Technical Topic

Nitration of Lubricating Oil

in Natural Gas Engines

Nitration is an undesirable condition which indicates that the oil in natural-gas-fueled engines is becoming saturated with the soluble and/or insoluble nitrogen oxide compounds.

The reaction of nitrogen with the base oil forms two kinds of nitrogen compounds: organic nitrates and nitro compounds. They are independent of the oxy-products that lead to oil oxidation, which is another form of oil degradation.

Organic nitrates comprise the most significant amount of nitrogen compounds in used gas engine oils. As oil is thrown onto the cylinder walls and wiped down, these compounds are washed into the crankcase where they play a major role in forming sludge and varnish. They are soluble in oil until an excessive level is reached, then they drop out to form light amber to maroon deposits around the rocker arm and valve assembly, and on piston skirts. These deposits also cause oil rings to stick, increase oil consumption, and shorten filter life.

Nitro compounds result from several conditions: piston blow-by caused by stuck, worn, or broken compression rings; scored or worn out-of-round liners; or exhaust gas leaking into the oil because of high valve guide wear or poor valve seating. Other causes include: leaking turbocharger seals; critical engine ignition and combustion patterns; or excessive service length of the oil.

A higher-than-expected concentration of nitro compounds means that there are unreacted nitrogen oxide gases in the oil. They will thicken the oil abnormally and cause premature dropout of varnish and sludge, evidenced by reddish piston skirt varnish and sludge in the lower compression ring grooves and oil rings.

Causes of Nitration

There is a correlation between the rate of nitration of a gas engine oil and a **combination** of operating conditions, such as air/fuel ratio, engine load, and oil temperature. Charts 1, 2, 3, and 4 show the effects of these factors on nitration.

Nitrogen oxides formed during combustion are also influenced by ambient air conditions, spark timing, and final combustion temperature. Field tests have shown that nitration increases when ambient air temperatures increase and/or loads are higher. While there are no specific data on the degree to which spark timing influences nitration, there are strong indications that it is one of the more important factors.

Of the various mechanical conditions which affect the rate of nitration, three are especially important: rate of oil makeup to the crankcase; poor ring sealing; and crankcase ventilation.

Although the **rate of oil make-up** alone does not affect nitration, the dilution of new oil and removal of nitrated oil through leakage changes the rate at which the bulk crankcase oil combines with nitrogen oxides and deteriorates. The higher the oil makeup rate in a given engine, the slower the rate of oil deterioration.

Blow-by of combustion gases into the crankcase adds to a buildup of nitro compounds in the oil. When **ring sealing** is poor, more highly nitrated oil will migrate back into the crankcase instead of out through the exhaust port.

Tests on laboratory engines have shown a correlation between **reduced crankcase ventilation** and oil deterioration. This suggests that nitro compounds in the oil may be more rapidly removed when crankcase ventilation is improved, thereby reducing deterioration.

Degradation Patterns

Four-cycle gas engines: Organic nitrates decompose rapidly at temperatures above 300°F. They are the main cause of oil deterioration in low-speed (below 700 rpm), four-cycle gas engines because cylinder wall temperatures usually are below 320°F, even in ebullient-cooled units. Where cylinder wall temperatures exceed 320°F, the higher temperatures promote oil oxidation which is the main cause of oil deterioration in small, high-speed, four-cycle gas engines.

Two-cycle gas engines: Oxidation is the main cause of deterioration in two-cycle engines with separate power cylinder lubrication systems. Nitrated products are scavenged out of the exhaust ports and thereby prevented from contaminating the crankcase charge. The presence of even moderate nitration in these units, however, is a strong indication that excessive oil feed to the cylinders is being scraped down into the crankcase.

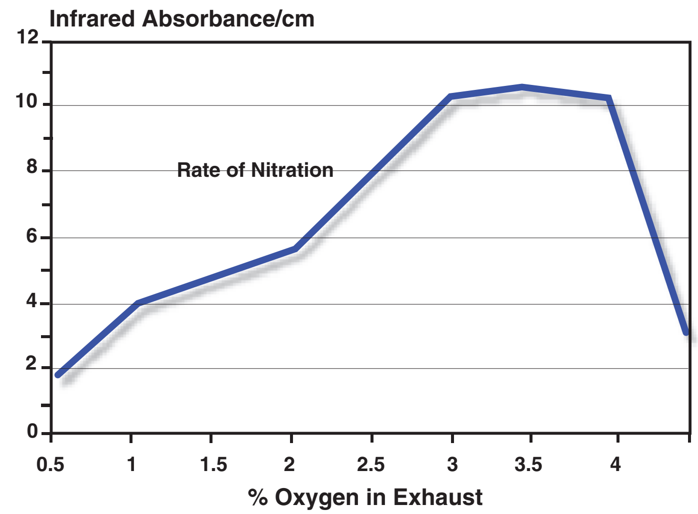

Chart 1. Effects of air/fuel ratio on nitration.
Varying the ratio from 0.5 to 2.5 to 4.2 percent oxygen in the exhaust of naturally aspirated, four-stroke engines confirms that a low rate of nitration may be maintained if the oxygen level is outside the 0.5 to 4.5 percent range, with nitration reaching a peak at 3.3 percent oxygen.

