ROLE OF SULFUR OXIDES IN WEAR AND DEPOSIT FORMATION IN ARMY DIESEL ENGINES

INTERIM REPORT
BFLRF No. 248

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Under Contract to

U.S. Army Belvoir Research, Development
and Engineering Center
Materials, Fuels and Lubricants Laboratory
Fort Belvoir, Virginia

Contract No. DAAK70-87-C-0043

December 1988

89 6

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
Unclassified	None

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT
N/A	Approved for public release;
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	distribution unlimited
N/A	

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
Interim Report BFLRF No. 248	

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
Belvoir Fuels and Lubricants Research Facility (SwRI)		

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
Southwest Research Institute 6220 Culebra Road San Antonio, Texas 78284	

8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
U.S. Army Belvoir Research, Development and Engineering Center	STRBE-VF	DAAK70-85-C-0007; WD 6 DAAK70-87-C-0043

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
Fort Belvoir VA 22060-5606	61102	1T1611 02AH51✓	FF(3)	

11. TITLE (Include Security Classification)

Role of Sulfur Oxides in Wear and Deposit Formation in Army Diesel Engines (U)

12. PERSONAL AUTHOR(S)

Naegeli, David W.; Marbach, Jr., Howard W.

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Interim	FROM Oct 85 TO Sept 87	1988 December	62

16. SUPPLEMENTARY NOTATION

17.	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Wear Combustion Deposits
			Sulfur Oxides Diesel Engines
			Diesel Fuels

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

In some locations outside the continental United States, U.S. military ground mobility equipment uses fuel with an increased sulfur content. Fuel sulfur has been identified as a primary contributor to diesel engine wear and deposits. The literature on the effects of fuel-bound sulfur on diesel engine wear indicates that sulfuric acid mist formed within the combustion chamber is responsible for corrosive attack of the cylinder bore and piston ring areas. Deposit formation has been more of a mystery in that the literature tends to support the theory that reaction of organically bound sulfur with the fuel and lubricant is the principal cause. Studies presented here suggest that sulfur dioxide (SO_2) formed in the combustion of fuel-bound sulfur is the primary cause of higher cylinder bore/ring wear and deposit formation in diesel engines.

(Cont'd)

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL
Mr. F.W. Schaekel	(703) 664-3576	STRBE-VF

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. ASBSTRACT (Cont'd)

Several bench-scale experiments were conducted to determine the effects of SO_2 on corrosion and deposit formation. It was found that iron sulfide is readily formed by an oxidation-reduction reaction between SO_2 and iron when moisture is present. Oil samples containing dissolved water and SO_2 were examined in a wear rig, and the results showed that concentrations of SO_2 as low as 0.05 percent caused significant increases in the size of the wear scar. Experiments were performed to determine the extent of reaction of SO_2 with hydrocarbons. Olefins were found to be very reactive with SO_2 and formed black insoluble tar-like products. Saturated aliphatics and aromatics were relatively unreactive with SO_2. Thermal stability bench tests showed that small amounts of SO_2 dissolved in both fuels and lubricants caused significant increases in deposit formation.

Engine tests were performed to determine the relative importance of SO_2 and sulfuric acid mist. Analysis of the exhaust gases sampled very near the exhaust port showed that at least 99 percent of the exhaust sulfur was SO_2. Sulfuric acid mist did not appear to be present in a significant amount; based on the accuracy of the measurements, its concentration could not have exceeded 0.5 percent.

Two engine tests were completed to further study the role of SO_2. In the first, SO_2 gas was injected into the intake manifold of a single-cylinder diesel engine at a concentration equivalent to that experienced when operating the engine on a fuel containing 2-percent sulfur. These results showed that SO_2 was responsible for the formation of deposits in the engine, but was only accountable for about 50 percent of the wear observed in similar tests using fuel-bound sulfur. This difference in wear is not understood, but it may result from the difference between a homogeneous and a stratified SO_2 concentration in the combustion chamber. The second test was performed in a three-cylinder diesel engine equipped with individual fuel injection systems for each cylinder. In this test, high-sulfur (3-percent) fuel was used in two cylinders, and neat fuel was used in the third cylinder. The results of this test showed that even though the three cylinders shared the same lubricant, the cylinders burning the high-sulfur fuel experienced considerably more wear and deposit formation than the cylinder operated on neat fuel. A kinetics modeling study is recommended to verify and quantify the role of SO_2.

The results of this investigation support a new theory that SO_2 is the principal cause of fuel sulfur induced wear and deposit formation in diesel engines. This information will aid lubricant researchers in formulating improved oils for use with high-sulfur fuel.

EXECUTIVE SUMMARY

Problems and Objectives: On certain bases outside the continental United States, fuels used in U.S. military ground mobility equipment may contain relatively high levels of sulfur. Fuel sulfur has been identified as a major contributor to diesel engine wear and deposit buildup. The engine literature indicates relatively broad acceptance of the theory that sulfuric acid mist formed in the cylinder during the combustion process is the primary cause of wear. Contrarily, the kinetics and thermodynamics of sulfuric acid formation indicate that sulfuric acid is unlikely to form in the cylinder at the high temperatures of combustion. Deposit formation is more of a mystery in that the literature suggests that reactions of fuel sulfur with the lubricant is the principal cause. The objective of the present study is to determine which sulfur-containing species are the primary causes of engine wear and deposit formation.

Importance of Project: There is clearly a need for a more basic understanding of the role of fuel sulfur in engine wear and deposit formation. Without a more in-depth understanding of the mechanisms of sulfur-induced wear and deposit formation in diesel engines, the potential to satisfy future needs by developing additives, more thermally stable lubricants, and improved metallurgy and engine design will be severely limited.

Technical Approach: Several bench-scale type experiments and full-scale engine tests were performed to determine the importance of sulfur dioxide in engine wear and deposit formation. Since previous work stressed the importance of sulfuric acid in engine wear, the approach taken in the present study was to perform experiments that tested the sulfuric acid theory against the possibility that sulfur dioxide, in fact, was responsible for most of the wear and also deposit formation.

Accomplishments: The results of this study support a new theory that sulfur dioxide formed directly in the combustion of fuel sulfur is responsible for the corrosive wear and deposit formation in diesel engines. It was found that the mechanism of corrosion by sulfurous acid, H_2SO_3, involves an oxidation-reduction mechanism; whereas sulfuric acid, H_2SO_4, simply behaves as an acid, causing galvanic corrosion. This difference in the corrosion mechanism may suggest new approaches for inhibiting the corrosion process, e.g., new possibilities may emerge in additive formulations and metallurgy that would not have been considered if sulfuric acid continued to be viewed as the major cause of corrosion. Considerable evidence is presented to show that dissolved sulfur dioxide in the lubricant is the major cause of increased deposits due to fuel sulfur. The fact that SO_2 appears to be the major cause of sulfur-related deposits seems to simplify the problem and should provide some new direction in solving the problem of deposits in diesel engines.

Military Impact: The benefit of this study is that it will provide direction for future research and development of lubrication additives, corrosion-resistant metallurgy, and improved engine design. Because sulfur dioxide causes corrosion by a different mechanism than sulfuric acid and also seems to be largely responsible for deposits, new approaches to the fuel sulfur problem may emerge that will eventually increase fuel availability in crisis situations and extend the life of vehicles in the field.

FOREWORD/ACKNOWLEDGMENTS

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I. INTRODUCTION AND BACKGROUND

In potentially strategic locations outside the continental United States, U.S. military ground mobility equipment uses fuel with increased sulfur content. Fuel-bound sulfur has been identified as a primary contributor to diesel engine wear and deposits. The literature (1-4)* on the effects of fuel-bound sulfur on diesel engine wear indicates that sulfuric acid mist formed within the combustion chamber is responsible for corrosive attack of the cylinder bore and piston ring areas. Deposit formation has been more of a mystery in that the literature (4) tends to support the theory that reaction of organically bound sulfur with the fuel and lubricant is the principal cause.

There is a definite need for a more basic understanding of the role played by sulfur in wear and deposit formation. A greater emphasis on the sulfur-containing species found in fuels and those formed in the combustion process that are responsible for wear and deposits may lead to the development of improved fuel additives and provide guidance in the materials and design aspects of future diesel engines.

Recent work (1) on the effects of heteroatoms on wear and deposits involved operating a single-cylinder diesel research engine using a highly controlled base fuel (JP-7) that was extremely low in sulfur and nitrogen. The engine lubricant was a synthetic polyalphaolefin material, also free of sulfur and nitrogen. Thus, wear and deposit effects observed during the 60-hour single-cylinder laboratory engine test were directly related to the heteroatom compound added to the base fuel. Through these controlled laboratory tests, wear and deposit effects were studied using four different types of known fuel sulfur compounds and two diesel fuels containing naturally occurring organic sulfur. Fuel sulfur type did not appear to directly influence wear rate. Support for this belief was also observed in the deposit-forming tendencies of most sulfur contaminants. The one exception was that the disulfide-type sulfur compounds appeared to produce slightly higher piston deposits. Fortunately, the type of sulfur in the fuel is not a great concern; this fact simplifies the procurement of diesel fuels.

In Frame's (1) investigation, four fuels contaminated with different nitrogen compounds had little or no effect on engine wear, but some of the nitrogen-containing fuels

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* Underscored numbers in parentheses refer to the list of references at the end of this report.

appeared to be associated with fuel injector deposits and fouling. In engine tests that had oxygen heteroatom compounds added to the base fuel in the form of naphthenic acids, higher engine wear was observed, but piston deposit formation remained at baseline levels. A fuel containing a combination of both known sulfur and nitrogen heteroatoms was tested, and no synergistic effects on wear or deposits were observed.

