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Synergism between particles of PTFE and hBN to enhance the performance of oils

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ABSTRACT

Solid lubricants (SLs) are known to enhance the tribo-performance of oils significantly. Current work focusses on issue of exploration of combination of SLs in different amounts along with dispersant (Polyisobutylene succinimide −1 wt% const.) for possible synergism. Hexagonal boron nitride (hBN) and polytetrafluoroethylene (PTFE) are known as anti-friction, Anti-wear additives. PTFE is also known as an effective extreme-pressure (EP) additive. A series of oils based on Group III (Gr III) as base oil containing PIBSI (1%) along with increasing amount of hBN (0–4%) and simultaneous decrease in PTFE (4–0%) were prepared.

The tribo-performance of oils was evaluated on 4 ball tester for EP (weld load) and anti-wear performance. Formulations were characterized for physical properties density, viscosity, flash point. Also the stability of oils was observed using Dynamic Light Scattering studies.

Results revealed the inclusion of these two SLs showed better tribo-performance (43% in Weld Load) than with presence of PTFE in oil. The characterization of wear and a possible wear mechanism was given by observing the worn surface under a scanning electron microscope and energy dispersive X-ray analysis.
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1. Introduction

Formulation of finished oil is one of the most complex and critical tasks since it contains multiple additives in judiciously balanced amounts with distinct performance expectations from each one of them. Classical definition of additive indicates that it has to be soluble in oil and has to enhance the function for which it is added and it must not be interfering with other additives antagonistically [1]. Many times there can be overlap of functioning of two additives and sometimes they show synergism also, which is most desired. However, today's finished oils may contain solid particles especially of nano-size and these are generally of solid lubricants (SLs) or metallic particles as anti-wear (AW), anti-friction (AF) and extreme pressure (EP) additives [2]. The research in this direction is slowly moving towards exploring the synergism/antagonisms of two types of particles or additives (may be soluble or insoluble) in oils and/or greases [3–26]. Table 1 shows the essence of efforts by the researchers in this direction.

Hexagonal boron nitride (hBN) is a well know SL and its particles (5 wt%) of different sizes 70 nm, 0.5 μm, 1.5 μm and 5 μm have been successfully exploited in canola oil. Nano-particles (NPs) performed best and lowered the coefficient of friction by 39%, pin wear by 71%, and surface roughness by 83%. [27]. Pin-on-disk tribometer was selected for tribological performance evaluation. Similarly, recent research in the authors' laboratory had indicated the significant potential of PTFE particles in various sizes (nano, submicron, micron etc.) in various concentrations as EP additive rather than AW additive in Gr II oil [28,29].

It was thought interesting to explore the potential of both types of particles together in various amounts in Gr III oil as EP or AW additive and to examine if any synergism is observed since such investigations are not reported in the literature. Keeping this in view, series of oils was developed by systematic variation of these two types of particles in combination and was evaluated for physical and tribological properties. Polyisobutylene succinimide (PIBSI) was also used as a dispersant in small amount (1%) based on the inputs from earlier investigations by the group for PTFE particles [30]. The details of work are discussed in the subsequent sections.

2. Materials and methodology

2.1. Selection of materials

2.1.1. Selection of hBN and PTFE particles

PTFE particles of micron size (12 μm) and hBN particles of nano size (70 nm) were selected in this study. Details of particles along with their suppliers and designations are shown in Table 2. The

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Table 1
Literature on synergism/antagonism of additives in oil and/or greases.

