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Effect of fullerene-like nanoparticles at low concentrations on the anti-wear properties of motor fuels

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Abstract

Motor fuels are the source of energy for internal combustion engines, and also a lubricant for friction units of the fuel equipment of automobile, aircraft and ship engines. The reliability and service life of the entire mechanism depend on the antiwear properties of fuels. Traditional anti-wear additives containing sulfur, phosphorus, chlorine, etc., are not applicable in motor fuels due to restrictions on emissions of toxic compounds. To improve the antiwear properties of lubricants, it is possible to use a new class of spatial carbon compounds - fullerene-like nanoparticles (FLNs).

This work shows that modification of liquid hydrocarbon motor fuels with fullerene-like nanoparticles (FLNs) increases the antiwear properties of fuels.

Key words: tribological characteristics of lubricants, motor fuels, antiwear additives, bearing capacity, fullerenes and fullerene-like nanoparticles

Introduction

Liquid motor fuels, a source of energy for internal combustion engines, are also a lubricant in the friction units of the fuel equipment of power mechanisms. The reliability of automobile, aircraft, and ship engines depends on the antiwear properties of such fuels [1].

The antiwear properties of lubricants can be improved by using surfactants, as well as unsaturated, aromatic or polycyclic hydrocarbons [2]. However, with a significant content of such components in fuels, their performance characteristics (viscosity, combustion efficiency, corrosivity, filterability, varnish deposits and carbon formation) deteriorate significantly.

Currently, special antiwear additives are added to lubricants to improve antiwear properties, which form chemical secondary structures on metal surfaces with high compressive resistance and reduced shear resistance. A wide range of compounds containing sulfur, phosphorus, chlorine, boron, and other heteroatoms are used as such antiwear additives [3, 4]. However, these additives cannot be used in motor fuels due to environmental restrictions on engine emissions [5]. Moreover, motor fuels are fundamentally different from oils in terms of the implementation of both lubricating effects. The oil is constantly (or for quite a long time) in the zone of frictional contact. The fuel passes through the friction zones of the fuel supply equipment in portions - once and for a short time (pieces of millisecond). For such periods of time, the chemical processes of the interaction of the components of the lubricant with metal surfaces cannot be fully realized.

New spatial nanostructures based on carbon are currently being considered as promising antiwear additives for lubricants. According to the recommendation of the International Union of Pure and Applied Chemistry (IUPAC), single- and multilayer closed spherical polyhedra consisting of carbon pentagonal and hexagonal faces (resembling a soccer ball in structure) are classified as fullerenes (or fullerene-like nanoparticles) [6].

The mechanism of action of fullerene-like nanoparticles on the tribological characteristics of lubricants is explained by the precipitation of fullerenes from the liquid phase on the contact surfaces during friction. It is assumed that a layer of ball-like fullerene nanoparticles formed on the friction surfaces transforms sliding friction into rolling friction with a decrease in the friction coefficient and minimization of wear out [7]. The role of the lubricating fluid in this case is reduced only to the delivery of fullerenes to the friction zone.

In accordance with such ideas, it should be expected that the positive effect of these additives on the tribological characteristics should increase as the contact surfaces are filled with fullerene particles. In turn, the precipitation of fullerenes accelerates with an increase in their concentration in the solution.

However, fullerene-like nanoparticles are very slightly soluble in hydrocarbon liquids based on alkanes [8]. The literature presents mainly the results of studies of the effect of C_{60} fullerene additives (at concentrations of 1–5 wt %) on the tribological properties of high-viscosity lubricants and oils, where sufficient stability of the compositions is ensured [9, 10].

Even in motor oils, which, for reasons of necessary thermal stability, are based on linear saturated hydrocarbons, fullerenes are poorly dispersed. The solubility of such compounds in aromatic solvents and vegetable oils with a high content of oleic acid is somewhat higher. Therefore, to improve the stability of fullerene components in motor oils, it is proposed to pre-disperse fullerenes in high-oleic vegetable oils, and then add these compositions to mineral oils. This technique was used, for example, during the project [10], where the optimal antiwear properties of lubricating oil were observed at the following ratio of components:

– 1% wt. fullerene C_{60};
– 10% wt. vegetable rapeseed oil;
– 89% wt. mineral motor oil M-10G2k.

