

Varnish Identification

Measuring oxidation products through temperature manipulation when particle counting

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When it comes to oil condition management in 2019, varnish is a hot buzzword. But what is varnish? Can this one word really be an accurate description for every sludge-like material that develops in your hydraulic or lubricating system? Varnish is a good generalisation for the conglomeration of sediment products that can build up after extended degradation of the base oil; it effectively describes that yellow/brown sludge that you may have noticed in tanks or on used filter elements.

What causes the formation of varnish?

Oil degradation describes the fracturing of oil molecules and the constituent additives; these broken molecules can ultimately stick to each other, as well as other contaminants present, to form varnish. But what is the cause of oil degradation in the first place? The process is called oxidation, which essentially describes the reaction of the base oil with oxygen.

There are many factors that can act as catalysts to this process, the first major contributor being contamination of various types. An obvious contaminant is solid particulates; whether it's environmental residue that's entered the system or wear metals, any form of solid material will aid the

varnish formation process. Oxidation products also stick to these contaminants to increase the quantity of sludge. A wide range of filtration is available, with the ability to assist in the removal of these harmful particulates.

Water is another common contaminant. Even dissolved water can heavily contribute to the oxidation process, we would recommend a maximum water saturation of 50% for your mineral-based oils in hydraulic and lubrication applications.

Finally, an often lesser-considered contaminant is air. The introduction of more oxygen containing materials will assist the unwanted oxidation process. Methods of water and gas removal are available, including a range of equipment based on the principle of vacuum dewatering; this enables the separation of water and gases from hydraulic and lubrication fluids.

As well as contamination, another factor can be excessively stressful system parameters. Pressures and temperatures that are beyond the fluid's capability can quickly cause the deterioration of the fluid. For example, excess temperatures can mean thermal degradation; it's important to remember that for every 10°C increase, the rate of reaction is doubled.

One final factor that is becoming an increasing risk, is electrostatic discharge (ESD) – this is a phenomenon where discharge sparking occurs within a system; this typically occurs in the filter housing. The temperature of the discharge spark is greater than 10,000°C. These sparks cause the oil molecule to “crack”, forming free radicals. These radicals continue to react with other oil molecules, oxygen and other radicals. The resulting oxidation products can then conglomerate to form the sludge-like material that we call varnish.



Figure 1: ESD graphic

Electrostatic Discharge (ESD)

What causes ESD? ESD occurs when the oil and filter become electrostatically charged. This happens due to a transfer of electrons between the materials; the reason for this transfer can be observed in the triboelectric series, identifying the electron affinity of the filter media and of oil. Filter media is typically glass-fibre, which will prefer to donate electrons and become positively charged, whereas oil will be more willing to receive electrons and become negatively charged. As these materials become separated, there is an increased voltage; once this exceeds 3kV/mm, discharge sparking can occur.

As well as contributing to varnish formation, these sparks can cause holes to be burnt into the filtration layers, this can effectively turn your 3µm filter into a 200µm filter. One possible solution considered to combat ESD is to make the filter conductive, but

this merely prevents the sparking from occurring at the filter. The charge continues to build up and can then discharge in more safety critical areas, such as the tank, where there is a risk of igniting the oil mist vapour and a resulting fire/explosion.

Oil conductivity plays a large role in the risk of ESD occurring. High conductivity oils, typically greater than 500pS/m, are less prone to ESD due to having more electron flow pathways. These oils tend to be the outdated Group I Base Oils, being more conductive due to the presence of heavy earth metals, such as Zinc. Low conductivity oils, typically less than 500pS/m, are more susceptible to ESD. These are usually the more heavily refined Group II and III Base Oils. As a result of this, measuring the conductivity of the oil is the initial parameter when identifying any risk of ESD.

