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TRIBOTECHNICAL CHARACTERISTICS OF CARBON-BEARING LUBRICANTS

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Abstract: The development of technology for manufacturing nanostructured substances in amounts that could suffice an interlaboratory research is a high priority task for the implementation of nanoproducts. The ultra dispersiblis clusters of synthetic carbon are used as on extra component in polymeric materials. The substances have a high dispersibility and activity of the surface. To study properties of mineral oils, modified ultra dispersiblis clusters of synthetic carbon is of interest. The present activity is devoted to the research of the modifying influence of ultra dispersiblis clusters of synthetic carbon on viscosity of the characteristic of mineral oils and their stability at various temperatures. In the preparation of diamond secondary suspensions not only statistic average sizes of particles should be taken into consideration, but also polydispersity parameters of nanodiamond particle population too.

Keywords: nanodiamond, sedimentation resistance, oil, properties.

1. INTRODUCTION

In a few dispersiblis nanodiamonds (DND) applications these are supposed to be employed as suspended in liquid low-molecular media. That is why the proposed technology provides the preparation of DND aqueous suspension as a final commodity product. On the other hand, some practices require a prior treatment of DND surface (e.g. in polymeric material science [1-3]). DND dry powders are more useful in such instances. It should be taken into account that economical expediency and sometimes process needs provide for DND dry powder manufacture for the customer followed by the preparation of DND suspension on site. So, the study on process of DND reversible recovery from commodity suspensions currently gains much importance in practice. It should be noted that so called technical diamond containing nanocarbon (TDCN) results from detonation synthesis and is composed of both crystal and amorphous nanocarbons. DND as itself is recovered from TDCN through a quite complex sequence of operations [2]. The sequence consists of at least stages of cleaning, drying, grinding and screening of fine fraction. The dispersity of the initial DND fraction obviously can not persist, the finished one being a set of DND aggregates ranging from nanometers to microns. Suspensions made of dry DND powder should not be inferior by their colloidal behavior to commodity ones. The target of the present research work was the preparation of DND secondary suspensions, as well as the study on factors influencing their sedimentation resistance.

2. EXPERIMENTAL

Dynamic light scattering was used for studying DND suspensions, "Coulter N4" (Coultronics, France), like other similar instruments on the principle of correlometer was employed to measure autocorrelation function of photomultiplier current induced by light scattered by suspended nanoparticles. To obtain DND aggregates mass part distribution by hydrodynamic sizes a before described method [4, 5] was used for the processing of autocorrelation functions measured. Due to the software available we could process up to 106 particles. The method also enables obtaining diffusion

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coefficients as well as hydrodynamic sizes of dispersiblis particles and associates in the suspension. Thus, the method of light scattering makes it possible to study parameters of number-average and mass-average distribution in structures not disturbed by external factors. This gives the clue to yield more reliable and complete data on dispersiblis systems than conventional techniques do (e.g. electronic microscopy). Nanodiamonds came from stock company "Almazny Zentr" (St.–Petersburg) and used with no pre-treatment. Suspensions were prepared by adding a calculated quantity of DND to distilled water with stirring over 30 min (magnetic stirrer). To study time of insonification for nanodiamond dispersity replicate portions of suspension were prepared to suit a number of time intervals. As ultrasound generator we used ultrasound bath Bramsonic 220 (50 W), the treatment was conducted in both correlometer cell and a separate vessel, time fixed by stopwatch. As base components for manufacturing lubricating materials the oils motor 15W40, transformer and industrial I–20A oils are used. The compositions are obtained by mechanical mixing of initial oils and modifier. As the modifier of the studied oils ultra dispersiblis clusters of synthetic carbon were used. The clusters are received by explosion technology. The dispersibility of a blend is made 200–300 nm, with a specific surface 350 m^2/g. The contents of ultra dispersiblis clusters of synthetic carbon in oil was 0.01–1.5%. The viscosity and temperature characteristics of modified oils were evaluated with the help of the viscosimeter VPG–2. The research of viscosity and temperature properties were conducted at the temperature of from 293 up to 363 K. To in the conditions of liquid-propellant thermostatic control. The influence of a blend on thermal stability of oils was evaluated by the results of the differential – thermal analysis (DTA). Oxidation-reduction processes in modified oils were evaluated with the method of IR-spectroscopy of passing. The experiments were conducted on the device Tensor–27.

