



# SOLIDS, LIQUIDS AND GASES

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In this bulletin we discuss solids, liquids and gases and how they relate to dirt, water and air - three of the most common contaminants found in oil. We look at what they are, what causes them, what damage they do, how we

detect them and how to prevent them from causing problems.

We were taught at school that there are three forms of matter: solids, liquids and gases. There is actually a fourth, plasma, but this form of matter is unlikely to be encountered on a daily basis. A plasma is a mass of charged particles or ions. Surprisingly, users of oil analysis are closer to coming in contact with a plasma than they may realise. The type of spectrometer that analyses oil for wear metals, contaminants and oil additives is known as an ICP or Inductively Coupled Plasma spectrometer. It is the very high temperatures achieved in the plasma that allow the atoms of iron or silicon, for example, to emit light of a characteristic frequency that can be measured and used to determine the concentration of the atom present in the oil.

I think that is enough physics for this bulletin so let us return to the three forms of matter that we are all familiar with: solids, liquids and gases. An ice block is a solid, if we warm it up a bit it will melt and turn into water which is a liquid and, if we heat it up even more, it will turn into steam which is a gas.

One of the biggest problems encountered in oil analysis is contamination and an oil contaminant can either be a solid, liquid or gas. This bulletin is going to look at one of each which make up the three most common contaminants found in oil: dirt, water and air. We are all familiar with dirt and water as contaminants but not everyone considers air as a problem, probably due to its somewhat ethereal nature.

## SOLID CONTAMINANTS

Let's start with the most common contaminant found in oil - dirt, sand, grit, dust, airborne dust, coarse dirt, soil or whatever you want to call it. It's that stuff you find in the garden or on the Durban beachfront. It is also very hard, very abrasive and very destructive, mechanically, if it gets into your oil. Good old road grit is harder than stainless steel.

Dust particles come in a wide array of sizes, from coarse dirt that we can see with the naked eye right down to sub-micron microscopic particles. A typical grain of sand will be about 500 microns or half a millimeter; dust from a cement factory might be about 5 micron in size. As a rough guide, the width of a human hair is about 50 microns.

Because dirt particles can be quite small they can become easily suspended in the oil - as we will see, it is the 10 to 20 micron sized particles that do the damage and these hardly ever settle out. What this means is that oil can very easily be turned into a grinding paste.

One might intuitively think that putting a handful of beach sand down the filler port on an engine might be an effective way of sabotaging the engine. Well, yes and no – the size of the dust particle is critical. The particle that will do the most damage is the particle with approximately the same width as the clearance between moving surfaces. Typically, in an engine, that will be between 10 and 20 micron or half to a quarter the width of a human hair.

Examples of clearances are given in the following chart:

Mechanical system	Typical clearance range
Ring to liner	0.3 – 7.0 micron
Big end bearings	0.5 – 20 micron
Main bearings	0.8 – 50 micron
Valve train	0.1 - 1.0 micron
Small end bearings	0.5 -15 micron
Gearing	0.1 -1.5 micron
Plain bearings	0.5 – 100 micron
Roller bearings	0.1 – 3.0 micron
Vane pumps	5.0 – 15 micron
Gear pumps	0.5 – 5.0 micron
Piston pumps	5.0 – 40 micron

This means that particles bigger than about 25 micron, in most cases, are too big to get between the moving surfaces to do any damage. Particles less than about 5 micron will sail right through the clearances without doing any damage at all. It is the particles that can get stuck between metal surfaces and cause three body abrasion that do all the damage. So, yes, a handful of beach sand may wreak havoc in an engine but the dirt would first need to be ground up to do really serious damage.

Fortunately, oil analysis has a number of ways of detecting dirt contamination. The chemical make-up of common or garden dirt is well established and it is usually a mixture of silicon and aluminium oxides. The ICP spectrometer mentioned in the opening paragraph of this bulletin can measure the amount of these elements in the oil easily and accurately. An increase in silicon is usually taken to indicate that dirt is getting into the oil. A word of caution here: dirt is not the only source of silicon

in an oil sample. The anti-foamant additive in the oil contains silicon as do silicone-based sealants and gaskets. Silicon is also found in the chemistry of coolants and is sometimes alloyed with aluminium to reduce the coefficient of expansion of pistons. For a rise in the silicon level to be caused by dirt entry it must be accompanied by a rise in aluminium, the other major component of dirt.