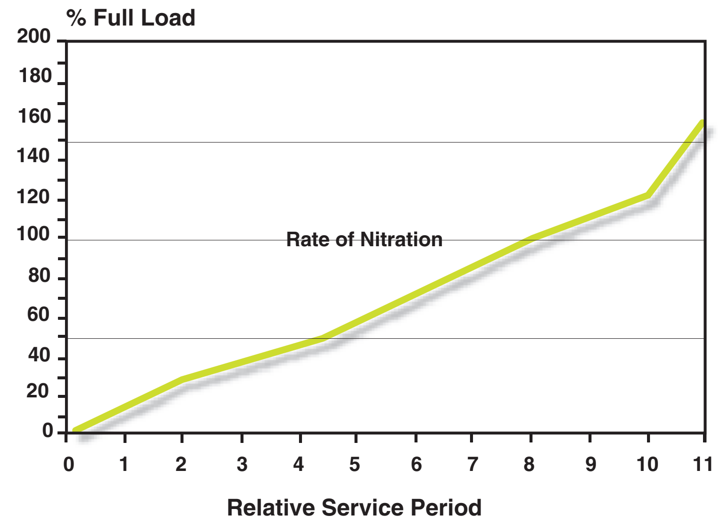

Chart 2. Effects of load on nitration
Improper air/fuel ratio and 2.5 percent oxygen in exhaust.

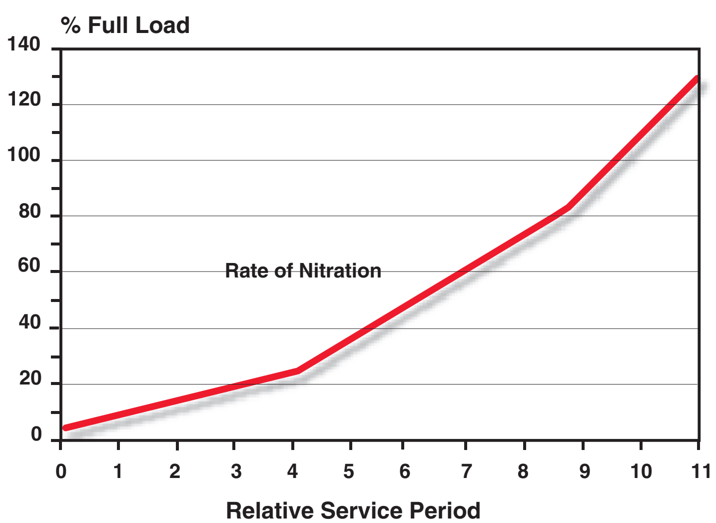

Chart 3. Effects of load on nitration.
An increase from 75 to 105 percent rated load causes a very sharp increase in the slope of the nitration curve even under a satisfactory air/fuel ratio and exhaust oxygen greater than 4.6%.

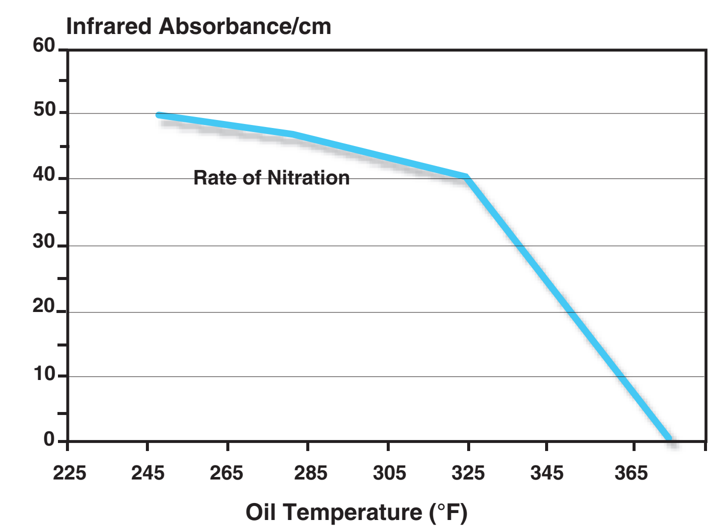

Chart 4. Effects of oil temperature on nitration.
Organic nitrates decompose rapidly when heated to temperatures above 300°F.

www.mobilindustrial.com

EN0761SH

Detection

Visual inspection of the rocker arm and valve assembly area and the piston skirt of an engine will reveal the amber-to-maroon-colored varnish deposits indicative of nitration. Nitration will also cause the oil control rings to stick and will form sludge in the crankcase.

