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Humidity Saturation Limits of Hydraulic and Lubrication Fluids

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In order to ensure the required plant availability, it is necessary to regularly check the degree of contamination due to solid particles and to monitor the water content in non-aqueous lubricants. Sensitive applications and components are often classified according to their tolerable limit of water content in milligrams/kilograms (mg/kg) or parts per million (ppm).

In the laboratory, this value is usually measured by the Karl Fischer method. The result is the sum of free and dissolved water. However, water only causes damage if it is free. Dissolved water is not a problem. Each lubricant contains dissolved water. Without knowledge of the respective limit of solubility (saturation) of the fluid in use, it is not possible to interpret the results from the Karl Fischer method. Thus, using proper measurement methods and determining the individual limit of solubility for water are important preconditions to implement modern maintenance strategies.

Free Water and Its Consequences

Free water accelerates oil degradation due to hydrolysis of ester-based fluids or the reaction of additives like zinc dialkyldithiophosphate (ZDDP) and calcium sulfonate. Sticky substances resulting from these reactions can lead to valve failure in control oil systems as well as decreased filter service life. Ice formation rarely creates problems. However, water causes increased wear due to cavitation within pumps and valves, corrosion and decreased load capacity of lubricant films. The service life of roller bearings already suffers at a relatively low level of water contamination. Ignoring this problem can result in serious damage with high costs.

Water Basics

Water in hydraulic and lubrication fluids can be found in all three physical conditions — solid, liquid and gas. Water in the form of gas is found within the surrounding air of the aggregates, as well as in dissolved form within the individual operating fluids. Water in liquid form usually should not be contained within lubricants because it will cause a rise in operating costs due to the problems mentioned previously.

To better understand the change in the physical condition from non-critical water vapor to harmful water drops, the most important laws should be examined in more detail.

Humidity (Relative Moisture)

The basic principles for gas are explained by Dalton's law (Figure 1).

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Daltons law

Nitrogen	77%
Oxygen	21%
Water vapour	1%
Other gases	1%

$$1000 \text{ mbar} = 770 \text{ mbar} + 210 \text{ mbar} + 10 \text{ mbar} + 10 \text{ mbar}$$

Brannenburg :

$$820 \times 77\% \quad 820 \times 21\% \quad 820 \times 1\% \quad 820 \times 1\%$$

$$P_{\text{sum}} = 820 \text{ mbar} = 632_{\text{N}_2} + 172_{\text{O}_2} + 8_{\text{w}} + 8_{\text{other}}$$

$$P_{\text{sum}} = P_{\text{w}} + P_{\text{rest}}$$

Figure 1: Dalton's law for air

Air principally consists of nitrogen and oxygen molecules, as well as smaller contents of other gases and water molecules. Within a closed room, these components would cause partial pressure to the walls. P_{w} is the partial pressure of water. If the distance between the molecules is large enough compared against their diameter, and if there are no other interactions, then Dalton's law applies. This means that the overall pressure of the air equals the sum of the partial pressure of all the components. If the saturation vapor pressure (P_{ws}) has set in within the air volume, the maximum number of water molecules is to be found within the gas. If the number of water molecules increases, this would cause condensation, i.e., water drops or water in liquid form. Practically, relative humidity plays the more important role. Figure 2 describes the relationship.

Relative Humidity(%) rH



„The relative Humidity is the ratio of water vapor pressure (P_{w}) and saturation vapor pressure (P_{ws}) at the present temperature [$P_{\text{ws}}(t)$]“

$$rH = \frac{P_{\text{w}}}{P_{\text{ws}}(t)}$$

$$\%rH = 100 \times \frac{P_{\text{w}}}{P_{\text{ws}}(t)}$$

Figure 2: Relationship between saturation vapor pressure (P_{ws}), partial pressure (P_{w}) and relative humidity (rH)

Saturation Vapor Pressure

Within an air layer above the surface of a certain liquid, a balanced vapor pressure would be the result if the air layer above is embedded. The value of the vapor pressure depends on the temperature and the type of liquid. The saturation vapor pressure limit prevails if the condensation level and the level of evaporation are balanced. A rise in temperature leads to a considerable increase in the saturation vapor pressure (Figure 3).

