Eurasian Chemico-Technological Journal 17 (2015) 295-300

Doping of Petroleum, Oil and Lubricants with Carbon Nanotubes as a Way to Improve the Performance of POL

I.V. Arkharova*[*] and I.V. Zaporotskova

Volgograd State University, Universitetskii prospect, 100, Volgograd, Russia

Article info

Received:
4 June 2015
Received and revised form:
28 July 2015
Accepted:
18 September 2015

Abstract

It is assumed that carbon nanotubes can be used as an additive, which will improve the operational properties and functional characteristics of lubricants. The doping of petroleum, oil and lubricants – semi – synthetic engine oil – with the carbon nanotubes, taken in various wt.% of additives, was carried out: 0.01; 0.1; 0.5 wt.%. The following physical and chemical characteristics were investigated: 1) viscosity of composite mix at a temperature of T = 25 °C (an initial state); 2) viscosity of composite mix after its aging at T = 160 °C on the mode of oxidation of the investigated samples of composite mix during 24 h; 3) the oxidation stability has been determined by the «acidity» and «acid number» parameters, these parameters have been carried out for the investigated samples of composite mix in an initial state and after aging. We assumed that doping of oil with carbon nanotubes will change some of oil's properties such as an indicator of viscosity, and chemical stability. The way of development functional and operational characteristics of lubricants by doping with carbon nanotubes was suggested. Results of researches showed that doping of carbon nanotubes causes change of such physical and chemical characteristics of lubricant as viscosity, acidity and acid number, alkaline parameter. Doping of lubricant with carbon nanotubes stops oxidation process and also leads to decrease of acidity and acid number in an initial state and for a state after aging. Besides, the carbon nanotube's presence has increased alkaline parameter after aging of composite mix that provides ability of oil to neutralize collateral sulphurous products and after aging during its exploitation. Thus, the researches proved positive influence of carbon nanotubes on the main functional characteristics of lubricants that allow us to recommend CNTs as new additives of liquid lubricant composite mixes.

1. Introduction

Petroleum, oil and lubricants (POL) are substances that are capable of decreasing frictional force and deterioration of friction surfaces, as well as increasing machinery loading capacities [1–2]. The primary use of lubricants is to reduce deterioration of friction surfaces and prolong service life of machinery components. These materials are also applied in sealing of clearance in cylinder – piston groups and abstracting heat from friction surfaces. In addition hereto, they protect metal surfaces from corrosion [3–4]. Various blends of liquid oils with different agents and additives are used as lubricants. Presence of dispersing additives in lubricants helps to hold a vast volume of insoluble impurities in finely dispersed uniform particles that are spread throughout POL in such a manner as to minimize risk of hazardous bottom impurities. As a result, such a lubricant having quite high level of viscosity contains minimal amount of insoluble impurities that might be hazardous.

Among qualitative functional characteristics of lubricants (lube oils) one should refer to density and viscosity, viscosity – temperature relation, pour point and flash point, lubricating capacity and chemical stability [5]. Lube oils shall possess high thermal – oxidative stability and sufficient anti-corrosive properties along with wear – reducing values and tolerable pumping ability at different ambient temperatures. Lube oils shall ensure maximum possible service life, and shall not create any deposits on components' surfaces [2].

---

[*] Corresponding author. E-mail: arkharova_irina@mail.ru

In order to satisfy the full package of requirements specified for lube oils, over the last years much attention was given to generate POLs with new features and specifications by means of introducing wide range of additives and surface – active substances. Attempts are made to study properties of lubricating materials modified with carbon filler, including carbon nanomaterials. Lubricants that have been injected with carbon nanoparticles acquire improved tribotechnical characteristics [6]. There are development projects that provide evidence of existence of a scope of use of fullerenes as new effective oxidation inhibitors of organic compounds and materials based thereon. The research [7] describes the lube – oil composition that includes nanoporous particles and is able to reduce friction, and thus, to increase fuel efficiency.

We assume that carbon nanotubes can be used as an additive that allows significantly improving performance properties and functional characteristics of petroleum, oil and lubricants [8–12]. The important peculiarity of carbon nanotubes (CNT) is connected with their unique sorption characteristics [13]. Given that a nanotube is a surface structure all its mass is concentrated on the surfaces of its layers. This determines abnormally high specific surface area of tubulens, which in turn, determines distinctive features of their electrochemical and sorptive characteristics [14]. Due to its unique features, carbon nanotubes are considered as an ideal dopant (doping material).

