SURFACE PLASMON RESONANCE - A PROMISING METHOD FOR ESTIMATING THE QUALITY OF MOTOR OIL

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Abstract: *Shown in this paper is the possibility to diagnose quality of motor oil by using the method of surface plasmon resonance (SPR) Investigated in this work were four samples of the motor oil Genuine 5w-30 dexos 2, namely: the fresh one and three ones taken after car mileages 180, 430 and 712 km. When measuring the kinetics of refraction indexes for the studied samples of used oil, the authors observed a characteristic "shoulder" caused by sedimentation of oxidation and wear particles on the surface of SPR device sensitive element, while in the case of fresh oil there took place only the temperature drift of the refraction index. It has been experimentally shown that using the SPR method improves more than one order (from* Δf_{min} *= 0.17 vol.% down to* Δf_{min} *= 0.0107 vol.%) the detection limit and enhances sensitivity of measuring the wear particles concentration in motor oil as compared with the refractometric method. Thus, it is experimentally proved that the SPR method can be offered to control quality of motor oils as well as the degree of wear inherent to interacting parts of machinery.*

Keywords: LUBRICANTS, MOTOR OIL QUALITY, SURFACE PLASMON RESONANCE, REFRACTIVE INDEX

1. Introduction

The problem of controlling quality of motor oils in the course of their development, production and operation in cars is topical [1]. In up-to-date cars, terms for changing used oil are regulated by the service manual with the periodicity indicated as a mileage or time of operation. For the most of cars, the first change should be carried out after the mileage of 2…3 thousand kilometers or after 6 months of operation, and in what follows after 10 thousand kilometers or 12 months of operation. However, in most of cases when changing the oil, car owners as well as operators in a service center do not know what is the current state of the replaced oil.

To estimate the character of changes in the qualitative indexes of oil, which have an effect on functionality of aggregate and can carry information of its technical state, it is necessary to obtain data usually got applying the standard [2] and specially developed [3] methods for testing. Performed in the work [4] were investigations of the rate of accumulation and concentrations of wear particles in the motor oil to timely determine the moment of intense wear of engine parts. The concentrations of measured wear products (iron) in oil were within the range 15 g/ton (~17 µg/ml) up to 300 g/ton (~340 µg/ml). While the technique based on weighing does not allow determining lower concentrations of wear products and needs far longer times.

Also known are optical methods for diagnostics of motor oils, which are based on the analysis of absorption spectra in the IR range. In [5], the authors studied absorption spectra of motor oils versus duration of their operation in the engine, temperature oxidation (170 °C) and the moisture (water) content. Also, it is known the resonance method [6], the essence of which is in determination of the resonance frequency inherent to an oscillatory circuit consisting of the inductance and capacitor, between plates of which the studied substance is placed. In the course of operation, the dielectric permittivity of the motor oil changes its value, which causes respective changes in the oscillatory circuit resonance frequency. However, these methods do not allow determination of wear products availability and, consequently, cannot provide information on the relative engine wear degree. So, they can be applied only to analyze the motor oil state.

It is believed that the optical method based on SPR phenomenon can serve as the competitive one, and it is the reason to study its capabilities in investigations of motor oil quality. Diagnostic facilities using this phenomenon possess high sensitivity to very low concentrations of studied substances (0.01…2 pg/ml) [7, 8] and high accuracy of measurements [9]. In [10], The SPR method was applied to determine refraction indexes of pure and used (three thousand kilometers mileage) synthetic motor oil Mobil Super 3000 fe sw-30. It was shown that there are essential differences between these two oil samples both in refraction indexes and in character of their changes in time. The refraction index of pure oil was increased with time, while that of the used one was increased, which was explained by the effect of temperature factor and sedimentation of the oxidation products onto a sensitive element of the measuring device. In that case, the authors did not study these oils at earlier stages of operation (below one thousand kilometers mileage) and did not perform the analysis of possible contribution of oxidation and wear products concentration.

