

## **Oxidation** *of oil and filtration of oxidation residuals in oil*

*The presence of oxidation residuals in oil is an increasing problem in various oil systems. The problem is enhanced by the trend of down-sizing oil reservoirs, increasing oil temperatures and prolonging oil change intervals. This article describes some of C.C.Jensen's experiences, solutions and results concerning the complex of oxidation problems. Further, phenomenons such as spark formation and creation of electrostatic tension in off-line oil filters are discussed.*

The oxidation of oil can be defined as degradation with oxygen as the reagent. However, the term oxidation is generally used to describe all types of oil degradation. All organic materials age; familiar examples may be butter turning rancid, newspaper paper (cellulose) getting yellow and wine getting tartar when developing vinegar.

The degradation processes of mineral oils are complex. A simple explanation would be that oxygen is reacting with the free radicals of the hydro-carbons which, in turn, form hydro-peroxides. Hydro-peroxides are unstable and soon broken down into ketones and water. The ketones oxidises further, forming aldehydes or organic carboxylic acids. The end products are acids, water and sludge. The acid causes corrosion and accelerated wear; the sludge increases the viscosity and blocks valves as well as other system components.

In the early 1970's C.C.Jensen A/S first encountered the problems connected with oxidation products/residuals, generally referred to as resin (US: varnish)<sup>1</sup>, in the lubrication oil on trunk engines (four-stroke diesel engines) running on heavy fuel. Since then we have seen similar problems in countless oil systems, and very often in connection with a very high thermal load on the oil. The term "oxidation product" covers a wide spectre of degradation products. *Varnish* can be described as a ropy, brownish or yellowish substance, which may cover metallic the surfaces of an oil system. *Sludge*, however, is found in the oil, is circulated with the oil flow and may settle if the surface tension of the oil, due to polar contents, is decreased (<20 mN/m). Darkish colour, bad smell, increased viscosity and acid content are common indicators of oxidized oil.

A high temperature caused oil degradation instigates the formation of gasses in the oil; a phenomenon utilized in the electrical power generation industry to trace faults in oil filled power transformers. In transformers oil oxidation is caused by the oxygen present in the oil. The surface of the paper-isolation material (thin strips of cellulose wound around the copper cores) in a transformer are often coated by a brownish substance, particularly in old transformers. This substance contains copper oxides and sludge. The sludge affects the cooling ability and the copper oxides are the result of a reaction between free copper ions and the oxygen in the oil. Consequently, one way to prevent these problems are to remove the oxygen from the oil. C.C.Jensen developed the CJC V30 VacuumFilter which reduces the oxygen content by a factor 20, hence decreasing the rate of oxidation. Tests have shown that the anti-oxidant additives (DBPC) in the oil are not removed by the vacuum treatment. However, it is not always a solution to remove the oxygen dissolved in the oil. In many systems oxygen (air) is entering the oil at such high rates that an equal rate removal would be uneconomical. In such systems oxidation itself cannot be prevented, but only the effect of the oxidation: the acceleration of the degradation process caused by the oxidation products as well as the malfunctioning valves etc.

### **Spark phenomenons and electrostatic charging of oil**

Both in industrial systems and onboard ships spark formation In oil tanks and between metal surfaces have, on rare occasions, been observed. These sparks are of course unwanted and the voltage can in fact be so high that injuries may occur. In order to explain these spark phenomena in practice, some theoretical basis knowledge is required:

When a fluid (oil) flows through a pipe which on the internal surface has the electric charge, zeta ( $\zeta$ )

[ref. 5], an electric current is created. The current induces a voltage difference,  $\Delta E$ , lengthwise in the pipe, defined by the following equation<sup>2</sup>:

$$(1) \Delta E = \Delta P \frac{\epsilon * \zeta}{\mu * \lambda}$$

Where  $\Delta E$  = voltage difference across pipe, V  
 $\Delta P$  = pressure drop across pipe, Pa  
 $\epsilon$  = permittivity of the fluid, F/m (F = Farad = A\*s/V)  
 $\zeta$  = (zeta) potential of pipe material, V  
 $\mu$  = fluid viscosity, Pa\*s  
 $\lambda$  = electric conductivity of fluid, S/m

