The Impact of Detergent Chemistry on TBN Retention

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Abstract

Historically, the characterisation of fresh and used diesel engine lubricants has been based on a limited number of analytical techniques. One of the most important methods of analysis has been total base number (TBN) measurement. Although TBN measurements are informative, easy, and quick, it can be misleading to base the judgement of an oil's performance solely on one criterion.

This paper offers some observations from a field test, showing that some detergent types gave unacceptable performance even though the TBNs were at an acceptable level. It is hypothesised that some detergents do not effectively neutralise all acidic species present in the lubricant, thereby reserving their own base, while in fact the oil may no longer provide sufficient protection against bearing corrosion. This hypothesis is supported by bench and engine test data. It is recommended that, at a minimum, total acid number (TAN) measurements be included in any analysis, and where time and cost permit, wear metals content, oxidation, soot content, and viscosity should also be evaluated.

Keywords

detergent, additives, engine oil, acid, total base number, total acid number

INTRODUCTION

Today's lubricants market offers a wide range of products for internal combustion engines. Many analytical techniques exist with which to characterise the individuality of these products and to confirm their compliance with specifications. Among the most frequently used characterisations are viscosity grade, TBN, sulphated ash level, and metals content. Historically, the level of acid neutralising base, or TBN, has been relatively high for heavy-duty diesel engine oils, because of the high sulphur content of diesel fuel. Recently, many governments have mandated the use of low sulphur fuel for diesel engines. Normally, such a mandate would be expected to lower TBN requirements;[1–4] at the same time, however, there is a drive towards extended service intervals (ESI),[5] which

Table 1 Difference between ASTM D-2896 and D-4739

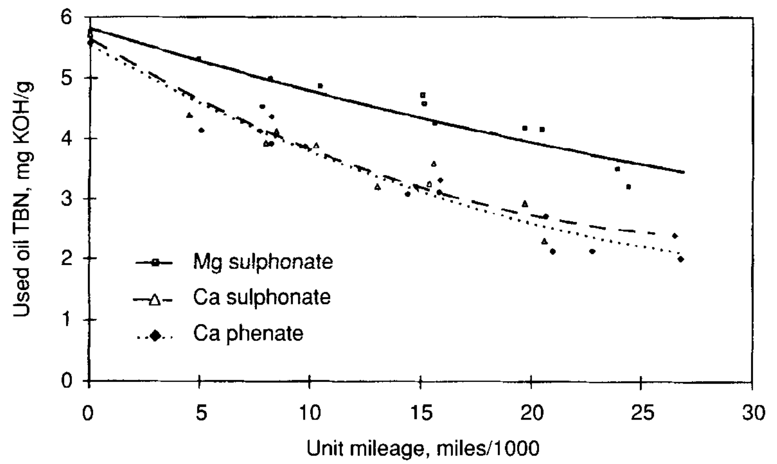
Additive type	*D-4739/D-2896 ratio (typical value)*
Phenate detergent	0.96
Sulphonate detergent	0.96
Ashless dispersant	0.48
Amine antioxidant	0.00

tends to push TBN requirement higher. As a result of these opposing demands, TBN requirements are being reconsidered.

In addition to using TBN for the characterisation of fresh lubricants, it is also employed to judge the condition of used oils. In many field applications with extended service intervals, TBN is measured to monitor used oil quality. This use of TBN became widespread at a time when today's sophisticated oil analysis methods were not available, and much higher sulphur fuel was in use, resulting in relatively stronger acids in the used oils. Several engine builders (OEMs) have set TBN limits for condemning used oil. One suggests that a reduction in TBN (by D-4739) to one-third of the initial value provides a guideline for the drain interval.[6] Another OEM requires fresh lubricants with a minimum TBN (by D-2896) of at least 20 times the fuel sulphur level for pre-chamber engines, 10 times for direct injection engines[7,8] and, furthermore, suggests a condemning limit of half that. In general, TBN is often used to describe the quality of fresh oils and to monitor the remaining life of used oils.