Particle counting can also be used to detect dirt entry, particularly coarse dirt. The particle counter shines a laser through the oil sample and particles cast shadows on a detector that can be counted. The instrument cannot distinguish between dirt and wear metals for example but once a high particle count has been noted, the oil can be filtered through a membrane and the remaining debris examined under a microscope. If dirt is found then corrective maintenance action can be taken before any serious wear takes place.

Although oil analysis is good at detecting dirt entry so that corrective action can be taken, it is far better to keep dirt out in the first place. It is a maintenance truism that it costs ten times as much to clean an oil that has become dirty than to keep the dirt out in the first place. Ensure that high quality breathers are used and that seals and gaskets are well maintained, treat all oil leaks as serious and be scrupulous with oil hygiene.

There are many other solid contaminants that can be found in oil such as soot, wear debris, process or environmental contaminants and oil residues. Dirt, however, is the most common and the most destructive.

## LIQUID CONTAMINANTS

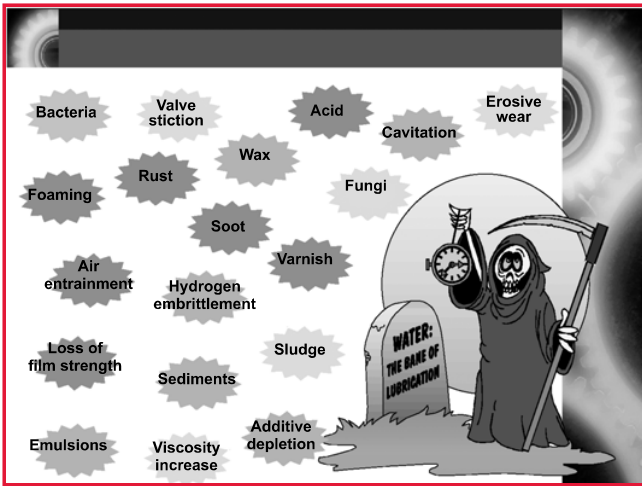
Let's move on to liquid contaminants. These could comprise coolants, fuels, greases, other oils and oil degradation by-products but by far and away the most common is water.

Water is both mechanically damaging in that it can cause corrosion or rust but it can also interact chemically with the oil causing it to break down in a process

known as hydrolysis. After dirt, water is the most common contaminant and most people are unaware of how aggressive water is, attacking both the machine and the lubricant. The following list shows how varied water's modes of attack are:

- Erosive wear
- Valve stiction
- Cavitation
- Corrosion
- Hydrogen embrittlement
- Sludge and soot deposits
- Additive depletion
- Viscosity increase
- Loss of film strength
- Acid formation
- Fungal and bacterial growth
- Wax deposits
- Emulsions
- Increase in air entrainment
- Foaming
- Sedimentation
- Additive precipitation

That's quite an impressive list of ways to do damage and all of them are fairly commonly encountered.



Water can enter a lubrication system in a number of ways such as contamination during top-up's or regular maintenance practices.

Oil compartments breathe so water may form as a condensate. Internal coolant leaks can occur in water cooled components. Washing or steam cleaning a component can introduce water into a system as can damaged seals, gaskets or breathers.

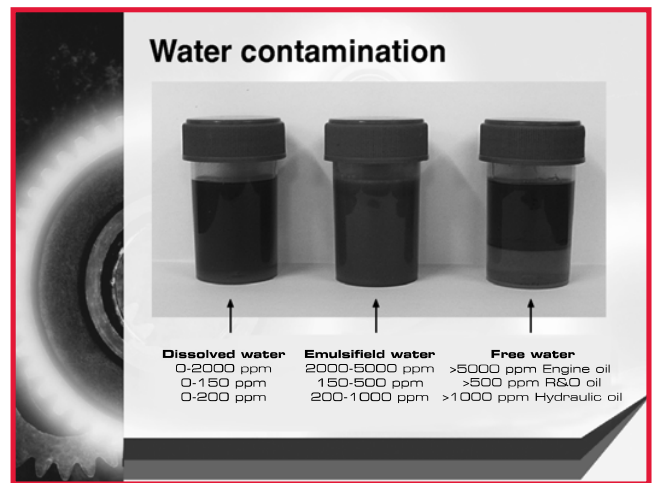
Remember, if oil can get out then dirt and water can get in; once again, treat all oil leaks as serious. Also, remember that no system is entirely sealed, if it were, then it would be impossible to take an oil sample!

