

ANL/ET/CP-99149

TRIBOLOGICAL BEHAVIOR OF NEAR-FRICTIONLESS CARBON  
COATINGS IN HIGH- AND LOW-SULFUR DIESEL FUELS\*

M. F. Alzoubi, O. O. Ajayi, O. L Eryilmaz, O. Ozturk, A. Erdemir and G. Fenske  
Energy Technology Division  
Argonne National Laboratory  
Argonne, IL 60439

The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory under Contract No. W-31-109-ENG-38 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

RECEIVED  
MAR 07 2000  
OSTI

August 1999

Paper to be presented at 2000 SAE International Future  
Car Congress, Arlington, VA, April 12-16, 2000.

---

\* Work supported by the Department of Energy, Office of Transportation Technology under Contract W-31-109-Eng-38.

## **DISCLAIMER**

**This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.**

## **DISCLAIMER**

**Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.**

# TRIBOLOGICAL BEHAVIOR OF NEAR-FRICTIONLESS CARBON COATINGS IN HIGH- AND LOW- SULFUR DIESEL FUELS\*

**M. F. Alzoubi, O. O. Ajayi, O. L. Eryilmaz, O. Ozturk, A. Erdemir and G. Fenske**  
Energy Technology Division  
Argonne National Laboratory  
Argonne, IL 60439

## ABSTRACT

The sulfur content in diesel fuel has a significant effect on diesel engine emissions, which are currently subject to environmental regulations. It has been observed that engine particulate and gaseous emissions are directly proportional to fuel sulfur content. With the introduction of low- sulfur fuels, significant reductions in emissions are expected. The process of sulfur reduction in petroleum-based diesel fuels also reduces the lubricity of the fuel, resulting in premature failure of fuel injectors. Thus, another means of preventing injector failures is needed for engines operating with low- sulfur diesel fuels. In this study, we evaluated a near-frictionless carbon (NFC) coating (developed at Argonne National Laboratory) as a possible solution to the problems associated with fuel injector failures in low-lubricity fuels. Tribological tests were conducted with NFC-coated and uncoated H13 and 52100 steels lubricated with high- and low- sulfur diesel fuels in a high-frequency reciprocating test machine. The test results showed that the NFC coatings reduced wear rates by a factor of 10 over those of uncoated steel surfaces. In low-sulfur diesel fuel, the reduction in wear rate was even greater (i.e., by a factor of 12 compared to that of uncoated test pairs), indicating that the NFC coating holds promise as a potential solution to wear problems associated with the use of low-lubricity diesel fuels.

## KEY WORDS

NFC Coating, High- and Low-Sulfur Diesel Fuel, Friction and Wear.

## INTRODUCTION

Various existing and forthcoming diesel engine emission regulations require the use of low-sulfur diesel fuels. This is because levels of various types of diesel engine emissions (gaseous and particulate) are dependent on the sulfur content of the fuel. In addition, sulfur is one of the elements that poison aftertreatment catalysts. Experience has shown that low-sulfur petroleum-base diesel fuels also have low lubricity [1,2]. With the impending widespread use of such low-emission diesel fuels, there is need for a solution to the low lubricity-problem associated with these fuels. One possible approach is application of performance enhancing, wear-resistance coatings to the surfaces of critical components that normally rely on the lubricity of the fuel.

One such coating is the diamondlike carbon (DLC), which has recently generated considerable interest for tribological applications in its various forms. These forms of carbon are metastable, amorphous, and contain both  $sp^2$  and  $sp^3$  hybridization structures. The ratio of  $sp^2$  to  $sp^3$  that results from the deposition technique [3-8] plays a key role in determining the tribological performance of DLC coatings. DLC films exhibit low friction, especially in dry environments [9,10], and even in vacuum [10]. The films also have high wear resistance, high hardness, good chemical inertness, and high thermal conductivity [11-12]. Amorphous carbon coatings with an extremely low friction coefficient (0.002), hence the name near-frictionless carbon (NFC), were recently developed at Argonne National Laboratory. These coatings are also hard and highly wear-resistant [13-14].

Current major applications of DLC coatings include magnetic hard disks, bearings, and other moving mechanisms. The diesel engine is another area where these coatings may find beneficial application. This paper investigates the friction and wear performance of Argonne's NFC coating when lubricated with diesel fuels containing various levels of sulfur. The results of this study will provide information on the application of this coating to enhance the performance of engine components operating with low-lubricity diesel fuels.