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Temperature and relative Humidity

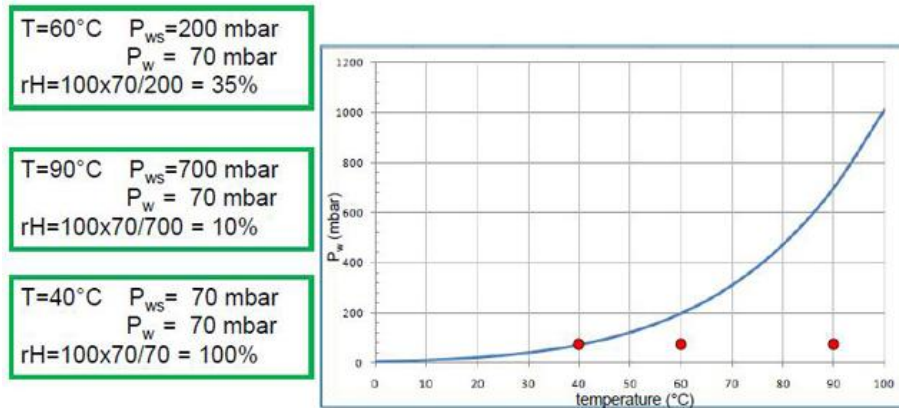


Figure 3: Example of the relationship between temperature and relative humidity

Water Activity

Water activity (a_w) serves as a measure for free water molecules contained in a material (liquid or solid). The mathematical correlation between the saturation vapor pressure and the water activity is shown in Figure 4. The water activity is defined as the quotient of the water vapor pressure above the material and the saturation vapor pressure above pure water.

Relative Humidity %rH \rightarrow Gas
Water activity $a_w \rightarrow$ Liquid

„The water activity a_w serves as a measure for free available water molecules within a certain material “

$$a_w = \frac{P}{P_0}$$

P – partial pressure of water within a substance bordering a certain material

P_0 – saturation vapor pressure of water at the same temperature

Figure 4: Water activity

The water vapor pressure above the respective material/fluid depends on the characteristics of the material, e.g., the base oil type and additives. The water activity changes depending on the actual content of freely moving water molecules and serves as a measure for the actual difference value compared to the saturation limit. This means it may increase or decrease during fluid usage depending on factors such as the change in additives or the generation of aging products. This aspect especially has to be observed when it comes to determining specific saturation curves for a certain oil type. Consequently, the mathematical relationship between the saturation limit value and water content (ppm) will change. Furthermore, water activity (saturation) is substantially dependent on temperature. Other than gases, the change due to pressure is negligible, since these are more or less incompressible fluids.

Methods to Determine Water Content

There are several methods to determine water content. These can be differentiated based on whether the content of water in dissolved form is measured or the absolute water content is determined, i.e., besides measuring dissolved water, free water also is taken into account. Common techniques include FTIR and the Karl Fischer method. In practice, simple screening

method.

Measurement of Humidity/Water Activity

Relative humidity is typically measured by means of electric sensors. With lubricants, mostly capacitive humidity sensors are used. Figure 5 shows the basic construction.

