

Analysis and Method of Quantification of Soot in Engine Oil

Yosuke OKUYAMA*
Wataru HOSHIKAWA*

Daichi SHIMOKOJI*
Ryuuji MATSUKADO*

Masashi MARUYAMA*

ABSTRACT

Soot in engine oil was isolated using a centrifuge and subjected to an intensive analysis. The atomic bonds of the carbon in the soot discharged from the engine under various driving conditions were analyzed, and it was determined that the greatest proportion of the bonds were C-C (carbon-carbon) sp^2 (graphite structure) bonds and H-C (hydrogen-carbon) bonds, with few C-C sp^3 (diamond structure) bonds.

It was shown that the ratio of H and C atoms (the H/C mole ratio) could be used as an alternative indicator for the hardness of the soot. In addition, the project studied the correlation between this alternative indicator of soot hardness and sliding wear in the engine.

A method of removing soft impurities and quantifying the soot components in isolation was also studied as a means of more precisely determining this correlation.

1. Introduction

Attention is today being focused on diesel engines, due to their significant effect in reducing CO₂ emissions. While they do emit less CO₂, diesel engines are also known to emit soot. The soot emitted from the tailpipes of diesel engines is a factor in pollution of the atmosphere^{(1),(2)}. Soot that infiltrates the crankcase as a blow-by gas mixes with engine oil and promotes sliding wear, resulting in a decline in engine durability^{(3),(4)}. Soot production can also increase in gasoline engines, for example when direct injection is used, and is known to promote sliding wear in these cases⁽⁵⁾.

Numerous papers have discussed the wear resulting from soot in engine oil as abrasive wear⁽⁶⁾. The particle diameter, hardness, and quantity of the soot are generally considered to be the factors influencing the degree of wear produced by the soot under conditions of engine lubrication⁽⁷⁾.

However, while many papers have pointed out the correlation between the particle diameter and quantity of soot and the level of sliding wear, almost none have

touched on the correlation between the hardness of soot and sliding wear^{(8),(9)}. This can be considered to result from the fact that because soot particles are microscopic, it is challenging to directly measure their hardness, and the extraction of individual soot particles from engine oil for measurement is impractical.

The research discussed in this paper analyzed the abrasive wear produced by soot in engine oil in relation to particle diameter, hardness, and quantity, the properties of the soot considered to be most relevant. In particular, the research determined an alternative indicator of soot hardness that displays a good correlation with sliding wear. In addition, the research proposed a new method of quantification enabling evaluation of the hard components of the soot, which have a significant effect on wear, in isolation.

2. Method of Procedure

It is necessary to focus on particle diameter, hardness, and quantity in order to understand the sliding wear produced by soot in engine oil. In the present research,

* Automobile R&D Center

the distribution of the particle diameters of the soot in engine oil was first analyzed, and the degree of effect on sliding wear within that distribution was determined. Next, to enable an indicator of soot hardness to be formulated, soot was extracted from engine oil and the atomic bonds and composition of the soot were analyzed.

In order to verify the validity of the alternative indicator, engines were subjected to bench durability tests and the correlation between hardness and wear was determined. Finally, focusing on the effect of the quantity of soot, a method of removing soft impurities from the soot to isolate the hard soot components that were considered to more readily promote wear was studied.

3. Tests

3.1. Analysis of Soot Particle Diameter

Engine oil containing soot was diluted with toluene, and laser diffraction scattering was employed to measure the distribution of particle diameters.

3.2. Unit Wear Tests for Particles of Different Diameters

Carbon black of different average particle diameters with a similar structure to soot was prepared and used in unit wear tests in order to determine the effect of soot particle diameter on wear. Block-on-ring and shell-four-