## **EXPERIMENTAL DETAILS**

### **Coating:**

The NFC coating was deposited on 50 x 40 x 10 mm steel flat test samples and 9.5-mm-diameter balls using an RF-plasma-assisted chemical vapor deposition (PACVD) method. The surfaces to be

coated were first sputter-cleaned in Ar plasma for 30 min. This was followed by a sputtering deposition of 50 to 70-nm-thick Si bond layer. The sputtering cleaning and deposition of a Si bond layer were used to ensure good adhesion between the NFC coating and the substrate material. A proprietary mixture of gas was then blended into the chamber to create the plasma for chemical vapor deposition of the NFC coating. A coating thickness of 1  $\mu\text{m}$  was deposited on both the ball and flat specimens.

#### Friction and Wear Test:

Friction and wear tests were conducted with ball-on-flat contact geometry in a high-frequency reciprocating test rig (HFRR). The ball specimens were 9.5 mm in diameter and the flat specimens measured 50  $\times$  40  $\times$  10 mm. Figure 1 is a schematic diagram of the test rig.

Tests were conducted at a normal load of 6.2 N, reciprocating frequency of 13.33 Hz, and a stroke length of 3 mm (giving an average speed of 0.08  $\text{m s}^{-1}$ ) for a total of 60,000 cycles, room temperature (25-27°C), and relative humidity of (20 to 25 %). The 6.2 N normal load produced an initial mean Hertzian contact pressure of  $\approx$  860 MPa and a maximum contact pressure of  $\approx$  1200 MPa for the steel-on-steel pair. (The hardness was 56 Rc for the flat, and 61 Rc for the ball. Tests were conducted with "low" (140 ppm) and "high" (500 ppm)- sulfur diesel fuels for the following four different material-contact combinations: (a) Uncoated ball/uncoated flat, (b) uncoated ball/NFC-coated flat (c) NFC-coated ball/uncoated flat, and (d) NFC-coated ball/NFC-coated flat. The fuel was applied by immersing both the flat and the ball in a bath of fuel during the test, creating a fully flooded contact.

The friction coefficient was continuously monitored in all tests by a strain gauge (LVDT) device. Ball wear was calculated from the dimensions of the wear scar measured by an optical microscope, at the conclusion of each test. Wear volume in the ball was estimated with the equation  $V_b = (\pi d^3)/64R$ , where  $d$  is wear scar diameter, and  $R$  is ball radius. The wear rate ( $W$ ) was calculated by normalizing the wear volume with the applied normal force and total sliding distance, i.e.,  $W = V_b / (F_n S)$ , where  $F_n$  is the applied normal force, and  $S$  is the total sliding distance.

## RESULTS AND DISCUSSION

## Friction

Figures 2 and 3 show the variation of friction coefficient with number of cycles for the high- and low-sulfur diesel fuels, respectively. With high-sulfur fuel, there was only a slight difference in friction behavior for the four different material combinations. For the uncoated ball and flat combination, the friction coefficient was  $\approx 0.09$ . When both ball and flat are coated, the friction coefficient during the tests was slightly reduced to  $\approx 0.08$ . When one of the surfaces was coated, the friction coefficient was  $\approx 0.085$ . Figure 3 shows the friction variation for tests with low-sulfur diesel fuel; friction coefficient behavior was very similar to that for high-sulfur fuel, but with slightly higher values. Figure 4 shows the average steady state friction coefficient for different contact pairs during tests with both low- and high-sulfur fuel.

## Wear

Figure 5 shows photo-micrographs of the wear scars on NFC-coated and uncoated balls tested with high- and low-sulfur diesel fuels. For tests with high-sulfur fuel, wear scar diameter on uncoated ball against uncoated flat was  $\approx 0.245$  mm, compared to 0.120 mm for NFC-coated pairs. Tests with low-sulfur fuel showed a similar trend to that of high-sulfur fuel, but with a slightly larger scar size.

Figure 6 shows average ball wear rates for different contact pairs tested with both high- and low-sulfur diesel fuels. The results showed that NFC significantly reduces the wear rate by almost 10 times compared to that of uncoated surfaces, and that the low-sulfur fuel produced slightly more wear than the high-sulfur fuel.

Low-sulfur diesel fuels are known to have poor lubricity. This study shows that the use of a surface coating, such as NFC in this case, is an effective method of overcoming the poor lubricity of low-sulfur diesel fuels. Although the coating did not change the friction coefficient significantly, it reduced the wear substantially. In fuel injector systems, wear and scuffing (which can sometimes be considered a form of severe wear) failures are much more important than the reduction of friction. Wear reduction was observed in every case in which one or both contacting surfaces were coated.