If we insert the values of a very clean gas oil and a used, water containing oil, filtered through a filter with a pressure drop of 2 bar, we get:

Static electric charge in ordinary cellulose fibres with two different oils		
Unit	Gas oil	Used, wet oil
Oil permittivity ( $\epsilon$ )	2.2 * 10 <sup>-11</sup> F/m	2.2 * 10 <sup>-11</sup> F/m
Viscosity ( $\mu$ )	0.001 Pa*s	0.05 Pa*s
Conductivity ( $\lambda$ )	10 <sup>-12</sup> S/m	10 <sup>-8</sup> S/m
Cellulose zeta-potential ( $\zeta$ )	10 mV	10 mV
Pressure drop (bar)	2	2
Maximum charging	44,000 kV	0.044 kV
Typical breakdown voltage at 1 cm	200 kV	300 kV
Risk of spark formation	YES	NO

**Table 1:** The values in this table are valid only by stationarity, i.e. no earthing to surroundings. Note the high risk of spark formation in the gas oil.

Off-line oil filters, including CJC Filters, have in technical literature been accused - by not entirely impartial organisations - of causing oil cracking due to spark formation [se ref. 2] (electric discharges creates approximately 3.6 \* 10<sup>-9</sup> mole gas per discharge, mainly hydrogen [ref. 1]). At C.C.Jensen we are convinced that the real cause of spark and oxidation phenomenons is to be found elsewhere than the off-line filters.

Static electric charge in a CJC cellulose filter with two different oils		
Unit	Gas oil	Used, wet oil
Oil permittivity ( $\epsilon$ )	2.2 * 10 <sup>-11</sup> F/m	2.2 * 10 <sup>-11</sup> F/m
Viscosity ( $\mu$ )	0.001 Pa*s	0.05 Pa*s
Conductivity ( $\lambda$ )	10 <sup>-12</sup> S/m	10 <sup>-8</sup> S/m
Cellulose zeta-potential ( $\zeta$ )	-0.1 mV	-0.1 mV
Pressure drop (bar)	2	2
Maximum charging	440 kV	0.00044 kV
Typical breakdown voltage at 1 cm	200 kV	300 kV
Risk of spark formation	YES	NO

**Table 2** shows that the maximum charge potential is far lower than for non-surface treated cellulose. Note that these values are valid only by in a theoretically ideal system without any form of earthing. In practice even a very weak earthing (e.g. 10 k $\Omega$ ) will completely eliminate the risk of sparking

Microscopically, a filter may be seen as a mass of more or less parallel tubes, which is why the above formula (1) can be used to describe the voltage difference occurring when oil flows through a filter. Note that the formula is also valid for a pipe, but only in stationary condition, i.e. a system completely isolated electrically and from which no current flows. In real life the generated voltages will be lower than suggested above, as the oil leaving the system is carrying electric charges, which means that the system is not electrically isolated. The cellulose, being a better electric conductor than the oil, acts as an earthing of the system. Thus a part of the generated voltage will be discharged through the cellulose.

It is important that the voltage difference, which may be generated if the system is not sufficiently earthed, is proportional to the differential pressure which, in turn, is proportional to the oil flow across a filter insert (or through a pipe). Equally, the voltage difference is proportional to the zeta-potential of the filter material. Another important factor is the difference between the charging of the filter housing and the charging of the filter material (the cellulose). An electrical charging of the filter housing is not harmful to the oil; only if the filter material (cellulose) is electrically charged and discharges (through sparking) to the filter housing can the oil be harmed.

