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YOU'RE ONLY AS OLD AS YOUR ANTIOXIDANTS SAY YOU ARE – PREDICTING THE REMAINING USEFUL LIFE OF YOUR LUBRICANT

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Lubricants do not last forever - a statement well understood by lubricant users all over the world. They are susceptible to the ageing process like most things on earth. An example of the aging process that is witnessed by everyone is the human skin. It ages with time and degrades by a process known as oxidation. Lubricants are no exception. Oxidation is currently being accepted as the major cause of lubricant ageing/degradation.

In a lubricant it is the chemical backbone that ages and undergoes this process of oxidation. A lubricant consists basically of two main components. It contains firstly a base oil (mineral oil) and secondly a cocktail of additives which are blended into this base oil. The chemical structure/backbone of the base oil is technically referred to as its hydrocarbon chain. The chief chemical constituent of human bones is calcium. Similarly the constituents of the hydrocarbon chains (chemical backbone of a base oil) are hydrogen and carbon. Hence the name hydrocarbon. Oxidation of this backbone results in increases in viscosity and Total Acid Number (TAN) and the formation of sludge and varnishes.

Using a lubricant until it is no longer useful is cost-effective but potentially catastrophic. However, if the rate at which it were ageing were known, therefore predicting its remaining useful life, it would be possible to schedule oil drain periods cost-effectively. Changes in operating conditions would be known prior to complete degradation of the lubricant and mechanical breakdown. An oil in use could therefore be used to its full potential. This can be achieved by the Ruler (remaining useful life evaluation routine) test. Understanding how your lubricant ages and knowing the rate at which it is ageing is an investment that will yield substantial returns.

BASE OIL (MINERAL OIL)

Base oil is the component of a lubricant that gives it its lubricating properties. Additives are blended into the base oil to enhance its lubrication, amongst other properties, thereby increasing its area of application. Mineral oil is generally used as a base oil for most lubricants and is a fraction of crude oil. There are three basic types of mineral oil, each type having a different oxidative stability. Most lubricants contain up to 90% base oil. The low cost, availability and lubricating properties of mineral oil make it an ideal candidate for lubricant base oils. Synthetic oils offer better oxidative stability and longer drain intervals. They do, however, also have their own set of disadvantages. Whether you are using a lubricant that is synthetic or mineral in nature, they still age.

WEARCHECK
CONDITION MONITORING THROUGH OIL ANALYSIS

OXIDATION

The oxidation reaction, with regards to this bulletin, refers to the reaction of oxygen with the backbone of the base oil. Oxidation is a three-step process. Figure 1 represents the oxidation reaction of a hydrocarbon chain. It is illustrated as one step for the purpose of this bulletin. 'C' represents carbon and 'H' represents hydrogen. The lines between them represent bonds, which can be described simply as a semi-permanent handshake between the two atoms. This handshake is broken by the process of oxidation, resulting in the incorporation of oxygen into the structure, hence the formation of an acid. In the reaction below, the end carbon of the hydrocarbon chain undergoes oxidation resulting in the formation of an acid. Oxidation may also take place in the middle of a hydrocarbon chain resulting in the formation of two acid products.

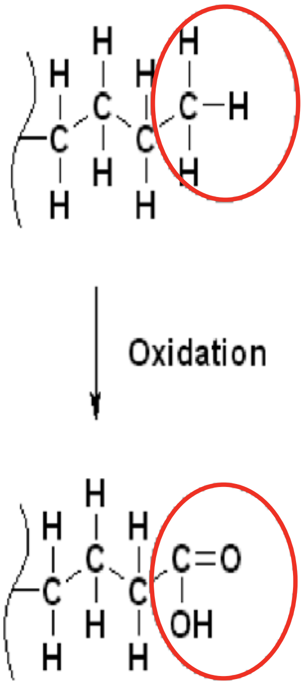


Figure 1: Oxidation reaction

When your skin ages, it is a result of oxidation taking place over a period of time. Oxidation of the skin can be accelerated by a number of factors, for example, the sun. If you expose your skin to UV rays, it will age more quickly. The same holds true for oil. The oxidation reaction is accelerated by a number of factors, including heat, moisture, entrapped air and certain metals.

WHAT PHYSICAL CHANGES ARE OBSERVED?

