Oxidation revealed: A deep dive into TOST testing

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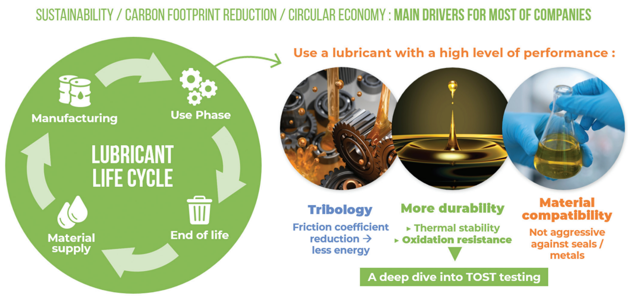
Introduction
Sustainability, carbon footprint reduction (CFR), and the circular economy are key drivers for most companies today, including those in the lubricants industry. Lubricants contribute to sustainability at various stages of their life cycle. A simplified lubricant life cycle encompasses at least four stages: material supply, manufacturing, blending, transportation, and the use phase, ending with end-of-life management.

Sustainability and CFR initiatives encourage lubricant manufacturers to transition from a cradle-to-gate lifecycle approach to a cradle-to-grave, and even cradle-to-cradle, if regeneration or re-refining processes are included. The selection of biobased or regenerated raw materials, which are biodegradable and non-toxic to aquatic microorganisms, plays a crucial role.

In the lubricant lifecycle, the use phase is particularly significant for carbon footprint reduction, although accurately calculating this benefit remains challenging. Various actions can be taken to extend oil life, such as monitoring the oil and equipment and performing regular maintenance operations. For optimal CFR benefits, high-performance lubricants are essential.

Enhancing lubricity and reducing wear by focusing on excellent tribological properties can help reduce the energy consumption. Additionally, improving compatibility and minimising destructive effects on materials like seals and metals are important considerations.



Developing lubricant formulations with high thermal stability and excellent oxidation resistance is vital for increasing oil durability. This is why oxidation resistance tests are so important. Among the numerous tests available to determine oxidation resistance in industrial oils, the Turbine Oxidation Stability Test (TOST) is one of the most widely used. This article, "Deep Dive into TOST Testing," reviews the classic TOST test and various adaptations for different types of lubricants and conditions.

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General principle of oxidation tests

Various methods are employed to assess the thermal stability and antioxidant properties of lubricants, with some techniques tailored to specific lubricant types. These methods aim to simulate oxidation phenomena under different operating conditions and within various mechanical components, all based on similar principles. The aging of oil is influenced by several factors:

- Thermal stress: varying temperatures
- Gas exposure: primarily air or oxygen, with differing flow rates or static pressures
- Presence of metal catalysts: either as solid metals or metal compounds like naphthenates introduced into the lubricant
- Presence of water

Oxidation stability is evaluated by monitoring several parameters:
- Changes in fluid characteristics (viscosity, acidity, additive depletion, metal concentration from catalysts, increase in carbonyl peak area via IR spectrometry, carbon residue, electrical properties)
- Quantification and appearance of insoluble materials resulting from oxidation (deposits, sludge, varnish)
- Corrosion assessment on metal specimens, including weight loss
- Pressure drops indicating induction time

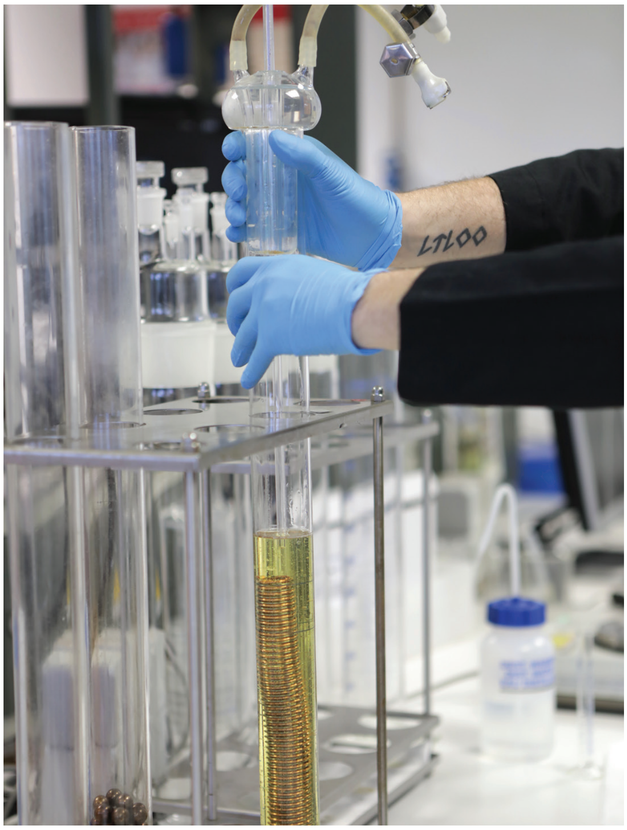
It's important to note that once a lubricant begins to deteriorate, the degradation process can accelerate rapidly due to associated exponential effects. Insoluble materials from oxidation can induce wear and friction, leading to increased insolubles and higher temperatures, which in turn reduce lubricant film thickness, further increasing wear and temperature. Rising acidity can cause corrosive effects on metal parts, increasing metal concentration that catalyses oxidation. Increased polarity due to oxidation can deteriorate surface properties, such as higher foaming stability and longer air release times. Additionally, water solubility increases, and electrical properties degrades.

