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On the tribochemical action of engine soot

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ABSTRACT

The tribological behaviour of soot was studied by means of a pin-on-disk tribometer coupled to a high-resolution wear measurement system (RNT). The soot particles were characterized by high-resolution transmission electron microscopy (HRTEM), energy electron loss spectroscopy (EELS), electron spin resonance (ESR) and X-ray photoelectron spectroscopy (XPS). The surfaces of the tribometer disks were analyzed by atomic force microscopy (AFM), Auger electron spectroscopy (AES) and prepared with focused ion beam (FIB) for high-resolution transmission electron microscopy (HRTEM). Our results show that wear does not depend on the mechanical properties of different soot particles, but is closely related to their reactivity and the amount of defect sites. A new wear model for Otto soot is proposed.

1. Introduction

Whether soot particulate emissions have a detrimental effect on the life of internal combustion (ic) engines, and how pronounced this effect is, has been disputed for a long time and continues to be of high interest to car manufacturers. Many conflicting, incomplete ideas and explanations about the properties and effects of soot particulates on the wear mechanism have been published. Rounds [1,2] showed that soot is not abrasive but adsorb anti-wear additives, thus diminishing anti-wear properties. Ryason et al. [3], however, concluded that soot particles are abrasive because they were found to generate grooves and breakouts in metal surfaces. The same idea was held by Nagai et al. [4] who showed that soot particles are very hard and act abrasively on metal surfaces. The authors also found that intensified exhaust gas recirculation (EGR) raises the soot concentration in oil, thus enhancing wear. Ratoi and Spikes [5] showed that dispersed Carbon Black rapidly abraded zinc dialkyldithiophosphate (ZDDP) reaction films. Gautam et al. [6] found more wear with soot contamination of the oil than without. Moreover, it was seen that higher soot concentrations in oil generates more wear whereas a higher concentration of phosphorus in the oil leads to less wear. Soejima et al. [7], Yamaguchi et al. [8], and Aldajah et al. [9] found that the presence of soot particles reduces the thickness and extension of anti-wear films and are abrasive. Truhan et al. [10] concluded that the chemical activity of soot particles and their reaction with ZDDP prevents the formation of liquid boundary layers on metal surfaces.

Part of the controversy found in the literature arises from the fact that the properties of soot particulate emissions very much depend on the thermodynamics of combustion in the engine and, consequently, on the final structure of carbonaceous matter, such as the average primary particle and aggregate sizes and size distributions, polydispersity, and the degree of graphiticity. This determines the rheological properties. The structural complexity of soots varies depending on the type of engine and its operating conditions. The same holds for experiments with well-defined industrial Carbon Black varieties which were used for controlled modification of the rheological properties of engine oils modified by adding specific quantities of a specific grade of Carbon Black. A wide variety of synthetic Carbon Black very different in size and structure are commercially available. Comparability of the findings about the influence of carbonaceous matter on oils makes it imperative that the same grade of Carbon Black is used in the experiments.

It must also be noted that the properties of soots vary, as is shown by comparing soot collected from the exhaust system of a passenger car with and without catalytic converter, on the one hand, with soot collected from the piston and the oil, on the other hand. In this study, this uncertainty is avoided by focusing on particulates collected right from the oil under identical conditions [11].

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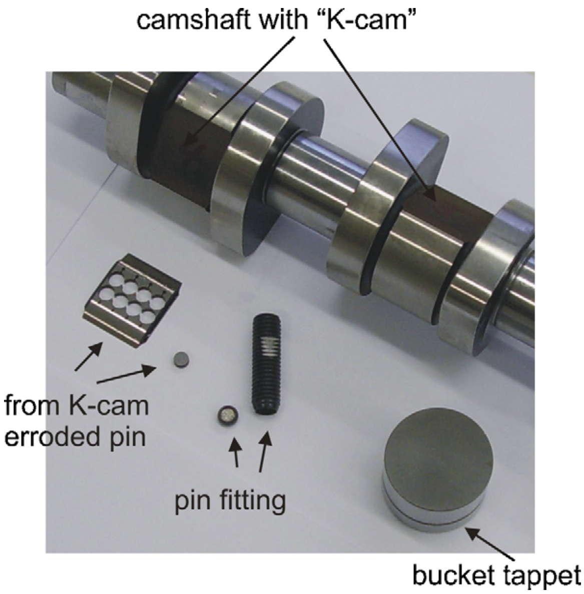

Fig. 1. Camshaft from K-cam eroded pin, pin fitting and bucket tappet.