The mechanism of fuel sulfur-related cylinder bore and ring wear is primarily a corrosion process believed to be caused by sulfuric acid formed from sulfur trioxide, SO_3, and water in the cylinder. Sulfuric acid, H_2SO_4, formation has been assumed to be the most important ingredient in the corrosion process because it is very stable, and its dewpoint temperature is such that condensation on a cylinder wall is favorable. It is postulated that sulfuric acid vapor condenses on the relatively cool cylinder walls and causes significant corrosion in areas of inadequate lubrication such as the upper cylinder bore. When engine tests were conducted at lower temperatures, i.e., by reducing the temperatures of the oil and coolant, it was found that the wear increased sharply. This increased wear also supports the theory of acid condensation on the cylinder wall. In view of these observations, it seems that the evidence is almost overwhelming that the corrosion is caused by sulfuric acid. However, there still remains the fundamental question of whether or not sulfuric acid actually forms in the cylinder. This question must be resolved so that improved methods of controlling fuel sulfur-related wear can be developed.

In diesel engine combustion, the fuel-bound sulfur is oxidized as the fuel burns. Sulfur dioxide forms rapidly in the flame zone, but the anhydride of sulfuric acid, SO_3, cannot form at flame temperatures because it is thermodynamically unstable at temperatures above 1300K. Fig. 1 shows the effects of pressure, temperature, and fuel/air ratio on the equilibrium concentration of SO_3 in a mixture of SO_2 and combustion gases.[2] Note that the fuel/air ratio scale corresponds with the temperature scale. The flame temperature was calculated by assuming that the initial temperature was 600°F (316°C). In diesel engine combustion, the pressure is very high, which increases the equilibrium concentration of SO_3. However, since temperature is the overwhelming effect, it seems very unlikely that significant SO_3 concentrations could form in the gas phase within the combustion chamber. It is important to keep in mind that the combustion process in a diesel engine is basically a diffusion flame. Diffusion flames burn at the stoichiometric

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$\dfrac{n_{SO_3}}{n_{SO_2}}$

$SO_{2\,(g)} + 1/2\,O_{2\,(g)} = SO_{3\,(g)}$

$$K_p = \frac{P_{SO_3}}{P_{SO_2}\sqrt{P_{O_2}}}$$

$$\frac{n_{SO_3}}{n_{SO_2}} = K_p\sqrt{n_{C_i}}$$

FUEL $(CH_{1.9})$; $T_0 = 600\,^{\circ}F$

$\dfrac{n_{SO_3}}{n_{SO_2}}$

50

10

5

1.0

0.5

P = 300 psia

OPERATING RANGE

0.10

P = 200 psia

0.05

| 1200 | 14 | 1600 | 18 | 2000 | 22 | 2400 | °F |

| 800 | 900 | 1000 | 1100 | 1200 | 1300 | 1400 | 1500 | 1600 | °K |

| 0.01 | 0.015 | 0.02 | 0.025 | 0.03 | 0.035 | F/A |
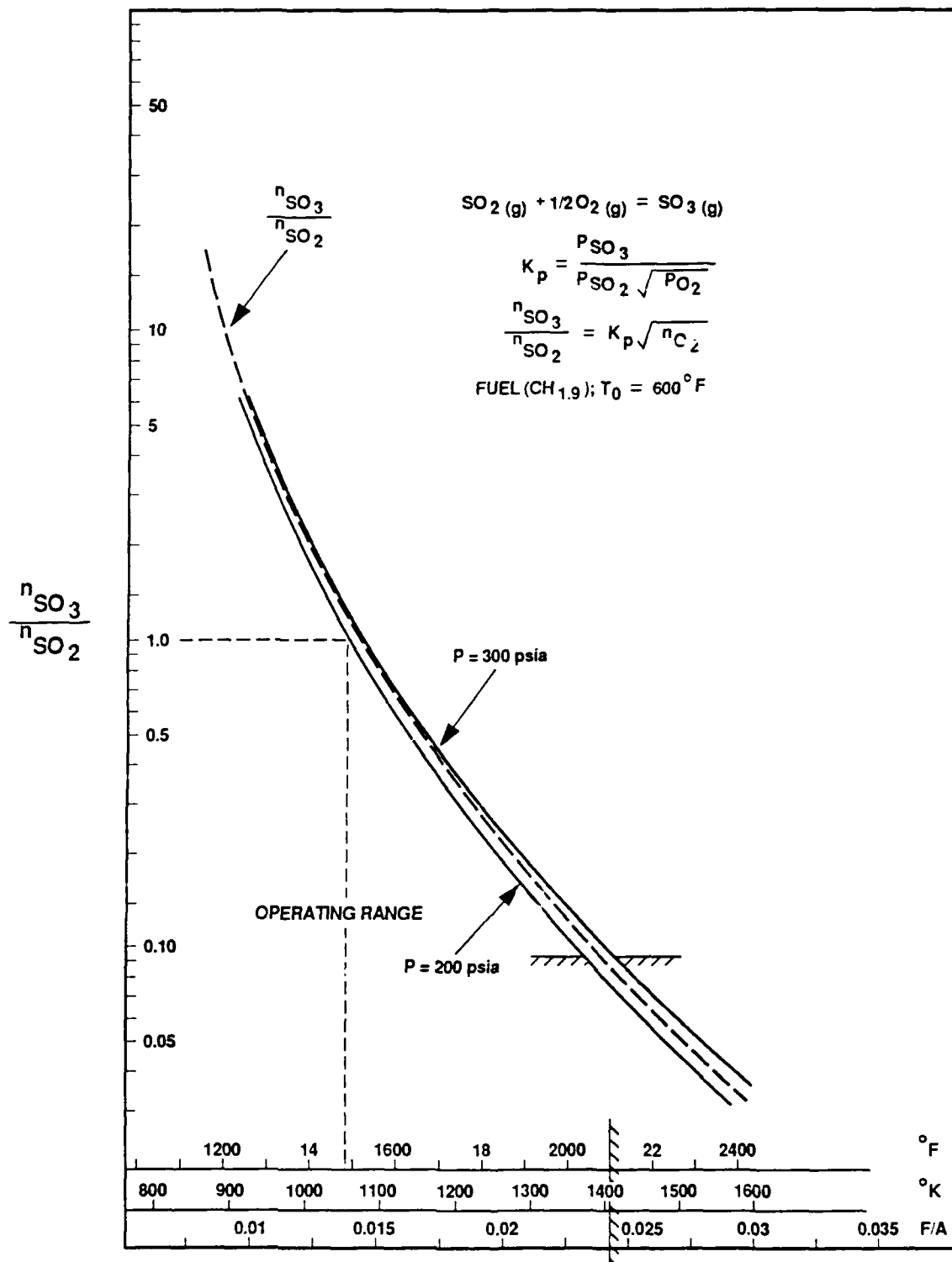
Figure 1. **Effect of temperature and fuel/air ratio on the**
SO_3/SO_2 mole ratio
(The fuel/air ratio scale corresponds with the flame temperature
that would be achieved assuming homogeneous combustion and
initial temperature of 600°F (316°C))

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fuel/air ratio, i.e., F/A = 0.065, so the actual flame temperature is much higher than that based on calculations using the overall fuel/air ratio.

The mechanism for the conversion of SO_2 to SO_3 remains relatively unknown. If, on one hand, SO_3 is formed by

$$SO_2 + O_2 = SO_3 + O$$
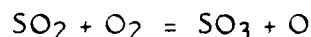
the rate of its production would probably be very slow. This reaction has a high activation energy because it involves the cleavage of the strong bond, 118 kcal/mole, in molecular oxygen; thus, it is very slow at temperatures below 1500K. On the other hand, the termolecular reaction of sulfur dioxide with oxygen atoms

$$SO_2 + O + M = SO_3 + M$$
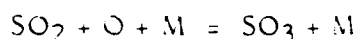
is essentially independent of temperature and increases in rate as the pressure, i.e., the third body, M, concentration, is raised. Although this reaction appears to be a likely candidate, it depends strongly on the oxygen atom concentration in the combustion chamber. Since oxygen atoms are present only when the temperature of the gas is close to the flame temperatures, i.e., at temperatures in which SO_3 is very unstable, it is highly improbable that this mechanism would account for its formation in the bulk gas phase environment of the combustion chamber.

A similar argument may be made for the reaction of SO_2 with OH radicals. The reaction of OH radicals with SO_2 is complex at ambient temperatures and is believed to be important in the formation of sulfuric acid in the atmosphere.(3) At flame temperatures the reaction

$$SO_2 + OH = SO_3 + H$$
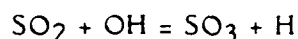
is probably very fast because the concentration of OH radicals is much higher than that of O atoms in the reaction zone.

One mechanism that could conceivably account for the formation of SO_3 in the gas phase is the diffusion of O atoms and OH radicals into the boundary layer on the surface of the

cylinder wall. The temperature in the boundary layer next to the surface of the relatively cold cylinder wall is expected to be less than 1000K. If SO_3 could be formed in the boundary layer, it would quickly scavenge water vapor and become sulfuric acid. While such a diffusion mechanism is possible, it is important to note the diffusion rates are exceedingly slow at high pressures. Hence, the diffusion of radical species into a lower temperature region would not only be slow, but reactions at high pressures would be very fast in bringing their concentrations down to equilibrium levels.

For the mechanism of condensation of sulfuric acid on the cylinder wall to be important, SO_3 must be formed in the gas phase. Based on the discussion above, this for nation does not seem to be highly probable. Aside from a relatively complex catalytic reaction involving chemisorbed SO_2 and O_2, it is difficult to conceive of a process that could result in the formation of detectable concentrations of sulfuric acid in the combustion chamber of a diesel engine. Therefore, the arguments given above suggest that the ring and cylinder bore wear in diesel engines is most probably caused by the abundant sulfur dioxide formed by the combustion of sulfur-containing fuels.

