Oxidation in lubricant base oils

The ageing of the oil

Oxidation is a common problem in many industries. When the oil is being used in a machine, it oxidizes over a period of time depending on the type of oil, the operational conditions and the environment. Oxidation can have negative effects on lubrication and hydraulic system, all of which may have serious consequences for the performance of the machinery. In this article you can read about the problems connected with oxidation.

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Deposit formation on key komponent

Oxidation is a complex primary chemical degradation process in the base oil. It can be defined as the chemical breakdown of the base oil molecules with oxygen as reagent where the principle source of oxygen is air.

The following parameters act as a catalyst:

- *Temperature*
- *Wear transition metals (wear particles)*
- *Water (both free and dissolved)*
- *Contaminants (in general and oxidation products)*

This process involves a series of chain reactions producing acid compounds that undergo further reactions forming polymeric compounds, which lead to sludge, lacquer, varnish, i.e. deposit formation.

The anti-oxidant additives, used in most oils, protect the oil from oxidation. They react with the intermediate oxidation compounds (i.e. partly degraded oil) and counteract the acid formation. As the oil oxidizes, the anti-oxidant additives are depleted over time and then the oil is exposed to oxidation. On the other hand, the principle source of oxygen (i.e. the oxygen from the atmosphere) may be inexhaustible.

Oxidation process in lubricant base oils

The base oil consists of a mixture of many different hydrocarbons. The oxidation process occurs when these hydrocarbons react with oxygen. It is a self-propagating process that occurs via free radicals.

Temperature is of great importance in oxidation. At lower temperatures (up to about 150 °C) the pattern of oxidation reactions may differ substantially from those at high temperatures.

In a general case it is assumed that oxidation of oil proceeds in three stages: initiation stage, propagation stage and termination stage.

The following model shows the oxidative degradation in lubricant base oils.

Initiation stage:
The hydrocarbons react with oxygen forming hydrocarbon free radicals. The reaction is catalysed by traces of transition metal ions like copper, iron, cobalt, chromium, etc.

Propagation stage:
The hydrocarbon free radicals react with oxygen forming peroxide radicals, that are highly reactive, and react further with hydrocarbons from the oil. This leads to hydroperoxides and hydrocarbon free radicals, which can react with oxygen.

Termination stage:
The hydroperoxides, formed in the propagation stage, cleave homolytically and form oxygenated compounds like aldehydes, ketones, alcohols and water. These compounds can react further forming organic acids and high molecular weight polymeric products. Further polycondensation and polymerisation of these products lead to insoluble products called sludge, which may precipitate as a thin film forming lacquers or varnish deposits on hot or cold metal surfaces.

Consequences of the oxidative degradation in lubricant base oils

Corrosion and wear
Acid formation will cause corrosion and wear in the internal surfaces of the machine. Water, which is also formed under the oxidation process, increases the corrosive effect of the acids.

Increase in oil viscosity
The oil viscosity increases due to the formation of oxidation products e.g. polymeric compounds and sludge. It will result in friction, wear and loss of energy.

Sludge and varnish
Sludge and varnish can result in valves blocking and orifices clogging. Once varnish deposits are formed on metal surfaces, it is very difficult to dissolve them even at high temperatures. These deposits are like a sticky