But for motor fuels, such methods of fullerene dispersion are unsuitable because of the deterioration of the filterability of fuels.

Up to this moment, in terms of scientific substantiation of the use of fullerene additives in fuels, a contradictory situation has developed:

- on the one hand, they should not settle on filters and precision surfaces of fuel equipment when fuel is supplied to the combustion chambers of engines;

– on the other hand, it is assumed that it is as a result of the deposition of fullerenes that their positive antiwear effect can be realized.

This contradiction prevents the use of fullerene-like nanoparticles in low-viscosity fuels with a predominance of saturated hydrocarbons (gasoline, diesel and aviation fuels). However, advertising materials recommend them as multifunctional additives, for example, to diesel fuels without justifying the permissible concentration limits.

In low-viscosity hydrocarbon fuels, solutions of fullerene-like nanoparticles are stable only when the content of these additives is up to dozens of ppm. Previously, in [11, 12], we showed that the addition of LPF even in the amount of several ppm to gasoline and diesel fuels significantly affects the energy efficiency of fuel combustion. When working with such additives, the engine efficiency increases up to 10-15% and, accordingly, fuel consumption per unit of useful power is reduced by 10-15%.

In the present work, the following questions are studied.

- Do the minimum concentrations of fullerene-like nanoparticles in hydrocarbon liquid motor fuels affect their anti-wear properties?

- If such an influence takes place, is it due to the deposition of fullerene particles on the friction surfaces or is there another mechanism of their action?

The clarification of these issues will make it possible to substantiate the strategy for the use of FLNs in low-viscosity motor fuels.

Materials and methods of experiment

Aviation turbine fuel Jet A-1 was used as the object of study. Some characteristics of the fuel taken for research are given below.

Physical and chemical parameters of aviation fuel Jet A-1.

Fractional composition:

✓ distillation start temperature, °C... 150
✓ 10% is distilled off at a temperature, °C, not higher... 165
✓ 50% is distilled off at a temperature, °C, not higher than ... 195
✓ 90% is distilled off at a temperature, °C, not higher than ... 230
✓ 98% is distilled off at a temperature, ° C, not higher than ... 250

Kinematic viscosity, mm^2/s: at 20 °C, not less than ... 1.3
Mass fraction of aromatic hydrocarbons, %, not more than ... 22
Concentration of actual resins, mg per 100 cm^3 of fuel, no more than... 3
Mass fraction of total sulfur, %, no more than ... 0.2

During the tests, fuel samples were used in a volume of 25 ml; samples were taken from one batch of fuel. Samples of fuels with additives of fullerene nanoparticles were prepared as follows. Fullerene-like nanoparticles were obtained by high-frequency discharge-pulse synthesis using a light hydrocarbon fraction of propane-butane as a feedstock [13]. To increase the stability of hydrocarbon solutions of FLNs, the resulting product was brominated in excess liquid bromine at room temperature for 72 hours. Residual bromine was distilled off in vacuum at 20°C.

The isolation of fullerene nanoparticles from the synthesis product and their size fractionation were carried out by extraction in absolute ethanol. The average size of isolated nanoparticles, according to estimates made by electron and atomic force microscopy, was 10–15 nm [11].

Solutions of fullerene nanoparticles in fuel were prepared using an ultrasonic low-frequency (22 kHz ± 10% kHz) disperser. From the resulting stable solution with the maximum concentration of FLNs, solutions with a lower concentration required for the study were prepared by adding calculated amounts of fuel.

The possible effect of the addition of fullerene nanoparticles on the antiwear properties of the fuel was assessed by the change in two tribological characteristics:

- wear indicator (registered by the diameter of the wear spot of mating steel balls);
- bearing capacity (registered by the value of the critical load to scuffing).