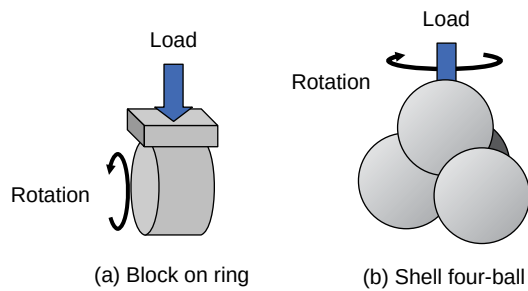


Fig. 1 Schematic of wear tester

Table 1 Wear test conditions

	LFW-1	Shell four-ball
Engine oil	ILSAC GF-4, 0W-20	ILSAC GF-4, 0W-20
Carbon black concentration (wt%)	0.2	0.2
Mean carbon black particle diameter (nm)	66, 95, 122	66, 95, 122
Load (N)	100	441
Operation time (min.)	180	60
Oil temperature (°C)	80	80
Rotation speed (rpm)	400	1200

ball tests were selected for employment. Figure 1 shows a schematic of the block-on-ring and shell-four-ball tests. Table 1 shows test conditions.

3.3. Method of Extraction and Quantification of Soot

A number of methods are available for quantitative analysis of soot in engine oil, including infrared spectroscopy, TG, and centrifugation⁽⁸⁾⁻⁽¹⁰⁾. Centrifugation was selected for use in the present research, because it enabled soot to be extracted and the properties of the extracted soot to be analyzed following quantitative analysis.

The research employed a centrifugation method in which the pentane-insoluble fraction extracted at a relative centrifugal force of 20 000 G was defined as the quantity of soot⁽¹¹⁾. In addition, the substitution of trichloromethane for pentane in order to remove the sludge precursors in the extracted insoluble fraction was also studied as a proposed method of quantifying soot in engine oil. Figure 2 shows the flow of procedures in the pentane-insoluble and trichloromethane-insoluble methods.

3.4. Analysis of State of Atomic Bonding in Soot

Electron energy loss spectroscopy (EELS) analysis is sometimes employed to identify the structures of representative carbon materials such as DLC⁽¹²⁾. In a broad

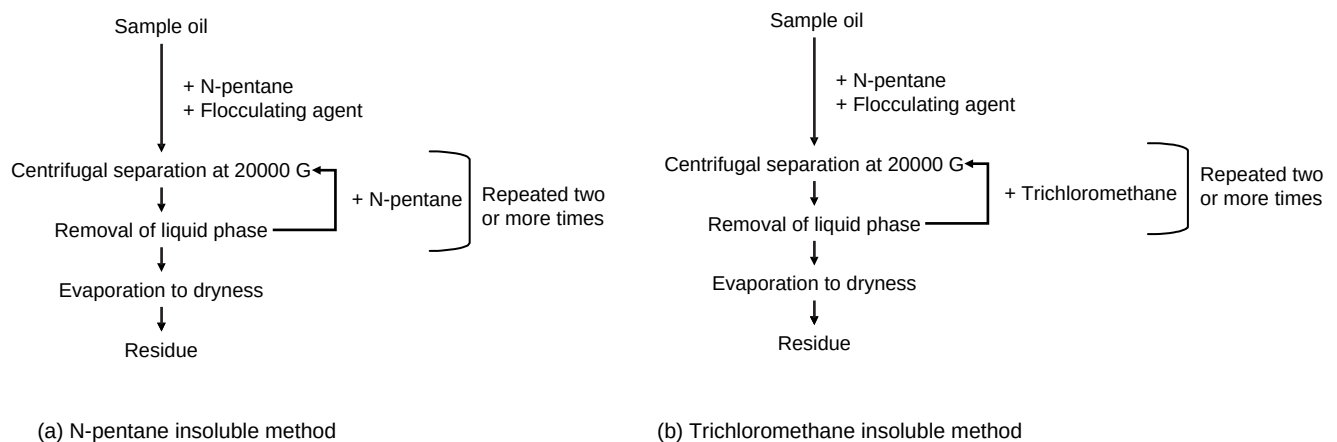


Fig. 2 Experimental procedure of soot quantitative analyses

Table 2 Engine specifications and test condition

Engine specs.	Number of cylinders and configuration	Inline 4
	Displacement	2354 cm ³
	Bore	87.0 mm
	Stroke	99.0 mm
	Compression ratio	10.5
Test condition	Speed	5000 rpm
	Grade	ILSAC GF-4, 0W-20
Engine oil	Spurious soot concentration (C element)	0.4 wt%
	Mean spurious soot particle diameter	100, 100, 120 nm

sense, the extracted soot can be taken to be a carbon material. An auger electron spectroscopy/reflection electron energy loss spectroscopy (AES-REELS) analysis was therefore conducted on the extracted soot.

