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# ANTIOXIDANTS SIGNAL LUBRICANT HEALTH

**Many lubricants such as gas turbine oils, biogas engine oils and polyurea-based grease depend on antioxidants to protect the base oil against severe oxidation and degradation. To provide improved protection, especially in thermally stressful environments, antioxidant chemistry has undergone a major transition in the last 10 years. Good examples are the change from mono-type antioxidant mixtures to synergistic mixtures of antioxidants, and the introduction of primary (radical scavengers) antioxidants to replace peroxide catchers such as zinc dithiophosphates.**

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Due to these evolutions, original equipment manufacturers and international standardization organizations have developed and implemented state-of-the-art testing methods that enable equipment users to monitor the life of their in-service lubricants. One reliable method for measuring antioxidant health is voltammetry, also known as the Ruler technique. This method provides an in-depth understanding of the condition, as well the degradation mechanisms, of oils.

**Introduction to Antioxidants**

Oxidation is the predominant reaction a lubricant undergoes in service, and it accounts for significant lubricant reliability and life problems. Oxidation is the major source of viscosity increase, varnish formation, sludge and sediment formation, additive depletion, base oil breakdown, filter plugging, loss of foam resistance, loss of demulsibility, acid number increase, rust and corrosion. Therefore, understanding and controlling oxidation is a major concern for the lubricant formulator.

Many tests are used to study the oxidation behavior of new fluids, including ASTM D2272 (RPVOT), D4310 (sludging), D943 (TOST) and D6514 (UOT). In-service oil analysis to measure the effects of oxidation include ASTM D6971 (Ruler), D7843 (MPC) and D664 (acid number). All these tools are an attempt to understand the fluid's behavior to this lubricant nemesis.

Virtually every lubricant formulation contains antioxidants. These additives are designed to be sacrificial, meaning they oxidize before any other component of the lubricant, thereby protecting it. This oxidative protection is the only thing saving the lubricant from premature failure.

Oxidation was originally defined as a reaction involving combination with oxygen. However, its definition has now been expanded to include any reaction in which electrons are transferred from a molecule. Iron rusting is a form of oxidation, where the reaction is between oxygen and iron. Combustion is a very rapid form of oxidation of a hydrocarbon producing water and carbon dioxide.

The typical final product of oxidation in slower reactions of a

Ruler instrument indicates antioxidant level.

hydrocarbon is an acid. Hydrocarbon oxidation to an acid involves complex steps where many different compounds are produced. When a hydrocarbon is allowed to oxidize without control (such as in an oxidation experiment like ASTM D2272), carbon dioxide and water are produced, just like in combustion.

The oxidation of a hydrocarbon involves three steps: initiation, propagation and termination. This process is followed by a condensation/rearrangement step that also increases a lubricant's viscosity and the insolubility of the by-product. The onset of oxidation can be controlled by limiting the source of oxygen, shortening the number of reaction cycles or adding alternate stopping methods. All of these methods are employed to some extent in lubricant formulations.

The oxidation initiation step is how it all starts. The faster or more common this step, the higher degree of oxidation the lubricant will experience. Initiation consists of the formation of a free radical, a molecular fragment having one or more unpaired electrons that are accessible to easily react with other hydrocarbons. Free radicals are usually short-lived and highly reactive.

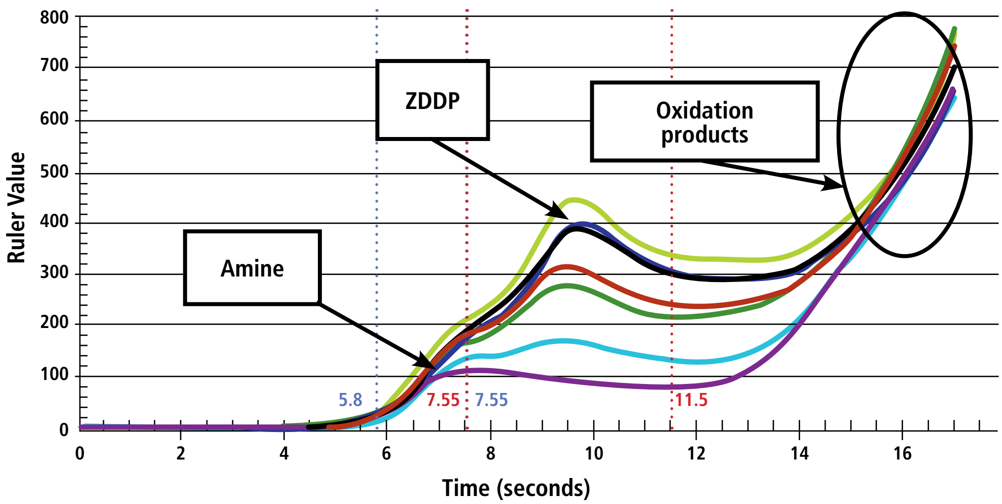
After a free radical has been formed, it can propagate the oxidation sequence. This step involves the formation of additional alkyl or peroxy radicals to continue the cycle of radical formation. Antioxidants break into the propagation step to terminate the process by forming stable radicals.