The bearing capacity of the fuel and the wear index were determined on a four-ball friction machine according to the method ASTM D2783 [14]. When choosing this method of tribological tests, we were guided by the following considerations. On this machine in the friction unit, the conditions of pure sliding with point contact are reproduced. On such an installation, the constancy of the initial conditions for individual measurements is ensured (the same physical, chemical and geometric characteristics of the frictional interface in the form of balls made of steel SH15 with a diameter of 12.7 mm with equal roughness parameters). Therefore, this method provides high reproducibility of results.

The wear index (diameter of wear spots of mating balls) was measured by the method of fixed loads with a normalized load of 100 N at a rotation frequency of 1500 min^{-1}. The wear scar diameters of the balls were measured at three different trial durations of 2, 3, and 5 min. After each measurement, the balls in the friction assembly were replaced with new ones.

The bearing capacity of fuels was determined by the value of the critical load to scuffing at the temperature of 20 °C, similarly to the ASTM D2596 method.

Characteristics of prototypes

Used alloying compositions of the following composition:

1 - Cr-B4C-Mo-C - 2% chromium, 1% boron carbide, 0.5% molybdenum and 0.4% carbon;

2 - Cr-Mo-V-C - 5% chromium, 1% molybdenum, 1% vanadium, 0.8% carbon;

3 - Cr-Mo-V-C - 10% chromium, 1% molybdenum, 1% vanadium, 0.8% carbon.

Visible defects, micro- and macrocracks are absent for the deposited layers.

From the above data on the chemical composition of the components it is clear that the main alloying elements are chromium with the addition of vanadium, molybdenum or boron carbide in the presence of carbon.

Results of research and discussion

According to those results of tribological tests shown in Fig. 1 and 2, the modification of liquid hydrocarbon fuels with low concentrations of FLNs improves the antiwear properties of fuels.

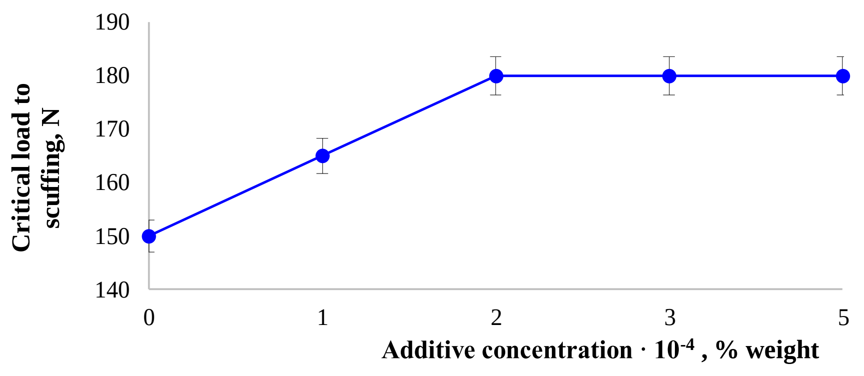

Fig. 1. Dependence of the bearing capacity of turbine fuel Jet A-1 on the concentration of the FLNs additive

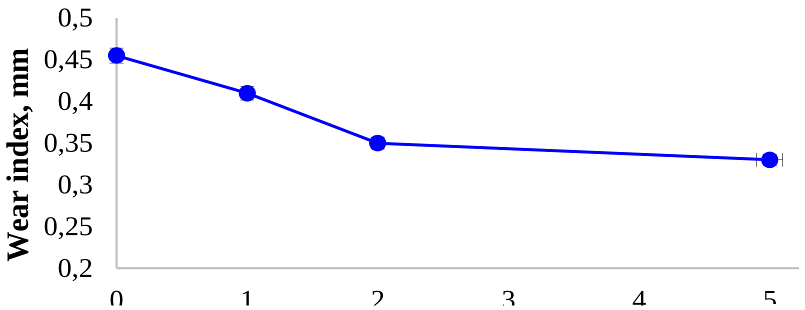

Fig. 2. **Dependence of the wear index on the concentration of the LPF in the turbine fuel Jet A-1: the duration of the tribological tests is 5 min**

