

Study of Degradation of Mineral Oils Products by FTIR Method*

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The degradation products of oils and decrease of additives content were studied by the FTIR method. The wavenumbers of oxidation, nitration, sulfonation products and antioxidant additives bands of infrared spectra of airborne engine mineral lubricants were precisely identified. These areas were identified on the basis of the analysis of 250 samples of the used oils of the oil MS-8P. Levels of degradation products of this oil were determined using mathematically generated calibration curves.

FTIR spectrometry is a fast nondestructive analytical method used for assessment of physical and chemical properties of the lubrication oils. It is suitable not only for qualitative but also for quantitative determination of the content of the degradation products and additives [1].

The motor lubricant oils are during their operation exposed to the high temperatures, pressures, and leaking of undesirable materials from outside, *i.e.* internal and external contamination. In oil after operation, products of chemical reactions, degradation products and contaminants (water, fuel, metals) are present and the content of additives is decreased. Monitoring of oil lubricant quality during its

using in machine ram probes oil life, its ability to protect engine and the condition of this engine, too [2].

Values of wavenumbers of absorbance bands of degradation products are variable in dependence on the oil type. These values for the used oil MS-8P were precisely identified while the wavenumbers of absorbance bands of subsistent various types of degradation or contamination were compared with literature data for other oils. Since there are no getatable standard reference materials of the similar type of oil, the calibration curves were constructed by mathematical procedure of applicative absorbance values of the new oil in studied areas.

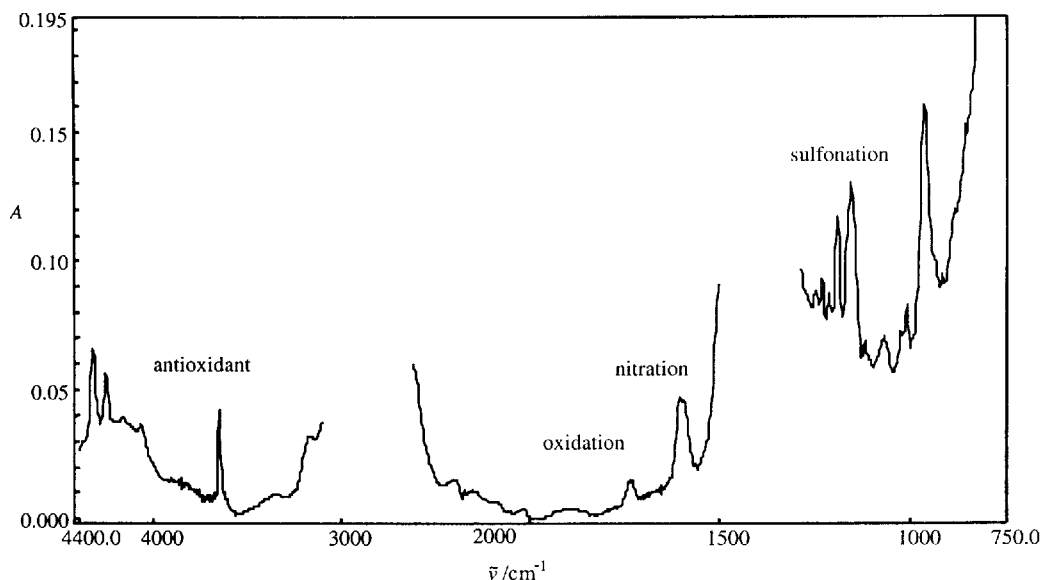


Fig. 1. Located areas of the infrared spectra of degradation products of mineral oil MS-8P.

