

STABILITY OF ULTRADISPERSE DIAMOND POWDERS IN OIL SUSPENSIONS

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ABSTRACT

Nanosized ultradisperse diamond powders (UDDPs) have shown potential for application in different industrial products. In lubricating oils they are introduced in the form of suspensions in organic liquids. Previously we have proposed an express method for determination of the concentration of powders in oil suspensions.

The aim of this work is to present our results on the application of the UV-VIS method for determination of the stability of UDDPs in oil and to compare the effect of different stabilizers used as lubricant additives and the influence of ultrasonic treatment on UDDP stability in oil.

The stability of UDDP suspensions has been followed for up to 75 days in storage. The obtained results show that powders containing soot are more easily stabilized than those with pure diamond. Ultrasonic treatment has an ambivalent effect and it is very important to determine correctly the time which would produce the required stability. Certain additives widely used in lubricants can ensure stability higher than that of a commercial product used for comparison. However, when preparing a concentrate for particular formulated oil the eventual effect of the additive package already present on the stability of UDDP in the doped oil should be considered.

Keywords: ultra disperse diamond powders, lubricants, UV-VIS spectrometry, oil suspensions, solid lubricants.

INTRODUCTION

Ultradisperse diamond powder (UDDPs) with dimensions in the nanoscale are produced by detonation of carbon-containing explosives under conditions of negative oxygen balance [1]. Because of their particle size, which is smaller by three orders of magnitude than the size of dynamically synthesized diamond, and specific conditions of formation, UDDPs exhibit some unique properties and especially a high and peculiarly manifested chemical activity. The latter allows for sur-

face modifications and outlines a wide range of potential applications [2, 3].

Different UDDPs 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]. In lubricants, which are of particular interest in this work, UDDPs are predominantly used in the form of suspensions [4]. The high surface activity leads to the aggregation of UDDP particles and to a varying stability of the suspensions,

depending on the type of the base oil (polar or non-polar), interaction with other additives, etc. In conventional lubricants (i. e., motor and gear oils, hydraulic fluids, etc.), the nano-sized UDDPs are presumably penetrating between the tribosurfaces, forming *in-situ* a film, which under boundary lubricating conditions ensures excellent load carrying and antiwear properties [5]. Benefits of decreasing the friction coefficient with 20 – 30 % and twice reducing wear are claimed [4-6].

However, evidence has been reported that the effect of UDDPs might be minimal and even negative [7]. Evidently, the practical benefits of UDDPs depend not only on the correct selection of the different additives and the formulation of the package, but also on the stability of the suspension and the concentration of UDDP in it, because the latter would determine to a great extent the amount of particles penetrating into the tribocontact and the formation of the lubricating film. For instance, it has been shown experimentally that addition of a fraction separated from UDDP containing soot, to an engine oil, led to decrease of the friction coefficient for bronze pairs by a factor of no less than two, whereas the addition of the unseparated UDDP exhibited abrasive properties [8]. The above observations clearly indicate that the stability of the oil suspensions of UDDPs is an important factor in the mechanism of their action.

Lubricant additives, containing UDDPs are offered on the market for the so-called “Do It Yourself (DIY)” application, which is typical for friction modifiers (e.g., MoS₂ and polymer suspensions for automotive oils). Under this market strategy, the client buys a small bottle of the product, which in the case of suspensions has to be vigorously shaken and added to the formulated oil under conditions of constant mixing of the oil and the additive (e.g., a running engine). Obviously, the stability of the additive suspension has an important role in DIY application, and will influence significantly its efficiency. The change of stability during shelf storage and its recovery after subsequent homogenization are key issues in selection of the methods for production of stable suspensions for the market.

The aim of this work is to present our results on the application of the UV-VIS method for determination of the stability of UDDPs in oil and to compare the effect of different stabilizers used as lubricant ad-

ditives and the influence of ultrasonic treatment on UDDP stability in oil.

EXPERIMENTAL

There are different methods that can be used to assess the stability of suspensions. Typically, they include some arrangement for storage and sedimentation, and a method for determination of the concentration of the solid phase from one or more points of sedimentation during the time of storage.