It is known that SO_2 has a high solubility in oils.(4) Since lubricants contain alkali dispersants, it is possible that both SO_2 and water dissolve in the lubricant film. When SO_2 combines with water, it forms an acidic sulfur dioxide hydrate (5) known in loose terms as sulfurous acid; it is a relatively weak acid that is comparable in strength with low molecular weight carboxylic acids. Engine tests (1) have shown that cylinder bore and ring wear increase when naphthenic acids are added to the fuel; it is equally possible that sulfurous acid could cause similar wear.

Although the literature favors the sulfuric acid theory, it is simply assumed that SO_3 is formed within the cylinder of the engine. Several measurements of sulfur oxides in diesel exhaust indicate that the conversion of SO_2 to SO_3 may range from as little as 1 percent to as much as 90 percent. However, this does not prove that SO_3 is formed in the cylinder where corrosive wear takes place. Thermodynamic calculations show that SO_3 is relatively unstable at higher temperatures and is unlikely to survive the hostile environment within the combustion chamber. The probability seems to be greater that SO_3 is formed in the exhaust system. The lower temperature in the exhaust system favors the formation of SO_3 because the equilibrium is shifted in that direction. Also, the exhaust system is made of steel, and its surface-to-volume ratio is high. Since the

walls are probably coated with Fe_2O_3, it is very possible that catalysis plays a role in the conversion of SO_2 to SO_3. Hence, high conversions of fuel-bound sulfur to sulfuric acid do not seem to originate from within the engine cylinder. In conclusion, it seems that there is a considerable question about the actual formation of SO_3 and sulfuric acid within the cylinder of the engine.

The purpose of the present study is to further investigate the role of sulfur oxides in wear and deposit formation in diesel engines. The results of this study suggest that sulfur dioxide (SO_2) formed in the combustion of fuel-bound sulfur is the primary cause of higher cylinder bore and ring wear and deposit formation in diesel engines. This finding is expected to have some bearing on the course of future research and the development of lubricants that will more effectively combat the effects of fuel sulfur.

II. OBJECTIVE

The purpose of this study was to use an exploratory approach involving several individualized experiments to determine the role of sulfur oxide chemistry in the corrosion-related cylinder bore and ring wear and reactions that lead to deposit formation in diesel engines. Previous studies based on engine tests emphasized measurements on the effects of sulfur concentration, sulfur type, engine temperature, etc., and concluded that sulfuric acid formation in the cylinder was the principal cause of cylinder bore and ring wear. However, an analysis of both the chemical and the diesel engine literature suggests that sulfuric acid may play only a relatively minor role and that the very abundant oxidation product, sulfur dioxide, could well be the chief cause of wear and deposit formation in diesel engines. This conclusion implies that future studies on cylinder bore and ring wear in diesel engines operating on high-sulfur fuels should consider sulfur dioxide as the corrosive agent rather than sulfuric acid.

III. APPROACH

This program was carried out from an exploratory stand point to determine the importance of sulfur dioxide chemistry in wear and deposit formation in diesel engines. Several experiments including both bench-scale type and full-scale engine tests were performed. Bench-scale experiments were carried out to determine the reactivity and

solubility of SO_2 in lubricants; wear measurements were made on lubricants contaminated with moisture and SO_2 using a BOCLE rig; and JFTOT tests were carried out to determine the effects of SO_2 contamination on the *thermal stability of fuels and lubricants.*

Measurements were made in a Petter diesel engine to determine the in-cylinder conversion of fuel sulfur to sulfuric acid mist. These measurements were performed using both sulfur-containing fuels and by adding sulfur dioxide to the air supply to the intake manifold of the engine. In 60-hour, full-scale engine tests, the effects of fuel sulfur and SO_2 added to the intake air on wear and deposits were evaluated. A DD 3-53 three-cylinder diesel engine equipped with individual *fuel injection systems for each* cylinder was used to determine if contamination of the lubricant with sulfur-containing combustion products was the sole cause of wear and deposits. In this test, a high-sulfur fuel was used in two cylinders and a neat fuel was used in the third cylinder. All three cylinders shared the same lubricant.

Although all the experiments described above had a similar goal, i.e., to show the potential of SO_2 to cause wear and deposits, the particular experimental procedures and apparatus used in the various areas of exploration were quite *dissimilar so they are* presented in the results section of this report.

IV. RESULTS

A. Engine Tests

There were basically three objectives of the engine testing; the first was to determine the importance of sulfuric acid in the wear mechanism, the second was to determine the importance of fuel-bound sulfur in the formation of deposits, and the third was to determine if the deposit formation and wear were the result of contaminants in the lubricant or caused by the relatively nascent combustion products formed in the cylinder. The approach used to determine the importance of sulfuric acid was to measure its concentration in the exhaust gases of a Petter diesel engine. Some of the earlier studies showed conversions of fuel-bound sulfur to sulfuric acid ranging from 10 to 90 percent, others report much lower yields, and thermodynamic calculations indicate that little or no sulfuric acid should form in the combustion chamber. To accomplish the second

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objective, tests were performed in a Petter diesel engine to measure the deposits and wear that result from the sulfur dioxide formed by the combustion of fuel sulfur.

In this test, a sulfur-free JP-7 fuel was used, and sulfur was introduced to the engine by injecting a flow of sulfur dioxide into the intake manifold. The purpose of this experiment was to eliminate possible effects of organic sulfur and to determine the importance of sulfur dioxide in the formation of deposits. To reach the third objective, tests were carried out in a Detroit Diesel (DD) 3-53 three-cylinder diesel engine equipped with individual fuel pumps and injection systems on each cylinder. In one cylinder, a blend of JP-7 fuel and tert-butyldisulfide containing 3-percent sulfur was used. Since all three cylinders shared the same oil sump, differences in wear and deposits among the three cylinders were attributed to the sulfur-containing combustion products formed in the cylinder.

B.   Sulfuric Acid Measurements

An analytical method was developed to measure the concentrations of sulfur oxides in the exhaust of a Petter diesel engine. Fig. 2 shows the apparatus used in these measurements. Basically, the method consisted of passing the exhaust gases through Trap A, filled with water, followed by Trap B, filled with 0.15 normal ammonium hydroxide. Each of the traps was equipped with impingers to enhance the dissolution of gases in the aqueous media. The volume of gas passed through the traps was measured with a wet test meter. Even though the object was to measure the relative concentrations of SO_2 and sulfuric acid mist, it was important to measure the volume and know that enough gas had passed through the traps. In theory, all the sulfuric acid mist is absorbed in Trap A; some of the SO_2 remains in Trap A also, but most of it is fixed in Trap B containing ammonium hydroxide.

The samples from the traps, each about 20 mL in volume, are analyzed for sulfite ion, SO_3, and sulfate ion, SO_4, by an ion chromatograph. The analysis must be performed promptly. If the samples are permitted to stand for any length of time, some of the sulfite ions will be oxidized to sulfate ion, and the sample will then have a falsely high level of sulfuric acid mist. This oxidation may be why unusually high levels of sulfuric acid have been found in exhaust samples in previous studies. The present study has shown that extreme care in preventing the oxidation of the sulfite ion is essential.
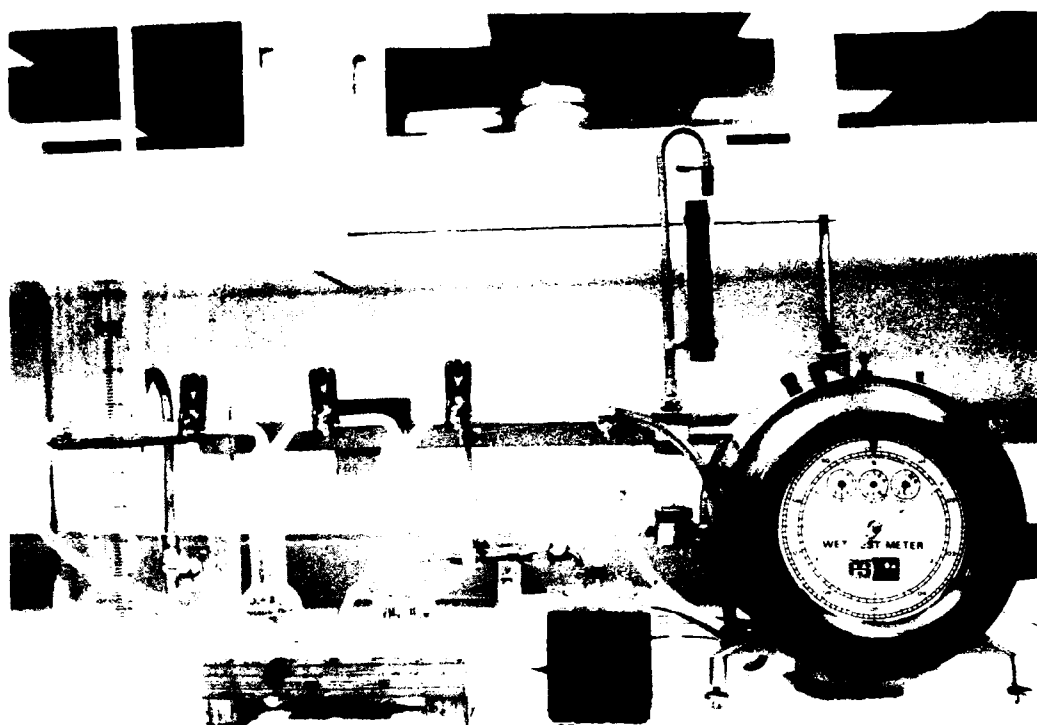
Figure 2. Apparatus for trapping out sulfur oxides from
diesel exhaust

Several bench-scale tests (see apparatus in Fig. 2) were made using mixtures of air and SO_2 to determine the accuracy of the method. The method provided a good measurement of the total sulfur oxides present in the air sample. In other words, it was apparent that all the SO_2 was absorbed by the water and ammonium hydroxide in the traps. Since the air sample contained only SO_2, it was hoped that only sulfite ion would be detected in the water trap. Unfortunately, a significant amount of sulfate ion was also found, indicating that some sulfite oxidation had occurred in Trap A before the solution could be analyzed with the ion chromatograph.

