

# Wear and electrical resistance on diesel lubricated surfaces undergoing reciprocating sliding

R.M. Crockett\*, M.P. Derendinger, P.L. Hug and S. Roos

Swiss Federal Laboratories for Material Testing and Research (EMPA), Ueberlandstrasse 129, 8600 Dübendorf, Switzerland

Tribological tests, using the high-frequency reciprocating rig (HFRR), were carried out on commercial diesel fuels with a range of lubricities as well as on solutions of methyl stearate and stearic acid in ultra-low-sulphur, additive-free diesel. The surfaces of discs used in the HFRR tests were measured with micro-Raman and time-of-flight secondary ion mass spectrometry (ToF-SIMS). These measurements showed that amorphous carbon was formed during reciprocating sliding, the structure of which was related to the lubricity as measured by the average wear scar on the ball. Magnetite ( $\text{Fe}_3\text{O}_4$ ) and hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) were also detected on the surfaces. In most cases, the detection of hematite in the wear track was also associated with low wear. However, hematite was found in the wear particles of all samples. The build up of a film, measured by electrical resistance, was attributed to the presence of hematite, which has a much lower electrical conductivity than magnetite.

**KEY WORDS:** diesel, lubricity, HFRR, tribotesting, wear

## 1. Introduction

The lubricating ability of diesel fuels has been the subject of a large number of investigations since the introduction of low-sulphur diesel [1,2]. Diesel pumps are lubricated by the fuel itself and rapid failure was observed as the natural boundary lubricants were removed from the fuel along with the sulphur [3]. These natural lubricants have been identified as polyaromatics as well as nitrogen- and oxygen-containing organic compounds [4,5]. The sulphur-containing compounds either have an adverse effect [4] or no effect [5] on the diesel lubricity.

As the anti-wear properties of diesel became more important, it was necessary to develop a fast, simple and cost-effective method to determine the lubricity of diesel [3]. The high-frequency reciprocating rig (HFRR), which measures the wear scar corrected for humidity ("WS1.4"), has become a popular tester for diesel fuel lubricity as it is versatile and widely available. The most promising features of the HFRR were the wide range of results obtained for different diesels, demonstrating a good degree of selectivity, and the positive response to boundary additives. However, a comparison of literature data has shown that there is a poor correlation between measurements with HFRR at 60 °C, the temperature used in the standardised test, and pump tests [6]. Analysis of the literature data also indicates a bias in the results. Of those results which do not correlate, a much larger number have good pump ratings and poor HFRR results than have poor pump ratings and good HFRR wear scar

values. This suggests that the HFRR is a more severe method than the pump test.

The mechanisms by which boundary lubricants improve lubrication vary with test methods and operating conditions. On the one hand, monolayers of the additive, usually carboxylic acids or methyl esters, form on the surface; thus preventing contact between the two metal surfaces and reducing wear [7,8]. Under other conditions, the formation of organometallic polymers from carboxylic acids on metallic surfaces has been observed [9]. The generation of iron salts of carboxylic acids, which may form solid lubricating surfaces on the metal, has also been investigated [10].

There have been a few investigations into the nature of the tribological system that is measured in the HFRR test [4,11]. Tests carried out on a hydrocarbon oil (isopar) with reciprocal sliding under different conditions from those generally used in the HFRR test showed that adsorption and decomposition of hydrocarbons led to carbon diffusion into the surface and that this provided some protection against wear [12].

In the HFRR test a steel ball undergoes reciprocating sliding against a significantly softer steel disc immersed in the diesel sample. The extent of wear on the surface of the ball is used as an indication of the lubricating ability of the diesel [13]. The friction coefficient is also measured during the test, as is the electrical resistance, which is given as "film" in percentage (referred to the resistance measurement when the two surfaces are separated as 100%). In the CEC standard for diesel lubricity [13] the "film" is referred to as film thickness. It is generally believed that a high film reading indicates the formation of a tribofilm by reaction of additives or the development of a hydrodynamic film that separates the metal surfaces. As there is no clear definition of what is being measured by "film (%)", a linear relationship

\*To whom correspondence should be addressed. E-mail: rowena.crockett@empa.ch

between the contact resistance and film thickness cannot be assumed.

In this paper, an investigation into the tribological system measured by the HFRR is described. The behaviour of stearic acid and methyl stearate in ultra-low-sulphur, additive-free diesel as well as the base diesel, and a range of commercially available diesels, was studied using micro-Raman and ToF-SIMS, in order to determine the mechanisms of wear. The chemical analyses also allowed insight into the relationship between film thickness, as determined by electrical resistance, and wear.