A doubling of the oil flow will double the pressure drop and consequently the generated voltage. Typical oils will have a breakdown voltage of 60 kV/2.5 mm [see for example IEC 60156 or ASTM D887]. This means that in an oil-filled gap of 1 cm there must be a voltage difference of no less than 240 kV before a spark over can occur. The very high temperature spark will break down the surrounding oil instantaneously, generating gasses - mainly hydrogen (H<sub>2</sub>) and carbon oxide gasses (methane, ethane, ethene and acetylene - with increasing temperatures). Some of the gas will dissolve in the oil. Hydrogen, however, (being the least soluble, the lightest and the most volatile of the gasses) will bubble to the surface

Off-line filter inserts have been accused of causing such spark overs. These accusations have, however, been proven to be subjective and unfounded. To date we have never been able to detect any electric charging of the hundreds of thousands of CJC Filters, which have been installed during the last 60 years, all over the world. **Likewise, measurements with hydrogen sensors on the automatic filter venting device have shown that no hydrogen is produced inside the filter housing. This means that there is no spark formation inside the filter housing and consequently no degradation of the oil.** The manufacture of CJC Filter Inserts is arranged to keep the zeta-potential of the CJC cellulose inserts as close to 0 mV as possible. This is achieved through, among other, regulating the pH value and various surface treatments of the cellulose mass. A low zeta-potential assures that the  $\Delta E$  (potential) in above formula is lower, thus avoiding electric charging.

In this context it is of utmost importance to distinguish between static charging of a filter housing and static charging of the filter material itself. Consequently, it is equally important to distinguish between spark overs **in** the oil and spark overs from the filter housing to its surroundings. The first would harm the oil because the spark is **in** the oil itself. The latter causes a spark over in the atmosphere and is nothing but an indication of inadequate earthing of the filter housing. If the filter is not correctly earthed, it may act as sort of Van de Graaff generator, generating an electric charge on the outside of the filter housing.

The calculations thus shows that an electric charging of the oil is possible. An electro-magnetic field across the oil (without spark overs) can cause an increase in the degradation rate, provided however that the electric field is fairly strong. The reason for this is that the molecules of the oil become polarized which facilitates the initiation of chemical processes [ref. 4].

### **Spark overs in oil**

A literature-study of static charging of fluids shows that the charging occurs when the electric conduc-

tivity is very low. Some writers say  $<10^{-7}$  S/m, which is a factor of 10 lower than the conductivity of ultra-clean water. Static electricity is generated under the following circumstances:

- By flow through a pipe
- By flow through a filter
- By sedimentation of water drops or dirt particles
- By ascending air bubbles

If the conductivity drops to below approximately 1 pS/m the static charge disappears due to a lack of ions to transfer the charge. The oil's degree of refining also determines the maximum charge per volume unit (C/L) that the oil can generate. The more refined and the less polyaromatics the oil contains, the lower is the charge potential. Earthing the electrically conducting components of an oil system does not completely prevent charging of the oil, but it does - and that is important - prevent spark overs between components/parts. The oil can "carry" electric charges because its low conductivity prevents discharging. The earthing of an oil flow system, on the other hand, does not have to be very good. Actually, the resistance to earth should just be less than 10 k $\Omega$ , which is not a very good earthing [ref. 6].

## Removal of Oxidation Residuals from Oil

### **Case Study 1**

*CJC Filter removes oxidation products from hydraulic oil*

#### **The System**

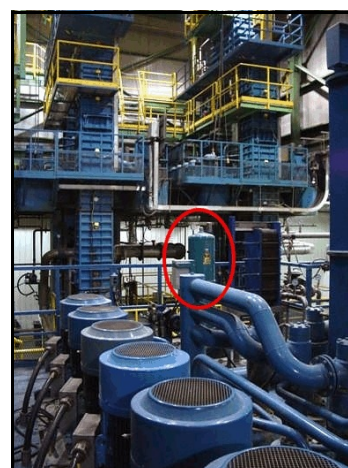
A hydraulic press at Millar Western Forest Products Ltd, Canada, pressing cellulose into large blocks to be used in the continued paper manufacturing process. A single paper-block weighs approximately 225 kg. The press operates with a hydraulic pressure of 200 - 250 bar and each press processes some 400 tons of cellulose per day with a scheduled down-time of 8 - 12 hours per month. In 2001 C.C.Jensen installed on the hydraulic system an HDU 27/54 Fine Filter with B 27/27 CJC Filter Inserts and a pump flow rate of 1,150 L/h<sup>3</sup>. There are 5 identical hydraulic systems with each 4,500 L of NUTP H 68 oil - a mineral oil based hydraulic fluid with good anti-wear properties. The CJC Filter was installed on one of these systems.

