ESTABLISHMENT OF THE POTENTIAL FOR THE FORMULATION OF HAZARDOUS THERMAL DECOMPOSITION PRODUCTS OF DEGRADED HYDRAULIC OILS USING MEMBRANE COLORIMETRY

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Abstract
The article is focused on the determination of the deposit formation potential of hydraulic oil using the Membrane Patch Colorimetry method. The determination of impurities does not only provide information about the amount of impurities in the oil. The color and intensity of the color can indicate what type of contamination may be involved. From experimental measurements, which provide important information in terms of degradation of hydraulic oil samples, it is clear that the lighter the color of the membrane after the passage of the hydraulic oil sample, the lower the measured Δ E value by the colorimeter and the higher the reliability and service life of the monitored components of machines and equipment.

Key words: *thermic degradation; colorimetry;insoluble contaminants; used hydraulic oil; index MPC.*

INTRODUCTION

Hydraulic oil is a fundamental carrier of information about the condition of key machine components, but it is a very often neglected and overlooked structural element, while the condition and cleanliness of the oil have a very significant impact on their reliability (*Chokelarb et al., 2024*). Hydraulic oil usually consists of petroleum or synthetic base oil and additives (from 0 to 5 %) that improve the service life and performance of the oil in aggressive environments. The base oil ensures an optimal hydrodynamic lubrication regime in the lubricant, which depends on viscosity and operating temperature. Antioxidants and anti-wear additives minimize oxidation on metal surfaces and treat surfaces with a protective film. Detergent-dispersant additives neutralize acidic oxidation products and prevent the deposition of impurities, thereby influencing the oxidation process.
Following the degradation of industrial oil in technical equipment is one of the most significant diagnostic methods, which can be used to characterize the aging state of the oil and also predict its remaining useful life (*Omiya et al., 2025*). Oil degradation is mainly influenced by the ongoing oxidation process, thermal degradation and chemical reactions that occur in real operating conditions of the machinery (*Kopčanová et al., 2020*). In addition, *Muhammad et al. (2020)* confirmed in their study that the oxidation rate increases in the presence of metal impurities and water molecules. This is manifested by the depletion of additives and subsequent oxidation of the base oil, which, due to chemical reactions between unstable oil components and oxygen, often leads to oil-insoluble degradation products, which subsequently begin to form deposits and sludges of various forms in the oil system - from soft jelly-like to sticky sludges to hard and shiny varnishes, the size of which is often less than 1μ (*Hong & Jang, 2023*). The former prevent heat dissipation, clog filters and narrow profiles or reduce the thickness of the lubricating film. The latter contribute to abrasion and wear. In addition, both increase the acidity of the hydraulic oil and pose a risk of corrosion. These degradation products are not measurable by conventional oil cleanliness grading procedures, which are only able to detect particles larger than 4 or 5 μm and thus provide information on only about 15 % of the total contamination of hydraulic oil. As a result, they are unable to identify varnishes or oxidation products, which can be as harmful to hydraulic oils as larger metal particles and other contaminants (*Kon et al., 2020*).
Regarding the measurement of insoluble contaminants in hydraulic fluids, the relevant standards for their determination are ASTM D4898:23 according to ISO 4405:22. These use gravimetric analysis, where the contaminated hydraulic oil is found in the standard porosity through a membrane filter of 0.45 and 0.8 μm, less common 0.2 μm, which means that they also capture oil degradation products of larger

dimensions, which change color from yellow to dark brown. After obtaining a membrane with a diameter of 47 mm, the result is calculated as the mass or mass captured on the membrane in mg.kg^{-1} mg.100 ml^{-1}. For monitoring the presence of soft sludge and subsequent determination of the concentration of insoluble contaminants in operating oils, the most widespread colorimetric method of the color of the membrane filter disc (MPC test), which is described in detail in the ASTM D7843:25 standard. However, this standard is currently used only for testing operating turbine oils (C*hokelarb et al., 2024*)
The aim of this article was to apply the principles generally used for the MPC test of turbine oils to the measurement of insoluble contaminants in samples of hydraulic oil of quality class HM and viscosity grade VG 46 as a function of time used in the circulation system of two shortening nodes of Baljer & Zembrod wood sorting and handling carts.