## 2. Experimental

Lubricity testing was carried out with the high-frequency reciprocating rig (PCS Instruments, London, England) according to CEC F-06-A-96 [13]. In this test, a steel ball is loaded and slides in a reciprocating motion against a stationary steel disc. The ball and disc were both of AISI 52100 steel. The ball had a diameter of 6 mm, a Rockwell C number of 58 to 66 and a surface finish of  $<0.05 \mu\text{m } R_a$ . The disc had a hardness of 190–210 HV30 and a surface finish of  $<0.02 \mu\text{m } R_a$ . In the tests, the discs are fully submerged in 2 mL of diesel fuel, which is maintained at a temperature of 60 °C. The load was 2 N, stroke length 1 mm and the reciprocating frequency was 50 Hz. Unless otherwise stated, the test duration was 75 min. The relative humidity was maintained between 50 and 55%. The ambient laboratory temperature was 22–23 °C. The wear scar values were measured with a microscope and corrected for vapour pressure to give the corrected average wear scar (WS1.4 value) according to the following equation

$$\text{WS1.4} = ((X + Y)/2) + \text{HCF}(1.4\text{-AVP}).$$

Where  $X$  and  $Y$  are the diameters of the wear scar on the ball in perpendicular directions in  $\mu\text{m}$ , HCF is the humidity correction factor in  $\mu\text{m}/\text{kPa}$  (60 for diesel fuel samples), and AVP is the mean vapour pressure during the test in kPa.

The repeatability of the method, which is determined from a round robin program, is given in CEC F-06-A-96 as

$$r = 139 - (0.1648 \times \text{WS1.4}).$$

The corrected average wear scar (WS1.4) is the value used to define the quality of lubrication of diesel fuels. The maximum value of WS1.4 permitted by the European Regulations (EN 590) is 460  $\mu\text{m}$ . The discs were washed with heptane before being measured with micro-Raman or ToF-SIMS.

Time-of-flight secondary ion mass spectra were recorded using a Physical Electronics 7200 ToF-SIMS system (Physical Electronics, Eden Prairie, Minnesota,

USA), equipped with an 8 keV  $\text{Cs}^+$  gun, which produces routine mass resolution on conductive samples of  $m/\Delta m > 5000$  at mass 27 (positive ion spectra). During the data acquisition process, ion doses were kept close to  $1.0 \times 10^{12}$  ions/ $\text{cm}^2$ , well below the static SIMS limit. The mass/charge ( $m/z$ ) range was calibrated using a set of low-mass ion peaks.

Raman spectra were measured with a Renishaw Raman Imaging Microscope (Renishaw plc Transducer Systems Division, Gloucestershire, England), equipped with a near-infrared laser (780 nm). All measurements were carried out with a magnification of 50 $\times$ . The intensities of the peaks were determined by fitting Gaussian curves.

Commercial diesels were obtained from various service stations in Switzerland. The base fuel, ultra-low-sulphur, additive-free diesel (Sweden Class 1, 3 mg/kg sulphur), was obtained from Deutsche Shell GmbH, Hamburg, Germany. Stearic acid ( $\geq 99.5\%$ ) and methyl stearate ( $\geq 99.0\%$ ) were obtained from Fluka Chemie GmbH, Switzerland, and used as received.

## 3. Results

### 3.1. Commercial diesels

There are three parameters given in the results of the measurement of diesel with HFRR. These are WS1.4, which is the measurement of lubricity [13], as well as the average coefficient of friction and the average film thickness over the 75 min that the experiment is carried out. The film thickness is a measure of the electrical resistance during the measurement, where 0% is the resistance when the ball and disc make contact in the absence of diesel and 100% is set with the ball and disc separated from each other. Figures 1 and 2 show the variation of the average film thickness and the average coefficient of friction with WS1.4, respectively, for 100 commercial diesels from service stations throughout Switzerland, measured between 1999 and 2002.

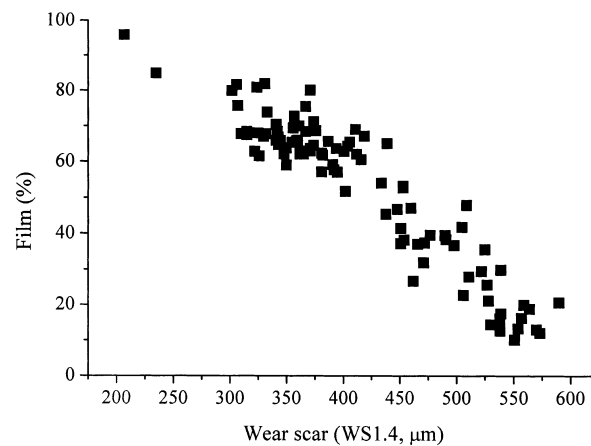


Figure 1. Film, as measured by electrical resistance in HFRR versus wear scar (WS1.4) for 100 commercial diesels.

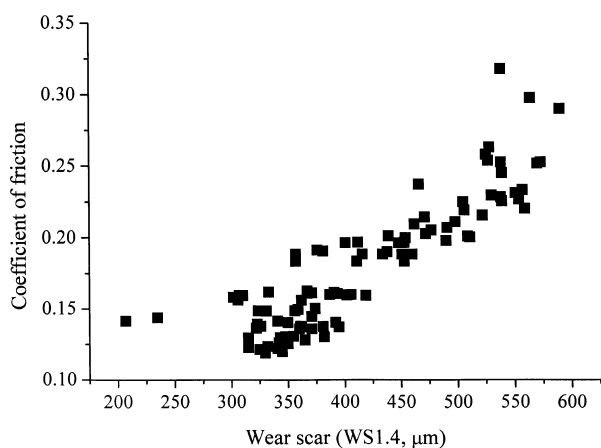


Figure 2. Coefficient of friction versus wear scar (WS1.4) for 100 commercial diesels.