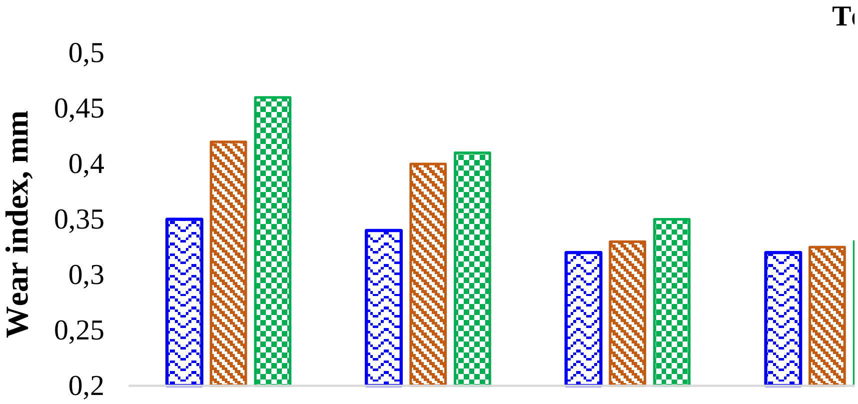

Fig. 3. Change in the wear index with an increase in the duration of the friction process in the turbine fuel Jet A-1: without additive (0) and at three different concentrations of FLNs (1, 2 and 5·10^{-4}, % wt.)

In the presence of fullerenes in the composition of the fuel, the bearing capacity increases and the wear index decreases. As the additive concentration increases, both of these tribological characteristics change no monotonically.

The bearing capacity increases most sharply in the initial range of the investigated additive concentrations, and then stabilizes. The optimal value of the FLNs concentration in terms of increasing the carrying capacity of the fuel was observed at 2·10^{-4} % wt., with a further increase in the FLNs concentration, this characteristic practically does not change.

The dependence of the wear index (wear scar diameter) on the additive concentration in the fuel is non-linear. As can be seen from the diagrams in Fig. 2, this indicator also decreases most sharply in comparison with tests in fuel without additives at FLNs concentrations in the region up to 2·10^{-4} % wt. At an additive concentration above this value, a decrease in the wear index is also observed (in contrast to the bearing capacity, which plateaued at this concentration), but this change is very weak.

The dependence of the wear index on the duration of the testing process is interesting (Fig. 3). This dependence is different for different concentrations of the FLNs additive in the fuel. In the absence of FLNs additives in the fuel and at their low concentrations, the wear indicator noticeably increases with an increase in the duration of tribological tests. At additive concentrations of 2 ppm and more, the amount of wear changes slightly with an increase in the duration of the friction process.

The results obtained can be explained as follows.

There is currently no generally accepted point of view on the mechanisms and processes underlying the various effects of ultra-low doses of additives on the behavior and properties of bulk phases (both liquid and solid). As a rule, the explanation of such effects can be reduced to one of two hypotheses.

According to one of these hypotheses, the effect of additives in micro quantities is caused by the concentration of the active ingredient in certain local volumes. As a result, the amount of a substance in such micro volumes can be several orders of magnitude higher than the initial average concentration in the solution, and the course of processes in these volumes is determined by the properties and behavior of the group of particles.

In the framework of another hypothesis, the influence of micro quantities of additional substances is associated with their coordinating (controlling) effect on the particles of the medium and the restructuring of the structural organization of these particles throughout the volume.

Based on such general ideas, it should be assumed that the effect of small doses of fullerenes on the antiwear properties of fuel can be due to the superposition of two different effects:

– Concentration of the additive substance in the most loaded areas of the friction surface due to the deposition of fullerenes.

– The coordinating effect of fullerenes on the molecules of the liquid phase with the rearrangement of the supramolecular structure of the fuel in the volume.

