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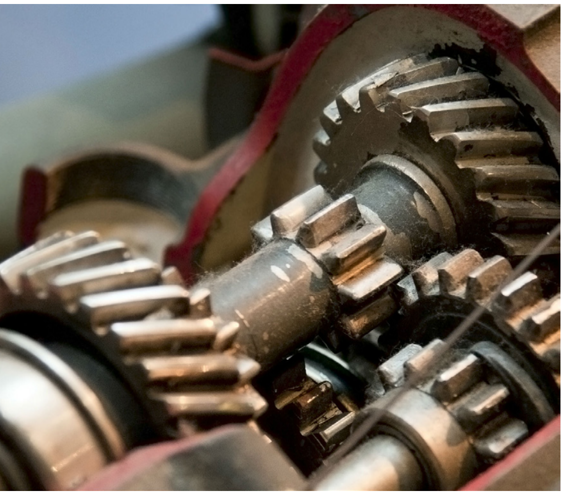
WHITE PAPER

Guide to Measuring TAN and TBN in Oil



Background

TOTAL ACID NUMBER

A high concentration of acidic compounds in a lubricant can lead to corrosion of machine parts and clogged oil filters due to the formation of varnish and sludge. When a lubricant breaks down, acidic by-products will be formed from the chemical decomposition of the base stock and additives in the presence of air and heat. Total Acid Number (TAN) is a measure of acid concentration present in a lubricant. The acid concentration of a lubricant depends on the presence of additive package, acidic contamination, and oxidation by-products. Occasionally, the depletion of an additive package may cause an initial decrease in TAN of fresh oil. However, the accumulation of oxidation by-products and acidic contaminants in an oil over time will always lead to an increase in TAN. This test is most meaningful in industrial machinery applications although sometimes it is recommended in engine applications along with Total Base Number (TBN).

TOTAL BASE NUMBER

Total Base Number (TBN) is a measure of alkaline concentration present in a lubricant. Engine oils are formulated with alkaline additives in order to combat the build-up of acids in a lubricant as it breaks down. The TBN level in a lubricant is targeted for its application. Gasoline engine oils are typically formulated with starting TBN around 5-10 mg KOH/g whereas diesel engine oils tend to be higher (15-30 mg KOH/g) due to the more severe operating conditions. Specialized applications, such as marine engines, may require >30 mg KOH/g. As the oil remains in service, this BN additive is depleted. Once the alkaline additives are depleted beyond a certain limit the lubricant no longer performs its function, and the engine is at risk of corrosion, sludge, and varnish. At this point it is necessary to top-off or change the oil.

Techniques for measuring TAN and TBN

THE FLUIDSCAN – INFRARED SPECTROSCOPY

Infrared spectroscopy uses a radiative source, a detector, and a computer to study the interaction of matter and light. The build-up of acids in a lubricant caused by oil degradation and oxidation can be detected by changes in the infrared spectrum. Oxidation and nitration products appear as peaks in the IR spectrum between 1600-1800 cm^{-1}. Because of the mixture of acids generated during the breakdown of a lubricant, there is not a single peak in the spectrum which can be correlated to TAN.

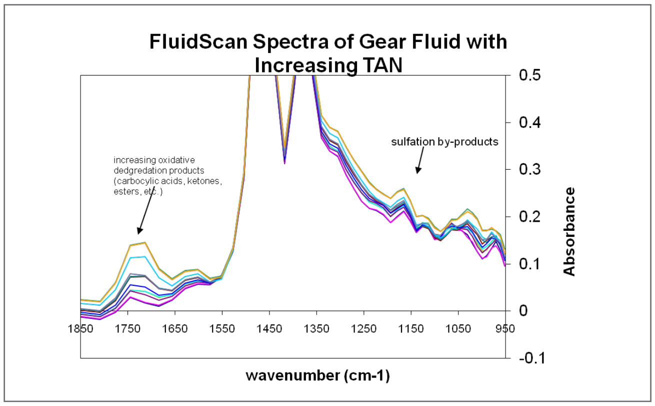
Changes in TBN are observed in the IR spectra as decreases in absorbance peaks related to the basic additives that are present in the engine oils, as well as changes to standard degradation peaks. The BN additives most typically used are calcium or magnesium sulphonates, phenates and salicylates. The specific BN additive package of a lubricant may contain any mixture of these, but they all have peaks in the 1000 and 1900 cm^{-1} region of the infrared spectrum.