MATERIALS AND METHODS

The quality of the hydraulic oil and indirectly the condition of the hydraulic circuit of the two shortening nodes of the Baljer & Zembrod timber sorting and transport equipment was monitored for 12 months, during which a total of 5 samples of the used hydraulic oil manufactured by Eni (Eni S.p.A., Rome, IT, Italy) of the HM quality class and VG 46 viscosity were taken from the tanks with a sampling frequency of approximately 500 operating hours according to the sampling procedure according to ASTM D4057-22 . The used petroleum-based hydraulic oil guarantees trouble-free operation even with strong temperature fluctuations thanks to its high viscosity index. The low pour point guarantees immediate readiness of the equipment for use at low ambient temperatures. It is also characterized by excellent wear protection and very good oxidation stability, as well as excellent anti-corrosion properties.
Special HDPE sample containers were used for sampling to prevent exposure to UV radiation from internal and external sources and the subsequent increase in the formation of deposits in the oil samples. Each sample had to contain at least 60 ml of the tested material, in accordance with the above-mentioned regulation. Since the oil taken was not returned to the machine during the analyses, it had to be topped up with new oil. Of course, the new oil did not have the same properties, so it was necessary to make a correction for the oil topping up before the analysis, which is described in detail in the publication by *Hönig et al.* (*2018*).
The hydraulic oil sample that was analyzed was stored for 68 to 72 hours (*ASTM D7843-25, 2025; ASTM D4057-22, 2022*) at 15 to 25 °C without access to light before determination. The measurement and evaluation of the potential of hydraulic oil to form hazardous thermal degradation products was carried out using a vacuum filtration unit with an electric vacuum pump Vacuubrand model MZ 1C (Vacuubrand GmbH + CO KG, Germany) Fig. 1 after thorough homogenization of the monitored sample in the laboratory of InterTriboDia, s.r.o. The preparation of the filtration set for measurement consisted of placing a membrane filter with a pore size of 0.45 μm into the funnel of the filtration unit. Subsequently, we filled the funnel of the filtration unit with 50 ml of a hydraulic oil sample to which we added 50 ml of the prescribed solvent based on hydrocarbons with an unbranched chain C5 to C9 with a boiling point of 35 to 60 °C. The mixture was thoroughly mixed for about 30 seconds and filtered through the membrane using vacuum (71± 5 kPa).

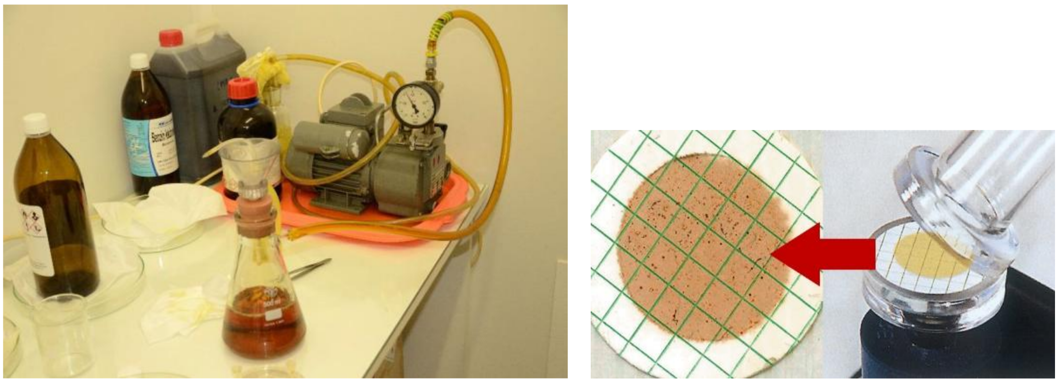

Fig. 1 Filtration kit for evaluating the potential for the formation of thermal degradation products

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The membrane color caused by the captured insoluble contaminants was measured colorimetrically on the International Commission on Illumination (CIE) L*a*b* color scale using a handheld visual spectrophotometer (MPC Color, Fluitec, USA) that provides results in the CIELAB color space – Fig. 2b. CIE L*a*b* is a three-dimensional color space that covers all colors perceived by human vision. For use in the digital world, it is usually mapped in practice to a three-dimensional integer space, and therefore the values of L*, a* and b* are often absolute values with a predefined range. The lightness value L * represents the darkest black at L * = 0 and the brightest white at L * = 100. The color channels a * and b * represent neutral gray at values a * = 0 and b * = 0. The a * axis represents the green-red component, green in the negative direction and red in the positive direction. The b * axis represents the blue-yellow component with blue in the negative direction and yellow in the positive direction. The a * value is positive towards red and negative towards green; b * is positive towards yellow and negative towards blue. L * is positive towards light and negative towards dark (Fig. 2a).

