

Physical stability of detonation nanodiamonds in liquid lubricants

G. St. Cholakov*, V. B. Toteva, St. D. Janev, St. G. Staykov, K. G. Stanulov

Department of Organic Synthesis and Fuels, University of Chemical Technology and Metallurgy, 8 boul. "Kl. Ohridsky", Sofia 1756, Bulgaria

Received January 10, 2011; Revised April 24, 2011

The aggregation of detonation nanodiamonds hinders their wider implementation and requires application-oriented studies and selection of stabilizers, which do not interfere with the rest of the components in the product in which they are used.

The aim of this work was to study the effect of typical lubricant additives on the sedimentation stability of nanodiamond powders in non-polar media (liquid paraffin). The low temperature stability of lubricating oils with nanodiamonds was also evaluated experimentally.

The used powders (nanodiamonds, ND and nanodiamonds with 40 % soot, NDS 40) were with sizes typical for commercial industrial nanodiamonds. Experimental evidence is presented that they contain a significant amount of aggregates with larger than nano-sizes.

Conventional laboratory mechano-chemical disaggregation, in the presence of experimentally selected best additives, ensure that more than 50 % of the NDS stays in the upper-most layer of the paraffin concentrate after 90 days of storage, while mild homogenization recovers around 70 % of the powder.

The mechano-chemical disaggregation was not so effective for ND. Similar stability was achieved when it was combined with a technology in which the concentrate was prepared from water suspension, by evaporation of the water in the presence of the stabilizer and some paraffin.

The NDS and ND powders slightly influence the low temperature stability of automotive oils, but their effect should be checked.

Keywords: detonation nanodiamonds; mechano-chemical disintegration; oil suspensions; sedimentation stability; lubricating oils, low temperature stability.

1. INTRODUCTION

Detonation of carbon-containing explosives under conditions of negative oxygen balance produces nanodiamond crystals with dimensions below 100 nm (NCDs) and/or below 10 nm (ultrananocrystalline diamonds, UNCD) [1], together with soot and other impurities, that have to be removed. Different purification methods have been suggested, but the most widely used involve treatment with oxidative agents in water suspension [2–4]. Soot might be only partially removed for some applications [5].

Depending on their size and specific conditions of formation, detonation diamonds might exhibit unique physical (highly developed surface) and chemical (active surface functional groups) properties [6]. These properties allow for a wide range of potential applications [5–8]. However, there are serious problems, which have to be solved in order to put nanodiamond production on an

industrial scale [9] and increase it significantly from the estimated 7 tons sold world-wide in 2008 [10].

The presence of active functional groups, obtained on the surface of both soot and nanodiamonds during their synthesis and/or purification, leads to formation in storage, of aggregates in which the original 4 – 5 nm sized nanoparticles, become chemically bonded [11]. There is evidence that aggregated particles with above micron dimensions are found in significant amounts in the water suspensions and dry powders offered on the market [8, 12].

Preserving the size and storage stability of the suspensions with disaggregated powders as a serious problem, especially in non-polar media, has been recognized fairly recently. It is complicated by the many interrelated factors, which influence its adequate solutions [13, 14]. The increase of the aggregates in storage compromises the inherent advantages of nanodiamond powders and seriously impairs their properties for different applications. Disaggregation methods and chemical

*To whom all correspondence should be sent.

E-mail: cholakov@uctm.edu

modifications for preserving the size and storage stability of the disaggregated powders in suspension have been suggested [5-14]. Typically, most surface groups are transformed into a particular type (e.g., $-\text{OH}$ or $-\text{COOH}$), which facilitates further chemical reactions – for instance, esterification [15]. More sophisticated modifications can produce hydrophobic, fluorinated, borated, etc. nanodiamonds [1, 3, 14–16].

However, the choice of a particular combination of methods should be application-oriented in terms of specific requirements for particle size and physical stability, possible interactions with other components in the final product, price-effect ratio, etc. Hereunder, we shall illustrate these specific requirements for the application of nanodiamonds in lubricants.

The interest in the lubricating properties of novel carbon materials stems from the present use of nanodiamonds for creating very efficient thin solid lubricating films on metal substrates, and to their potential “ball bearing effect” when introduced as suspensions in lubricants [5, 17–20]. The typical application in the former case is lubrication in vacuum (e.g., in space) and in the latter case more conventional and much less expensive products - lubricating oils, greases, etc. are targeted.

Numerous lubricating additives with nanodiamonds are being advertised on the market. Their positive effect on lubrication reported in different publications, can be characterized as significant [17–20] or very high [5, 21, 22], though at least in one paper [23] negative results for a nanodiamond additive in automotive oils are presented.

Nanodiamonds can be used in two types of conventional lubricating products: liquid (i.e., oils) and plastic (i.e., greases, pastes, etc.). Modern liquid lubricants are synergistic combinations of hydrocarbon and/or synthetic base oils, and additives which ensure adequate performance according to a preset specification. The chemical types of the used components depend on the particular application of the oils [24]. Moreover, different producers might employ chemically different additive compounds to achieve the lubricating, oxidation, rheological, etc. properties of their products [25].

Solid additives that can be solubilized in micelles of organic surfactants and form stable colloid solutions are incorporated into the respective lubricating oils in their production [26]. Micro- and nano-sized solid particles of metals,

MoS_2 , graphite, fluorine polymers, etc. [27] for liquid lubricants are offered as “Do It Yourself (DIY)” oil suspensions, which the consumer might add to commercial oils. Nanodiamonds fall in the same category and presently are commercialized as concentrated suspensions in oil [28, 29].