PROS:

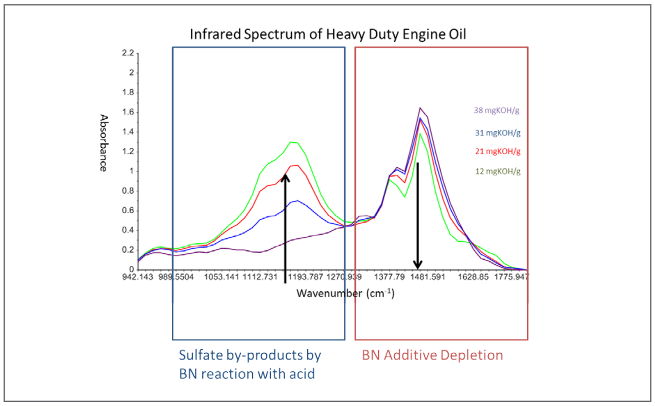
- Can be done in the field
- No solvents
- Fast results
- Very low cost per sample
- Any operator can get good results
- Precalibrated for over 90% of oils
- Only requires 2 drops of oil

CONS:

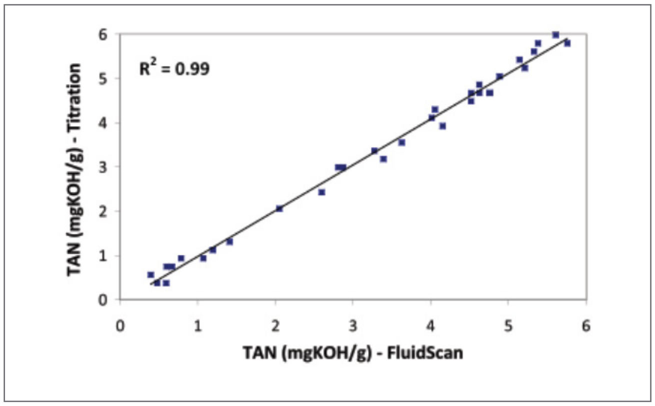
- Oil must fit into a pre-calibrated family
- Very sooty samples (>3%) cannot be measured



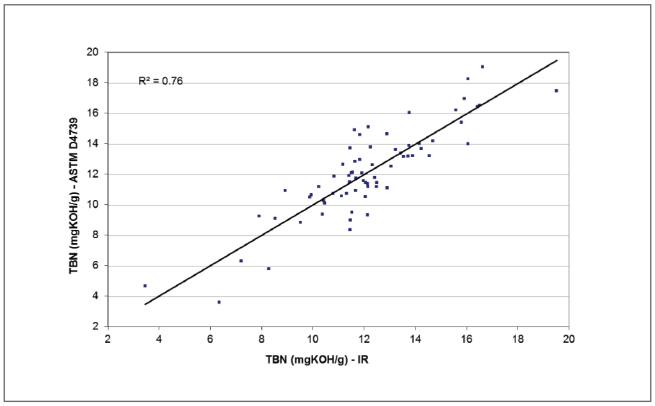
The FluidScan spectra show an increase in the oxidation and sulfation byproducts with increasing TAN for gear oils.



The FluidScan spectra show depletion of the BN additive and an increase in the sulfate by-products with decreasing TBN for heavy duty engine oils.



Comparison of FluidScan TAN measurements with Titration TAN measurements shows excellent correlation.



Comparison of FluidScan TBN measurements with Titration TBN measurements shows excellent correlation.

The FluidScan is a portable handheld spectrometer used to measure oil condition and chemistry. On the FluidScan, hundreds of new and used lubricants of widely varying type and level of degradation have been gathered into a sample library. Their infrared spectrum was recorded along with their TAN and/or TBN value using a standard ASTM titration technique (D4739 for TBN and D664 for TAN). Next, multivariate data analysis techniques are used to relate the known TAN or TBN to the infrared spectrum. The end-result is quantitative readings of TAN and TBN using infrared spectroscopy.

