LUBRICATING OILS WITH DETONATION NANODIAMONDS

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SUMMARY

The present work investigates the influence of suspensions with nanodiamonds on the oxidation stability, and lubricating properties of an automotive gear oil and a motor oil.

- The blend of soot and 40 % diamond showed a very significant pro-oxidation effect in the gear oil, but the stability of the motor oil practically remained unchanged. The pure nanodiamond concentrates improved twice the oxidation stability of the motor oil. In the formulated gear oil the concentrate with a polysuccinimide stabilizer did not change the oxidation stability, while that with a sulfonate stabilizer impaired it.

- The tested suspensions did not show impressive positive influence on the lubricating properties, except in a few cases. The explanation of the obtained results seems to lie in the relatively small amount of really nano-sized fraction in the powders. The successful deaggregation is important not only for the physical stability of the concentrates, but also a pre-requisite for a breakthrough in improving the properties of lubricants containing them.

Keywords; nanodiamonds; motor oils; gear oils; tribology, lubrication.

Introduction.

Detonation of carbon-containing explosives under conditions of negative oxygen balance produces blends of soot and diamond-like carbon (DLC) with dimensions in the nanoscale [1].

The interest in the lubricating properties of novel carbon materials (fillerenes, nanotubes, carbon onions, nano-diamonds, etc.) is related to their well documented application for building up thin solid lubricating films on metal substrates [2 - 4]. Relatively new studies aim to incorporate them in the conventional liquid lubricants and achieve a "ball bearing effect", i.e., the particles to act as small hard balls in the tribo-contact, as metal balls do in a bearing [5].

The typical application of thin films, produced from nanodiamonds is lubrication in vacuum (e.g., in space). The targeted conventional lubricants with nano-diamonds are polishing pastes, greases and lubricating oils [4], though at least one patent has been issued for transformer oils with nanodiamonds possessing enhanced thermal conductivity and dielectric properties [6].

Different products, containing nanodiamonds on the market range from pure diamond powders to products containing also soot in different proportions, depending on the depth of removal of the soot originally present after the detonation synthesis [3]. To liquid lubricants, which are the particular interest of this work, the powders are predominantly added in the form of oil suspensions [4]. The high activity of the powder surface functional groups leads to the aggregation of the particles and to a varying stability of the suspensions, depending on particle size, the suspension base oil (polar or non-polar), interaction with stabilizers, etc.

It should be noted that if nanodiamonds are targeted as lubricating additives, but in a particular lubricant they cannot achieve a lubricating effect comparable to that of DLC solid films in vacuum, their use does not make sense, both from economic point of view, and from the point of view of eventually influencing negatively other properties of the lubricant [7, 8].

Therefore, studies devoted to the lubricating effect of suspensions with nanodiamond powders, determined in different tests and lubricants, providing evidence for their interactions with suspension stabilizers and other additives in the formulated lubricant, etc. are very important for their application.

In our previous studies on such suspensions we have firstly developed an express method for evaluation of the concentration of nanodiamonds and blends with soot in oil suspensions by UV-VIS spectrometry [9]. We have subsequently used this method to follow the sedimentation stability of the suspensions in the presence of typical lubricant additives and packages for up to 90 days [10].

In order to improve the physical stability of the suspensions we have tested different combinations of particular additives and packages, and developed new technological steps in the preparation of the suspensions [8]. We have also reported on the oxidation stability of lubricants containing nanodiamond – soot blends and pure nanodiamonds, and approaches for affecting positively the established pro-oxidant effect of the powders [7].

The aim of the present work was to investigate the extreme pressure (EP) and the antiwear properties of samples which have shown best physical and oxidation stability in our previous work.

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Experimental.

Preparation of the powder suspensions in oil.

The powders used in all our studies were received from the Department of Space Material Science, Space Research Institute of the Bulgarian Academy of Sciences under the provisions of a joint project. According to the participating team from this Department, the powders have been obtained in a pilot installation by controlled explosion and annealing of the soot, following improved versions of their patented technology [11]. The laboratory compositions for our work were prepared with two powders - one containing around 40 % diamond (to be called further "DB 40"), and - one containing pure nanodiamond.

The Laboratory of Organic Reactions of Microporous Materials of the Institute of Organic Chemistry of the Bulgarian Academy of Sciences is the other collaborator in the joint project. The relevant to our studies part of the work of this team is on the characterization of the powders and the development of methods for modification of their surfaces.

The concentrates used in this work were the samples which achieved best chemical and physical stability, as described in [7 - 10]. There we present in detail the methods for the preparation of the concentrates, and the method for evaluation of their stability, the powders and the additives used, the physical stability of the concentrates and the low temperature stability and oxidation stability of the lubricating oils containing them, etc. More information about the powders we have used is provided in publications of our collaborators [11 - 13].