The aim of this work is to study possibilities for simultaneous control both the state of motor oil and wear degree of car engine parts at early stages of its operation as well as determination of oxidation and wear products concentration with high sensitivity and productivity.

2. Prerequisites and means for solving the problem

2.1. The model of effective medium that describes availability of oxidation and part wear products in motor oil

The motor oil with oxidation and wear products can be represented by the model of suspension containing a disperse filler. Knowing the values of refraction indexes for pure and used oils, one can determine the impurity percentage. Let us consider the pure motor oil as a matrix, and oxidation and wear products as filler. The most spread approaches to describe this system are the Wiener limits as well as Maxwell-Garnett and Bruggeman models. In these approaches, they introduce the conception of "effective medium" with some efficient refraction index, the value of which lies between those of matrix and filler. Wiener's limits [11] describe boundary values of the efficient refraction index in the model of layered structure (Fig. 1a) [12]. In this case, the medium efficient refraction index depends on direction of the field electric component. If it is oriented along the normal to composite layers, then the composite dielectric permittivity is defined by Exp. (1), but if it is parallel to composite layers – by Exp. (2). The refraction indexes for these two cases of field component directions are the Wiener limits, and they can be determined as roots of respective dielectric permittivities.

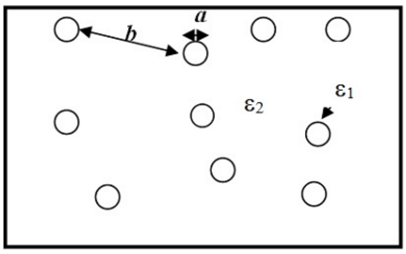
$$\varepsilon = f_1\varepsilon_1 + f_2\varepsilon_2, \qquad (1)$$

$$\frac{1}{\varepsilon} = \frac{f_1}{\varepsilon_1} + \frac{f_2}{\varepsilon_2}, \qquad (2)$$

where, f_1 and f_2 are volume fractions of suspension components;
ε is the relative dielectric permittivity of suspension;
ε_1 and ε_2 are relative dielectric permittivities of suspension components.

Since oxidation and wear products are located chaotically in motor oil, this approach can be applied only for determination of the possible range for suspension efficient refraction index values. The approaches by Maxwell-Garnett and Bruggeman seem to be more efficient, since they were developed especially for media with chaotically located of filler particles in the matrix. The main condition of applicability of the Maxwell-Garnett approach [13] is a small size ***a*** of nanoparticles in comparison with distances between them ***b***, and, as a consequence, their low volume concentration ***f*** in the total substance mass (Fig. 1b).

a)



b)

Fig.1. *Model of the layered structure (a) for determination of limits characteristic for efficient refraction index by Wiener for the suspension with the composition dielectric permittivities: ε_1 – filler and ε_2 – matrix. The model for a composite (b) in approaches by Maxwell-Garnett and Bruggeman [12].*

Within the framework of Maxwell-Garnett model, the medium has a dielectric permittivity related with permittivities of components by Exp. (3). The Bruggeman model [14] is applied when volume fractions of components f_1 and f_2 are in relation from 1/3 up to 2/3, which corresponds to the case of high concentrations:

$$\frac{\varepsilon - \varepsilon_2}{\varepsilon + 2\varepsilon_2} = f\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2}, \qquad (3)$$

where, f is the volume fraction of nanoparticles in suspension;
ε – relative dielectric permittivity of suspension;
ε_1 and ε_2 are relative dielectric permittivities of nanoparticle substance and matrix, respectively.

As initial data for modeling, one can use optical constants of synthetic motor oil and the main component of wear products – iron. Since in accord with the set task it was necessary to control quality of oil at early stages of operation, when the concentration of oxidation and wear products is low, we used the Maxwell-Garnett approach for determining the wear products concentration.

2.2. Structural schematic of the experimental setup and method of investigations

The experimental setup (Fig. 2) consisted of the thermostat (Fig. 3b), where the SPR refractometer "Plasmon-71" (developed in Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine) (Fig. 3a) and container with motor oil samples were placed.