I am sure you are familiar with the saying that oil and water don't mix. Well, that is only true up to a point. Very small amounts of water are capable of being dissolved in oil which means that water can exist in oil in three distinct forms: dissolved, emulsified and free.

The amount of water that can be dissolved in oil will depend on the type of oil, its additive chemistry, the age of the oil, its level of degradation and the number, type and concentration of contaminants - the chemistry is far from simple. The following chart gives an idea of how much water can dissolve in the different classes of oil:

Oil type	Dissolved	Emulsified	Free
Engine	Up to 2000 ppm	2000 – 5000 ppm	> 5000 ppm
Hydraulic	Up to 200 ppm	200 – 1000 ppm	> 1000 ppm
Gear	Up to 500 ppm	500 – 2000 ppm	> 2000 ppm
Turbine	Up to 150 ppm	150 – 500 ppm	> 500 ppm

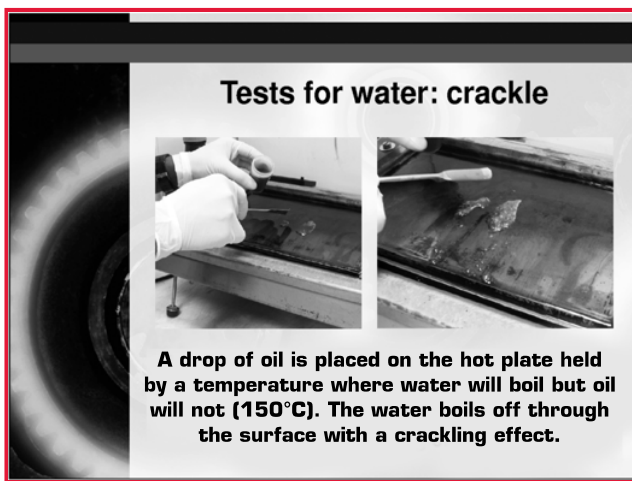
Note that 1 ppm is equivalent to 1/10 000th of one percent so that 1 000 ppm is 0.1%.



As with dirt, water contamination is very easily detected in an oil sample. Water may be destructive in many ways but it can also be detected in a variety of ways in the laboratory.

All samples are screened for water; we can do this because the screening tests are cheap, easy, quick and effective. All engine samples undergo FTIR (Fourier Transform Infra Red) analysis for the detection of combustion by-products and oil degradation. This test can also be used to screen for the presence of water as well as quantifying it. As the test gets done on all engine samples anyway the water screen is carried out at no extra cost, time or labour and has a detection limit of about 500 ppm. All molecules vibrate and the FTIR spectrometer works by measuring the frequency of these vibrations.

All other sample types are subjected to what is known as the crackle test. A few drops of oil are placed on a hot plate at about 150°C. At this temperature water will boil but oil will not, if there is any water present in the oil it will boil off through the surface of the oil, spitting and crackling as it does so. A good technician should be able to detect water down to 500 ppm (0.05%) and a lot of samples can be screened quickly, cheaply and accurately. This is also a test that can easily be done in the workshop.



Once a sample fails one of the screening tests, an actual water determination can be carried out. If the screening test indicates that the amount of water present is around 1% or less, the sample is subjected to a Karl Fischer titration. In this test the oil sample is heated to drive off any moisture in the oil. The vapours then enter a reaction vessel where they are automatically titrated against special reagents designed to detect

water. The instrument can then give a digital readout of the amount of water present. This instrument is astonishingly accurate and can measure water down to below 10 ppm (1/1 000th of 1%). For most industrial and automotive applications water is measured to an accuracy of 0.1% or 1 000 ppm and is reported accordingly. If greater accuracy is required this can be provided for with a special sample kit. Extra accuracy is important for refrigeration compressors and insulating oils.

