NMR Study of the Fresh and used Transformer Oils

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Abstract

Using nuclear (proton) magnetic resonance spectroscopy (NMRs) and relaxometry (NMRr) were studied fresh and used transformers oils. Changes in the molecular composition content was determined upon oil aging. Dependences of NMR spectra and NMR-relaxation parameters –spin-spin T_{1i}, relaxation times were received for transformers oils. Experimental results are interpreted on the base of exchange dynamical model.

Introduction

Great amounts of used alternating current (AC) transformer oils (TO) is currently increasing. So, the problem of their re-refining becomes particularly urgent and the petrochemical quality standards pertinent to their quality are becoming more stringent. Fresh TO compositions are known to manufacturers, while this information about used oils is unavailable.

We have made an estimation of the chemical composition of fresh (FTO) and used transformer oils (UTO) on the basis of comparative analysis of them using NMRs and NMRr methods. NMR-spectra provides detailed information regarding HC structure of oil and confirm some data obtained by FTIR spectroscopy. 1H NMR spectroscopy is a quantitative analytical method to study aging of motor oil and to get insight into the chemical processes which occur during aging. But high resolution NMR-spectroscopy is, in general, not applicable in industrial environments, because of the large size and big weight of the magnet system, the necessity to use a cryogen, the hazard of stray magnetic fields of superconducting magnets and their high cost [1].

NMR-Relaxation Proved its Uniqueness as a Powerful Method Equally Suitable for Refined Scientific Investigations and for routine analysis and control. It has several advantages over others; possibility for simultaneous measurement of several physchemical parameters; nondestructive and non contact opportunity of control and automation, short time of measurement. The international standard test method for hydrogen content of middle distillate petroleum products by low-resolution pulsed NMR-spectroscopy, especially for hydrogen content determination in aviation fuels ASTM D7171-05 [2] was elaborated.

Method of NMR-relaxation offers robustness and analysis rapidity. It gives information about relaxation parameters of the every phase of the ODS: spin-lattice T_{1i} and spin-spin T_{2i} relaxation times, populations of their proton phases P_{1i} and P_{2i}, correlation times τ_{c} (times of life in the molecular position); correlation times between proton exchanges τ_{cp};

interatoms distances r_{ij}; temperatures T_{phi} of the phase transitions; degree of the protons phases ordering, derived from relaxation times ratio S = T_{1i}/T_{2i} and others [3].

Here we present the study by NMR-methods transformer oils: fresh TO (FTO) GK-1 with the density ρ_{08} = 850 kg/m^{3} and used transformer oil (UTO), which density appeared to become ρ_{08} = 874 kg/m^{3}. The color of FTO is yellow-green, and red of UTO.

Spectra 1H of Fresh I and used II Transformer Oils

Spectra 1H of fresh I and used II transformer oils GK-1 obtained on Tesla-100 NMR-spectrometer at resonance frequency 100 MHz are presented at Figure 1 and Figure 2 (I and II). Deuterated chloroform (CDCl)_{3} was applied as a solvent.

Figure 1. Spectra 1H of the Fresh Oil GK-1

Figure 2. Spectra 1H of the used Transformer oil GK-1

From spectra was established, that in UTO compare to FTO spectra summary line intensity of methyl CH_{3} + methylene –CH_{2}- groups at chemical shifts δ ∼ 0.7-1.0 ppm and δ ∼ 1.3-1.7 ppm decreased from 84.4% to 77.9% on 6.5%. Average carbon chain length (CL) strongly affects other quality parameters, such as viscosity, higher heating value etc. [4]. Especially, content of –CH_{2}- groups decreased from 52% to 44%, the length of –CH_{2}- chains decreased from CH_{2}/CH_{3} = 1.604 for FTO to 1/3 for UTO. So the paraffinic hydrocarbons in the
FTO are more linear and have longer chains than those in the UTO. In UTO appeared the following substances (which were not present according to NMR-spectra in pure TO: R-CH₂-NR-N< and R-CH₂-COO- at chemical shifts $\delta = 2.3-2.5$ ppm, which spectra line intensity is 0.19% from summary square of lines in spectra; R-CH₂-COOH and –C=CH₂-OR at $\delta = 2.5-3.0$ ppm with intensity 0.33%; was observed great increase of spectra line intensity on 3.3% for aromatics in the wide range of chemical shifts $\delta = 6.6-7.4$ ppm.

