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Factors Affecting Water Solubility in Oils

Water can occur in three phases within an oil system, depending on the chemistry of the oil in question. This goes for both mineral and synthetic oil. In general, oils dissolve some water. However, each oil has its specific water-saturation point beyond which excess water becomes either emulsified or free. Therefore in various oil-systems, one may have to deal with dissolved, emulsified, and/or free-water.

A solution is a thermodynamically stable state, where solvating forces homogeneously mix all the molecules present in the solution. The type and amount of additives mostly determine the water solubility of new oils, whereas oxidation products have a remarkable effect on the solubility of aged oils.

Oil composition

Pure base oils have very limited solubility, which is related to the ratios of paraffin, naphthenic, and aromatic compounds. The saturation point at 20 °C varies from approximately 30 parts per million (ppm) of paraffin oils to over 200 ppm of fully aromatic liquids, but it is typically between 40 to 80 ppm. Solubility may increase significantly with the use of additives. The typical value for new lubrication oil is <500 ppm. Oxidation products also increase solvating efficiency. Mineral-based transformer oils typically have very little additives and therefore have low solubility like base oil, whereas lubrication oils with greater amounts of additives generally have much higher solubility (Figure 1).

The overall absorption forces and water content of the solution in the equilibrium state are determined by Gibb's energy of mixing. On the molecular level, the absorption forces are binding forces between the water molecules and the molecules in the oil matrix. Water molecules are polar by nature, so the interaction forces increase with the increasing polarity of the matrix molecules, such as additives and oxidation products.

Temperature

The dependence of solubility on temperature is almost always exponential (Figure 1). Hot oil dis-

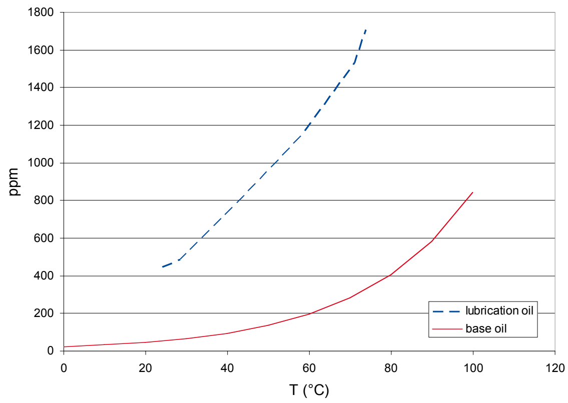

Figure 1: Average water solubility of mineral base oil and one lube oil as function of temperature.

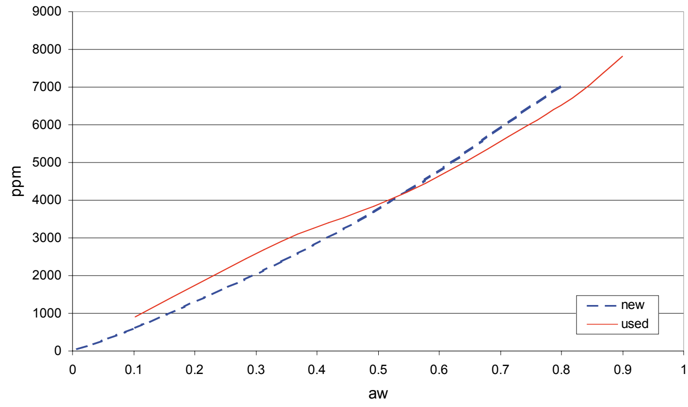

Figure 2: Solubility of fresh and used engine lubrication oil.

solves greater amounts of water. The hotter the oil, the greater the water absorption from air to oil in the same humidity conditions. This should be noted in any system setup, as airborne moisture contamination is one of the most common water sources.

Aging of oil

Lubricating oil circulating in high-speed systems deteriorates with time due to oxidation. Oil characteristics - presence of oxygen, catalysts present, and the temperature levels to which the oil is exposed - determine the rate of the aging process. In lubrication oil systems, air is always present, and the metal debris from machine construction and the moisture present are catalysts for the aging, that is, oil deterioration process. Aging processes are equilibrium reactions, and therefore the decay rate of oil is a function of activity of water rather than absolute water content. High temperatures and mechanical stresses, e.g. in the bearings, also accelerate the process.

Free water / emulsion

When water content in oil reaches the saturation point of that oil, it separates out and free water is formed, resulting in a two-phase system. Free water is commonly considered as the number one contaminant of oil. Water corrosion and cavitation type damages are mainly consequences of the free water phase.

Under a high mixing ratio or presence of surfactant additives (i.e. wetting agents that lower the surface tension of a liquid, allowing easier spreading, and the interfacial tension between two liquids), water may form an emulsion with oil. An emulsion is a mixture of two unblendable substances, where one substance is dispersed in the other. Because of surfactants, micro-size water droplets are homogeneously mixed in oil, forming an emulsion. The surfactants are chemicals that have both hydrophilic (a molecule that can bond with water) and hydrophobic (a molecule that is repelled by water) natures and thus are soluble to both phase water and oil. They form micelles (liquid particles) over the water droplets that convert the droplets "soluble" in oil. Surfactants may be added to oils to form emulsion, or some additives may act as emulsifiers, although added for different purposes.

Moisture measurement

Traditionally, water in oil has been measured by Karl Fisher titration (a method for determining the moisture content of a sample) and expressed in ppm, which is the total absolute water content, thus not giving any indication whether water is dissolved or free. However, due to differences in oil types and difficulty in predicting aging effects, ppm values are often not sufficient. Therefore, relative values like water activity (aw) are useful parameters for setting alarms in control systems.

Capacitive thin film sensors give this value without temperature corrections or oil-type calibrations. The active film of the sensor absorbs water molecules, which change the dielectric constant (i.e. a measure of the ability of a material to resist the formation of an electric field within it) of the film. The absorption is proportional to the equilibrium relative humidity of oil, thus indicating the margin to saturation.

The Vaisala HUMICAP® thin film polymer sensor products are beneficial in applications where the water amount must not exceed solubility limit, i.e. free water has to be avoided. The sensor is very sensitive even to negligible amounts of water and other small polar molecules. Therefore, the active polymer film and the sensor structure have to be such that the additives and oxidation products in oil do not disturb the measurement. The latest generation of the Vaisala HUMICAP® sensor is developed for demanding moisture measurement in liquid hydrocarbons. The sensor's excellent chemical tolerance provides accurate and reliable measurement over a wide measurement range.

ppm conversion

If the solubility of a specific oil is known through the whole operating temperature range, the measured relative moisture value can be converted to absolute water content (ppm_W). However, we must note that the conversion is valid only if the water solubility of the oil does not change. In lubrication systems the solubility changes with time regardless of the system maintenance (Figure 2). In such cases, conversion to fresh oil does not give a true value of the water amount. However, an oil regeneration process may fully restore the original water solubility level of the oil. ●