There is a need for systematic studies of engineering problems, concerning the whole field of application of nanodiamonds in non-polar media and pertaining not only to lubricants. These include specification of acceptable particle size and sedimentation stability, compatibility of stabilizers/modifications with other compounds in the same product (e. g, base oil and lubricant additives), influence of the powders not only on the targeted functional properties (e.g., lubrication), but also on other important properties of the final product (e. g., low temperature properties, oxidation stability), etc.

Previously, we developed a method for UV-VIS determination of the concentration of nanodiamond powders in non-polar media [28], and applied it for estimation of the sedimentation stability of suspensions of nanodiamonds with soot (NDS) and pure nanodiamonds (ND), stabilized with different surfactants [29].

The aim of this work is to study the effect of typical lubricant additives on the sedimentation stability of ND and NDS in non-polar media (liquid paraffin). The low temperature stability of lubricating oils with nano-diamonds is also evaluated.

2. EXPERIMENTAL

2.1. Nanodiamond powders and concentrated suspensions in liquid paraffin

We used two powder samples, produced in the Space Research Institute (SRI) of the Bulgarian Academy of Sciences – a blend of nanodiamond and soot, containing 40 % nanodiamond (denoted as NDS 40) and – pure nanodiamonds (denoted as ND). In SRI, after the detonation, soot from both powders had been removed by treatment with a boiled mixture of sulfuric acid and potassium bichromate, followed by moderate thermal oxidation with HNO_3 and washing with de-ionized water to pH 7. The water suspensions of the powders had been finally subjected to ultrasonic treatment.

The average particle size distribution of the used powders, obtained from SRI as water suspensions (Fig. 1), was determined by photometric sedimentation analysis with a Shimadzu Centrifugal Particle Size Analyzer, Type SA-CP-2.

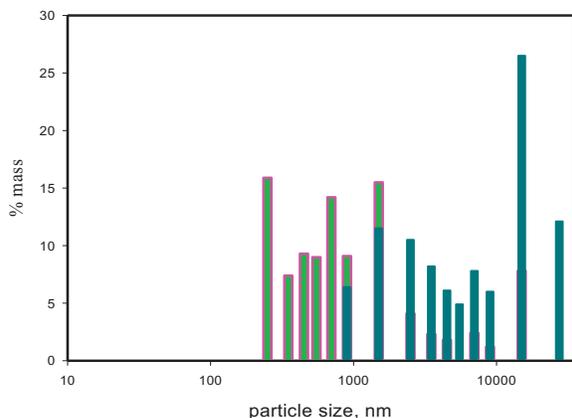


Fig. 1. Size distribution in the used nanodiamond samples: ■ - ND; ■ - NDS 40.

The NDS 40 sample has considerably larger aggregates than the ND sample, some of which are more than 10 microns in size. Both samples are comparable to the typical commercial industrial nanodiamonds, analyzed by Osawa [12], with dynamic light scattering. More information about the used powders can be found in publications by our colleagues from SRI [30–32].

Evidently, the aggregates in both samples used could be crushed and chemically modified by sophisticated techniques. However, for our studies on implementation of nanodiamonds in conventional automotive oils, it was important to start our work with the sizes, typical for commercial powders, available at a reasonable price.

The suspensions in liquid paraffin (kinematic viscosity at 40 °C = 32.82 mm² s⁻¹; density at 20 °C = 842.5 kg m⁻³; its GC analysis is given in [28]), were prepared either from the dry powders, or from their water suspensions. When the model suspensions were prepared from dry powders, firstly a paste containing approx. 20 % powder was obtained by homogenizing weighed amounts of powder and liquid paraffin with a laboratory homogenizer with shearing blades for 10 sec at rotation speed of 10 000 rpm. For mechanochemical disintegration, the respective stabilizer was included in the paste, which was then disintegrated in six subsequent 10 sec. runs for a total of one minute. The applied technology for the particular pastes is noted in the respective Tables. The concentration of the powder in all pastes was determined in parallel by the UV-VIS method, and gravimetrically, after centrifugation of the suspensions in hexane. In the latter case, the hexane was removed from the separated oil phase in a

rotary vacuum evaporator, and from the powder – in a vacuum drying oven.

The powder suspensions in paraffin were prepared by weighing calculated amounts of the respective paste, stabilizer(s) and liquid paraffin in laboratory flasks, followed by mixing with a conventional laboratory stirrer for 30 min at 60 °C, conventional laboratory ultrasonic treatment, and again mechanical stirring under the described conditions. The preparation of oil suspensions from water suspensions of the powders is described later in the text.

2.2. Stabilizers and lubricating oils

Nanodiamond powders might be stabilized with different surface-active substances [33]. However, it is an advantage if the stabilizers are compounds involved in the potential application of the powders. Therefore, in continuation of our previous studies [29], in the present work we have tested the combinations of the additives and packages, typical for gear and automotive oils, shown in Table 1. The influence of the powder suspensions on the pour point temperatures was studied in three typical petroleum oils. The first one was SAE 90 base oil (SAE is the US Society of Automotive Engineers), used as received by the manufacturer – the “Prista Oil” Company, Bulgaria. The second oil was prepared in our laboratory by dissolving a required amount of the auto gear oil package 1 in the base oil at concentration, recommended by the package producer for SAE 90 API GL 5 automotive gear oil (API is the American Petroleum Institute). The third oil was a commercial sample of SAE 15W/40 API SJ/CF engine oil, bought from a gasoline station. It is mineral oil based and widely used in gasoline and diesel engines on the road in many countries.