Were obtained more detailed spectra on the Bruker Avance 400 spectrometer [5].  

Figure 3. Part of the NMR-Spectra for Water Line in TO at $\delta = 4.5-4.56$ ppm

Figure 4. Part of the NMR-Spectra for Aromatics in TO at $\delta = 6.25-7.5$ ppm

At figure 3 is presented the part of the NMR-spectra line for water peaks in TO at $\delta = 4.5-4.56$ ppm measured at $T = 20^\circ$C. Here I – for FTO (GKO, 2007); II – TO after 37 years of use, for this sample also temperature was increased to $T = 90^\circ$C and then after heating for 2 hours, was recorded spectra IIa, then after one hour after cooling the sample to $T = 90^\circ$C was recorded spectra IIb; III – FTO after thermotreatment during 8.5 hours at temperatures 115-135°C in glass retort with free access of air; IV – FTO with addition of 0.1 ml of distilled water in 12 ml of oil with following treating by ultrasonic; V – thermo treating analogous to III, but with addition to 100 ml of oil pieces of copper and steel wires. Peak at $\delta = 4.5$ ppm correspond to water protons in the true solution in TO, and peak at $\delta = 4.55 \pm 0.02$ ppm correspond to water molecules, aggregated in drops, dispersed in TO. With increase of temperature to $T = 90^\circ$C, integral intensity of the peak at $\delta = 4.55 \pm 0.02$ ppm decreased, but at $\delta = 4.5$ ppm increased. This mean, that with temperature increase part of the colloidal water decrease and part of soluble water is increased. At cooling takes place the reverse process.

At figure 4 presented part of the NMR-spectra for aromatics in TO at $\delta = 6.25-7.5$ ppm in samples I-III. Maximal intensity of peaks have samples II and IIa, minimal – FTO (sample I). In white mineral oil (sample B) signal from aromatics is absent. So it is seen, that increase of exploitation date from 37 to 54 years practically does not influence on arene concentration in $^1H$ NMR spectra. It can be explained by grouping of arenes in colloidal and then in solid particles, which then precipitate. It was confirmed [5] by relaxation measurements.


Spin-lattice $T_{1\text{L}}$, spin-spin $T_{2\text{S}}$, relaxation times and their proton populations $P_{1\text{L}}$ and $P_{2\text{S}}$ are useful for characterization of dynamical processes in oils. For measurements of NMR-relaxation was used designed by us [6] relaxometer NMR-NC-1 with resonance frequency $v_o = 14.34 \text{ MHz}$. Temperature of measurements was maintained with accuracy $\pm 0.2^\circ$ at 25°C by thermo stabilization unit [7].

For $T_{1\text{L}}$ and $P_{1\text{L}}$, determination spin-echo recovery sequence $90^\circ-\tau-90^\circ-\tau-180^\circ$ of Hahn was used. For $T_{2\text{S}}$ and $P_{2\text{S}}$ measurements $90^\circ-\tau-(180^\circ-2\tau-\tau)\_n$ sequence of Carr-Purcell-Mayboom-Gill [8] was applied, eliminating the influence of self-diffusion and protons exchange. Experimental error of measurements was $\pm 3\pm 4\%$ for relaxation times and signal amplitudes recurrence $\pm 1\pm 2\%$, depending from accumulations number $n$ of NMR-spin-echo amplitudes and error could be decreased in $(n)^{1/2}$ times using $n$ accumulations. Sample probe head has $\varnothing 20$ mm, so the sample volume $V$ for probe filling height $h = 3.5$ cm was $V = 11$ cm³, large enough to get representative probe. Coefficient of sensibility $K = v^3 V$ [MHz·cm³] in our NMR-relaxometer is $K = 2250$ MHz·cm³, that is near to $K = 3970$ MHz·cm³ of MARAN-23 (Oxford, UK) with higher frequency $v = 23$ MHz, but less probe diameter $\varnothing 18$ mm and volume 8 cm³.

