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**FLUORESCENCE SENSOR FOR CHARACTERIZATION OF  
HYDRAULIC OIL DEGRADATION**

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**Abstract**

*Measurements of fluorescence emission of oil were used to develop a technique and sensor for detecting hydraulic oil quality in operation. Test results for hydraulic oils corroborate very well with optical emission spectrometry, particle counter, optical microscopy, total acid number, and viscosity test results. Fluorescence emission ratio parameter was found to be independent of dust and iron contaminant concentration in oil without additive, but dependent on oil chemical degradation. Basing on measurements of this parameter it is possible to detect degradation of oil before severe wear in a tribosystem. The study clearly shows that fluorescence emission ratio gives sufficient information to characterize and evaluate oil quality. The technique and sensor developed are found valid for evaluating hydraulic oil degradation. The sensor can monitor the oil oxidation during operation with high accuracy. It is reliable in operation and can be used for monitoring the oil quality in hydraulic systems of compressors and turbines.*

**Keywords:** *Tribosystem, oil efficiency, monitoring method, on-line device, fluorescence method*

**1. INTRODUCTION**

The analysis of lubricant in tribosystems is ever more widely used at industrial and transport plants [1]. Oil performance degradation causes corrosion, carbon formation, the loss of oil lubricity, filter clogging, and the elevation of local temperatures on friction surfaces thus accelerating the wear of friction units. The on-line monitoring of the condition of the lubricant makes possible not only its more effective usage but also the prevention of mechanism failure.

Oil oxidation is one of the main causes of oil performance degradation. To assess the degree of oxidation under laboratory conditions the standard for the total acid number (ISO 6618)

and the Fourier-spectroscopy method [2] are used. Fluorescence spectral analysis is also used in laboratory to determine the oil quality [3, 4]. In contrast to IR analysis fluorescence spectral analysis gives data on the general oil condition rather than evaluates the concentration of individual components.

Relatively cheap UV and short wavelength sources came into the market that provided conditions for the development of new fluorescence methods and devices for the on-line monitoring of oil condition.

The measurement of the fluorescence intensity and the excited state lifetime are basic

fluorescence methods used to evaluate oil condition in real time.

The effect of a high optical density of the oil on the fluorescence intensity is the main drawback of the fluorescence methods based on the measuring of the oil fluorescence intensity. To overcome it special methods for determining of the oil fluorescence characteristics are applied in devices for oil performance monitoring [5].

The fluorescence methods based on the measurement of the excited state lifetime involve time or frequency analysis or their modifications. The method of time-resolved fluorescence spectroscopy is one of such modifications [6–8], which does not need the oil optical density to be considered. However, it is rather complicated for on-line monitoring based on device built into the oil line or portable device. Moreover, expensive equipment is required to implement the method.

## 2. CONCEPT OF ON-LINE METHOD

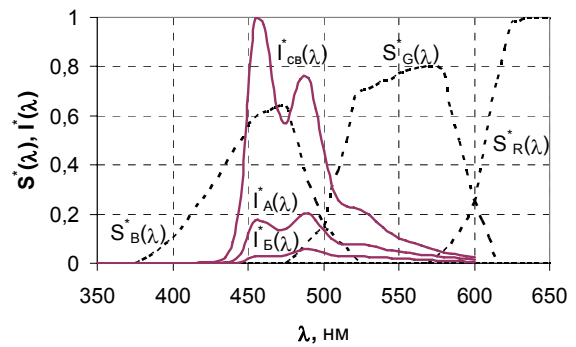
The fluorescence of oil as any organic substance is caused by energy transitions in  $\pi$ -orbitals of C=C bonds. In addition, conjugated  $\pi$ -systems require lower excitation energies than isolated bonds due to a higher mobility of  $\pi$ -electron and hence they are excited more easily. Therefore, aromatic and polyaromatic compounds are main sources of the fluorescence of organic substances [9].

The growth of the number of cycles of aromatic compounds or the length of double bond chains increases the mobility of  $\pi$ -electron and shifts the absorption and emission spectra towards the longer wavelengths. Intramolecular and intermolecular interactions affect considerably the fluorescence intensity. Intramolecular energy transfer can decrease or even annihilate the fluorescence of a molecule. Intermolecular interactions govern fluorescence quenching [10].