If the screening test indicates that the amount of water present might be greater than 1% then an amount of the sample is weighed out and reacted with a chemical called calcium hydride. When this chemical comes in contact with water it reacts and releases hydrogen gas, the volume of which can be measured using a simple manometer and will be proportional to the amount of water present.

Finally, if the oil is grossly contaminated with water (>25%) then simply placing the sample in a measuring cylinder and measuring the height of the two layers will give a fair estimation of the amount of water present.

Note that some fire retardant oils are formulated with water present, usually at a level of around 40%. These oils look clear and there is no separation into oil and water layers. Measuring the amount of water in these lubricants actually gives an indication as to the health of the oil rather than the presence of water being a bad thing.

The same rules, practices and precautions apply to keeping water out as to keeping dirt out. One extra consideration might be the installation of desiccant breathers to remove water before it gets into the lubricated system.

## AIR CONTAMINATION

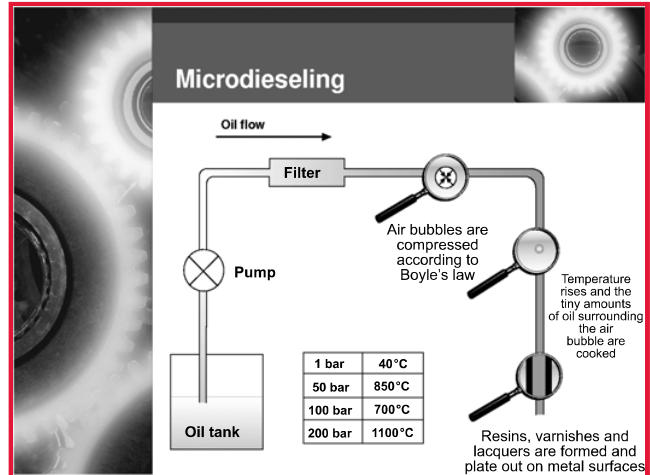
We now come to our last contaminant, air, which most people don't even think of as a contaminant. It can, however, be just as destructive as dirt or water.

Like water, air can exist in the lubricant in a number of ways: dissolved, entrained,

foam and free. Up to about 10% of an oil's volume may be due to dissolved air. This normally shouldn't be a cause for alarm but it may result in spongy operation of hydraulic systems. Entrained air, which is probably the most damaging, consists of tiny bubbles of air carried by the oil and often results in a cloudy appearance. Foam exists as a stable layer of larger air bubbles on the surface of the oil and can result in corrosion, vapour locks and high compressibility and may not be a problem in itself but may indicate excessive air entrainment. Foam may also make up as much as 30% of an oil's volume. Foam is often more of a cosmetic problem rather than a cause of mechanical distress. Free air is simply a large pocket of air trapped in a dead leg somewhere in the system and is not usually an indication of a problem but may contribute to corrosion and vapour locks.

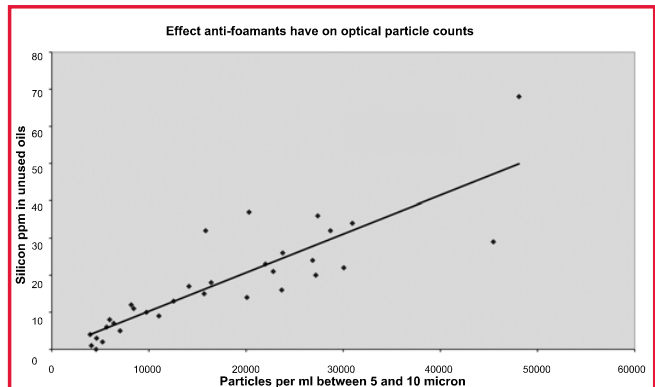
There are a number of causes of air contamination but probably the most common is the presence of water. The water lowers the surface tension of the oil, allowing air bubbles to separate into lower volume bubbles that are easily suspended in the oil. Other contaminants can have a similar effect, particularly very finely powdered particulates. Other causes include the loss or deactivation of anti-foamant additives, using the wrong viscosity oil for a particular application, poor reservoir design and perhaps the most common, suction line leaks.