Although the data is scattered, there is a clear trend towards a higher value for film thickness with decreasing wear scar size (WS1.4). Therefore, the data (figure 1) indicate that diesels with good lubricities also tend to result in a high average electrical resistance between the surfaces during the measurement. The average coefficient of friction also shows a trend towards higher values with increasing wear scar (figure 2).

Micro-Raman measurements were carried out for ten commercial diesels, with a range of wear scar values from 315 to 573  $\mu\text{m}$ . All ten of these diesels had sulphur contents lower than 50 mg/kg and showed a good agreement between the wear scar and average film thickness (table 1). Figure 3 shows the surface of the wear tracks on the discs used in the HFRR tests for diesels 1 and 10, taken with scanning electron microscopy.

No peaks were detected in Raman spectra measured outside the area of wear particles on the discs. The Raman spectra showed that the wear particles around the wear track on the discs were very inhomogeneous. Figure 4(a) and (b) show two of the spectra measured on wear particles produced during the HFRR measurement

Table 1  
Sulphur content and HFRR values for ten commercial diesels.

Sample	Sulphur (mg/kg)	WS1.4 ( $\mu\text{m}$ )	Average film (%)
1	22	315	68
2	25	335	61
3	9	361	63
4	14	380	56
5	12	404	49
6	31	454	55
7	11	472	35
8	18	515	13
9	30	551	18
10	27	573	9

of sample 10. The peaks at 290, 408, 497, and 607  $\text{cm}^{-1}$  indicated the presence of hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), whereas the peak at 667  $\text{cm}^{-1}$  was assigned to magnetite ( $\text{Fe}_3\text{O}_4$ ) [14]. The broad peaks at higher wavenumbers, from about 1200 to 1700  $\text{cm}^{-1}$ , are very similar to those observed in measurements of amorphous hydrogenated carbon (a-C:H) coatings. In the spectra of a-C:H coatings there are usually only two peaks at approximately 1300–1380  $\text{cm}^{-1}$  and 1520–1570  $\text{cm}^{-1}$ . However, this same area in the spectra (figure 4) of wear particles contained three peaks at approximately 1330, 1450, and 1570  $\text{cm}^{-1}$ . The peak at ca. 1570  $\text{cm}^{-1}$  was assigned to the G mode of amorphous carbon, which results from the in-plane bond stretching motion of pairs of carbon  $\text{sp}^2$  atoms. The peak at ca. 1330  $\text{cm}^{-1}$  is designated the D peak and is a breathing mode, which is forbidden in perfect graphite and only becomes active in the presence of disorder. The G peak occurs for all  $\text{sp}^2$  sites, whereas the D peak is always related to the presence of six-membered aromatic rings [15]. The third peak at 1450  $\text{cm}^{-1}$  could not be unambiguously assigned but may result from mixtures of long alkanes trapped in the amorphous carbon. All other spectra measured outside the wear track on the disc, formed in the HFRR test of sample 10, contained one or more of the three identified

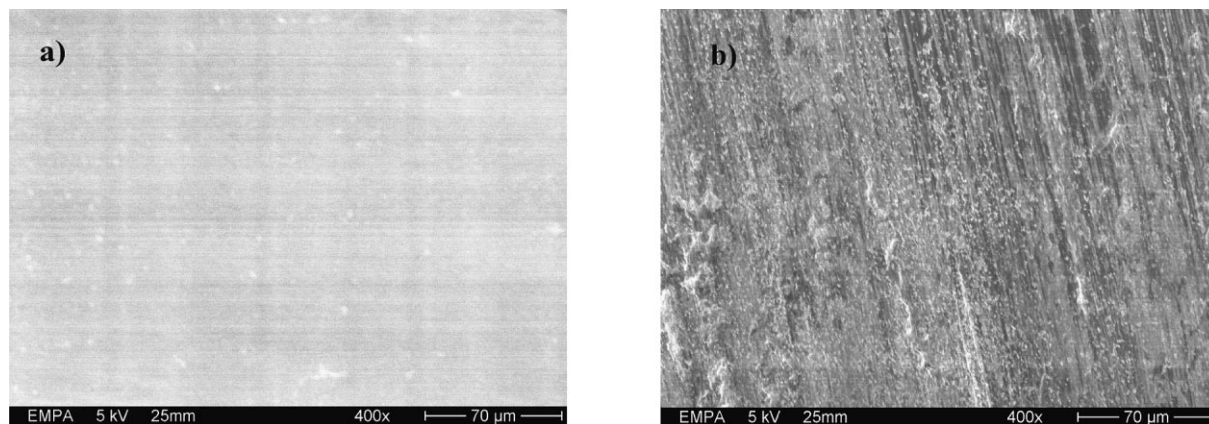


Figure 3. SEM pictures of the wear tracks on the discs used in the HFRR tests of: (a) the commercial diesel 1, with the lowest wear scar value, and (b) the commercial diesel 10, with the highest wear scar value.