2.3. Methods of analysis

The method for the estimation of the concentration of NDS 40 and ND in oil concentrates with UV–VIS has been described in detail in [29]. The sedimentation stability [28] was studied by determination with UV–VIS of the concentration of the powder in the upper 0.5 cm layer of the paraffin concentrates, stored in closed laboratory test tubes. The tubes were kept at room temperature in the laboratory. Samples for the sedimentation stability studies were taken after 0, 20, 75 and 90 days of storage, thus characterizing, respectively, initial, short, medium and long-term stability in their potential application. Additionally, recovery of the stability of the concentrate after

long-term storage was tested after 1 min stabilization of the 75 or 90 days samples with a

Table 1. Description of the lubricant additives and packages tested as stabilizers.

Stabilizers	Description by the supplier ^a
Gear oil package 1	Additive package for automotive gear oils, containing S, P, N
Gear oil package 2	Additive package for automotive gear oils, containing S, P, N
Motor oil DD package 1	Overbased Ca detergent + N-containing dispersant
Motor oil DD package 2	Detergent and dispersant (DD) additive package
Finished motor oil package 1	Motor oil additive package, containing S, P, N, B, Zn, Mg
Finished motor oil package 2	Motor oil additive package, containing S, P, N, Zn, Ca, Mg
Motor oil additive 1	Thermostable polyalkenyl succinimide dispersant
Motor oil additive 2	Overbased Ca alkylaryl sulphonate
Motor oil additive 3	Neutral Ca alkylaryl sulphonate

^a) The single capital letters are the symbols of the respective chemical elements.

conventional laboratory tube-shaking machine. Thus, it is also application-oriented, though in DYI applications vigorous shaking of the pack, often containing a ball, is used. The FT-IR spectra of all liquid samples were recorded with a “FT-IR Equinox” spectrophotometer (“Bruker Corporation”) in thin film, and those of the powders – in the standard thin tablets, prepared with KBr.

The amount of calcium in the additives and the oils was determined by inductively coupled plasma atomic emission spectrometry (ICP AES), following the ASTM D 4951 method on a “Varian Vista MPX”, with a detector with CCD matrix. Sulphur was determined by the ASTM D 4951 method and checked with Wavelength-Dispersive X-Ray Fluorescence Spectroscopy (ASTM D 4927 method). The reason for determination of sulphur by two methods was that its concentration turned out to be somewhat higher than that given by additive manufacturers. Both methods confirmed the sulfur concentrations presented in the respective Table.

The pour point temperatures were determined according to the ASTM D 97 method.

3. RESULTS AND DISCUSSION

3.1. Stability in liquid paraffin of NDS 40 suspensions, stabilized with lubricant additive packages and additives

Our previous work with individual additives and additive packages [28] implied that succinimide dispersants and alkylarilsulphonate detergents are promising stabilizers for concentrated suspensions that can be used in lubricants. More importantly, it demonstrated that engine oil additive packages, which contain such additives, have also a stabilizing effect. The tested gear oil packages and additives could not stabilize the suspensions. Inorganic alkalinity, solubilized in the overbased sulphonates showed a negative effect as compared

to the neutral sulphonates tested. For polymeric dispersants the presence of an imide group improved stability. Table 2 summarizes the most important results for suspensions, containing 3 % NDS 40. The stability at 15 min after preparation is given as an indication of the easiness of initial dispersion. The Table includes also a binary combination of the better stabilizers, which within experimental error [28], does not show synergistic action of additives 1 and 3.

In general, the amount of stabilized powder after short-term and medium-term storage in all samples is low, but the recovery after 75 days for some of them is satisfactory.

The above observations determined our further experiments, namely we studied systematically the short-term stability of gear oil package 1 with combinations of three engine oil additives. In engine oils these additives are expected to adsorb on soot and prevent its flocculation. It was important to establish if there might be antagonism between the gear oil package and the engine oil additive stabilizers, which might compromise their effect. The amount of NDS 40 was decreased, in order to estimate the effect of lower powder concentrations. Fig. 2 shows the obtained results. With the lower powder concentration the short-term stability is improved. For all samples the stabilizing effect decreases with decreasing the amount of the stabilizer. However, the polyalkenyl succinimide additive 1 shows some positive effect (i.e. higher stability than the proportional to its concentration), while the other two additives have a negative effect. Thus, this additive is more appropriate for stabilizing NDS 40 in gear oils. This is important because additives without metal are preferred in these oils.

3.2. Stability of NDS 40 paraffin suspensions, prepared with binary additives and mechanochemical disintegration.

Our next experiments were targeted on tested systematically combinations of the two best improving medium and long-term stability. We

Table 2. Stability of paraffin suspensions of 3 % NDS 40^a.