An issue that further complicates the TBN question is the fact that two commonly accepted measurement methods are used: ASTM D-2896, often used for fresh oils, and ASTM D-4739, for used oils. The two methods are similar in that they involve adding a measured amount of acid to the oil until all of the base has been consumed. The TBN is calculated from the amount of acid required to neutralise the lubricant completely. The difference between the two methods comes in the choice of acid used and the solvent in which the oil is dissolved to run the test. D-2896 uses a stronger acid that does D-4739, and a more polar solvent system. The combination of stronger acid and more polar solvent results in a more repeatable method. For some lubricant additive types, D-4739 does not measure all the base that is present. **Table 1** shows some typical values for the ratio of TBN by D-4739/TBN by D-2896. In general, D-4739 gives a lower result, but the difference between the two methods is not consistent. The D-4739 results are low for all ashless additives, especially for some amine oxidation inhibitors. Regardless of these differences, we have chosen to show TBNs only by D-4739 (unless noted otherwise) as it has become an accepted procedure for used oils.

Figure 1 Field test used oil TBN (D-4739)



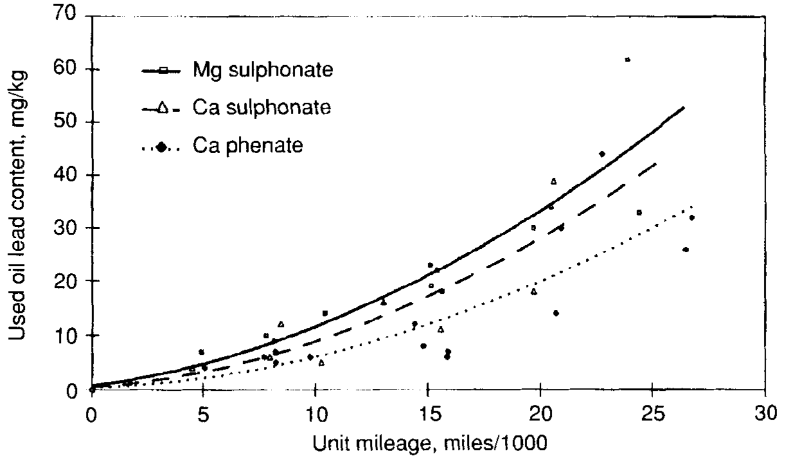
TBN analysis is one of the most commonly used means for characterising a lubricant. In this paper, a number of cautionary observations from bench, engine, and field testing will be discussed, and the paper will

1. demonstrate the limitations of the approach that uses TBN only;
2. show the importance of several related methods for the analysis of new and used oils; and
3. underline that a thorough characterisation of a used engine lubricant requires a complement of analyses consisting of TBN, TAN, wear metals content, oxidation, soot content, and viscosity.

FIELD TEST OBSERVATIONS: Field test description

In an ongoing field test, a number of different detergent technologies are being compared at equal dosage in the same baseline formulation. The test fleet uses Cummins N-14 engines to power 65-ton GVW units, which run fully loaded. The test oils are rotated through the units, which are run until the oil level drops to 2 gallon below the maximum mark; no oil is added during the drain period. This approach allows the units to accumulate 20,000–25,000 miles without disturbing the oil ageing process. During the drain period, oil samples are taken and analysed for, among other parameters, TBN, TAN, and wear metals.