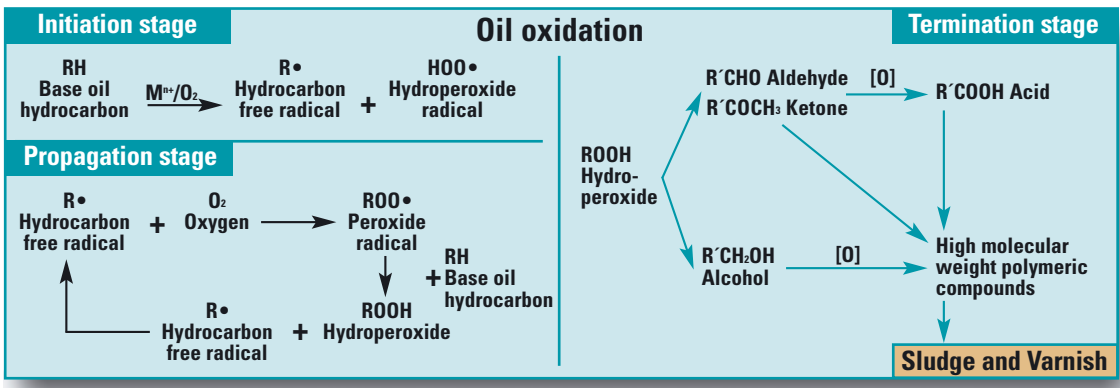

Diagram showing the oxidative degradation in lubricant base oils

References

- "Chemistry and Technology of Lubricants" - R.M. Mortier and S.T. Orszulik - Blackie Academic & Professional
- "Longer life for Hydraulic Fluids" - P.V. Madhavan, Fluid Power Engineering & Technology Guide - Machine design, December 6, 1990

material that will trap hard contaminants creating a "sandpaper surface", which can cause accelerated wear in the components. In addition to this, varnish acts as an insulator, reducing the effect of the heat exchangers which again means higher temperatures and accelerated reaction rates.

Measuring oxidation in lubricant base oils

Oxidation by-products (aka soft particles) are compounds of molecular sizes less than 1 micron, which cannot be measured by conventional particle counting methods.

TAN analysis (total acid number) and viscosity testing can be used as indicators of oxidation but they cannot determine whether or not the oil is oxidized. Dark color, and sour, putrid odor usually indicate oxidation.

There are several methods to monitor oxidation in the oil. Generally, these methods are used to either determine oil degradation products from the oil or the consumption of anti-oxidants in the oil. The latter is used to predict when the onset of oxidation will occur.

The following are examples of methods to monitor the oxidative degradation:

FTIR analysis
(Fourier Transformation Infrared Spectroscopy)
This analysis is based on the principles of molecular spectroscopy. It can verify oxidation in lubricants by identification of functional groups (e.g. ketones, carboxylic acids) in molecules.

QSA
(Quantitative Spectrophotometric Analysis)
The oxidation by-products are isolated from the oil sample and a quantitative spektrophotometric analysis of the isolated contaminants is carried out in order to determine the degree of oxidation.

Ultracentrifuge test
This test uses the gravitatory forces to extract and settle the contaminants of the oil. The sediment is compared with a sedimentation rating system to determine oxidation.

Gravimetric analysis
This analysis examines oxidation by measuring the weight of residual components. The oil sample is treated with the solvents pentane (hexane), toluene and pyridine to determine the oxidation products.

Colorimetric Analysis:
This analysis examines the color of contaminants collected on membrane filters by a colorimetric device.

The following are examples of methods to monitor the consumption of anti-oxidant additives:

FTIR analysis
(Fourier Transformation Infrared Spectroscopy)
This analysis, mentioned above, can monitor the additive depletion.

RULER test
(Remaining Useful Life Evaluation Routine)
It measures the remaining anti-oxidants by voltametric analysis.

RBOT test
(Rotating Bomb Oxidation Test)
It measures the oil´s resistence to oxidation under prescribed conditions.

Removal of oxidation products using filtration systems

The key to prevent oil degradation is to remove the oxidation by-products before they can react further and form insoluble slugde and varnish deposits. These compounds are very difficult to remove by the conventional mechanical filters because we are dealing with submicron particles with a high level of solubility in hydrocarbons.

Electrostatic filters and cellulose filters can remove oxidation products, because oxidation compounds are polar - i.e. have electrically positive and negative poles.

The electrostatic filters remove the oil contaminants using the principles of electrostatic and electromagnetism. The cellulose filters, on the other hand, utilize the characteristic that the cellulose material is also polar. The oil degradation products are attracted and retained by the poles of the cellulose fibers.

Oxidation is a common problem in many industries

Adsorption of oxidation by-products in the CJC™ Fine Filter: Resin in the oil attracts to the polar fibres in the filter mass and are retained

• "Using Oil Analysis to Control Varnish and Sludge" http://www.noria.com/learning_center/category_article.asp?articleid=59
• "New Varnish Test Improves Predictive Maintenance Program" http://www.practicingoilanalysis.com/article_detail.asp?articleid=761&relatedbookgroup=OilAnalysis