**Types of Antioxidants**

Antioxidants protect the base oil by either scavenging radicals or decomposing hydroperoxides into stable products. Two main categories of antioxidants are available in the industry: primary and secondary.

Primary antioxidants act by removing the radicals and are better known as radical scavengers. Amines and phenols are common types of primary antioxidants and have a typical concentration of 0.3 to 0.7 percent in turbine oils.

Secondary antioxidants eliminate peroxides (hydroperoxide decomposers) to form nonreactive products that do not participate in further oxidation. Zinc dithiophosphates and sulfurized phenols belong to this class of antioxidants. Typical concentrations of zinc dithiophosphates antioxidants in automotive crankcase lubricants reach a maximum of 1.5 percent. Carbamates are also used as secondary antioxidants, and sulfurized carbamates provide additional antiwear protection.




Ruler graphs trending the life of in-service diesel oils show the formation of oxidation products and depletion of amines and ZDDP. Oxidation products can be produced even though there is still antioxidant support remaining in the fluid.

*Source: Fluitec*

Mixed antioxidant systems add two or more antioxidants to a fluid, typically providing increased antioxidant effect in excess of that provided by either additive individually. For this reason, antioxidants are often used in synergistic mixtures to extend lubricant life.

In a mixed system, one antioxidant sacrifices itself to preserve and regenerate the other. An example of this behavior is the synergy between amines and phenols where the phenol depletes early while the amine is more stable. Another example is the combination of primary and secondary antioxidants that remove both

*Continued on page 36*

*Continued from page 33*
radicals and hydroperoxides.

### Measuring Antioxidants

The method for monitoring the amount of antioxidants in lubricants is based on voltammetric analysis where a small sample is extracted with an electrolyte in solvent and placed in an electrolytic testing solution. Results are based on current, voltage and time relationships in a three-electrode sensing system. The dissolved antioxidants oxidize electrochemically (lose an electron) based on their oxidation potential, resulting in an oxidation reaction that can be used to predict the remaining useful life of a grease or fluid.

As described by ASTM test methods D6810, D6971 and D7520, the voltammetric method is performed with a commercially available voltammograph called the Ruler. This instrument can be used both in the laboratory and in the field.



With the wide variety of antioxidants available today, it is important to select the appropriate mixture of electrolytes, which acts as a carrier for the electric current to the different antioxidants. Commercial electrolytes solutions can be divided into three categories.

Neutral electrolytes mixtures are for amines, ZDDP and phenols. Basic electrolyte mixtures are used for phenolic antioxidants. Acidic electrolyte mixtures are specifically for overbased formulations (engine oil containing phenates and salicylates) where the overbasing is reacted to leave the original phenol to be analyzed. This electrolyte mixture detects ZDDP, phenols and amines.

### Correlation to Other Methods

During the last decade, synergistic mixtures of antioxidants have been introduced as the way to meet increased lubricant performance requirements. Consequently, the industry needs new test methods to better monitor the remaining activity of these antioxidants. The knowledge gained helps OEMs and standardization organizations be more proactive by understanding the lubricant degradation process, rather than to set action limits based simply on oxidation testing.

Oxidation test methods such as the Rotating Pressure Vessel Oxidation Test (RPVOT) and Pressurized Differential Scanning Calorimetry (PDSC) can provide information that is indirectly linked to the measurement of antioxidants. The correlation between RPVOT and voltammetric methods has been the subject of several research projects that show good