3. RESULTS AND DISCUSSION

A typical picture of number average distribution of DND particles in commodity suspensions is shown in Fig. 1. As it evidences, the used technology for DND recovery results in a population of clasters with asymmetric monomodal distribution of aggregates by size, shifted toward the region of large-sized particles. In other words, the population of DND claster aggregates features a continuous set of particles present in the range from 1 nm up to micron sizes.

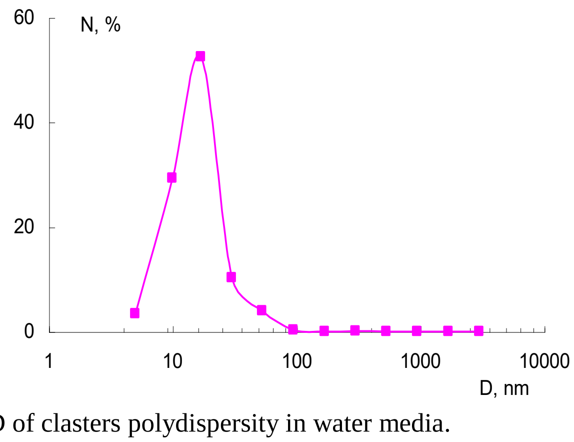


Figure 1. Typical curve of DND of clasters polydispersity in water media.

In view of classical concepts in quantum mechanics, the physics of condensed state and crystal physics analyzed the structure features, habitus and energy state of dispersed particles obtained by mechanical dispersion of semi-finished and condensation of atomic or molecular components. Based on different methodological approaches subject to Einstein's equations, the criterion of the Debye temperature, the uncertainty principle, Schrodinger equation, etc. is suggested an analytical expression for determining the dimensional boundary L_0 of particle transition of the condensed medium from macro- to nanostate which is characterized by specific parameters of thermal physical and energy performance: $L_0 = 230^{-1/2}\theta_D$,where the θ_D - Debye temperature [6]. This expression allows realizing estimates of various parameters of nanoparticles of various substances and chemical compounds and justifying technological modes of production and application. Analysis of the characteristics of the process of obtaining nanosized particles using the theory of point groups and closest packing enable to establish the most probable habitus due to crystal-chemical prehistory. It is implemented physical justification of activity of nanoscale particles of different habitus caused by crystal-chemical structure of semi-finished product and the type of crystal lattice [7]. It is established the effect of the existence of uncompensated charge at the nanosized particles of different structure which promotes the formation of ordered quasi-crystalline structures in boundary layers and improves the performance of deformation-strength, tribological and protective properties of technical products of the functional polymer nanocomposites.

As a rule, the number of large – sized particles (over 200 nm) is insignificant – under 0.5%. Nevertheless, they can much contribute to DND mass. The sedimentation resistance of the said particles is low and they are first to settle out of the suspension markedly differs from a calculated one.

Let us look into a possible increase in nanoparticle share through generally recommended US field application. As a first approximation we chose a suspension concentration that would provide practically complete separation of DND aggregates in the dispersion medium (0.002% mass).

The data on number average diameter of DND aggregates (D_{mean}) against insonification time are shown in Fig. 2. The humped curve passes through the local minima at 4.7 and 20 minutes of insonification at min value of D_{mean} equal to 22.6 nm.

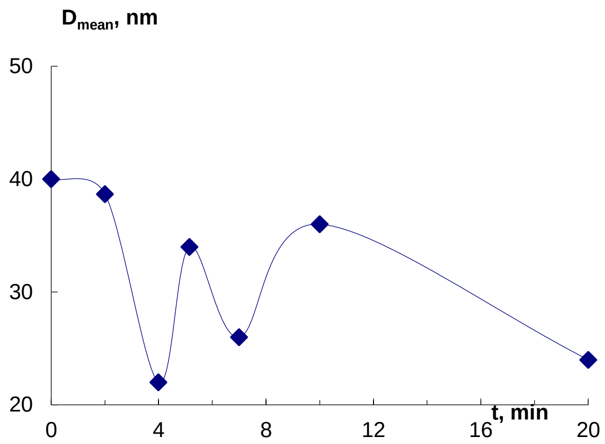


Figure 2. Time insonification influence on $R_{mean}$of DND (C = 0.002 mass. %).