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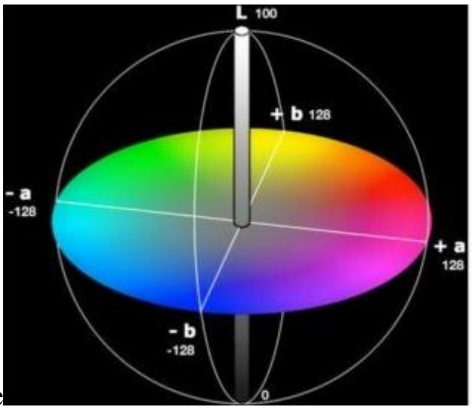

Fig.2 a- CIE LAB color space (L*a*b*) b – handheld visual spectrophotometer

The higher the L value, the higher the concentration of black particles in the oil. The black color can be caused by soot particles, which can indicate microdieseling, spark discharge or intense overheating of the oil in a certain place. The higher the a value, the greater the risk of corrosive particles forming deposits and sludges or a decrease in the additive content of the base oil. Finally, the higher the b value, the more prone the oil is to sticky deposits. This color space system is created by plotting the rectangular coordinates L*, a*, and b*, which are defined by equations (1) - (4).

$$L^* = 116 * \left(\frac{Y}{Y_n}\right)^{\frac{1}{3}} - 16 \quad (1)$$

$$a^* = 500 * \left[\left(\frac{X}{X_n}\right)^{\frac{1}{3}} - \left(\frac{Y}{Y_n}\right)^{\frac{1}{3}}\right] \quad (2)$$

$$b^* = 200 * \left[\left(\frac{Y}{Y_n}\right)^{\frac{1}{3}} - \left(\frac{Z}{Z_n}\right)^{\frac{1}{3}}\right] \quad (3)$$

$$\frac{X}{X_n}; \frac{Y}{Y_n}; \frac{Z}{Z_n} > 0.01 \quad (4)$$

where Xn, Yn, Zn are the ternary values that define the color of a normally white object as a reference material, which is a clean, unused and dried membrane, while the tristimulus values X, Y and Z define the resulting color of the membrane after the insoluble contaminants in the used oil sample have been captured. The results were expressed as ΔE according to equation (5), which means the color difference.

$$\Delta E_{ab}^* = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2} \quad (5)$$

where Δ L is the difference in lightness, Δ a is the difference in the red and green light spectrum, Δ b is the difference in the yellow and blue light spectrum

RESULTS AND DISCUSSION

The quick darkening of the samples hydraulic oil and the change in its natural odor were the impetus for us to confirm the presence of thermal degradation products by vacuum filtration based on the methodological steps outlined in the previous chapter. These products can change the chemical and physical properties of the hydraulic oil, thereby affecting its quality and performance in the circulatory system of the working equipment. The measurement result was the determination of the potential of the analyzed oil to form thermal degradation products and the level of severity of thermal degradation. To increase accuracy, the measurement of each sample was performed three times and the average value was reported as the result.

The calculated ΔE value, obtained according to equation (5), can then be evaluated according to the membrane color scale and severity. Severity 0, or good condition, means a very low probability of deposit formation and represents a ΔE value in the range of 0 to 2. Satisfactory condition, severity 1 indicates a low potential for the formation of degradation products with a ΔE value of 3 to 10. Warning condition with severity 2, or even medium potential for deposit formation, does not yet show a deposit formation problem, but they may start to form when the hydraulic oil cools, ΔE from 11 to 25. At this level, more frequent monitoring of the oil charge is recommended. With significant deposit formation with severity 3 (ΔE in the range of 26 to 45), there may already be an increase in temperatures in the machine's hydraulic system and operational problems. At this level of severity, it is recommended to take corrective measures, which are confirmed by a detailed oil analysis. If the ΔE value reaches critical numbers (severity 4 and ΔE value above 45), it already represents a high potential for the formation of degrading impurities, and intensive cleaning is necessary to prevent soft sludge from remaining on the walls of the machine's hydraulic system components. In urgent cases, the oil charge may even have to be replaced and the entire circulation system cleaned.