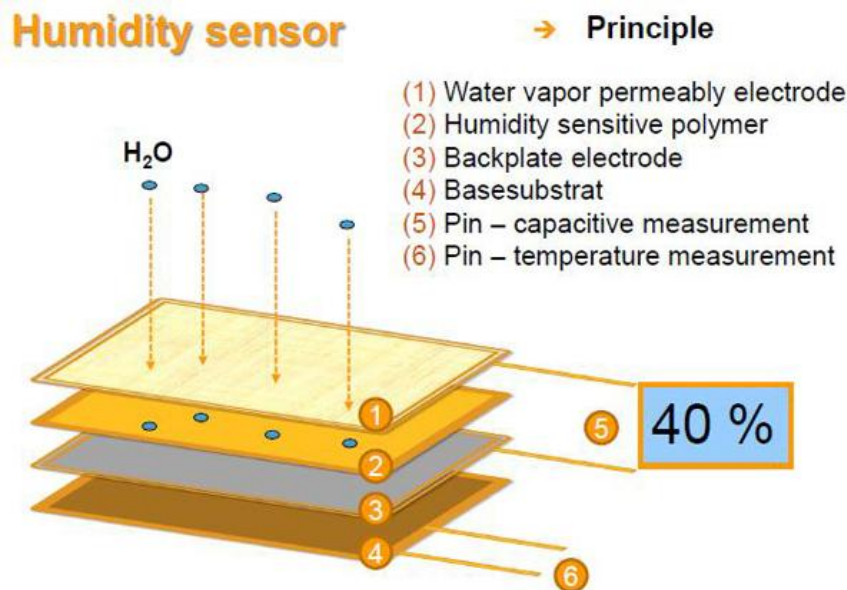


Figure 5: Principle construction of a capacitive humidity sensor

A water-vapor-permeable electrode serves as a contact layer for the sample. Below this electrode, which is coated with noble metal, there is the dielectric, whereby the electric characteristics adjust depending on the relative humidity. Its counterpart is situated below on a base substrate made of glass or plastic. Its construction is similar to a plate capacitor. Due to the diffusion of freely movable water molecules, a balance of moisture sets in. The result is always compared against the maximum solubility of the media (saturation).

Calculating the correlation to the absolute water content in ppm or mg/kg is possible only by knowing the limit of solubility and by determining the saturation curve (Figure 3). The accuracy of the available sensors is between 2 and 5 percent relative humidity.

Determination of Water Using FTIR

FTIR is based on the fact that absorption of individual molecules within the lubricant varies dependent on their typical linkage. The FTIR device compares the spectrum of the current sample with the respective fresh oil data. The spectrum of a used oil sample contaminated with water differs from the fresh sample regarding its OH oscillations at a wave number between 3,650 to 3,150 cm⁻¹. By means of the band intensities or the area calculation within this wave number range, it is possible to determine the water content according to the Beer-Lambert law (Figure 6).

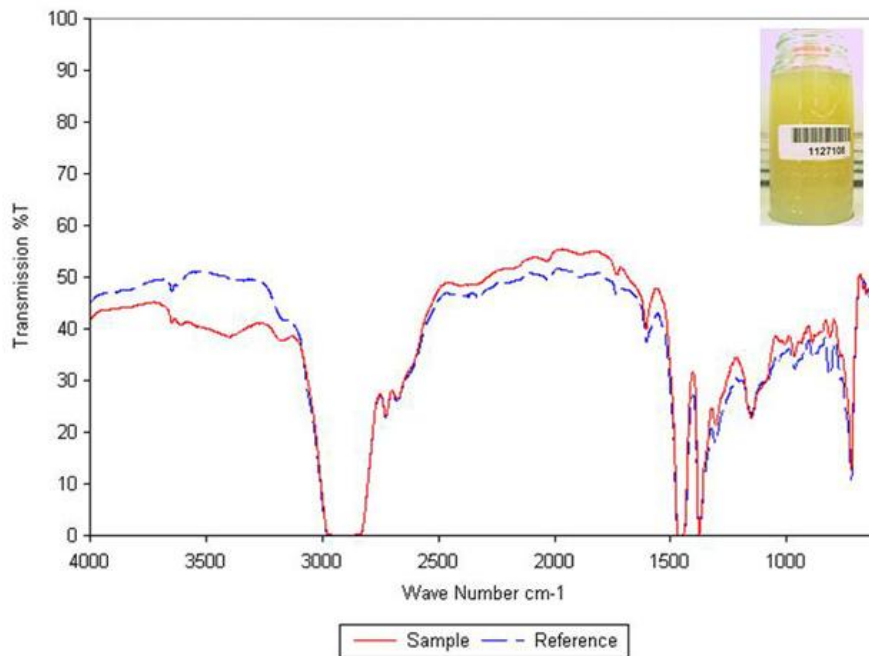


Figure 6: Fresh and used oil spectra of an HLP oil containing 2,265 ppm water

If the fresh spectrum becomes modified due to a change in the lubricant contents, or if the used lubricant is mixed with another type, or if OH groups rise due to oil degradation, considerable differences with regard to the calculated water values can occur. Therefore, it is necessary to take into account all possibilities when evaluating FTIR results to avoid wrong interpretations. Consequently, the minimum limit of 1,000 ppm seems plausible. The maximum limit is reached when water droplets appear inhomogeneous. Using this method for lubricants with a saturation limit below 1,000 ppm should be avoided.

Determination of Water According to the Karl Fischer Method

To precisely determine the water content within lubricant or hydraulic oils is not easy. Some substances require titration. Coulometric titration according to Karl Fischer is based on an electrochemical method. The device consists of two components – the Karl Fischer titrator and an integrated oven. A certain amount of the oil sample is filled into a glass vial and hermetically sealed via a septum (Figure 7). The glass vial is then placed into the oven, and the septum is punctured with a cannula. Nitrogen is poured into the sample and afterward into the titration vessel. Due to the heating process, water within the oil sample is evaporated (water vapor). With this method, only the water vapor that was absorbed by the stream of nitrogen is led into the titration vessel. Side effects due to additives are fully avoided.