Let us follow the effect of DND concentration on the structure of suspension (relationships between nanoparticle relative part (N %) and mass part (M %)). From before experiments we choose 20 mins as a basic time of insonification. In addition, we narrow the nanoparticle range under examination to under 200 nm in B – the most useful in practice.

The tabulated data (Table 1, regime 1) evidence that practically all of DND aggregates are within the range of nanosizes, N percentage being close to 100 and hardly varied over the range. Their mass part, however, does not exceed 5%. Thus, the vast majority by mass of DND particles are within few large-sized aggregates that stay unbroken under the chosen conditions. It is noteworthy that D_{mean} values, little varying in the range of concentrations to 0.1% mass, sharply drop (almost 2-fold) at c=0.5% mass. It evidences for the presence of a local structure of suspensions of nanosized DND particles that is influenced by concentration.

As our calculations chow, at c=0.5% mass the polydispersity curve has a narrow peak of 0–32 nm in width and the maximum at 18 nm. At lower concentrations smearing of the peak takes place (maximum 30–40 nm, width 0–178 nm). Low value of M% is connected with a narrow number average DND distribution (c=0.5% mass). The former is calculated for a wider range and, consequently, produces too high data while averaging.

Be back to the Table 1. Note again that almost all DND aggregates are within nanosize range; a number of larger particles is small and can be neglected (if say nothing of their mass). On could suppose that a suspension structure like this would bring about its high resistance to sedimentation. However, we experienced that the suspensions stay stable not longer than for 2.5 hours (4 hrs for those with c=0.5% mass). We focus on the part played by large particles to reveal factors that may account for the low sedimentation resistance. First, the difference in geometric dimensions brings about different diffusion mobilities of the particles. As nanodispersed particles are the quickest, the probability of their collision with slowly moving large ones is very high in the diffusion process. High surface activity of nanoparticles would lead to almost irreversible aggregation of finely- and low-dispersed collided particles. Theoretically, there is a continuous spectrum of low-dispersed particles. The closer surface energy of particles is, the lesser is the probability of irreversible aggregation of particles of this spectrum. In the general case the aggregation of large particles is reversible. Therefore, the processes of segregation would mainly occur at the expense of release of statistic average-sized particles. With all this allowed for, the whole process of aggregation – segregation gives rise to a suspension structure that is characterized by a decreased part of finely dispersed fraction and enriched in fraction of mean-sized particles.

Table 1. Polydispersity of DND suspensions against concentration and insonification regime.

Concentration, % mass	Regime1*			Regime 2*		
	D_{mean}, nм	N %	M %	D_{mean}, nм	N %	M %
0.002	44.4	99.9	4.9	24.7	99.9	19.2
0.01	43.1	99.8	3.9	244.0	52.0	6.6
0.1	36.4	99.9	2.3	123.4	93.5	32.1
0.5	21.4	99.8	1.9	30.0	99.7	45.4