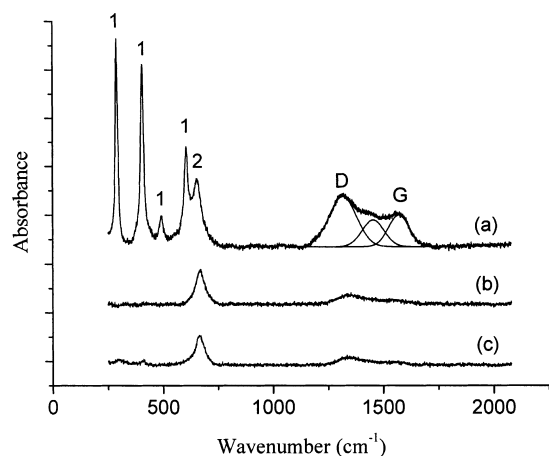


Figure 4. Raman spectra of wear particles around the wear track (a) and (b) and of the surface in the middle of the wear track (c). 1:  $\alpha$ - $\text{Fe}_2\text{O}_3$ , 2:  $\text{Fe}_3\text{O}_4$ , D and G: disorder and graphite peaks of amorphous carbon. The Gaussian fits for the D and G peaks are shown in (a).

sets of peaks, for hematite, magnetite and amorphous carbon, with varying intensities. Only magnetite was detected in all Raman spectra of the wear. The other nine samples showed essentially the same behaviour. Hematite, magnetite and amorphous carbon were detected in the wear particles produced in each HFRR experiment. However, Raman spectra were recorded for samples 1 and 2 which contained only amorphous carbon and no magnetite.

The area inside the wear track, for sample 10, was significantly more homogeneous than the area of wear particles, with only slight differences in the intensities of the amorphous carbon peaks relative to the intensity of magnetite (figure 4(c)). The areas at the end of the track contained larger proportions of amorphous carbon than areas in the middle. Hematite was not detected inside the track.

The spectra measured in the middle of the wear tracks produced in the HFRR test of the diesel varied from sample to sample. Whereas no hematite could be detected in the track for samples 8, 9 and 10, it was clearly visible in the spectra measured for the other seven samples. In order to establish the variation in the amount of hematite relative to magnetite, the ratio of the intensity of the hematite peak at  $408\text{ cm}^{-1}$  to the sum of the peak area at  $408\text{ cm}^{-1}$  and the magnetite peak area at  $667\text{ cm}^{-1}$  was calculated for each Raman spectrum (table 2). As the shape of the range of peaks assigned to amorphous carbon varied visibly with each sample, the ratio of the intensities of the D and G peaks was also calculated (table 2).

### 3.2. Boundary additives in ultra-low-sulphur diesel

Commercial diesels contain varying amounts of a large number of additives. There was also no information available on the type of lubricity improver that had

Table 2  
Ratio of the intensity of D to G peaks and proportion of hematite on surfaces lubricated with commercial diesels (n.d.: not detected).

Sample	Amorphous carbon $I_D/I_G$	Relative hematite $I_{408\text{ cm}^{-1}}/(I_{408\text{ cm}^{-1}} + I_{667\text{ cm}^{-1}})$
1	0.61	0.21
2	0.79	0.20
3	2.17	0.20
4	0.66	0.17
5	1.95	0.11
6	2.83	0.17
7	3.61	0.03
8	2.90	n.d.
9	4.39	n.d.
10	3.65	n.d.

been used. Therefore, in order to simplify the system being studied, solutions of methyl stearate and stearic acid in ultra-low-sulphur, additive-free diesel (ULSD) were measured. Both of these are widely considered to have good lubricities, although methyl stearate leads to poorer HFRR results than stearic acid. A wear scar (WS1.4) of  $668\text{ }\mu\text{m}$  was measured for the base fuel, ULSD, with the HFRR test. A solution of  $500\text{ mg/kg}$  methyl stearate in ULSD gave  $517\text{ }\mu\text{m}$  and a solution of  $500\text{ mg/kg}$  stearic acid in ULSD gave a value of  $273\text{ }\mu\text{m}$ . In order to follow the development of wear, tests were carried out using the same conditions as described in CEN F-06-A-96 [13], but were stopped at 2, 5, 10, 20, 75, and 150 minutes. A new ball and disc were used in each case. Figure 5 shows the results of these measurements for ULSD and the two solutions containing methyl stearate and stearic acid. From the two minute point, the increase in wear for ULSD and the methyl stearate in ULSD are essentially the same up to 20 min and a significant difference in the wear rate is measured at 40 min. In the measurements of stearic acid in base