No	Stabilizers ^b	Stability, % of initial			
		15 min	20 days	75 days	Recovery, 75 days
1	Auto gear oil package 1	47.54	0.0	-	-
2	Auto gear oil Package 2	44.53	3.1	-	-
3	Engine oil DD ^b package 1	99.02	54.0	11.9	37.2
4	Engine oil DD Package 2	95.49	42.8	20.5	61.8
5	Finished engine oil package 1	76.26	54.6	7.2	81.7
6	Finished engine oil package 2	90.59	56.7	12.9	74.0
7	Engine oil additive 1	89.92	17.6	9.1	65.1
8	Engine oil additive 2	85.62	37.0	11.1	34.1
9	Engine oil additive 3	97.22	61.5	19.2	84.0
10	0.50 Add. 1 + 0.50 Add. 3	93.94	36.9	24.3	54.4

^a) From dry powder, without mechano-chemical disintegration.

^b) “DD” stands for “Dispersant and Detergent” – i.e. packages of dispersant and detergent additives for engine oils that can be bought separately.

Table 3. Stability of 3 % NDS 40 suspensions from paste, with additives 1 and 3^a

Sample	Stabilizers (mixtures in mass ratios)	Sedimentation stability, % of initial			
		20 days	75 days	90 days	Recovery, 90 days
25	Motor oil additive 1	71.46	58.51	57.07	72.98
26	0.75 Add. 1 + 0.25 Add. 3	77.57	62.33	60.94	75.43
27	0.50 Add. 1 + 0.50 Add. 3	59.50	45.61	40.72	60.87
28	0.25 Add. 1 + 0.75 Add. 3	66.01	-	51.72	67.73
29	Motor oil additive 3	62.59	63.34	59.80	67.32

^a) From dry powder, with mechano-chemical disintegration.

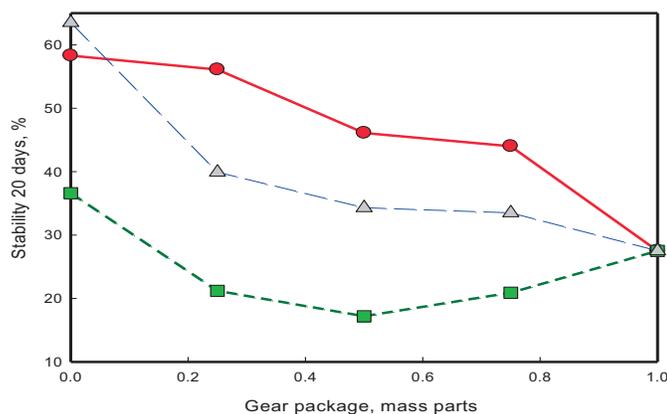


Fig. 2. Stability of paraffin suspensions of 2 % NDS 40 with mixtures of gear oil package 1 and engine oil additives: (●)-additive 1; (■)-additive 2; (▲)- additive 3.

stabilizers, including them in the pastes and increasing the disintegration time with the view to achieve mechano-chemical crushing of some aggregates. Table 3 presents the obtained results.

It shows that more than half of the powder stays suspended even after 90 days of storage. The recovered stability is somewhat lower than the best results achieved previously. The observed synergism for sample 26 and antagonism for

sample 27 needs further studies, although the respective result in Table 1 provides some relevant evidence for the latter sample. However, we decided not to perform such studies at this stage because of the modeling approach of this work, done in paraffin. In a DIY product the used oil for the suspensions would be of higher viscosity and the recovery more effective, thus minimizing the practical importance of the observed effects.

Our next task was to study the effect of the applied mechano-chemical disintegration of NDS 40. For this purpose, the oils and the powders from the pastes with individual additives had been separated by centrifugation and the respective FT-IR spectra had been recorded. Fig. 3 shows the FT-IR spectra of additive 1, the oil (liquid paraffin) and the powder, obtained by centrifugation of the paste from which the suspension with additive 1 had been prepared.

The spectrum of additive 1 (Fig. 3, up) among the peaks of hydrocarbon groups, shows two peaks characteristic for succinimides: vibrations of -NH- groups (a wide peak at 3448.7 cm^{-1}) and vibrations of >C=O groups (a sharp peak at 1704.9 cm^{-1}). In the oil spectrum (Fig. 3, up) the first peak disappears, and the second one (at 1705.7 cm^{-1}) has a much lower intensity.

In the spectra of the crushed NDS 40 powder (Fig. 3, down) the -NH- peak is identified at 3442.5 cm^{-1} , and the peak of the >C=O groups is at 1697.5 cm^{-1} . These peaks are not present in the spectra of the liquid paraffin or the NDS 40 powder used to prepare the suspension (Fig. 3, down). Thus, the FT-IR spectra on Fig. 3 confirm the assumption that additive 1 has been adsorbed on the powder during the preparation of the paste.

Table 4. Active elements in Additive 3, its paste with NDS 40^a, and the oil from the paste after centrifugation.

Samples	Concentration, %	
	Sulphur	Calcium
Additive 3	5.16	2.78
Oil portion of paste	1.04	0.55
Oil, obtained from the paste by centrifugation	0.23	0.17
Calc. reduction in separated oil as compared to oil in paste, %	77.9	69.1

^a) From dry powder, with mechano-chemical disintegration.

The adsorption of the alkylaryl sulphonate additive 3 is supported by FT-IR spectra (peak of S=O vibrations for the additive at 1212.4 cm^{-1}). However, the spectra are not presented here, because the adsorption of additive 3 is confirmed more profoundly by the data presented in Table 4. According to these data a significant portion of additive 3 is not present in the oil, obtained after centrifugation, and presumably has been adsorbed on the surface of the powder. The effect of the mechano-chemical dis-integration of NDS 40 in the presence additive 1 on the powder size distribution is presented in Fig. 5.