In our work we have chosen to store our compositions in capped laboratory glass test tubes with a height similar to the bottles in which such products are sold. The tubes were kept in the laboratory in vertical position under indirect light and at room temperature for 75 days. After 20 and 75 days of storage, the upper 0.5 cm layer of each test tube was homogenized, and a sample was taken from it. These samples were then diluted with n-hexane and the concentration of UDDP in them was estimated by the UV-VIS method, described in [9]. The initial stability of the suspensions was determined by the same method. The data for the stability analysis were complemented by the results for changes of the concentration of the powder in the hexane dilutions, measured after 15 minutes storage in the measuring cell of the UV-VIS apparatus [9]. Finally, after the 75 days of storage, all test tubes which still had some powder in their upper 0.5 cm layer were transferred onto a laboratory reciprocating shaking machine which effectively homogenized the concentrates in vertical direction for one minute. The “recovered” stability of the concentrates was determined by taking a sample from the upper 0.5 cm layer and estimating the powder concentration in it, as described above.

The samples, the stability of which was tested in the present work, included a commercial lubricating concentrate containing UDDP and a considerable number of lubricating suspensions made in the authors’ laboratory by weighing on an analytical balance and subsequent homogenization with a mechanical stirrer for 60 min at 50 – 60° C. The homogenization was done in laboratory jars of approx 200 cm³ volumes with sealed caps, which were labeled and used for longer storage. Whenever a portion of the suspensions had to be taken from a jar (e.g., for stability analysis), manual stirring of any sediment at

the bottom of the flask, followed by at least 10 min homogenization with a mechanical stirrer was applied.

Liquid paraffin was used as a model base oil of all concentrates [9]. It was chosen, because it is widely used in modeling of liquid lubricants and is colorless, which is an advantage for the UV-VIS analysis. Preliminary tests, as well as our experience showed that concentrates prepared with hydrocarbon base oil, would have a higher stability. Stability of formulated oils doped with the studied concentrates is not an object of this work, but it is believed, that in general it will be higher than that of the concentrates.

The concentrates were obtained either from pastes containing liquid paraffin and UDDP, by diluting a prescribed amount of the respective paste with liquid paraffin and eventually adding different stabilizers, or by direct mixing of liquid paraffin, UDDP and stabilizers. Pastes of approx. 30 % concentration were prepared with a mechanical disintegrator with blades and plates, at a fixed speed of rotation of 10000 RPM.

The commercial concentrate was used as bought from the retailer. Samples from it were transferred and stored in a laboratory jar from the original container, after vigorous shaking, as prescribed by the retailer, and

then the concentrate in the jar was homogenized as were the laboratory concentrates.

All UDDPs were received from the Department of Space Material Science, Space Research Institute of the Bulgarian Academy of Sciences under the provisions of the 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 [10, 11]. Most of the laboratory compositions were prepared with an UDDP, containing around 60 % diamond (to be called further "UDDP 60). Two UDDP 60 samples contained chemically bounded boron, and one – copper. These samples were prepared by the Laboratory of Organic Reactions of Microporous Materials of the Institute of Organic Chemistry of the Bulgarian Academy of Sciences, who is the other collaborator in the joint project. Samples of not modified pure diamond powder were employed in some of the compositions.

The proposed method was tested on concentrates obtained by direct weighing of components and/or from pastes, with and without stabilizers, with and without additional stabilization by a conventional laboratory ultrasonic device and/or an ultrasonic disintegrator.

Table 1. Codes and Description of the Lubricant Additives and Packages Tested as Stabilizers.

Code	Description
Stabilizer 1	Thermally stable polyalkenyl succinimide, TBN = 17.7 KOH.g ⁻¹
Stabilizer 2	Polyisobutylene succinic anhydride, MW 1300
Stabilizer 3	Overbased phenate, TBN = 260 mg KOH.g ⁻¹
Stabilizer 4	Overbased Ca alkylaryl sulphonate, TBN = 300 mg KOH.g ⁻¹
Stabilizer 5	Overbased Ca alkylaryl sulphonate for EP oils, TBN = 400 mg KOH.g ⁻¹
Stabilizer 6	Overbased Ca alkylaryl sulphonate + N containing additive, TBN = 320 mg KOH.g ⁻¹
Stabilizer 7	Neutral Ca alkylaryl sulphonate, TBN = 30 mg KOH.g ⁻¹
Stabilizer 8	Additive package for automotive gear oils, containing S, P, N.
Stabilizer 9	Motor oil additive package, containing S, P, N, Zn, Ca, Mg, TBN = 77 mg KOH.g ⁻¹ .
Stabilizer 10	Motor oil additive package, containing S, P, N, B, Zn, Mg, TBN = 114 mg KOH.g ⁻¹
Stabilizer 11	Overbased Mg alkylaryl sulphonate, TBN = 400 mg KOH.g ⁻¹ .
Stabilizer 12	Additive package for industrial oils, containing S, P, N.
Stabilizer 13	Detergent and dispersant additive package for motor oil formulation
Stabilizer 14	Primary palmityl amine, commercial chemical of <i>purum</i> grade
Stabilizer 15	Oleic acid, commercial chemical of <i>purum</i> grade
Stabilizer 16	Neutral Ca alkylaryl sulphonate, TBN = 14 mg KOH.g ⁻¹
Stabilizer 17	EP additive, containing B, synthesized in the authors' laboratory
Stabilizer 18	Oleyl butylate, synthesized in the authors' laboratory
Stabilizer 19	Zn dithiophosphate for industrial gear oils