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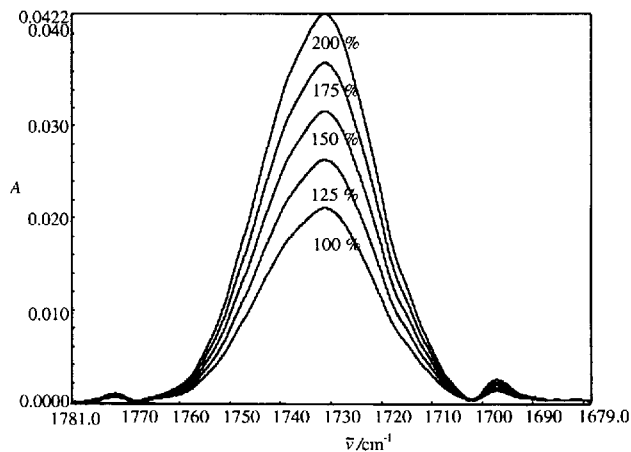


Fig. 2. The dependence of the height of oxidation absorption band on the amount of oxidation products.

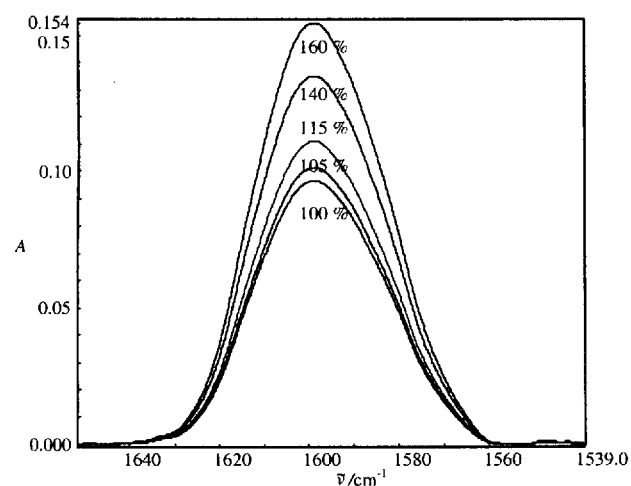


Fig. 3. The dependence of the height of nitration absorption band on the amount of nitration products.

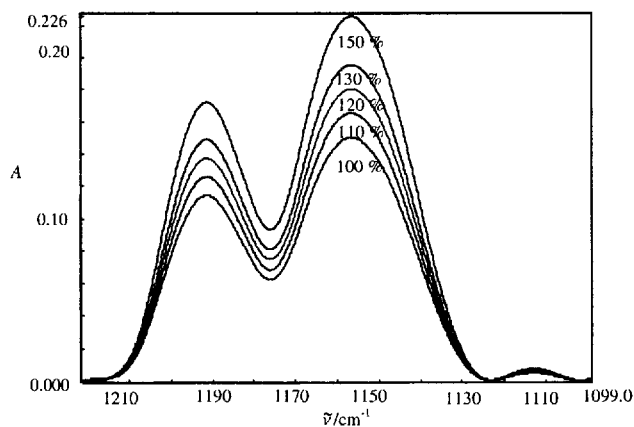


Fig. 4. The dependence of the height of sulfonation absorption band on the amount of sulfonation products.

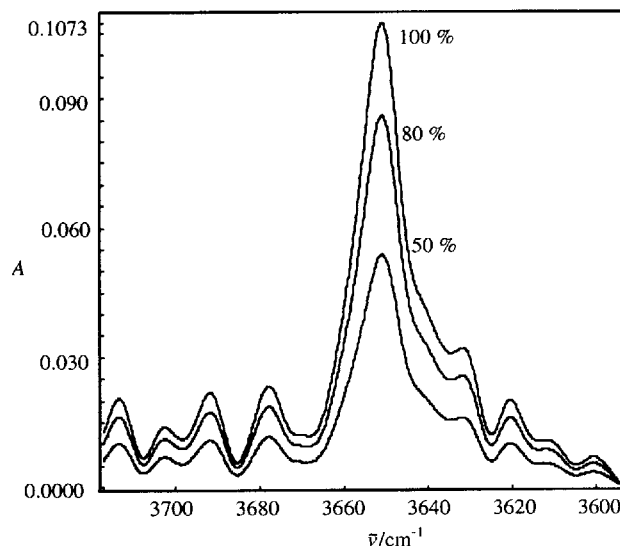


Fig. 5. The dependence of the height of absorption band of antioxidant additives on the amount of antioxidant additives.