Additives and Oils.

Table 1 presents the chemical type and typical properties of the additives we have used in our studies.

We have oriented our experiments towards express and reproductive estimation of the influence of the powders in two widely used oils: an automotive gear oil, formulated by addition to a SAE 90 base oil of a commercial package in the concentration recommended by its producer for the API GL 5 specification, and a commercial sample of SAE 15W/40 API SJ/CF mineral based motor oil.

The used abbreviations designate respectively, the viscosity classification of the Society of Automotive Engineers (SAE), and the performance category of the American petroleum Institute (API).

Methods for testing the lubricating properties.

The performance of gear oils for manual transmissions is determined by standard specifications, e.g. by ASTM D 5760 or for military applications - MIL-2105E. Table 2 lists some of the relevant laboratory tests from these specifications in which lubricating properties of automotive gear oils are evaluated.

The lubricating properties of engine oils are evaluated mostly in engine tests, as described, for instance, in ASTM D 4485. One of the modelling tests, for instance, in which wear is accessed together with oxidation, dispersant, detergent ability and corrosion resistance, is the ASTM D 6335 method of test. I

It is not an objective of this work to review the numerous tests for engine oils, which are frequently elaborated and replaced. Table 2 is intended mainly to certify the use for express, reproducible laboratory tests, such as the simple four ball machine tribometer, on which we have conducted our experiments.

All tests for the evaluation of the DB and pure nanodiamond concentrates were done on a "SETA EP Four Ball Machine", following strictly the ISO 20623 method. We have acquired considerable experience in the performance and interpretation of such tests while developing additives and lubricants [14 - 16].

The standard EP parameters were determined in 10 s runs at each applied normal load (a weight of 1 kg was considered to correspond to a load of 10 N). In addition the average wear scar diameters after 60 min runs, starting from room temperature were measured as indicative of antiwear properties.

The Flash Temperature Parameters (FTP) was calculated in the usual manner in each run. The maximal value of FTP, suggested as an approximate value of the highest working temperature in the contact after which the lubricant will fail [17], was also included in the results.

All tested samples were compared for additions of 5 % concentrate not to the neat oil, but to the neat oil with 5 % liquid paraffin. This is due to the fact that paraffin is used as the model base oil of our concentrates. The influence of real-life hydrocarbon and/or synthetic base oils in the concentrates and the influence of the amount of the concentrate on performance will be the object of our future work.

Results and Discussion.

Tables 3 and 4 present, respectively, the results for the lubricating properties of the automotive gear oil and the engine oil with the concentrates.

As seen from Table 3, in the formulated gear oil only the suspension of DB 40, stabilized with additive 1 shows a clear improvement of the EP properties, as expressed by the ISL, FTP and the LWI. It, however, does not influence the weld load, and the antiwear properties (WSD after the 60 min test). The rest of the results with either additive and/or powder are within the limits of precision of measurement of the respective parameters.

In the engine oil (Table 4) the suspension of DB 40 with additive 1 repeats its positive influence on initial seizure load, FTP and the load wear index, but again does not influence either the weld load or the wear scar diameter after 60 min.

The lubrication films eventually formed by the pure nanodiamonds, seem stable and hard enough to bring up the weld load with one loading step.

Looking for explanation of the overall not very impressive performance of the powders, we hereunder present the transmission electron microscope (TEM) photos of the initial DB 40 powder, and the DB 40, obtained from the paste prepared in the presence of additive 2, as described in [8] after centrifugation of the oil (Fig. 1 and Fig. 2).

The two figures show that the diamond phase in both blends (Fig. 1a and Fig. 2a) is aggregated, although the individual mono crystals are with sizes in the nanoscale. The photos on both figures show the edge of an aggregate.

Our previous studies [7] with X ray diffraction (XRD) and X ray photo electron spectrometry (XPS) indicated that the aggregation is eventually realized with the participation of the graphite or graphitoid phase. This is in conformity with the findings in [18, 19]. Our work [8] also demonstrated that when preparing the paste of DB 40 in the present of the additives a significant amount of them is adsorbed on the surface of the powder. This seems to be confirmed by the above TEM photos as well. Moreover, it seems that some minor mechano-chemical crushing of the aggregates also might have been done.

In their recent work [20], Wu et al. reviewed previous studies on lubrication with different nanoparticles, and pointed out that the achieved effect depends on the size, shape and concentration of the particles. In the experimental part of their work with a Plint-Cameron machine, they also could not achieve impressive results with nanodiamonds, as compared to the lubrication effect of the other pnanoparticles they tested.

The importance of size and shape was confirmed also by the work of Chukaeva [21], who had shown experimentally that addition of a particular fraction separated from a nanodiamond to an engine oil, lead to decrease of the friction coefficient for bronze pairs by a factor of no less than two, whereas the addition of the unseparated powder exhibited abrasive properties.