Since the primary purpose of this measurement was to determine the sulfuric acid content of diesel engine exhaust, special steps were taken to prevent the oxidation of sulfite ion in the water trap. In a recent study, Erwin (5) found that several low molecular weight carboxylic acids were, in fact, quite effective inhibitors of the oxidation of sulfite ion; glycolic acid was found to be a particularly strong inhibitor. Irwin's measurements showed that a 0.4-percent aqueous of glycolic acid was optimal in preventing the oxidation of sulfite ion. It was found that the replacement of the water in the first trap with the glycolic acid solution greatly reduced the oxidation of sulfite

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ion. While this change significantly improved the measurement, it was, nevertheless, important to use every method possible to reduce the rate of oxidation of sulfite ion in the first trap.

Trial analyses were performed on SO_2/air mixtures to determine if purging the contents of Traps A and B would lower the rate of oxidation of sulfite ion in Trap A. TABLE 1 gives some typical data obtained in these analyses.

TABLE 1. Analysis of Sulfur Oxides

Sample Number	Trap A		Trap B		Air Purge, liters	N_2 Purge, liters	% Sulfur as H_2SO_4
	SO_3	SO_4	SO_3	SO_4			
1	171	25	216	0	0	0	5.11
2	78	1	400	29	10	0	0.17
3	31	23	400	1	20	0	4.25
4	21	10	494	11	30	0	1.56
5	26	18	458	9	0	20	2.96

The purpose of purging the traps with air and nitrogen was to drive the dissolved SO_2 in Trap A into Trap B. Since sulfite ion is easily oxidized, lowering its concentration in Trap A would help to prevent the formation of sulfate ion. The results in TABLE 1 show that there was considerable oxidation of sulfite ion in Trap A. Only sample 2 gave an acceptably low level of sulfuric acid. Purging the solution with air and/or nitrogen had little effect on the yields of sulfuric acid. Note also that there was considerable scatter in these measurements.

While investigating these results further, it was realized that most of the oxidation in the samples occurred in the time that lapsed between acquiring the sample and performing the analysis with the ion chromatograph. In the procedure used, the samples from Traps A and B were poured into glass vials and carried to another laboratory for ion chromatographic analysis. The vials contained air in the vapor space above the solutions taken from Traps A and B. If the samples stood for any length of time before the analysis was performed, dissolved oxygen in the solution would oxidize the sulfite

ion. Therefore, purging with an inert gas such as nitrogen could have been very beneficial since it would tend to displace the dissolved oxygen in Trap A.

In subsequent trial analysis of SO_2/air mixtures, the samples in Traps A and B were purged with nitrogen, and a new technique was used to minimize contamination with oxygen when the sample was taken from Trap A for analysis. A syringe with a 0.45-micron uniflo filter was used to extract the sample from Trap A. The syringe and filter assembly shown in Fig. 3 was particularly useful in retrieving diesel exhaust samples from Trap A because that sample was grossly contaminated with soot. The soot had to be removed before the sample could be analyzed with the ion chromatograph. Since the syringe was also compatible with the injection port of the ion chromatograph, this method of transferring the sample eliminated any further contact with oxygen and freed the sample of particulate contamination.

Figure 3. The syringe and 0.45-micron uniflo filter device used to retrieve dissolved diesel exhaust samples from Trap A in Fig. 2

A last question that arose in the analysis technique was the possibility that the concentration of oxygen in the gas samples might have an effect on the oxidation of sulfite ion to sulfate ion while the gas was being purged through Trap A. To address this concern, gas blends of nitrogen and SO_2 containing 5-percent and 21-percent oxygen were prepared and analyzed in duplicate. It was found that the conversion to sulfuric acid was 0.53 percent in the sample containing 5-percent oxygen and 0.38 percent in the sample containing 21-percent oxygen. These measurements showed that the concentration of oxygen in the sample had little or no effect on the amount of sulfate ion detected in Trap A.

The refinements in the technique, along with more prompt analysis, reduced the oxidation of sulfite ion in Trap A by almost an order of magnitude below the first

attempts to analyze sulfur oxides and, thus, greatly improved the accuracy of the analysis. Several analyses of SO_2/air samples provided a baseline that could be used to compare with analysis of actual diesel exhaust. Obviously, the SO_2/air samples did not contain any SO_3 or H_2SO_4, but the results still showed that about 0.5 percent of the sulfur was present in the form of sulfuric acid. A GC-Mass Spectrometric analysis showed that the SO_2 used in this study contained less than 100 ppm of SO_3. Hence, it was concluded that if sulfuric acid was actually present in the exhaust of the Petter engine, the exhaust analysis method described above would have to show a conversion of fuel sulfur to sulfuric acid greater than a baseline value of 0.5 percent.

As mentioned above, a Petter Model PH1W single-cylinder, four-cycle, direct injection, water-cooled diesel was used in the study of exhaust sulfur oxides. Petter engine characteristics are given in TABLE 2.

TABLE 2. Petter PH1W Engine Characteristics

Displacement	659 cm^3 (40.2 CID)
Bore and Stoke	87.3 mm x 110 mm
Compression Ratio	16.5:1
Piston	Aluminum
Piston Rings	3 Rectangular Compression Rings, 1 Oil Control
Oil Capacity	2.84 L (no oil filter used)

Before each test was performed, the liner was honed and the piston cleaned to remove deposits, and the engine was rebuilt with new piston rings. Following a short break-in on neat JP-7 fuel, the engine oil (polyalphaolefin) was changed, and the test was started. The test procedure consisted of 60 hours of steady-state operation, accumulated 8 hours per day for 7.5 days with a 16-hour overnight shutdown each day. Typical engine operating conditions used in most of the tests are given in TABLE 3. Engine oil level was adjusted to full at the end of each day, and a small sample of the used oil was drawn for wear metals analysis.

TABLE 3. Petter Engine Operating Conditions for Exhaust Analysis

Operating Condition	Setting
rpm	1800
Load, ft-lb	28 to 29
Bhp	9.6 to 9.8
Oil Temp, $^{\circ}C$	74 to 78
Coolant In, Temp, $^{\circ}C$	80
Coolant Out, Temp, $^{\circ}C$	82 to 83
Exhaust Temp, $^{\circ}C$	550 to 575
BSFC, lb/BHp hr	0.387 ± 0.005
Piston Temperature*, $^{\circ}C$	
Top Land (thrust and antithrust)	182
Skirt Top (thrust and antithrust)	131

* Determined by temperature-sensitive plugs.

At first, the engine was operated on a JP-7 fuel containing 1.0-percent sulfur added in the form of tert-butyldisulfide (TBDS). Later the fuel sulfur content was increased to 2.0 percent, and, in some of the tests, JP-8 was used as the base fuel instead of JP-7.

The exhaust samples were taken as close as possible (ca. 6 in. (15 cm)) to the exhaust port of the engine to minimize the low-temperature gas phase oxidation of SO_2 in the exhaust line. The results of repeated measurements at the operating conditions given in TABLE 3 are shown in TABLE 4. Note that the calculation of wt% sulfur in the form of sulfuric acid was performed by dividing the moles of sulfur in the form of sulfate ion in Trap A by the total moles of sulfur in Traps A and B, and multiplying by 100.

It is apparent that the levels of sulfuric acid in the exhaust are very low. When the baseline of 0.5-percent conversion to sulfuric acid is compared with the average value of 0.81 percent from exhaust measurements, the difference, 0.31 percent, lies well within the standard deviation of the baseline measurements, so it seems that there is virtually no sulfuric acid in the exhaust. In addition to the measurements near the exhaust, some measurements were also made about 6 feet downstream in the exhaust. These

TABLE 4. Analysis of Sulfuric Acid in Exhaust

Sulfite Ion, mg/L		Sulfate Ion, mg/L		% Sulfur* as H_2SO_4 Acid
Trap A	Trap B	Trap A	Trap B	
160	782	13.4	106	1.07
110	754	8.8	156	0.73
31	680	9.0	60	0.98
29	580	6.0	112	0.71
66	992	9.9	34	0.75
20	944	4.9	56	0.40
223	958	9.1	41	0.62
12	566	7.3	73	0.94
10	1523	21.3	53	1.11
12	1058	10.1	107	0.72

* The wt% of sulfur as sulfate ion in Trap A. Average = 0.81 percent.

measurements showed conversions to sulfuric acid ranging from 2 to 4 percent, indicating that there was some oxidation of SO_2 to SO_3 in the exhaust gases. In previous studies, measurements of sulfur oxides in the exhaust showed relatively high conversions to sulfuric acid. In view of the results of the present study, it appeared that the high conversion rates observed in previous studies were either caused by SO_3 formation in the exhaust system, or they may possibly have been the result of problems with the method of analysis.

