Study Committee D1

Materials and Emerging Test Techniques

Paper D1-PS2-10608

The Degradation Degree Control of the Hydrocarbon Base of Mineral Oils Using the Specific Degradation Marker in their Infrared Spectrum

M.Sh. Garifullin[1], Y.N. Slobodina [1], A.R. Bikzinurov [1], R.A. Giniatullin[2]

[1] Kazan State Power Engineering University, [2] Kazan National Research Technological University

Motivation

- Traditional methods of diagnosis of mineral transformer oils (MTO) do not allow to control the state and the process of destruction of the hydrocarbon base of oils. One of the mechanisms of oil degradation is the formation of double C=C bonds in hydrocarbon molecules.
- The purpose of the study is to study changes in the content of unsaturated hydrocarbons with double C=C bonds in various MTO using infrared (IR) spectroscopy

Method/Approach

- Preparation of MTO samples: fresh, old operational and artificially aged oils; operational oils purified with adsorbents.
- Selection of spectral range and conditions for measuring IR absorption spectra of oils.
- Study of intensity of characteristic IR absorption bands related to unsaturated C=C bonds of hydrocarbon molecules in different oils.

Objects of investigation

Different types of mineral transformer oils:

- Fresh transformer oils of various grades;
- Artificatively aged oils;
- Old operational oils;
- Operating oils which have been purified with various adsorbents.

Experimental setup & test results

- Apparatus for artificial oxidation of oils APSM-1.
- Adsorbents of three types: a - KSKG; b - AS230Sh; c - Fuller's Earth.
- IR-Fourier spectrometer TENSOR-27 (Bruker).

Obtained (prepared, measured)

- Samples of oils with different degrees of thermal degradation: 1; 2; 3; 4.
- Samples of old operational oils: I, II, III and IV.
- Oils purified with adsorbents: Ia, IIa, IIIa; Ib, IIb, IIIb; IVc.
- IR spectra of fresh, old and adsorbent-purified oils.

Discussion

- The intensity of characteristic IR absorption bands in the region of 4750÷4500 cm^{-1} related to C=C bonds in hydrocarbon molecules in old operational and artificially oxidized transformer oils is significantly higher than in fresh transformer oils.
- After adsorption purification of old oils, the intensity of the characteristic absorption bands decreases insignificantly.

Conclusion

- The process of thermodestruction of transformer oil is accompanied by an increase in the number of C=C bonds in the transformer oil.
- The content of unsaturated hydrocarbons in the mineral transformer oil characterizes the irrecoverable degree of destruction of its hydrocarbon base.
- With the help of IR spectra of mineral transformer oils in the region of 4750÷4500 cm^{-1} one can control the change in the total content of C=C groups in the oils.
- A method of differentiating fresh mineral transformer oils produced by hydrocracking technology from reduced oils is proposed.

Study Committee D1

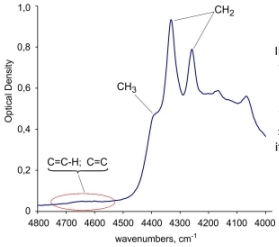
Materials and Emerging Test Techniques

Paper D1-PS2-10608

The Degradation Degree Control of the Hydrocarbon Base of Mineral Oils Using the Specific Degradation Marker in their Infrared Spectrum

(continued)

IR absorption spectrum of mineral oil in the range 4800÷4100 cm^{-1}

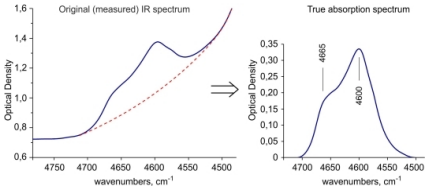


IR spectrum was measured in the cuvette with a thickness of 0.4 mm.

To analyze the region of the spectrum highlighted in red, it is necessary to increase the thickness of the cuvette to 5÷10 mm.

In the region of 4750÷4500 cm^{-1} there are characteristic absorption bands of unsaturated hydrocarbons with double C=C bonds.

IR absorption spectrum of mineral oil containing unsaturated C=C groups



Left - original (measured) IR spectrum, right - after removal of background approximated by Gaussian curve.

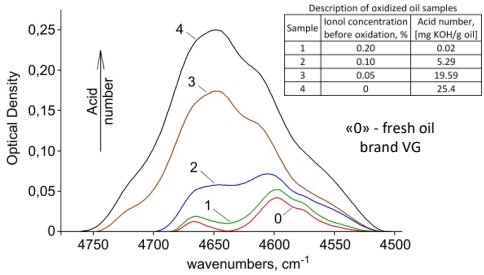
The absorption bands with peaks around 4665 and 4600 cm-1, which refer to the vibrations of =C-H and C=C groups of unsaturated hydrocarbons, act as analytical bands.
A 10 mm thick cuvette was used for measurements, the windows material was CaF2.

Preparation of samples of oils with different degrees of thermodestruction

Oxidation conditions for the oils:
- oxidation temperature – 150 °C;
- oxidation time - 14 hours;
- oxygen supply rate - 200 ml/min.

The decrease in the degree of thermo-oxidation was simulated by reducing the initial concentration of the oxidation inhibitor 2,6-di-tret-butyl-4-methylphenol, referred to as Ionol additive, in the oil.
The initial concentration of Ionol in the prepared samples of VG oils was 0.2 %, 0.1 %, 0.05 % and 0 %.