It is possible to single out the influence of these two effects on the basis of the fact that their action should be reflected differently on different tribological characteristics.

Indeed, the bearing capacity is a characteristic of the instantaneous state of the tribosystem. When measuring this characteristic, tribological tests are short-term (test time is 10 s). Therefore, this characteristic should not be affected by the rather inertial process of deposition of fullerene particles from the liquid phase onto the contact surfaces. Changes in this tribological characteristic of fuel in the presence of fullerenes in it are mainly due to processes occurring in the liquid phase, and not on the surface of solids.

When determining the wear indicator (wear scar diameter), the process of tribological testing is relatively long (from several minutes to 1 hour). Therefore, this indicator can depend both on processes in the liquid phase and on the slow-in-time phenomenon of deposition of fullerene nanoparticles from solution onto solid surfaces.

The obtained results of the study indicate that the change in tribological characteristics when FLNs is added to the fuel is indeed due to the superposition of two effects.

An increase in the fuel carrying capacity is observed only with an increase in the concentration of fullerenes up to 2 ppm. With an increase in the concentration of FLNs in the solution above 2 ppm, this tribological characteristic practically does not change.

Apparently, this effect can be associated with the formation of the domain structure of solvent molecules around the center-forming nanoparticles of the additive [18, 19]. At the additive concentration limit of 2 ppm, saturation is reached, i.e. filling the entire volume of the solution with such domain formations. In the region of an increased concentration of the additive (exceeding 2 ppm), clustering of the particles of the additive between themselves is possible, which is accompanied by a decrease in the effectiveness of the effect of such associates on the properties of the solution compared to the efficiency of individual nanoparticles [14].

However, the wear indicator continues to decrease somewhat with an increase in the content of fullerenes in the solution above 2 ppm. The change in the wear index in this concentration range can apparently be explained by the deposition of fullerene nanoparticles on the friction surface. However, the influence of this effect on the antiwear properties of the fuel under the given conditions of tribological testing is less significant than the effect of nanoparticles on the change in the structure of the liquid phase.

Conclusions

1. Modification of liquid hydrocarbon motor fuels with fullerene-like nanoparticles (FLNs) increases the antiwear properties of fuels.

2. The effect of low concentrations of FLNs on the antiwear properties of liquid hydrocarbon fuels is mainly associated with the effect on the structure of the liquid phase and, to a lesser extent, with the deposition of fullerene nanoparticles on the friction surface.

3. Based on the obtained results, a strategy for the use of FLNs in hydrocarbon liquid motor fuels is substantiated. In such petroleum products, additives based on fullerene-like nanoparticles are advisable to use at concentrations of several ppm. A further increase in the concentration of the additive does not lead to a significant increase in antiwear properties, but may impair the efficiency of engines due to deposits on filters and on working surfaces.

References

1. Hsieh P.Y., Bruno T.J. A perspective on the origin of lubricity in petroleum distillate motor Fuels. *Fuel Processing Technology*. 2015. V. 129. P. 52–60.

2. Likhterova N.M., Seleznev M.V., Goryunova A.K. Tribologicheskiye kharakteristiki sovremennykh aviatsionnykh kerosinov. Neftepererabotka i neftekhimiya. 2019. № 7. S. 35–40.

3. Zhang J., Spikes H. On the Mechanism of ZDDP Antiwear Film Formation. *Tribol. Lett.* 2016. V. 63. P. 3–27.

4. Rastogi R.B., Maurya J.L., Jaiswal V. Phosphorous free antiwear formulations: zinc thiosemicarbazones–borate ester mixtures. *Proc. IMechE, Part J: J Engineering Tribology.* 2012. V. 227. P. 220–233.

5. The technical regulations for automobile gasoline, diesel, ship and boiler fuels. Cabinet of Ministers of Ukraine, 2013, 22p.