## Conclusions

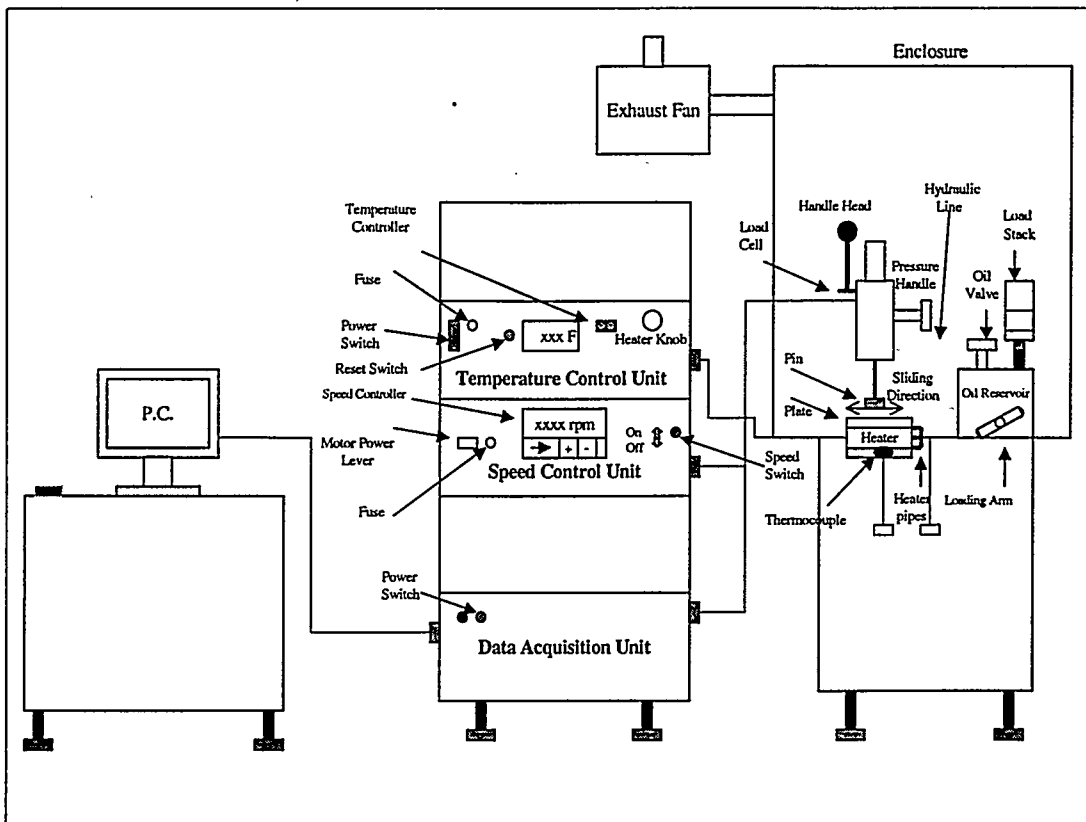
The use of low-sulfur diesel fuel is being required to reduce diesel engine emissions for compliance with existing and new regulations. Low-sulfur fuels are also more beneficial for after-treatment catalysts, but they tend to also have low lubricity, thus making fuel injection components vulnerable to early failure. The use of Argonne's NFC coating was shown in this study to be an effective means of preventing such failure.