Air entrainment can have a number of negative effects on the lubricating properties of the oil. Air contains oxygen so increasing the amount of air will increase the potential for oxidation of the oil. It can also increase the thermal degradation of the oil. Tiny air bubbles can be compressed by mechanical action to very small volumes which, in turn, generates very high temperatures. The tiny film of oil surrounding the air bubble will then char in a process called microdieseling that produces varnish. The presence of air also reduces the heat transfer properties of the oil, resulting in overheating. Air breaks down oil films, causing wear by displacing lubricant layers. As already mentioned, air contamination can result in poor hydraulic control. Certain oil mixtures can also result in air problems.



One of the most common anti-foamant additives is a chemical called poly-methylsiloxane (PMS). This chemical contains silicon, which explains why oil fresh out of the drum contains between 5 and 15 ppm silicon. This is not dirt but an additive blended into the oil by the oil company. It is important to note that this compound is added in vanishingly small quantities in order to do its job, just 10 ppm. It is also important to note that overdosing with this additive can actually cause air release problems. This is one of those additives that have to be just right.

PMS has a very high molecular weight and can form groups of molecules called micelles. This results in what is sometimes called the 'fish eye effect' and the additive can actually be detected by the particle counter. The following graph shows a clear correlation between the 5-10 micron particle count and the amount of silicon in a selection of oils taken from our new oils library. It is also the only additive that has the potential to be removed from the oil by ultra-fine filtration.

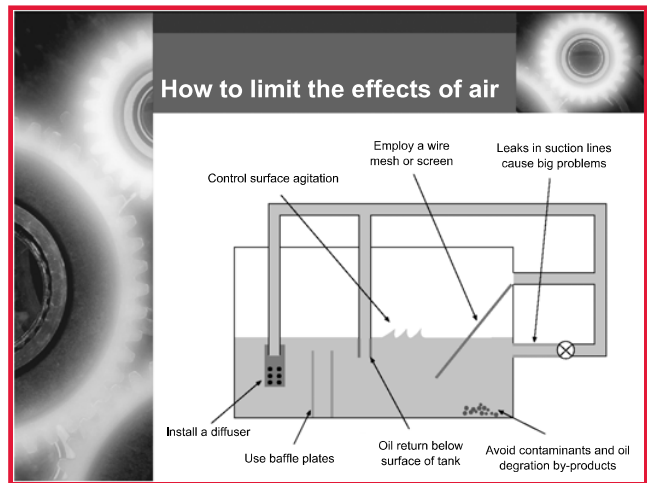


PMS has a very low surface tension and is what is known as a surfactant. It attaches itself to the air-oil interface and causes it to break down, causing the foam to collapse. If overdosing occurs then many of these large molecules attach themselves to the air bubbles and cause them to sink in the oil, resulting in poor air release properties.

When foaming or air entrainment occurs, there is a knee jerk reaction to blame the oil rather than look for contamination or a mechanical source of the problem. Invariably the cause is either water or a suction line pulling air into the system. However, blaming the oil does not require any troubleshooting. PMS is also available as a supplemental additive that equipment owners can use for sweetening sumps. It is vitally important that if additive depletion is the cause of foaming, then the dosage has to be spot on and most plants do not have the capabilities to add at a level of 10 ppm or ensure correct dispersion of the additive. Overdosing will result in poor air release properties of the oil - you will actually make the problem worse.

There are two very separate tests that can be done on an oil sample to measure air/oil properties. The first is an anti-foaming test which, in effect, looks at putting the oil in a blender, looking at the amount of foam on the surface of the sample and measuring how long it takes the foam to collapse. In the case of the air release test, the amount of time it takes for the entrained air level to drop to 0.2% is measured.

Keeping air out of oil basically comes down to good system and reservoir design. Ensure there are no leaks on suction lines, control surface agitation, employ a diffuser on the uptake line, use wire mesh on the return line, ideally the return line should be below the surface of the reservoir, limit the amount of oil degradation and contamination and baffle plates should be installed in the bottom of the sump. A long sump residence time will also mean that air has time to be released.



This bulletin clearly demonstrates one of the most important principles of successful proactive maintenance: Once your oil is contaminated, it costs ten times more to clean it up than it does to keep it contaminant-free in the first place. If you can keep your oil clean and dry, you will be assured of many trouble-free years, hours or kilometres of operation.

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