Figure 2 Field test used oil lead content

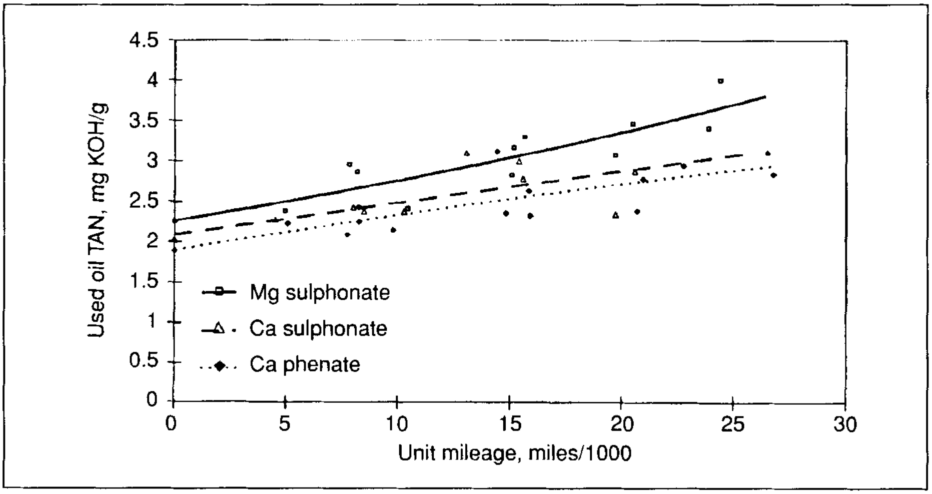


Test results and discussion

Results of the TBN analyses are shown in **Figure 1**. These TBNs were measured according to D-4739, as there was little discrimination between used oils with D-2896. Three detergent technologies are compared in this evaluation. TBN depletion rates for a calcium sulphonate and a calcium phenate were found to be similar. A magnesium sulphonate, however, behaved differently; its TBN depletion rate was slower. These findings support work done by other researchers in the GM 6.5L engine test.[9] Based on TBN observation alone, one might conclude that the magnesium sulphonate oil has better ESI capabilities. However, the wear metals analyses show a different picture. The used oil lead content, shown in **Figure 2**, indicates that the lead corrosion rate is highest for the magnesium sulphonate-containing oil, intermediate for the calcium sulphonate, and lowest for the calcium phenate.

One explanation for the difference in TBN retention is that magnesium sulphonate (or sulphonates in general), possibly being a weaker base in a lubricating oil environment, may not neutralise all acids, thus reserving base which shows up as higher TBN. Other researchers have also reported differences in acid neutralisation capability for various detergent types.[10] If this were true, one would expect that the use of magnesium sulphonate alone might result in a higher level of corrosive bearing wear. Also, a higher TAN level for the magnesium sulphonate oil would be expected. The TAN (D-664) analyses on the used oil samples, **Figure 3** (overleaf), support the above hypothesis. TAN levels for the sulphonate detergents increase more rapidly throughout the drain period.

Figure 3 Field test used oil TAN (D-664)



Summary of field testing

It can be concluded that a judgement about the quality of a lubricant, and especially on its capabilities as an extended service interval oil, cannot be based solely on TBN measurement. Several other used oil characteristics need to be taken into account. In the next sections, the results of some bench test work, triggered by the field test observations, will be discussed.

BENCH TEST OBSERVATIONS: Hypothesis

It was suggested above that differences in the used oil lead content observed in a field test could be correlated with differences in TAN increase. At the time of writing, there are only speculations as to the reason for these differences in TAN. One possibility, as suggested above, is that magnesium sulphonate does not neutralise weak acids as fully as the calcium detergents, therefore reserving base which appears as a higher TBN. A further, related scenario is that base oil, in the presence of magnesium sulphonate alone, oxidises more rapidly (see below) than in the presence of calcium detergents. Oxidation of base oil generates 'weak' acids that would show up as TAN if not neutralised. In addition, there is the added possibility that some acids afforded by combustion blow-by are similarly weak and not neutralised by magnesium sulphonate.

Fresh samples of the oils that were used in the field test were evaluated in several bench tests to appraise this hypothesis. We chose one acid neutralisation test and three oxidation tests for this purpose.