## References

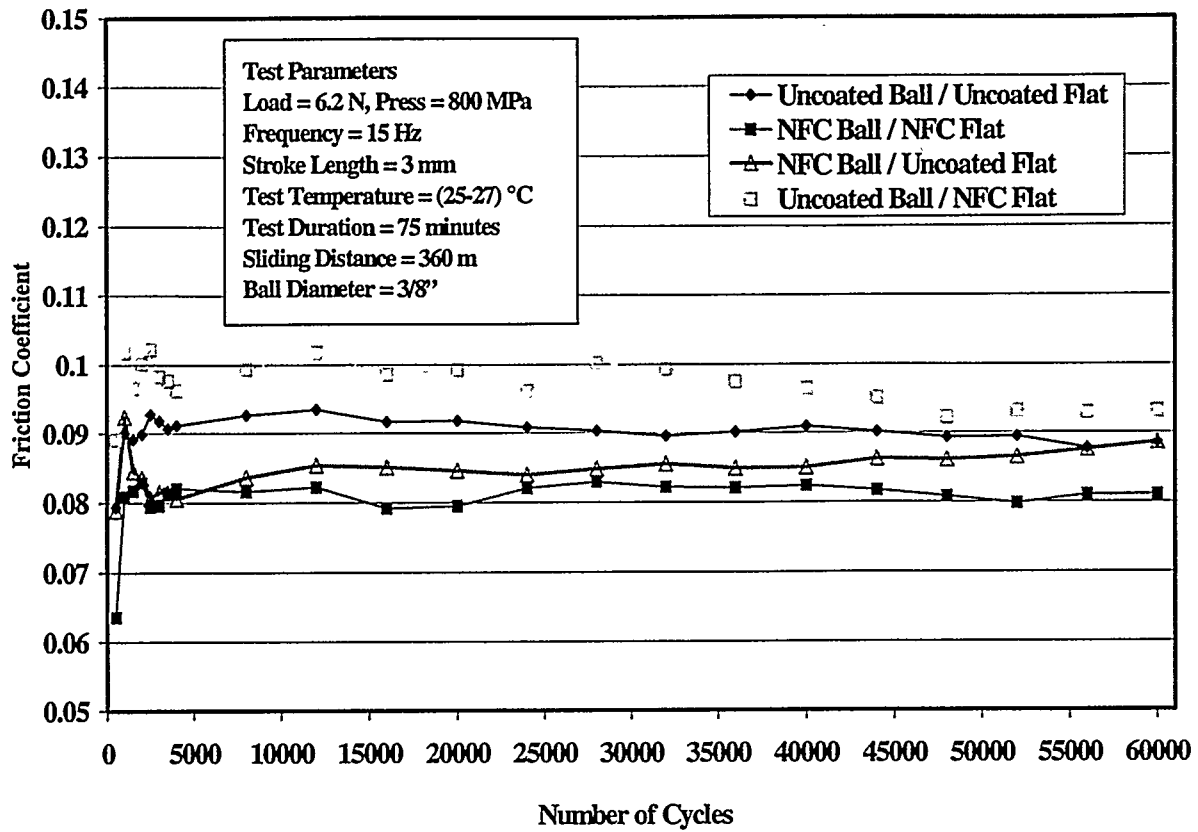
- [1] M. Nikanjam, Diesel Fuel Lubricity: On the Path to Specifications, Chevron Products Company, SAE Paper, 1999-01-1479.
- [2] D. Wei and H.A. Spikes, The Lubricity of Diesel Fuels, *Wear Transactions*, 111 (1986) 217-235.
- [3] J.F. Braza and T.S. Sudarshan, *Surface Modification Technologies* (T.S. Sudarshan and J.F. Braza, eds.), The Institute of Materials (1992), 801.
- [4] H. Tsai and D.B. Bogy, *J. Vac. Sci. Technol.*, A5 (1987) 3287.
- [5] *Properties and Characterization of Amorphous Carbon Films*, *Mater. Sci. Forum*, 52-53 (1990).
- [6] *Proc. NATO Advanced Study Institute, Diamond and Diamondlike films and Coatings*, I1 Ciocco, Castelvechio Pascoli, July 22-Aug. 3, 1990, Plenum, New York, 1991.
- [7] *Proc. 1<sup>st</sup> Euro. Conf. On Diamond and Diamondlike Carbon Coatings*, Crans-Montana, Sept. 17-19, 1990, in *Surf. Coat. Technol.*, 47 (1991).
- [8] D. Dowling, T. Kelly and M. Ahern, *Technol. Ireland*, 22(9)(1991) 54.
- [9] A. Erdemir, M. Switala, R. Wei, and P. Wilbur, *Surf. Coat. Technol.* 79 (1991) 17.
- [10] A. Grill, *Surf. Coat. Technol.*, 94-95 (1997) 507.
- [11] Syed Q.A. Rizvi, *Friction, Lubrication and Wear Technology*, *ASM Handbook*, 18 (1990) 102 and 103.
- [12] D. Godfrey, *Boundary Lubrication, Interdisciplinary Approach to Friction and Wear*, P.M. Ku, ed., *NASA Special Publication SP-181*, 1968, p 335-353.