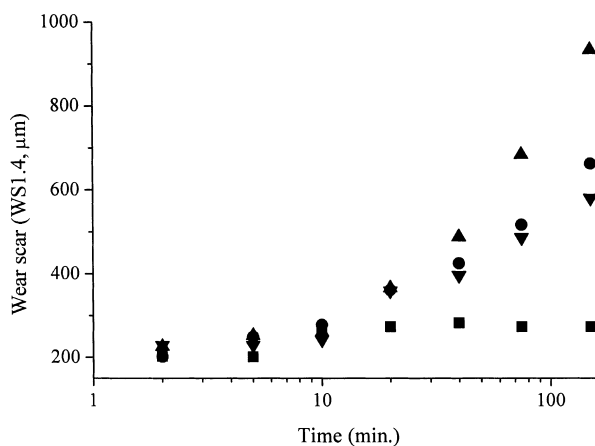


Figure 5. Wear scar (WS1.4) versus time for ultra low sulphur diesel (▲),  $500\text{ mg/kg}$  methyl stearate in ULSD (●),  $1000\text{ mg/kg}$  methyl stearate in ULSD (▼) and  $500\text{ mg/kg}$  stearic acid in ULSD (■).

fuel, a difference in the wear, in comparison to ULSD, is already noticeable at 20 min.

There was no build up of the film in the measurement of ULSD up to 150 min (average film 11%). A film was apparent for both solutions of methyl stearate (average film 53%) and stearic acid (average film 93%). In the case of methyl stearate, the value for the film thickness was unusually high for such a poor WS1.4 value. In the measurements of the stearic acid solution, the formation of the film corresponded approximately to the time where the wear no longer increased. However, the wear values measured for the methyl stearate solution continued to increase after the film had formed.

The same set of experiments was carried out on a solution of 1000 mg/kg methyl stearate in ULSD in order to determine whether an increase in concentration would lead to a levelling of the wear values as with stearic acid. However, with the higher concentration, the lubricity as determined by WS1.4 improved, but the wear value continued to increase up to 150 min (figure 5).

The Raman spectra measured on the discs used for the HFRR measurements of the methyl stearate and stearic acid solutions showed variations with time. The most noticeable change was in the amount of hematite detected by Raman. The variations in the spectra over the surface of each wear track were larger than in the case of the commercial diesels. Therefore, spectra were measured for at least four different spots in each wear track. The average ratio of the intensities of the D to G peaks of the amorphous carbon and the proportion of hematite are given in table 3 along with the standard deviations for each sample. In both cases there was little significant change in the ratio  $I_D/I_G$  with time. However, there was a significant difference between the values measured for the surfaces lubricated with methyl stearate in ULSD and stearic acid in ULSD.

The Raman spectra measured on the wear track in the discs used for the HFRR test on ULSD for 75 min contained mostly magnetite with only a very weak signal

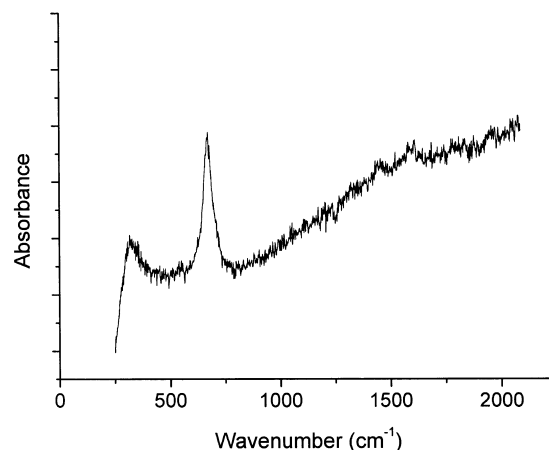


Figure 6. Raman spectrum of the surface in the middle of the wear track on a disc used in the HFRR measurement of ultra low sulphur diesel (75 min.).

for amorphous carbon (figure 6). However, the discs used for 5 and 10 min had wear tracks with small dark spots, of ca.  $10\ \mu\text{m}$  diameter, on the surface which contained hematite and larger amounts of amorphous carbon. The ratio  $I_D/I_G$  was ca. 2.8 at 5 min and ca. 7.2 at 10 min and the proportion of hematite was ca. 0.3 and 0.2, respectively.

ToF-SIMS measurements were also carried out on the discs used in HFRR tests for ULSD and the solutions of stearic acid and methyl stearate (500 mg/kg). There was little difference between the spectra of the surfaces in the middle of the track and the wear particles. In all cases, fragments assigned to alkyl- and alkylene-iron-ions were detected, i.e.,  $\text{CH}_3\text{Fe}$  ( $m/z$  70.97),  $\text{C}_2\text{H}_5\text{Fe}$  ( $m/z$  84.98),  $\text{C}_2\text{H}_3\text{Fe}$  ( $m/z$  82.96),  $\text{C}_3\text{H}_5\text{Fe}$  ( $m/z$  96.98), and  $\text{C}_4\text{H}_7\text{Fe}$  ( $m/z$  111.00). The spectra of the wear track and wear particles produced in the HFRR measurement of the stearic acid solution contained weak signals assigned to iron stearate ( $m/z$  339.23). This was not found in the case of methyl stearate (figure 7).

