WEARCHECK® The Leaders in Oil & Fuel Analysis

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ACIDS AND BASES, THE "SPY VS. SPY" OF THE LUBRICATION GAME

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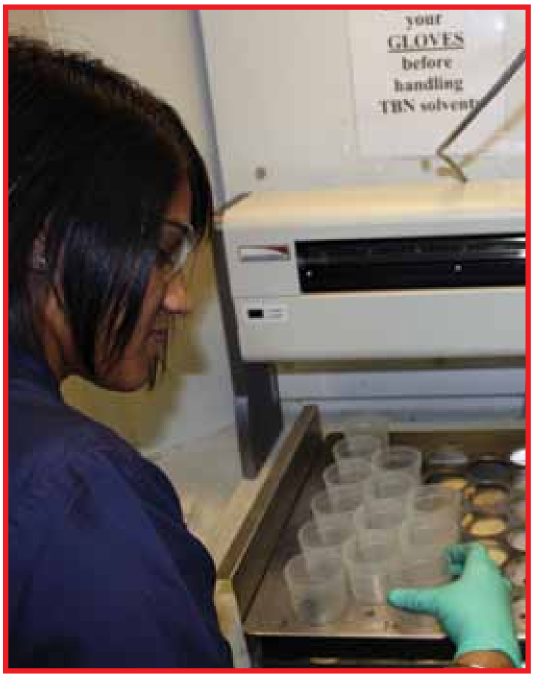

A Total Base Number (TBN) machine in operation in a WearCheck laboratory

MONITORING OIL DEGRADATION

Introduction

In many ways, the properties of acids and bases are embodied by the classic cartoon strip, "Spy vs. Spy", which was first published in Mad Magazine in 1961. This Technical Bulletin will help you understand what acids and bases are all about, why they need to be assessed, methods of assessment and what these parameters have to do with industrial and mobile equipment.

If the amount of acid or base present in your oil is unfavourable, then the oil – or more critically, the machine – can be damaged. It is thus essential to understand these terms with reference to oil analysis in order to get the best life from your assets by reducing downtime and minimising costly repairs.

What are acids and bases?

Acids are typically corrosive substances which have several complex definitions. They typically are a source of hydrogen ions. Think of acids as Spy 1. Bases are the species that acids preferentially react with, think of these as Spy 2 in terms of the analogy that will be used in this Technical Bulletin. Spy 1 and Spy 2 actively seek one another out to destroy each other. In the story of acids and bases, they destroy each other by forming less reactive salts. Again, definitions of bases are numerous and complex. Bases are sometimes referred to as alkalis, such as in alkaline batteries. Alkalis are water-soluble bases comprising, in part, metals from the first two columns in the periodic table. In oils, bases would be the correct term for alkalis as the compounds are oil-soluble rather than water-soluble. In aqueous systems, which is where pH is defined, acids have a low pH (less than 7) while bases have a high pH (greater than 7). Neutral substances have a pH of 7.

Acid – TAN

Acid in oil is generally referred to as TAN or Total Acid Number. In recent times, there has been a move in some circles to drop the "Total" and simply call the test Acid Number (AN). Either way, this is a measure of the concentration of acids in the oil. Some acids are classified as 'strong', like mineral acids such as hydrochloric or sulphuric acid. Some acids are much milder, including many organic acids. A common example of an organic acid is acetic acid, which is the key component in vinegar. TAN does not look at the strength factor of the acid; rather, it describes the number of acid molecules present. Think of it as the size rather the potency of Spy 1's arsenal. The strength of the acid (strong vs. weak) would be akin to the potency of Spy 1's arsenal. TAN is measured in units of the number of milligrams of potassium hydroxide required to neutralise a gram of oil (mg KOH/g).

In an engine, there will be both mineral acids, which are present from the combustion process, as well as organic acids as a result of thermal oxidation of the oil. During combustion, which is a high pressure, high temperature event, the sulphur that is present in the diesel (or petrol) will react with oxygen in the air in the cylinder, instantly forming SO_2 and SO_3 gases. Combustion also releases another by-product: water. The SO_2 and SO_3 dissolve into the water, forming sulphurous and sulphuric acids. Nitrogen and oxygen in the air, which normally do not react with each other, also come into play courtesy of the combustion conditions, forming various nitrous oxides. These in turn also dissolve in the water, resulting in nitrous and nitric acids. Nitric and sulphuric acids are the big guns in Spy 1's arsenal.