- [13] A. Erdemir, G. R. Fenske, Effect of Source Gas and Deposition method on Friction and Wear Performance of DLC Films, *Surface and Coatings Technology* 94-95 (1997) 525-530.
- [14] A. Erdemir, G. R. Fenske, Tribological Properties of Hard Carbon Films on Zirconia Ceramics, *Tribology Transactions*, V 39(1996), 3, 735-744.



**Figure 1. Reciprocating Wear Test Machine**



**Fig. 2** Variation of friction coefficient with number of cycles with high- sulfur diesel

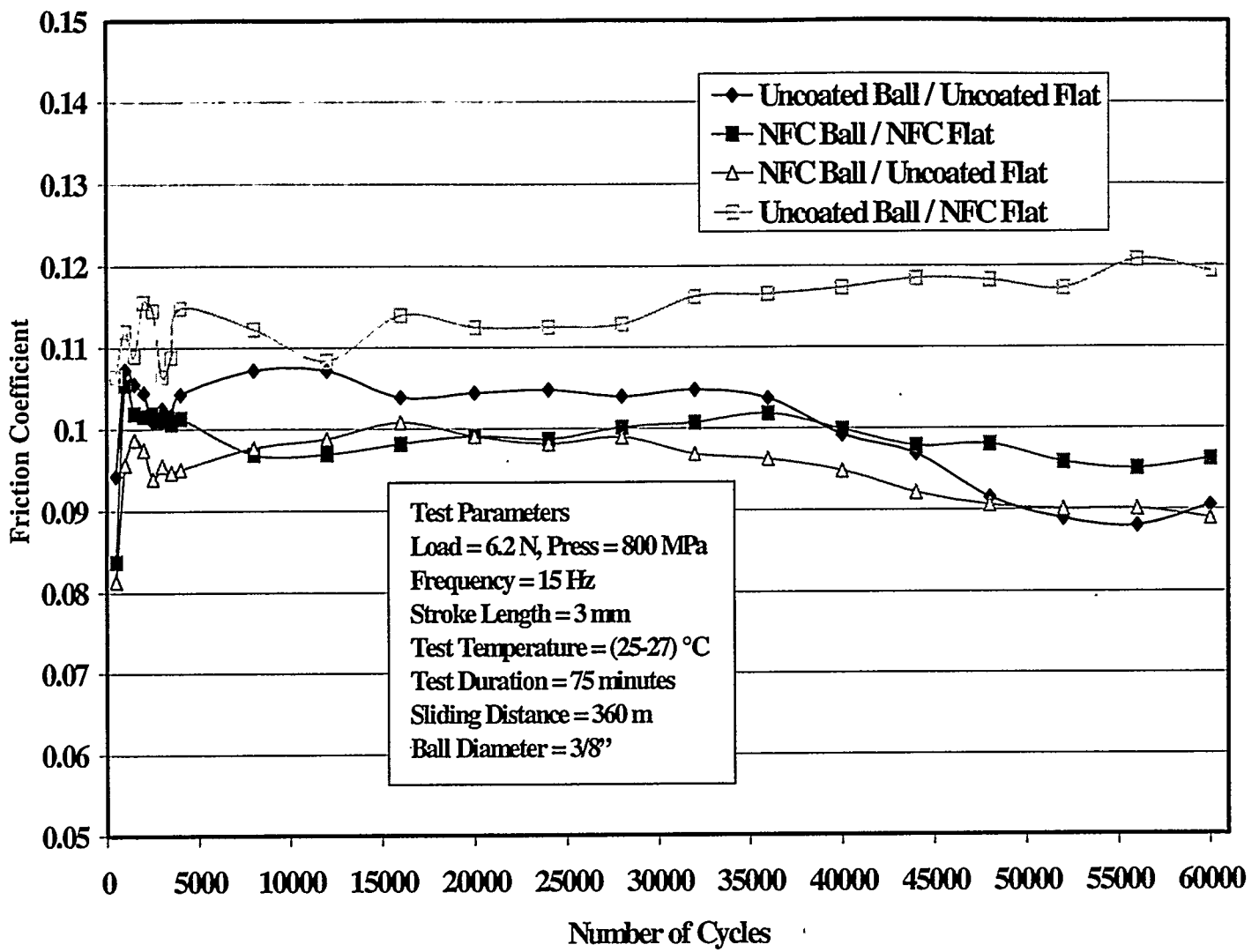


Fig. 3 Variation of friction coefficient with number of cycles with low-Sulfur diesel