Table 3

Ratio of intensity of D to G peaks and proportion of hematite relative to magnetite in Raman spectra measured on the surface of discs used in HFRR tests for methyl stearate and stearic acid in ULSD (n.d.: not detected).

Time min.	Methyl stearate in ULSD		Stearic acid in ULSD	
	Amorphous carbon $I_D/I_G$	Relative hematite $I_{408\ \text{cm}^{-1}}/(I_{408\ \text{cm}^{-1}} + I_{667\ \text{cm}^{-1}})$	Amorphous carbon $I_D/I_G$	Relative hematite $I_{408\ \text{cm}^{-1}}/(I_{408\ \text{cm}^{-1}} + I_{667\ \text{cm}^{-1}})$
2	$4.98 \pm 2.43$	n.d.	$0.93 \pm 0.19$	n.d.
5	$2.04 \pm 0.88$	$0.02 \pm 0.02$	$0.85 \pm 0.26$	$0.05 \pm 0.02$
10	$4.58 \pm 1.36$	n.d.	$0.73 \pm 0.3$	$0.07 \pm 0.02$
20	$2.26 \pm 0.11$	$0.08 \pm 0.05$	$0.51 \pm 0.18$	$0.11 \pm 0.04$
40	$2.68 \pm 0.47$	$0.14 \pm 0.09$	$1.00 \pm 0.22$	$0.18 \pm 0.05$
75	$2.17 \pm 0.35$	$0.19 \pm 0.04$	$0.66 \pm 0.13$	$0.18 \pm 0.03$
150	$2.55 \pm 0.04$	$0.23 \pm 0.03$	$1.25 \pm 0.11$	$0.20 \pm 0.01$

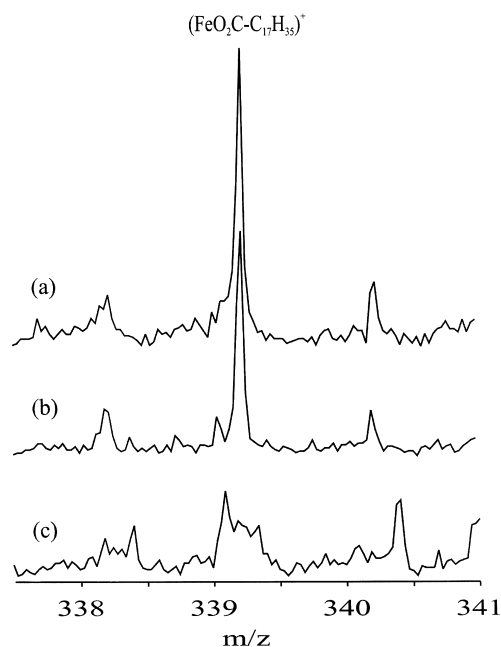


Figure 7. ToF-SIMS spectra of iron stearate in the wear particles (a) and in the wear track (b) formed during the HFRR test on stearic acid in ULSD, along with the same region in the spectrum measured on the wear track formed during the HFRR test on methylstearate in ULSD (c).

## 5. Discussion

Magnetite has been observed previously on surfaces following lubricated sliding [12]. In that case, a hydrocarbon oil, isopar, was used as the lubricant. Isopar probably has a similar lubricity to ULSD, which also resulted in a wear surface containing almost exclusively magnetite after 75 min. However, those diesels with a better lubricity gave wear surfaces which also contained hematite. Both hematite ( $\alpha$ - $\text{Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ) are hard, brittle iron oxides, which commonly occur in the corrosion products of steel [16]. These are formed on the surface of steels during sliding by the reaction of dissolved oxygen with the nascent iron surface [17].

Hematite is a semiconductor with a band gap of 2.2 eV, whereas magnetite, with a band gap of only 0.1 eV, displays almost metallic properties [16]. The electrical resistance of hematite ( $10^6 \Omega \text{cm}$ ) [18] is much larger than that of magnetite ( $0.005 \Omega \text{cm}$ ) [19]. Figure 8 shows the variation in the relative intensity of the hematite Raman signal relative to the sum of the magnetite and hematite peaks versus the film thickness which is measured by the HFRR for the commercial diesels. The film thickness at the end of the test was used, and not the average film, as the Raman measurements can only describe the surface at the end of the test. There is clearly a trend towards higher film thickness with an increasing proportion of hematite relative to magnetite.