- The formation of acids results in the corrosion of metal surfaces. A high TAN is indicative of this.
- Hydrocarbon chains in the base oil with the help of additives interact optimally, resulting in an ideal viscosity. Changes in the structure of the hydrocarbon chain result in an increase in viscosity.
- Association of oxidation products such as the various acids may lead to the formation of sludges and varnishes and a decrease in lubricity.
- The load-bearing ability of the lubricant decreases as hydrocarbon chains are cleaved.

PROTECTION OF THE BASE OIL

Many anti-ageing creams are available on the market to reduce the appearance of wrinkles on your skin. Sun block provides our skin with protection from oxidation that is accelerated by the sun. These products contain moisturisers, UV blockers, collagen and various other chemicals which reduce the affects of ageing. Lubricant experts exploit the same approach in protecting the base oil. Additives are blended into the base oil providing it with protection from high temperatures, pressures and long hours of use. Lubricant additives increase the life span of an oil and its area of application.

Additives include:

- Antioxidants (anti-oxidation)
- Antiwear agents
- Viscosity index improvers
- Rust/corrosion inhibitors
- Demulsifiers
- Extreme pressure additives
- Antifoam agents
- Detergents/dispersants

Oils also include an acid-neutralising additive reserve. This reserve may include the above additives, which exhibit a dual function. It is responsible for neutralising any acids formed in the oil. A measure of this reserve is determined by the Total Base Number (TBN) test. It can be seen that most of these additives are present to combat the effects of oxidation. We will take a closer look at antioxidants and how they protect the oil from oxidising.

ANTIOXIDANTS

Antioxidants are sacrificial in nature and deplete with time. They deplete first before the base oil begins to oxidise. Studies reveal that after 70-80% of the antioxidant reserve is depleted, physical changes within the oil begin to occur. Antioxidants act by targeting particular steps in the oxidation reaction. The type of antioxidant used is dependent on the intended application of the lubricant. There are three main classes of antioxidants illustrated in Table 1.

Class	Description	Examples
Primary: free radical scavengers	During the first step of oxidation, highly reactive chemicals are formed. These continue to react in a manner that ultimately produces acids. Primary antioxidants react with these reactive chemicals first, resulting in the formation of stable complexes.	Amines, hindered phenols
Secondary: peroxide decomposers	In the second step of oxidation, the highly reactive chemicals formed in the first step react with oxygen to produce peroxides. Secondary antioxidants are involved in the removal of these peroxides.	Phosphates and thiophosphates (ZDDP, alkyl phosphites and alkyl phosphates) including sulfides and polysulfides (phenothiazines, dithiocarbamates and sulfurised isobutylenes)
Mixed antioxidants	When two antioxidants are blended into a lubricant often the protection they offer is greater then the sum of the action of the individual antioxidants. In other words 1+1>2. Certain mixtures involve the depletion of one antioxidant resulting in the preservation and sometimes synthesis of the other.	Mixture of hindered phenols and amines

Table 1 : Various types of antioxidants and their action

A CLOSER LOOK AT ZDDP

ZDDP (zinc-dialkyl-dithiophosphate) has been used in oils since the 1940's. It was originally developed as an antiwear additive but was also found to be a very good antioxidant. The additive is still used today. The structure of ZDDP is illustrated in Figure 2. Alkyl groups may contain between 1 and 14 carbons.

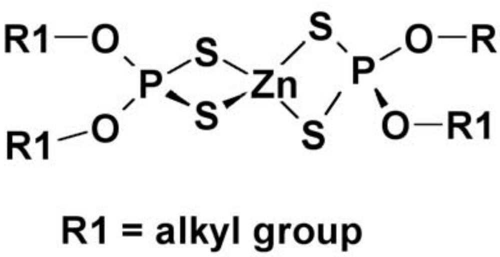


Figure 2: Monomeric structure of ZDDP

TO RECAP

In this bulletin we have so far established and illustrated a number of principles:

- Lubricants do age
- Oxidation is the major cause of this ageing process
- Antioxidants protect the lubricant from oxidation
- The oxidation process and the action of antioxidants

The age of the lubricant is therefore related to antioxidant concentration. The sacrificial nature of antioxidants means they are consumed with time and their concentration is an indication of the age of the lubricant.