* see the text

On the basis of the above model of DND suspension structure we assume that the sedimentation resistance can be enhanced through an artificial removal of the largest particles (e.g. by filtration at the simplest). Indeed, upon the filtration of DND suspension (after prior US treatment) through a metal filter with cylindric pores of d=0.5 mcm the sedimentation resistance goes up to 48 hrs. Let us examine the relations of the structure of DND suspensions to insonification regime. The insonification and successive rest during suspension stability result, as above assumed, in a structure enriched with DND aggregates of medium size. As it follows from the proposed mechanism of aggregate formation, they are structured of a core with a shell of fine particles around. There is no contradiction in the assumption that the structure of aggregates arisen is instable toward shift loads. Repeat insonification can then contribute to the destruction of the aggregates and favour in this way an increase in mass part of finely dispersed particles. To this end, the insonified DND suspension was kept for 2 hvs and re-insonified. One can see that the repeat insonification made it possible to get much higher values of fine particle mass part. Optimum results are attained for c=0.5% mass, where the share of under 200 nm sized particles is 45.4% mass. The researches were conducted at the temperature of 293±5 K. At the concentration of the modifier 1 % and more the value of a kinematic viscosity of oil I-20A begins to increase. The kinematic viscosity of motor oil 15W40 is increased unsignificantly up to 379.4 mm^2/c with the adding up to 1% of the modifier. In comparison with a pure one kinematic viscosity is equalled 346 mm^2/c for pure oil. The kinematic viscosity of transformer oil is increased up to 28mm^2/c at the contents of a blend 1%, the kinematic viscosity of initial oil is equalled 22.3 mm^2/c. The dependece is of a parabolic kind. For the definition of viscosity and temperature properties of modified oils have conducted measurements of kinematic viscosity at temperatures from 293 up to 363K (table 2).

The viscosity and temperature characteristics are stabilized for modified oils. The given effect is observed at the concentration of the modifier more than 1% for motor oil. Stability of modified oils to thermal destructive was evaluated by the methods of the differential - thermal analysis. The adding of a blend to industrial oil results in deboosting of speed of a course thermooxidating destructive of modified oils.

The method IR–spectroscopy establishes appearance of the additional absorption bands in the area 500–1000 cm^{-1}. In a IR–spectrum the additional absorption bands seem to testify the chemical interaction between molecules of lubrication and clusters of carbon. The addinq up of the modifier in the oils under consideration does not result in change thermooxidating properties of oils.

Thermooxidating properties of the invesfiqated objects were determined by the change of optical density of the absorption band 1740 cm^{-1}. In a course of theexperiment it was established, that the dependence of optical density of the absorption band 1740 cm^{-1} of pure oil on time of heat treatment has the same kind, as for modified oils subjected to heat treatment at the same temperature (Fig. 3).

Table 2. A kinematic viscosity of modified oils depending on temperature and concentration of the modifier.

Temperature in K	Contents of a blend in oils in mass shares(long), %								
	Industrial			Motor			Transformer		
	0	0.01	0.1	0	0.01	0.1	0	0.01	0.1
293	88.4	89.7	90.85	346	347.4	352.6	22.3	22.6	23.5
303	52.1	52.3	53.6	188.5	189.8	193.4	14.9	15.3	16.1
313	32.5	34.6	35.7	112.1	113.2	114.9	10.1	10.7	13.7
323	20.8	22.2	23.8	67.6	67.9	69.9	7.3	7.9	9.1
333	14.6	15.6	16.9	42.3	43.2	44.8	5.1	5.8	7.2
343	9.8	10.4	11.6	25.5	26.6	27.6	3.9	4.6	5.2
353	5.6	6.5	7.3	15.7	17.1	18.2	2.7	3.2	3.7
363	3.8	4.6	5.1	8.9	9.4	10.3	1.9	2.3	2.7

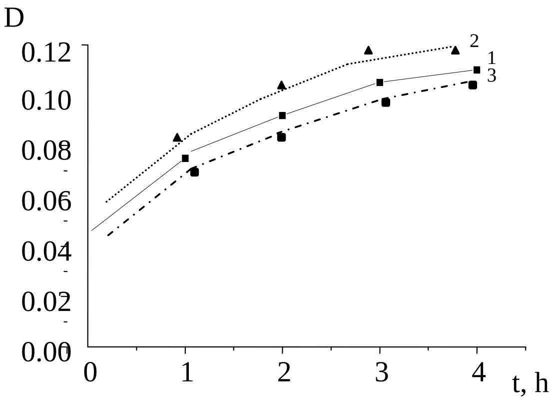
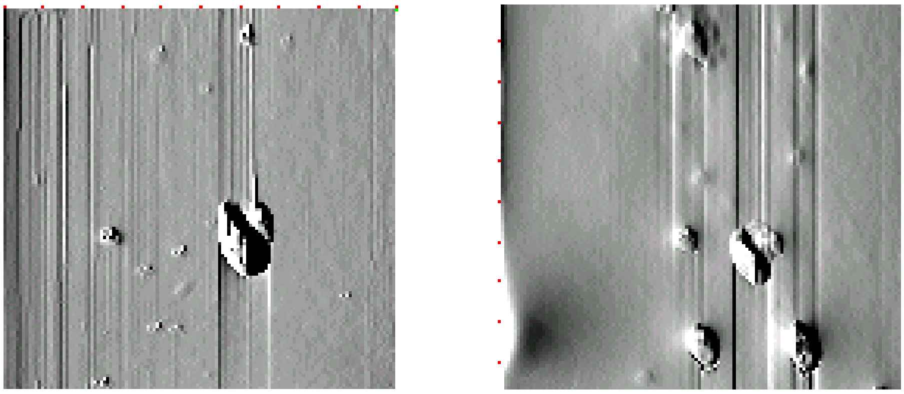