Figure 3 shows the principle of AES-REELS. An electron loss energy near structure (EELS) spectrum with the background removed, representing the low energy loss side of the EELS spectrum, was obtained from the electron energy loss spectrum for the extracted soot. Using the spectra of diamond and graphite as benchmark materials, and glassy carbon as an amorphous carbon, a peak fit was performed using the method of least squares. The ratio of hydrogen-carbon (H-C), carbon-carbon (C-C) sp^2 , and carbon-carbon (C-C) sp^3 bonds in the extracted soot was estimated from the peak fit results.

3.5. Analysis of Soot Composition

The insoluble fractions extracted by centrifugation were burned to enable analysis of the organic elements composing them.

3.6. Bench Engine Durability Test Using Oil with Added Artificially-produced Soot

Engine oils to which carbon black had been added were used in a durability test on a K24A engine. Table 2 shows the engine specifications, test conditions, engine oil grade, and carbon black properties.

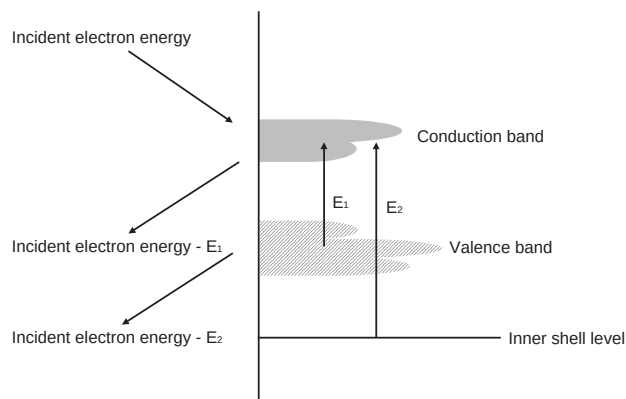


Fig. 3 Principle of EELS (schematic of energy loss and transition process in EELS)

4. Results and Considerations

4.1. Analysis of Properties of Soot in Engine Oil and Determination of Hardness Indicator

Figure 4 shows the results of measurements of the mean particle diameter of soot in engine oils recovered from the market, for both gasoline and diesel engines. Figure 4 indicates that in the case of both gasoline and diesel engines, the mean diameter of soot discharged from the engine that has accumulated in the engine oil is roughly 100 nm.

Unit wear tests were next conducted using carbon black of different mean diameters in order to determine the effect of changes in the diameter of soot particles on wear. Figure 5 shows the results of these unit wear tests. As Fig. 5 shows, under block-on-ring and shell-four-ball sliding conditions, changes in the particle diameter did not produce any observable effect on wear.

Next, the atomic bonding state of the pentane-insoluble fractions, extracted from the engine oils that were recovered from the market, was analyzed in order to determine an indicator for hardness. Figure 6 shows a three-dimensional phase diagram generated from the results of AES-REELS analysis of the pentane-insoluble fractions. The phase diagram shows that if the ratio of C-

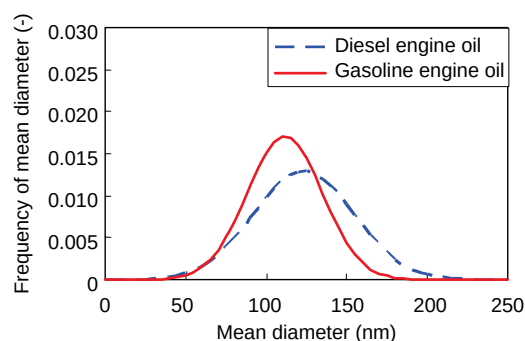


Fig. 4 Field research on mean soot particle diameter in recovered deteriorated diesel and gasoline engine oil