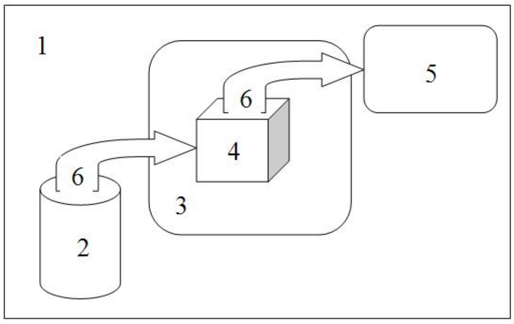
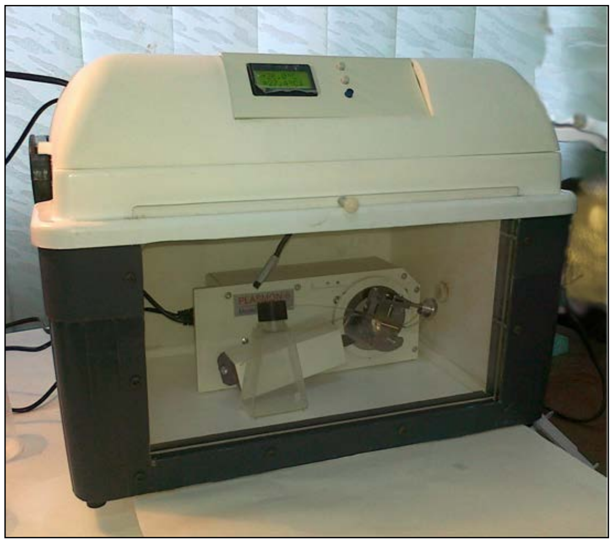


Fig.2. *Schematic experimental setup: 1 – thermostat; 2 – container with a motor oil sample; 3 – SPR refractometer; 4 – measuring cell of the refractometer; 5 – oil-gun pump; 6 – connecting pipes for pumping oil in and out.*

a)



b)

Fig.3. *Appearance of the SPR refractometer (a) and thermostat (b) with refractometer and motor oil container.*

Operation surface of the refractometer sensitive element is made of the gold film with the thickness 50 ± 2 nm deposited on a glass substrate. To excite surface plasmons in the gold film, we used *p*-polarized light from a semiconductor injection laser diode with the wavelength 850 nm. Necessary conditions for excitation of surface plasmons were provided by changing the angle of laser light incidence onto the sensitive element surface. The angular dependence of reflected light intensity $R(\theta)$ serves as a main device original characteristic. To determine the refraction index of motor oil samples and its changes in time, specified in this device are two operation modes: Multiple and Slope. Changes in the analyte refraction index cause a shift of the $R(\theta)$ minimum.

In the Multiple mode that was used in experiments, we performed periodical measurements of $R(\theta)$ characteristics to determine the angular shifts of their minima $\Delta\theta$, which is necessary for calculations of the refraction index inherent to the studied substance. The minimum of the measured characteristics was approximated with the polynomial of the 2-nd degree to reduce the measurement errors caused by a finite step of angular scanning the reflection characteristic. Then, we determined the angular position of the minimum for the approximating polynomial θ_{min} and calculated the respective refraction index that was considered as the result of these measurements.

We carried out the measurements of the refraction indexes for four samples of synthetic motor oil Genuine 5w-30 dexos 2, namely: before using it in the car engine (fresh) as well as after its operation for the mileages 180, 430 and 712 km (used). Being based on assumption that the wear products will be deposited onto the surface of refractometer sensitive element under the gravity force action, we performed measurements of kinetics (changes in time) of the refraction index for the studied samples by using the SPR refractometer “Plasmon-71”. In addition, we measured the same samples with the optical refractometer RL3.

