



HOW DO OILS DEGRADE?

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Oils have a finite lifetime - they will eventually degrade and/or become contaminated and will need to be changed. Lubricants consist of a base stock that can either be mineral or synthetic. In the case of synthetic base stocks, these are a family of compounds that are manufactured in a laboratory to have precisely the properties that the chemists and engineers want. Mineral base stocks are derived from crude oil that comes out of the ground and is refined to produce a base stock that can do the desired job. Synthetic bases are superior to mineral ones but are much more expensive.

The other component of a lubricant is the additive package. This is a range of twenty or more chemicals that the refinery blends with the base stock so that it can do its job. Most additives are sacrificial in nature 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 numerous Technical Bulletins 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:

- ◆ Neutralisation
- ◆ Shear down
- ◆ Hydrolysis
- ◆ Oxidation
- ◆ Thermal degradation
- ◆ Water washing
- ◆ Particle scrubbing
- ◆ Surface adsorption
- ◆ Rubbing contact
- ◆ Condensation settling
- ◆ Filtration
- ◆ Aggregate adsorption
- ◆ Evaporation
- ◆ Centrifugation

Neutralisation: Although the sulphur levels of fossil fuels have been reduced dramatically over the last ten years, many fuels still contain small amounts of sulphur and some parts of the world still use fuels with sulphur in excess of 0.5%. Residual fuels used in marine applications can have sulphur contents very much higher than this.

During combustion the sulphur is oxidised to form sulphur oxides which in turn react with water vapour (also a combustion by-product) to form sulphur acids. These acids are neither good for the machinery (engine) nor the oil. Engine oils are blended with

additives that neutralise these acids. They are typically over-based sulphonates of calcium or magnesium and this is where these results come from on an oil analysis report.

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

Nitrogen fixation from the atmosphere can generate nitrogen-based acids through a 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.



A technician testing oil samples for neutralisation additives

Shear down: it is vitally important that the temperature at which viscosity is measured be noted, as viscosity changes with temperature. As temperature increases, the viscosity decreases. To further complicate matters, different oils thin out at different rates as the temperature increases. This introduces the concept of a viscosity index or VI. The VI of an oil is a unitless number that gives a measure of how quickly the viscosity will change with temperature. Oils with a low VI will thin out more rapidly than oils with a

higher VI as temperature increases.

The VI of an oil can be increased in a number of ways. Typical mineral multigrade oils have an additive, VII or viscosity index improver, which is a long chain organic polymer that remains tightly curled up when it is cold. As the temperature increases the polymers uncoil and retard the thinning action of the increase in temperature. Very highly refined mineral oils have a naturally high VI as the refining process removes the components of the crude oil that have poor VI properties.

Unfortunately these long organic polymers that uncoil when the oil heats up are not completely shear stable. This means that when the compounds are subjected to high shearing forces, such as may be encountered in an automatic transmission, they start to break up, resulting in a permanent viscosity loss. Oils that achieve a high VI through the refining process or by virtue of their synthetic base stock are not subject to this phenomenon.

Hydrolysis: Hydrolysis quite literally means 'water cutting' and is the reaction of water with certain additives that cause them to break down. This is a chemical reaction of water that alters the chemical make-up of the additive or base stock. As an example, esters are formed by the chemical reaction of an acid with an alcohol and the subsequent loss of a water molecule.

This reaction is reversible and water can be added to an ester to break it back down into its constituent alcohol/acid parts. The process would be known as hydrolysis.

Water can be responsible for the breakdown of ester-based synthetic base stocks but can also react with additives such as zinc dithio diphosphate, 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 base stock of the oil and is the reason that even very clean and well-maintained oils eventually wear out and need to be changed. Oxidation is the reaction between the oil's base stock (and its additives) and the oxygen that is found in the atmosphere. The air that we breathe is about 20% oxygen. It is this gaseous element that permits us to live on planet earth and is also responsible for the combustion of fuels that takes place in the cars we drive and the buses, trucks and bulldozers that we 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 faster the oil will oxidise.