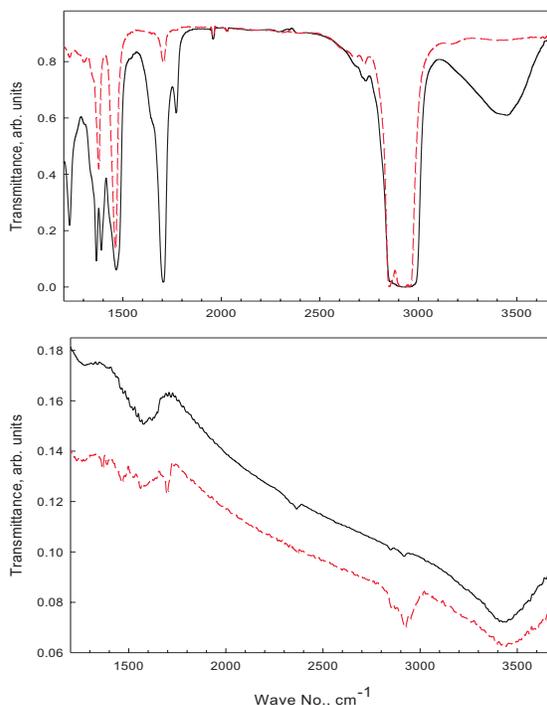


Fig. 3. FT-IR spectra indicating adsorption of the polyalkenyl succinimide additive 1 on the NDS 40 powder. Up: Straight line - Additive 1 (thin film); Dashed line - oil, separated from the paste, containing additive 1 (thin film). Down: Straight line - NDS 40 powder (tablet); Dashed line - NDS 40 powder, separated from the paste (tablet).

3.3. Sedimentation stability of liquid paraffin suspensions with pure nanodiamonds.

Table 5 presents the results for the sedimentation stability of the paraffin suspensions of pure nanodiamond powder (ND), prepared with additives 1 and 3.

The pastes for the first two samples were obtained from dry powders, without mechano-chemical stabilization. As expected, the results were not satisfactory. The next two samples were prepared with mechano-chemical disintegration, as those with NDS. A certain improvement was achieved, but the effect was lower than for the NDS samples. The last two samples were prepared from water suspensions of the ND powder, into which portions of paraffin and additive were added, and the water was evaporated. The rest of the paraffin and additive needed to prepare pastes with approx. 20 % powder were then added, and the pastes were mechano-chemically disintegrated. The developed

Table 5. Sedimentation stability of paraffin suspensions with nanodiamond powder (ND).

Sample	Technology	Sedimentation stability, %			
		20 days	75 days	90 days	Recovery
30	Dry powder, paste with Add. 1	23.80	-	16.00	30.00
31	Dry powder, paste with Add. 3	39.12	-	28.20	56.90
32 ^a	Dry powder, paste with Add. 1	54.75	37.83	28.70	70.43
33 ^a	Dry powder, paste with Add. 3	44.60	37.27	31.81	86.70
34 ^a	Water suspension and paste, add. 1	68.20	44.60	46.50	79.10
35 ^a	Water suspension and paste, add. 3	82.60	70.50	65.20	84.70

^a With mechano-chemical disintegration.

Table 6. Active elements in Additive 3, its paste with ND^a, and the oil from the paste after centrifugation

Samples	Concentration, %	
	Sulphur	Calcium
Additive 3	5.16	2.78
Oil portion of paste	2.58	1.39
Oil, obtained from the paste by centrifugation	1.51	0.58
Calc. reduction in separated oil, as compared to oil in paste, %	58.53	41.73

^a From water suspension, with mechano-chemical disintegration.

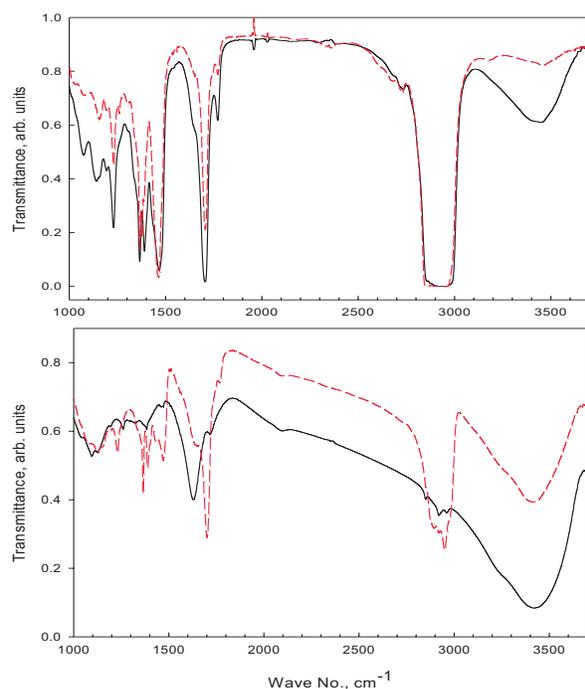


Fig. 4. FT-IR spectra indicating adsorption of polyalkenyl succinimide additive 1 on pure nanodiamond. Up: FT-IR spectra (thin films) of additive 1 - straight line and the oil, separated from the nanodiamond paste containing it - dashed line. Down: FT-IR spectra (tablets) of the used nanodiamond - straight line and the nanodiamond, separated from the paste containing additive 1 - dashed line.

preliminary treatment of the water suspensions brought up the stability of the ND suspensions to the levels achieved with the NDS powder.