In most other components, the acid present is likely to be predominantly organic. Here, with the help of elevated temperatures and catalysts such as iron and copper (two common wear metals), oxygen is included into the hydrocarbon back bone of the oil. This results in the formation of carboxylic acids. These further destabilise the oil and result in thickening of the oil and decreasing its effectiveness in performing lubrication functions, which, in turn, causes premature wear and often failure in these components. As the oil thickens, so it is no longer pumped efficiently and oil starvation may result, especially on start-up. A sustained build-up of acids will also result in potential for accelerated rust, corrosion and oxidation. The inclusion of oxygen into the hydrocarbon chain results in the formation of carbon oxygen bonds, which chemists refer to as carbonyl bonds. More on these later.

Chillers are a bit of an exception, especially where synthetic ester-based oils are used. Introduction of moisture sees a number of chemical reactions where the by-products are hydrochloric and/or hydrofluoric acids and strong mineral acids. These have a similar devastating effect on oil as sulphuric and nitric acids. Hydrofluoric acid is also exceptionally toxic. The down side of chillers compared to engines is that the inclusion of water is not anticipated in chillers as it is not part of expected operating conditions. Consequently, the oil formulation does not have the appropriate additives to deal well with high acid loading caused by the inclusion of water. The high acid environment then leads to copper being leached in the system and deposited on iron surfaces, including bearings. Amongst other problems, this can result in bearing failure.

Other sources of acid include certain additives. The common anti-wear additive ZDDP (zinc dialkyl dithiophosphate) is weakly acidic in nature – as are many EP (extreme pressure) additives. One may think a new oil would always have a TAN of near zero. If the above additives are present, the starting TAN may well be over 2.0. This does not indicate a problem, and in fact represents a properly formulated oil, depending on the application. Moreover, in these oils, instead of seeing a gradual and continuous rise in the TAN, one can actually expect a slight drop in TAN compared with the new oil as acid additives are depleted. A tipping point is reached as the oil starts to oxidise, and then the TAN will begin to increase again, passing the original starting point and continuing to increase until the oil is changed.

Measurement of TAN

The American Society for Testing and Materials (ASTM) defines several methods for measuring TAN. Two commonly employed methods are ASTM D664 and ASTM D974. Both methods are titrations. A titration is a process where a reagent of known concentration is added to a sample of unknown concentration. The reagent has an active ingredient that reacts with a component of the sample that is under investigation. The point in the titration where just enough of the reagent is added to the sample to completely react with all the components being analysed is called the end point. This is determined by colour change of an indicator present, electrically via an electrode system or by very small temperature changes. The volume of reagent used to reach the end point and its concentration, as well as a known amount of sample, allow for determination of the unknown in the sample. In the case of TAN, a strong base is added to the sample to determine its acid number. The base is typically potassium hydroxide or tetrabutyl ammonium hydroxide.

With ASTM D664, a potentiometric titration is used.

This is where the titration end point is determined using an electrode system. During the initial phase of the titration, the millivolts of the electrode change quite slowly with the addition of the titrant. As the end point is approached, the rate of change of the millivolt response increases through to a maximum at the end point, then the rate of change decreases again. This results in an inflection at the end point on which software is able to detect and report. D664 is suitable for all types of samples, however it is slow, and end point detection can be problematic resulting in less precision and accuracy of results. The electrodes also need a lot of care and maintenance to give satisfactory results.

ASTM D974 is a colourmetric titration where the end point is detected by an observed colour change. An indicator chemical is selected that changes colour in a specific pH range that must be matched to the end point. With strong acids and bases, this is in the pH 7 range. However, as one is dealing with weak acids in most oils, a higher pH range is more desirable. ASTM D974 is highly suitable for most oils. Streamlining of the TAN assessment methods affords rapid and cost effective analysis which is accurate and reproducible. This is essential to the users of oil analysis for condition monitoring purposes. ASTM D974 is, however, unsuitable for oils that mask the colour of the indicator. This is the case for crank-case oils from diesel engines.

The method used for TAN analysis does have a bearing on the results. As a result of this, WearCheck and its associated laboratories use ASTM D664 for engine oils where customers request TAN and ASTM D974 for all other instances where a TAN is required.

Another way of measuring carboxylic acid build-up in the oil is to monitor the oxidation level by Fourier Transform Infrared Spectroscopy (FTIR). This is achieved by quantifying the carbonyl group through the measurement of its stretch frequency at around 1710 cm^{-1} in the spectrum. This is routinely done for all engine samples analysed by WearCheck.