Figure 4 Acid neutralisation test TAN increase (D-664)

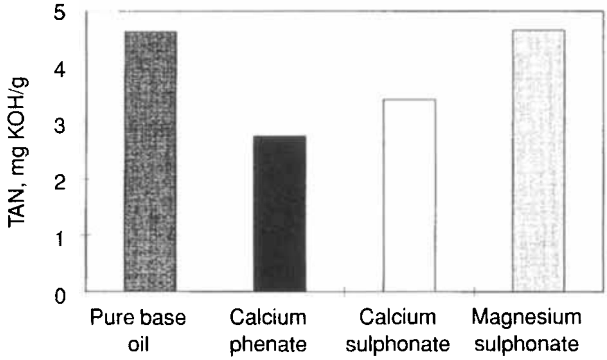


Figure 5 Modified IP-48 TBN/TAN (D-4739/D-664)

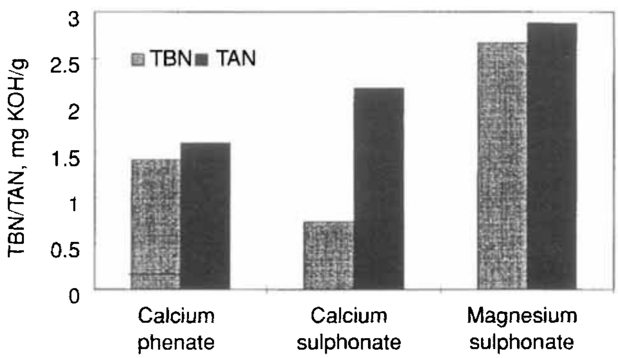
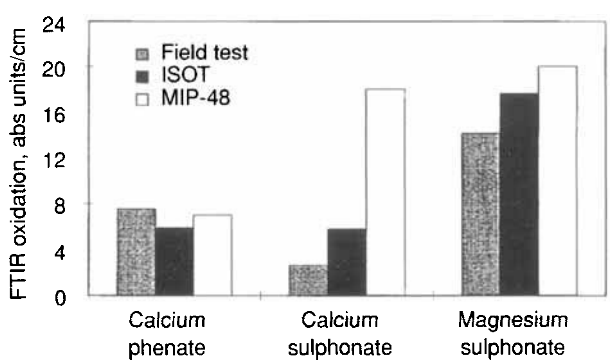


Figure 6 Field test versus ISOT and MIP-48 oxidation



Acid neutralisation test

The same three field test formulations, identical in every way except for the detergent, were treated with 5 TAN of oleic acid, a weak organic acid. In addition, the same amount of acid was added to base oil as a reference case. As shown in **Figure 4**, the magnesium sulphonate did not reduce TAN at all over the base oil case. The greatest reduction in TAN was observed with calcium phenate, but calcium sulphonate also afforded a meaningful reduction in TAN by D-664. This is the same ranking as the TAN increase observed in the field test.

High-temperature oxidation bench test

A high-temperature oxidation bench test, the Modified IP-48, was run on the three field test oils to examine the impact of oxidation on base depletion, e.g., in the hotter regions of the engine. This test was run for 4 h at 200°C in the presence of air but no metal catalyst.

Figure 5 shows the TBN and TAN of these three oils at the end-of-test (EOT). Severe TBN depletion occurred with all three oils, but, like the field test, magnesium sulphonate showed the highest EOT TBN. It also showed the highest EOT TAN, demonstrating again that magnesium sulphonate does not neutralise acidic oxidation products as effectively as calcium phenate.

The relative degree of oxidation of the test oils in the Modified MIP-48 bench test is shown in **Figure 6**. The relative ranking of the calcium phenate and magnesium sulphonate is consistent with the field test data, but the calcium sulphonate, which behaved as well as the calcium phenate in the field, did not look very good in the high-temperature MIP-48 test.