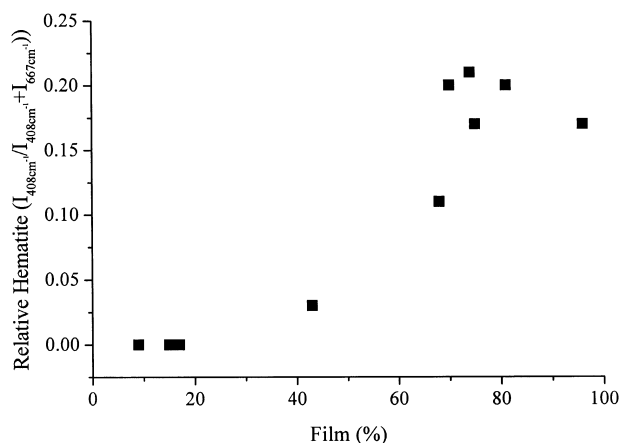


Figure 8. Proportion of hematite versus film thickness at end of HFRR measurement of ten commercial diesels.

The formation of hematite over time was determined by stopping the HFRR test at various times. Figure 9 shows the variation in the proportion of hematite and the build up of the film over time for the solutions of methyl stearate and stearic acid in ULSD. This suggests that the film, which is measured by electrical resistance, is a measure of the amount of hematite on the surface.

The amount of hematite found on the surface of the disc used in the HFRR test of methyl stearate in ULSD is high compared to the commercial diesels with similar wear scar values (WS1.4). However, the result of the HFRR test in the case of methyl stearate is unusual in that the average film is also very high for a solution with such a low lubricity.

Hematite was found in the wear particles on all the samples, regardless of the measured lubricating ability. Therefore, the formation of hematite does not lead to an improvement in the wear characteristics of the surface. This was further confirmed by the observation that the wear values for the test of methyl stearate in ULSD continued to increase after hematite could be detected on the surface in the wear track. On the other hand, in the test for the stearic acid solution, the wear values remain constant shortly after the increase in the film thickness.

The relationship between the detection of hematite in the wear scar and the lubricating ability of the diesels suggests that in those cases where the diesels have a good lubricity, the hematite is protected against wear. This is probably achieved by the formation of an amorphous carbon coating on the surface. The changes in the relative intensities of the D and G peaks in the Raman spectra, assigned to amorphous carbon, with time are shown in table 3. For both the methyl stearate and the stearic acid solutions there appears to be little significant change over time. However, the scatter of the data for methyl stearate is significantly higher than that of stearic acid. It was assumed that the ratio of intensities was also constant for the ten commercial diesels. Therefore, if there is a relationship between the

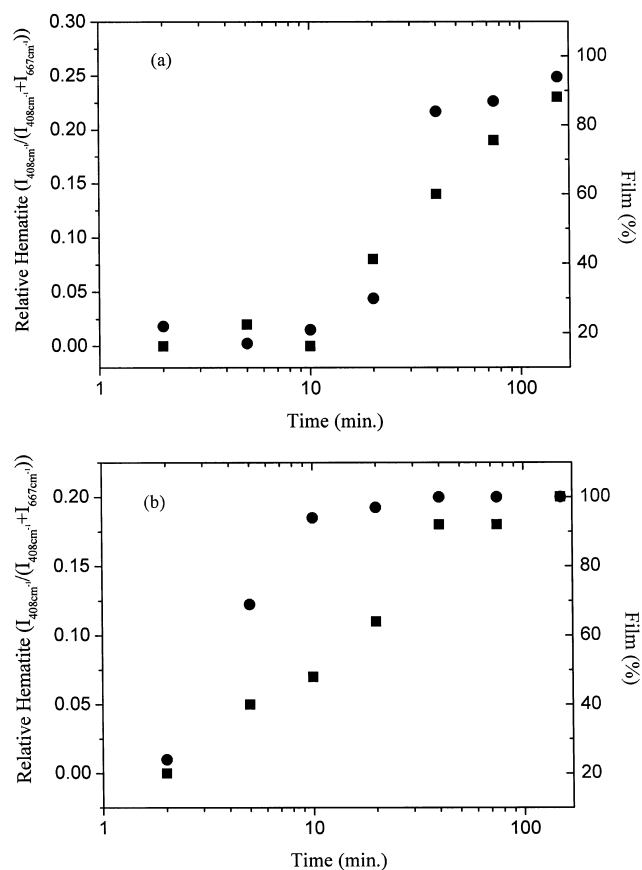


Figure 9. Proportion of hematite (■) and film thickness (●) at end of HFRR measurements for methyl stearate (a) and stearic acid (b) in ULSD.

wear-scar value and the amorphous carbon, this should be evident at the end of the experiment. Figure 10 shows the variation in  $I_D/I_G$  with the wear scar for the commercially available diesel fuels. There is a trend towards lower  $I_D/I_G$  ratios, and a larger graphitic content, with decreasing wear scar, and, thus, higher lubricity.

The observation of lower wear with lower  $I_D/I_G$  ratio is in apparent contradiction to measurements on a-C : H films [20] in which the wear rate was shown to increase with decreasing  $I_D/I_G$  ratio. However, the wear rate in this case [20] refers to the wear on the amorphous carbon coating, which cannot be renewed during the sliding process. In the HFRR experiment, the wear scar is a measure of the wear to the steel ball and the amorphous carbon supplied by the lubricant can be renewed throughout the measurement. If the coatings with lower  $I_D/I_G$  ratios have a lower shear strength, they can be preferentially removed from the surface leaving the iron oxides intact. The high wear rate of these coatings, therefore, leads to the low wear rate of the steel. This was further supported by the observation that for diesels with good WS1.4 values (samples 1 and 2) very large amounts of amorphous carbon were detected in the wear around the track.