The latter measurements were performed to demonstrate advantages of the SPR method in solving these tasks. The instrumental errors δn in measurements of the refraction index by using the devices RL3 and “Plasmon-71” are as follows: ±0.0002 and ±0.00001, respectively. For each sample of motor oil, the SPR refractometer was used to perform a series of 10 sequential measurements, which enabled to determine the limits of methodical errors when measuring the refraction index. These limits are ±0.00002. Using the values of optical constants for iron n_{Fe} = 3.0476 and k_{Fe} = 3.7819 [15] for the laser wavelength 850 nm and the method described in [16], we calculated the relative dielectric permittivity for iron ε_{Fe} = 2.7180, which is necessary for modeling.

3. Results and discussion

The refraction index values for the samples of motor oil Genuine 5w-30 dexos 2 were experimentally determined with the devices “Plasmon-71” and RL3 (Table 1). The difference between values of refraction indexes measured using the above devices is caused both by its dispersion and by the fact that optical refractometer gives the value of bulk refraction index, while the SPR refractometer gives the surface one.

Table 1. Results of measurements and data processing

No. sample	Car mileage, km	Measured refractive index		Dielectric permittivity	Concentration of nanoparticles, vol.%
		"Plasmon-71"	RL-3		
1	0	1,45643		2,12119	0
2	180	1,45664	1,4692	2,12180	0,1121
3	430	1,45695	1,4696	2,12270	0,2776
4	712	1,45742	1,4698	2,12407	0,5284
5	87	1,45645		2,12125	0,0107

Adduced in Table 1 are also the calculated values of the relative dielectric permittivity ε for the studied samples as well as results of calculations for the bulk concentration f of nanoparticles related to wear products in accord with the Maxwell-Garnett model. The errors of ε and f calculations are ±0.00005 and ±0.0005, respectively.

The dependence of motor oil refraction index on car mileage (Fig. 4) has a linear character and can be approximated by a linear function with the high matching factor (R^2 = 0.9973), which enables, using this function, to calculate the minimum car mileage necessary to control quality of motor oil and to determine the bulk concentration of wear products. Shown in the fifth line of Table 1 are this minimum car mileage and the respective value of the bulk concentration for oxidation and wear products in motor oil determined using the SPR method with the errors in measurements of the refraction index ±0.00002.

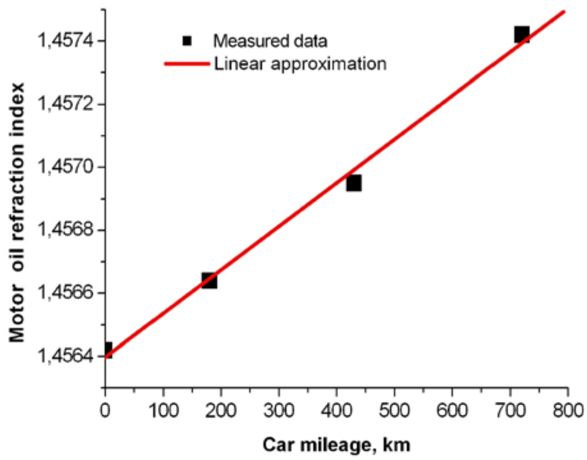


Fig.4. *Dependence of the refraction index for the samples of synthetic motor oil Genuine 5w-30 dexos 2 on duration of its operation in the car engine and the result of linear approximation of this dependence with the function* $y(x)=A+B\cdot x$, *where* A = 1,456, $B = 1.382\cdot10^{-6}$, *matching factor* R^2 = 0.9973.

The difference between refraction index values inherent to the samples of used motor oil determined with the optical refractometer corresponds to errors of measurements by using this device, which provides its resolution by wear products concentration Δf_{min} = 0.17 vol.%. While the resolution of the SPR refractometer equals to Δf_{min} = 0.0107 vol.%, which improves by more than one order (16 times) the detection limit, *i.e.*, considerably enhances sensitivity of measuring the wear products concentration in motor oil.

4. Conclusions

Application of the SPR method improves the detection limit and enhances sensitivity by more than one order from Δf_{min} = 0.17 vol.%. down to Δf_{min} = 0.0107 vol.%, when measuring the concentration of wear products in motor oil, as compared with the known refractometric method. It enables to determine availability of these products at early stages of car exploitation.

5. Literature

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