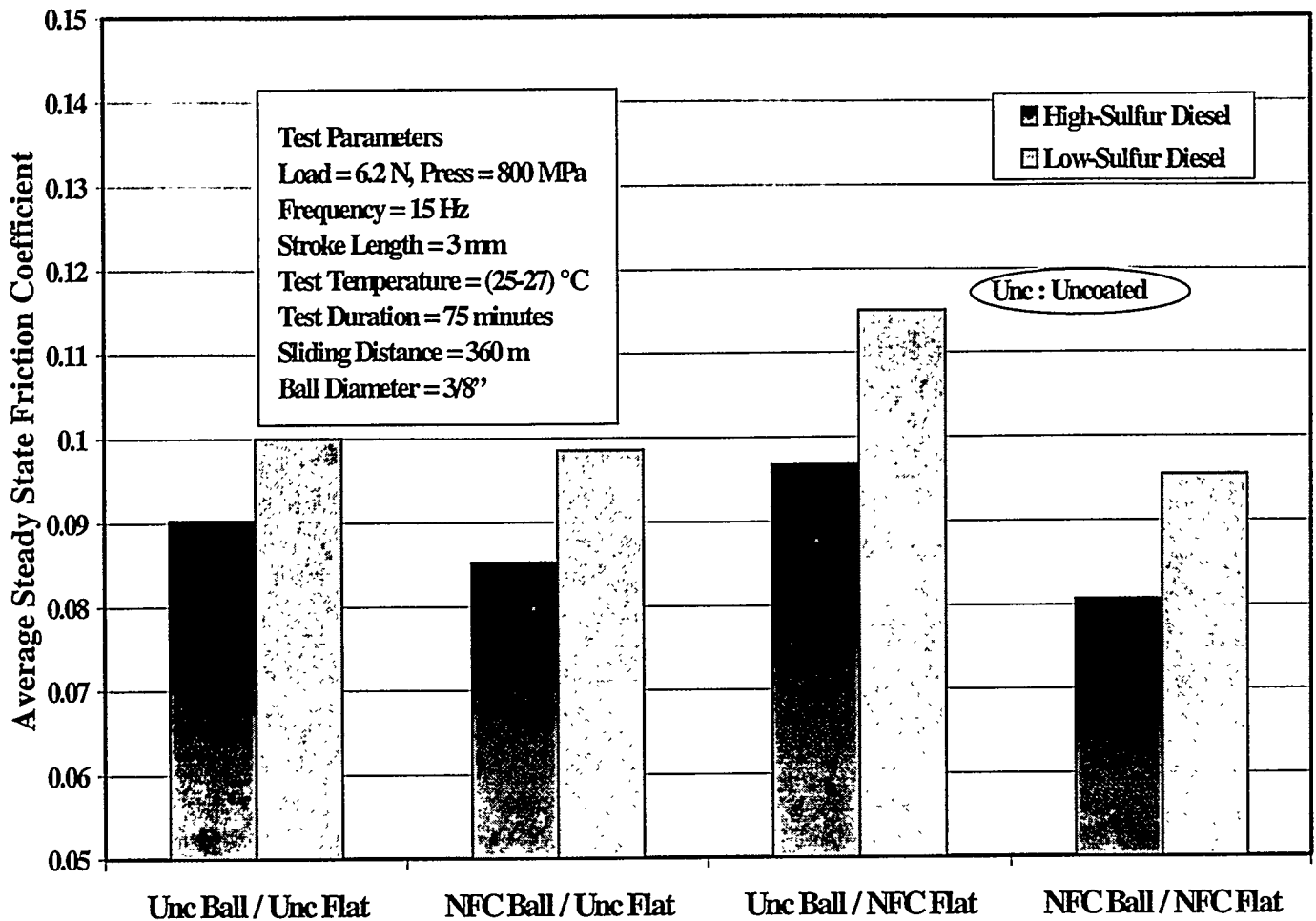
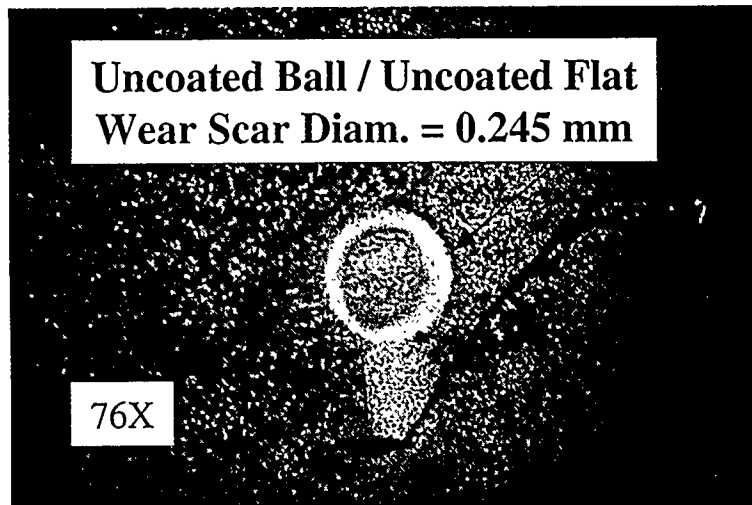