Prior to the filter installation the owner observed the following problems/symptoms:

- Valves not working or sticking
- Deposit coating on components
- Darkening of the oil
- Increasing problems with varnish ever since first observation in 1988

the latter, however, most probably caused by increased production and loading of the machines.

In spite of an oil cleanliness (ISO 4406) of 15/12/10, i.e. a fairly clean oil as far as particles are concerned, they experienced problems. An ultra-centrifuge analysis of each oil sample (24 h at 40,000 rpm; a gravity exposure of more than 20,000 G) showed large quantities of varnish in the oil. On that basis the CJC Filter was installed.



*III. 1: A Sunds Slabs Press with the CJC HDU 27/54 Filter installed (red circle).*

### The Problem

As virtually the total oil volume of 4,500 L is in circulation during a pressing cycle there is a Risk of local "hot spots" in the hydraulic system. The general system oil temperature was not elevated. The high compression pressure could also instigate a micro-diesel-effect or an adiabatic compression of air bubbles. Both result in oxidation of the oil.

### The Test Record

Samples were drawn at 3 months intervals:

- 0 months      Start up
- 3 months      Samples ultra-centrifugated
- 6 months:      Filter housing dismantled  
Filter inserts replaced (the first set was not yet saturated, but had to be sent to the lab for analyses)  
FTIR and other tests of the filter inserts  
Filtration restarted
- 9 months:      Samples ultra-centrifugated
- 12 months:    Samples ultra-centrifugated, and the CJC Filter was disconnected from the hydraulic system
- 12+3 months: Samples ultra-centrifugated

After 6 months of operation samples were taken from the filter insert material and sent to an independent laboratory for analyses. The objective was to find out which materials/substances the filter might have removed from the oil.

After 12 months the filter was removed from the system and installed on another of the 5 presses. 3 months after the filter had been moved an ultra-centrifugation sample was drawn from the first press. The objective was to establish how efficiently a CJC Filter removes varnish (resins) and to quantify this.

### Types of Analyses

- ICP analysis to determine the elements/materials removed by the filter
- Gravimetric analysis where varnish (resins) is removed from the filter media
- FTIR analysis (Fourier Transformation InfraRed spectroscopy) to determine whether oxidation residuals - if any - have been removed from the oil.

### The Result

The ICP analysis shows that no additives have been removed from the oil. The gravimetric assessment of the varnish content - a process whereby the remaining oil in used filter material is extracted by means of the solvents hexane and heptanes, leaving the non-soluble oxidation residual products. The volume of the latter is weighed to establish the dirt-holding capacity of the filter.



III. 2: The CJC Filter with housing dismantled. After 6 months of operation. The dark, shiny colour of the filter inserts indicates oxidation products.



III. 3: The CJC Filter Insert after 12 months' test (6 months after insert replacement). When compared with ill. 2 it is clear that the oil was more clean during the last 6 months of the test, thus depositing less of the brown oxidation products.

(in gram, representative sample)	Total mass	Filter mass	Varnish mass	Relation varnish mass / filter mass
Sample 1	310139	150416	159723	106
Sample 2	324575	162115	162460	100
Average	317357	156266	161092	103

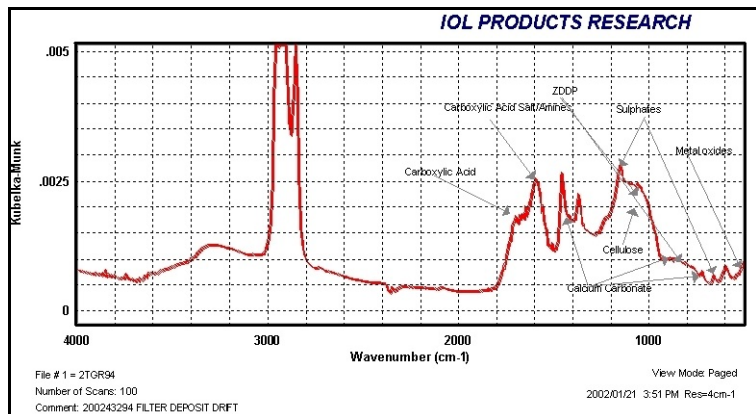
Table 3: In the course of the first 3 months the filter inserts retained 1.03 times their weight of oxidation products and particles. CJC Filter Inserts have been seen to have a dirt-holding capacity of 1.91 times their proper weight, i.e a type 27/27 (height x diameter in cm) with a dry weight of some 4 kg can retain almost 8 kg of oxidation products and particles.