Figure 7: Karl Fischer titrator with sample vials

Water Saturation Level of Different Fluid Types

The saturation limit of a lubricant depends on the material's qualities, e.g., base oil type, additives, contamination or components due to degradation. The limit value changes in relation to the actual number of free water molecules. This parameter varies during the operating life of hydraulic and lubricating fluids depending on the changes in the fluid. This aspect is especially relevant when it is necessary to determine oil-specific saturation curves, because the mathematical relationship between the saturation limit and the water value in ppm of the fresh product might change after some time in use.

With regards to motor oils, this usually means that the water solubility at the same temperature decreases, because additives are consumed and thus are no longer available to bind water molecules. For most hydraulic fluids and circulation lubricants, water solubility increases when the fluids are in use because of the increase in the number of polar constituents resulting from the rise in aging products. They, in turn, can bind additional water molecules.

At the Oelcheck laboratory, several hundred oil samples with different additive packages and various viscosities have been analyzed. The absolute water content was determined by the coulometric Karl Fischer method, while the water activity (relative humidity) was determined by water sensors. Oversaturated samples were excluded. Among the fresh oil samples, used oil samples from various components have been analyzed. Figure 8 shows some typical saturation levels of different hydraulic fluids. Narrow ranges are seen due to altering additive packages and different influences. Figure 9 shows the limit values of common lubricants.