Abbreviations and symbols: TBN – total base number. The single letters are the symbols of the respective chemical elements.

The studied stabilizers were conventional additives or additive packages, produced by well recognized additive companies and recommended for formulation of different lubricants (e.g., motor oils, automotive and industrial gear oils, etc.) or compounds related to them, some of which were synthesized in the authors' laboratory. All concentrates contained approx. the same amount of UDDP, which has been identified from published data as typical for UDDPs. Table 1 shows the codes, used in the authors' laboratory for the different stabilizers, and a concise description, as provided by the respective companies from which they have been bought.

Table 1 shows that the chosen stabilizers are typical for the detergent, dispersant, EP etc., additives or their packages, used for formulation of lubricants in which UDDPs might be added.

RESULTS AND DISCUSSION

The concentrations of the powder in the samples taken for analysis after storage were estimated with the empirical correlations described in [9]. In this work we have proposed different correlations for estimation of the powder concentration, as follows

Table 2. Stability of UDDP 60 Concentrates prepared with different stabilizers ($\bar{A}_{15}/\bar{A}_0 > 60\%$ [9]).

Sample No	Description of Concentrate	Stability, % of the initially weighed amount of powder in the concentrate			
		15 min*	20 days	75 days.	Recovered stability
1	Stabilizer 1, 2.0 %	89.9	18.29	9.1	65.1
2	Stabilizer 2, 2.0 %	78.8	5.2	0.0	-
3	Stabilizer 3, 2.0 %	88.5	5.8	0.0	-
4	Stabilizer 4, 2.0 %	85.6	36.6	11.1	34.1
5	Stabilizer 5, 2.0 %	88.5	32.1	11.8	24.1
6.1	Stabilizer 6, 2.0 %	99.0	54.4	11.9	37.2
6.2	Stabilizer 6, 2.0 %	92.0	-	-	-
7.1	Stabilizer 7, 2.0 %	97.2	-	-	-
7.2	Stabilizer 7, 2.0 %	97.0	61.5	19.2	84.0
7.3	Stabilizer 7, 2.0 %	88.1	-	-	-
7.4	Stabilizer 7, 2.0 %	83.2	-	-	-
9	Stabilizer 9, 2.0 %	90.9	56.6	12.9	74.0
10	Stabilizer 10, 2.0 %	76.3	55.8	7.2	81.7
11	Stabilizer 11, 2.0 %	79.9	4.8	0.0	-
16	Stabilizer 13, 2.0 %	95.5	42.8	20.5	61.8
18.1	<i>Commercial Sample</i>	85.1	44.3	0.0	48.7
18.2	<i>Commercial Sample</i>	86.1	48.0	0.0	34.5
20	Stabilizer 16, 0.5 %	55.8	2.0	0.0	-
21	Stabilizer 16, 1.0 %	84.1	5.8	0.0	-
22	Stabilizer 16, 2.0 %	80.9	30.9	9.0	31.0
23	Stabilizer 16, 3.0 %	92.0	45.4	9.8	39.3
24	Stabilizer 16, 3.5 %	92.8	72.1	16.4	40.2

Abbreviations and remarks: US – ultrasonic treatment (laboratory device); USD – ultrasonic treatment (disintegrator device), the time of treatment in minutes is shown after the abbreviation. *Italic* – the stabilities of the commercial samples were calculated as % of the calculated initial amount of powder. All concentrations were calculated with model 2 [9].

* Stabilities after 15 min were determined in the cell of the UV-VIS apparatus in hexane-diluted samples.

(\bar{A} is the UV-VIS absorption of the sample diluted with *n*-hexane):

Model 1: C_{uddp} in hexane, % = $0.0738 * \bar{A}$ - for UDDP 60 samples without stabilizers.