Oil oxidation causes the rapid modification of unsaturated aromatic molecules with oxygen-containing groups. As a rule, the oxidation of aromatic molecules leads to the formation of oxygen bridges (alkyl- and aryl-ethers) and general increase in polarity. All these factors result in higher delocalization of  $\pi$ -electron that increases the relative number of emitting centers in the long-wave region and for this reason the emission spectrum shifts towards the longer wavelengths.

This phenomenon of the fluorescence spectrum shift caused by oil oxidation has formed the ground for the method of the on-line monitoring of oil condition developed at the V. A. Belyi Metal-Polymer Research Institute (MPRI) in collaboration with the Korean Institute of Science and Technology (KIST).

Figure 1 shows changes in the spectra of the relative fluorescence intensity measured with the fluorometer (Model K2, ISS Co., USA) at the excitation wavelength of 300 nm for fresh hydraulic oil DTE-24 ( $I_{fr}^*(\lambda)$ ) and two samples (*A* and *B*) of used oil ( $I_A^*(\lambda)$ ,  $I_B^*(\lambda)$ ), the operating time of oil *B* being longer than that of oil *A*. The relative fluorescence intensity decreases in the short-wave region and increases in the long-wave one, i.e. with prolonging the duration of oil operation the spectrum shifts towards longer wavelengths.



**Figure 1:** Spectra of relative fluorescence intensity of fresh oil and two samples (*A* and *B*) of used hydraulic oil and relative spectral sensitivity of RGB photodiode in red, green, and blue ranges.

To evaluate the oil oxidation degree the diagnostic parameter  $F$  is used that characterizes the shift of the spectrum as the ratio of the fluorescence intensity  $I_{\Delta\lambda l}$  measured in the longer wave range to the fluorescence intensity  $I_{\Delta\lambda sh}$  measured in the shorter wave range:

$$F = \frac{I_{\Delta\lambda l}}{I_{\Delta\lambda sh}}. \quad (1)$$

The shift of the fluorescence spectrum towards the long-wave range depends on the oil oxidation degree and does not depend on the oil temperature and optical density.

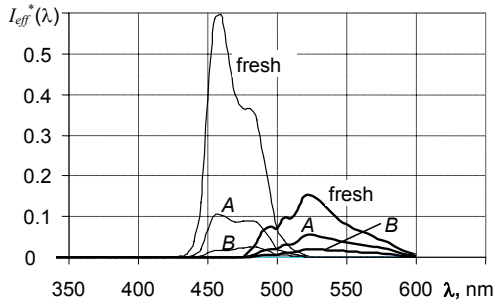
The fluorescence intensity in the short- and long-wave ranges is measured with the color sensor (RGB photodiode) that has recently come into the market. It is capable of measuring simultaneously the intensity of oil fluorescence

in three spectral ranges, i.e. red, green, and blue. For example, one of such detectors is Color Sensor MCS3AT whose relative spectral sensitivities in the red  $S_R^*(\lambda)$ , green  $S_G^*(\lambda)$ , and blue  $S_B^*(\lambda)$  ranges are shown in Figure 1.

The effective spectral fluorescence intensity  $I_{eff}(\lambda)$  (the spectral intensity transformed into the electric signal by the RGB photodiode) is the product of the spectral fluorescence intensity  $I(\lambda)$  of oil and the spectral sensitivity  $S(\lambda)$  of the photodiode [11]:

$$I_{eff}(\lambda) = I(\lambda)S(\lambda). \quad (2)$$

Figure 2 presents the calculated relative effective spectral intensity of fluorescence  $I_{eff}^*(\lambda) = I_{eff}(\lambda) / I_{max}$  ( $I_{max}$  – maximal spectral intensity of oil fluorescence). The effective spectral intensity in the red range ( $\Delta\lambda_R = 590\text{--}750$  nm) is zero and the ratio of the effective fluorescence intensities in the green ( $\Delta\lambda_G = 490\text{--}610$  nm) and blue ( $\Delta\lambda_B = 400\text{--}510$  nm) ranges increases as the duration of oil operation becomes longer.



**Figure 2:** Relative effective spectral fluorescence intensity of fresh oil and two samples (A and B) of used hydraulic oil.