Advanced technical facilities, their units and machinery operate only on formulated oils, i.e. oils that contain additives and agents introduced in a form of synthetic and mineral ingredients to base oil that provide the latter with required features [8]. Modification of petroleum, oil and lubricants with carbon nanotubes allows them to obtain dramatically new properties. Oil doped with carbon nanotubes obtains certain expected properties such as change of viscosity index and improvement of chemical stability. This is the reason why studying possible potential of improvement of operational properties of petroleum, oil and lubricants, and lube oils in particular, doped with carbon nanotubes, as well as analyzing some properties of derived compositions is of great interest.

2. Experimental

POL synthetic blend motor oil Lukoil Super 10w–40 was doped with carbon nanotubes of different weight percentage: 0.01; 0.1; 0.5 wt.%. The physical-chemical properties of carbon nanotubes are described in paper [14]. We used carbon nanotubes produced at the TISNUM factory for experimental research. The procedure of producing oils with carbon nanotubes of different weight percentage (so–called compositions) was as follows. Before being introduced into oils carbon nanotubes were subjected to ultrasound treatment in ultrasonic bath of type «YX – 3560». The target of ultrasound treatment was to break initial large aggregates of nanoparticles into smaller ones. After ultrasound procedure, test oils were doped with carbon nanotubes in the proper proportions. For this purpose oils were heated up to T = 30–40 °C (this temperature range has no significant effect on oil quality), and then carbon nanotubes were added. This procedure was accompanied by continuous mechanical mixing by means of titrating apparatus TPR–M–UHL–4.2 in order to have thorough dispersion of particles.

The following physical and chemical properties of a created composition were studied:

1) Viscosity of the composition at a temperature of T = 25 °C (initial condition);

2) Viscosity of the composition after its aging at a temperature of T = 160 °C with oxidation behavior of sample components of the composition over a period of 24 h;

3) Oxidation stability determined by such parameters as “acid capacity” and “acid number” of sample components of the composition in their initial condition and after aging.

In order to evaluate impact of admixture of carbon nanotubes on functional characteristics of petroleum, oil and lubricants we studied samples of base oil without additives (so – called base samples).

Viscosity was measured by means of capillary viscosimeter at a temperature of T = 25 °C. The low tip of a vertically fixed capillary tube went down to 2–3 mm below liquid level in an oil container. Oil was sucked in with a rubber bulb up to the midpoint of the upper expansion of capillary viscosimeter, after that we measured drain time of 3.6 mL of liquid between marks with a stopwatch. Poiseuille equation was used to calculate viscosity value [15]:

$$\eta = \frac{\pi \cdot \Delta P \cdot R^4 \cdot \Delta t}{8 \cdot V \cdot l} \qquad (1)$$

where ΔP – differential pressure, Pa; R – capillary radius, m; Δt – liquid drain time, s; V – volume, m^3; l – capillary length, m.

Results of viscosity calculations for the base sample and compositions with different content of carbon nanotubes are listed in Table 1.

Table 1

Viscosity value of base sample, compositions in initial condition and after aging, σ – mean square deviation

Carbon nanotubes content, wt.%	Viscosity ± σ, mPa · s			
	Initial condition	Initial condition	After aging	Viscosity fluctuation
0	193.35 ± 4.68	0	213.14 ± 1.28	0
0.01	206.77 ± 4.80	+13.42	195.39 ± 1.05	-17.75
0.1	220.42 ± 2.57	+27.07	193.35 ± 1.66	-19.79
0.5	229.51 ± 3.47	+36.16	189.70 ± 2.09	-23.44

Similar tests were carried out for the samples that had been artificially aged at the following mode: selected samples were aged at a temperature of 160 °C while stirring constantly with help of titrating apparatus TPR–M–UHL–4.2. Oil is able to reach this temperature only on sides of cylinder barrels in the motor; however, its residence time therein is quite low. Thus, continuous presence of oil at such temperature ensures fast aging of oil during its oxidation.

During oil oxidation process almost all its physical, chemical and operating parameters change, such are the following: viscosity, flash point, coking capacity, water content, alkali base number and acid number, content of non – dissolved residue and wear products [16]. One of the main factors negatively affecting oil quality is its continuous aging. Over the course of aging one notices increase of corrosiveness, formation of deposits, inability to initiate cold start – up, and loss of oil pumping ability. Speed of this negative process can be gradually decreased by introduction of an effective antioxidant additive. When oil is oxidized acid number rises, and alkali base number reduces. Balance between alkali base number and acid number determines degradation factor (aging) of oil during its use [17].

