Evaluation of a Field Test Method for Total Base Number Determination in Lube Oils

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Total base number in diesel lubricating oils is a critical parameter for determining the effectiveness of the oil in protecting the engine from acids formed during combustion. Existing test methods require trained personnel and well equipped laboratories, and these methods utilize solvents and chemicals such as chloroform, toluene, and perchloric acid that are either toxic or environmentally regulated. These reagents must be made fresh at intervals of days or weeks and used reagents present a difficult and expensive disposal problem. These multiple barriers to performing TBN testing often lead to a frequency of testing which is much less than most maintenance schedules call for. At Dexsil we have recently developed a test kit for determining TBN that eliminates the use of hazardous constituents, is stable for at least a year, tests for actual TBN and is completely portable so that it can be used on ships or other remote locations that do not have full laboratory services available.

The new test kit combines parts of ASTM methods D-2896 and D-4739 as well as some new procedures to provide a test which eliminates the use of dangerous chemicals, is completely pre-packaged, extends the shelf life to at least a year, and provides results that are comparable to the established methods. Each test kit consists of:

1) A sampling syringe for obtaining an accurate amount of the sample to be analyzed.

2) One pliable polyethylene test tube containing two breakable glass ampules. one ampule contains a diluent, isooctane, and an emulsion breaker while the other contains a specific amount of hydrochloric acid in isopropyl alcohol.

3) A second pliable test tube that contains seven ml of an aqueous extraction solution and a glass ampule containing a pH indicator.

4) A micro-burette that contains a solution of sodium hydroxide of known concentration and which is imprinted with a scale of TBN numbers ranging from 0 to 20.

5) A plastic pipette.

6) A plastic filter containing a plug of polypropylene wool.

TESTING PROCEDURE

After shaking the sample well to assure homogeneity, the sampling syringe is used to transfer a fixed amount of the sample to the first of the polyethylene test tubes (tube #1). The ampule containing the isooctane diluent is then broken by squeezing the sides of the pliable tube and the tube is shaken to mix the sample with the diluent. The second ampule which contains the alcoholic HC1 is broken next and the resulting mixture is shaken well to assure that the acid reacts with the entire sample. Next, the aqueous extraction solution is poured from tube 2 into tube 1. The cap is replaced on tube 1 and the mixture containing the sample, solvent, HC1, and aqueous extraction solution is mixed vigorously by shaking the tube. The tube is turned upside-down on its cap and the aqueous phase is allowed to separate from the hydrocarbons. The aqueous extract is then decanted through the polyethylene filter into tube 2. Tube 2 is filled up to a 5 ml line engraved on the side of the tube and the micro-burette is screwed into the test tube. The pH indicator ampule in the tube is broken introducing the indicator into the aqueous solution. The titrant in the micro-burette is then added dropwise to the solution. As soon as the solution changes color from magenta to yellow, the titration is stopped and the TBN number is read off the side of the burette at the point where the burette plunger stopped.

ASTM method D-2896 utilizes a back titration technique on difficult to analyze oils. This back titration provides a much more reliable, more easily detected end point than does the forward titration for either 2896 or 4739. D-4739, however, has the advantage of using hydrochloric acid instead of perchloric acid and therefore provides a more accurate reading of useful residual base. The test kit uses a back titration and hydrochloric acid to provide both an easy to detect, precise end point and an accurate, conservative reading of actual residual base. The major difference between the test kit and the ASTM methods is that with the kit method, the final titration is performed in the aqueous phase. This means that the pH indicator color change is almost instantaneous and also allows oils of any color to be run by this calorimetric technique. In the past, dark oils have prevented calorimetric tests from being widely used because the titration was always run in the organic phase. An aqueous titration results in a solvent system that does not require chlorobenzene or chloroform because an organic phase potentiometric reading is not necessary.

Part of the reason for the poor reproducibility of method D-4739 (21%) is that the operator is required to prepare and standardize a number of reagents, all of which have an effect on the final outcome. To run one sample by this method, the operator must standardize the acid and the non-aqueous buffers, verify the output and performance of the electrode, and run a blank on the titration solvent. Then the operator must interpret an inflection point that is quite often barely discernible and can be effected by the quality of the electrode and solvents being used. By using pre-packaged standardized reagents, the test kit method eliminates most of the sources of this error and can therefore provide more consistent results from test to test.

Specific acids used in testing for TBN, such as perchloric and hydrochloric can provide significantly different results when testing for residual base. In short, stronger acids detect the weaker bases which may not be detected by a weaker acid. The interpretation of these weaker bases as contributing to TBN may provide an unrealistic result as the weaker bases, such as calcium nitrate, may not serve to protect the engine at all. The chart below is an extension of one provided by J.R. Barnes in his paper entitled "Importance of Railroad Diesel Engine Oil TBN and its Relevance to LMOA Generation 5 for Salicylate Oils" which was published in the September 1991 edition of Lubrication Engineering.