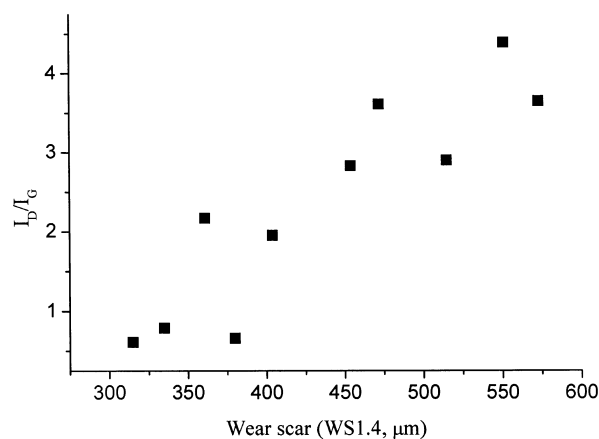


Figure 10. Ratio of D to G peaks in Raman spectra measured in the middle of wear tracks, on the discs, versus the wear scar on the ball (WS1.4) produced by reciprocating sliding lubricated with commercial diesel fuels.

The measurements on ULSD for 5 and 10 min show the presence of hematite and amorphous carbon with large  $I_D/I_G$  ratios in the wear track. The surfaces of these samples were very uneven and were covered with scratches indicating abrasive wear caused by particles of the hard iron oxides. Additionally, the low diffusion of oxygen at the contact during sliding would have slowed the formation of iron oxides and promoted severe adhesive wear. In the diesels containing additives, the oxygen could be supplied by the additive, thus preventing adhesive wear [21]. Some areas on the discs used for ULSD tests were possibly protected against wear by an advantageous distribution of pressure, that is, the spots of hematite may have been in small holes, caused by adhesion or abrasion, protected by surrounding areas of magnetite.

The wear scar value for solutions of methyl stearate in ULSD improved when the concentration was doubled, however, the detected hematite and  $I_D/I_G$  ratios remained basically the same. In the HFRR measurement the speed of the ball against the disc changes during each stroke as the ball has to stop and start at the end of the track. In the middle of the track the lubrication may be in the mixed regime and therefore result in some degree of elastohydrodynamic lubrication. It has been shown that the HFRR test is to some extent dependent on viscosity [22]. Thus, it is possible that the improvement in lubricity on increasing the concentration of methyl stearate was the result of a higher viscosity and that the ester does not provide protection to the surfaces in the HFRR test in the same way as the acid, by forming a protective amorphous carbon coating. Additionally small amounts of iron stearate were detected on the surfaces lubricated with stearic acid in ULSD, which may provide additional protection to the surfaces. The iron stearate could have been formed by reaction with or complexation of hematite [16]. No iron stearate was detected on the surfaces lubricated with methyl stearate, indicating that

the ester did not hydrolyse to the acid under the conditions used in the HFRR test.

ToF-SIMS showed that alkyl and alkylene iron were also formed during contact of surfaces in the HFRR lubricated with ULSD and solutions of stearic acid and methyl stearate in ULSD. The formation of graphitic-type carbon and cracking of hydrocarbon molecules on iron surfaces has been observed during ball-on-flat tests on multialkylated cyclopentane oil [23]. Amorphous carbon has also been detected, with Raman spectroscopy, on surfaces lubricated with Pennzane based greases following four-ball measurements [24]. However, oils and greases have a much better lubricity than diesel oil and are used in more severe conditions.

## 5. Conclusion

Although the amorphous carbon coating will also have an effect on the electrical resistance across the surface, the decisive factor appeared to be the presence of hematite. The hematite did not result in better wear behaviour, but remained longer on the surface as a result of the formation of an amorphous carbon coating which provides protection. Low  $I_D/I_G$  ratios were associated with good lubrication as measured by the HFRR. Therefore, the structure of the coating was influenced by the type of lubricity improver added, although amorphous carbon was also formed from ultra low sulphur, additive free diesel. The lubricity improver is not necessary to produce amorphous carbon, which may have been formed from the alkanes in the diesel in the HFRR test. The additive influenced wear behaviour by deciding the graphitic character of the carbon.

The dependence of the wear scar value (WS1.4) on the formation of products similar to those identified for tests on oils and greases suggests that the HFRR test may be too severe for diesel. This severity appears to be caused by the high wear rate of the softer disc which produces a more reactive surface. It has been shown that acids do not improve lubrication on nascent iron surfaces [25]. Therefore, in the HFRR test, the iron

required for decomposition of the hydrocarbons must come from the wear particles formed during sliding and not from complete removal of the oxide surface.

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