We defined acid content and acid number of a base sample of the synthetic motor oil and examined a composition based on this oil and carbon nanotubes. Test material was presented by samples of compositions with different amount of carbon nanotubes in initial condition and compositions after aging. Acid content and acid number were calculated in accordance with GOST 5985 – 79 [18]. Test approach was the following. A cone flask was filled with 50 mL of 85% ethyl alcohol, after it was shut with backflow water cooler, and the content was boiled for 5 min. Nitrazine yellow indicator was added. Alcoholic solution of potassium hydroxide 0.05N neutralized by hot alcohol 0.05N, resulting in color change from yellow to green. Then, the flask was filled with 50 mL of test material, and the mixture was also boiled with back-flow water cooler for 5 min. After that hot mixture was titrated until colors changed. Acid content is valued in mm of potassium hydroxide (KOH) that is required for neutralizing acids contained in 100 mL of POL [18]. Acid content level is calculated with the following formula:

$$K = \frac{V_2 \cdot T \cdot 100}{50} \tag{2}$$

where V_2 – volume of potassium hydroxide solution used in titration, ml; T – titer of 0.05N potassium hydroxide solution, mg/mL; 50 – volume of tested POL, mL [18].

Acid number is calculated, as follows:

$$K = \frac{V \cdot T}{m} \tag{3}$$

where V – volume of alcoholic solution of potassium hydroxide used in titration, sm^3; T – titer of alcoholic solution of potassium hydroxide, mg/sm^3; m – sample mass, g [15].

Calculated volumes of acid content and acid number of tested samples are presented in Tables 2 and 3.

Table 2

Acid content value of base sample in initial condition and after aging, σ – mean square deviation

Carbon nanotubes content, wt.%	Acid content ± σ, mg KOH/100 mL			
	Initial condition	Change of acidity	After aging	Change of acidity
0	0.6 ± 0.03	0	0.66 ± 0.01	0
0.1	0.8 ± 0.05	+0.2	0.72 ± 0.02	+0.06
0.1	0.26 ± 0.03	-0.34	0.6 ± 0.04	-0.6
0.5	0.36 ± 0.01	-0.21	0.1 ± 0.02	-0.56

Table 3

Acid number value of base sample, composition in initial condition and after aging, σ – mean square deviation

Carbon nanotubes content, wt.%	Acid number ± σ, mg KOH/g			
	Initial condition	Change of acid number	After aging	Change of acid number
0	0.0073 ± 0.0003	0	0.0080 ± 0.0001	0
0.01	0.0097 ± 0.0005	+0.0024	0.0087 ± 0.0002	+0.0007
0.1	0.0031 ± 0.0003	-0.0042	0.0073 ± 0.0004	-0.0007
0.5	0.0044 ± 0.0001	-0.0029	0.0012 ± 0.0002	-0.0068

3. Results and Discussion

Viscosity values of tested samples (base oil sample without carbon nanotubes and compositions with different content of carbon nanotubes) in initial stage and after aging at a temperature of T = 25 °C are referenced in Table 1. Viscosity fluctuation graph depending on weight percentage of PNT in a composition in initial condition and after aging is shown in Fig. 1

With increase of weight percentage of CNT in the composition (initial condition) viscosity of the latter increases as well (Fig. 1, curve 1). Provided weight percentage of nanotubes rises in the composition after aging (Fig. 1, curve 2) viscosity value lowers down in comparison with value of oil without CNT (base sample). It should be noted that degradation rate of a composition due to aging is not high, as it is similar to viscosity value of oil without added CNT. Results obtained related to acid content and acid number are presented in Tables 2 and 3 and Figs. 2 and 3 correspondingly. Analysis of the results has shown that addition of CNT in weight percentage 0.01 wt.% leads to increase of degradation rate of the composition both in initial condition and afteraging, i.e. oil ages too quickly and loses its properties at undesirably fast rate.

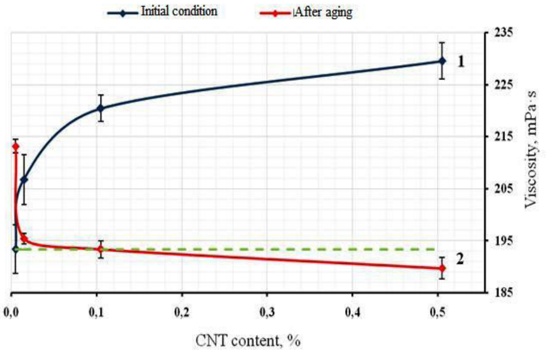

Fig. 1. Viscosity fluctuation graph depending on weight percentage of PNT in a composition in initial condition and after aging.