Based on the above 1:1.03 relation between mass of varnish retained and cellulose mass we can determine that a standard CJC B 27/27 insert with a dry weight of 4 kg can remove at least kg of dirt, water and resins from the oil. By the second replacement of inserts the relation had almost doubled so that almost 8 kg of oxidation products and particles could be retained.

The FTIR analysis of the filter insert material that had been in use for 6 months, showed that the filter insert contained:

- ZDDP (residual of consumed additive)
- Carboxide acid (oxidation residuals at 1,720 cm<sup>-1</sup>)
- Sulphates (1,160 and 606 cm<sup>-1</sup>)
- Calcium carbonate
- Metal oxides
- Cellulose (the filter media itself)

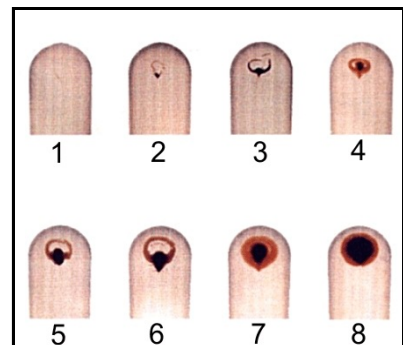
The pictures of the high speed centrifuged oil samples show that the CJC Filter has removed the oxidation products which deposit at ultra-high-speed centrifuging. These are the oxidation products which would cause e.g. valves to block. We have found a report [ref. 7] describing the removal of oxidation products by means of an electrostatic filter on exactly the same type of system (bale press with identical oil and oil volume). The centrifuged samples from the electrostatic filtration show a minor improvement after 18 months of filtration. The CJC Filter produced a significantly higher reduction of oxidation products and after just 12 months of filtration.



III. 4: The FTIR analyses of CJC Filter Insert material show, among other things that the filter material retains organic acids and sulphates - the initial stages of sulfation (formation of sulphuric acids).

By using a 8-step system, developed by Mobil Oil, to classify ultra-centrifugation samples, the oxidation degree of an oil can be visually established.








- 1-3 indicate a healthy oil
- 4-5 indicate the first signs of resins deposits
- 5-6 indicate that the frequent oil sampling and analysis is required
- 7-8 indicate that the oil has a strong tendency to deposit varnish/resins (oxidation products) in the oil system.



III. 5: The 8-step system for classifying ultra-centrifuges samples, developed by Mobil Oil.

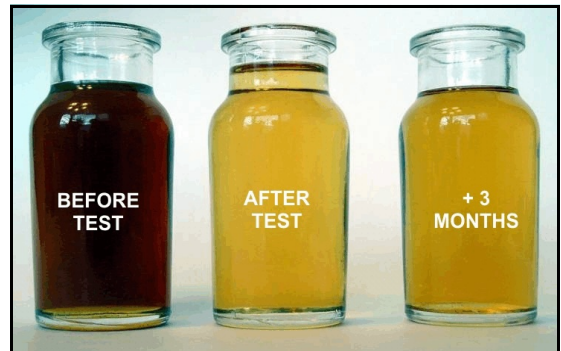
By comparing the CJC samples in ill. 4 with the classification spec-

imens in ill. 5 it is evident that the CJC Filter reduces the oxidation degree of the oil from a clear category 8 to a category 1-2. This means that the lifespan of the oil is extended and that the Risk of varnish/resin formation and depositing is minimized.

CJC HDU 27/54 Off-line filter					
Electrostatic filter [ref. 7]					
Time	Start	3 months	9 months	12 months CJC / 18 months Electrostatic	3 months after filtration stop.

**Table 4** shows that the CJC Filter improves oil condition from category 8 to category 1-2, whereas the electrostatic filter failed to improve oil condition to more than category 6.