TBN

Going back to the original discussion and the comparison to Spy vs. Spy, we have had a good look at Spy 1. Now we turn our attention to Spy 2, the counterpart of acid, which is base. The measurement of base in oils is covered by the term base number (BN) or total base number (TBN). The base number of an oil is a measurement of how much acid the oil can deal with before it is overwhelmed. Whereas acid number is universally applicable to all oils, base number is almost uniquely focused on engine oils. The reason for this is that the amount of acid generated in a crank-case is quite considerable compared to other lubricated compartments. The base number comes about primarily from the addition of detergents to the oil. These take the form of sulphonates, phenates or salicylates of calcium, magnesium, barium or sodium. The most common of these is calcium sulphonate. In marine oil applications, overbased calcium carbonate may be used. A secondary contribution to the TBN comes from dispersants that may be present in the form of polyisobutylene succinimide (PIBS).

Engine oils formulated for diesel engines will typically have a starting TBN of around 8 – 15 mg KOH/g and this will be lower for petrol engines. The ideal starting TBN will factor in the engine make and model, as well as the fuel being used. Engine OEMs will specify an oil in a region taking these factors into account. Marine engines will typically need a starting TBN much higher than this, and oils with a starting TBN of 80 are not unheard of. This is required as the fuels used in marine applications are less refined and have much higher sulphur levels. This results in more acid from combustion and hence more additive is required to cope.

The TBN of an oil will reduce during use and should this drop below a critical threshold, it is recommended that the oil is changed. Again making use of the Spy vs. Spy analogy, in this instance, Spy 2 has become compromised, and, without replacement, Spy 1 is going to cause mayhem. The limits used depend on who is consulted. An old rule has been based on when the TBN value has halved. This was perhaps more useful in the days of high sulphur fuels. Another approach is to say when the TAN and TBN values meet. This is good in theory but the determination of the TAN of a degraded oil is not only somewhat unreliable but also an expensive test. The reason for the lack of reliability is that the end point of the titration becomes very diffuse and it becomes impossible to pinpoint. One must then rely on secondary methods of end point detection.

Currently WearCheck adopts a rather cautious approach on the basis that oil is cheaper than machines. Should the TBN drop below 4, the oil will be condemned. If the system has a very large sump capacity, it would be possible to sweeten the oil with the appropriate additive, however WearCheck doesn't typically recommend this action due to a range of potential issues. If the TBN is between 4 and 6 then, depending on the system, the oil may be considered acceptable. If the TBN is above 6, there would be no cause for concern. There are two exceptions here – gas engines and marine engines. In gas engines, the OEM generally will set a lower limit on TBN and this should be adhered to; and in marine applications, due to the high sulphur fuels, half the starting TBN would be a better guide.

Measurement of TBN

The units of TBN are the same as those of TAN, i.e. mg KOH/g. However, it must be noted that, unlike in the case of TAN where a strong base is added to the oil to neutralise it, in the case of TBN a strong acid is added to the oil. There are two commonly-used ASTM methods - namely ASTM D2896 and ASTM D4739. ASTM D2896 uses a very strong acid - perchloric acid - in a titration with the oil sample and solvent. Perchloric acid will react with TBN additives as well as very weak bases and wear metals. It is more commonly used for new oils. When employed with used oils, the wear metals and very weak bases present in the sample will elevate the TBN, resulting in an overestimation of the effective base reserve of the oil. Spy 2 appears better off than it really is. As a result, WearCheck uses ASTM D4739 as its default base number method. In this titration, hydrochloric acid is used to neutralise the base components present in the oil, resulting in a more realistic assessment of the oil. As trending is important and the two methods do give different results, WearCheck will also use ASTM D4739 for new oils as well. Both methods are supported by WearCheck.

Titration is slow, expensive and also produces environmentally-unfriendly waste streams. Consequently, alternative methods are also developed to assess TBN. FTIR can be used to predict the TBN value. WearCheck has developed its own TBN prediction models for use in the majority of its laboratories. This method successfully predicts the TBN on the vast majority of used oils to within 1 TBN unit of the ASTM D4739 titration result. The model is derived using chemometerics and partial least squares modelling. In WearCheck's program, any sample with a predicted TBN of less than 6 will automatically get sent for a titration test using ASTM D4739 to ensure the highest level of certainty of the status of the TBN in the oil.

Conclusion

By understanding the acid base chemistry of lubricating oils, unique insights can be gained into the oil's chemistry, which has a major impact on the equipment it lubricates. When the battle of acids and bases gets out of hand, and acids dominate, oils thicken dramatically and corrosion, rust and other wear modes destroy equipment. By using a quality oil analysis program, such as that offered by WearCheck, these vital parameters can be measured and alarms raised to ensure timeous action is taken to reduce cost and improve equipment up time – in short, minimising stress, reducing costs and adding money to the bottom line.

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