Most of the measurements of sulfur oxides were made using the operating conditions given in TABLE 3, i.e., the same conditions used in an earlier study by Frame.(1) However, some work was done at different operating conditions, varying coolant temperature and load. Several studies (4,6) have shown that operating conditions such as load and, especially, coolant temperature have a more marked effect on cylinder bore and ring wear when sulfur is present in the fuel. For example, lowering the coolant temperature normally reduces the wear rate, but when sulfur is present, the wear rate tends to increase considerably. These observations have led workers to believe that lowering the coolant temperature increases the formation of sulfuric acid in the combustion chamber. If sulfuric acid concentrations are increased as the result of lower

combustion temperatures and reduced temperatures at the cylinder walls, it is possible that this increase would also be observed in the exhaust gases.

Engine tests were performed at coolant outlet temperatures as low as 110°F (43°C), and the exhaust gases were analyzed for SO_2 and sulfuric acid content. Tests were also carried out to determine the effects of rpm and load on the conversion of fuel sulfur to sulfuric acid in the exhaust gases. All these measurements gave basically the same result. There was no detectable sulfuric acid in the exhaust.

These measurements are quite conclusive in that they show that very little, if any, sulfuric acid is formed in the combustion chamber of a continuously operating diesel engine. Since sulfuric acid concentrations in the combustion chamber appear to be exceedingly low, the results suggest that sulfur dioxide plays a more important role in cylinder bore and ring wear. This is not to say that sulfuric acid is totally unimportant in cylinder bore and ring corrosion. In cases where the engine has been turned off, the remaining combustion condensates left in the cylinder contain sulfur oxides in aqueous solution that would most probably oxidize to sulfuric acid.

C. Effects of Sulfur Dioxide

Both engine tests and bench-scale experiments were performed to determine the role of sulfur dioxide in deposit formation and wear. Two full-scale 60-hour engine tests were performed in which sulfur dioxide gas was introduced into the intake air stream of the Petter engine. In these tests, the JP-7 fuel, the polyalphaolefin lubricant, and the operating conditions given in TABLE 3 were the same as those used by Frame (1) in a previous study. These conditions were used because the objective was to compare the results of adding SO_2 to the inlet air with the results obtained by Frame (1) on JP-7 fuel with various added sulfur compounds. The concentration of SO_2 in the inlet air was made equivalent to that which would be formed in an engine burning a fuel containing 2-percent sulfur.

In addition to the measurements of engine wear and deposit formation performed by Frame, samples of the inlet air and exhaust gases were analyzed for sulfur oxides, including sulfuric acid. Also an iron coupon was placed in the crankcase of the engine. At the end of the test, the iron coupon was examined for corrosion using electron

microscopy. The coupons were then compared with bench-scale corrosion experiments using similar iron coupons. The results of these measurements are discussed in the section of this report that addresses corrosion chemistry and mechanisms.

While the tests were in progress, gas samples were taken for analysis of sulfur oxides from both the air inlet to the engine and the exhaust port. It is well established in the results presented previously that sulfuric acid is negligible in the combustion of fuels containing sulfur. However, it was thought that there might be more significant formation of sulfuric acid in an experiment where the SO_2 was in the air before it reached the combustion chamber. TABLE 5 gives the results of the analysis of samples taken while the tests were in progress.

TABLE 5. Ion Chromatographic Analysis of Inlet and Exhaust
Gases for SO_2 and SO_3 in Petter Engine

Sample No.	Sulfite, mg/L		Sulfate, mg/L		% Sulfur as SO_4 in Trap A
	Trap A	Trap B	Trap A	Trap B	
E1	310	6600	140	45	1.65
E2	500	4200	75	80	1.38
E3	640	8000	125	170	1.17
E4	650	7200	120	120	1.24
E5	690	8000	50	195	0.47
E6	760	8900	100	170	0.84
E7	680	8200	100	110	0.92
E8	810	8500	90	125	0.79
E9	990	8300	80	40	0.71
E10	960	8100	88	165	0.79
E11	650	6800	89	140	0.97
I1	490	8300	30	245	0.28
I2	620	8000	31	435	0.29
I3	620	7800	31	425	0.29
I4	440	8100	80	565	0.73
I5	670	10000	40	320	0.30
I6	650	8600	35	390	0.30
I7	1030	8400	35	215	0.30
I8	620	6700	45	160	0.50

E = exhaust sample; average = 0.99-percent conversion to H_2SO_4.
I = air intake sample; average = 0.37-percent conversion to H_2SO_4.

The results in TABLE 5 reconfirm that only a small amount of sulfuric acid is formed in the combustion chamber. In this test, the SO_2 was given a greater opportunity to oxidize the SO_3 than in the tests using fuel-bound sulfur. The concentrations of sulfuric acid in the exhaust are similar to previous tests; 0.81-percent conversion of sulfur to sulfuric acid in the test using fuel-bound sulfur and 0.99-percent conversion in the test where SO_2 was introduced into the intake air stream. The analysis of the SO_2-contaminated intake air provided an excellent baseline for the sulfuric acid formed in the process of performing the analysis. Accounting for the baseline, these results indicate that the amount of sulfur in the form of sulfuric acid in the exhaust, near the exhaust port, is less than 0.6 percent. This result places considerable doubt in the theory that sulfuric acid is solely responsible for corrosive wear in diesel engines operating on fuels containing sulfur.

Upon completion of the test, the engine was disassembled and examined for wear and deposit buildup. Ring wear was measured, and a standard Coordinating Research Council (CRC) weighted total deposit piston rating was performed. The used oil was analyzed for degradation and contamination buildup using standard ASTM tests. Deposits were washed from the piston and intake valve with heptane and then dimethylformamide (DMF). Heptane- and DMF-soluble deposits were recovered using a vacuum rotary evaporator to remove the solvents. The deposits from the heptane and DMF washings were then weighed and analyzed to determine their chemical compositions.

TABLES 6, 7, and 8 summarize the engine test results and give a comparison with previous test results reported by Frame (1) using JP-7 fuel and various added sulfur compounds. Engine wear was evaluated based on used oil iron content and measured piston ring end-gap change; cylinder liner wear was not discernible among the tests. Fig. 4 shows the history of iron buildup in the used oil of Tests I and II. Two tests were performed because the used-oil iron content appeared to be unusually low in the first test. The irregular, but, for the most part, monotonic increase in the used-oil iron content is typical of other wear studies. Comparison of data in TABLE 6 shows that the average used-oil iron content measured in Tests I and II was about 51 percent of that found in previous tests using JP-7 fuel containing 2-percent sulfur. Based on the work of Frame, the used-oil iron contents of Tests I and II were similar to or just slightly above the values that were found for the same JP-7 fuel containing 1-percent sulfur.

TABLE 6. Petter Engine Tests - 2% Fuel S

Fuel Heteroatom Type	JP-7 None*	JP-7 + 2% S as Fuel Additives* Range	JP-7 + 2% S as SO$_2$ Test I	JP-7 + 2% S as SO$_2$ Test II
<u>Avg. Operating Conditions</u>				
Test Hours	60	60	60	60
rpm	1800	1800 to 1806	180	1803
Load, lb-ft	29	29 to 30	29	29
Bhp	9.8	9.8 to 10.1	9.9	10.0
Oil Temp, °C	79.1	74.4 to 79.1	75.1	76.1
Exhaust Temp, °C	605	584 to 624	563	552
Oil Consumption, lb/hr	0.228	0.229 to 0.346	0.213	0.362
<u>Results</u>				
Used Oil Fe, ppm	52	231 to 268	146	162
Ring End Gap Change, in.				
Top	0.001	0.001 to 0.006	0.003	0.002
2	0.001	0.006 to 0.016	0.004	0.006
3	0.003	0.008 to 0.013	0.005	0.006
Avg. Ring Gap Change, in.	0.0016	0.006 to 0.010	0.004	0.0047
Piston WTD Rating	151	222 to 245	240	212
Piston Lacquer Demerit	3.2	3.5 to 5.5	7.7	6.8
Ring Sticking	None	None	None	None

* Test results from Frame.([1])

TABLE 7. Petter Piston Deposit Composition - 2% Fuel S

Fuel Heteroatom Type	JP-7 None*	JP-7 + 2% S as Fuel Additives* Range	JP-7 + 2% S as SO$_2$ Test I	JP-7 + 2% S as SO$_2$ Test II
Piston/Int Valve <u>Deposit Analyses</u>				
Heptane-Soluble Deposit, wt g	1.75	1.63 to 2.52	0.27	1.89
Composition, wt%				
C	85.4	85.1 to 85.3	83.3	84.7
H	14.1	14.3 to 14.4	6.6	13.2
N	0.11	0.14 to 0.42	0.98	0.23
S	0.12	0.17 to 0.56	2.7	3.06
Dimethylformamide (DMF) - Soluble Deposit, wt g	0.74	0.92 to 1.60	1.08	1.15
Composition, wt%				
C	67.1	53.0 to 59.7	65.6	64.9
H	5.0	5.0 to 8.4	4.8	4.2
N	3.9	1.1 to 5.6	3.6	3.3
S	0.6	3.1 to 3.3	4.4	3.0

* Test results from Frame.([1])

TABLE 8. Used Oil Properties - Petter Engine - 2% Fuel S

Fuel Heteroatom Type	JP-7 None*	JP-7 + 2% S as Fuel Additives* Range	JP-7 + 2% S as SO$_2$ Test I	JP-7 + 2% S as SO$_2$ Test II
__Used Oil Analyses__				
K. Vis, cSt, at 40°C	34.32	34.95 to 37.00	34.4	35.3
at 100°C	6.67	7.39 to 9.30	8.8	7.0
TAN	0.2	0.74 to 1.4	0.90	0.97
Insolubles, wt%				
Pentane "A"	0.71	0.81 to 1.11	1.54	1.82
Toluene "A"	0.53	0.73 to 0.94	1.41	1.72
Pentane "B"	0.69	0.81 to 1.10	1.53	1.84
Toluene "B"	0.28	0.61 to 0.94	0.74	1.05
Elements				
Fe, ppm	52	231 to 268	146	162
Cu, ppm	15	20 to 23	<10	<10
Pb, ppm	<60	<60	<60	<60
S, wt%	<0.01	0.02 to 0.04	0.04	0.04
Differential IR, Oxidation Absorbance at 1710 cm^{-1}	NIL			