For every 10°C increase in oil operating temperature, the rate at which the oil oxidises is doubled 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 quite a long life time. Temperature really only 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 much damage? When crude oil is taken from the ground it contains many, many different chemical compounds yet a lot of these chemicals are closely related. The crude 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 in the presence of oxygen, the base stock reacts and forms compounds that are known as peroxides which, in turn, form another class of compounds called free radicals. Both peroxides and free radicals are highly reactive species and cause the formation of acids and sludge and make the viscosity of the oil increase. This increase in viscosity of the oil is due to another chemical process known as polymerisation which simply means the sticking together of the smaller fractions of the base stock to form fractions of larger chemicals which have

higher boiling points and higher viscosities.

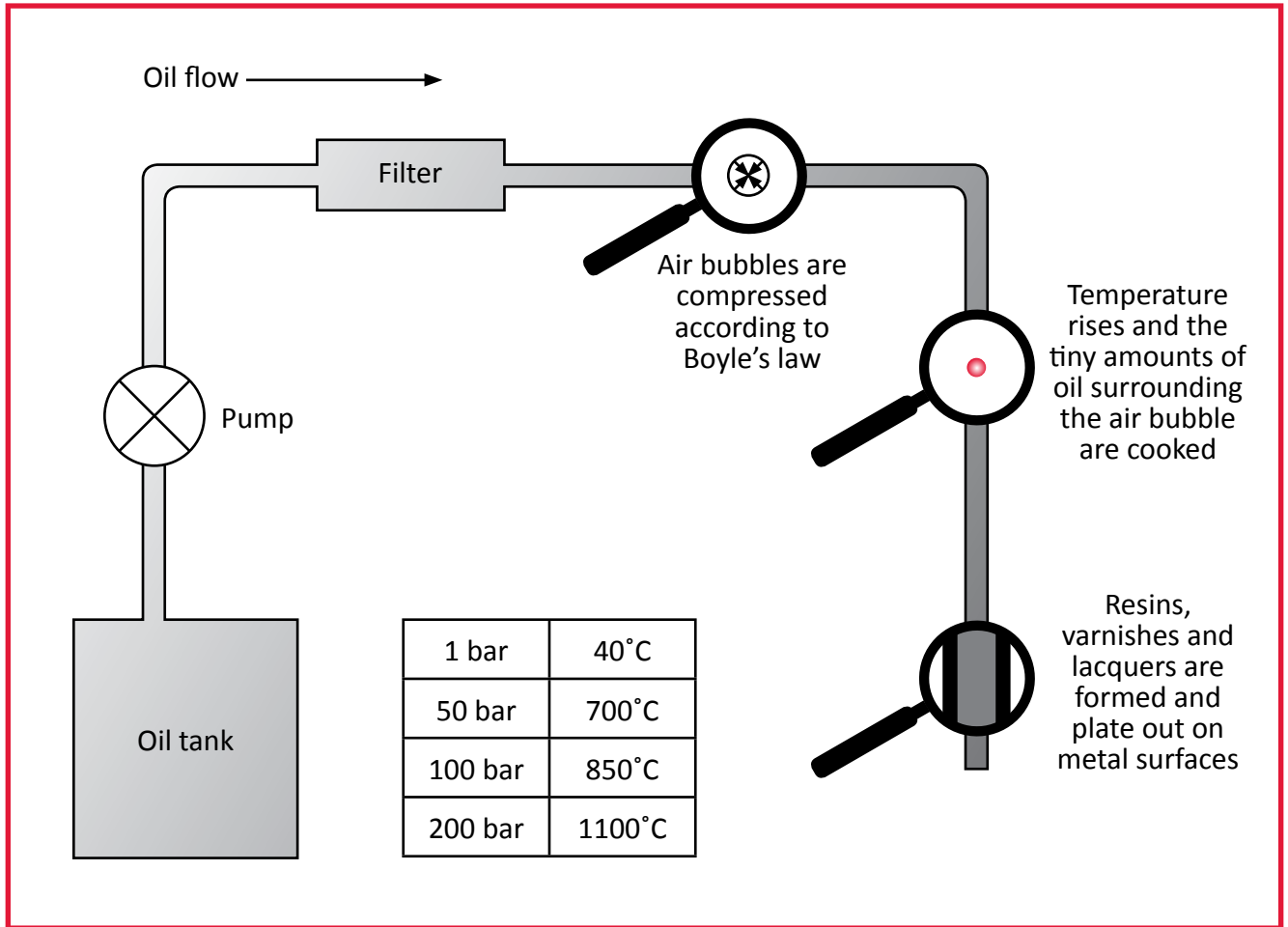
A question that is often asked is 'What is the maximum temperature that this oil can withstand?' Unfortunately there is no answer as the lifetime of the oil is not only dependent on operating temperature but time as well. So, what we need to know is, how hot and for how long? An engine oil might happily deal with 150°C for an hour or so but degrade severely at 100°C over a longer period of time.