Model 2: C_{uddp} in hexane, % = $0.025262 * \bar{A}^{0.60}$ - for UDDP 60 samples with stabilizers and $\bar{A}_{15} / \bar{A}_0 > 60\%$.

Model 3: C_{uddp} in hexane, % = $0.036763 * \bar{A}^{0.52}$ - for UDDP 60 samples with stabilizers and $\bar{A}_{15} / \bar{A}_0 < 60\%$.

Model 4: C_{dia} in hexane, % = $0.068742 * \bar{A}^{1.03}$ - for samples with unmodified pure diamond of medium stability.

Two of these correlations (model 2 and model 3), relevant to the present work have been used. Model

2 was used for all UDDP 60 concentrates with $\bar{A}_{15} / \bar{A}_0 > 60\%$ (Table 2). Model 3 was used to calculate the initial concentrations and the concentrations after 15 min sedimentation in the cell of the UV-VIS apparatus for concentrates with $\bar{A}_{15} / \bar{A}_0 < 60\%$ (Table 3).

The stabilities of the concentrates with $\bar{A}_{15} / \bar{A}_0 < 60\%$ after 20 and 75 days and the recovered stabilities after storage for 75 days and homogenization were initially calculated with both models. Model 3 calculates nearly two times higher stabilities than model 2, however, visual observation of the respective test tubes and the fact that none of the relevant concentrates contained powder in the upper 0.5 cm of the test tubes after 75 days, lead to the conclusion that model 2 is more appropriate, so only these results are shown in

Table 3. Stability of UDDP 60 Concentrates Prepared with Different Stabilizers ($\bar{A}_{15} / \bar{A}_0 < 60\%$ [9]).

Sample No	Description of Concentrate	Stability, % of the initially weighed amount of powder in the concentrate			
		15 min*	20 days	75 days	Recovered stability
8.1	Stabilizer 8, 2.0 %	73.2	-	-	-
8.2	Stabilizer 8, 2.0 %	80.9	0.0	-	-
12	Stabilizer 12, 2.0 %	69.7	3.1	0.0	-
17	Stabilizer 14, 2.0 %	70.3	10.8	0.0	-
19	Stabilizer 15, 2.0 %	59.6	0.0	-	-
25	Stabilizer 17, 2.0 %	69.4	4.3	0.0	-
26	Stabilizer 18, 2.0 %	60.3	1.9	0.0	-
29**	<i>Stabilizer 19, 2.0 %</i>	<i>91.0</i>	<i>10.3</i>	<i>0.0</i>	-

* See remarks for Table 2; concentrations for 15 min were calculated by model 3 [9]. The rest of the concentrations were calculated by model 2 [9].

** *Italic* – calculated with model 2, which however predicts for this particular sample with unusually high uncertainty [9].

Table 4. Stability of Concentrates with Modified UDDP 60.

Sample No	Description of Concentrate	Stability, % of the initially weighed amount of powder in the concentrate*			
		15 min*	20 days	75 days	Recovered
23	Stabilizer 16, 2.0 %, UDDP	80.9	30.9	9.0	31.0
35	Stabilizer 16, 2.0 %, UDDP Cu	75.2	19.7	12.5	31.5
27	Stabilizer 16, 2.0 %, UDDP B ³⁺	79.9	24.7	10.0	30.2
28	Stabilizer 16, 2.0 %, UDDP BO ₃	59.2	25.3	6.5	15.9

* The concentrations of the powder in samples 23 and 35 were calculated with model 2 [9]; for samples 27 and 28 model 3 was used.

Table 5. Stability of Concentrates after Ultrasonic treatment.

Sample No	Description of Concentrate	Stability, % of the initially weighed amount of powder in the concentrate			
		15 min*	20 days	75 days	Recovered stability
23	Stabilizer 16, 2.0 %, no treatment	80.9	30.9	9.0	31.0
30	Stabilizer 16, 2.0 %, US 10 min	86.1	59.7	34.6	72.0
31	Stabilizer 16, 2.0 %, US 20 min	69.0	46.7	22.2	84.4
32	Stabilizer 16, 2.0 %, US 30 min	83.5	65.6	39.1	82.7
33	Stabilizer 16, 2.0 %, US 40 min	86.5	58.2	36.6	73.2
34	Stabilizer 16, 2.0 %, US20 min + USD20 min	97.3	52.2	38.1	63.0
24	Stabilizer 16, 3.5 %, no treatment	92.8	72.1	16.4	40.2
36	Stabilizer 16, 3.5 %, USD 5 min	90.7	53.6*		
37	Stabilizer 16, 3.5 %, USD 10 min	89.5	-		
38	Stabilizer 16, 3.5 %, USD 15 min	92.7	-		
39	Stabilizer 16, 3.5 %, USD 20 min	93.5	61.5*		

Abbreviations and remarks: US – ultrasonic treatment (laboratory device); USD – ultrasonic treatment (disintegrator device), the time of treatment in minutes is shown after the abbreviation.