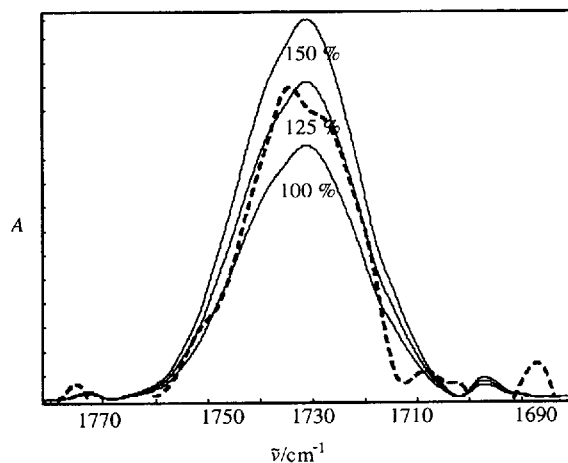


Fig. 6. The comparison of oxidation absorption band of real sample and mathematically generated absorption bands of oxidation products of the fresh oil. — Mathematically generated values; - - - real sample.

EXPERIMENTAL

The oil MS-8P (Mineral Shell-8P, engine oil for turboprop subsonic aircraft, made in Russia) has been studied. Experiments were realized by using infrared spectrometer with Fourier transformation, Spectrum 1000 (Perkin—Elmer), in the middle area of spectrum, from 750 to 4400 cm^{-1} . Spectrum 1000 is a single-beam spectrometer with resolution from 2 to 8 cm^{-1} , internal detector LiTaO_3 , the divider of beam from KBr material, and HeNe laser. Mineral lubricant oil samples were measured in BaF_2 cell with thickness of 0.10 mm. Spectra of new and degraded oil samples were scanned 16 times for creating spectra aver-