Fig. 4 shows the FT-IR spectra of the polyalkenyl succinimide additive 1, the oil (liquid

paraffin) and the powder, obtained by centrifugation of the paste from which the suspension with additive 1 had been prepared.

The two characteristic peaks of additive 1: vibrations of $-NH-$ groups (a wide peak at 3448.7 cm^{-1}) and vibrations of $>C=O$ groups (a sharp peak at 1704.9 cm^{-1}) are clearly seen on Fig. 4 (up). Their intensity in the oil centrifuged from the paste is lower, though not so profound as in Fig. 3. Fig. 4 (down) also shows the appearance of the characteristic additive peaks, though the wide peak at $3100 - 3600\text{ cm}^{-1}$ might include $-OH$, $-NH_2$ and $>NH$ groups present on the original nanodiamond powder surface, as well. In general the spectra with nanodiamonds are more complex than with the NDS 40 blend. They suggest more complex interactions between the additive and the functional groups on the nanodiamond surface.

Table 6 presents the content of the active elements in the alkylaryl sulphonate additive 3, its nanodiamond paste, and the oil from the paste after centrifugation. Again a considerable amount of the additive is not present in the oil, centrifuged from the paste, and has remained on the nanodiamond powder surface.

Fig. 5 presents the effect of the mechano-chemical disintegration in the presence of additive 1 on the size distribution of both the NDS and ND powders. The analysis was performed on samples taken from the respective freshly prepared paraffin suspensions. The comparison with Fig. 1 clearly shows that the larger aggregates have been crushed, with effect similar to ball milling [33].

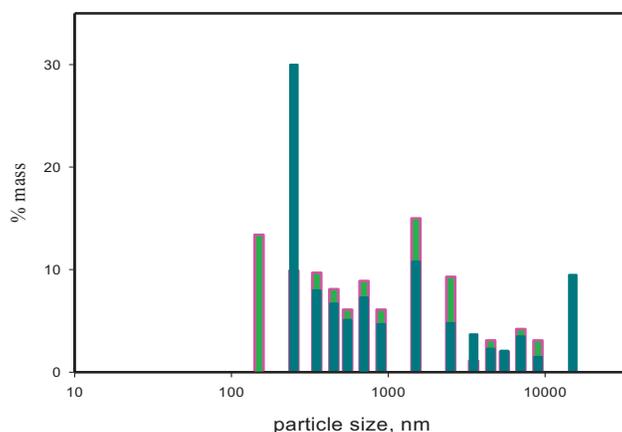


Fig. 5. Size distribution of the mechano-chemically disintegrated nanodiamond samples: ■ - ND in the presence of additive 1; ■ - NDS 40 in the presence of additive 1.

Table 7. Pour temperatures of lubricating oils with NDS 40 and ND.

Sample	Pour point, °C
Base gear oil (specification) +	(less than -18)
no additive	-19
5% liquid paraffin	-19
5 % concentrate of NDS 40 with Additive 1	-19
5 % concentrate of NDS 40 with Additive 3	-19
5 % concentrate of ND with Additive 1	-19
5 % concentrate of ND with Additive 3	-18
Automotive gear oil SAE 90 API GL 5 (specification) +	(less than -18)
no additive	-20
5% liquid parafin	-19
5 % concentrate of NDS 40 with Additive 1	-19
5 % concentrate of NDS 40 with Additive 3	-16
5 % concentrate of ND with Additive 1	-17
5 % concentrate of ND with Additive 3	-17
Motor oil 15W/40 API SJ/CD (specification) +	(less than -27)
no additive	less than -32
5% liquid paraffin	less than -30
5 % concentrate of NDS 40 with Additive 1	less than -30
5 % concentrate of NDS 40 with Additive 3	less than -30
5 % concentrate of ND with Additive 1	less than -30
5 % concentrate of ND with Additive 3	less than -30

3.4. Low temperature stability of lubricating oils with NDS and ND

As shown in the introduction, the effect of nanodiamonds on lubricating properties has been widely studied. However, the requirement that they should not impair the rest of the important properties of the original lubricant – oxidation stability, low temperature and anticorrosion properties, demulsibility, etc. seems to be neglected. Chou and Lee [19] recently showed that addition of nanodiamond particles, depending on their size and the additives in the lubricant, might increase the viscosity of lubricating oils. Hereunder, we present results on the influence of nanodiamond concentrates on the low temperature stability of three oils, accessed by their pour point

temperatures (Table 7). The pour point temperature is indicative of depletion at low temperatures of high molecular mass *n*-alkanes from the oil. Experimental data of the influence of the powders on this phenomenon is needed, because the particles might become centers for the crystallization of the alkanes.

The results in Table 7 show that, within the error of the analysis, the concentrates slightly influence the pour point temperatures of the oils. This is very important, especially for multi-grade fuel economy engine oils, which have to pass more sophisticated tests related to low temperature properties [24, 25]. In any case, our results show that the pour point temperature should always be tested when developing nanodiamond suspensions for different

oils, because particular combinations of powder stabilizers and lubricant additive packages might impair the low temperature properties of the doped oil.

