Application of FT-IR spectrophotometry in the assessment of changes in composition of greases induced by mechanical action

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Introduction

Increased mechanical forces generated in friction pairs requires, in order to ensure reliable operation thereof, application of lubricating agents that contain improvers [1, 2]. During operation the lubricating agent is subjected to a number of factors that cause irreversible changes in composition and loss of functional properties [3, 4]. In view of the above the selection of a fast method of analysing the chemical composition of the lubricating agent during its use becomes a major issue. One important criterion of selecting such method is the small size of the sample taken for analysis from the friction pair during the use of the lubricating agent, as is also the speed of carrying out the analysis, that is the short time needed to assess the condition (changes in composition) of the lubricating agent in question [5÷7].

The purpose of the research undertaken was to verify the applicability of infrared spectrophotometry to monitor changes in the chemical composition (content of additives, oxidation products) in greases subjected to tribological loads generated during tribological tests.

Subject and procedure of the study

The object of the study was a model composition of grease with a mineral oil base with no additives (M-0) and compositions containing 1%, 3%, 6% and 10% RC additive based on organic sulphur compounds.

Tribological tests of the greases were carried out using a 4-ball tester under the following conditions: spindle speed – 500 rpm, friction pair load – 40 kG, test duration – 60 min. Upon completing the test, the friction pair was disassembled, the test balls were washed with n-hexane and the diameter of the wear scar was measured under an optical microscope.

Chemical composition of greases was determined using an FT-IR 6200 spectrophotometer (Jasco, Japan). The IR spectra were obtained by the reflective method using a diamond crystal, spectral range 4000 to 600 cm^{-1}, resolution 4 cm^{-1}. Spectral tests were performed on greases before and after tribological tests.

Test results

Identification of loss of lubricating additives

In the first stage specific bands of the RC additives used were identified (Fig. 1).

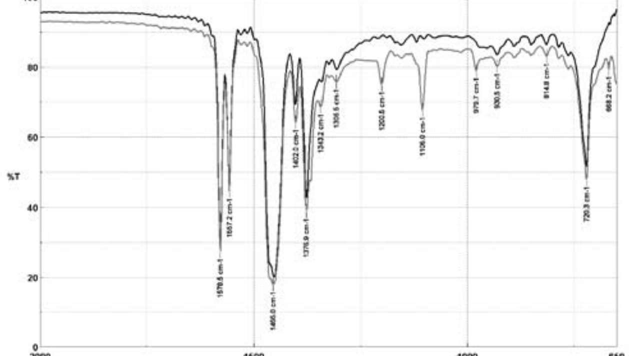

Fig. 1. IR spectra of greases: M-0 (1) and M-10RC (2)

Analysis of the spectra indicated the bands produced by the additive: 1105 cm^{-1} (C=S stretching vibrations) and 1200 cm^{-1} (C-H bending vibrations in –S-CH_3 group). In order to evaluate the analytical suitability of the bands mentioned, the relation between the additive content in grease and absorbance in these spectral bands was studied. The surface of the area between the baseline and the absorption curve was calculated by integrating for the bands mentioned. The relation between the surface area corresponding to the RC additive and its content in the grease is shown in Figure 2.

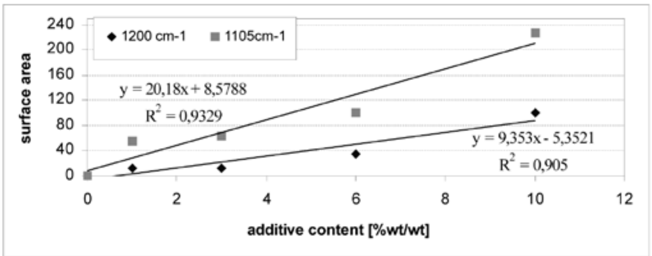

Fig. 2. Surface area corresponding to the RC additive vs. RC additive content in grease

The results obtained were subjected to statistical analysis (using mathematical tools provided by Excel spreadsheet software) and regression functions were fitted. The function equations are shown in the graph. It was found that the derived function equations had relatively high coefficients of linear determination ($R^2>0.9$). The linear relationship between absorbance (expressed by the surface area under the peak) and additive concentration satisfies the Beer-Lambert law, which states that there is a proportional relationship between the surface area under the peak, specific for the given compound, and its concentration in the sample.

The developed procedure for determining the content of additives in the model grease compositions was applied in the study of chemical structure changes caused by mechanical action in greases subjected to tribological tests.