* after 29 days. The experiment is continuing with all four concentrates.

Table 6. Stability of Pure Diamond Concentrates Compared with Relevant UDDP 60 Concentrates.

Sample No	Description of Concentrate	Stability, % of the initially weighed amount of powder in the concentrate			
		15 min	20 days	75 days	Recovered stability
1UMD	Stabilizer 16, 2.0%, US 20 + USD 20	87.2	44.4	28.0	66.2
14 UMD	Stabilizer 16, 2.0 %, US 30	-	23.8	16.0	30.0
2 UMD	Stabilizer 16, 2.0%, US20	63.4	18.1		
10UMD	Stabilizer 16, 3.5%, US20	93.1	27.9		
11UMD	Stabilizer 7, 2.0 %, US20	73.8	20.8		
12 UMD	Stabilizer 4, 2.0%, US20	78.8	10.6		
31 UDDP	Stabilizer 16, 2.0 %, US 20 min	69.0	46.7	22.2	84.4
24 UDDP	Stabilizer 16, 3.5 %	92.8	72.1	16.4	40.2
7.3 UDDP	Stabilizer 7, 2.0 %	97.0	61.5	19.2	84.0
4 UDDP	Stabilizer 4, 2.0 %	85.6	36.6	11.1	34.1

Abbreviations and remarks: US – ultrasonic treatment (laboratory device); USD – ultrasonic treatment (disintegrator device), the time of treatment in minutes is shown after the abbreviation. UMD - unmodified diamond.

Table 3 and Table 4. This observation is not surprising since it might be expected that after the aggregates of larger dimensions are settled during the first days, the suspensions in the upper layer of the samples become more stable. Model 2 turned also to be more appropri-

ate for the estimation of the same stabilities for the concentrates with pure diamond powder (Table 5), than model 4 developed in [9] for such concentrates. This fact needs further investigation, which will be organized with more diamond concentrates.

Results for parallel samples in Table 2 (i.e., samples 6, 7 and 18) show that the stabilities are reproduced with an uncertainty corresponding to that of the respective correlation [9]. Still, it is evident that many of the concentrates developed in the authors' laboratory are comparable to or considerably more stable than the commercial concentrate. The samples in which the influence of the amount of stabilizer has been assessed improve their stability along with the increased stabilizer concentration.

Table 4 compares the results for the concentrates prepared with modified UDDP 60 powders.

As seen from Table 4, the concentrate, containing boron in the form of BO_3 shows worse ability for recovery after prolonged storage. Within the respective uncertainty of the results, the rest of the stabilities are comparable to that with the unmodified powder.

Table 5 presents the results for the effect of the ultrasonic treatment on stability.

The results in Table 5 indicate an ambivalent effect of the ultrasonic treatment on the stability of the concentrates and imply that an optimal time of treatment should be established for each particular composition and device. Similar observations have been reported for suspensions in water [12] and for seeding of diamond like carbon films from different solvents [13].

Table 6 shows the stability of concentrates with pure diamond powder.

The series of experiments with diamond powders are not completed yet, but the results obtained till now seem to be encouraging for the development of stable concentrates with such powders.

CONCLUSIONS

The obtained results show that powders containing soot are more easily stabilized than those with pure diamond. Certain additives ensure stability higher than that of a commercial product used for comparison. Typical detergent lubricant additives provide higher stability than dispersants. However, as might be expected, dispersants ensure in general better stability after 15 minutes of storage and better recovery of the stability after prolonged storage. There are additives, which cannot stabilize UDDP. So, when preparing a concentrate for a particular formu-

lated oil, the additive package already present in the oil should be considered from the point of view of its eventual effect on the stability of UDDP in the doped oil.

Ultrasonic treatment has an ambivalent effect on stability and it is very important to determine correctly the time which would produce the required stability.

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