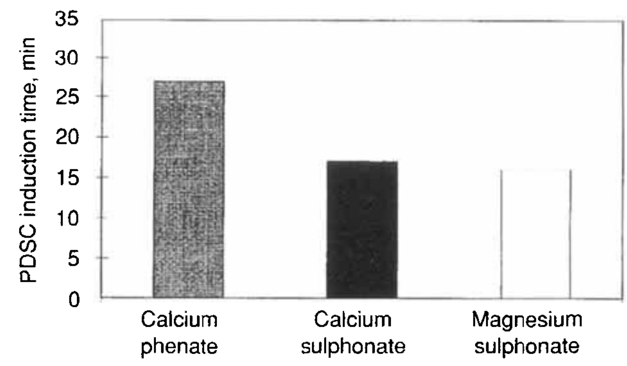
Oxidation bench tests

Oxidation was also studied in the Indiana Stirring Oxidation Test (ISOT). The results were measured using Fourier Transform Infra-Red (FTIR). The FTIR results of both bench tests and the field test are shown in **Figure 6**. Although the ISOT reaction temperature (170°C) is higher than the field sump temperature (90–110°C), the oxidation levels are of the same order of magnitude, suggesting that the severity of the ISOT is comparable to that of the field.

PDSC test

To supplement the conclusions drawn from the Modified IP-48 and the ISOT bench test, the same field tested oils were evaluated in a Pressurised Differential

Figure 7 PDSC comparison of detergents



Scanning Calorimetry (PDSC) bench test. An isothermal test mode (200°C) was used, with the oxygen pressure set at 100 psi. The induction times are shown in **Figure 7**. The induction time for the calcium phenate is long, indicating good oxidative stability. The magnesium sulphonate gave a short induction time, which indicates poor oxidation stability. This is in line with previous observations from the ISOT, and supports the idea that the magnesium either promotes oxidation, or is not an effective inhibitor. Where the ISOT and the PDSC differ is in the relative ranking of the calcium sulphonate. This might be as a result of the difference in temperature at which the oils are evaluated in the two tests.

Summary of bench testing

Although the correlation between field and bench test is not perfect, both field and bench test data indicate that the magnesium sulphonate-containing oil gave higher oxidation levels, and the calcium phenate-containing oil gave lower oxidation levels. The performance of the calcium sulphonate-containing oil seems to depend on the operating temperature of the test. In the field test (90–110°C) and the ISOT (170°C), the calcium sulphonate performs as well as the calcium phenate. However, in the Modified MIP-48 (200°C), and the PDSC (200°C), the oxidative stability of the calcium sulphonate is not adequate, and its performance is similar to that of the magnesium sulphonate. In general, the bench test data support the hypothesis that differences exist between detergents in their acid neutralisation and antioxidant capacities.

Table 2 Mack T-9 test oils

Test oil description	*TBN (D-4739)*	*Detergent type*
A. Internal reference	6.08	All Ca
B. Low TBN – all Mg	6.97	All Mg
C. Low TBN – Ca/Mg	6.09	Ca/Mg (3:1)
D. High TBN – Ca/Mg	9.83	Ca/Mg (6:1)

ENGINE TESTING

We compared the field test results with results from several engine tests. Test results from one American and one European engine test will be discussed in the following sections.

Mack T-9

The most interesting data came from the (American) Mack T-9 test, which was designed to be a cylinder-liner and piston-ring wear test. The Mack T-9, more than any other PC-7 engine test, has the character of an extended service interval test. During the test's 500 h, most of the TBN is depleted. TAN increases, in some cases causing a corresponding increase in lead, most likely from bearing corrosion. Four test oils, listed in **Table 2**, were compared. With respect to the cylinder-liner wear, there was no discrimination, but oils B and D did give 35 and 20% lower piston-ring weight loss, respectively, than did A and C, which were about equal.