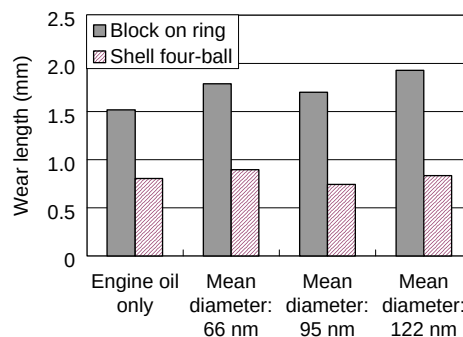


Fig. 5 Wear tester result with carbon black of different mean diameters

C sp^3 bonds increases, the structure becomes closer to that of diamond, and the substance becomes ultra-hard. If the ratio of C-C sp^2 bonds increases, the structure becomes closer to that of graphite, and the substance becomes hard.

However, if the ratio of H-C bonds increases, the substance should become soft. As Fig. 6 shows, analysis of the bonding state of carbon atoms in soot discharged from the engine that had accumulated in engine oil indicated that the soot contains few C-C sp^3 bonds, and a high proportion of C-C sp^2 and H-C bonds. In addition, the distribution width of the C-C sp^2 bond / H-C bond ratio is greater than that of the C-C sp^2 bond / C-C sp^3 bond ratio. Given this, it was conjectured that understanding the ratio of C-C bonds and H-C bonds would be more important than conducting a detailed analysis of the state of C-C bonds in developing an index for the relative hardness of the pentane-insoluble fraction in engine oil. The project therefore focused on the mole ratio of carbon and hydrogen atoms (the H/C mole ratio), and verified the usefulness of the H/C mole ratio as an alternative indicator for hardness. Specifically, artificially-produced soots with different H/C mole ratios were used in engine bench durability tests, and the existence of a positive correlation between the H/C mole ratio and engine sliding wear was demonstrated.

4.2. Verification of Validity of Hardness Indicator in Engine Durability Tests

Three types of artificial soot were prepared and added to engine oils to produce carbon concentrations of 0.4 wt%. These oils were used in engine bench durability tests. The inner rotor of the oil pumps was studied to quantify the level of engine wear. Figure 7 shows a photograph of the complete oil pump. When wear progresses in the inner rotor, the oil pressure in the main

gallery declines. This decline occurs because of idling of the oval-shaped shaft that penetrates the inner rotor and is used for rotor drive. Figure 8 shows photographs of inner rotors following the completion of durability tests. As Fig. 8 shows, there was conspicuous wear of the interiors of the inner rotors for artificial soots with H/C mole ratios of 0.35 and 0.5. No wear could be found in the case of the artificial soot with a H/C mole ratio of 0.6 after 150 hr of testing. These results can be considered to indicate that the earlier the decline in oil pressure occurs, the more severe the wear.

Figure 9 shows the correlation between the time elapsed in durability tests until the decline in oil pressure occurs and the H/C mole ratio. Figure 9 indicates that there is a tendency for the time elapsed until the oil pressure drop to become shorter and the degree of wear more severe the lower the H/C mole ratio and the higher the carbon ratio of the soot. A precise correlation can therefore be established between the H/C mole ratio of the pentane-insoluble fraction of the soot and engine wear, and it can therefore be considered to represent an effective indicator of hardness.