It can be concluded from the literature that the wear mechanism induced by the presence of soot is not fully understood yet. More fundamental knowledge is needed. Thus, the properties of soot and their influence on wear were in the focus of our studies.

This study examined the effect of different types of soot on the wear of cam and cam follower materials. A pin-on-disk test was employed because this tribo-system has unidirectional motion. A variety of analytical techniques were employed to measure soot morphology and chemical properties, friction, wear and chemical reactions on the wear surfaces.

2. Experimental details

2.1. Materials and oils

In all tribological experiments (Fig. 1), a case-hardened pin (16MnCr5) 5.2 mm in diameter eroded from the K-cam of a camshaft was run against a nitrided disk (bucket tappet); various fully formulated commercial lubricants (Fuchs Titan 5W30) were used.

The oils used for the tribological tests were fresh oil, Carbon Black oil, Carbon Black centrifuged oil, and two oils which were loaded with soot by dynamometer engine tests and sampled at different running times. One set of oil samples were aged using a spark ignition internal combustion (ic) engine which uses the thermodynamic Otto cycle and one set which was generated by an auto ignition ic engine in a Diesel cycle. We will refer to these oils in short as Otto and as Diesel engine oil. Carbon Black oils were obtained as concentrates (Mira Corp.) and then diluted with fresh oil. The concentration of soot in the oils is shown in Table 1.

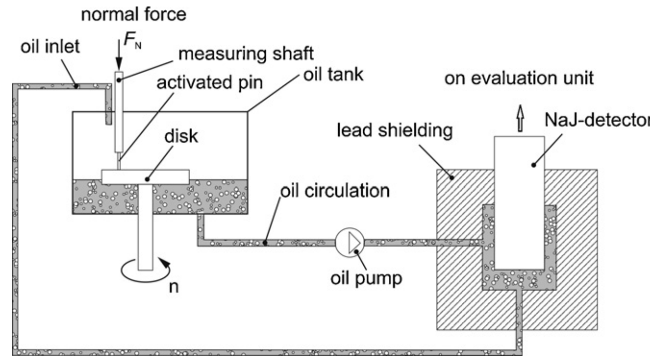

Fig. 2. Schematic representation of the setup for the pin-on-disk wear testing machine.

2.2. Pin-on-disk tribometer

A custom-built pin-on-disk tribometer (Fig. 2) was employed for the tribological experiments. Wear was measured continuously by the radionuclide wear measurement technique [12]. The nominal contact pressure in all experiments was 13 MPa; the sliding velocity 0.3 m/s; the oil temperature was kept constant at 120 °C; and the duration of all experiments was 40 h.

2.3. Analytical methods

High-resolution transmission electron microscopy (HRTEM; Jeol 2010F) was used to study the nanostructure and the surface structure of soot particles as well as the surface structure of the tribometer disks on the first nanometer of the surface. HRTEM was accompanied by electron energy loss spectroscopy (EELS) to obtain information about the binding of carbon atoms to their nearest neighbours. EELS spectra supplied additional information about the morphology and elemental composition of the soot samples.

Electron spin resonance (ESR) furnished information on the number of unpaired electrons within the soot particles. The spectra were recorded by an ELEXSYS 500-10/12 spectrometer with a frequency of 9.5 GHz at 77 K and room temperature.

X-ray photoelectron spectroscopy (XPS; Leybold MAX 100) was conducted to study the chemical composition and chemical states in the topmost atomic layers of soot particles.

Atomic force microscopy (AFM; Veeco Dimension 3100) was used to analyze the topography of the wear track.

Depth profiles of the elemental composition on the first 100 nanometers of the disks were measured by Auger electron spectroscopy (AES; Auger Nanoprobe PHI 680).

In addition to AFM and AES, lamellae of the tribometer disks for high-resolution transmission electron microscopy (HRTEM) were prepared by the focused ion beam technique (FIB; FEI Strata FIB 205).

Table 1
Soot concentration in oils used for wear tests.

Name	Soot concentration (wt.%)	Phosphor (mg/kg)	Silicium (mg/kg)	Sulphur (mg/kg)
Fresh oil	0.00	641	<10	2100
Carbon Black (CB)	1.01	628	8	2170
CB centrifuged	0.01	630	3	2090
Diesel engine oil	2.61	542	59	1560
Diesel engine oil	4.72	970	26	1990
Otto engine oil	0.54	469	41	1540
Otto engine oil	0.94	582	41	1950