**III 6:** This picture shows that the oil colour went from dark, an indication of oxidation, to the light colour of fresh oil. A control sample was taken 3 months after test finish when the CJC Filter had been moved to another press. That sample showed that the oil had slightly worsened, but was still far better than before filtration start.



## Removal of Oxidation Products from Lubricating Oil

### Case Study 2

#### The System

Laboratory test-system with 100 L of used lubrication oil from a two-stroke marine diesel engine.

#### The Problem





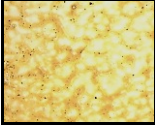
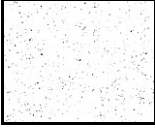




The oil contained particles and oxidation residual products. The shipowner reported that the lube oil generally did not live as long as previously experienced. A particle size distribution analysis proved the majority of the particles to be less than 0.8 µm (micron) in size.

#### The Test

A CJC HDU 15/25 FineFilter with A 15/25 Inserts was used with a flow rate of 45 L/h. The size ration filter insert / oil volume is equal to the ratio between the largest CJC Filters and the system lube oil volume onboard a vessel. The test objective is to remove the oxidation products.

**The Result**

Particle size distribution analyses are carried out before and after the oil is passed through the filter 200 times. The oxidation products have a particle size of 0.2 to 0.8 µm, and consequently the filter β-value is not very high. To make the particle distribution analyses the oil is dissolved in n-pentane and successively vacuum-filtered through membranes of still smaller pore-size (from 12 down to 0.2 µm). As the oil virtually did not contain particles larger than 0.8 µm, only membranes smaller pored than 0.8 µm are depicted in table 5.

Membrane pore size:	0.2 µm	0.4 µm	0.6 µm	0.8 µm
Before filtration				
100 times through filter (3 times after addition of dust)				N/A
200 times through filter				N/A

**Table 5:** Filtration of oxidation products in a diesel lube oil. The membranes show that the CJC Filter removes oxidation products (brown coating) down to below 0.4 µm in size. Further, the addition of particles (the two lower rows) that the CJC Filter retains test particles down to below 0.4 µm.

Note that the brown coating of the membranes disappears after filtration, except on the 0.2 µm membrane. Halfway through the test dust was added (ISO Fine Test Dust 12103-1, A2) to the oil in order to detect how efficiently the CJC Filter retains particles of 0.6 µm and smaller. It is shown that the CJC Filter removes particles as small as 0.2 µm, however with a higher efficiency on 0.4 and 0.6 µm particles.

**Oxidation residual products in oil can be caused by one or several of the following factors:**

- Aeration of the oil (air bubbles or dissolved oxygen)
- Adiabatic compression of air bubbles in the oil (local overheating)
- Overheating in all of the oil system
- Sparks form static electricity
- Pollution with anti-frost fluid
- Soot
- Hydrolysis (degradation with water as reagent) - also known as acid hydrolysis. Actually condensate, ingress or water deriving from the degradation of the oil.
- Pollution with grease lubricants
- Nitration
- Hot surfaces
- Sulfation (fuels, H<sub>2</sub>S, H<sub>2</sub>SO<sub>4</sub>)
- Corrosion
- Incompatible additive packages from two of more oil types
- Low quality base oil

## Conclusion

It can be concluded a risk of spark overs in an oil filter do exist, but it is a small risk - and in an CJC Filter even insignificant.

There is no evidence that spark overs have ever occurred inside a CJC Filter. On the contrary, the oil filtration the filtration of the oil is an important assistance in extending oil lifetime. The following facts prove this:

The CJC Filter can remove oxidation products from both hydraulic and lubricating oils. There is no generation of hydrogen (H<sub>2</sub>) inside a CJC Filter housing.

*Henrik Hallberg Jensen, M.Sc., C.C.Jensen A/S*

## Notes

1. Other English terms for oxidation products are: deposits, lacquer, gums, tars.
2. The equation is derived from Poiseuilles law, applied on Poissons law. See derivation in [ref.3].
3. Further information on <http://www.cjc.dk/index.php?m=p&pid=28>, and on <http://www.cjc.dk/index.php?m=p&pid=212>.

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- 8] [http://www.noria.com/learning\\_center/category\\_article.asp?articleid=59](http://www.noria.com/learning_center/category_article.asp?articleid=59)