There are several additional risk indicators, one being the workload at the filter; if the low conductivity accompanies a workload greater than 0.1L•min⁻¹cm⁻², the chance of sparking greatly increases. Secondly, colder conditions can be problematic as conductivity positively correlates with temperature, so it may be that during cold start-ups the conductivity is significantly lower than the recommended 500pS/m and as a result the charge build up can occur. Furthermore, the oil condition can be a great pointer that ESD has already occurred. The main aspect of this article is looking at oxidation products and it's already been explained that ESD is a cause of varnish formation; therefore an increased level of varnish is a potential indicator for ESD. We can also look and listen for physical signs; when ESD is occurring, there can be some clear indicators that the sparking is taking place. For one, if you can get near the filter housing, you may actually hear the sound of the electrical discharges continually occurring. Additionally, the filter element itself will display signs of burning damage; a process which can be easily handled by a laboratory with the experience of analysing used filter elements.

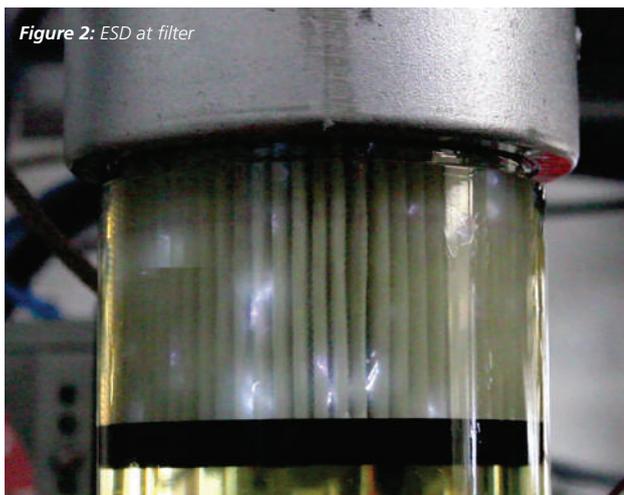


Figure 2: ESD at filter

Once a risk of ESD occurrence has been identified, what can be done to remove this? Because the charge build up is a result of a huge number of interactions at the filter element, this is the target area for change. It has already been explained that simply making the filter conductive is not a solution, therefore it is essential that the interaction process is stopped at the source; by preventing the electron transfer in the first place, the charge does not build up and the risk of sparking is mitigated. This technology is not available from every filter supplier, so it is best to enquire about the ESD prevention process built into filters prior to acquisition.

Why is varnish a problem and why does it need to be measured?

The build up of sludge in a system can be damaging in many ways, the first key issue being malfunctioning valves. Sludge can prevent the normal functioning of valves, causing sticking of spools, the end result of which can be serious, especially if the valves in question are required for a safety function. Another problem is the blocking of filters; typical inline pressure filters are developed to filter out solid particulates of various shapes and sizes. Many use depth filtration, where multiple layers are used to filter out a complex range and large quantity of contaminants. This level of technology can result in a

more expensive filter, but it is still cost-effective when performing its intended duties. However, instead of using the full range of filtration media embedded, varnish will stick to the exterior of the filter; this causes premature blocking and increased costs due to higher frequency of element changes.

More critical issues caused by varnish includes the reduction in lubrication gaps; the incompressible nature of oil is the reason it is used for these high pressure and power applications. Lubrication gaps are the pockets of lubricant that prevent direct metal-to-metal contact in the system, therefore preventing wear and extending the lifetime of components. If oxidation products begin to deposit in these areas, the amount of lubrication is reduced and the level of wear can drastically increase.



Figure 3: Example of contaminants in a filter

Lastly, but just as important, is the obstruction of heat transfer. Due to the nature of varnish, it's solubility in the oil is dependent on the operating temperature. At higher temperatures the sludge can remain dissolved, but at lower temperatures it can become free. Because of this, varnish will typically deposit on

colder surfaces, such as cold elbows in the system, tank walls or any cooling devices. If a cooler is subject to sludge build up, the heat exchange capability will be reduced; this will raise the system temperature and further contribute to the oil ageing process.

If these symptoms are occurring within a system, what can be done to confirm that varnish is the cause?