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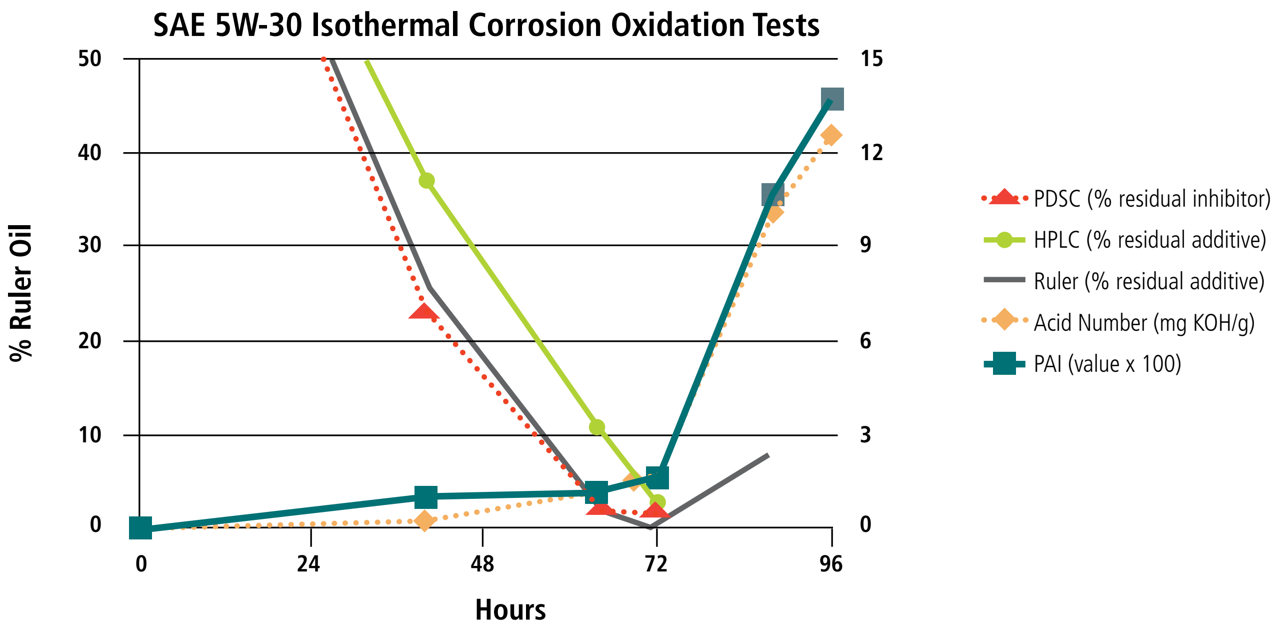
Plot shows the correlation among different oxidation tests.

*Source: Fluitec*

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correlation for phenolic formulations in API Group I oils.

However, there is less correlation between voltammetry and other indirect measurements for synergistic mixtures of phenol-amines and long-life Group II oils. Rather, voltammetric techniques provide more accurate results, faster data acquisition and a more thorough understanding of the oxidative health of the fluid.

Ruler technology can be used as a trending tool for any lubricant application using antioxidants. General guidelines for interpreting results for turbine, compressor and other rust and oxidation oils are:

- **Amine only formulations:** Warning limit at 50 percent remaining, condemning limit at 25 percent.
- **Phenol only formulations:** Warning limit at 50 percent remaining, condemning limit at 25 percent.
- **Amine-phenol formulations:** Warning limit when amines are at 50 percent remaining, condemning limit when amines are at 25 percent.
- **Amine-phenol depletion ratios:** Under oxidative conditions, phenols regenerate amines, thereby depleting first. If amines are depleting at the same rate or faster than phenols, water is entering the reaction, causing this unusual mode of degradation.

**Future Trends**

In situ replenishment of antioxidant packages for in-service turbine oils has been proven to be an effective method of extending oil life, provided sufficient up-front testing is done. The Ruler is one of the key tests in qualifying in-service oil for antioxidant replenishment and in monitoring the fluid once it is in use.

As an example, Ruler results from two turbine oil antioxidant replenishment qualification tests are showed that replenishment had the desired effect of increasing antioxidant concentration in one case but not in the other. It is important to note that several other performance tests are necessary before an oil can be qualified for antioxidant addition.

When adding antioxidants to in-service turbine oils, Ruler testing is a critical tool to monitor the depletion of these additives. Ideally, refortified antioxidants should deplete at a rate similar to that of antioxidants in new turbine oils.

Antioxidant monitoring can be performed in a multitude of lubricants, ranging from jet turbine oils to natural gas engine oils to hydraulic fluids. And appropriate electrolytic testing solutions have been designed to accommodate the spectrum of lubricant formulations. As in any oil analysis, tracking trends is crucial, and understanding the health of the individual antioxidants in the oil can also trigger supporting analytical tests. □

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