WEAR CHECK AFRICA
A member of the Set Point group

TECHNICAL BULLETIN
ISSUE 40

WEARCHECK
CONDITION MONITORING
THROUGH OIL ANALYSIS

IF YOU CAN'T STAND THE HEAT . . .

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Earlier this year we published a Technical Bulletin on the ups and downs of viscosity. This was an important topic to cover as the viscosity of an oil is its most fundamentally important property. Both physical and chemical degradation can cause a change in the viscosity of an oil and, in terms of an increase in viscosity, poor combustion and sludging have been covered extensively in a number of Technical Bulletins. This Technical Bulletin will deal with high temperature operation and the effect it has on the rate of oxidation and, in turn, the degradation of lubricating oils and consequent increase in their viscosity.

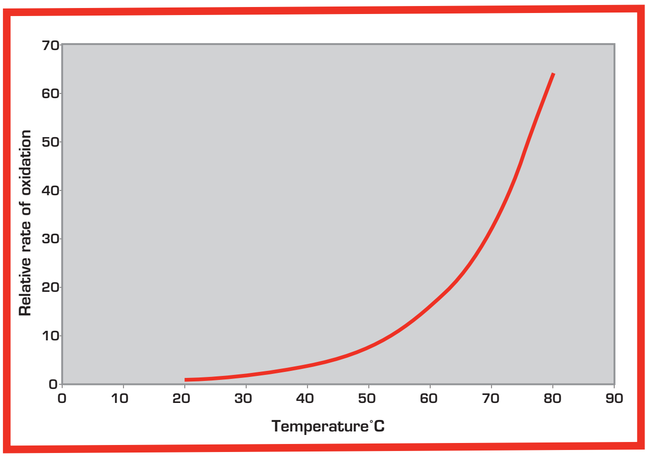
Oils do not last for ever but with the right base stock, carefully blended additive package, correct usage, clean environment and good maintenance practices, an oil can last for a very, very long time. However, even in an ideal situation, the oil will eventually wear out and the most common cause for this is high temperature operation or the oil being subjected to heat over an extended period of time which might, in itself, not even amount to overheating.

Lubricants can certainly be declared unfit for further use due to the presence of external contaminants, dirt and water being the most common and destructive examples. Internal contaminants such as wear debris and combustion by-products are also very destructive to both the component and the oil. Oil additives are, by their nature, sacrificial and eventually wear out or get used up and the loss of such additive activity can signal that an oil needs to be changed due to lubricant degradation.

CAUSES OF OVERHEATING

However, it is oxidation that 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 and take oil samples from. 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 lifetime of the oil is halved. This situation is not quite as dire as it sounds as oils naturally have quite a long lifetime. 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. The graph below illustrates the relationship between temperature and oxidation.