Significant efforts have been made to develop improved methods for evaluating the oxidation resistance of lubricants. The Turbine Oxidation Stability Test (TOST) is widely used for industrial lubricants, and numerous variants of this original method have been developed.

TOST Tests and variants

Classic TOST

The ASTM D 943 method, known as TOST, was developed in 1943 and remains widely used to predict the oxidation life of various oils, including anti-wear hydraulic, R&O, and turbine oils. The test involves heating the oil with copper and iron catalysts, adding water to simulate steam condensate, and introducing oxygen to accelerate oxidation. Oxidation is measured by the increase in the acid number of the oil.



The procedure involves placing 300 ml of test oil and catalyst coils into a heated bath at 95°C, adding 60 ml of distilled water, and using a water-cooled condenser to prevent water vapour loss. Oxygen is bubbled through the oil at 3 l/h, and periodic samples are taken to determine the acid number. The test concludes when the total acid number (TAN) reaches or increases by 2.0 mg KOH/g, indicating the "oxidation lifetime" of the oil.

This method is widely used for specifications such as ISO 8068, DIN 51515-part 1 L-TD, Siemens TLV 901304, Mitsubishi MS4-MA-CL 001 002 003, and General Electric GEK 107395A. Uninhibited oils typically fail within 200 hours, while high-quality oils can exceed 5,000 to 10,000 hours. However, the correlation between this test and actual field performance can vary.

The ASTM D943 test has an upper limit of 10,000 hours, with values beyond this considered nonstandard extensions. An alternative to the classic TOST, known as anhydrous TOST, is conducted without water and is suitable for lubricants not prone to water contamination. ISO 4263-3 provides an anhydrous procedure for synthetic hydraulic fluids of categories HFDU, HEES, HEPG, and HETG.

Sludge TOST

One limitation of the original TOST method is its focus solely on acid number, which overlooks the potential for oils to deteriorate by producing insolubles and sludge. The ASTM D4310 test, known as the Determination of the Sludging and Corrosion Tendencies of Inhibited Mineral Oils, is a modified alternative to ASTM D943. It assesses the tendency of inhibited mineral oils to form sludge during oxidation.

The test follows the conditions outlined in ASTM D943. After 1000 hours, the test is stopped, and the oil and water layers are separated and filtered. The weight of insoluble material is measured gravimetrically using a 5-micron pore size filter. Copper content in the oil, water, and sludge phases can be determined using appropriate methods.

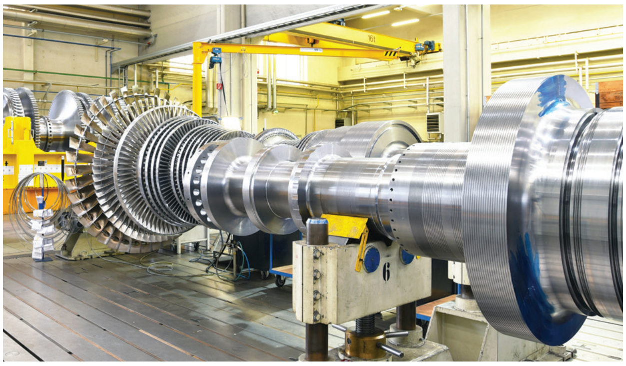
Primarily used for specification purposes, this method indicates the potential for oil to form insolubles or corrode metals during field service. However, a direct correlation with field performance has not been established.