Thus, in the first instance the effective lubrication with particles, including also nanodiamonds, depends on their capability to penetrate the tribocontact. Moreover, the diamond particles are abrasive and if they cannot enter the contact, the result most likely would be increased wear. This assumption for the role of the supply of the particles into the contact was also supported, for instance, by the recent work of Matsumoto et al. with onion-like carbon added to synthetic polyalpha-olefine oil [22]. In their friction experiments with a ball and plate contact, changing the diameter of the balls and increasing contact pressure produced worse results.

Coming back to the results of our work, the probable cause for the non-impressive lubricating performance of the tested powders seems to be that the aggregates, most of which are in the micron range, in the specific conditions of the four ball machine experiments, cannot enter the tribocontact in sufficient quantities. The several cases when certain positive effects have been obtained seem to indicate the presence of particles, small enough to enter the contact, while a sufficient supply of these particles can be realized within the duration of the test.

The above considerations and examples from other authors show that our findings display performance, which is not only due to the powders and tribometer we are using, but are rather an illustration of a more common problem. In any case, our results again emphasize the fact, demonstrated by the results of other authors as well, that the successful deaggregation of the particles should be a primary task, from the point of view of lubrication and application of nanodiamond powders in lubricants.

Conclusions

The work presented above may be summarized as follows:

- The evaluation of the lubricating properties of the three oils, containing suspensions of a nanodiamond blend with soot, and of pure nanodiamonds and two different lubricant additives, used as stabilizers, did not show impressive positive results, except in a few cases.

- The possible explanation of the obtained results seems to lie in the relatively small amount of really nanosized fraction in the powders,as demonstrated in the presented TEM studies. This seems to be a common problem in the full application of such powders, and in lubricants, in particular.

- The successful desaggregation is important not only for the lubrication performance of nanodiamond powders, but as our previous work demonstrated, also for the physical stability of the concentrates and their influence on the oxidation stability of lubricants containing them.

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Table 1
Characteristic properties of the additives, used as stabilizers.

No	Property	Additive 1	Additive 2	Method
	Chemical type	Polyalkenyl succine imide	Alkylaryl Ca sulfonate	-
1	Kinematic viscosity, $mm^2 s^{-1}$			ISO 3104
	- at 25 °C	-	2600	
	- at 40 °C	-	850	
	- at 100 °C	500	45	
2	Density at 15 °C, $kg m^{-3}$	917	986	ISO 12185
3	Pour point temperature, °C	-	-12	ISO 3016
4	Flash temperature, °C	210	155	ISO 2592
5	Total base number, mg KOH g^{-1}	17.7	30	ASTM D 2896
6	Contents of:			
	- Nitrogen, %	1.84	-	ASTM D 4629
	- Calcium, %	-	2.78	ASTM D 4951
	- Sulfur, %	-	5.16	ASTM D 4927
7	- diluent oil, %	< 60	< 60	-
8	Recommended concentration, %	0.5 – 5.0	0.5 – 3.0	-

Table 2. Lubricating properties of automotive gear oils, according to different specifications

No.	Property	Limits	Method
1	EP properties, EP Four Ball Machine - Mean Hertz Load, N - Average Wear Scar Diameter (WSD), mm	 > 750 < 0.5	EN ISO 20623 10 sec. run 60 min, at 75 °C and 400 N
2	Scuffing load capacity, FZG machine. - failing load stage	11	ASTM D 5182
3	High Torque Test. Condition of gear teeth Condition of half-shaft and axle housing	The performance of the oil shall be superior to that of the CRC reference oil RGO 104.	IP 232, proc. B
4	High speed shock test.	The performance of the oil shall be superior to that of the CRC reference oil RGO 110.	Chrysler Avenger test rig

Table 3
Lubricating properties of the automotive gear oil with DB-40 and nanodiamond concentrates.

No.	Sample	ISL, N	FTPmax	WL, N	LWI, N	WSD 60 min, mm
SAE 90 API GL 5 automotive gear oil +						
1	none	1260	305.8	5000	652	not tested
2	5 % paraffin	1260	315.6	4000	609	0.44
3	5 % DB 40 with Additive 1	1600	332.5	4000	666	0.45
4	5 % DB 40 with Additive 2	1000	269.5	4000	565	0.41
5	5 % nanodiamond with Add. 1	1000	278.7	4000	595	0.41
6	5 % nanodiamond with Add. 2	1000	269.5	4000	592	0.45

Table 4
Lubricating properties of the automotive gear oil with DB-40 and nanodiamond concentrates.

