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Structure and chemistry of crankcase and cylinder soot and tribofilms on piston rings from a Mack T-12 dynamometer engine test

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ABSTRACT

Structure and chemistry of soot extracted from the crankcase and cylinder wall and tribofilms on piston rings of a Mack T-12 engine test were examined. XANES spectra recorded on soot samples indicate the presence of thermo-oxidative and tribochemical decomposition products in engine oil indicative of interaction between piston ring and soot samples. HRTEM indicates the presence of nanoparticles of calcium phosphate compounds, ZnO and Fe_2O_3 embedded at the surface of the turbostratic soot structure possibly responsible for third body wear. Abrasive grooves were found on the piston ring indicative of abrasive wear mechanism as a dominant wear phenomenon. In addition, significant differences in chemical composition of crankcase soot, cylinder soot and piston ring tribofilms were elucidated.

1. Introduction

Over the last three decades, heavy-duty diesel engines have evolved to comply with tighter pollution mandates and customer requirement [1]. Modifications in engine design have changed the combustion chamber and crankcase environment and hence have impacted development of heavy-duty engine oil technology [2]. Engine lubricant quality is very important to help ensure engine durability, engine performance and reduce maintenance downtime [3]. Over last three decades, various engine lubricants qualification tests have been developed and introduced to evaluate the heavy-duty engine lubricants performance. Beginning in the late 1980s, a new Mack genuine oil specification and American Petroleum Institute (API) heavy-duty engine lubricants category was introduced with each new U.S. heavy duty, on highway emission specification such as Mack T-7, T-8, T-8A, T-8E, T-9, T-10, T-11 and T-12 [2,4,5]. These tests simulate various field operations of the diesel engine and are employed by the engine oil formulators to evaluate and optimize their products.

In 2004, new U.S. NO_x emission standards resulted in most U.S. heavy-duty engine manufacturers adopting cooler EGR to lower NO_x emission to 2 g/bhp h [1]. Heavy duty engine manufacturers could not use retarded timing injection to achieve stringent NO_x restriction mandates; hence use of cooled EGR was inevitable [2]. EGR replaces the available oxygen, delays the ignition and produces more soot in the combustion chamber along with contaminants through exhaust recirculation that degrades the lubricants in the crankcase [2,6–9]. To evaluate the effectiveness of engine oil in protecting the engine in various harsh environments, engine oil formulators have been using diesel engine dynamometer engine tests. For example, Mack T-7, T-8 and T-11 were designed to evaluate the soot laden viscosity increase, while Mack T-9, T-10, T-12 were developed to evaluate the effectiveness of lubricating oil in reducing wear of piston liner, bearing wear and oil oxidation with higher EGR ratio [2]. Accumulation of soot due to EGR in the harsh environment of the crankcase requires effective engine oil formulation to mitigate the wear of engine components and extend the drain interval [4,6,10–19].

In the previous studies by Patel et al., an interaction between crankcase soot and decomposition products of lubricating oil was reported [20,21]. The crankcase soot used for characterization was extracted from the used crankcase oil acquired during drain interval from commercially operated diesel trucks and hence represented realistic field operation of diesel engine [20,21]. Characterization of drain interval crankcase soot using XANES, HRTEM, Synchrotron radiation, X-ray diffraction, and Raman spectroscopy has provided information on the structure and composition of soot. These studies have suggested that mechanically embedded hard nanocrystalline particles of calcium phosphate, hydroxyapatite, ferric oxide along with amorphous zinc polyphosphate, and crystalline calcium sulfates were present in the turbostratic structure of soot. In a related study it was shown that carbon black treated under milling and oxidizing conditions could be used as a surrogate for crankcase extracted soot; however, the treatment could not incorporate debris from tribofilms into the soot structure [22,23].

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Table 1
Operating parameters for Mack T-12.

Parameter	Phase 1	Phase 2
Time (h)	100	200
Speed (rpm)	1800	1200
Fuel rate (kg/h)	59.2	63.5
Torque[a] (N m)	1349	2576
Oil gallery temperature (°C)	88	116
Oil sump temperature (°C)	93	129
Coolant outlet temperature (°C)	66	108
Intake manifold temperature (°C)	90	80
EGR rate (%)	35	15
Air/fuel ratio	23.6	21.1
Soot (wt%)	4.0–4.6 at 100 h	6.0 at 300 h

[a] Uncontrolled parameters, typical value.

The current study examines the soot induced wear mechanism in controlled Mack T-12 dynamometer engine tests. This test method was developed to evaluate the wear performance of engine oils in turbocharged and inter-cooled four-cycle diesel engines equipped with EGR and running on ultra-low sulfur diesel fuel [2]. The Mack T12 test uses a Mack E-TECH V-MAC III diesel engine with Exhaust Gas Recirculation (EGR). The Mack T-12 is a procedure that evaluates oil's ability to minimize wear of the cylinder liner, piston rings and bearing wear in engines with EGR. The Mack T-12 is part of the API CJ-4 performance category of engine oil procedures, and it simulates heavy-duty, on-highway post 2007 truck operations. A warm-up and a 1-h break-in are followed by a two-phase test consisting of 100 h at 1800 r/min and 200 h at 1200 r/min, both at constant speed and load conditions. The operational parameters of the Mack T-12 test are summarized in Table 1.