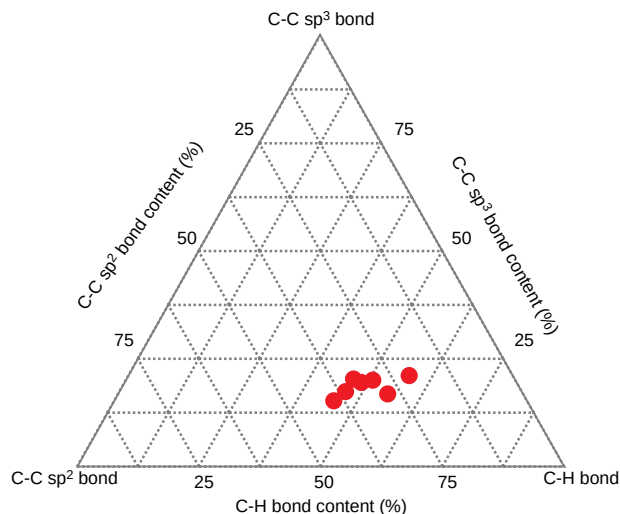


Fig. 6 Phase diagram of carbon atom binding state in soot

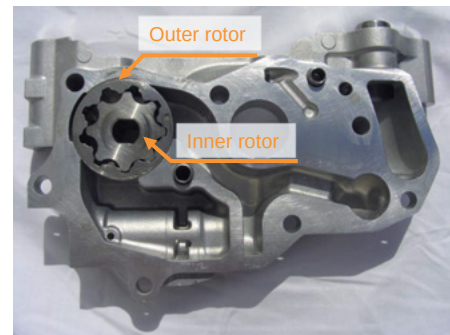


Fig. 7 Oil pump

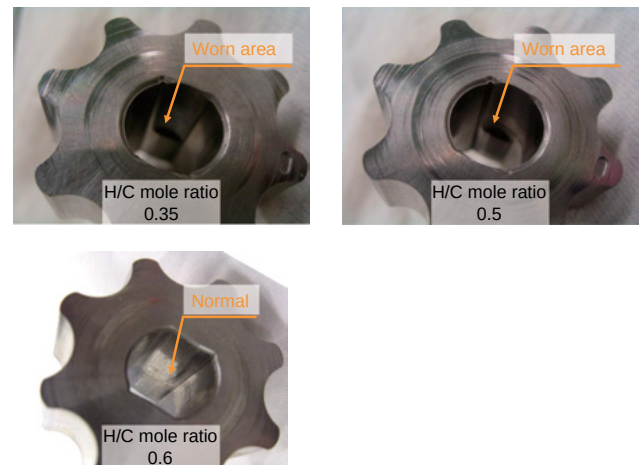


Fig. 8 Worn parts

4.3. Study of Method of Quantification of Soot that Evaluates Hard Components Only

As indicated above, the difference in H/C mole ratios represented an issue when determining a correlation between the quantity of pentane-insoluble substances in engine oil and engine wear. This can be considered to be due to the fact that sludge precursors were extracted from the oil together with the soot. A method of minimizing differences in the H/C mole ratio of the substances extracted from the oil by removing sludge precursors as much as possible and extracting pure soot was therefore proposed.

Figure 10 shows the H/C mole ratios of pentane-insoluble fractions and trichloromethane-insoluble fractions extracted from diesel vehicle and gasoline vehicle engine oils recovered from the market. As Fig. 10 shows, the H/C mole ratios of the trichloromethane-insoluble fractions display a sharper distribution curve than those of the pentane-insoluble fractions. This indicates that the method of using trichloromethane-

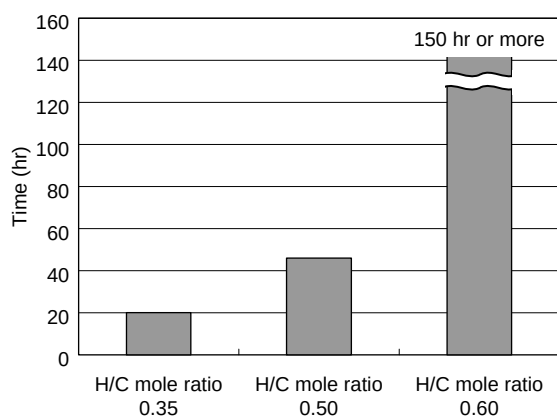


Fig. 9 Time until oil pressure reduction with soot of different H/C mole ratios

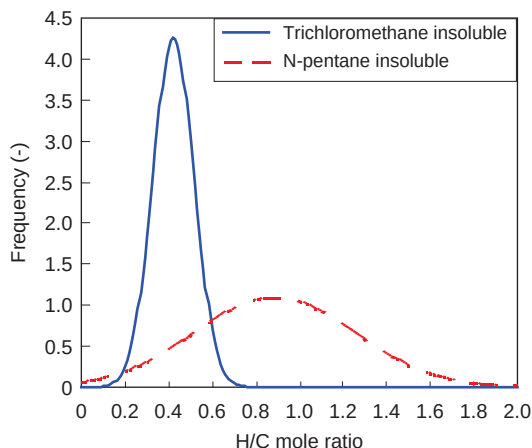


Fig. 10 Result of H/C mole ratio analyses with trichloromethane and n-pentane insoluble