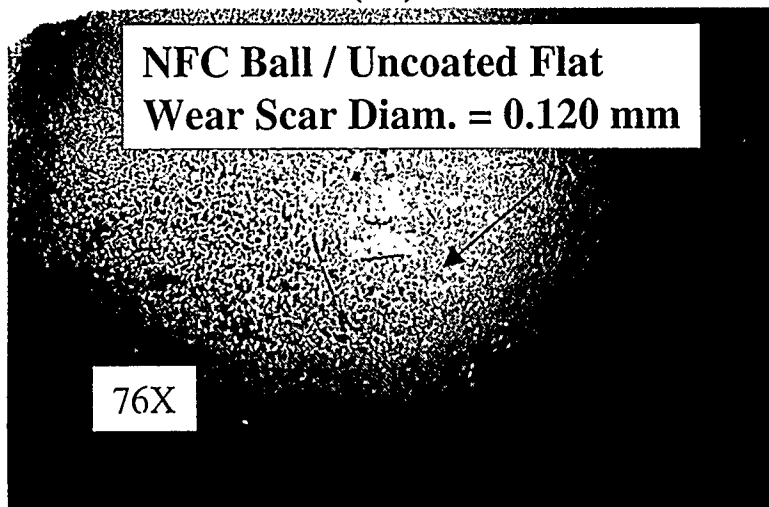
Fig. 4 Average steady state friction coefficient for different for surface contact pairs

**Fig. 5. Wear scars of NFC-coated and uncoated balls tested with high- and low sulfur diesel fuels**

**High-Sulfur Diesel Ball Scars**

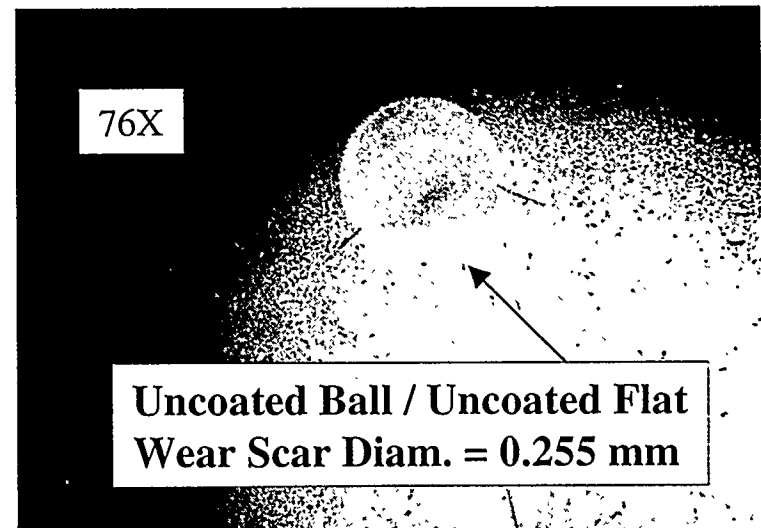


(a)

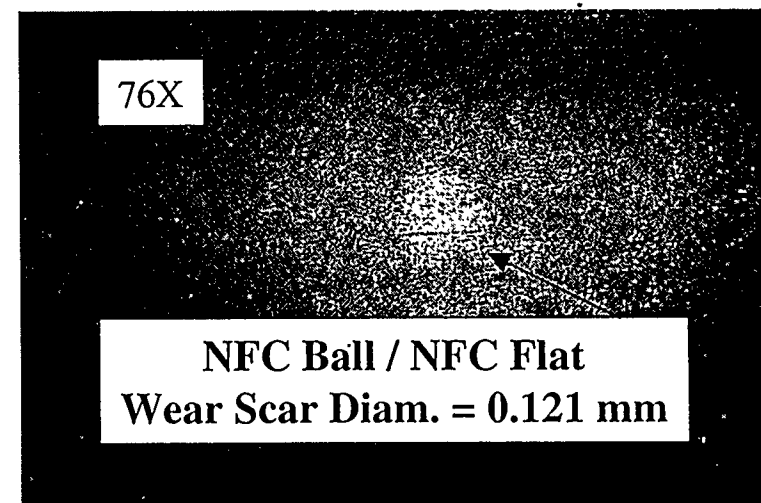


(b)