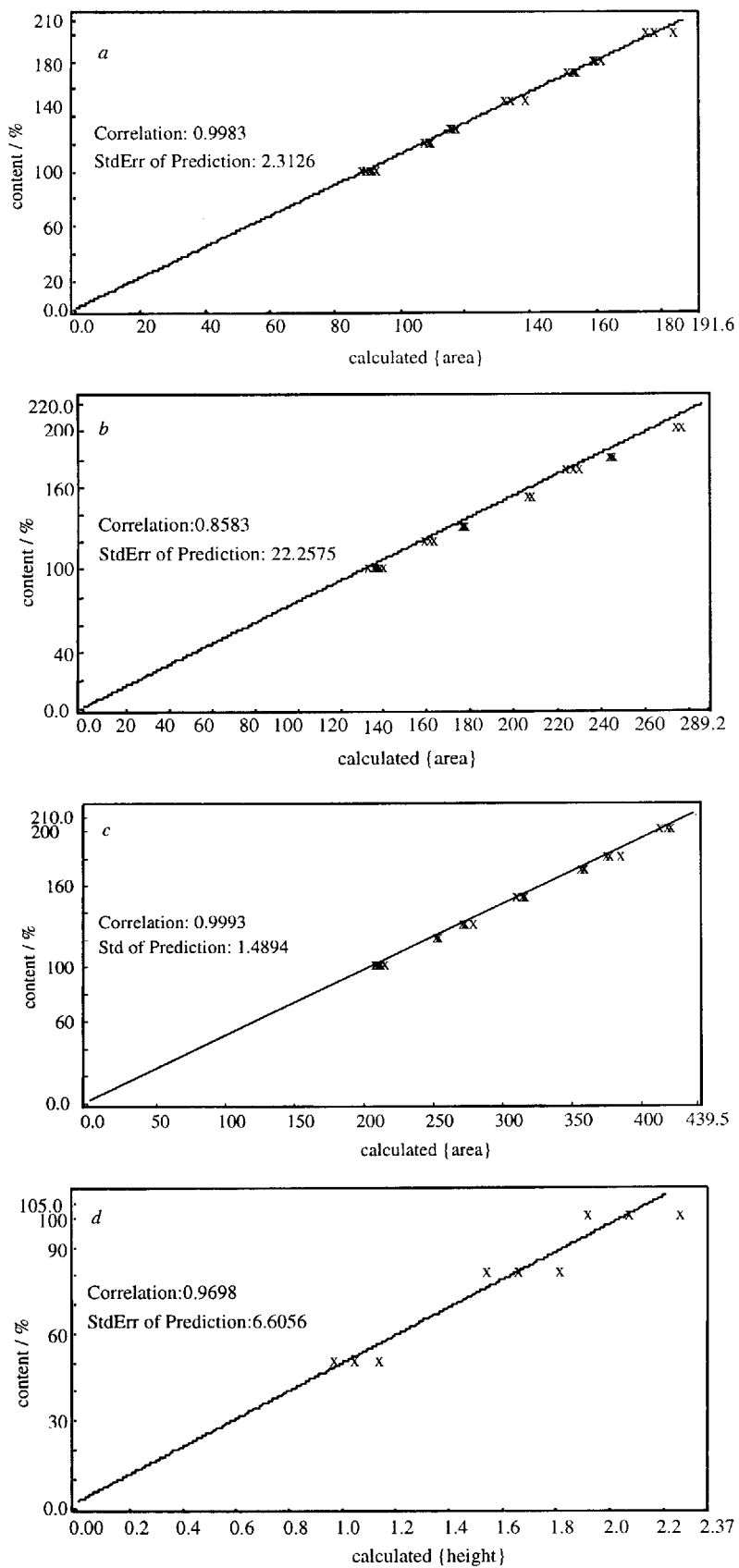


Fig. 7. The calibration curve of oxidation (a), of nitration (b), of sulfonation (c), of antioxidant additives (d).

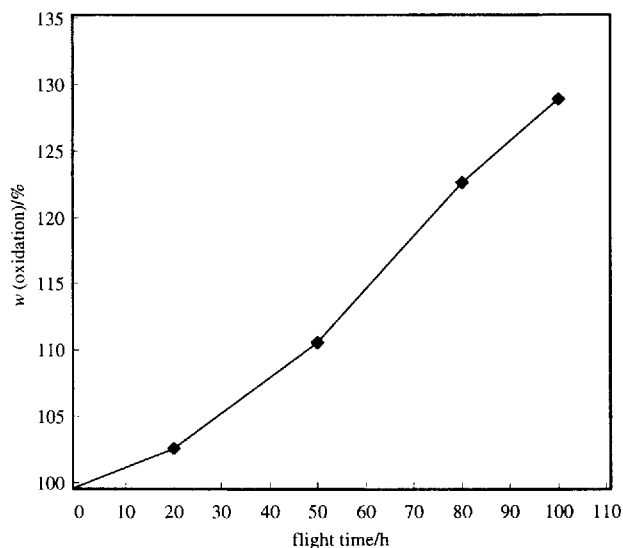


Fig. 8. The dependence of content of oxidation products in mineral oil MS-8P on flight time.

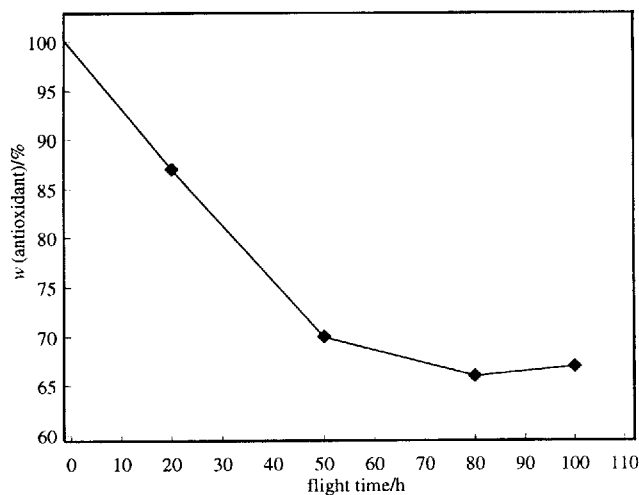


Fig. 9. The dependence of antioxidant additives content in mineral oil MS-8P on flight time.

ages. These spectra were measured in comparison with background spectrum that was 16 times scanned, too.