The TBN (D-4739) curves of the intermediate oil samples, shown in **Figure 8** (overleaf), indicate once again that the calcium-containing oils have a higher rate of TBN depletion than does the all-magnesium oil. The end-of-test TBN level of the all-calcium internal reference oil dropped to near zero; the low TBN calcium/magnesium oil dropped to 1.2, whereas the all-magnesium oil dropped only to a level of 2.2. Clearly, the TBN depletion rates of the calcium-containing oils raised some concern over what might have happened to the bearings. Indeed, the used-oil lead-content curves, shown in **Figure 9** (overleaf), demonstrate that the internal reference oil did give the highest lead content; the curve starts increasing after only 200 h. The second worst, however, was not a calcium-containing oil, but the all-magnesium oil. In conclusion, among oils of the same general formulation (i.e., excluding the reference oil), the ranking of oils is again reversed, going from the TBN plot to the used oil lead comparison.

Figure 8 Mack T-9 used oil TBN (D-4739)

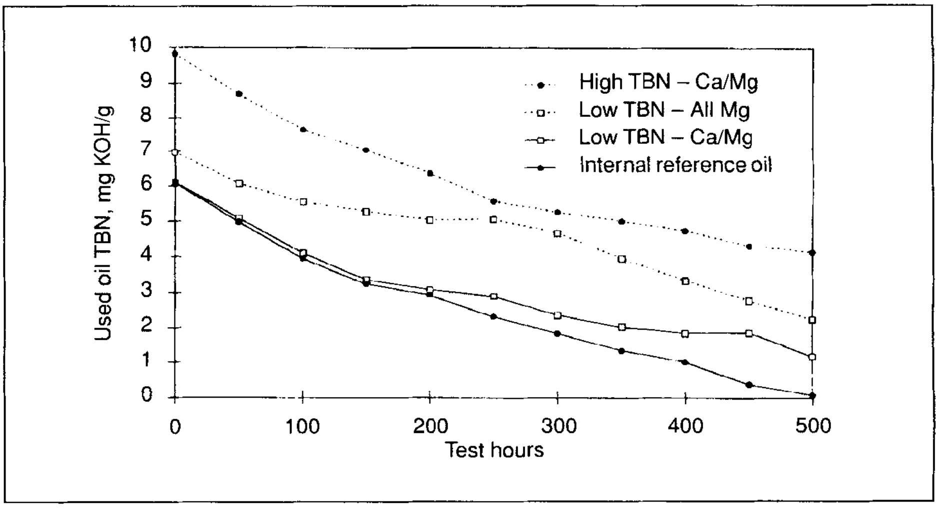


Figure 9 Mack T-9 used oil lead content

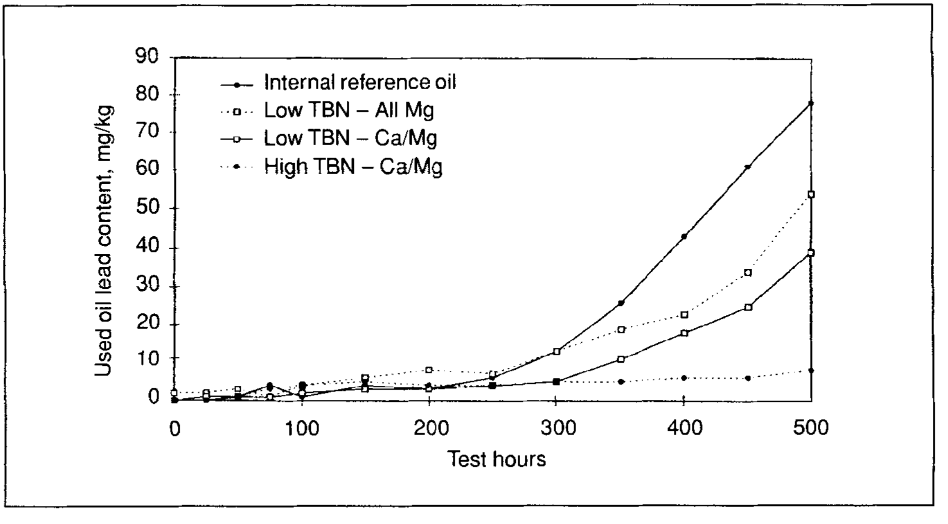
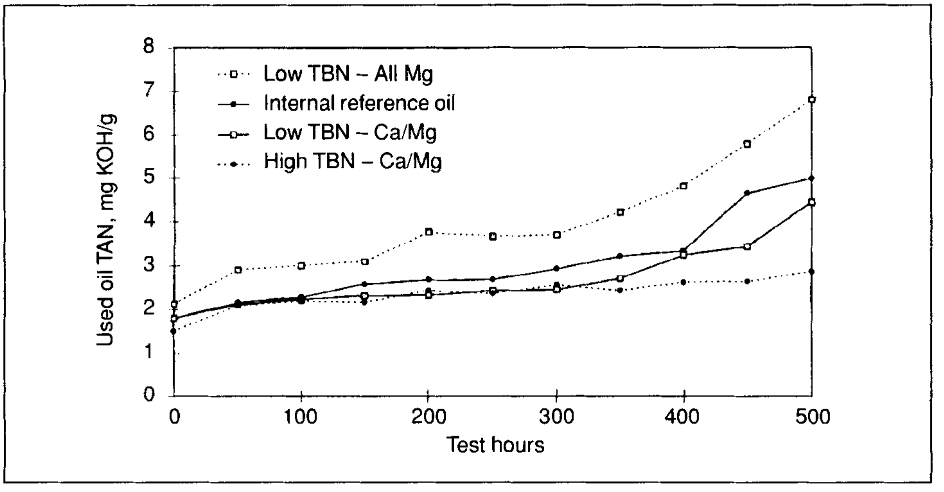


Figure 10 Mack T-9 used oil TAN (D-664)



The TAN increase curves were plotted (**Figure 10**) in an attempt to understand what caused the lead level to increase for the all-magnesium oil, even though its end-of-test TBN level stayed well above 2. As can be seen, the initial TAN for the all-magnesium oil was slightly high, but then increased significantly compared to all other oils. Again, this suggests that acidic species in the oil are not being completely neutralised by the magnesium-based detergent.

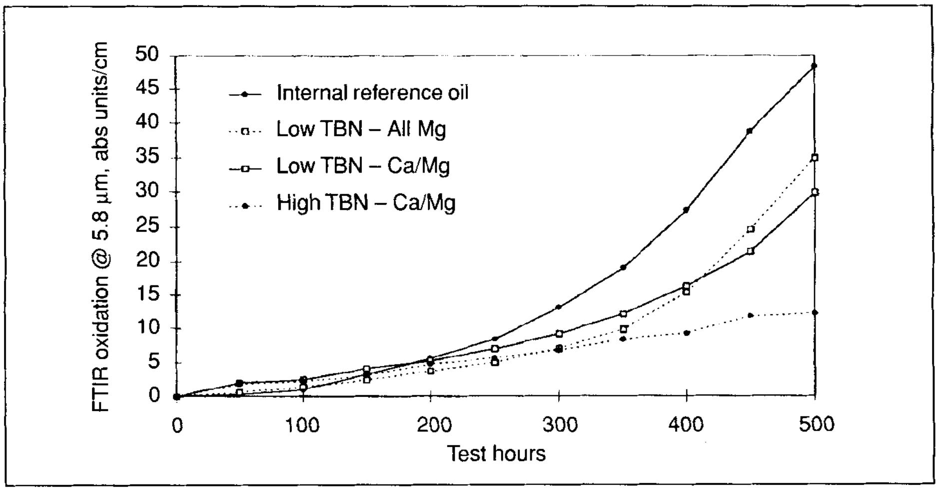
Next, the oxidation levels were compared, similar to what was done in the bench test section. These oxidation levels, shown in **Figure 11** (overleaf), appear to relate very well to the observed used oil lead contents, lending support to the idea that the oxidation of the base oil created the acids that resulted in both the TAN increase and the corrosion of the lead bearing material.