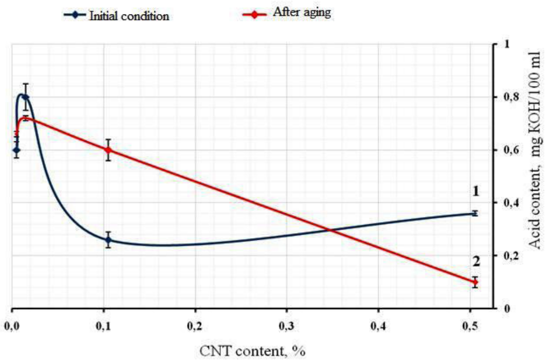

Fig. 2. Graph of acid content variation depending on weight percentage of CNT in the composition in initial condition and in the composition after aging.

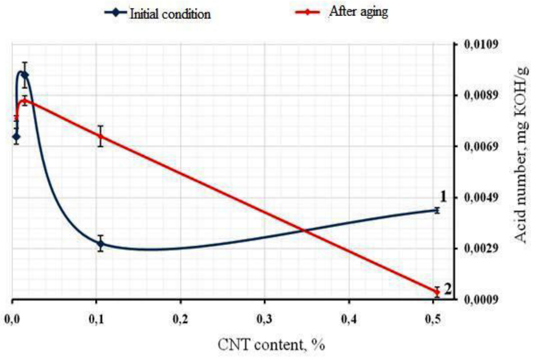

Fig. 3. Acid number variation graph depending on weight percent age of CNT in the composition in initial condition and in the composition after aging.

Further increase of CNT content in the composition not only stops oxidation process, but also results in decrease of acid content down to range 0.26–0.36 mg KOH/100 mL in the initial condition and down to minimum value of 0.1 mg KOH/100 mL after aging. It stands to mention that aging process of the composition that contains 0.01 wt.% CNT does not cause such rapid increase of acid content in comparison with the similar composition in initial condition. With a rise of CNT content up to 0.5 wt.% the referenced value decreases by 6.7 times compared to oil without CNT addition in the initial condition.

The principle of the graph of acid number variation depending on CNT weight percent age in the composition in initial condition is similar to the graph in Fig. 3 (curve 1). It should be noted that change of acid number of the composition after aging has the tendency to decrease. In addition the above its values decrease by 6.7 times in comparison with the oil without CNT.

On the basis of analysis of results obtained it may be concluded that introduction of small percent age of CNT (0.01 wt.%) initiates reduction of oxidation stability of the lubricant. It is stated that 0.5 wt.% can be considered as desired content of carbon nanotubes for artificially aged composition; with this content acidity and acid number reach their minimal values.

Due to the most important property of oil is its stability to neutralize sulfurous by products (sulfuric acid and sulfurous acid), and therefore to slow down corrosion damage to a motor, impact of CNT on alkali parameter was studied in qualitative test. The procedure of determination of alkali parameter by color was as follows. A glass container was filled with 25 mL of distillated water, a slip of yellow indicator paper and 2 mL of solvent toluene. One to two drops of tested oil was added to the container that was afterwards plugged with a cap and carefully shaken. Derived solution was set still for 3–5 min following which we evaluated change of solution color in the container. Change of colors helps to identify alkali number this solution has, for instance, yellow color of the solution means there is less than 1.5 mg KOH/g; green color – from 1.7 to 2.5 mg KOH/g (wherein light green is 1.7 and dark green is 2.5). The analysis of chosen compositions has shown that alkali number reduces when base sample ages (without CNT). However, increase of weigh percentage of CNT from 0.01 to 0.5 wt.% enhances coloring of the composition both in its initial condition and after aging, therefore providing evidence of increased alkali parameter. As can be seen from the above, introduction of carbon nanotubes effects positively the ability of oil to neutralize sulfurous byproducts even after aging.

4. Conclusion

The present research proposes improvement of functional and performance characteristics of petroleum, oil and lubricants by adding (doping with) carbon nanotubes that possess unique physical and chemical properties including sorption and antioxidant. The test results of compositions based on synthetic motor oil added with carbon nanotubes of various weight percentage content and oil without CNT (base sample) at a temperature of T = 25 °C have shown that injection of carbon nanotubes changes such physical and chemical properties of lubricants as viscosity, acid content and acid number, alkali parameter. These indicators of POL quality increase in the process of oil aging which has been proven by results obtained for artificially aged base sample. Doping lubricants with carbon nanotubes not only stops oxidation process but also reduces acid content and acid number in initial condition and after aging. Moreover, their presence increases alkali parameter after aging of the composition, therefore making it possible for oil to neutralize sulfurous by products while in operation even after its aging.

