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Characteristics of diesel engine soot that lead to excessive oil thickening

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ABSTRACT

This is a study of soot from a heavy duty diesel (HDD) engine test designed to evaluate the soot handling ability of a lubricant. This study aims to understand what properties of diesel soot produced under certain conditions contribute to loss of viscosity control through examination of the morphology, nanostructure and oxygen functionalization of particulates obtained from two heavy duty diesel engine tests with different levels of EGR. Particulate samples obtained from the used engine oil that lost viscosity control at relatively low soot levels showed that the soot in this case was more graphitic and had lower oxygen functionalization.

1. Introduction

Engine oils used in diesel engines are composed of a base oil and additives such as detergents and dispersants. The dispersants help maintain soot and other insoluble products of combustion in suspension. Dispersant is composed of a polar head, which adsorbs on the soot surface and a long chain moiety, which prevents soot particles from coming in contact with each other.

To meet heavy duty diesel engine emission regulations, engine manufacturers are incorporating exhaust gas recirculation systems in their engines. In these systems, a portion of the exhaust gas is cooled and recirculated to the intake of the engine. Under these conditions, severe increase in the engine oil viscosity has been observed even at relatively low soot levels (Fig. 1).

The driving force behind this phenomenon is not well understood. Possible scenarios driving the loss of viscosity control include: (i) competitive reactions between dispersant and other polar lubricant additives such as the detergent for sites on the surface of the soot, (ii) the production of 'unreactive' soot, which does not readily adsorb dispersant, or (iii) changes in temperatures bringing about dispersant desorption from the soot surface.

This study pursues the second scenario. It is proposed that soot produced during a heavy duty diesel engine test with EGR is 'unreactive' leading to poor surface coverage by the dispersant (Fig. 2), thus, allowing particle agglomeration to occur. 'Unreactive' soot could mean two things: either the soot is graphitized (structural impediment to dispersant function) or has low surface oxygen content (chemical impediment to dispersant function).

The extent of graphitization of soot determines soot reactivity [1]. Graphitization of soot is determined by the length and orientation of graphene layers comprising the soot nanostructure. The surface oxygen functionalization refers to the amount of oxygen bonded to the soot surface. It is well established that oxygen surface complexes mediate soot–dispersant reactions. Therefore, along with the nanostructure, the surface oxygen functionalization of particulate samples will be examined.

The nanostructure of soot depends on its origins and thermal exposure. The degree of graphitization refers to the length and orientation of graphene layers, which make up the soot primary particle. With increasing graphitization, graphene layer dimensions become larger and curvature is decreased. In addition, interlayer spacing of carbon sheets approach spacing observed in the graphite lattice [2].

The degree of graphitization influences the soot surface properties. Studies of highly oriented pyrolytic graphite (HOPG) show that it has high structural uniformity and surface homogeneity and in turn, reacts poorly with other molecules [3]. Similarly, more graphitized soot is less reactive than its amorphous counterpart [1]. It follows that more graphitic soot is less reactive with the dispersant molecules in an engine lubricant.

The increased reactivity of less graphitic soot is explained by the edge carbon atom density. Edge carbon atoms are the carbon atoms on the exterior of the polyaromatic layers (Fig. 3). They are typically aryl C–H atoms and are more reactive than basal carbon atoms because of greater accessibility and partial saturation of valences. Hence, they are predominantly sites for hydrogen atom

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extraction and O_2 and OH addition [1,3]. In disordered carbons, the edge carbon atom density goes up. In turn, the overall reactivity of the carbon increases.

A soot dispersant molecule consists of a polar group and a high molecular weight non-polar group. The polar group associates with a soot particle, while the nonpolar group keeps the particles suspended in the oil. Soot–dispersant interactions are mediated by polar atoms or groups on the soot surface. As such, polar oxygen complexes on the soot are binding locations for dispersant. Examples of such groups are shown in Fig. 4.

Soot particles consist of 80–90 wt% carbon. Thus, concentrations of other atoms are low. However, they tend to concentrate at the soot surface giving the particles their polarity [4]. After surface oxidation of graphitic carbons, oxygen functional groups are found predominantly at edge carbon atoms [5]. Likewise, in diesel soot, it is expected that oxygen groups will largely be at edge carbon atoms. The level of surface oxidation of soot is also dependent on temperature and gas phase species concentration. As a result, engine operating conditions, which control temperature and species concentration in the cylinder, likely influence soot surface oxidation and ultimately, dispersion in engine oil (Fig. 4).

