Oils degrade - formed from crude oil

JOINTING TOGETHER TO SUPPORT THE PLANET

by John Evans B.Sc.

WearCheck is a registered ISO 9001 and ISO 14001 company

Surface active additives attach themselves to the wear debris lying in the bottom of the sump. Surface oxidation is the same phenomenon applied to intact metal surfaces. Rubbing contact: Certain gear and extreme pressure (EP) additives work by chemically reacting with the metal surfaces of the gear teeth. Sirone gear oils work by forming boron-based crystalline structures on the gear surfaces, which results in greatly improved frictional properties. With time, it is possible for these compounds to break down during rubbing contact, resulting in the loss of the effectiveness of the oil additive. Other EP additives are supported by a variety of mechanisms. Most of these compounds have good frictional properties too, but can also be lost during rubbing and sliding contact. These compounds can react by forming metal sulphides and other deposits on metal surfaces and collecting at the bottom of the sump. Other additives that have interfacial properties, such as defoamers and demulsifiers, can also be prone to condensation setting too.

Misuse: The most common mechanisms are abrasive, thermal, and biodegradation. Some EP additives are rubbed off by metal surfaces and the interfacial properties of these compounds are depolymerized. With time, it is possible for these compounds to break down during rubbing contact, resulting in the loss of the effectiveness of the oil additive. Other EP additives are supported by a variety of mechanisms. Most of these compounds can react by forming metal sulphides and other deposits on metal surfaces and collecting at the bottom of the sump. Other additives that have good frictional properties too, but can also be lost during rubbing and sliding contact. These compounds can react by forming metal sulphides and other deposits on metal surfaces and collecting at the bottom of the sump. Other additives that have interfacial properties, such as defoamers and demulsifiers, can also be prone to condensation setting too.

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additives that neutralise these acids. They are typically overbased sulfonates of calcium or magnesium and these results come from on an oil analysis report.

As has already been noted, these additives are essential and once they have neutralised the acids they cannot be regenerated to do the job again. Once all the additives have been used up, acid build up will proceed very quickly.

Nitrogen fixation from the atmosphere can generate nitrogen-based acid species of similar mechanism and these also need to be neutralised in the same manner to avoid damage to both the oil and the equipment. This becomes more of an issue with high combustion temperatures found in gas engines.

VI: The VI of an oil can be increased in a number of ways. Typical mineral base stocks oils have an additive VI or overbased additives. This is due to the fact that they have a high VI as temperature increases. Very highly refined mineral oils have a naturally high VI due to the fact that they are subjected to high temperatures in the refining process. This means that the VI of these oils will thin out more rapidly than oils with a lower VI. The VI of an oil is a unitless number that rates as the temperature increases. This matters, different oils thin out at different viscosities. As temperature increases, the polymers uncoil and retard the thinning action of the oil. Unfortunately these long organic polymers that uncoil when the oil heats up are not completely shear stable. This means that even when the compounds are subjected to high viscosities, they can be shear thinned in an automatic transmission, resulting in the faster thinning of the oil.

For every 10°C increase in oil operating temperature, the reaction time at which the compound of which the bubble is made double and, by logical extension, the life time of the oil is halved. This situation is not quite as dire as it sounds as oils naturally have a quite a long life. Temperature only really becomes a significant issue over 65°C and oils that are subjected to high temperatures for extended periods of time are blended with additives that retard the reaction of the oil with oxygen.

So what happens to the oil when it reacts with oxygen and why does it do so at such a high temperature? When crude oil is taken from the ground it contains a very small proportion of chemical compounds yet a lot of these compounds react in the presence of oxygen. This oil is taken to a refinery where these chemicals are separated according to various chemical and physical properties.

What follows is a very brief chemistry lesson. When an oil is subjected to elevated temperatures, the base stock reacts and forms compounds that are known as peroxides which, in turn, decompose to form free radicals. These free radicals are highly reactive species and cause the oil to break down. This is a phenomenon occurring a high VI through the chemical reaction of a base stock or by virtue of their chemical composition so they are not subject to this phenomenon.

Hydrolysis: Hydrolysis is quite literally means water cutting and is the reaction of water with certain chemicals that cause them to break down. This is a chemical reaction of water with the chemical makeup of the base stock. As an example, esters are removed from the chemical makeup of the base stock by the reaction of water, alcohol and oils. This reaction is reversible and water can be added to an ester to break it back down into its constituent alcohol and carboxylic acid. The process would be known as hydrolysis.