Performance indicators, such as excessive oil consumption and shorter filter life can be indications of nitration inside the engine.

Infrared absorbance, commonly known as an IR scan, is a rapid, qualitatively accurate method of differential analysis which determines inherent chemical changes in used oil, as well as the amount and nature of the contaminants. In the process, a sample of used lubricant is compared to a reference sample of new oil. Infrared rays are passed through cells of 0.1mm (0.003937 in) in thickness, which contain the samples. The net difference in the chemical composition is recorded. The Mobil Signum oil analysis laboratory program uses infrared absorbance to determine nitration contamination levels by looking at both trends and sudden changes. Table 1 shows unsatisfactory engine conditions that can be caused by nitration and nitro compounds, as detected by Signum oil analysis.

Troubleshooting

The following is a general troubleshooting guide for various nitration conditions.

Nitration: Check trend leading up to the condemning value. If the value is the result of a gradual increase, the cause may be either: a) the combustion mixture, which may be improved by adjusting the air/fuel ratio; b) slightly low bulk oil temperatures; or c) minor ignition problems, such as spark plugs, wiring, or timing.

Rapid increases in nitration values are caused by the same problems as above, but to a more severe degree. On two-cycle engines, check for excessive power cylinder oil-feed rates.

Nitration tendency: Indicates improper ignition and combustion, which may be caused by:

- Unfavorable air/fuel ratios
- Uneven fuel/air distribution
- Poor scavenging
- Detonation or preignition
- Unbalanced loads and firing pressure
- Faulty ignition, spark timing, spark plugs
- High blow-by
- Leaking fuel valves
- High combustion pressure
- Engine overloading; improper cooling
- Low oil temperatures
- Excessive cylinder oil scrape-down (two-cycle)

Nitro compounds: Check hours since overhaul; values tend to be high following overhaul. While these values will not condemn oil, they suggest operating problems. Possible causes could be:

- Piston blow-by or turbocharger seal leakage
- Excessive power cylinder oil-feed rates (two-cycle engines)

Correcting the Problem

Laboratory tests and field-sample analyses show that gas engine oils become unfit for service when the concentration of organic nitrates approaches five percent. Excessive amounts of organic nitrates act as oxidizing agents that rapidly accelerate oil oxidation. Continued build-up of nitration products will deteriorate the oil.

Check air/fuel ratio: Low rates of nitration may be maintained if the oxygen level in the exhaust is outside the range of 0.5 to 4.5 percent, with nitration reaching a peak at 3.3 percent oxygen.

Oil temperature: Decreasing the oil temperature from 150°F to 135°F appears to boost nitration appreciably. This may be due to the heating effect on the oil film exposed to nitrogen fixation. Oil temperatures from the engine should not be lower than 150°F, and preferably greater than 160°F, if organic nitration is to remain at a moderate level.

Organic nitrates decompose rapidly at temperatures above 300°F; therefore, they are not retained in oil films when the cylinder wall temperature exceeds 320°F. Oil oxidation, however, is related directly to high engine temperatures, as in high-speed, four-cycle gas engines where cylinder wall temperatures exceed 320°F.

Adjust load: High loads and load imbalance between cylinders will increase nitration. An increase from 75 to 105 percent of rated load can sharply increase the slope of the nitration curve.

Unsatisfactory Condition	Causes of Condition as Identified by Signum Oil Analysis									Verified by Engine Analyzer
	Vis.	Water	Glycol	Oxidation	Nitration	Nitro	Coking	Insol.	Metals	
Sludge - Cold, Hot	X	X		X	X			X		
Varnish	X		X	X	X			X		
Carbon - Soot, Coke, Varnish				X	X		X	X		
Ring Sticking			X	X	X		X			X
Blow-by	X				X	X				X
Poor Combustion				X	X		X	X		X
Filter Plugging		X	X	X	X		X	X		
Poor Air Filtration									X	
Coolant Leaks		X	X						X	X
Liner Wear									X	X
Ring Wear									X	X
Bearing Wear									X	X

Table 1. Identification of unsatisfactory engine conditions using Mobil Signum oil analysis.
Unsatisfactory conditions caused by nitration and nitro compounds are indicated in the "Nitration" column. Note the correlation of some conditions with engine analyzer results.

For further information on Signum Used Oil Analysis and Mobil Pegasus gas engine oils, contact us at www.mobilindustrial.com or call us at 1-800-MOBIL-25.