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LUBRICANT INDUCED METAL CORROSION - AN ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY APPROACH

Abstract

Corrosion costs are above 3.3 trillion US $ worldwide affecting infrastructure such as highways, bridges, buildings, oil pipelines and industrial machining. Corrosion so far has severe consequences like down times, maintenance costs and security issues. Concerning lubricants a lot of research has been carried out the last decades by manufacturers of machines and lube formulators to protect metals against corrosion but each time a formulation is changed because of legislation, raw material availability or technical justifications, costly long term field tests most often have to be performed. Electrochemical Impedance Spectroscopy (EIS) is a method at the forefront of technology that supports the lubricant and metal industry identifying potential challenges of lubricant corrosiveness, corrosion tendencies of metals and additive performance.

Key words: *lubricant, corrosion, electrochemical impedance spectroscopy*

The main advantages of Electrochemical Impedance Spectroscopy (EIS) are speed, precision and reproducibility. It is able to measure corrosion tendencies at a broad range of temperatures from -70°C up to +240°C taking an in-depth look at decisive details such as additive activation mechanisms. Combining electrochemical impedance spectroscopy with various methods such as REM (Reflection Electron Microscopy), EDX (Energy Dispersive X-Ray Analysis) and ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy) it is able to obtain the full picture that R&D laboratories can draw. Alternating current (AC) methods measuring impedance are well known since years in sensor industries and used for example as online-sensors to determine the condition of lubricants. Concerning online-sensors the impedance measurement is performed at specific frequency spots measuring properties such as conductivity and susceptibility. Steps further depicting detailed information of corrosion tendencies EIS is used where test specimens are measured using frequencies between 0.1 Hz and 1 MHz giving a full spectrum. Performing frequency dependent measurement is making sense because impedance strongly depends on frequency. The electrochemical system reveals important information about mechanisms in lubricant formulations contributing to overall impedance by frequency response analysis. In general EIS is very similar to FT-IR spectroscopy where vibrational excitation of covalently bonded atoms and groups are induced and absorption spectra are recorded. In case of EIS dipolar moments of molecules and charged ions interact with the electromagnetic field. Obtaining ionic movement and polar interactions EIS perfectly fits to analyze corrosion and corrosion tendencies.

Think of lubricant formulations made of several compounds containing sulfur carriers highly corrosive to copper and you would like to know if your formulation containing coin metal passivators performs well. In this case EIS is capable of measuring the charge transfer resistance R_{ct} which is directly correlated to the corrosion tendency of the metal and lubricant under investigation. Focusing on R_{ct} formulators are able to optimize treat rates gaining margin. Screening temperatures between -70°C and +240°C one can focus if additives might get activated by temperature forming highly corrosive matter. Think of a formulation used at oil temperatures between +25°C and +50°C. If your formulation produces highly corrosive matter at +70°C you do not have to take care, but what if activation takes place at +40°C? Better you perform tests such as EIS to be sure and prevent severe security issues and costs.

In principle the measurement cell used is made of two metal pipes plugged together fixed into a Teflon holder. At the top of the pipes a Randel-Screw is used to fix both pipes and assure a well defined space between both electrodes. Between the electrodes the lubricant is filled in till the top of the outer pipe. Contact is taken using crocodile cramps at the top and left extends of the copper pipes. The assembly is shown in Figure 1.

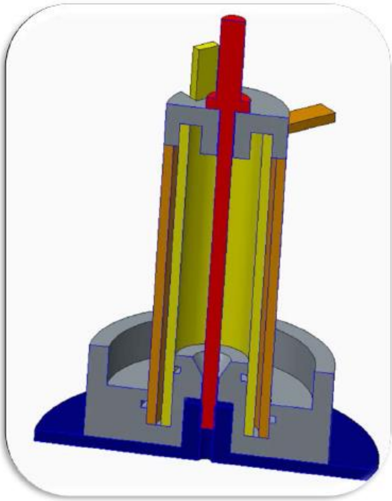

Figure 1: Measurement cell used to record an impedance spectrum

Heating and cooling the test specimen is performed using a climate chamber where the cell is placed into a faraday cage to optimize signal / noise ratio. According to ISO TR 16208 the spectrum is analyzed evaluating charge transfer resistance R_{ct}, electrolyte resistance R_s and double layer capacitance C_{dl}.