In conclusion, our research has proven that carbon nanotubes have positive effect on main functional and performance characteristics of petroleum, oil and lubricants, and that allows recommending use of CNT as new additives to liquid lubricating compositions.

References

[1]. I.A. Buyanovskiy, I.G Fuks, T.N. Shabalina, Neft' i gaz [Oil and Gas], Moscow, 2002. – 230 p. (in Russian).

[2]. Kh.A. Khussein, V.G. Mel'nikov. Zhurnal regional'nogo otd. RAEN [Journal of Regional Dep.]. – Ivanovo: IGKhTU (2007) 62–67 (in Russian).

[3]. Kh.A. Khussein, V.G. Mel'nikov. Fizika, himija i mehanika tribosistem [Physics, chemistry and mechanics tribosystems], Volgograd State University Press, Volgograd 6 (2007) 18–22 (in Russian).

[4]. A.V. Volkov, V.A. Godlevskiy, N.I. Zamyatina, Kh.A. Fiziko–khimicheskaya mekhanika protsessa treniya [Physico-chemical mechanics of friction processes], Volgograd State University Press, Volgograd, 2008. p. 118–121 (in Russian).

[5]. Topliva, smazochnye materialy, tehnicheskie zhidkosti. Assortiment i primenenie: Spravochnik [Fuels and lubricants, technical liquids. The range and applications]: Directory / I.G Anisimov, K.M. Badyshtova, S.A. Bnatov etc.; Ed. V.M. Shkol'nikova. Ed. 2nd Revised. and ext. – M.: Publishing Center "Tekhinform", 1999. – 596 p.

[6]. M. Lyuty and etc. Nanostrukturnye materialy [Nanostructured materials] – 2002: Belarus –Russia. Abstracts 2nd Scientific and technical seminar 24–25 October 2002. – M.: IMET RAN, 2002. – S. 44 (in Russian).

[7]. Lubricating oil composition for friction reduction that includes nanoporous particles: pat. Russian

Federation: B82B C10M C10N / Lee Hyeung Jin; Cho Yong Rae; patent applicant and holder SK LubricantsCo., Ltd. 2012145479/04; applic. 16.03.11; publ. 10.04.14, Journal 10 (in Russian).

[8]. A.V. Eletskiy, Uspekhi fizicheskikh nauk [Advances of physical sciences] 167 (9) (1997) 945–972 (in Russian).

[9]. S. Reich, C. Thomsen, J. Maultzsch Carbon nanotubes. Basic concepts and physical properties. Wiley, VCH Verlag, Berlin, 2003.

[10]. P. Harris, Carbon Nanotubes and Related Structures. New Materials for the XXI Century. Tekhnosfera, Moscow, 2003, 336 p. (in Russian).

[11]. A.V. Eletskiy, B.M. Smirnov. Uspekhi fizicheskikh nauk [Advances in Physical Sciences] 165 (9) (1995) 977–1009.

[12]. P.N. Djachkov Carbon nanotubes: morphology, properties, applications. Binom, Moscow, 2010. – 196 p. (in Russian).

[13]. A.V. Eletskiy. Uspekhi fizicheskikh nauk [Advances in Physical Sciences] 174 (11) (2004) 1191–1231 (in Russian).

[14]. I.V. Zaporotskova, Carbon and noncarbon nanomaterials and composite structures on its base: morphology and electron properties. Volgograd State University Press, Volgograd, 2009, 490 p. (in Russian).

[15]. D.V. Sivuhin, General course of physics. Textbook. – M.: FIZMALIT, 2005. – 544 p. (in Russian).

[16]. K.K. Papok, N.A. Ragozin, Dictionary of fuels, oils, lubricants, additives and special fluids]. 4th ed., Trans. and ext. Moscow, Chemistry, 1975. 392 p. (in Russian).

[17]. A.A. Voynov, Yu.V. Gus'kov, The manual for laboratory works / Ed.: A.A. Voynova. – Penza: Izd – vo PGU, 2011. – 56 p. (in Russian).

[18]. GOST 5985–79. Nefteprodukty. Metod opredeleniya kislotnosti i kislotnogo chisla. – Vzamen GOST 5985 – 59; vved. 01.01.1980. – M.: Standartinform, 2009. – 6 s.