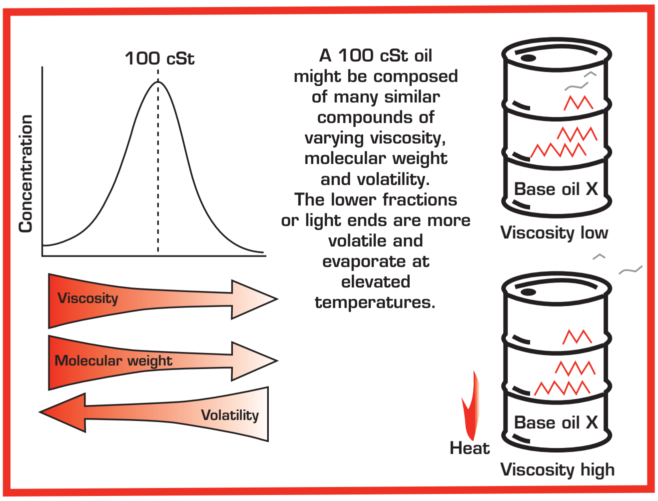


Oxidative stability

PROBLEMS CAUSED BY OVERHEATING

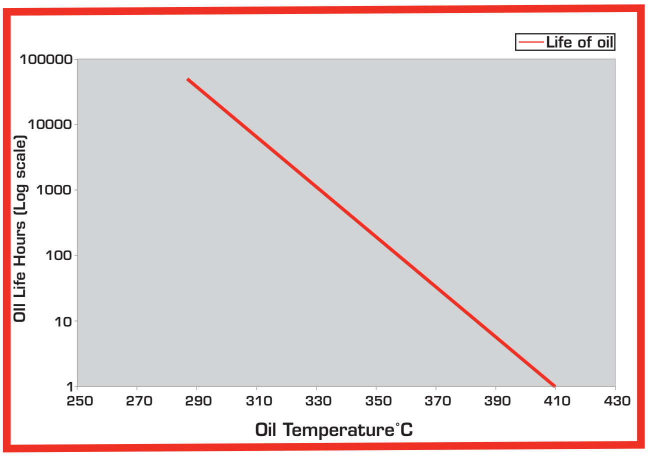
So what happens to the oil when it reacts with oxygen and why does it do so much damage? When crude oil is taken from the ground it contains many, many different chemical compounds, yet a lot of these chemicals are closely related. The crude oil is taken to a refinery where the chemicals are separated according to various chemical and physical properties. A barrel of crude may contain the components that make up the gas you use in your skottel braai, petrol, paraffin, diesel, hydraulic oil, engine oil, gear oil and even the tar you find on the roads. All these different fractions belong to the same class of chemicals and are separated on the basis of volatility or boiling point. Even a highly refined engine oil will contain a narrow range of these compounds.

What follows is the first of two very brief chemistry lessons. 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 the 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 that have higher boiling points and higher viscosities.



Volatility

The ability of an oil to resist oxidation is known as its oxidative stability, as shown in the graph on the left. However, the viscosity of an oil can increase in the presence of heat but without oxygen actually being present - this is known as thermal stability. As shown above, the lighter fractions have lower boiling points and are therefore more volatile. If the oil is subjected to high temperatures in the absence of oxygen then the lighter fractions can evaporate and the nett effect is an increase in viscosity without the oil actually being oxidised. The graph below illustrates this.



Thermal stability

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 will degrade severely at 100°C over a longer period of time.

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 problem of high viscosity is a reduced ability of the oil to act as a coolant. A lubricant has many functions but some of the main ones are to reduce friction and wear, remove contaminants, behave as a structural material, transmit power and act as a coolant. It is the loss of this last feature that can set up both a vicious and a viscous circle. The oil is expected to flow freely in order to disperse and remove frictional and operational heat. If a small amount of overheating results in a slight increase in viscosity, then the oil is less able to act as coolant due to the increased viscosity and reduced fluidity. This, in turn, results in slightly more overheating which, in turn, results in more problems, creating a domino effect. The degradation of the oil in the picture below can occur in a surprisingly short period of time.

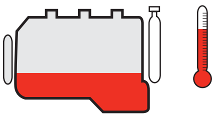
Sludge

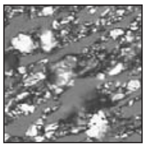
So what actually happens to the oil when subjected to high temperature operation? The results are:

- an increase in viscosity as already discussed either due to oxidation, polymerisation or the loss of light ends
- an increase in acidity and, in turn, a reduction in Total Base Number as well as an increase in wear readings due to the loss of fluidity and an increase in acidity.

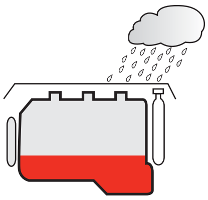
But it is not just high temperatures and the length of time that the oil is subjected to this that can cause oxidation and an increase in viscosity; there are quite a few factors that can exacerbate the situation.

The presence of air, water and wear metals can all accelerate the rate of oxidation and oil degradation along with an increase in acidity. Both air and water can act as a ready source of oxygen and wear metals such as iron and copper can have a catalytic effect on the rate of oxidation. The illustration below shows the effect of temperature, water, air and wear debris on oxidation and acid formation rates.





Catalyst	Acid number
None	Low
Iron	Moderate
Copper	Moderate
Copper + water	Very high