Laboratory testing is the definitive solution to determining whether oxidation products are at fault, and there are a variety of tests to consider.



The MPC (Membrane Patch Colourimetry) Test – traditionally developed for turbine lube oil applications, this procedure extracts any insoluble contaminants onto a filter membrane and assigns an index value based on colour; essentially, the darker the membrane, the greater the risk of varnish deposition in the system. The number scale is typically interpreted as follows:

- 0-30 Good – No apparent varnish problem at the moment.
- 31-50 Action – Increased value due to soft contaminants caused by oil degradation. Varnish deposition on bearings, valves and gears as well as reduced filter lifetimes are to be expected.
- >50 Critical – MPC value has drastically increased due to soft contaminants caused by advanced additive depletion and oil oxidation. Varnish has deposited on bearings, valves, tank and gears. Very short filter lifetimes are to be expected.

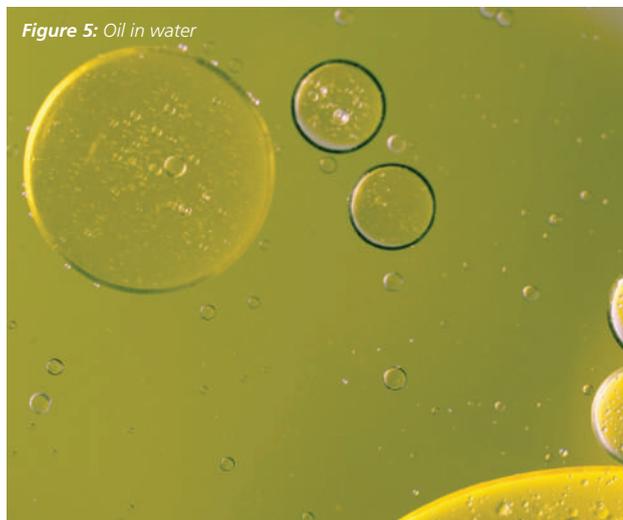
The RULER (Remaining Useful Life Evaluation Routine) – a technique using linear sweep voltammetry that measures the phenolic and aromatic amine antioxidants; by comparing used and new samples, a percentage of useful remaining antioxidant content can be obtained. These antioxidants act as a scapegoat for the base oil, reacting with oxygen before any harm comes to the oil itself; therefore it stands to reason that, if the antioxidants have depleted, the rate of base oil oxidation will increase and more varnish will build up within the system. A final analysis of note here is Fourier Transform Infrared Spectroscopy (FTIR).

Spectroscopy; through infrared absorbance, different compounds can be identified thanks to their unique spectroscopic signatures. Oxidation products are one such set of compounds that can be observed through FTIR; identifying spectrum peaks around the 1750 cm⁻¹ region typically translates to the presence of these materials.

Many different tests are available and choosing a wider range of analyses will provide the most information to allow for a greater informed decision. Once tests have confirmed the presence of varnish, what can then be done to mitigate this damaging material? A variety of options are available, dependant on factors such as oil volume, budget and accessibility. Typically on large volumes, the varnish can be removed from the oil via conditioning units. These units are able to efficiently remove these oxidation products by cooling the oil and filtering out the precipitated varnish. Where the oil volume is low, it may not be cost effective to pursue this; in these instances, an oil change and complete system flush is recommended.

As the title of this article suggests we are looking at using traditional optical particle counters as a measurement technique for varnish by manipulating the test temperature, either online or in laboratory settings, to determine the particle distribution in the

oil. This is achieved through the use of a light source emitting a beam through the oil, which is detected by a photo diode opposite. As a particle breaks the beam, this gets registered. This is repeated thousands, or millions, of times to provide a particle count.