No.	Sample	ISL, N	FTPmax	WL, N	LWI, N	WSD, mm
SAE 15w/40 API SJ/CF motor oil +						
1	none	1260	336.8	2000	436	not tested
2	5 % paraffin	1000	363.6	2000	348	0.46
3	5 % DB 40 with Add. 1	1600	452.1	2000	615	0.48
4	5 % DB 40 with Add. 2	1000	269.5	2000	346	0.66
5	5 % nanodiamond with Additive 1	1260	296.6	2500	443	0.49
6	5 % nanodiamond with Additive 2	1260	315.6	2500	444	0.54

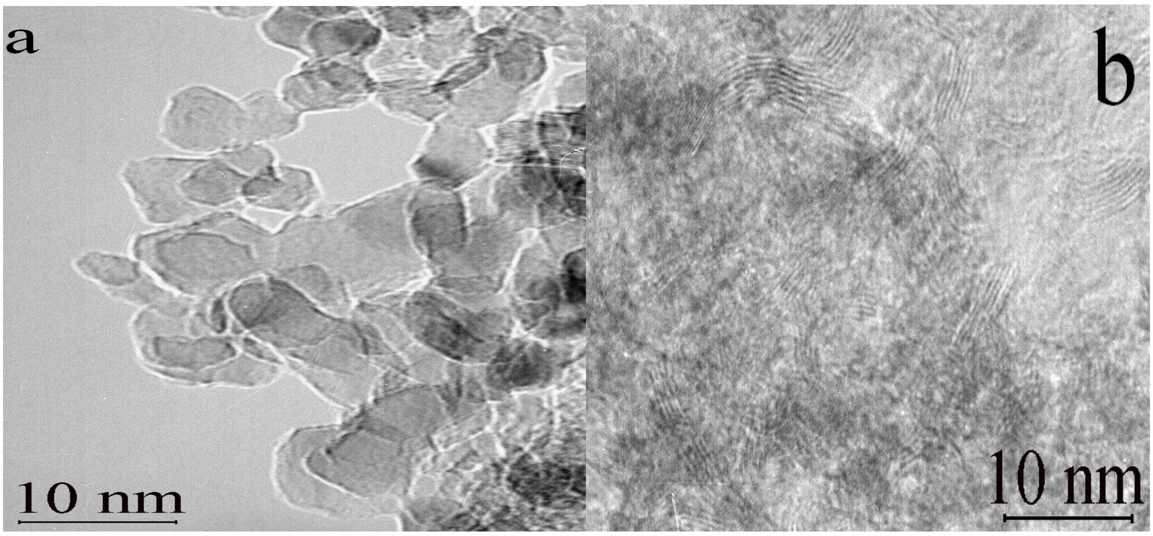

Figure 1. TEM photos of the diamond (a) and the soot (b) from DB 40.

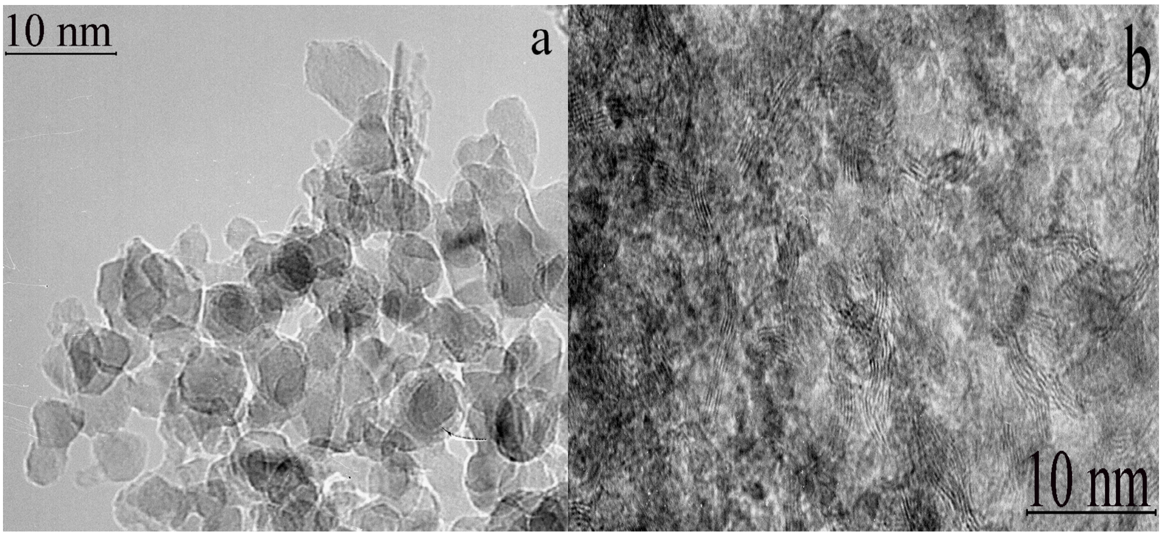

Figure 2. TEM photos of the diamond (a) and the soot (b) from DB 40
separated from paste with Add. 2 by centrifugation.