Dry TOST

Despite their superior oxidation resistance and thermal stability, Group 2 and Group 3 base oils can still experience varnishing issues, primarily due to their lack of aromaticity, which affects their solvency and ability to keep insolubles in solution. To mitigate these problems, several precautions should be taken:

- Enhance antioxidant (AO) formulations, balancing phenolic and aminic antioxidants.
- Consider using a co-base oil to improve performance.
- Avoid conditions that initiate radical formation, such as hot spots and electrostatic discharge.
- Regularly monitor the oil, perform top-ups, and use filtration methods like electrostatic cleaning.

The Dry-TOST test, developed by Mitsubishi Heavy Industries (MHI), is a variant of the standard TOST test designed to address issues related to varnish and sludge formation in turbine oils. Unlike the standard TOST, the Dry-TOST test is conducted without water and at a higher temperature of 120°C. This approach aims to better simulate the conditions that lead to varnish and sludge formation in turbine oils.



In this test, six to eight tubes containing 360 ml of oil sample (without water) are heated at 120°C with oxygen in the presence of an iron-copper catalyst. Over time, each tube is removed, and the sample is analysed using Test Method D2272. Insolubles are measured until the RPVOT (Rotating Pressure Vessel Oxidation Test) residual ratio falls below 25%.

The passing criterion is to maintain less than 100 mg/kg of insoluble material at an RPVOT value corresponding to 25% of the new oil. This 100 mg/kg limit was determined by MHI based on their field experience with turbines and hydraulic control systems

MHI's 50/50 Mix Test in Dry-TOST

Mitsubishi Heavy Industries (MHI) aims to understand the influence of top-up oils by applying the same criteria to a 50/50 mixture of new and oxidised oil. This approach simulates real-world conditions where turbine oils are periodically topped up with fresh oil.

The procedure involves preparing oxidised oil by subjecting it to the Dry-TOST method until it reaches an oxidation level (RPVOT ratio between 50% and 30%). The oxidised oil is then mixed with new oil in a 50/50 ratio. This mixed oil undergoes the Dry-TOST method again to evaluate combined oxidation stability and sludge formation tendencies.

This method better simulates conditions in turbine systems where oils are periodically topped up, providing a more accurate prediction of long-term performance. It also helps understand how additives

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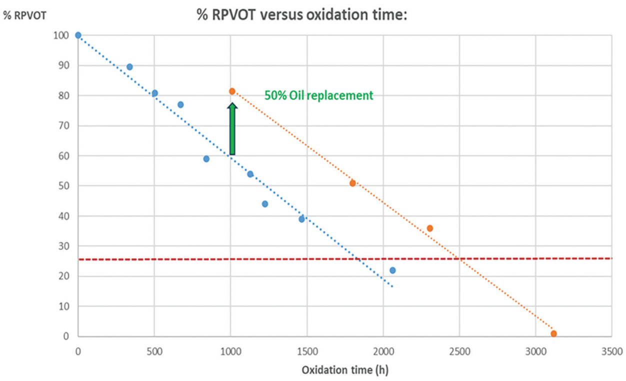
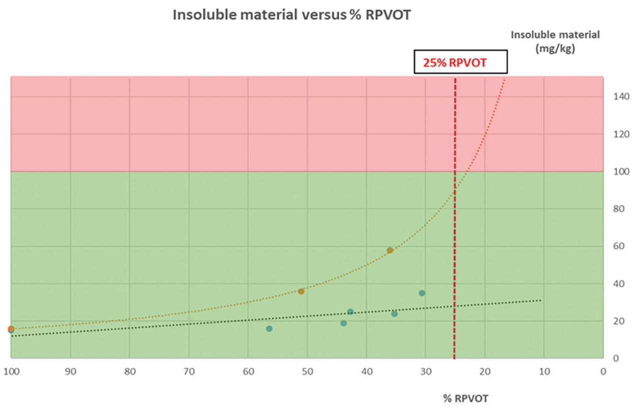
in the new oil interact with oxidised oil, potentially improving formulations to reduce sludge and varnish formation. The benefit is enhanced predictive capability and optimised additive packages to improve the stability and cleanliness of turbine oils. This test offers a more realistic assessment of the oil's performance over time.