The output signals of the RGB photodiode in the red  $J_R$ , green  $J_G$ , and blue  $J_B$  ranges are proportional to the effective fluorescence intensity and are found from the formulas:

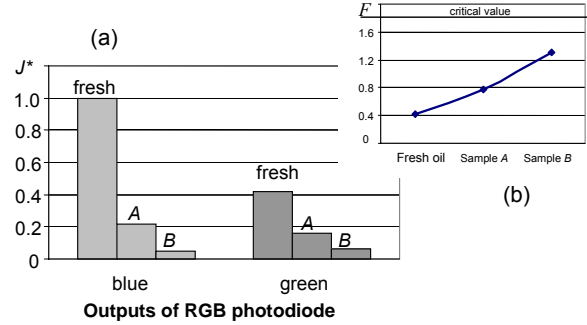
$$J_R = \int_{\Delta\lambda_R} I_{eff}(\lambda) d\lambda = I_{max} S_{max} \int_{\Delta\lambda_R} I^*(\lambda) S^*(\lambda) d\lambda, \quad (3)$$

$$J_G = \int_{\Delta\lambda_G} I_{eff}(\lambda) d\lambda = I_{max} S_{max} \int_{\Delta\lambda_G} I^*(\lambda) S^*(\lambda) d\lambda, \quad (4)$$

$$J_B = \int_{\Delta\lambda_B} I_{eff}(\lambda) d\lambda = I_{max} S_{max} \int_{\Delta\lambda_B} I^*(\lambda) S^*(\lambda) d\lambda, \quad (5)$$

where  $S_{max}$  is maximal spectral sensitivity of photodiode.

The calculated outputs of the RGB photodiode are shown in relative units in Figure 3, a.



**Figure 3:** Output signals of RGB photodiode in relative units (a) and parameter  $F$  as function of oil operation duration (b).

Variation in the parameter  $F$  with increasing the oil operation duration is shown in Figure 3, b. Later, the parameter  $F$  is compared to its critical value for a particular mechanism and finally the conclusion is drawn on the oxidation degree and efficiency of oil.

### 3. HYDRAULIC OIL MONITORING

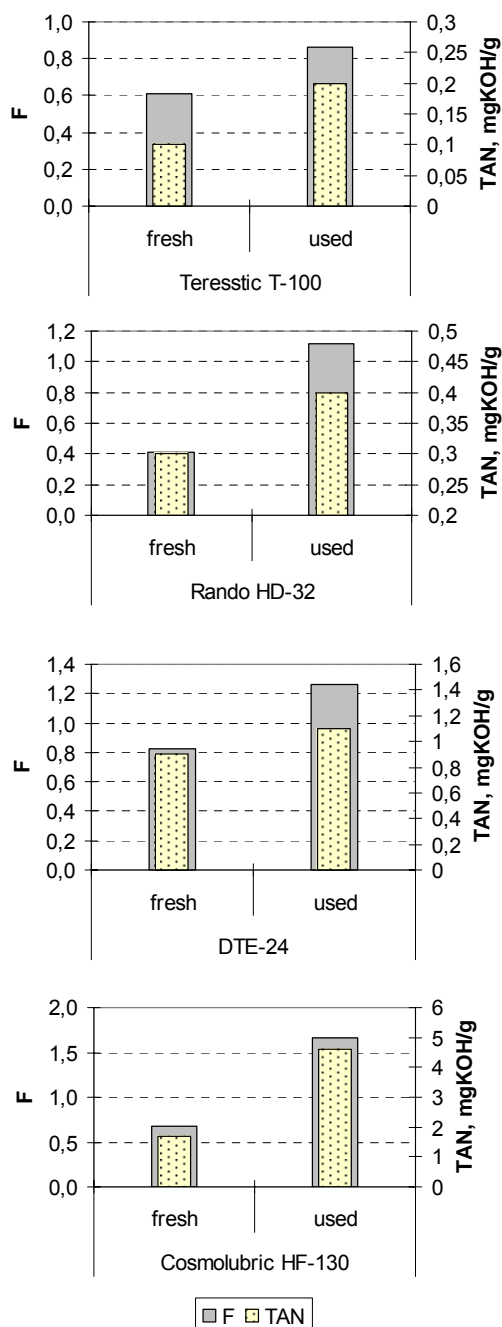
The method has been implemented by means of the fluorescence sensor Fluor-2 developed at MPRI and produced at KIST. The UVdiode LED3-UV-395-30 with the wavelength of 395 nm is used as the exciting emission source and the RGB photodiode Color Sensor MCS3AT serves as the detector. The sensor can be used as a portable device under laboratory conditions or built in the oil line. The data recording and processing are driven by a microcontroller according to specially developed software. The diagnostic parameter  $F$  is indicated on the monitor of the electron unit. When the parameter  $F$  exceeds its critical value the signal flashes which means the oil should be replaced.