POTENTIOMETRIC TITRATION

Metrohm Fully Automatic TAN and TBN Titration System

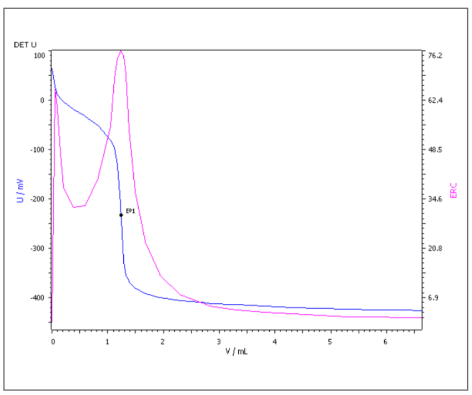
The most widely accepted techniques for measuring TAN or TBN are the potentiometric titration methods. Potentiometric titration is very accurate and can measure many different sample types without regard to color or the presence of contaminants. It does involve solvents and careful technique and is best performed by a well-trained chemist. The cost of equipment can be reasonable, but the most user-friendly and easy to maintain systems tend to be fairly expensive. The need to purchase solvents and to dispose of waste can also make it more costly compared to other methods.

PROS:
- The industry standard
- Accurate
- Tolerant of difficult samples (color, contaminants)

CONS:
- Requires expensive equipment
- Requires solvents
- Requires a skilled operator
- Can require up to 4 g of sample.
- Must be performed in a lab
- Relatively high cost per test

TAN

For TAN, the commonly accepted test method is ASTM D664 which involves dissolving the sample in toluene and isopropanol with a bit of water and titrating that solution with alcoholic potassium hydroxide. A glass electrode and reference electrode are placed in the solution and connected to a voltmeter/potentiometer. The titration endpoint is reached when a well-defined inflection point is found or the meter reading in millivolts corresponds to a buffer solution.



Potentiometric determination of TAN (blue = titration curve, pink = ERC)

TBN

ASTM D2896 is the accepted method for TBN for new and used oils. The sample is dissolved in chlorobenzene and glacial acetic acid and titrated with perchloric acid in glacial acetic acid. The endpoint is determined by potentiometric titration with a glass indicating electrode inside the solution and a reference electrode connected with the sample solution by a salt bridge.

Another method ASTM D4739 is also accepted for measuring TBN in used oils. The titrant in D4739 is a milder acid than in D2896, hydrochloric vs perchloric, which can result in lower TBN results if there are weak bases present in the sample that the hydrochloric acid will not neutralize. The BN additive is a relatively strong base, so the inclusion of weaker bases in the measurement is not important when looking at the lifetime left in the lubricant.

COLORIMETRIC TITRATION

Colorimetric titration methods can be used as long as the oil is not dark. For these methods, the endpoint is detected by a visible color change through the use of an indicator which reacts to a change in pH. For TBN measurement, it can be challenging due to the dark nature of crankcase oils, especially when soot may be present.

In ASTM D974, a sample is dissolved in toluene, p-naptholbenzene, and isopropyl alcohol containing water. Then the solution is treated with KOH or HCl until a color change occurs to indicate the endpoint. The amount of KOH or HCl added to reach the endpoint determines the TAN or TBN. ASTM D3339 is a similar method to ASTM D974, except that it is designed for a smaller sample size (2 g vs 20 g).

PROS:

- Accurate
- Does not require expensive electrodes

CONS:

- Cannot be used in dark or contaminated oils
- Requires solvents
- Requires a skilled operator
- Must be performed in the lab
- Relatively high cost per test

FIELD TEST KITS

Test kits are available as a convenient first line test for TAN or TBN. The kits contain premeasured reagents and the result is measured as a color change by eye. In some cases the kits contain a predesignated amount of KOH or HCl titrant so that they provide a qualitative pass or fail response. In other kits, titrant syringes will come marked with graduated increments already converted to TBN or TAN units. The user starts with a known volume of sample in a test tube, and then adds aliquots of KOH/HCl reagent and observe for color change. When the solution changes color, they check the number on the syringe next to the plunger and that is their TBN or TAN.

PROS:

- Can be done in the field
- Premeasured materials
- Fast results

CONS:

- Cannot be used in dark or contaminated oils
- Requires solvents
- Requires a skilled operator
- Moderate cost per test

Summary

Monitoring TAN and TBN is an important test for measuring lubricant condition. There are several methods available ranging from expensive laboratory methods to quick field tests. In a laboratory setting, methods are chosen based on the highest accuracy and repeatability that can be achieved with a decent throughput. Out in the field, it is most important to get a trustworthy result quickly enough that preventative or corrective maintenance action can be taken before major equipment failure. The best method to use depends on the application need.

References:

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3. "Overview of FluidScan Handheld Infrared Oil Analyzer," White Paper, spectrosci.com
4. "Determination of the total acid number in petroleum products," Metrohm, Application Bulletin AB-404_1_EN

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