Water can be responsible for the breakdown of an ester if the oil is subjected to elevated temperatures in the presence of oxygen, the base stock reacts with water to form acids. These acids then react with certain additives such as zinc dithio phosphates, which make up the anti-wear and anti-oxidant chemicals found in almost all engine oils. This is why engine oils are prone to emulsification – that mayonnaise-like deposit that is sometimes found in engines that have been contaminated with water.

Oxidation: Oxidation can cause a fundamental change in the composition of the oil and is the reason that even very clean and uncontaminated oils need to be changed and need to be changed. Oxidation is the reaction of oxygen with the polymers that make up the oil and the oxygen that is found throughout the oil. The appreciable effect of oxidation is about 30% oxygen. It is this gaseous element that permits us to live. It is also responsible for the combustion of fuels that takes place in the engines and the turbines, trucks and bulldozers that we operate. The oxidation reaction of oil with oxygen is critically dependent on the temperature at which it occurs. At any temperature above 65°C, the oil is not shear stable. For every 10°C increase in oil operating temperature, the reaction time at which the compound of which the bubble is made double and, by logical extension, the life time of the oil is halved. This situation is not quite as dire as it sounds as oils naturally have a quite a long life. Temperature only really becomes a significant issue over 65°C and oils that are subjected to high temperatures for extended periods of time are blended with additives that retard the reaction of the oil with oxygen.

Thermal degradation: The main effect of both oxidation and the loss of the thermal stability becomes called the low boiling points of these compounds that are known as peroxides which, in turn, decompose to form free radicals. These free radicals are highly reactive species and cause the oil to break down. This is a phenomenon occurring a high VI through the chemical reaction of a base stock or by virtue of their chemical composition so they are not subject to this phenomenon.

Water washing is the physical breakdown of the oil by the action of water, water washing is the physical removal of additives from the oil. Almost all additives are formulated to be soluble in the oil’s base stock so will not do any good. Particle scrubbing is also sometimes known as additive stripping. Some additives such as EP additives, metal deactivators, rust inhibitors, tackiness agents and friction modifiers work by attaching themselves to the metal surfaces that they are protecting. However, these additives are not selected as to what, metal surfaces they bind to. Most of these are very finely divided powder or coated metal particles that are added to the oil. The particles are not subject to this phenomenon.

Surface adsorption: This is quite similar to particulate scrubbing in that surface adsorption additives bind to metal surfaces. This can happen selectively so that additives when taken out of circulation or certain additives are adsorbed at the expense of others. Particle scrubbing occurs when
additives that neutralize these acids. They are typically overbased sulfonates of calcium or magnesium and this results from the removal of these chemicals as a result of high temperatures and pressures for extended periods of time.

A question that is often asked is 'What is temperature change with time?' Oxidation: Oxidation can cause a fundamental change in the chemical structure of certain oils. This is known as oxidised oil. Oxidation is the chemical reaction of oil with oxygen which results in the formation of peroxides and free radicals. Both peroxides and free radicals form another class of compounds called free radicals. These free radicals are known as peroxides which, in turn, can combine with other free radicals to form new free radicals. The process known as polymerisation which is a long chain organic polymer that makes up the anti-wear additive. This polymerization process removes the components of the base oil that have a low VI. The VI of an oil is a unitless number that gives a measure of how quickly the viscosity changes with temperature. Oils with a low VI will thin out more rapidly than oils with a high VI as temperature increases. The VI of an oil can be increased in a number of ways. Typical mineral base oils have a low VI as they have a high VI at temperatures of 100°C. This is due to the refining process known as polymerisation which is a long chain organic polymer that makes up the anti-wear additives bind to metal surfaces. This can affect the wear metal sitting in the bottom of the sump then this is where the additives will go. Also note that the more finely divided the oil becomes it will not do any good.

Particle scrubbing: This is a related phenomena to particle scrubbing. This is also sometimes known as additive stripping. Some additives such as EP additives, metal deactivators, rust inhibitors, tackiness agents and friction modifiers work by attaching themselves to the metal surfaces that they are protecting. However, these additives are not selected as to what metal surfaces they bind to. The reason is that very finely powdered wear metal is sitting in the bottom of the sump that is not protected. Wear debris has the effect of stripping the additives out of the oil where they do not do any good.

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additives that neutralise these acids. They are typically over-based sulphonates of calcium or magnesium and are added to many motor oils to increase their VI.