CONCLUSIONS

The sedimentation stability of the studied nanodiamonds (ND) and their blends with soot (NDS) in paraffin was estimated after 20, 75 and 90 days of storage. Recoverability of the initial stability by mild homogenization was also tested. Typical additives for automotive gear and engine oils, their packages and binary combinations were evaluated as stabilizers. The obtained results show:

- Dispersant and detergent additives for engine oils and their packages are effective stabilizers. Succinimides and neutral sulphonates showed best results.

- The ND sample was more difficult to stabilize than its 40 % blend with soot (NDS 40), which can be explained with the fact that these additives are designed to disperse soot and coke particles.

- Mechano-chemical disaggregation with a laboratory homogenizer with razor blades was also evaluated. Both tested additives adsorbed on the surfaces of NDS 40 and ND, and some of the larger aggregates were crushed.

- With the selected stabilizers and mechano-chemical disaggregation more than 50 % of the NDS stayed in the upper layer of the paraffin concentrate after 90 days of storage, with recovery of around 70 % of the initial stability with mild homogenization. Higher stability is expected when more viscous hydrocarbon oils are used for the concentrates.

- The mechano-chemical disaggregation was not so effective for ND. Similar to the NDS results were achieved, when it was combined with evaporation of the water in the presence of the stabilizer and the paraffin.

- The NDS and ND powders slightly influence the low temperature stability of tested lubricating oils, but their effect should always be checked.

Acknowledgement: *The authors acknowledge with gratitude that the present work was supported by a grant from the Bulgarian National Science Fund under the provisions of Project No. NT 3-03/2004.*

REFERENCES

1. B. I. Kharissov, O.V. Kharissova and L. Chávez-Guerrero. Synthesis Techniques, Properties, and Applications of Nanodiamonds, *Synth React Inorg M*, **40**, 2, 84 (2010).
2. V. Yu. Dolmatov, M. V. Veretennikova, V. A. Marchukov, and V. G. Sushchev. Currently Available Methods of Industrial Nanodiamond Synthesis. *Phys. Solid State*, **46**, 4, 611 (2004).
3. S. Osswald, G. Yushin, V. Mochalin, S. O. Kucheyev, and Yu. Gogotsi. Control of sp²/sp³ Carbon Ratio and Surface Chemistry of Nanodiamond Powders by Selective Oxidation in Air. *J. Am. Chem. Soc.* **128**, 11635 (2006).
4. P. A. Vityaz. The State of the Art and Prospects of Detonation-Synthesis Nanodiamond Applications in Belarus. *Phys. Solid State*, **46**, 4, 606 (2004).
5. V. E. Red'kin. Lubricants with Ultradisperse Diamond-Graphite Powder. *Chem. Technol. Fuels Oils*, **40**, 3, 164 (2004).
6. *Ultrananocrystalline Diamond Synthesis, Properties, and Applications*. Eds. O. A. Shenderova, D. M. Gruen, William Andrew Publishing, New York, U.S.A, 2006.
7. O. Auciello, A. V. Sumant. Status review of the science and technology of ultrananocrystalline diamond (UNCD™) films and application to multifunctional devices. *Diamond Relat. Mater.*, **19**, 699 (2010).
8. A. M. Schrand, S. A. Hens, A. C. Suzanne and O. A. Shenderova. Nanodiamond Particles: Properties and Perspectives for Bioapplications, *Crit. Rev. Solid State Mater. Sci*, **34**, 1, 18 (2009).
9. V. V. Danilenko. Nanodiamonds: Problems and Prospects. *J. Superhard Mat.*, **32**, 5, 301 (2010).
10. A. Vul. Detonation nanodiamonds. New Challenges and Applications. 2nd International forum on nanotechnologies, *Rusnanotech 09*, 6-8 october 2009, Moscow.
11. A. S. Barnard. Self-assembly in nanodiamond agglutinates. *J. Mater. Chem.*, **18**, 4038 (2008).
12. E. Osawa. Monodisperse single nanodiamond particulates. *Pure Appl. Chem.*, **80**, 7, 1365 (2008).
13. M. V. Korobov, M. M. Batuk, N. V. Avramenko, N. I. Ivanova, N. N. Rozhkova and E. Osawa. Aggregate structure of "single-nano buckydiamond" in gel and dried powder by differential scanning calorimetry and nitrogen adsorption. *Diamond Relat. Mater.*, **19**, 665 (2010).
14. V. N. Mochalin and Yu. Gogotsi. Wet Chemistry Route to Hydrophobic Blue Fluorescent Nanodiamond. *J. Am. Chem. Soc.*, **131**, 4594 (2009).
15. A. Krueger, Th. Boedeker. Deagglomeration and functionalisation of detonation nanodiamond with long alkyl chains. *Diamond Relat. Mater.*, **17**, 1367 (2008).
16. W.-W. Zheng, Yi-H. Hsieh, Yu-Ch. Chiu, S.-Jhu Cai, Ch.-L. Cheng and Ch. Chen. Organic functionalization of ultradispersed nanodiamond: synthesis and applications. *J. Mater. Chem.*, **19**, 8432 (2009).
17. M. Amaral, C.S. Abreu, A.J.S. Fernandes, F.J. Oliveira, J.R. Gomes, R.F. Silva. Nanodiamond-based tribosystems. *Surf Coat Tech*, **204**, 1962 (2010).