These counters can be calibrated to a variety of standards, but for this research task, we are looking at ISO 4406:2017 (Hydraulic Fluid Power – Fluids – Method for coding the level of contamination by solid particles); this standard categorises particles by size and quantity, resulting in a three digit classification system. This is one of the defining standards in the industry and it is available online, but essentially it allows for the easy comparison of contamination levels – the higher the value, the greater quantity of particles at that size range. For example, an ISO 4406 code of 17/14/11 could translate to:

- 17 – 101,232 particles >4µm per 100ml of fluid
- 14 – 13,333 particles >6µm per 100ml of fluid
- 11 – 1,564 particles >14µm per 100ml of fluid

Whereas a higher code of 21/18/15 could translate to:

- 21 – 1,324,412 particles >4µm per 100ml of fluid
- 18 – 172,113 particles >6µm per 100ml of fluid
- 15 – 31,321 particles >14µm per 100ml of fluid

Particle counters are typically operated at the system temperature, or at room temperature in laboratory conditions, but what if we could manipulate this temperature and observe any differences in results as a measure of oxidation products?

This was the premise of our research in the HYDAC Fluid Care Laboratory. Our initial hypothesis being that fresh oil samples will have low MPC values and negligible differences between the particle count at 20°C and 80°C. In samples with high MPC values, they will also display a decrease in the particle counts at the two temperatures, such as 22/20/15 at 20°C and then 19/18/15 at 80°C. This would indicate that the deposits dissolve back into the oil at higher temperatures. Alternatively, it is expected that there will be some instances where the high MPC value is not reflected in the particle counts. This would indicate that the colour is not due to “varnish”, but perhaps due to typical solid contaminants or staining of some kind.

The study involved 100 real oil samples from a variety of industrial applications, including Power Generation, Pulp and Paper, Oil Manufacturers, Injection Moulding. Each of these samples was subjected to MPC and Particle Count (20°C & 80°C) testing. Results were plotted as “MPC” against “% Difference Between the No. Particles >4µm at 20°C and at 80°C”.

The findings of this research can be seen in the following chart:

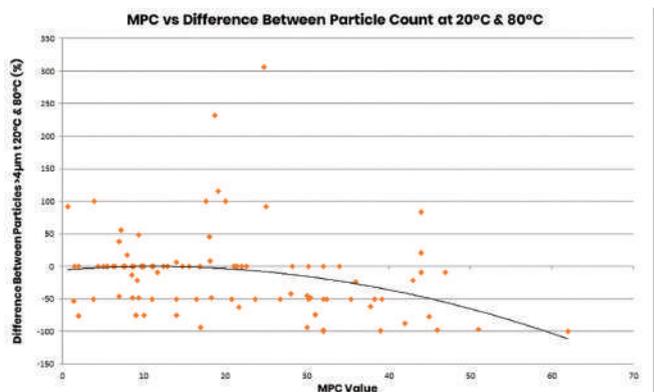


Figure 6: Results of MPC vs Difference between particle count

Figure 7: Varnish build up



As can be seen, the findings show that as the MPC value increases, the No. Particles $>4 \mu\text{m}$ at 80°C decreases compared to 20°C . Some of this data was much more extreme, such as a change from 23/16/8 (20°C) to 13/11/7 (80°C) with an MPC value of 62; in cases such as this we can infer that most, if not all, of the colour of the membrane was due to oxidation products. Conversely, some of the results contradicted our main hypothesis, an example being a change from 14/12/9 (20°C) to 15/13/9 (80°C) with an MPC value of 44; in these instances, we can conclude that the colour of the filter was due to completely insoluble particulates or staining.

To summarise, varnish (oil oxidation products) is a serious threat to machinery condition and needs to be monitored appropriately. MPC is a reasonable measure of varnish potential within a system but further verification of MPC testing is important; this

can be achieved through Particle Counting at 80°C as well as 20°C . If a high MPC value accompanies a decrease in the Particle Count, we can confirm the presence of varnish.

The ending point here is that manipulating the temperature while particle counting provides us with another string to our analytical bow; the more testing that is available, the more knowledge we have and ultimately we have more control over our hydraulic and lubrication worlds.



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