* Test results from Frame.(1)
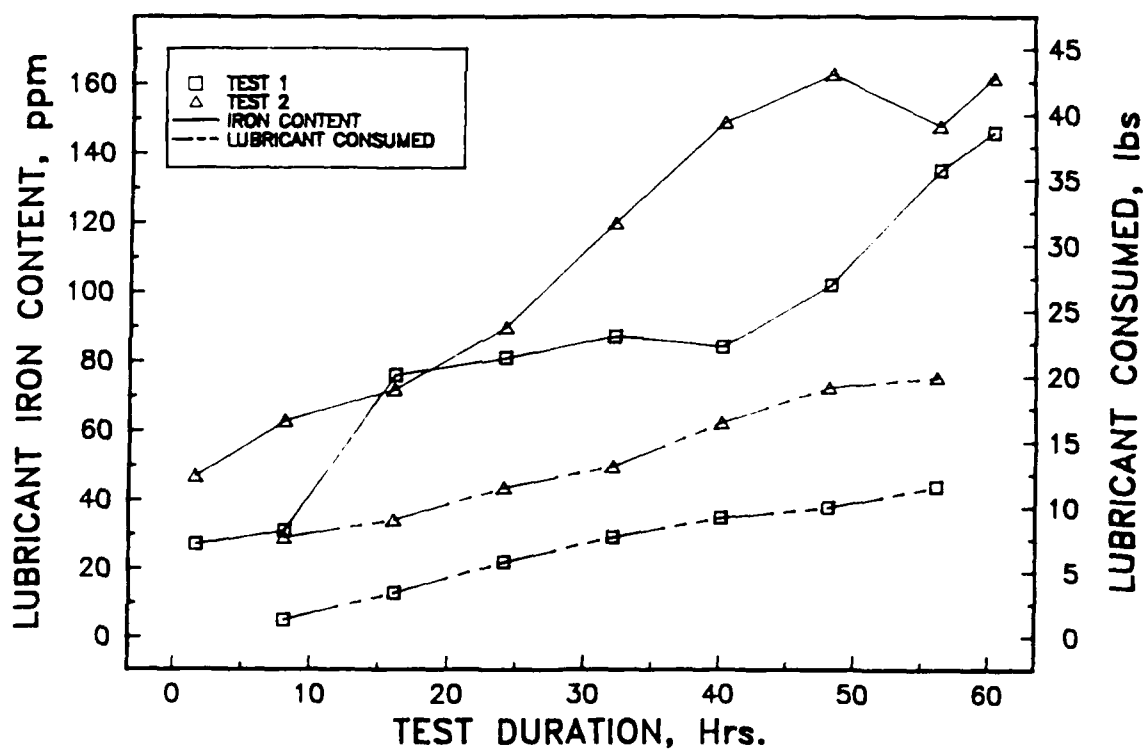
Figure 4. __Iron buildup in the lubricant and the consumption of lubricant during the Petter engine wear tests__
(Sulfur was added by introducing SO$_2$ into air intake stream)

One can only speculate on the reason why the wear is much higher when the sulfur is bound in the fuel. One possible reason is that the combustion process in a diesel engine is highly stratified, so there are large fuel concentration gradients in the combustion chamber. When sulfur is part of the fuel, the diffusion-type burning process may result in relatively high concentrations of SO_2 in various regions of the combustion chamber. If part of the fuel spray impinges on the cylinder wall before it is allowed to burn, it will evaporate from the wall and burn in a zone relatively close to the wall. This burning may result in a relatively high partial pressure of SO_2 near the wall, which would significantly increase the dissolution of SO_2 into the oil film.

In a study by Broeze and Wilson (7), it was found that wear in a single-cylinder Caterpillar diesel engine was nonlinearly dependent on the concentration of sulfur in the fuel. Their results in Fig. 5 show that there is virtually no difference in cylinder bore
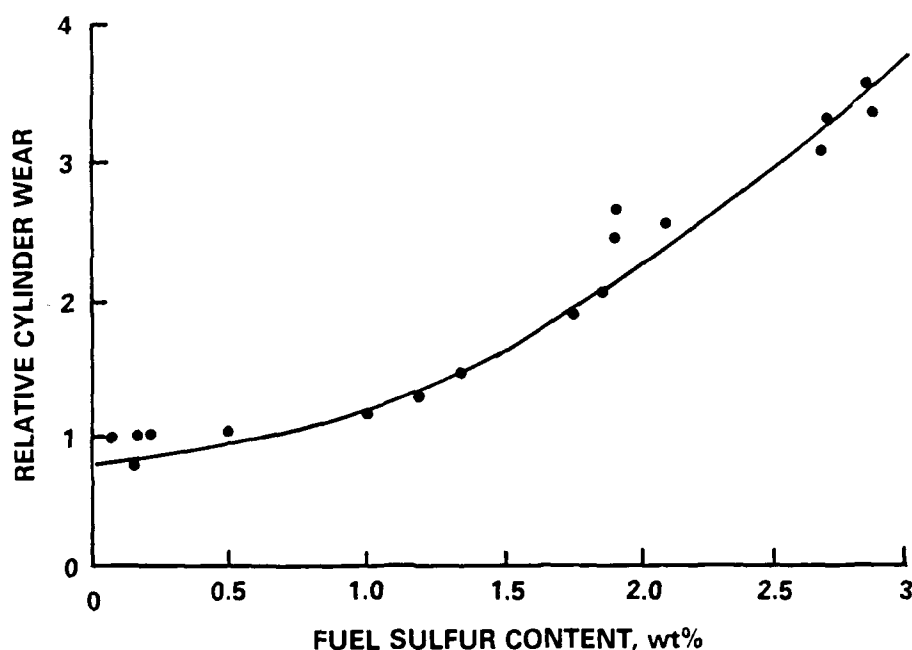
Figure 5. Effect of fuel sulfur on cylinder bore wear (7)

wear for fuels in the 0- to 0.5-wt% sulfur range. However, bore wear started to increase substantially as the fuel sulfur content was raised above 1 percent. Since the concentration of SO_2 in the combustion chamber is directly proportional to the sulfur content of the fuel, and the amount of SO_2 dissolved in the oil film is proportional to the partial pressure of SO_2, the fact that there is a nonlinear dependence of wear on sulfur content suggests that the wear rate may be dependent on the SO_2 concentration to a

power greater than unity. From the standpoint of chemistry, the mechanism of the corrosion process appears to be a complex reaction involving more than one SO_2 molecule.

If cylinder bore and ring wear is, in fact, nonlinearly dependent on the SO_2 concentration in the combustion chamber, it is reasonable to assume that the heterogeneous nature of the combustion process in a diesel engine would tend to create regions of higher than normal concentrations of SO_2, which would, in turn, result in a higher wear rate than if the SO_2 was homogeneously distributed in the combustion chamber. For the present, this explanation is the only one that can be offered for the relatively low wear rates measured in the engine tests where the source of sulfur is SO_2 in the intake air.

It is well known that fuel sulfur increases the formation of deposits on combustion chamber surfaces, especially on the piston and the valve tulip. The mechanism of deposit formation has never been understood, but it has been casually suggested that deposits form as a result of incomplete combustion and the partial oxidation of hydrocarbons and sulfur compounds in the fuel.

Comparison of the results given in TABLES 6, 7, and 8 shows that the deposits formed in Tests I and II are essentially the same as those formed in a similar tests where the sulfur was bound in the fuel. Piston cleanliness, as determined by Weighted Total Deposit (WTD), was independent of whether the sulfur was added in the form SO_2 or was fuel bound. The Lacquer Demerit was a little higher in Tests I and II where SO_2 was added to the intake air, but, nevertheless, fell close to the range of values reported by Frame for fuel-bound sulfur tests. The compositions of the heptane- and DMF-soluble deposits given in TABLE 8 for Tests I and II were similar to the range of values obtained in tests with fuel-bound sulfur. The determination of the heptane-soluble deposit in Test I appeared to be erroneous because the weight of the sample was much smaller than that found for the base fuel. However, the heptane-soluble deposit weight measured in Test II was in good agreement with the range of values reported by Frame for fuel-bound sulfur tests. The sulfur content of the heptane-soluble deposit obtained in Tests I and II was significantly greater than that of the fuel-bound sulfur tests. There is no explanation for this other than the fact that the residence time of SO_2 in the combustion chamber was more than twice as long in Tests I and II.

The composition and weight of the DFM-soluble deposits obtained in Tests I and II were in good agreement with the range of values measured in the fuel-bound sulfur experiments. Since the DFM deposits are generally considered to be the best indicator of lubricant thermal stability, the results given in TABLE 7 suggest that sulfur dioxide plays a major role in deposit formation in diesel engines. For further discussion of the effects of SO_2 on deposit formation, see Section IV.G of this report entitled "The Effects of Sulfur Dioxide on Lubricants."

The results given in TABLE 8 show that the viscosity and total acid number (TAN) of the used polyalphaolefin oil samples from Tests I and II fell within the range of values obtained in the same engine from the fuel-bound sulfur tests. However, the pentane and toluene insolubles found in the used oils were higher in the samples from Tests I and II than they were in the fuel-bound sulfur tests. The higher concentration of insolubles in Tests I and II is probably the result of a greater residence time of sulfur dioxide in the engine. Because sulfur dioxide is present in the cylinder during the compression, combustion, and part of the intake and exhaust strokes, there is a greater opportunity for the dissolution of sulfur dioxide and reaction with the oil. For further discussion of the effects of sulfur dioxide on lubricants see the results of the bench-scale experiments in Section IV.G of this report.