IR absorption spectra of samples of oils with different degrees of thermodestruction



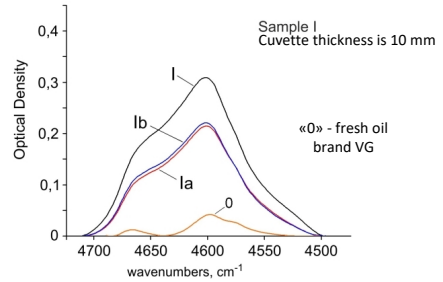
Description of oxidized oil samples

Sample	Ionol concentration before oxidation, %	Acid number, [mg KOH/g oil]
1	0.20	0.02
2	0.10	5.29
3	0.05	19.59
4	0	25.4

Experiment on adsorption purification of mineral oils

- Three samples of oxidized transformer oils were used - Samples I, II and III.
- Adsorption purification was carried out using silica gels of 2 grades: KSCG (hereinafter - type a) and AS 230Sh (hereinafter - type b).
- Purification was carried out by settling the oils in a closed container filled with silica gel for 100 hours without stirring. The ratio of oil mass to silica gel mass was 2 : 1. The samples of oils purified with KSCG silica gel are designated Ia, IIa and IIIa. The oils purified with AS230Sh silica gel were designated as Ib, IIb and IIIb.
- The old transformer oil, sample IV, was purified with Fuller's Earth at a waste oil regeneration facility. The purified sample was designated IVc.

IR spectra of oils based on Sample I



Sample	Silica gel type	Acid number, mg KOH/g
I	–	0.04
Ia	KSKG	<0.01
Ib	AS-230Sh	<0.01

Study Committee D1

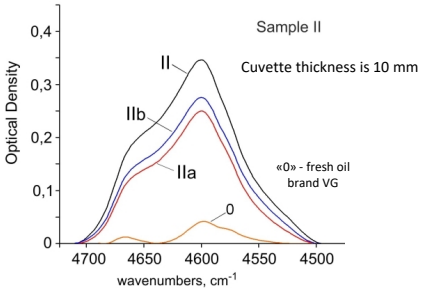
Materials and Emerging Test Techniques

Paper D1-PS2-10608

The Degradation Degree Control of the Hydrocarbon Base of Mineral Oils Using the Specific Degradation Marker in their Infrared Spectrum

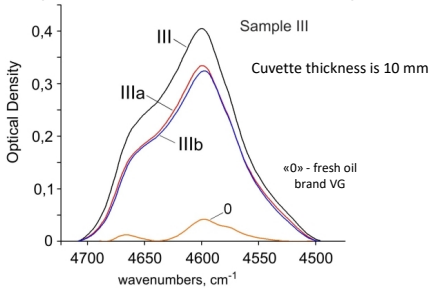
(continued)

IR spectra of oils based on Sample II



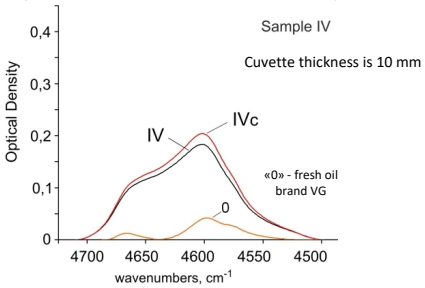
Sample	Silica gel type	Acid number, mg KOH/g
II	–	0.08
IIa	KSKG	<0.01
IIb	AS-230Sh	<0.01

IR spectra of oils based on Sample III



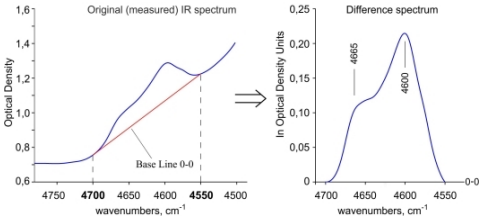
Sample	Silica gel type	Acid number, mg KOH/g
III	–	0.14
IIIa	KSKG	<0.01
IIIb	AS-230Sh	<0.01

IR spectra of oils based on Sample IV



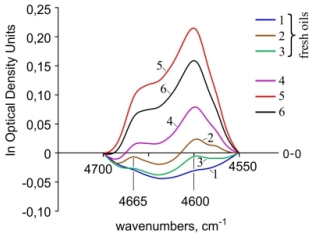
Sample	Adsorbent	Acid number, mg KOH/g
IV	–	0.02
IVc	Fuller's Earth	<0.01

Algorithm of converting the original IR spectrum into a difference spectrum



The baseline, labeled as 0-0, is drawn through the two points of the spectrum corresponding to wave numbers 4700 and 4550 cm^{-1}.

Difference IR spectra of various mineral transformer oils



1, 2, 3 - fresh GK, VG and Nytro 11GX oils, respectively;
4 - aged Nytro 11GX oil; 5 - decommissioned aged oil; 6 - reclaimed oil.

Conclusion

- One of the mechanisms of degradation of mineral transformer oils is the formation of unsaturated C=C bonds in hydrocarbon compounds.
- To monitor changes in the content of C=C groups in the hydrocarbon base of the oil it is convenient to use the characteristic absorption bands in the IR spectrum of oils in the region 4750÷4500 cm^{-1}.
- Using IR method, it is shown that adsorption purification does not allow to remove unsaturated compounds from mineral oil completely.
- An algorithm is proposed, which allows differentiating fresh mineral transformer oils produced by hydrocracking technology from reconstituted oils by IR spectra.