An example of a gear oil measurement between +0°C and +100°C is shown in Figure 2. The Arrhenius-Plot where the natural logarithm of conductivity ln(σ) is plotted against the reverse of temperature 1000/*T* is used for in depth analysis. For liquid electrolytes, as lubricants are, ln(σ) versus 1/*T* should give linear behavior where the slope is associated to the activation energy of charge transfer at the cell electrodes (equivalent to corrosion tendency). Everything different from a straight line can be attributed to a system change such as chemical reactions (e.g. corrosive matter formed) or phase changes (e.g. pourpoint).

In our case at +40°C the plot shows a significant change in slope pinpointing to formation of highly reactive species. At elevated temperatures +80°C and above surface layers are formed and the slope flattens. After heating up to +100°C reactive species still remain in the oil depicted as significant higher conductivities cooling down again to +0°C.

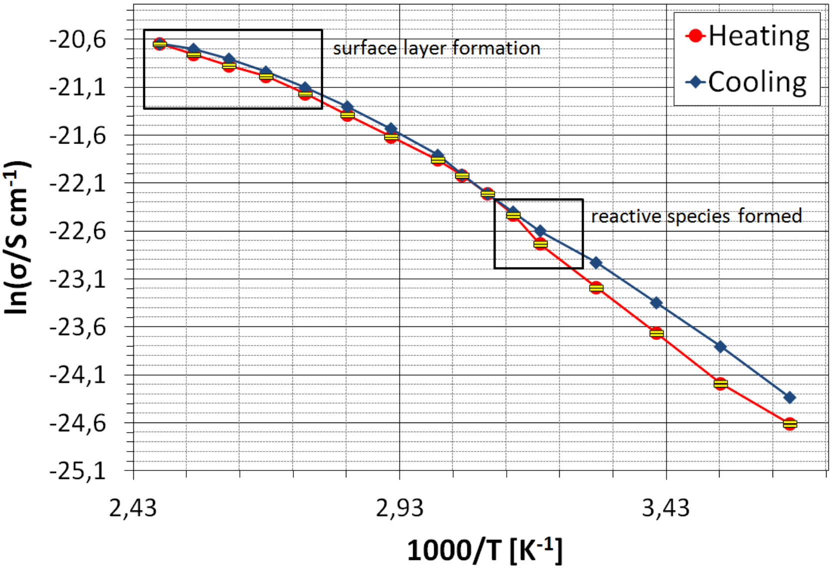

Figure 2: Arrhenius-plot of conductivity calculated from charge transfer resistance (R_{ct}). Calculated uncertainties are shown as yellow bars

Figure 3 shows a raster electron microscope picture after oxidative aging of the gear oil which was performed using rancimat technology where the sample was exposed to heat, increased volumes of air and a copper stripe catalyst over 4 weeks.

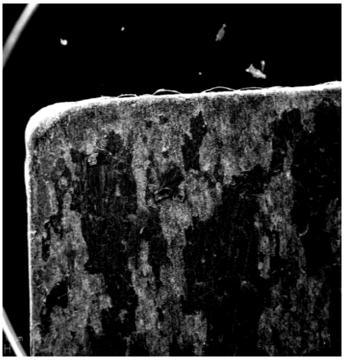

Figure 3: REM picture taken after aging oil and copper test specimen in a rancimat depicting severe pitting corrosion and surface layer formation

Generally, an investigative approach shown in Figure 4 should be followed. It covers several variables that can be varied such as temperature, materials, preparation and shelf life from which detailed overview about correlation effects which might take place can be obtained. Being able to use different kind of metal electrodes and checking almost each working fluid, combinations as shown in Figure 5 can be used for analyzing corrosion tendencies.