To gain insight on how long a lubricant in current use should last, the concentration of antioxidants in the new oil must be known. This is its antioxidant reserve. The next factor that needs to be known is the rate at which this reserve is used up. This is done by monitoring the depletion of the reserve with respect to time, hence determining the rate at which it is being used up. Normal depletion rates are therefore identified. This requires testing of the oil in use at frequent intervals. With these two pieces of information known, the theoretical time it will take for the antioxidant reserve to be depleted can be calculated. This information also highlights abnormal operating conditions, which are identified by a higher than normal rate of depletion. The root cause of the abnormality can then be investigated and corrected.

THE RULER

The Ruler (remaining useful life evaluation routine) is a modern and cost-effective method of evaluating the antioxidant reserve of a lubricant. It exhibits good correlation with RPVOT, FTIR, TBN, viscosity and TAN tests. The method was initially developed to measure the remaining useful life of gas turbine engine lubricants and has now been developed for a large range of lubricants. Its ability to measure the relative remaining antioxidant concentration of a lubricant provides the lubricant user with vital information, which ultimately leads to substantial cost savings.

The Ruler device uses an electroanalytical method known as voltammetry in determining the relative antioxidant concentration of a lubricant. Voltammetry is based on the measurement of an electric current with respect to varying an applied voltage (potential).

Its action can be illustrated as simply giving the test solution an 'electric shock', with slowly increasing voltage until the antioxidants in the solution react. The 'stronger' antioxidants will react only with a larger applied voltage compared to the 'weaker' antioxidants. The Ruler therefore has the added ability of distinguishing between different antioxidants. The greater the reaction during the electric shock, the larger the amount of that particular antioxidant present.

Figure 3: The Ruler instrument

DETERMINATION OF THE RUL

The remaining useful life (RUL) of used oil is determined by measuring a new and used oil sample and comparing the peak areas on the voltammogram. The new oil is regarded as containing 100% antioxidants and the used oil is compared to this. If the peak area of the used oil is determined to be half the size of the peak area obtained for the new oil, it is regarded to have 50% RUL. Different percentages will be obtained for the different antioxidants present and the total %RUL will be the mean of these values. Different antioxidants may deplete at different rates.

THE BENEFITS OF THE RULER

COST SAVINGS

Knowing the protection capability of your lubricant, compared with its representative new oil, provides the lubricant user with essential information. Maintenance intervals can be well planned and abnormal operating conditions identified before lubricant or mechanical breakdown. An added advantage is that lubricants can be used to their full potential, thereby saving operational costs.

EFFECTIVE ROOT CAUSE INVESTIGATION

Knowing the amount of antioxidants present in your lubricant, coupled with the results of various tests employed in oil analysis, allows for the construction of a clearer image of what is happening to your lubricant's chemistry. A better understanding of this enables effective root cause investigations and provides added insight into condition monitoring.

EXTENDED OIL DRAIN PERIODS WITHOUT RISK

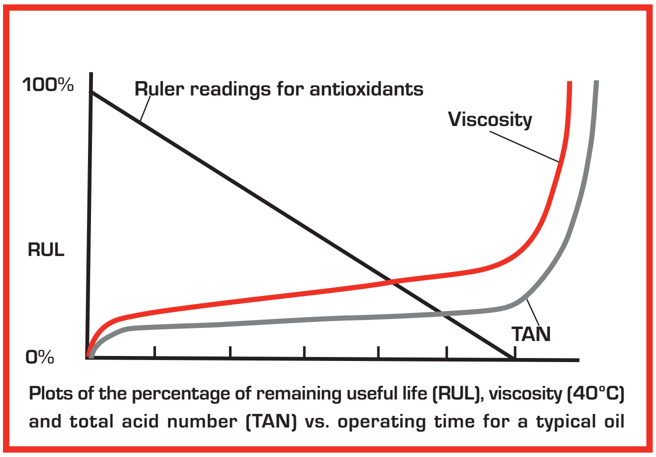
Maintenance managers and foremen are generally wary of extending oil drain periods. The risk of mechanical breakdown when the oil has degraded is a luxury that cannot be afforded. Other operators may be in a Catch 22 situation. The cost of replacing large volumes of oil before they have reached the end of their useful life is significant. The risk of mechanical failure due to allowing the oil to degrade until its breaking point is also significant. Knowing the RUL of the oil will satisfy these concerns.

