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PTFE based nano-lubricants

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ABSTRACT

Polytetrafluoroethylene (PTFE) is known as a high performance engineering polymer as well as a solid lubricant. The literature contains several papers that report on the effects of nano-sized solid lubricant additives, but no systematic studies have been published on the effects of nano-sized PTFE particles. This paper first describes the methodology for preparing nano- and micro-PTFE particles that were blended into a 150 N API Group II base oil. The particle sizes were 50 nm, 150 nm, 400 nm and 12 μm, and the particle concentrations were 4, 8 and 12%. Formulations were characterized for physical properties and tribological behavior. Physical properties included density, viscosity, pour point, and flash point. Tribological characteristics were (1) weld load tests (a four-ball EP method to determine load carrying capacity), (2) anti-wear properties (using a different four-ball test method) and (3) friction (using an Optimol-SRV III oscillating friction and wear tester). Results from tribological testing of the experimental oils and bearing steel test specimens showed that PTFE particles can significantly improve the weld load, as well as anti-wear and friction reduction properties. The smaller the size of PTFE particles and the higher their concentration, the greater was the performance improvement. The topography and surface chemistry of the test specimens were examined using scanning electron microscopy, and the improved quality of the tribo-films formed on the counter faces was seen to correlate with performance improvements.

1. Introduction

Performance of a lubricant is enhanced in multiple ways by adding a combination of additives such as anti-friction, anti-wear, extreme pressure, anti-oxidant, anti-corrosion, detergent etc. Ever increasing severity in operating conditions and advances in equipment technology coupled with raising lubrication requirements are the key reasons for the exploration of new kind of additives and optimization of their concentrations. Nano-Particles (NP_S) are regarded as the most plausible prospect to meet these demands. The enhanced performance due to addition of NPs in composites, oils, fluids etc. is essentially because of the high surface area/volume ratio leading to extensive interaction between tribo contact points and lubricants containing NPs [1 and cross refs in it]. A large number of papers have reported on the positive effects of NPs in selected oils for reducing friction and/or wear [1–21]. When some NPs were added into the base oil, their anti-friction (AF) and anti-wear (AW) properties improved significantly. Wu et al. [2] and Choi et al. [3] reported that the nano-oils with Cu NPs reduced the friction coefficient (μ) of SAE 30 oil and raw oil respectively. Inorganic fullerene like (IF) NPs [5–7] mixed with oil also reduced the μ. Rapoport et al. [6] reported that IF WS_2 NPs mixed with oil improved tribological properties.

The size of NPs (such as Cu, IF-WS_2, ZnS, PbS) shows positive effect on tribological properties, mostly in the range of 2–120 nm [2–15]. Interestingly smaller size of NPs did not necessarily lead to better properties as reported in the case of gold particles, where 20 nm sized particles were more effective in reducing μ and wear than those of 5 nm size. It was argued by Chinas-Castillo et al. [8] that the smaller NPs were unable to prevent asperity–asperity interaction to the extent 20 nm particles did. On the contrary, Liu et al. [9] reported that studies on dialkyldithiophosphate (DDP) modified Cu NPs of two sizes in liquid paraffin led to the conclusion that smaller size (2 nm) was more effective in reducing wear by virtue of better quality of protective film. In further work by Liu et al. [10–15] involving studies on a wide range of colloidal solid NPs using a four-ball tribotester, claimed that during friction process the deposition of tribo-chemical reaction products by NPs led to an AW boundary film reducing shearing stress. The mechanisms of friction and wear reducing properties of NPs in oils had been reported as colloidal effect, rolling effect, protective film or third body effect. The studies on mechanism of colloidal NPs in oils by Chinas-Castillo et al. [8] indicated that NPs penetrate in a thin film or elasto-hydrodynamic (EHD) film mainly by a mechanical entrapment. The boundary film formed due to rolling of NPs was of at least one or two times thicker than the size of NPs.

Some papers also reported the effect of concentration of NPs in oils. A low concentration of NPs is sufficient to improve the desired property of oil. Table 1 indicates the essence of some of the research papers on this aspect.

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Literature survey indicates that in spite of well accepted fact that PTFE is very effective solid lubricant, no efforts are put to explore the potential of PTFE NPs as an additive in lubricating oil. Hardly any comparative studies are done to provide an insight on the influence of size effect by comparing the performance of micro-lubricant (MLs) and nano-lubricants (NLs) with varying sizes of the same additive particles. This becomes more important when such studies are reported for high performance polymer composites [25]. In view of the foregoing, few MLs and NLs were prepared with micron and nano-sized PTFE particles in varying concentrations (4, 8 and 12 wt%). Four-ball tester and SRV oscillating friction and wear tester were used to evaluate the performance of these oils. The results are reported in the subsequent sections.

2. Materials and methodology

2.1. Selection of material

2.1.1. Selection of PTFE particles

Details of PTFE powders of four different sizes along with designations are shown in Table 2. Field emission scanning electron micrographs {(FESEM), (ZEISS, Supra 55)} of three particles (N, S_{SS} and S_{SB}) are shown in Fig. 1 [25]. Particle size distribution graph (Malvern Mastersizer 2000) of biggest particles (designated as M) is shown in Fig. 2.