All measured IR spectra were adjusted by FTIR spectrometer software Perkin—Elmer Applications Spectrum v3.02 followed by mathematical operations: Absorbance (converting transmission data into absorbance data), Blank region (clearing away some regions of the spectrum), Interpolate (cutting out the spectrum current region), Smooth (smoothing to the current region of the spectrum), Baseline (performing baseline correction of the spectrum), and Offset (shifting the spectrum so that the Y-value of minimum point becomes zero) [3, 4].

DISCUSSION

On the basis of literature data [2, 5, 6] four basic regions of degradation process of mineral oil in infrared spectrum were identified. The main attention was given to those wavenumbers of mineral lubricant IR spectra, in which the absorption bands concern the following degradation products.

In the oil MS-8P, the products of oxidation process caused by oxygen (carbonyl and carboxyl compounds) were monitored in the area of $\bar{\nu} \approx 1730 \text{ cm}^{-1}$; products of nitration process (organic nitrate) were monitored at $\bar{\nu} \approx 1600 \text{ cm}^{-1}$ and products of sulfonation (sulfate compounds) occurred in the region of $\bar{\nu} \approx 1150\text{--}1200 \text{ cm}^{-1}$. The decrease of antioxidant additives was monitored in infrared area of $\bar{\nu} \approx 3650 \text{ cm}^{-1}$. There are the areas in which the degradation processes of the oil MS-8P, like oxidation, nitration, sulfonation, and decrease of antioxidant additives are indicated, as shown in Fig. 1. After identification of the applicative values of the wavenumber the samples of fresh oils, or

oils, which were regarded as fresh (max. 8 h used in the lubricant system of engine) were analyzed. Similar procedure was used for analysis of degradation oil samples. Spectra of degraded oils were compared with spectra of fresh oils.

Since there are no oil MS-8P reference materials, which could be used for the preparation of the calibration curves, it was necessary to use the spectra of fresh oil by support of software equipment. For creating the calibration curves, the data of fresh oils were used. Their spectra were taken as the base for calculation. The calibration curves were constructed from these basic spectra by multiplying the absorbance values of the absorption bands for four basic regions and the suitable numerical constants were used.

Absorption bands of monitored infrared spectrum areas, which are shown in Figs. 2—4, were formed by multiplying the absorbance band value of this fresh oil, which presents 100 %, by decimal number from 1.0 to 2.0. As seen from Fig. 5, the absorption bands of antioxidant additives were obtained by multiplying the absorbance value by decimal number that was smaller than 1.0. In Fig. 6 are compared the absorption bands of oxidation products by mathematically generated oil spectra with absorption band of real degradation oil sample.

Calibration curves obtained by mathematical generation are summarized in Figs. 7a—d. From the viewpoint of the tribological diagnostics important is the comparison of the oxidation and degradation level, as well as the decrease of antioxidant additives with the data of fresh oil. Figs. 8 and 9 show the original and increased content of the oxidation products and the decrease of additives content in dependence on engine flight time.

CONCLUSION

The absorption band position values of degradation mineral oil products are known from literature only approximately. By identification of absorption bands of degradation products and additives by the suitable process, the right values of their wavenumbers in IR spectrum of oil MS-8P were determined.

Calibration curves were developed on the basis of mathematically generated absorptions, which were obtained from absorbance of fresh lubricants. Developed method was used for quantitative estimate of properties of the degradation airborne mineral oil in dependence on flight time. By comparison of absorption values of degraded and fresh oils of the designate type, the level, the degree, and the rate of the process of degradation were determined.

Therefore, the analysis of the degradation oils by the FTIR method enables to determine both the current condition and the operating life of the oil.

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