OPTIMISING NEW TECHNOLOGY

Oil experts are continuously developing new blends of lubricants and new types of additives aimed at extending oil drain periods and increasing the resilience of oil to increasingly harsh conditions. The capability of determining how long an oil will last will enable maintenance managers to take maximum advantage of this new technology where existing oil grades may contain new blends of additives and base oil.

PROACTIVE DECISION-MAKING

One of the most powerful benefits of the Ruler is its ability to allow lubricant users to make proactive decisions. Tests like viscosity, TAN, FTIR-oxidation and TBN provide the user with information on the present nature of their lubricant. Significant changes in results are observed after the lubricant has already begun to degrade. Monitoring antioxidant depletion allows the user to establish normal rates and make decisions on when to expect the lubricant to degrade. Users can therefore make decisions on whether to change the lubricant or monitor its state more frequently until it is considered to be at the end of its useful life. Graph 1 illustrates the general response of the Ruler compared to TAN and viscosity tests.



Graph 1: Ruler compared with TAN and viscosity

Graph 2 represents a voltammogram from the Ruler instrument of a commonly used diesel engine oil. This multigraph illustrates the depletion of antioxidants with time. The oil was aged under laboratory conditions and samples taken at frequent intervals. It can be seen how the antioxidant peak decreases with time. The tallest peak represents the new oil and the lowest peak represents oil aged for 30 hours under laboratory stressed conditions. After 30 hours the antioxidant concentration has depleted to 36.2% of the new oil. Antioxidants depleted within hours due to the extreme stress placed on the oil for the purposes of the experiment.

Graph 2: Voltammogram of a laboratory-stressed diesel engine oil

TURBINE OIL APPLICATION AND RPVOT

The rotating pressure vessel oxidation test (RPVOT) method is an established reliable method of measuring the oxidative stability of a lubricant, especially turbine oils. RPVOT exposes the lubricant to extreme temperature, pressure and high levels of oxygen in the presence of a copper catalyst. The time taken for the lubricant to oxidise is measured. The RUL can be determined by measuring the time taken for oxidation to occur during analysis of a representative new oil and comparing it with results achieved from the analysis of the oil in use. The drawbacks of RPVOT are that it is expensive and a single test may take up to 600 minutes. With new additive blends, RPVOT tests may take between 800 to 3000 minutes. Turbine oils containing synergistic mixtures of antioxidants are being investigated as they are thought to yield inconsistent results and are being considered unsuitable for RPVOT. The Ruler does a test within 17 seconds excluding sample preparation. The Ruler test is very much cheaper and quicker than the RPVOT test.

WHICH TYPES OF LUBRICANTS CAN BE TESTED BY THE RULER?

- Hydraulic oils
- Transmission and gear oils
- Compressor oils
- Industrial lubricating oils
- Greases
- Industrial gas turbine lubricants
- Industrial steam turbine lubricants
- Phenolic antioxidants in steam turbine oils
- Phenolic antioxidants in pump bearing oils
- Combustion engine lubricants – diesel, automotive, gas engine, marine
- Aircraft engine oils
- Ester-based hydraulic fluids

Note: The above list serves as a guideline of the applicable lubricants for Ruler analysis. Some lubricants, depending on their intended application, may not be viable for Ruler analysis. Certain types of greases developed for low temperature use may have a low concentration of antioxidants or may not have antioxidants at all. They have been designed for protection against wear and high pressures which is of greater importance in their specific application than oxidation.

POINTS TO REMEMBER

- The decision of when a lubricant should be changed is subject to an accumulation of oil analysis data. The Ruler test should be coupled with other oil analysis tests.
- A sample to be tested has to be submitted with a new oil to be used as a reference.
- Samples that have undergone severe oxidation may produce unreliable results.
- The test is accurate to ±10%.
- >10% water content in a lubricant may affect Ruler results.

The phrase "You are as old as your arteries" can well be applied to lubricants. Your lubricant is as old as its antioxidants say it is. The fact is, however, that the condition of your arteries is not the only area you should focus on. Similarly, complete understanding of the condition of a lubricant requires information from various different tests to create a clear picture of its current state. Greater information known about the lubricant allows for more precise decision-making. The Ruler instrument is a key ingredient in providing a clearer picture and predicting the future.

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