Spin-echo amplitudes $A_s$ envelopes dependences in Hahn and CPMG-methods after the amplitude detection has forms, described by equations:

$$A_s(t) = 1 - A_s\{P_{1\text{L}}\exp(-t/T_{1\text{L}}) + P_{1\text{S}}\exp(-t/T_{1\text{S}})\} \quad (1)$$

$$A_s(t) = A_s\{P_{2\text{S}}\exp(-t/T_{2\text{S}}) + P_{2\text{L}}\exp(-t/T_{2\text{L}})\} \quad (2)$$

By measurements of transverse magnetization using solid echo $(90^\circ-\tau-90^\circ-\tau-\text{echo})$ was observed component, described by equation:

$$A_s(t) = A_s\{P_{2\text{S}}\exp(-t^2/T_{2\text{cS}}^2)\} \quad (3)$$

where $P_{1\text{L}}, P_{1\text{S}}, P_{2\text{S}}, P_{2\text{L}}, P_{2\text{cS}}$ correspond to populations of protons, participating in several types of molecular...
motions which determine relaxation times $T_1$ and $T_2$. From measured spin-echo amplitudes data logarithm was taken, and then the curve was decomposed on three linear components, corresponding to relaxation times $T_{1i}$ and $T_{2i}$ with $P_{1i}$ and $P_{2i}$ of two proton phases $A$ and $B$ with high and lower mobility of molecular fragments of oils. Besides proton populations obtained from $T_1$ and $T_2$ differs (especially for phase $A$). This will be discussed later.

According to our measurements at temperature $T = 25^\circ C$, FTO has relaxation times of the phase A equal to $T_{2A} = 297 \pm 12$ ms and $T_{2B} = 98 \pm 4$ ms phase B with corresponding proton populations $P_{2A} = 0.51 \pm 0.02$ and $P_{2B} = 0.49 \pm 0.02$; UTO has $T_{2A} = 723 \pm 20$ ms and $T_{2B} = 437 \pm 17$ ms with proton populations $P_{2A} = 0.92 \pm 0.02$ and $P_{2B} = 0.08 \pm 0.02$.

For all TO characteristic sufficient dependence of relaxation times from distance $t_{0i}$ between $180^\circ$ pulses in the range 1400-2000 $\mu$s, which corresponds to frequency $(t_{0i})^{-1}$ of $180^\circ$ pulses. This is inherent to the exchange processes between protons in the $A$ and $B$ phases with chemical shifts $\delta_A$ and $\delta_B$ in this samples. This result together with the fact, that $T_{2A} = 297 \pm 12$ ms and $T_{2B} = 98 \pm 4$ ms in FTO lower, then $T_{2A} = 723 \pm 20$ ms and $T_{2B} = 437 \pm 17$ ms in UTO is the indication, that FTO has colloidal ordered structure, while UTO contain low weighted molecules, perhaps as a result of destruction of aliphatic hydrocarbons (HC).

Indeed, as it was shown by $^1H$ NMR spectra, HC content (methyl -CH$_3$ and methylene -CH$_2$ groups) decreases from 84.4% in FTO to 73.8 % at UTO of (methane and naphthenic molecules) summarily on 10.6%. Also in UTO appeared 3.21% of polyaromatics. Used oil HC are more branched, because the ratio of spectra line intensities between CH$_3$-C and /-C-CH$_2$-C groups sufficiently changed from 0.623 in FTO to 0.93 in UTO. The results coincide with results of [9].

At the same time, in the work [10] was shown, that after the expenditure of antioxidant 'lonol' in transformer oil, aging process is accompanying by paramagnetic centers formation, which lead to appearance of asphalt-tar compounds. Interactions of PC with diamagnetic molecules lead to formation of particles of dimensions 100-10 000 nm in UTO with maximum at 1000 nm (compare to 0.1 to 100 nm colloid structures with maximum at 5.5 nm). This particles become visible and change the color of FTO changed from yellow-green to red in UTO.

Dependences of spin-spin relaxation rates $R^2 = T_2^{-1}$ from $(t_{0i})^{-1}$ in the range 200-2000 $\mu$s are presented at figure 5.