TBN Methods: What Do They Measure?[1]

	D2896	D664	D4739	Test kit
ACID:	Perchloric in Acetic Acid	Alcoholic HCl	Alcoholic HCl	Alcoholic HCl
SOLVENT:	Chlorobenzene/ Acetic Acid	Hydrocarbons	Toluene/IPA/H20	Toluene/IPA/ chloroform
MEASURES:	Strong bases Weak bases	Strong bases Some weak bases	Strong bases Some weak bases	Strong bases Some weak bases
EXAMPLES FRESH OIL:	All detergent base All dispersant (amine) base	All detergent base Most dispersant base	All detergent base Most dispersant base	All detergent base Most dispersant base
EXAMPLES USED OIL:	Most Ca, Mg salts of degradation products	Very few Ca, Mg salts of degradation products	Some Ca, Mg salts of degradation products	Some Ca, Mg salts of degradation products

EVALUATION

To evaluate the test kit method, it was compared directly to ASTM methods D-2896 and D-4739. Both new and used oils from diesel engines were run in triplicate on each method. TBN values varied from 0 to 17. Oils with TBN values greater than 20 were not run because these are out of the pre-set range of the test kit method (these can be run by the test kit but the sample size must be reduced.) The averages of the three runs on each oil with each method are given in the table below.

Comparison of New and Used Oils by Three TBN Methods
(TBN average of 3 runs each sample for each method)

Sample	Oil Type	D4739	D2896	Test Kit
A	New	1.31	0.90	0.85
B	New	7.05	7.87	7.53
C	New	12.45	14.78	13.62
D	New	11.20	12.44	11.58
E	Used	3.79	6.79	5.42
F	Used	9.61	13.55	11.36
G	Used	4.64	6.37	5.26
H	Used	13.05	16.76	15.50

The table illustrates that, in most instances, the older an oil is, the greater will be the difference between the TBN values determined by a method utilizing hydrochloric acid compared to a method using perchloric acid. This difference is due to the various species contributing to total base that are present in the oil, not just the age of the oil itself.

The following samples were obtained from diesel locomotives and had been in service for an extended period. Notice the spread of about four TBN units between methods 4739 (hydrochloric acid) and 2896 (perchloric acid). The test kit results fall somewhere in between the two, generally closer to 4739 than 2896.

Used Diesel Railroad Oils
(TBN average of 3 runs each sample, each method)

Sample	D4739	D2896	Test Kit
8503	4.21	8.22	6.0
8512	4.03	8.48	5.7
8513	2.54	6.87	4.9
8516	2.54	6.89	4.3
8523	5.56	6.89	4.3
8540	7.25	11.12	9.5
8542	6.89	10.70	8.5

When compared to ASTM methods D-4739(664) and D-2896, the relative advantages to the test kit method are:

It does not require instrumentation or a trained analyst and can therefore be run as often as is desired.

The test is entirely portable and can be performed on site in six minutes allowing tests to be run more frequently at lower cost.

It contains no hazardous solvents, so it reduces health risks and disposal costs,and it facilitates compliance with environmental regulations.

No calibration or standardization is required - prepackaged reagents assure consistency from test to test. No additional reagents or containers are necessary.

A back titration is performed in the aqueous phase which permits a definitive calorimetric end point.

A long shelf life means that test kits can be stored and used whenever they are needed.

The test kit measures actual total base number - it is not looking for only a specific additive, but actually measures all constituents that are contributing to total base reserves.

There are some disadvantages to the test kit that must be considered when choosing an analytical method.

The test kit uses a volumetric sampler to measure the amount of oil that is introduced into the test. This means that oils which have a density significantly different from 0 9 g/ml will result in answers which are biased high for higher density oils and low for lower density oils. This can be avoided if a balance is available to weigh the sample. If all that is needed is to know the difference in TBN between a new oil sample and a used one (change in TBN), then density is not even a factor, and the kit will give accurate results on any fluid.

The range of the kit is limited from 0 to 20 TBN units. Higher TBN oils can be run, but these require that a smaller sample size be used or that the oil be cut with a 0 TBN diluent.

There is no hard copy record of the TBN result such as is provided by an automatic titrator equipped with a printer. The operator must manually record all results.

Conclusion

By employing relatively simple technology, a TBN test kit has been developed that circumvents many of the problems associated with more traditional testing methods. Its portability and low cost make it ideal for any location that does not have trained technicians or automated TBN analysis available. It works on every brand and type of diesel lubricating oil that has been tried and gives accurate results with any additive package. It is easy to use, requires no calibration or standardization, and a sample can be run in six minutes. It eliminates the use of chlorinated solvents and has a long shelf life that makes it suitable for use on ships or other remote facilities that may not have full time access to a laboratory. Even well equipped laboratories find that the test kit method is faster, easier, and more accurate than even automated titrations.

This technology has recently been adapted to testing for total acid number (TAN) and a TAN test kit is also available covering a range of 0 to 2 TAN units with resolution of 0.1 TAN. It has been shown to correspond well with ASTM method D-664.

[1]Table (except for test kit data) from J.R. Barnes, "Importance of Railroad Diesel Engine Oil TBN and its Relevance to LMOA Generation 5 for Salicylate Oils" Lubrication_Engineering, Vol. 47, 9, 713-722.