**Low-Sulfur Diesel Ball Scars**



(c)



(d)

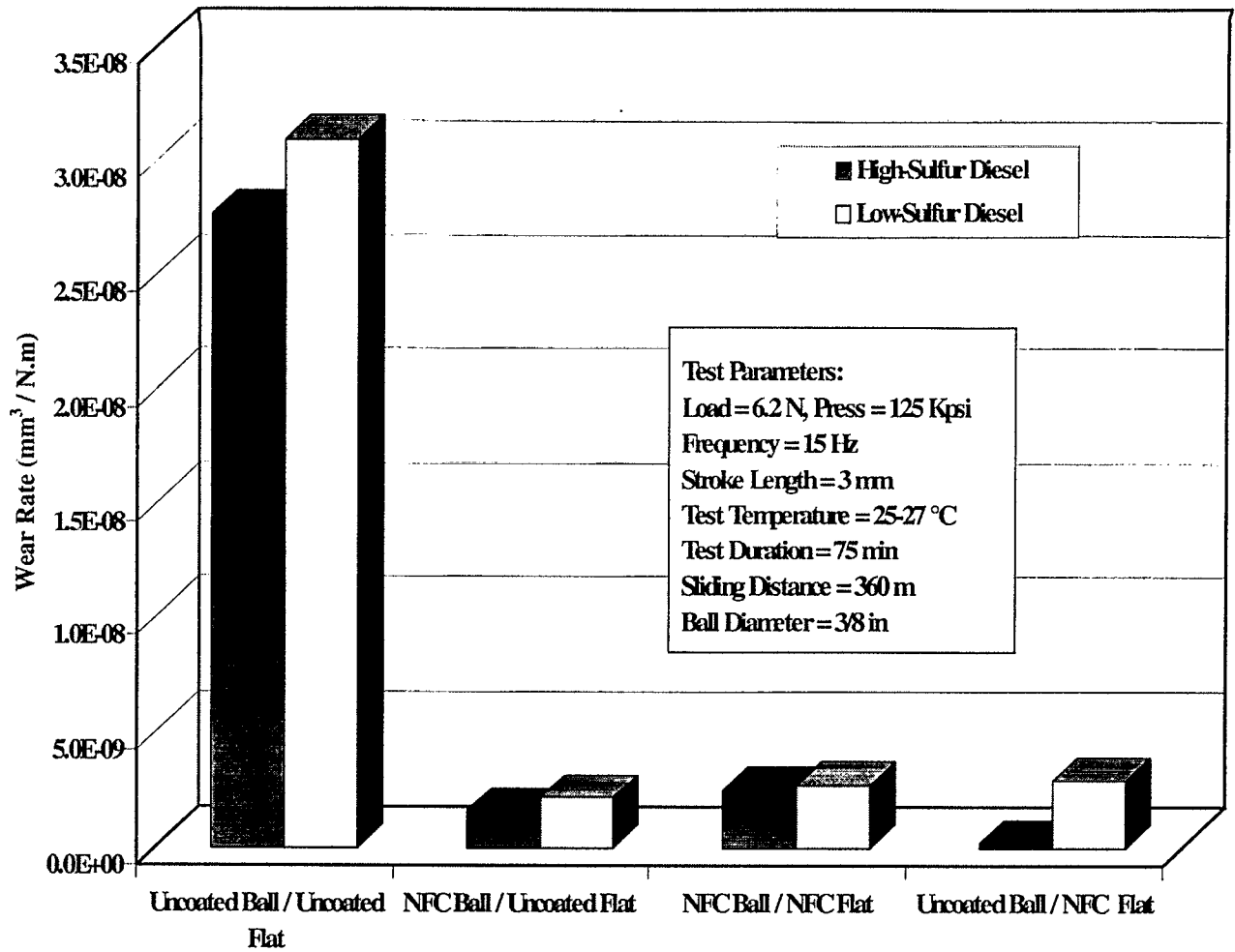


Fig. 6 Wear rate vs. surface contact pairs for high- & low- sulfur diesel