The impact of engine parameters, design and operating conditions on soot related engine oil viscosity increase has been studied for over two decades [6–12]. Covitch et al. [6,7] investigated the effect of fuel chemistry and injection timing on the severity of Mack T-7 engine tests. Findings indicated higher API gravity fuel resulted in lower lubricant viscosity increase at the end of the 150 h test. In addition, they found advancing injection timing for a given fuel resulted in higher viscosity increase [6,7]. A decade later, Bardasz et al. studied oil thickening in different engines and with varying operating conditions [8–11]. They determined oil viscosity growth is dependent on both engine type and operating conditions. Recently, Penchaliah et al. observed that among four contaminants in a lubricant (soot, oxidation, moisture and sulfuric acid), oxidation and soot exhibited the largest impact on viscosity [13].

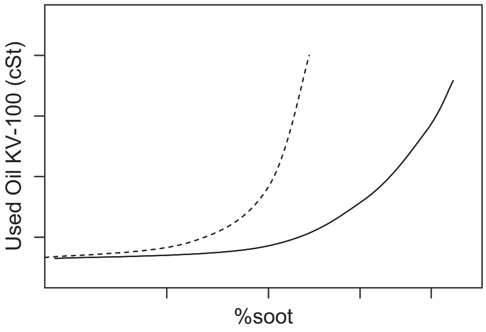

Fig. 1. Representation of the rapid increase (- - - -) in oil viscosity in a heavy duty diesel engine test compared to more desirable viscosity control (—).

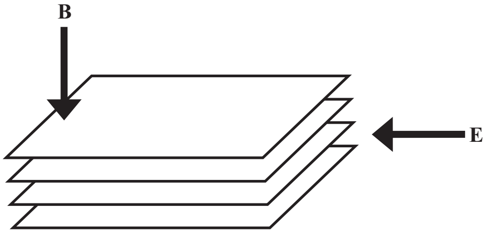

Fig. 3. Sketch of the basal and edge planes of the graphitic domain.

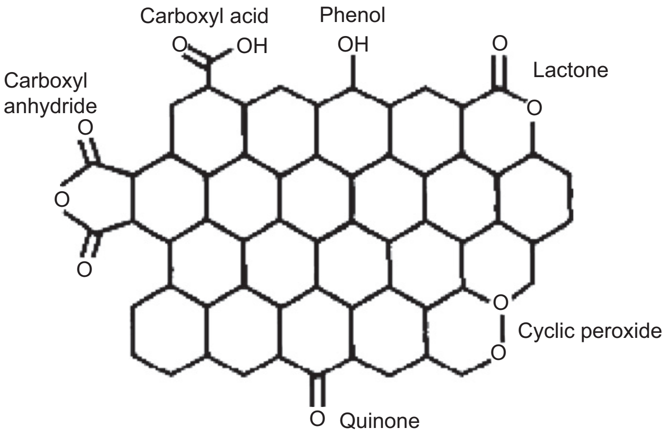

Fig. 4. Sketch of various surface oxygen complexes that may be present in carbon structures.

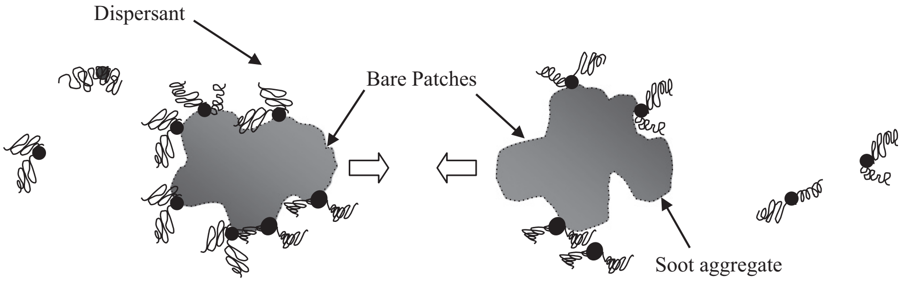

Fig. 2. Sketch depicting incomplete surface coverage by the dispersant allowing soot agglomeration to occur.

Growth in soot aggregate size and concentration in engine oil contribute to viscosity increase. Experimentation with oil formulations demonstrated that basic lubricant additives control soot particle growth more effectively. Increasing dispersant levels or total base number better controlled the viscosity changes [9]. These findings suggested soot–dispersant reactions are similar to acid base reactions [7,9].

In the past, the dependence of engine oil viscosity increase on particle size and concentration has been studied without much consideration to the underlying properties of soot. Earlier work has been limited to transmission electron microscopy (TEM) and quasielastic light scattering (QELS). Consequently, previous work has not addressed why at similar soot levels, more severe particle agglomeration and in turn, viscosity increase can occur.

The literature contains extensive studies of soot nanostructure. Methods such as near-edge X-ray absorption fine structure spectroscopy (NEXAFS) [14–17], high resolution transmission electron microscopy (HRTEM) [18–22], electron energy loss spectra (EELS) [22] and Raman spectroscopy [22–24] are utilized to probe soot nanostructure providing information about the degree of graphitization whether quantitatively or qualitatively. HRTEM