6. Lyubchuk T.V. Fulereny ta inshi aromatychni poverkhni (struktura, stabil'nist', shlyakhy utvorennya). K.: Vydavnycho-polihrafichnyy tsentr "Kyyivs'kyy universytet". 2005. 322 s.

7. Tuktarov A.R., Khuzin A.A., Dzhemilev U.M. Fullerenosoderzhashchiye smazochnyye materialy: dostizheniya i perspektivy (obzor). Neftekhimiya. 2020. T. 60, № 1. S. 125–147.

8. Yeletskiy A.V. Fullereny v rastvorakh. Teplofizika vysokikh temperatur. 1996. T. 34, № 2. S. 308–323.

9. Ginzburg B.M., Baydakova M.V., Kireyenko O.F., Tochil'nikov D.G., Shepelevskiy A.A. Vliyaniye fullerena C60, fullerenovykh sazh i drugikh uglerodnykh materialov na granichnoye treniye skol'zheniya metallov. Zhurnal tekhnicheskoy fiziki. 2000. T. 70, Vyp. 12. S. 87–97.

10. Kravtsov A.G. Modelirovaniye formirovaniya maslyanoy plenki na poverkhnosti treniya pri nalichii fullerenovykh dobavok v smazochnom materiale i yeye vliyaniye na skorost' iznashivaniya tribosistem. Problems of Tribology. 2018. № 1. S. 69–77.

11. Polunkin YE.V., Pylyavs'kyy V.S., Bereznyts'kyy YA.O., Kamenyeva T.M., Levterov A.M., Avramenko A.M. Pokrashchennya khimmotolohichnykh vlastyvostey dyzel'noho palyva mikrodobavkoyu vuhletsevykh sferoyidal'nykh nanochastok. Kataliz ta naftokhimiya. 2020. №. 29. S. 59–64.

12. Increasing surface wear resistance of engines by nanosized carbohydrate clusters when using ethanol motor fuels / O.O. Haiday, V.S. Pyliavsky, Y.V. Polunkin, Y.O. Bereznytsky, O.B. Yanchenko, A. Smolarz, P. Droździel, S. Amirgaliyeva, and S. Rakhmetullina. *Mechatronic Systems 1*. London, 2021. P.89-99. URL: https://doi.org/10.1201/9781003224136-8

13. Rud' A.D., Kuskova N.I., Boguslavskiy L.Z., Kir'yan I.M., Zelinskaya G.M., Belyy N.M. Strukturno-energeticheskiye aspekty sinteza uglerodnykh nanomaterialov vysokovol'tnymi elektrorazryadnymi metodami. Khimiya i khimicheskaya tekhnologiya. 2013. T. 56, Vyp. 7. S. 99–104.

14. Yadav G., Tiwari S., Jain M.L. Tribological analysis of extreme pressure and anti-wear properties of engine lubricating oil using four ball tester. *Materials Today*. 2018. V. 5, No. 1. Part 1. P. 248–253.

Пилявський В.С., Полункін Є.В., Гайдай О.О., Янченко О.Б. Вплив фулереноподібних наночастинок у малих концентраціях на протизносні властивості моторних палив

Моторні палива є джерелом енергії для двигунів внутрішнього згоряння, а також мастилом для вузлів тертя паливної апаратури автомобільних, авіаційних і суднових двигунів. Від протизносних властивостей палив залежить надійність і термін служби всього механізму. Традиційні протизносні присадки, що містять сірку, фосфор, хлор тощо, не застосовуються в моторних паливах через обмеження на викиди токсичних сполук. Для покращення протизносних властивостей мастильних матеріалів можливе використання нового класу просторових вуглецевих сполук – фулереноподібних наночастинок (ФНЧ).

У даній роботі показано, що модифікація рідких вуглеводневих моторних палив фулереноподібними наночастинками (ФНЧ) підвищує протизносні властивості палива.

Ключові слова: трибологічні характеристики мастильних матеріалів, моторні палива, протизносні присадки, несуча здатність, фулерени та фулереноподібні наночастинки