SN	Oil/Grease	Additives	Wt%	Synergism/Antagonism/Other	Ref.
1	Light neutral HVI oil	• ZDDP Polymers (AKP 84. AKP-86, AKP-88, AKP-80, AKP-6878) • Complex esters (AKL-44, AKL-28, AKL-45, AKL-X, AKL-33) • Mixtures	0.005 0.25 0.5 (Total additives)	• ZDDP alone was effective only at higher conc. • Esters more effective than polymers as AW. Wear reduction-18 to 44%. • **Max synergism** for 0.1% polymers (lower conc.) and ZDDP 0.01% (higher conc.). • Higher conc. of complex esters (0.5%) with ZDDP (0.005–0.01%) showed **better AW** response.	[3]
2	Number 3 Li or Ca based greases	• Ca- petroleum sulphonate • $CaCO_3$ • Calcium acetate • MoDTC	2 2 2 4	• P_b increasing efficiency- $CaCO_3$ > Ca- acetate > Ca pet. sulphonate. • MoDTC and Ca-pet. sulphonate or Ca acetate - **synergistic** as AW in Li- greases, but not for Ca- greases. • μ of MoDTC-grease < MoDTC and Ca- grease.	[5]
3	Mineral oil	• Metallic stearates (Cr, Cu, Al, Pb, Sn, Na, Li) • MoS_2 (size < 5 μ) • Graphite (size < 10 μ)	–	• Anti-seizure properties- Pb stearate > MoS_2. • Metallic stearates- good AW at lower loads, but it differs significantly at higher loads. • Stearates of Sn and Pb- best overall tribo-performance. • Graphite and MoS_2 –more effective at higher loads than lower loads. • **Synergism** for combinations of stearates with MoS_2-graphite- more effective as AW & AF. • **Antagonism-** stearates of Na and Sn with graphite-MoS_2 on wear at high loads.	[8]
4	Mixture of HVI 300 neutral and 800 neutral base stock	• ZDDP • OBS • NS • Phenate • PIBS	0.3 (fixed) and 0.5–2 (varying) 0.5–5 – 2–10 2–10	• Synergism for AW- ZDDP-OBS and ZDDP-phenate and antagonism for ZDDP-PIBS. • Synergism- detergency and AW- for ZDDP & OBS (1:5) • Synergism for ZDDP-OBS-phenate combination (1:5:10)-ideal for the sustinence of ZDDP-OBS. • Synergism for optimized doses of ZDDP-OBS-NS-phenate (overbased)-PIBS (1:5:7:10:6)- for improved detergency and AW	[10]
5	HVI paraffinic mineral oil, 150 neutral base oil	• Mo based FM (MoDTP, MoDTC, MoAC) • S containing EP (SIB, DBDS, SF, ESD)	Mo (0.05 and 0.1%) S (0.25–1.0%)	• Synergism- as AW for 0.05% Mo in combinations. • Synergism -MoDTC in combination with SIB and ESD above 0.5% S • Antagonism- in combination with DBDSas AF • Synergism -All four EP additives with MoAC at 0.25% S.	[11]
6	Lithium based and organo claybased grease	• MoS2 • Graphite	l-5 Total 5% (20:80 to 80:20)	• Both- equally good as AW/EP for Li- grease • Synergism -For Li- grease, MoS2-graphite- in WL for 40:60 while for AW- at a 60:40 • In organo clay grease, the combination showed synergism in EP but antagonism in AW.	[13]
7	HVI paraffinic mineral base oil, 150 neutral base oil	• Mo based FM (MoDTP, MoDTC, MoAC) • Sulphur containingEP (SIB, DBDS, SF, ESD)	Mo (0.05 and 0.10) S (0.25, 0.50, 0.75 and 1.00)	• Antagonism-Combination of MoDTC and DBDS for WL which decreased by 10–11%. • Synergism- MoDTC with SF and ESD for load-carrying capacity by 11–13%. AW (better by 10–16%) on addition of MoDTC at 0.05–0.10 wt% MO • Synergism- for MoDTC at the 0.05% Mo level and SIB at the 1.0% S, as EP and AW (improvements 39% and 12.5%, respectively).	14]
8	Paraffinicmineral oil base oil	• ZnDTP • MoDTC • Mixture	Mo (700 ppm) Zn (1000 ppm)	• Synergism –As AF for a combination of ZnDTP and MoDTC.	[16]
9	Paraffinicmineral oil	• ZDDP • B agent (Borate ester) • H agent (Heterocyclic compd)	1% (Total concentration)	• H-agent-better EP additive than B-agent. • Synergism for AW for BH-agents; better than ZDDP	[17]
10	Paraffin oil	• ZDDP • Cu-DDP (Cu core-8 nm)	4 4	• Cu NPs -better than ZDDP as AW, AF & load-carrying capacity • Synergism- due to reaction film and deposited film of Cu during friction process.	[18]
11	S-free Mobil J 500 base oil	• ZDDP • MoDTC • MoDTP • Mixture	0.5% (Total Conc.)	• **Synergism** -EP and AW performance was in the order ZDDP + MoDTC > MoDTP > MoDTC > ZDDP • ZDDP + MoDTC showed synergism for lowest μ	[20]
12	Ti-complex greases	• Benzoic acid/stearic acid • Sebacic acid/stearic acid • PTFE (70–90 nm) • TiO_2 (< 10 nm) • SiO_2 (< 30 nm)	17 0.5–3	• Optimum conc. as AF and AW for PTFE (2%), TiO_2 (0.5%) and SiO_2– (1.5 wt%). • For benzoic acid/stearic acid Ti grease with optimal conc. of PTFE, TiO_2 and SiO_2, μ-reduced by 34.58, 22.97, and 24.47%, respectively, and the WSD by 4.95, 4.35, and 1.80%, respectively. • **Synergism-** between Ti sediment and adsorbing film accounts for the reduction of friction and wear.	[24]
13	Mineral oilPAOGrease (Li, Polyurea, I40A)	• DND (120 nm, 90 nm and 10 nm) • PTFE (0.1–1.0 μ, 1–2 μ, 5 μ) • Cu	0.13, 0.3, 0.7, 1.6 4 0.5	• DND + PTFE-significant improvement as EP and AF properties of greases and oils due to synergistic effect. • Smaller particles of DND (10 nm)- better AF for PAO-based oil than 120 nm.	[25]
14	Solvent refined mineral oil (MVIS 250) gear oil	• CaBN (50–100 nm) • T321	0.1–0.4 1–3	• **Synergism-** for AF-for 0.4% CaBN and 1.5% T321 Lowest μ (0.071) for 0.1% CaBN and 1.0% T321. • P_b and P_D improved due to CaBN and T321 into oil.	[26]

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