Figure 3. Dependence of optical density of the absorption band 1740 cm^{-1} of mineral oil on time of oxidation in at T = 493 K. 1) oil I–20A, 2) oil I–20A + 0.01% of a blend, 3) oil I–20A + 0.1% of a blend.

The increase of viscosity at adding up of a blend is explained by the formation of adsorption linkes between molecules of oil and particles of the modifier. With the increase of the concentration of a blend in oil the number of links between the molecules of oil and the clusters of the modifier is increased, which in its turn increases viscosity of oils. According to the references the adsorption links are stable and at increased temperatures, and this is confirmed by viscosity and temperature tests and the data of the differential - thermal analysis. By the method of a atomic-load-carrying microscopy the a structure of lubricating materials filled by a blend was studied. The surface of pure oil is of a smoothed kind. The adding 0.01% of a blend results in appearance in oil of globular objects with the sizes 0.1-4 mcm. The further increase of in the concentration of a blend results in increase of quantity of such objects per unit area at the decrease of the average size up to 0.1–2 μm. (fig. 4).

The clusters of synthetic carbon change the tribotechnical characteristics of initial oils. The factor of friction of a pair steel 45 – steel 45 decreases by 10–15 of % at the concentration of the modifier 0.01%. The further increase in the contents of the modifier reduces the value of a factor of friction. However at the concentration of 3% and above sharp increase in the value of a factor of friction is observed. This effect might be explained by the fact that at the concentration of clusters more than 3 % the sizes of conglomerates, formed in oil, become larger, than the thickness of a lubricating layer, therefore the clusters of synthetic carbon play a role of abrasive particles. The factor of friction of the pair steel SH 15-PEND decreases in 1.5–2 times at the concentration of a blend in the oil 0.005%. The further adding up of the modificator increases a factor of friction.



a) b)

Figure 4. Morphology of a surface of a substrate, with a marked oil layer containing ultra dispersiblis clusters of synthetic carbon. a) 0.01% of a blend; b) 0.1% of a blend (25×25 a μm).

4. CONCLUSION

In the preparation of diamond secondary suspensions not only statistic average sizes of particles should be taken into consideration, but also polydispersity parameters of nanodiamond particle population too. Even a minor amount of large sized undistroyable aggregates of particles markedly brings down the sedimentation resistance of suspensions. Sedimentary instable large aggregates are rich in finely and low-dispersed particles. Time of insonification in a complicated manner influences the pattern of polydispersity curve for nanocarbon particles in suspensions. Time of optimum insonification can be found and, thus, a maximum part of nanodiamonds reached ranging 0–100 nm that is of much importance in practice. Left–assembly processes in suspensions combined with the periodical insonification can be a key to bring a max possible mass part of nanodiamond particles in secondary suspensions to a highly dispersed state. On the basis of the conducted research it is possible to make the following conclusions: the adding up of ultra dispersiblis clusters of synthetic carbon in a structure transformer, motor 15W40 and industrial I–20A of oils results in the increase of kinematic viscosity; the viscosity and temperature characteristics of oils at the modification by a blend are stabilized. Small concentration of a blend (0.005–0.01%) improve the tribotechnical characteristics of mineral oils. At concentration more than 3% of a blend on abrasive wear of contrbody takes place in the oil.

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