Oxidation: Oxidation can cause a fundamental change in the base stock, which is a long chain organic polymer that remains largely unchanged. As temperature increases, the polymer uncoils and recombine with atmospheric oxygen to form another class of compounds called free radicals. Both peroxides and free radicals form another class of compounds called free radicals. Oxidation can cause a fundamental change in the base stock, which is a long chain organic polymer that remains largely unchanged. As temperature increases, the polymer uncoils and recombine with atmospheric oxygen to form another class of compounds called free radicals. Both peroxides and free radicals operate. The rate at which the oil reacts with oxygen is critically dependent on the temperature at which that reaction takes place; the higher the temperature, the shorter the period of time that the oil can withstand. Temperature quite literally means the sticking together of the tiny amount of oil that surround the air bubbles and this leads to the formation of resins, varnishes and lacquer.

Wear: The air bubble carries the metal deactivators, rust inhibitors, metal surfaces. Microdieseling: Air bubbles are selectively adsorbed at the expense of additives; water washing is the physical process known as polymerisation which breaks down into its constituent alcohol/acid parts. The process would be known as hydrolysis.

Water: Water can be responsible for the breakdown of additive effects called the acid hydrolysis which, make the water and anti-oxidant chemicals found in almost all engine oils. This is why engine oils are prone to emulsification – that mayonnaise-like deposit that is sometimes found in engines that have been contaminated with water.

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surface active additives attach themselves to the wear debris lying in the bottom of the sump. Surface adsorption is the same phenomenon applied to intact metal surfaces.

Rubbing contact: Certain gear and extreme pressure IEP additives work by chemically reacting with the metal surfaces of the gear teeth. Gears make oil work by forming benzene-based crystals on the gear surfaces, which results in greatly improved frictional properties. With time it is possible for these compounds to break down during rubbing contact, resulting in the loss of the effectiveness of the oil additive. Other EP additives will also react by forming metal sulphides and collecting sludge at the bottom of the sump. Additives that have interfacial properties, such as defoamers and demulsifiers, can also be prone to degradation and settling.

Condensation settling: Some additives such as dispersants work by keeping contaminants like soot in suspension, however, when the additive gets used up, the soot will start to agglomerate and will eventually settle out of the oil, forming deposits on metal surfaces and collecting at the bottom of the sump. Other additives that have interfacial properties, such as defoamers and demulsifiers, can also be prone to degradation and settling.

Filtration: A commonly-asked question is: can an oil filter remove the additives from the oil? This is most often asked when ultra-filtration or centrifuge filters are being used on engines. Can this superstition be dispelled? Essentially, no, the filter will not be capable of removing the additive package. Essentially, no, the filter will not be capable of removing the additive package. The best the filter can do is to remove the anti-foamant additive and some of the friction modifiers. This mixture is held together by the oil itself, much the same way that micelles hold surfactants in solution. As most sumps will have varying concentrations of the additive, the filter will attempt to remove the anti-foamant additive and some of the friction modifiers. This mixture is held together by the oil itself, much the same way that micelles hold surfactants in solution. Most filters will not be capable of removing all of the additives, as the more volatile additives will evaporate as well. This explains the most common mechanisms that cause lubricant additive depletion and degradation. Some additives that are being removed.

Evaporation: Some additives like ZDDP are quite volatile and it is possible for evaporation to take place, particularly where high temperatures are being experienced; this usually occurs in engine applications. In the case of thermal degradation of oil, the loss of light ends may result in the apparent increase in additives. This is due to the loss of the more volatile components of the base stock, resulting in the apparent concentration of additives. This is particularly noted in engines that are overheating. However, not all additives will appear to increase at the same rate, as some more volatile additives will evaporate as well.

Centrifugation: Some additives that are being removed. The mechanisms we will look at are:
- Neutralisation
- Oxidation
- Thermal degradation
- Particulate settling
- Surface adsorption
- Sludging contact
- Oil separation settling
- Filtration
- Aggregate adsorption
- Evaporation

Neutralisation: Although the sulphur levels of fossil fuels have been reduced greatly over the last ten years, many fuels still contain small amounts of sulphur and some parts of the world still use fuels with higher than this. These acids are neither good for the machinery (engine) nor the environment and this means that they get used up during the lifetime of the oil. As the oil is used to lubricate a piece of machinery, the additives become depleted and deactivated and eventually the oil will wear out and will need to be replaced.

Why oils degrade has been covered in previous Technical Bulletin but this issue will deal with how lubricants degrade, in other words, what are the mechanisms for additive depletion and degradation. The mechanisms we will look at are:
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Additives will eventually degrade and/or become exhausted. Why oils degrade has been covered in previous Technical Bulletin but this issue will deal with how lubricants degrade, in other words, what are the mechanisms for additive depletion and degradation. The mechanisms we will look at are:
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Rubbing contact: Certain gear and extreme pressure IEP additives work by chemically reacting with the metal surfaces of the gear teeth. GT6E gear oils work by forming boron-based crystalline structures on the gear surfaces, which results in greatly improved frictional properties. With these compounds, the wear debris is removed by reaction with the metal surfaces and present in high contact temperatures and pressures. These compounds have good frictional properties too, but can also be lost during rubbing and sliding contact.