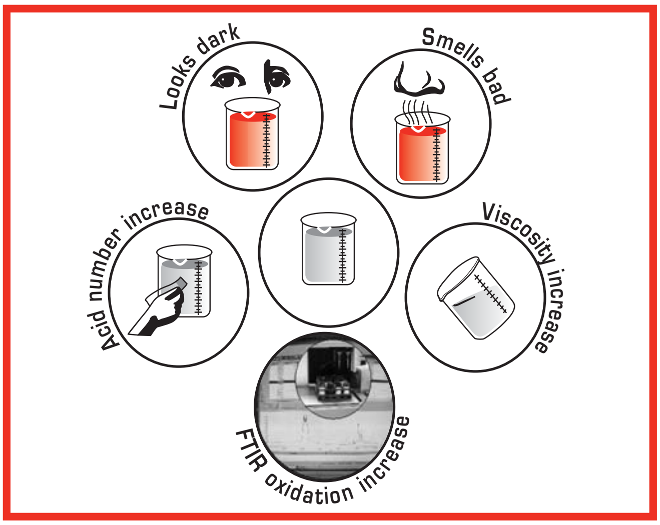


% Air	Relative acid number
0	0,10
3	0,15
6	0,25
9	0,50
12	0,60

Catalytic effects

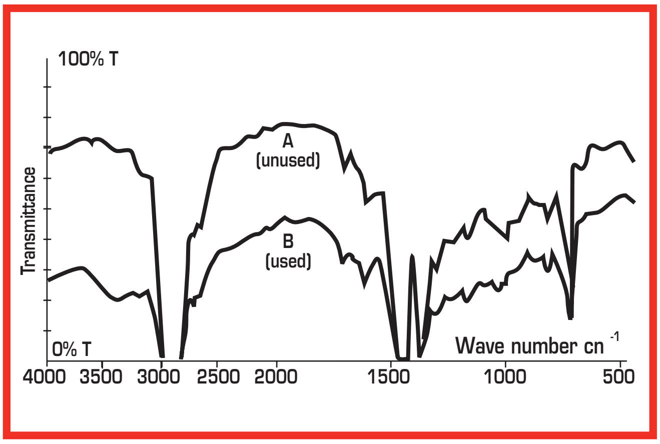
DETECTING OVERHEATING

We have already determined the causes of overheating and the problems it creates but how do we look for the clues that this process is taking place? Surprisingly, some of the answers do not require a fancy laboratory at all. We have already noted that the viscosity of the oil will increase and this can sometimes be quite visible but at the same time the oil will darken in colour and will take on a pungent, sour odour due to the formation of acids and higher molecular weight compounds. On a more scientific side, the percentage viscosity increase can be measured, as can the acidity. An instrument called the FTIR (Fourier Transform Infra Red) spectrometer can actually measure the amount of oxygen that has reacted with the oil.



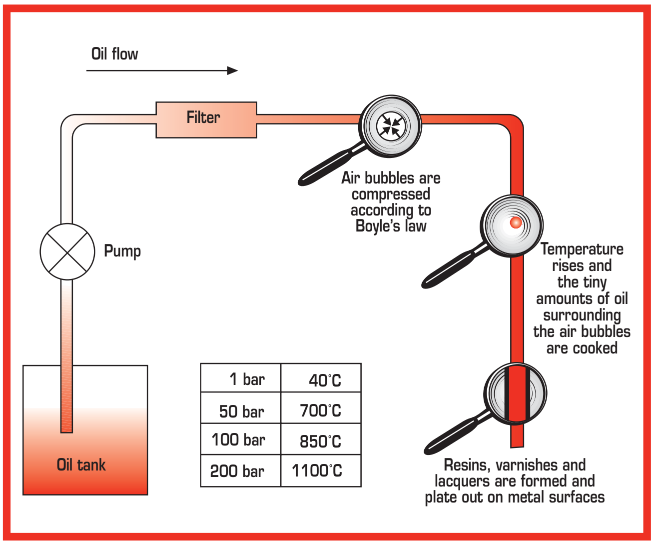
Detecting overheating

The operation of the FTIR has been covered in a number of other technical bulletins but basically a spectrum of new oil is compared with that of the used oil; oil that has reacted with oxygen gives a distinctively different signature to oil that has not.



Measuring oxidation

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 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. The diagram below illustrates what happens.

