAMA	1	Oil 2	58		83	119	
	2	Oil 4	62		102	117	
	3	Oil 5	5.6		7.4	20	
Lubrizol	4	'Low Impact'	52	82		106	
	5	'Conventional'	105	124		149	
	6	'Low Impact'			82	91	
	7	'Conventional'			107	78	
Afton	8	FT-33	70				
	9	FT-33			77	72	
	10	FT-33			73	71	
	11	RBR-10443-L-02	15				
	12	RBR-10443-L-02			22	19	
Oronite	13	Low PEI	15				
	14	Low PEI			24	36	

Earlier samples

The data in Table 3 can also be plotted to view the change in the values of PEI(165-T) with time of exposure to the volatilizing conditions. This is shown in Figure 2 and the atypical 48-hour test response of the 'Conventional' oil is evident.



The eight matrix oils tend to separate into two groups regarding the whole range of PEI(165-T) values. Another view is that there are also some oils which still seem to be somewhat increasing in PEI(165) at the 48-hour period. These four were chosen for 64-hour analyses by the Task Group.

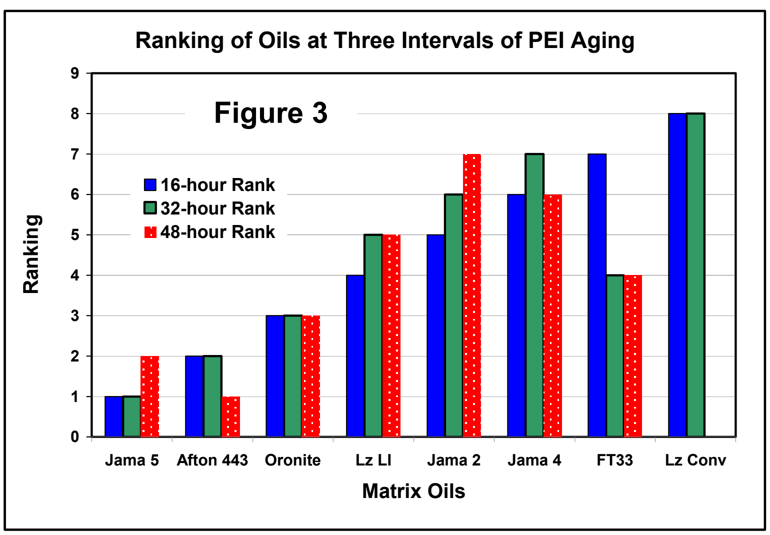
Analysis of Data

Time-Variable PEI(165-T) Study

Inasmuch as three of the four sources of the matrix oils had different engine tests and protocols, there is no common engine test for correlation. However, the essential question that the Task Group sought to answer with this study was whether the longer volatilization exposure time would significantly change their relative values.

One of the Task Group members considered the need and suggested simply comparing PEI(165-T) data on a ranking basis at all three exposure time intervals. This approach answers the question of whether there are significant changes among the phosphorus emission tendencies of the matrix oils.

Figure 3 shows this comparison

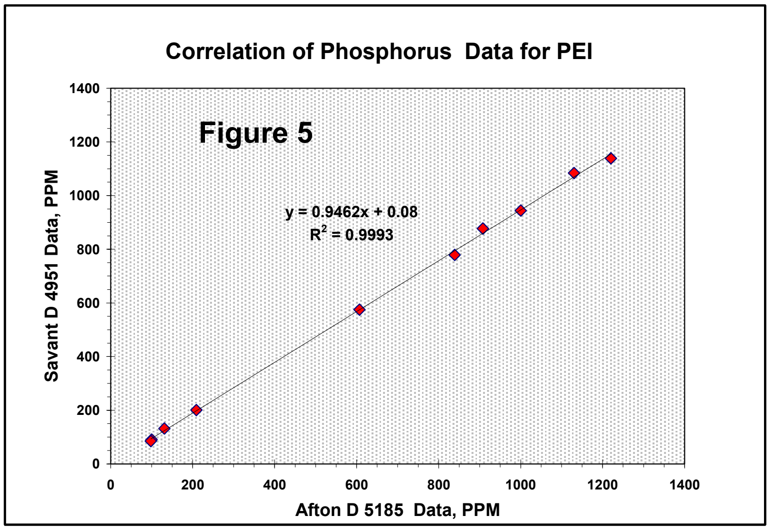


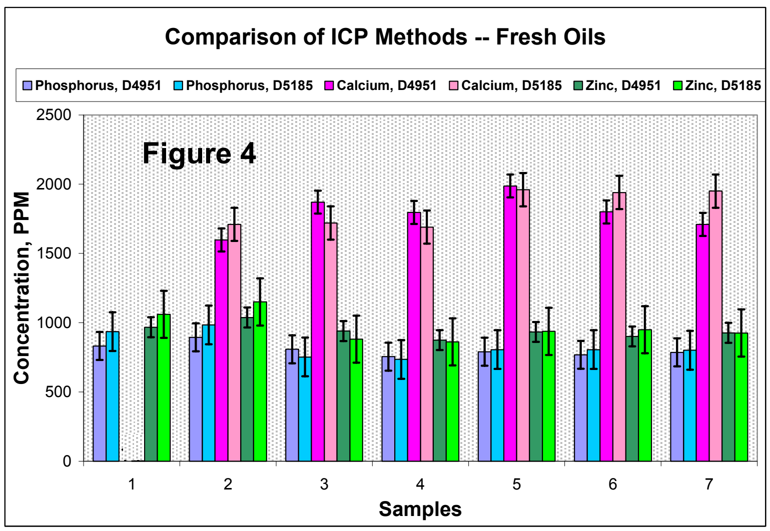
With the exception of FT-33, an un-typical oil without detergents, the remaining seven oils show consistent individual rankings. The minor variations shown most likely reflect inexperience with these new PEI(165-T) protocols as well as the forced pace of accumulating the data.

From this point of view, it would seem that the basic question of improvement of the performance of the PEI(165-16) (which has already shown acceptable correlation in several studies) by extending the time of exposure is questionable.

Comparison of Elemental Analysis Methods

Data obtained using ASTM Methods D 4951 and D 5185 are graphically shown in Figures 4 and 5 for seven fresh samples and ten volatilized samples respectively.





The cooperative ICP data obtained make it evident that there is no meaningful difference between the two methods. What difference there may be as shown by the slope of the best line in Figure 5 is likely to be in favor of ASTM Method D 4951 which is stated to be the best method for the determination of oils not carrying wear contaminants. Method D 4951 is also less affected by so-called viscous matrix effects because of the higher dilution ratios.

Conclusions to the First Task Group Report

The Task Group has been successful in bringing the desired data forth for consideration of the Parent ESCIT. Still to be reported are the PEI analyses that were selected at the last phone conference meeting of the Task Group as well as the ICP analyses very recently submitted by Intertek.

These pieces of information will be covered in an amended version of this report.

Appendix 1
Scope and Objectives

Scope

The Scope of the Phosphorus Emissions Bench Test Task Group is to determine the optimum test length for the PEI(165) protocol to obtain best correlation with field and engine tests.

The Scope of the Task Group also includes the setting of Objectives.

Objectives

1. To determine, through designed bench studies utilizing the Selby-Noack instrument, the optimum test length that will provide best correlation with data from taxi fleet and engine data.
2. To report the data gathered to the parent ESCIT group with recommendations regarding a subsequent round robin conducted under the auspices of ASTM Committee D02 and its Subcommittee B, Section 7.