An engine oil sample with a very high viscosity due to overheating

Thermal degradation: The main effect of both oxidation and the loss of the thermal stability (sometimes called the loss of light ends) is an increase in viscosity. Increased viscosity can result in oil pump cavitation, poor fluidity on start-up, increased energy consumption and the reduction of the oil's ability to shed water and release air. Poor fluidity, due to increased viscosity and cold starts, is when the majority of engine wear takes place.

Another phenomenon that is related to overheating and can result in oil degradation is micro-dieseling. Air can exist in oil in four forms, dissolved, entrained, foam and free. It is the microscopic bubbles of entrained air that cause the problem. These bubbles can be compressed, according to Boyle's law, to very high pressures which, in turn, can create



Microdieseling

very high temperatures on a microscopic scale. These high temperatures can actually burn the tiny amounts of oil that surround the air bubbles and this leads to the formation of resins, varnishes and lacquers.

Water washing: Whereas hydrolysis involves the chemical 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 have limited solubility in aqueous (water) solutions. However, some additives are selectively soluble in water; this means that some of the additives can become dissolved in the water which will cause them to be removed from the oil. As water is not generally soluble in oil in high concentrations, this process results in the water washing of additives from the oil. Hydrolysis is the chemical degradation of additives; water washing is the physical depletion.

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 selective as to what metal surfaces they bind to. If there is a lot of very finely powdered wear metal sitting in the bottom of the sump then this is where the additives will go. Also note that the more finely divided a mass is, the greater its surface area. Wear debris has the effect of stripping the additives out of the oil where they do not do any good.

Surface adsorption: This is quite similar to particle scrubbing in that surface active additives bind to metal surfaces. This can happen selectively so that additives are taken out of circulation or certain additives are selectively adsorbed at the expense of others. Particle scrubbing occurs when

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 (EP) additives work by chemically reacting with the metal surfaces of the gear teeth. Borate 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 that contain sulphur and phosphorus react by forming metal sulphides and phosphides on the gear surface under the high contact temperatures and pressures encountered. These compounds have good frictional properties too, but can also be lost during rubbing and sliding contact.

Condensation settling: Some additives such as dispersants work by keeping contaminants like soot in suspension, however, when the additives get 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 defoamants 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 centrifugal filters are being used on engines. Can this super-fine filtration damage the oil additive package? Essentially, no, the filter will not remove additives. It is possible for a filter to remove the anti-foamant additive as the molecules are quite big and can form micelles, however, the other additives will all be well less than one tenth of a micron



Sludge like this is often found at the bottom of many sumps

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 that are being removed.

Aggregate adsorption: Often the laboratory will be presented 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 size) wear debris (usually iron), coarse dirt, a trace of water and some oil residues. This mixture is held together by the oil itself, much the same way that milk might hold flour together in a batter. The bottom of most sumps will have varying concentrations of this sludge and surface active additives will be attracted to these aggregates and be removed or stripped from the oil. The oil residues will also be part of the lubricant's additive package.

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 the more volatile additives will evaporate as well.

Centrifugation: Components that are fitted with centrifugal filters, usually engines, may be prone to additive loss by filtration. Once again, these will tend to be additives that have 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 contaminants.

This explains the most common mechanisms that cause lubricant additive depletion and degradation. As can be seen, the process is quite complex and there are many competing mechanisms that are taking place at the same time. Lubrication technology is very intricate and each can of oil is a very delicate and sophisticated blend of many chemicals that all have very specific jobs to do. The base stock is also an elaborate mix of compounds. Additives can often compete with each other for active sites in an attempt to do the jobs that are required of them. Likewise, the degradation of the oil is also a complex web with many competing processes taking place at the same time. Even the best oil, in the best equipment, operating in an ideal environment with perfect maintenance practices will eventually degrade, wear out and need to be changed.

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