Hydraulic

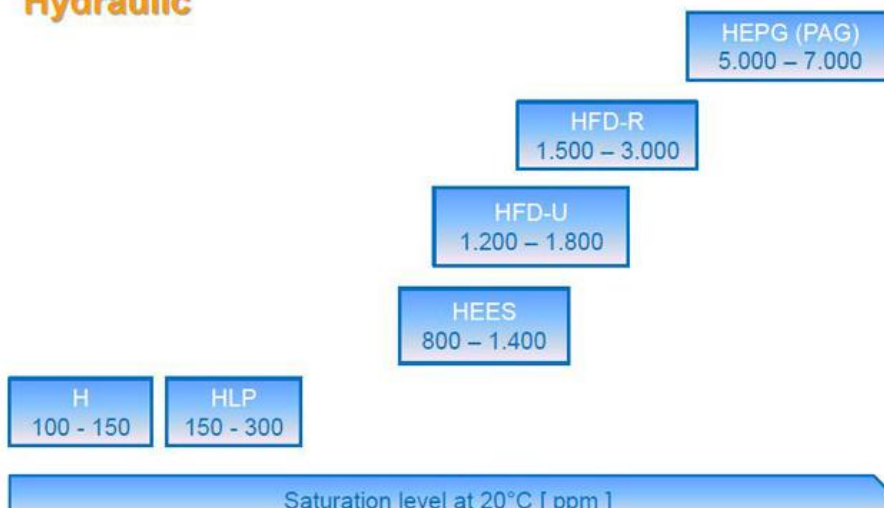


Figure 8: Water saturation ranges of various hydraulic fluids

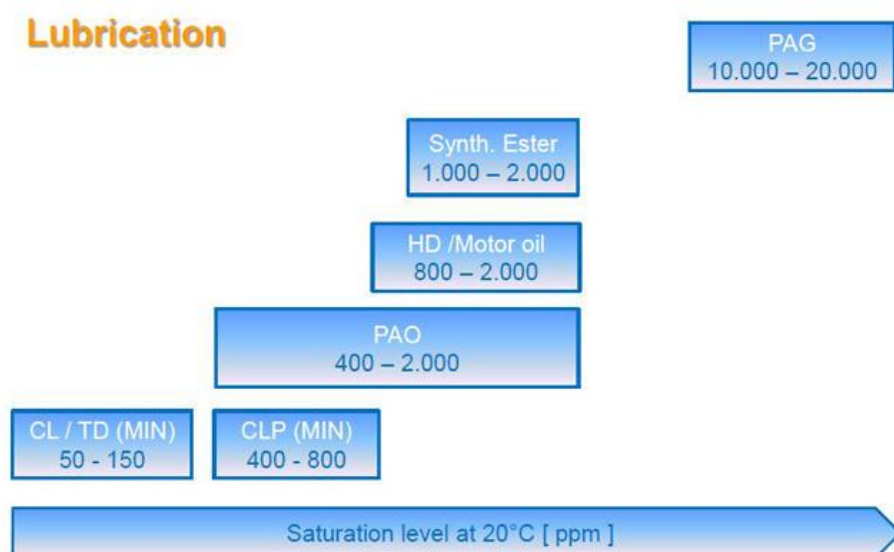


Figure 9: Water saturation ranges of various lubricants

Specification and Limit Values

Aware of the negative consequences caused by free water within hydraulic and lubricating fluids, several manufacturers and standards organizations have published guidelines and limit values regarding the allowable water content. Tables 1 and 2 show some examples for synthetic and mineral oil-based fluids.

Specification Mineral Oil	Water content absolute
Hydraulic (DIN 51524)	500 ppm
Lubrication (FAG / SKF)	300 / 200 ppm
Turbine (DIN 51515)	150 ppm
Isolating Fluid	10 ppm

Table 1: Limit values of the water content of mineral oils (detection according to the Karl Fischer method)

Specification Synthetic Fluids	Water content absolute
Hydraulic (HEES)	1000 ppm
Lubrication (PG)	5000 ppm

Table 2: Limit values of the water content of synthetic fluids (detection according to the Karl Fischer method)

Limit values are only given for the absolute water content. Indeed, it has to be proven that certain limit values have not been exceeded. This led to the correlation between the values of the humidity sensors in percent rH and the absolute water content (ppm or mg/kg) being determined and saved as "calibration." So far, standards for maximum relative humidity levels are only indicated by a few manufacturers of filters and humidity sensors.

Adapting the saturation range of the humidity sensor to the actual water content of the fluid is the only way to ensure that the humidity sensor is calibrated for the specific fluid.

to determine saturation curves, and the mathematical correlation could be neglected.

Figure 10 shows an explanation with plausible limit values for the use of humidity sensors based on measured values (relative humidity).

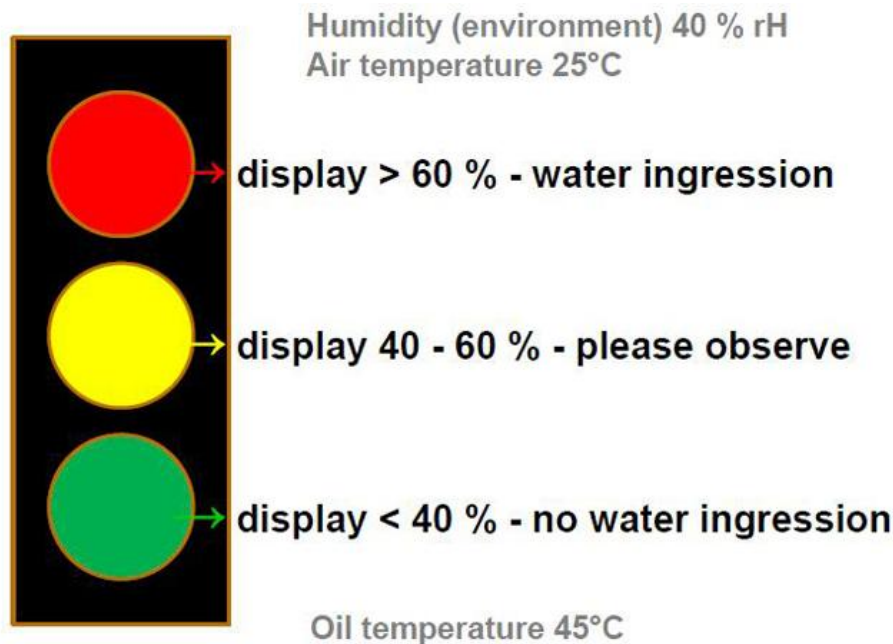


Figure 10: Example of a simple estimation of the relative humidity of lubricants

Remember, water is usually the liquid source of lubricant contamination. Measuring and observing the relative moisture/water activity can serve as an early indicator of the possible development of harmful free water. In order to assess the risk and to initiate necessary measures to prevent serious damage, it is useful to know the saturation level of the liquid in use. Therefore, it is recommended to stipulate additional limit values regarding the maximum relative moisture in comparison to the saturation value.

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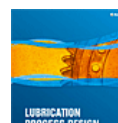
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