Measured data are presented in Fig. 3 and 4 and represent a summary of the observed formation of insoluble degradation products, which differ in different levels of staining of filter membranes in used hydraulic oil samples during the operating period in the open hydraulic circuit of shortening nodes of handling equipment for sorting and transporting wood logs. For illustration of described process selected values are shown in Tab. 1 and Tab.2.

Fig.3 Detail of the membranes of the hydraulic oil samples with captured thermal degradation products of the shortening node of the handling line I

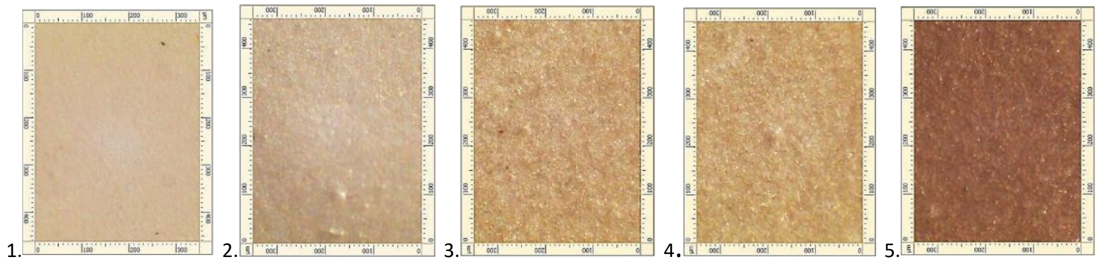

Fig.4 Detail of the membranes of the hydraulic oil samples with captured thermal degradation products of the shortening node of the handling line II

Tab.1 Membrane color value and severity level in the samples of used hydraulic oil in the circuit of the shortening node of the line I

Oil sample after	500 hours	1000 hours	1500 hours	2000 hours	2500 hours
Insoluble thermal degradation products					
Severity level	2	3	3	3	3
Insoluble MPC (ΔE)	16.25	26.71	27.09	28.14	34.57
Control limit ΔE	30		Abnormal limit ΔE	60	

Tab.2 Membrane color value and severity level in the samples of used hydraulic oil in the circuit of the shortening node of the line II

Oil sample after	500 hours	1000 hours	1500 hours	2000 hours	2500 hours
Insoluble thermal degradation products					
Severity level	2	2	3	3	3
Insoluble MPC(ΔE)	14.12	21.33	28.38	29.93	35.41
Control limit ΔE	30		Abnormal limit ΔE	60	

At operating temperature, the degradation products in the oil are dissolved or form small particles that are problematic to effectively quantify using standard tests. Degradation products, which result in the formation of deposits in the oil system and for this reason represent one of the most dangerous contaminants in circulation systems, were also monitored in the publications of the authors *Pravda et al. (2024)*; *Hong & Jeon (2022)*. They arise mainly from overheating or sharp local overheating of the oil. Modern lubricants, group II and III, form deposits more frequently than in the past (*Hobbs et al. 2021*). According to *Livingstone & Cavanaugh (2015)*, one of the reasons is the use of base oils with lower solubility, higher polarity or new additive formulations. For this reason, it is necessary to use modern analytical methods to regularly monitor the cleanliness and varnish and sludge formation potential of the oil, which can also include the membrane color evaluation method for determining total impurities (MPC test).

CONCLUSIONS

There are multiple ways a hydraulic oil can fail, forming deposits. Oxidation is the most common and well-known degradation pathway. Other mechanisms may also aid in degrading hydraulic oil, such as micro-dieseling, electrostatic spark discharge (ESD), or reactions with incompatible fluids or contaminants that migrate into the system. Traditional contamination monitoring practices do not always provide a sensitive and timely warning to machine and oil users of the potential for deposits in the machine's circulation system and their causes. As a result, a set of standard oil charge sample analyses may not provide a warning of when the oil will begin to degrade and form varnish or sludge.

If we focus on the visual aspect of hydraulic oil degradation products, especially oxidation products, we see colors ranging from yellow to brown, gray to black. If an oil sample is filtered through a test membrane with a porosity of 0.45 μm or less, oil degradation products will remain trapped inside the membrane and on its surface. The membrane is colored after filtration, and the more impurities there are in the oil, the richer and darker the color of the membrane. For oil fillings that require high oil purity, which include hydraulic system fillings in particular, it is appropriate to use the CPA method together with the

MPC method, which measures both reflected light and transmission through the membrane in the RGB color space.

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