D.   The DD 3-53 Engine Test

The purpose of this experiment was to determine if sulfur-oxide contaminants accumulated in the oil contribute significantly to the wear and deposit formation in diesel engines. A multicylinder engine with separate fuel-injection systems for each cylinder was used to compare the wear and deposit formation from a sulfur-free fuel in one cylinder and a high-sulfur fuel in the other cylinders. Since all cylinders share the same oil sump, effects of sulfur-dioxide contamination of the lubricant on wear and deposit formation can be compared with the effects of in-cylinder combustion products.

The engine used in this experiment was an iron block, two-cycle Detroit Diesel, Model 3-53; its characteristics are described in TABLE 9. The engine was fully instrumented and coupled to a laboratory test stand dynamometer. The test was conducted using the U.S. Army 210-hour wheeled-vehicle test cycle modified for the needs of this program. This test cycle, described in TABLE 10, provides alternating periods of full power and

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TABLE 9. DD 3-53 Engine Characteristics

Engine Type	Two-cycle compression ignition, direct injection uniflow scavenging
Weight (dry), kg (lb)	431 (950)
No. of Cylinders, arrangement	3 in line
Displacement, liter (cu in.)	2.6 (159)
Bore and Stroke, cm (in.)	9.84 X 11.43 (3-7/8 X 4-1/2)
Cylinder Block Material	Cast iron (cast iron liners)
Rated Power, kW (Hp)	72.3 (97) at 2800 rpm
Maximum Torque, Nm (lb-ft)	278 (205) at 1800 rpm
Compression Ratio	21 to 1
Fuel System	Unit injector (N 50 needle valve), primary and secondary engine filters
Governor	Variable speed with throttle controls
Oil Filter	Full-flow single filter
Oil Cooling	Integral heat exchanger using 100-percent jacket-coolant flow
Piston Description	
Material/Design	Cast iron/trunk type
Ring Configuration	1 - Fire ring (rectangular)
	2 - Compression rings (rectangular)
	3 - Oil rings
Piston Cooling	From jet in top of connecting rod

TABLE 10. Wheeled-Vehicle Test Cycle

Period	Time, hr	Load, %	rpm	Coolant, °F (°C)
1	2	100	2400	160 (71)
2	1	0	1500	100 (38)
3	2	100	2400	160 (71)
4	1	0	1500	100 (38)
5	2	100	2400	160 (71)
6	1	0	1500	100 (38)
7	2	100	2400	160 (71)
8	1	0	1500	100 (38)
9	2	100	2400	160 (71)
10	10	--------------------Shutdown--------------------		

cold idling with overnight shutdown. A complete description of the wheeled-vehicle test cycle procedure is given in the Appendix.

Prior to the test, the engine was assembled with new parts, and baseline measurements were made of the cylinder bore and piston diameters, the piston ring gaps, and the bearing weights. Each of the three cylinders in the engine was equipped with individual fuel injection pump systems. A neat Jet A fuel with less than 0.01-percent sulfur was used in cylinder No. 1, and a blend of Jet A and tert-butyldisulfide with a sulfur content of 3.0 percent was used in cylinder Nos. 2 and 3. With regard to lubricant exposure to combustion-product contaminants, the fueling of the three cylinders was equivalent to operating the engine on a fuel containing 2-percent sulfur.

A grade-40 bright-stock lubricant with an API engine service classification SA was used in the test. The properties of this additive-free lubricant are listed in TABLE 11. While the test was in progress, small samples of the oil were taken every 7 hours for analysis

TABLE 11. Properties of Grade 40 Lubricant
(API Engine Service Classification SA)

Property	ASTM Method	New Oil
K. Vis at 40°C, cSt	D 445	143.88
K. Vis at 100°C, cSt	D 445	13.99
Viscosity Index	D 2270	93
Gravity, °API at 60°F	D 287	28.6
Flash Point, °C	D 92	293
Total Acid No. (TAN)	D 664	0.01
Total Base No. (TBN)	D 664	0.09
Element, %		
Ca	XRF*	ND**
N	D 4629	0.012
P	XRF	<0.01
S	XRF	0.21
Zn	XRF	ND

* XRF = X-Ray Fluorescence.
** ND = Not Determined.

of wear metals. Larger oil samples were taken at 70, 154, and 210 hours for a more complete lubricant quality analysis employing standard ASTM tests. Every time an oil sample was taken for analysis, the oil level was measured and restored to its original level. TABLES 12 and 13 give the respective analysis of wear metals and the determinations of lubricant quality. Fig. 6 shows that both the iron in the used oil and the consumption of oil increased with reasonable consistency throughout the test. The rate of oil consumption was calculated from the slope of the line shown in Fig. 6. It is apparent from the results that the wear rate remained relatively constant throughout the test and that secondary factors such as the buildup of abrasive particulates had little or no influence on the rate.

After the test was complete, the engine was disassembled and all the important parts were gauged according to the standard CRC rating and weight determinations. The results of these measurements, given in TABLE 14, show that the cylinder Nos. 2 and 3 operating on the high-sulfur fuel experienced substantially more wear and deposit formation than cylinder No. 1, which was only exposed to the combustion products of neat Jet A. Fig. 7 shows only light scuffing on cylinder No. 1, whereas cylinder Nos. 2 and 3 experienced heavy scuffing, lacquer buildup, and deposits formed in the inlet air ports.

Bore and ring wear was more than twice as great in cylinder Nos. 2 and 3 than in cylinder No. 1, but rod-bearing wear appeared to be about the same for all the cylinders. The combustion environment in cylinder Nos. 2 and 3 appeared to be considerably more hostile than in cylinder 1 because the faces of the rings on piston Nos. 2 and 3 were not only burned but also chipped. Fig. 8 shows the chipping on the edges of the ring faces, as indicated by the circles.

Compared to piston No. 1, piston Nos. 2 and 3 had much higher WTD ratings. These differences, which were quite substantial, are shown in Fig. 9. While piston No. 1 showed only light scuffing, there was heavy lacquer buildup on the skirts and much more carbon deposition in the land and groove areas of piston Nos. 2 and 3. There is no doubt that the high-sulfur fuel in cylinders 2 and 3 had a marked effect on piston cleanliness.

TABLE 12. Analysis of Wear Elements in the Used Oil

Hours	Elements			
	Fe, ppm	Cu, ppm	Cr, ppm	S, %
0	<10	<10	<10	0.21
7	<10	<10	<10	0.21
14	<10	<10	<10	0.21
21	<10	<10	<10	0.21
28	27	<10	<10	0.20
35	ND*	ND	ND	ND
42	35	<10	<10	0.22
49	50	<10	<10	0.23
56	42	<10	20	0.22
63	43	<10	32	0.24
70	46	<10	22	0.24
77	82	<10	18	0.24
84	85	17	25	0.23
91	87	20	25	0.23
98	77	22	50	0.23
105	85	<10	32	0.22
112	85	<10	47	0.23
119	85	<10	47	0.24
126	120	24	36	0.23
133	145	33	45	0.23
140	138	24	28	0.23
147	120	30	42	0.23
154	125	19	27	0.24
161	132	22	30	0.23
168	127	20	27	0.23
175	126	14	18	0.22
182	190	37	40	0.24
189	207	35	37	0.23
196	204	21	30	0.26
203	199	35	19	0.26
210	212	32	30	0.25

* ND = Not Determined.
Note: All recorded values for Pb were less than 60 ppm; Sn values were not determined.

TABLE 13. Lubricant Quality Analysis

| Test Duration, hr	New	70	154	210
K. Vis at 40°C, cSt	143.9	125.7	133.9	150.8
K. Vis at 100°C, cSt	14.0	13.0	14.2	15.5
Viscosity Index	93	97	104	105
Total Acid No. (TAN)	0.01	0.56	0.47	0.57
Total Base No. (TBN)	0.09	<0.01	<0.01	<0.01
Insolubles, wt%				
Pentane A	ND*	ND	ND	0.63
Toluene A	ND	ND	ND	0.57
Pentane B	ND	ND	ND	0.67
Toluene B	ND	ND	ND	0.51
Carbon Residue, wt%	ND	0.46	0.60	0.74
Sulfated Ash, wt%	ND	0.03	ND	0.06
Element				
Ca, ppm	ND	ND	ND	ND
Cu, ppm	<10	<10	19	27
Cr, ppm	<10	22	27	31
P, ppm	<0.01%	ND	ND	72
Pb, ppm	<50	<50	<50	<50
Sn, ppm	ND	ND	ND	18
S, %	0.21	0.24	0.24	0.24
Zn, ppm	ND	ND	ND	14
Fe, ppm	ND	46	125	212