2.1.2. Base-oil selected

As per current practice in the lubricant industry, there is a trend to move away from API GP I to GP II/III base oil categories as the later offers better viscosity–temperature stability, oxidation resistance, lower volatility and superior low temperature rheology. Hence 150 N Group II base oil was selected as a base-stock for all further studies. This was regarded as parent oil (designated as O_P). O_P was used for preparing various nano- and micro-oils based on additions of PTFE powders of different sizes and in different concentrations as per Table 2.

Table 1
Information from literature on an optimum dose of selected NPs for best performance of oils.

S. no.	NP	Size (nm)	wt%	Optimum conc. (wt%)	Ref.
1	WS_2	10–15	0–2	2	[5]
2	IF-WS_2	–	1, 5 and 10	10	[7]
3	ZnS-DDP coated	4	0.05–0.4	0.1	[12]
4	LaF_3-DDP coated	6	0.05–1.5	1	[14]
5	PbS-oleic acid capped	8	0.05–0.4	0.2	[15]
6	Cu	2	0–1	1	[16]
7	Ni	20	0.5, 1 and 2		[17]
8	CuO	30–50	0.5, 1 and 2	1	[18]
	ZnO	20		0.5	
	ZrO_2	20–30		0.5	
9	Nano-diamond	20	0.05, 0.10 and 0.15 g/l	0.05 g/l	[19]
10	Zinc borate	20–50	0.5–2	1.5	[20]
11	ZrO_2	< 50	0.1, 0.5 and 1%	0.5	[21]
12	TiO_2	40	0.01–1.4	0.25	[22]
13	Cu	25	0.5 and 2	0.5	[23]
14	Ni	10	0.25–3	0.25	[24]

2.2. Preparation of oil suspensions with PTFE

PTFE is a solid lubricant with very low surface energy and generally when added to any mineral base oil, it tends to settle down. There are various routes to improve suspension stability of such mixtures/blends such as preventing coagulation through inter-particle repulsion; slowing down sedimentation by increasing the viscosity of the continuous phase; making the material solid-like by creating a network structure; using an inter phase solvent/dispersant to improve the stability through the stirrer, the ultrasonic bath, the ultrasonic disruptor and the high-pressure homogenizer etc. [26].

In the present study probe sonication was used for dispersing nano- and micro-particles in a parent oil. Ultrasonic wave is a pressure wave that propagates through a medium, resulting in a vast amount of energy dissipation, and violent collapse of gas and vapor bubbles (termed as "acoustic cavitations"), which possibly induces many physico-chemical effects. Sonic Vibra Cell Ultrasonic Liquid Disperser was used for sonication. Ultrasonic waves at frequency of 20 kHz and 750 W were employed for selected durations (variable parameter). The ultrasonic probe (diameter 12 mm) was dipped in selected medium in such a way that it was immersed inside at the depth of 2–3 cm.

During initial trials, PTFE-oil suspensions were made with 1 and 2% (by wt.) of PTFE with respect to the parent oil. However, after initial tribo-studies, it was observed that it did not lead to significant difference in a tribological performance. Hence higher amounts (4, 8 and 12 wt%) were selected. The procedure adopted for developing micro- and nano-suspensions is as follows.

(a) **For micro-suspensions**—The selected quantity of PTFE (16 g) and parent oil (184 g) was divided in 4 lots (4 g of PTFE and 46 g of parent oil each). A paste of PTFE with small amount petroleum ether (40–60 °C) was slowly mixed with the medium of suspension (petroleum ether) (approx 150 ml in a beaker of 250 ml) followed by a sonication for selected time (duration 30, 45, 60 and 90 min). Base oil was then slowly added in installments and sonicated for a minute followed by addition of next installment. Similarly second, third and fourth lots were sonicated. Finally the whole suspension was transferred in one beaker and the complete blend was sonicated for 1 h (when the temperature reached 50 °C, it was automatically cut off and blend was allowed to cool). Then the suspension was sealed and allowed to stand for 7 days. The absence of solid precipitate in the oil was regarded as a good suspendability of PTFE in the oil. It was observed that the sonication time influenced the stability of suspension significantly. Oils sonicated for 30 and 45 min showed precipitation of PTFE

Table 2
Details of selected PTFE powders and micro- and nano-oils [25].

S. no.	Designations of PTFE powders	Supplier	Size as per suppliers' data	Concentration (wt%) and type of PTFE used in parent oil	Designation of oils based on particle size
1	N (nano-size)	Shanghai SMEC Trading Co. China	30–50 nm	(i) N—4%	O_{N4}
				(ii) N—2% and S_{SS} 6%	$O_{N2\text{-}SS6}$
2	S_{SS} (submicron small size)	Shanghai SMEC Trading Co. China	100–150 nm	S_{SS}—4, 8 and 12%	O_{SS4}, O_{SS8}, and O_{SS12}
3	S_{SB} (submicron big size)	Shanghai SMEC Trading Co. China	300–400 nm	S_{SB}—4, 8 and 12%	O_{SB4}, O_{SB8}, and O_{SB12}
4	M (micron size)	Sigma Aldrich	12 μm	M—4, 8 and 12%	O_{M4} O_{M8}, and O_{M12}

Note: Base oil was designated as O_P.