Mack T-12 uses higher EGR ratio compared to other Mack lubricant tests. It is well established that higher EGR ratio increases wear of engine components [2]. Moreover, soot enters the lubricant with exhaust gas in the form of blow-by, or it is deposited on piston and cylinder walls and subsequently scrapped off by the second groove rings and oil ring and deposited into the crankcase oil. Thus, soot scrapped off from the piston and cylinder wall and extracted from the crankcase oil can provide comprehensive insight of interaction of soot with lubricating oil and decomposition products of lubrication oil. In addition, characterization of piston ring can also provide significant understanding of the interaction between piston rings and soot and provide insight of the dominant wear mechanism of piston cylinder due to interaction with soot.

To characterize the cylinder soot, crankcase soot and piston rings, X-ray Absorption Near Edge Structure Spectroscopy (XANES) and High Resolution Transmission Electron Microscopy (HRTEM) together with Scanning Electron Microscopy (SEM) were used to study the wear tracks and tribofilms generated on the 2nd groove piston ring.

2. Experimental technique

2.1. Diesel soot extraction

Used diesel engine oil was acquired from Mack T-12 lubrication qualification dynamometer test. Crankcase soot was extracted from the sump oil and was diluted using hexane as solvent in 50 wt% dilution. The mixture was centrifuged at 12,000 rpm for 2 h. The supernatant was discarded and remaining residue of soot was washed with hexane, which was followed by centrifuging at 12,000 rpm for 2 h. This process was repeated until oil was removed completely and constitute crankcase soot. In addition, a black color substance stuck on the top land, the second land, the third land, under crown and cylinder wall areas was scrapped off using spatula. This black color substance was diluted with hexane as solvent in 50 wt % dilutions. A similar centrifuging method was used, as mentioned above, to remove oil. The residue from the centrifuging operation was further cleaned using a Soxhlet extraction method for 48 h using hexanes as solvent. The extracted black color substance was then dried and ground using a mortar and a pestle to break up the agglomerates for further analysis. Since it was scrapped off from the various areas of piston and cylinder, hereafter it is referred to as “cylinder soot”

2.2. XANES spectroscopy

XANES experiments were carried out at Canadian Light Source, Saskatoon, Canada, using the 2.9 GeV storage ring and at The Synchrotron Radiation Center, Wisconsin, Madison, using the 800 MeV storage ring. Three beam lines were used at Canadian Light Source to obtain K and L shell absorption edge spectra. Phosphorous, sulfur and calcium K absorption edges were recorded using the Soft X-ray Micro-characterization Beam line (SXRMB) covering region of 1700–10,000 eV with photon resolution of 0.2 eV and beam spot size of 4 mm $\times$ 300 μm. Phosphorus and sulfur L-edge spectra were obtained using the Variable Line Grating-Plane Grating Monochromator (VGM-PGM) beam line covering region of 5–250 eV with photon resolution of 0.2 eV. The PGM beam spot size is 500 μm $\times$ 500 μm. Zinc L edge spectra were obtained using the Spherical Grating Monochromator (SGM) beam line that covers the energy range between 250 and 2000 eV with photon resolution of 0.2 eV in 100 μm $\times$ 100 μm spot size. XANES spectra were acquired using a Total Electron Yield (TEY) mode and a Fluorescent Yield (FY) mode. Calcium L edge was obtained at the Synchrotron Radiation Center (Wisconsin, Madison) using HERMON beam line covering 64–1400 eV with 0.2 eV resolution.

2.3. High resolution transmission electron microscopy

High-resolution transmission electron microscopy of the diesel soot was conducted using a Hitachi H-9500 microscope at an accelerating voltage of 300 kV with a lattice resolution of 0.18 nm. High-resolution lattice images of crystalline nanoparticles and the turbostratic structure of soot were acquired. Energy-dispersive X-ray spectra were acquired from selected regions to determine the chemical makeup of different regions within the soot particles.

2.4. Scanning electron microscope (SEM)

A Hitachi S-3000N variable pressure scanning electron microscope was used to acquire the magnified image of wear tracks. Samples were kept under high vacuum and secondary electron beam was focused on the wear tracks to acquire the image. Wear track image was acquired at 1000 $\times$ magnification.

3. Experimental results

3.1. Phosphorous L edge

Phosphorous L edge XANES spectra recorded in Total Electron Yield and Fluorescence Yield modes on crankcase soot, cylinder soot and tribofilm of piston ring are shown in Fig. 1. The L-edge for phosphorus probes electronic transitions from the 2p orbitals to unoccupied higher levels and d orbitals [24]. The P L-edge TEY absorption spectra provide information from the top 5–10 nm [25] compared to the P K-edge TEY spectra, which provides information from the top 100 nm. To help elucidate the chemistry of the soot samples and tribofilm sample, we compare the spectra of the soot