18. C.A. Charitidis. Nanomechanical and nanotribological properties of carbon-based thin films: A review. *Int J Refract Met H*, **28**, 51 (2010).
19. C.-C. Chou, S.-H. Lee, Tribological behavior of nanodiamond-dispersed lubricants on carbon steels and aluminum alloy, *Wear*, **269**, 11–12, 757 (2010).
20. D. X. Peng, Y. Kang, R. M. Hwang, S.S. Shyr, Y.P. Chang. Tribological properties of diamond and SiO₂ nanoparticles added in parafin. *Trib. Int.*, **42**, 911 (2009).
21. V. Yu. Dolmatov. Detonation Nanodiamonds in Oils and Lubricants. *J. Superhard Mat.*, **32**, 1, 14 (2010).
22. M. G. Ivanov, S. V. Pavlyshko, D. M. Ivanov, I. Petrov, O. Shenderova. Synergistic Compositions of Colloidal Nanodiamond as Lubricant Additive, *J. Vac. Sci. Technol.* **B 28**, 4, 869 (2010).
23. Y.Y. Wu, W.C. Tsui, T.C. Liu. Experimental analysis of tribological properties of lubricating oils with nanoparticle additives. *Wear*, **262**, 819 (2007).
24. *Lubricant additives: chemistry and applications*. Ed. L. Rudnick, 2nd ed., CRC Press, Taylor & Francis, Boca Raton – London - New York, 2009.
25. *Chemistry and Technology of Lubricants*. Eds. R. M. Mortier, M. F. Fox, S. T. Orszulik, 3rd ed., Springer, Dordrecht - Heidelberg - London - New York, 2010.
26. J. Galsworthy, St. Hammond and D. Hone. Oil-soluble colloidal additives. *Curr Opin Colloid In*, **5**, 274 (2000).
27. *Nanolubricants*. Eds. J. M. Martin, N. Ohmae, John Wiley & Sons, Ltd, 2008.
28. G. St. Cholakov, N. Georgiev, Chr. Ivanova, K. G. Stanulov. Stability of Ultradisperse Diamond Powders in Oil Suspensions. *Journ. Univ. Chem. Techn. Met.*, **40**, 4, 299 (2005).
29. G. St. Cholakov, N. Georgiev, Chr. Ivanova, K. G. Stanulov. An Express Method for Estimation of the Concentration of Ultradisperse Diamond Powder in Oil. *Journ. Univ. Chem. Techn. Met.* **40** (2005), 4, 291 - 298.
30. D. Mitev, R. Dimitrova, M. Spassova, Ch. Minchev, S. Stavrev. Surface peculiarities of detonation nanodiamonds in dependence of fabrication and purification methods. *Diamond Relat. Mater.*, **16**, 776 (2007).
31. T. Tsoncheva, V. Mavrodinova, L. Ivanova, M. Dimitrov, S. Stavrev, Ch. Minchev, *J. Mol. Catal. A: Chem.* **259**, 223 (2006).
32. V. Mavrodinova, M. Popova, I. Kolev, S. Stavrev, Ch. Minchev. Effect of the preparation conditions of Ni-supported shock-wave synthesized nanodiamond catalysts. FT-IR and catalytic considerations. *Appl. Surf. Sci.* **253**, 7115 (2007).
33. Y. Zhu, X. Xu, B. Wang, Zh. Feng. Surface modification and dispersion of nanodiamond in clean oil. *China Part*, **2**, 3, 132 (2004).

ФИЗИЧЕСКА СТАБИЛНОСТ НА ДЕТОНАЦИОННИ НАНОДИАМАНТИ В ТЕЧНИ СМАЗОЧНИ МАТЕРИАЛИ

Г. Ст. Чолаков*, В. Б. Тотева, Ст. Д. Янев, Ст. Г. Стайков, К. Г. Станулов

Катедра „Органичен синтез и горива”, Химикотехнологичен и металургичен университет, бул. “Климент Охридски”, София 1756, България

Постъпила на 10 януари, 2011 г.; коригирана на 21 април, 2011 г.

(Резюме)

Агрегирането на детонационните нанодиаменти спъва по-широкото им използване и изисква изследвания, ориентирани към конкретното приложение, и стабилизатори, които да не взаимодействат негативно с останалите компоненти на продукта.

Основната цел на работата беше да изследва ефекта на типични присадки за смазочни материали върху седиментационната стабилност на нанодиаментни прахове в неполярна среда (течен парафин). Оценена беше експериментално и нискотемпературната стабилност на смазочни масла с нанодиаменти.

Използваните прахове (нанодиаменти, ND и нанодиаменти с 40 % сажди, NDS 40) бяха с размери, типични за продаваните индустриални нанодиаменти. Представени са експериментални резултати, че те съдържат значително количество агрегати с по-големи от нано размери.

При използване на лабораторно механо-химическо дезинтегриране, в присъствие на експериментално подобраните най-добри присадки, над 50 % от NDS 40 остават в най-горния слой на парафиновия концентрат след 90-дневно съхранение, а около 70 % от праха се суспендират отново след умерено хомогенизиране.

Механо-химичното дезинтегриране не беше толкова ефективно при ND. Подобна стабилност беше постигната, когато то беше комбинирано с технология за приготвяне на концентрата чрез изпаряване на водата от водна суспензия в присъствие на стабилизатора и известно количество парафин.

Праховете NDS 40 и ND слабо влияят върху нискотемпературната стабилност на изпитаните смазочни масла, но техният ефект трябва винаги да се проверява.