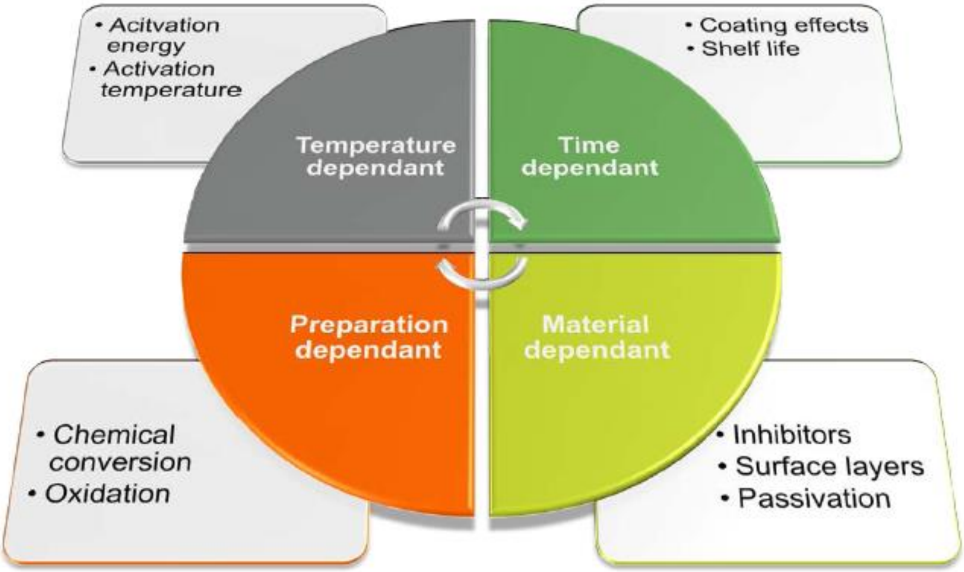

Figure 4: Investigative approach digging deeper clarifying corrosion mechanisms

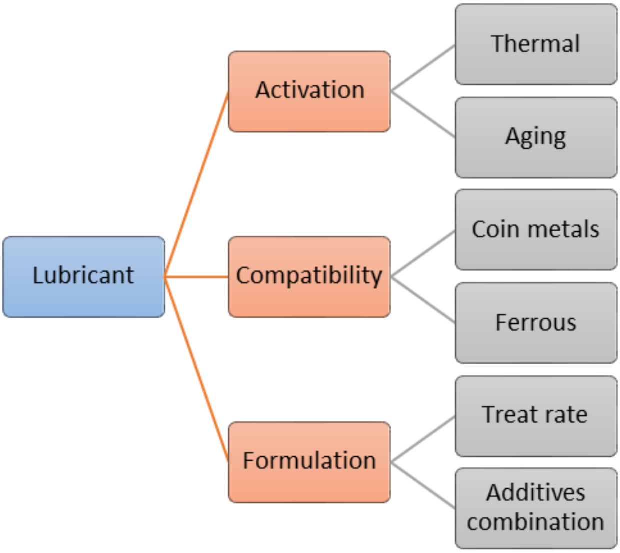

Figure 5: Strategy investigating corrosion effects combining different materials, formulations and temperatures

Conclusion

EIS bundled with various methods such as REM, EDX and ICP-OES, correlation of electrochemistry with optical and elemental analysis reveals detailed information about corrosion mechanisms pinpointing problems which may occur in everyday applications. Electrochemical impedance spectroscopy is capable analyzing additive performance, metal compatibility covering inhibitors (e.g. Cu-Inhibitors), metal surface passivation, coating formed, activation temperatures of e.g. sulfur carriers and activation energies of corrosive matter.

Therefore EIS assists revealing important information concerning additive treat rates, corrosion mechanisms and correlative material effects. EIS can be used to make the right decisions formulating lubricants and choosing materials mastering challenges of tomorrow.

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