The method efficiency was evaluated in laboratory study when testing fresh and used mineral hydraulic oils, i.e. Teresstic T-100 taken from a hot rolling mill, oil Rando HD-32 taken from the input unit of a hydraulic system, and oil DTE-24 and synthetic oil Cosmolubric HF-130 taken from a hot rolling mill. Values of the parameter  $F$  were compared to the total acid number (TAN) found by the standard laboratory method (ISO 6618).

The measurement results (Figure 4) demonstrate a good correlation between the diagnostic parameter  $F$  and TAN that indicates a

high validity of the results of estimating the oxidation degree of hydraulic oil by the fluorescence method developed.

monitor oil condition in hydraulic systems, compressors, and turbines.



**Figure 4:** Correlation between diagnostic parameter  $F$  and total acid number  $TAN$  when analyzing oils: Teresstic T-100; Rando HD-32; DTE-24 and Cosmolubric HF-130.

#### 4. CONCLUSIONS

The fluorescence method allows for monitoring the oil oxidation in equipment operation with high reliability. The sensor is distinguished by simple design, reliability, and low cost. The method and sensor can be used to

#### REFERENCES

- [1] Markova, L.V., Myshkin, N.K., Semenyuk, et al. Methods and instruments for condition monitoring of lubricants, *J. of Friction and Wear*, 2003, Vol. 24, No. 5, 50–59.
- [2] Barnes, M. The lowdown on oil breakdown, *Practicing Oil Analysis Magazine*, 2003, <http://www.practicingoilanalysis.com>.
- [3] Stellman, C.M., Ewing, K.J., Bucholtz, F., and Aggarwal, I.D., Monitoring of the degradation of a synthetic lubricant oil using infrared absorption, fluorescence emission and multivariate analysis: a feasibility study, *Lubrication Eng.*, 1999, Vol. 56, No. 3, 42–52.
- [4] Keller, M.A. and Saba, C.S., Monitoring of polyphenyl ether lubricants using fluorescence spectroscopy, *Applied Spectroscopy*, 1990, Vol. 44, No. 2, 256–268.
- [5] Kong, H., Han, H.-G., Yoon, E.-S., Markova, L., Myshkin, N., and Semenyuk, M., US Patent 7136155, publ.14.11.2006.
- [6] Fantasia, J.F. and Ingrao, H.C., Paper 10700-1-X, *Proc. 9<sup>th</sup> Intern. Symp. on Remote Sensing of the Environment*, Ann Arbor, 1974, 1711–1745.
- [7] Camagni, P., Colombo, A., Koechler, C. et al. Fluorescence response of mineral oils: spectral yield vs absorption and decay time, *Applied Optics*, 1991, Vol. 30, No. 1, 26–35.
- [8] Hegazi, E.M., Hamdan, A.M., and Mastromarino, J.N., US patent 6633043, <http://www.uspto.gov>, 2003.
- [9] Pradier, B., Largeau, C., Derenne, S. et al., Chemical basis of fluorescence alteration of crude oils and kerogens. Microfluorimetry of an oil and its isolated fractions; relationships with chemical structure, *Org. Geochem.*, 1990, Vol. 16, Nos. 1–3, 451–460.
- [10] Wehry, E.L., Structural and environmental factors in fluorescence. In *Fluorescence: Theory, Instrumentation and Practice*, New York: Marcel Dekker, 1967, 37–132.
- [11] Miroshnikov, M.M., *Teoreticheskie osnovy optiko-electronnykh priborov* (Theoretical Foundations of Optical-Electron Instruments), Leningrad: Mashinostroenie, 1977.