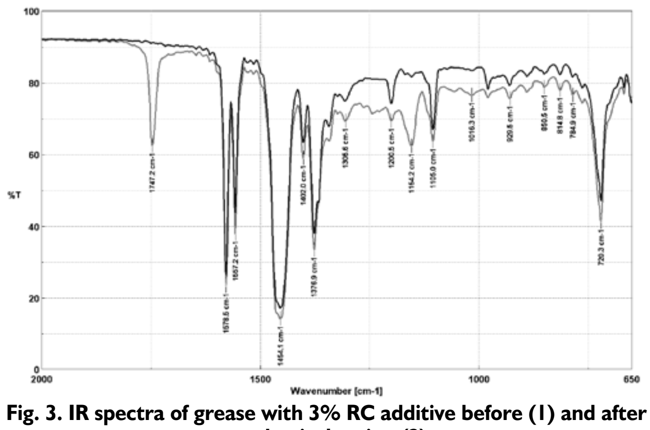

Fig. 3. IR spectra of grease with 3% RC additive before (1) and after mechanical action (2)

The analysis of spectra of grease compositions obtained before and after the mechanical action showed that the intensity of bands corresponding to the additives has decreased (Fig. 3). It was also found that the 1105 cm^{-1} band is not specific, because it lies in the area, which is typical for oxygen-containing oxidation products (C-O) and is obstructed by bands corresponding to the formed products of ageing.

Quantitative changes in the band corresponding to the grease additive is shown in Figure 4. They are presented as the surface area under the peak corresponding to the RC additive, before and after tribological tests.

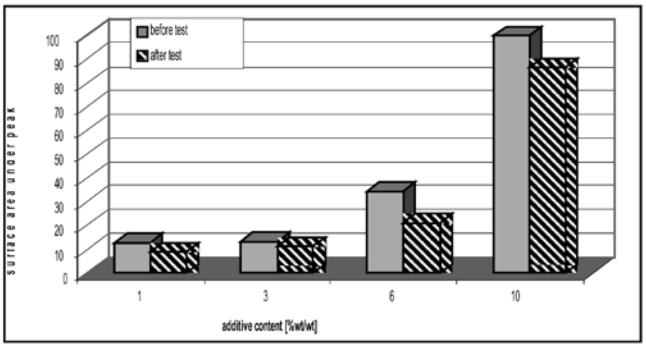

Fig. 4. Surface area under the peak vs. content of additive in grease before and after tribological tests

The data obtained indicated that in all cases there was a decrease of intensity in the 1200 cm^{-1} band, the largest decrease (by ca. 60%) in the case of grease containing 6%wt/wt additive. The smallest decrease was observed in the case of grease composition with 3% additive.

Identification of oxidation products

Bands, specific for oxygen-containing products of oxidation (1747 cm^{-1}), appear after tribological tests in the IR spectra of greases containing 1% and 3% additive. The intensity of these bands increased with increasing content of additive in the grease (Fig. 3). On the other hand, the spectra of greases containing 6% and 10%wt/wt RC additive showed bands of low intensity, not dependent on additive concentration. The appearance of oxidation products may be responsible for the good anti-wear properties of greases, defined by the diameter of the wear scar, that contain 1 and 3%wt/wt of RC additive. Increase in the surface area under the peak of oxidation products was concomitant to the decrease of the diameter of the wear scar in the friction pair. Figure 5 shows the relationship between the surface area under the peak specific for oxidation products and the diameter of the wear scar at various concentrations of the additives in greases after tribological tests.

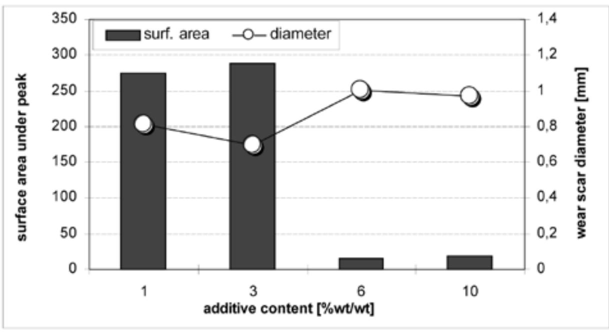

Fig. 5. Relationship between the surface area under the peak specific for oxidation products and the diameter of the wear scar at various concentrations of the additives

The spectral examination of the greases subjected to tribological tests has shown that upon mechanical action some grease components were oxidized to oxygen containing organic compounds that form an organic film on the surface of the metal, which inhibits wear of the lubricated friction pair.

The results obtained indicate that anti-wear efficiency, defined by the diameter of the wear scar, is not only the function of additive concentration.

Conclusions

The tests performed have shown that infrared spectrophotometry is an efficient and fast method for assessing the changes in chemical composition of greases subjected to mechanical action. The linear relationship between the surface area under the peak specific for the additive and its content in the grease may constitute a reliable means of monitoring changes in additive content under operating conditions. The applied measurement method enables evaluation of both quantitative and qualitative changes in the structure of the grease, and it may therefore be used to monitor changes in the content of key grease components, which determine useful life of the grease.

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