insoluble fractions enables selective quantification of hard soot components and the more precise establishment of a correlation with wear.

5. Conclusion

- (1) It was found that the carbon atoms in soot in engine oil display few carbon-carbon sp^3 bonds (diamond-structure) and a large proportion of carbon-carbon sp^2 (graphite structure) and hydrogen-carbon bonds.
- (2) A correlation was determined between the H/C mole ratio and engine wear, and the H/C mole ratio can therefore be considered a useful indicator of the relative hardness of soot in engine oil.
- (3) The removal of sludge precursors by means of centrifugation using trichloromethane was found to be a useful method of quantification of soot in engine oil.

References

- (1) Chiba, I., Kaneko, I., Matsui, R., Ishihara, Y., Matsukado, R.: Development of Low Emission Diesel Engine with DPF System, Honda R&D Technical Review, Vol. 17, No. 2, p. 65-70
- (2) Kanda, T., Kobayashi, S., Matsui, R., Sono, H.: Combustion Technologies for Euro IV-compliant Direct Injection Diesel Engine, Honda R&D Technical Review, Vol. 16, No. 2, p. 139-146
- (3) Jao, T.: Soot Characterization and Diesel Engine Wear, ITC Nagasaki, p. 1981-1986 (2000)
- (4) Kurihara, I.: Dizuru Enjinyu no Kaihatsu Doukou to Yuchusuno Konntoruru Gijutsu, Nisseki Mitsubishi Technical Review, Vol. 43, No. 4, p. 168-174 (2001) (in Japanese)
- (5) <http://www.jsae.or.jp/08std/std03.html>, JSAE Hyojunka Chosa Houkokusho, Enjinnoiru Bunnkakai, May 2005- Feb. 2006, Gasorine Enjinnyu Mamoushikennhou Hyojunka Chosa (in Japanese)
- (6) Yamamoto, H.: Research on Hardness of Soot Contaminated in Diesel Engine Oil, JSME annual meeting 2003(3), p. 137-138 (2003)
- (7) Sasada, T.: Effect of Dust Particles on Wear of Materials, Proceedings of JAST Tribology Conference (Tokyo), p. 25-26 (2008)
- (8) Kagaya, M.: Study on Diesel Soot (Part I), Journal of the Japan Petroleum Institute, Vol. 40, No. 5, p. 482-487 (1997)
- (9) Kagaya, M.: Study on Diesel Soot (Part II), Journal of the Japan Petroleum Institute, Vol. 40, No. 5, p. 488-493 (1997)
- (10) Kagaya, M.: Study on Diesel Soot (Part III), Journal of the Japan Petroleum Institute, Vol. 40, No. 5, p. 494-499 (1997)
- (11) <http://www.jsae.or.jp/08std/std03.html>, JSAE Hyojunka Chosa Houkokusho, Enjinnoiru Bunnkakai, May 2006- Feb. 2007, Jidoushayou Gasorinn

Enjinnkikann Junnkatsuyu no Chehnnmamou
Shikennhouhou Kaihatsuno Hitsuyousei Kenntou (in
Japanese)

- (12) Watabe, T.: The Application of AES-REELS in the Study
of the Chemical Bonding State and Structural Analysis
of Carbon Materials, Kobe Steel Engineering Repots,
Vol. 55, No. 1, p. 65-69 (2005)

■ Author ■



Yosuke OKUYAMA



Daichi SHIMOKOJI



Masashi MARUYAMA



Wataru HOSHIKAWA



Ryuuji MATSUKADO