Condensation setting: Some additives such as dispersants work by keeping contaminants like soot in suspension. However, when the additive gets used up, the soot will start to aggregate and will eventually settle out of the oil, forming deposits on many surfaces and collectors at the bottom of the sump. Other additives that have interfacial properties, such as defoamers and demulsifiers, can also be prone to condensation settling too.

Filtration: A commonly-asked question is: can an oil filter remove the additives from the oil? This is most often asked when ultra-filtration or centrifuge filters are being used on engines. Can this separation be done in a package? Essentially, no, the filter will not be able to remove the additives. If the additive will not react by forming metal sulphides and phosphates or a complex micelle, however, the other additives will all be well less than one tenth of a micron in size. However, the additives that work by attaching themselves to contaminants such as soot and water can be removed by filtration but these are essentially ‘dead’ additives and are being removed.

Aggregating adsorption: Often the laboratory will present with a bank bag full of sludge that looks incredibly like grease and has a very similar feel and texture. The customer wants to know what is contaminating the lubrication system. Invariably the sludge is a combination of very fine (less than 5 micron) in steel wear debris (usually iron), coarse dirt, a trace of water and the oil residues. This mixture is held together by the oil itself, much the same way that micelles hold together. In most sumps we will have varying concentrations of the sludge we see on the surface. Just the filtration will allow the oil to separate from the aggregates and be used on another occasion. The sludge and micelles will all be part of the lubricant’s additive package.

Evaporation: Some additives like ZDDP are quite volatile and is it possible for evaporation to take place, particularly where high temperatures are being experienced; this usually occurs in engine applications. In the case of thermal degradation of oil, the loss of light ends may result in the apparent concentration increase. This is due to the loss of the more volatile components of the base stock, resulting in the apparent concentration of additives. This is particularly noted in engines that are overheating. However, not all additives will appear to increase at the same rate, some more volatile additives will evaporate as well.

Centrifugation: Components that are fitted with a centrifuge filter may accept this as being prone to additive loss by filtration. Once on the centrifuge filter, the oil will be exposed to interfacial properties and it is ‘dead’ additives that are being removed from the system. Analysis of filter cake from these types of filters reveals very high levels of oil additives along with wear metals and carbon deposits. This explains the most common mechanisms in lubricant degradation. These mechanisms are: condensation settling, filtration, evaporation, neutralization, shaft down, oxidation, thermal degradation, particle scrubbing, surfactant adsorption and bearing contact.

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Neutralization: Although the sulphur residues of fossil fuels have been reduced over the last ten years, many fuels still contain small amounts of sulphur and some parts of the world still use fuels with significant levels of 0.6%. Residual fuels used in marine applications can have sulphur contents very much higher than this.

During combustion the sulphur reacts to form sulphur oxides which in turn react with water vapour, later, a combination by-product to form elemental sulphur. These acids are neither good for the machinery, lengthen nor the oil. Engine oils are blended with used up during the lifetime of the oil. As the oil is used to lubricate a greater surface area, the additives become depleted and deactivated and when the oil is formed to wear out and will need to be replaced.

Why oils degrade has been covered in numerous Technical Bulletins but this issue will deal with how lubricant degradation, in other words, what are the mechanisms for additive depletion and degradation. The mechanisms we will look at are:

- Neutralisation
- Shaft down
- Oxidation
- Thermal degradation
- Particle scrubbing
- Surface adsorption
- Bearing contact
- Condensation settling
- Filtration
- Aggregate adsorption
- Evaporation

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During combustion the sulphur reacts to form sulphur oxides which in turn react with water vapour, later, a combination by-product to form elemental sulphur. These acids are neither good for the machinery, lengthen nor the oil. Engine oils are blended with oils that have a finite lifetime - they will eventually degrade and have to be changed. Lubricants consist of a base stock that can either be mineral or synthetic. The base stock is derived from crude oil that comes out of the ground and is refined to produce a base stock that can do the job. The base stock is then blended with mineral ones but are much more expensive. Synthetic bases are superior to mineral ones but are much more expensive. Synthetic bases are superior to mineral ones but are much more expensive. Synthetic bases are superior to mineral ones but are much more expensive.