According to [11] the dependence for relaxation rate $(T_{2A})^{-1} = R_{2A}$ for protons in one of proton phases must exist the following relation:

$$(T_{2A})^{-1} = (T_{20A})^{-1} + P_A P_B (\delta \delta \omega \omega)^2 \tau_e^{-1} \left(1 - (2 \pi / t_{0i}) th (\pi / \tau_e)\right)$$

(4)

where $(T_{20A})^{-1}$ - relaxation rate in the absence of exchange, $\delta \delta \omega \omega$ - chemical shifts difference between "$A'"$ and "$B'$" - groups exchanging protons, $\tau_e^{-1}$ - average time of proton "living" in one position - exchange correlation time, and $(\pi / \tau_e) th (\pi / \tau_e)$ in equation (4) can be neglected, so it transforms to:

$$R_{2A} = (T_{20A})^{-1} + P_A P_B (\delta \delta \omega \omega)^2 \tau_e^{-1} \left(1 - (2 \pi / t_{0i})\right)$$

(5)

Or can be rewritten as:

$$R_{2A} = R_{20A} + P_A P_B (\delta \delta \omega \omega)^2 \tau_e^{-1} - P_A P_B (\delta \delta \omega \omega)^2 \tau_e^{-1} / t_{CP}$$

(6)

Our measurements in the samples at fig.5 show, that in agreement with theory [11], the increase of relaxation rates $R_{2A}$ (curves 1 for pure TO and 2 for used TO) in both samples at $t_{CP} > 1600 \mu$s is observed. For $t_{CP} > 1600 \mu$s exchange with correlation coefficient $R^2 = 0.93$ and square mean error $S = 0.055$ the $R_{2A}$ for FTO and UTO are described by equations:

$$R_{2A} = 4.52 - 0.00173/t_{CP}$$

(7)

$$R_{2A} = 1.98 - 4.2210^{-5}/t_{CP}$$

(8)

Exchange processes are clearly seen at $t_{CP} < 714$ (s$^{-1}$), $t_{CP} > 1400 \mu$s, so we shall calculate exchange parameters in this range. For FTO from eq.(5) with $R_{20A} = 3.25$, $P_A P_B = 0.5104$ $= 0.25$ and eq.(6) with $R_{20A} = 1.37$, $P_A P_B = 0.05$ we have the which give in FTO for $t_{CP} > 625$ s$^{-1}$ $\tau_e = 5.4-10^{-3}$ sec and $\delta \delta \omega \omega = 0.153$ ppm, which can be attributed to exchange between conformations of methylene -(C-CH$_2$-) proton chains at $\delta = 1.4$ and 1.25 (1 ppm) $= 100 \text{ Hz}$ chemical shifts. For UTO $R_{20A} = 1.37$, $P_A P_B = 0.95-0.05$ $= 0.0475$. So we have $1.37 + 0.0475 (\delta \delta \omega \omega)^2 \tau_e = 1.98$ and $0.0475 (\delta \delta \omega \omega)^2 \tau_e$ $= 4.2.10^{-5}$, from which we obtain calculated $\tau_e = 6.9-10^{-5}$ sec and $\delta \delta \omega \omega = 0.44$ ppm, which is attributed to the fast exchange between new oxidized compounds (for instance $R_2$-CH-COOH) at $\delta = 2.6-2.8$ and aromatic protons at $\delta = 7.1$ ppm. This our results on chemical shift positions coincide with results of paper Kupareva, et al [8].

As to relaxation times, according obtained results, we can say, that $T_{2A} = (R_{20A})^{-1}$ = 307 ms can be attributed to methylene -(C-CH$_2$-) proton chains at $\delta = 1.4-1.25$ ppm in FTO. In UTO relaxation times $T_{2A} = (R_{20A})^{-1}$ = 730 ms can be attributed to $R_2$-CH-COOH groups with $\delta = 2.6-2.8$ (with mean amount $P_A = 0.51$), measured $T_{2B} = 98$ ms with mean amount $P_B = 0.49$ can be attributed to aromatic protons at $\delta = 6.9-7.9$ ppm.
So can be made a conclusion that correlations between chemical characteristics of fresh and used oils can be used for optimization and upgrading technology of re-refining UTO by blending with the new additive packages. Can be selected the regulation and type of re-refining processes taking in consideration molecules in TO, between which exchange takes place.

Conflicts of Interest

There are no conflicts to declare.

References