Example of test results

The graph below illustrates the determination of oxidation lifetime based on a 25% RPVOT ratio and the impact of replacing 50% of the oil:



The following graph illustrates the impact of top-ups on the increase of insoluble materials:



Based on the information provided by these graphs, we can conclude that regular top-ups combined with oil monitoring can significantly extend the oil's life. However, precautions should be taken to avoid the accumulation of insoluble materials. If regular top-ups are performed, it is advisable to combine them with efficient oil filtration.

TOPP (Turbine Oxidation Performance Prediction)

TOPP has been developed by Fluitec to assess the physical and chemical alterations of turbine oil. This test is an alternative to the Dry-TOST, evaluating extended parameters at different oxidation states for 12 weeks when the test is carried out at 120°C and including tests like Viscosity, TAN, RPVOT, RULER and MPC.

By using the same accelerated oxidative process specified in ASTM D7873, alongside standardised test methods such as FTIR, MPC, RULER, RPVOT, insoluble material content, TAN, viscosity, metals, and deposit evaluation, the results and findings can be correlated to actual field performance.

Ammonia TOST

Ammonia has a Global Warming Potential (GWP) and Ozone Depletion Potential (ODP) of zero. It is commercially available worldwide, can be produced in a greenway and has an acceptable energy density, making it an environmentally friendly choice.

Oxidation tests using ammonia in combination with air have been developed primarily for two purposes:

Inertness to ammonia for compressor oils (ammonia compressors)

The aim of this test is:

- To ensure that lubricants do not react chemically with ammonia, which can lead to the formation of harmful deposits and reduce the efficiency of the compressor.
- To confirm that the lubricant maintains its properties and performance in the presence of ammonia.

In this test, a mixture of air (8.6 l/h) and ammonia (1.4 l/h) bubbles through 300 ml of oil in the presence of a copper coil. Water (0.1%; 0.3 ml) is added at the beginning of the test and every 24 hours. The test runs for 150 hours at 125°C, and the oil is analysed at the end of the test based on the following criteria:

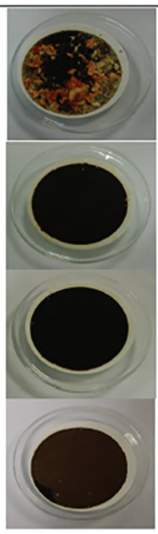
- Total Acid Number (mg KOH/g)
- Organic Insolubles (wt%)
- Soluble Copper (ppm)

Ammonia contamination can lead to rapid oxidation of the oil. This occurs when aqueous ammonia in the oil reacts with copper alloy components, producing oil-soluble copper complexes that act as powerful catalysts. The consequences are overheating, deposit formation, and sticking.

The following table represents an oil that is not compatible with ammonia:

TAN before (mg KOH/g)	Tan after (mg KOH/g)	Total insoluble * (% W/W)	Copper content (PPM)	Catalyst aspect
0	0,03	0,16	23	dark brown, slightly tarnished

* total = filtration residues + material adhering on glass

Sample after test:	Reactor after test:	Filter(s)
		

Oxidation of engine oil in the presence of ammonia

Ammonia is emerging as one of the most promising zero carbon fuel options for deep-sea shipping. Currently, there is no official oxidation bench test method to evaluate the interaction between engine lubricants and ammonia.

Based on existing literature, oxidation stability tests on marine engine oil in the presence of ammonia should monitor classic parameters such as kinematic viscosity, Total Acid Number (TAN), Total Base Number (TBN), Fourier Transform Infrared Spectroscopy (FTIR), insolubles, and metals (ICP-OES) analysis. Additionally, it may be relevant to include performance tests for corrosion, deposit formation, and tribology evaluations such as anti-wear and extreme-pressure properties.

Conclusion

In conclusion, TOST tests and their variants are versatile tools applicable to various oils, including turbine, hydraulic, and compressor oils. Oxidation testing is crucial for assessing the oxidation and thermal performance of lubricants under severe conditions to try to predict real-world performance. While real-world performance is best evaluated through engine or field tests, these are very expensive and limited in the number of tests that can be conducted within a short period. Therefore, bench tests are widely used for evaluating new additives and formulated lubricants. It is important to consider multiple parameters such as insoluble material, viscosity, acidity, additive depletion, and varnish tendency.

The significance of regular top-ups has been demonstrated, showing that they can extend the oxidation lifetime of oils. However, precautions must be taken to prevent the accumulation of insoluble materials. Additionally, assessing the remaining performance of altered oils in terms of deposit formation, wear properties, and material compatibility is crucial for ensuring long-term lubricant effectiveness.

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