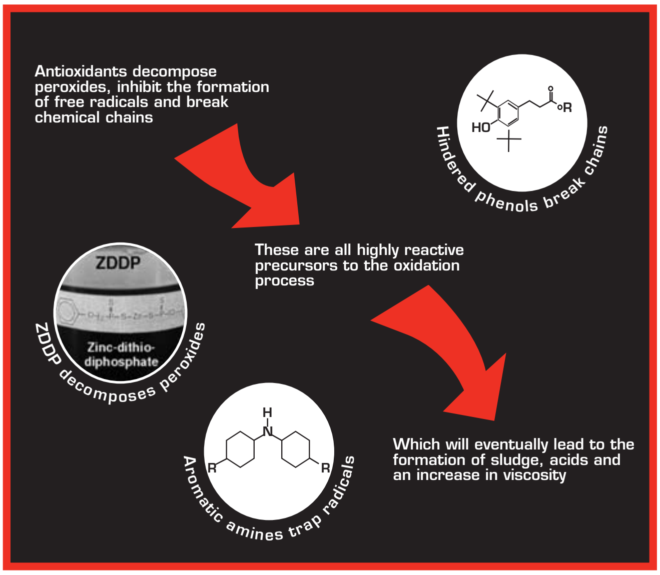


Micro-dieseling

LIMITING THE EFFECTS OF OXIDATION

This would appear to be a fairly grim picture that has been painted thus far but things are not as bad as all that. As has already been mentioned, oils have a reasonable resistance to oxidation and temperatures need to be relatively high in order to do serious damage. However, lubricants that are subjected to prolonged and elevated temperatures are blended with a series of chemicals called antioxidants that retard the effects of heat and the oil's reaction with oxygen.

Please bear with me whilst we have the second of our brief chemistry lessons. In our last lesson it was noted that oxidation causes the formation of peroxides and free radicals and at the same time the base stock starts to polymerise. Antioxidants fall into three broad classes of compounds: dithio-phosphates which decompose peroxides, aromatic amines that trap free radicals and hindered phenols that break the chains that lead to polymerisation. The end result is the postponement of the oil's oxidation and the extension of its useful life.



Antioxidants and how they work

It is interesting to note that the additive known as ZDDP (Zinc Dithio Di Phosphate) has been used in oils since the 1940s. It was originally developed as an anti-wear additive and it is very effective in doing that job but, as it turned out, it was also a very good antioxidant. The additive is still used extensively to this day as the chemists have struggled to find other additives that can do such a good job at such a reasonable cost - and that is the end of the chemistry lessons!

TROUBLESHOOTING

Now that we know what oxidation is, what causes it, what effects it has on the oil, how we can detect it and how we can limit its effects – we now need to know what we can do to troubleshoot an overheating problem should one exist. Simply changing the oil is not going to make the problem go away; the cause needs to be treated not the symptoms. In the spirit of an ISO 9000 corrective action report: troubleshoot the problem, trace the cause, eliminate it and ensure that it cannot happen again.

The following is a list of basic items to look at if an engine is experiencing overheating:

- Thermostats and radiator shutters
- Radiator fins and cores
- Water pump efficiency
- Coolant level
- Radiator pressure relief valve
- Fan and V belts
- Thermostatic fan
- Engine loading
- Cooling fins
- Engine cleanliness
- Water hoses
- Pressure test cooling system
- Oil cooler passages
- Air entrainment – oil and coolant
- Coolant capacity
- Coolant concentration
- Coolant activity
- Coolant mixtures

It is quite possible that the effects of overheating may be as a result of severe ambient conditions rather than a mechanical fault or a problem with the cooling system. Ambient temperatures in excess of 60°C are not unheard of and will degrade an oil very quickly. In situations such as this, reducing the oil drain period may be one solution. It may also help to increase the oil sump capacity, which will result in more anti-oxidant chemicals being present to do the same job, to increase the capacity of the cooling system or to introduce an oil cooler.

THE CASE FOR SYNTHETIC OILS

So, if you can't stand the heat... (a saying sometimes attributed to President Harry S Truman) ... then the other solution in situations such as this would be to use a synthetic rather than a mineral oil. Mineral oils are produced by refining crude oil to achieve just the right fractions or base stock to do a particular job and are enhanced by the addition of additives. This process, however, is not perfect and some undesirable components get left behind. Synthetic oils are designed by chemists in the laboratory to have all the necessary desired properties and none of the undesirable ones. Often excellent basic stocks are achieved even before the oil companies blend their additives in. The down side, of course, is that synthetic oils are more expensive than mineral oils but it is fairly easy to produce a synthetic base stock with a very high resistance to oxidation.

One of the advantages of using a synthetic lubricant is extended oil drain periods due to the excellent natural resistance to oxidation. On the other hand, extended oil drain periods that have led to severe oil degradation will have exactly the same effect on the oil as overheating.

Whatever the solution, one that works and is cost effective needs to be found because persistent overheating and the damage that it does to both the oil and directly to the engine, will eventually result in premature failure.

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