An interesting observation is that the absolute level of TAN at which the lead content starts to increase appears to be different for the different detergent chemistries. Based on this observation, it is not recommended to set an absolute TAN level as a pass/fail criterion for lubricants, just as no single condemning limit is appropriate for TBN.

OM 364A

One of the key tests in the European engine oil specifications is the Mercedes-Benz OM 364A. This test, designed to be a bore polish and piston deposits test, has a duration of 300 h. The TBN is measured for oil samples taken every 50 h. In this engine test, three oils with the same detergent level, but different ratios of calcium phenate/calcium sulphonate, were compared. Data presented

Figure 11 Mack T-9 end-of-test oxidation



previously suggest that a sulphonate has better TBN retention than a phenate. The TBN drop during the three engine tests, measured using the ASTM D-664 method, is plotted in **Figure 12**. The data show that the TBN drop increases when there is more calcium phenate in the detergent mix. This would support the earlier conclusion that calcium phenates are more effective in neutralising acids than are sulphonates, and as a result, lose their TBN at a faster rate.

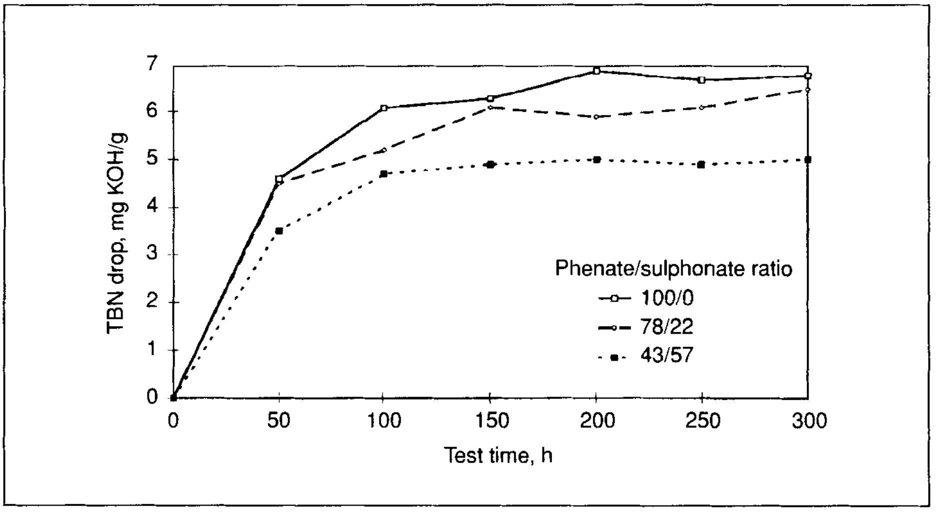
Summary of engine testing

From piston-ring weight loss and TBN depletion, one would conclude that a 'magnesium-only' formulation and a high TBN oil (**Table 2**, B and D, respectively) were the best performers in the Mack T-9 test. However, once used oil lead content and TAN increase are taken into account, a slightly different conclusion is drawn. The magnesium-based oil, although good in preventing ring weight loss, gave higher levels of bearing corrosion. Data from a European engine test, the OM 364A, support the hypothesis that calcium phenate is more effective in neutralising acids, and therefore loses its TBN at a faster rate.

CONCLUSIONS

It is not possible properly to characterise a lubricant and judge its suitability for extended service intervals on the basis of TBN retention alone. The ability to control TAN and oxidation need also to be evaluated because of the potential impact on bearing corrosion.

Figure 12 OM 364A TBN drop (D-664)



Each of the evaluated detergent types has strengths and weaknesses. The work presented in this paper suggests that some detergents with good TBN retention are less effective in neutralising acids and may cause lubricants to be less oxidatively stable.

Formulation of a high-performance diesel engine oil should be possible using each of the detergent options evaluated in this paper, provided that the other components in the additive package are carefully selected and balanced for optimised performance.

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