* ND = Not Determined.
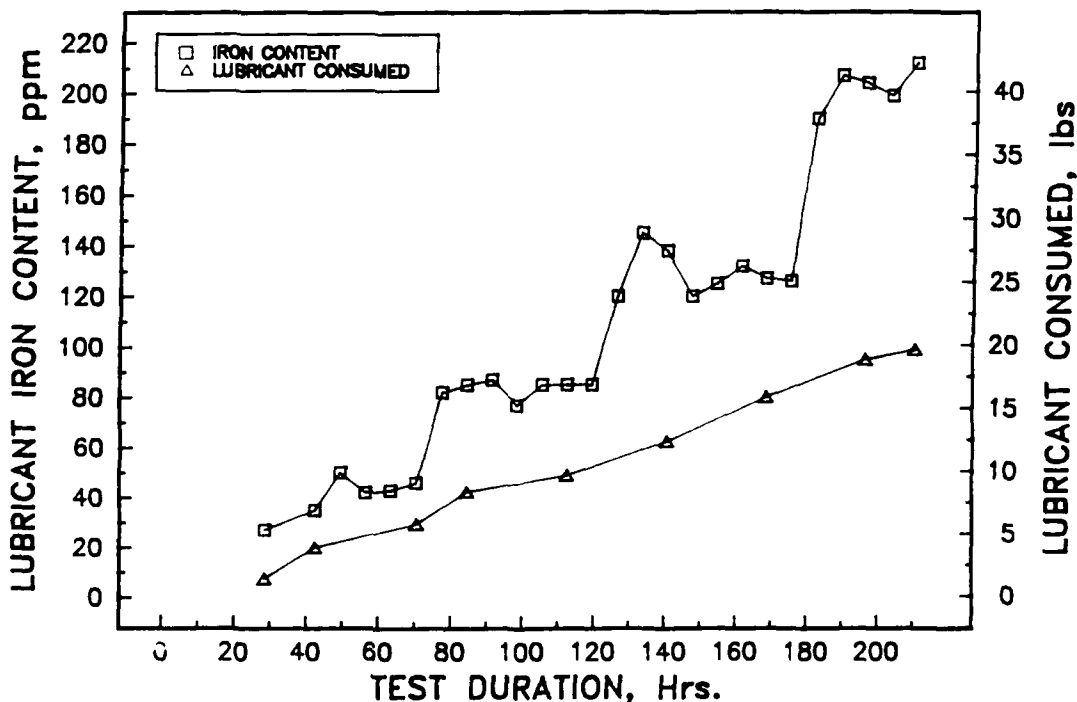
Figure 6. Iron buildup in the lubricant and the consumption of lubricant during the DD 3-53 engine test

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TABLE 14. Measurements of Wear and Deposits in the DD 3-53 Engine

	Piston		
	No. 1	No. 2, 3% S	No. 3, 3% S
Piston WTD Rating	274.0	335.2	360.0
Cylinder Liners			
% Port Restriction	2	12	10
% Scuffed			
Thrust	2	3	3
Antithrust	2	22	29
% Total Scuffed	2	12.5	16
% Glazed	0	0	0
% Lacquer	0	100*	100*
Cylinder Liner			
Avg Wear Loss, in. (mm)	0.0004 (0.0102)	0.0009 (0.0229)	0.0008 (0.0203)
Piston Ring Wear Loss, in (mm)	0.023 (0.5842)	0.044 (1.12)	0.043 (1.09)
Rod Bearing, gm	0.0635	0.0832	0.0702
Ring Face Condition, % Ring Face Burn			
1	5	8**	5**
2	22	7**	14**
3	34	14**	28**
4	24	16**	50**
Piston Surface Condition			
Top Land	N	N	N
Skirt	15% Scuff	Heavy Lacquer	Heavy Lacquer
Piston Pin	N	N	N
Fuel Injectors and Pump	OK	Failed at 175 hr	Failed at 175 hr
Main Bearing, wt loss, gm			
1	0.0230	--	--
2	0.0483	--	--
3	0.0454	--	--
4	0.0319	--	--

* Heavy Lacquer.
** Chipped.
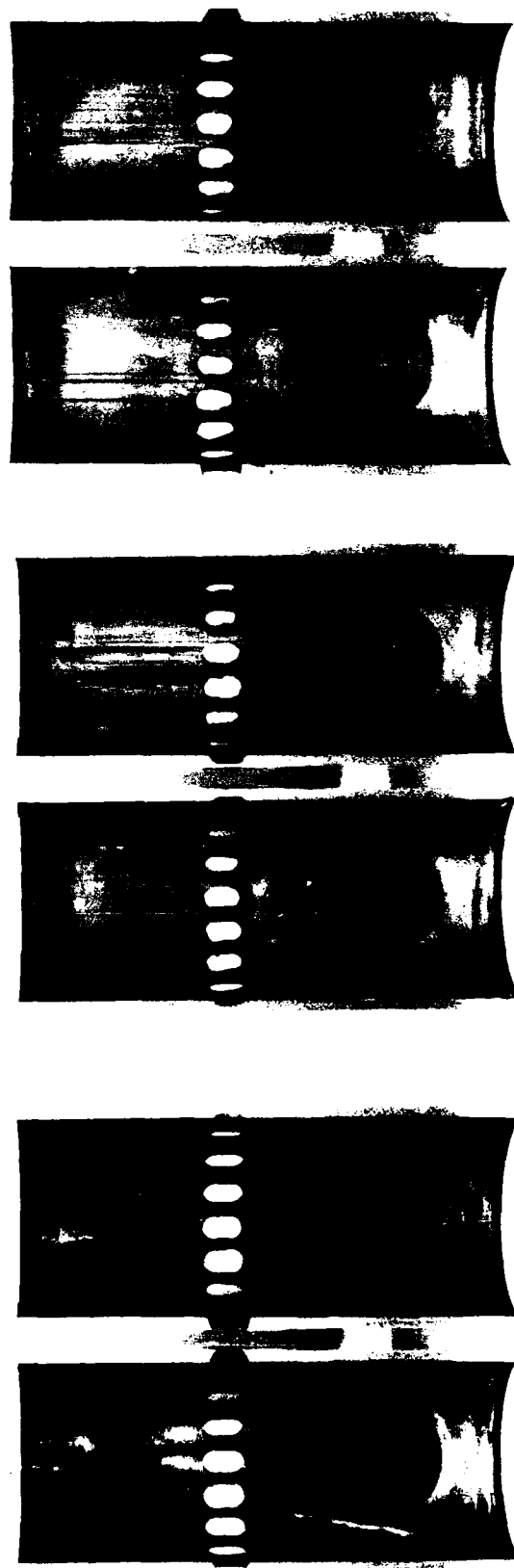
a. Cylinder No. 1 operated on neat Jet A

b. Cylinder No. 2 operated on Jet A containing 3-percent sulfur

c. Cylinder No. 3 operated on Jet A containing 3-percent sulfur

Figure 7. Condition of cylinders in the DD 3-53 engine

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1
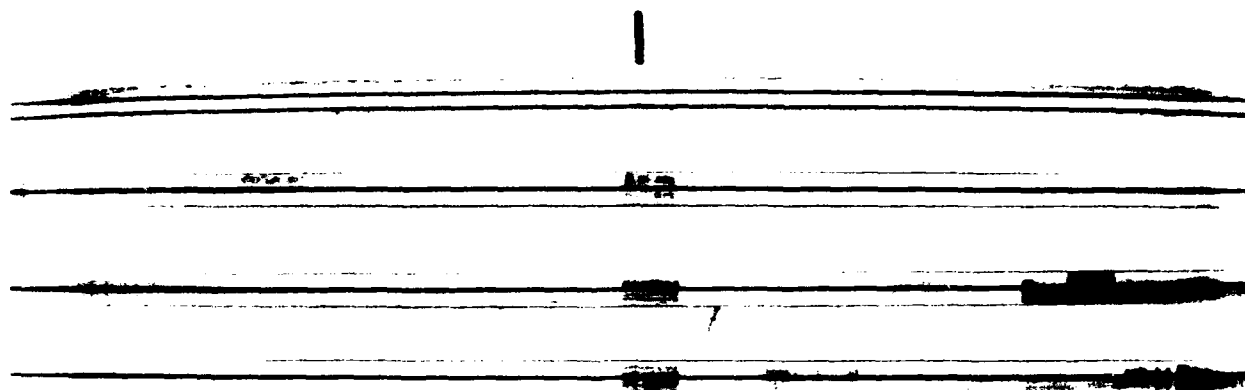
a. Rings of piston No. 1 operated on neat Jet A

2

b. Rings of piston No. 2 operated on Jet A containing 3-percent sulfur

3

c. Rings of piston No. 3 operated on Jet A containing 3-percent sulfur

Figure 8. Condition of the rings in the DD 3-53 engine
(Chipping in Figs. b and c are highlighted by circles)
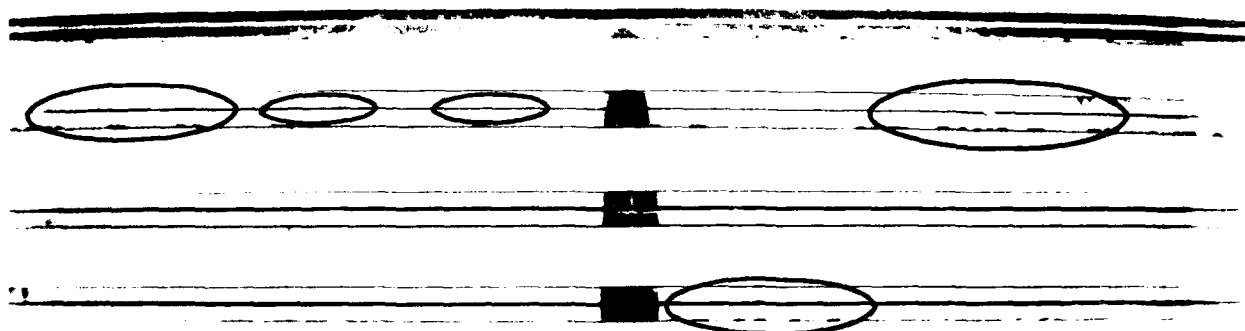
a. Piston No. 1 operated on neat Jet A

b. Piston No. 2 operated on Jet A containing 3-percent sulfur

c. Piston No. 3 operated on Jet A containing 3-percent sulfur

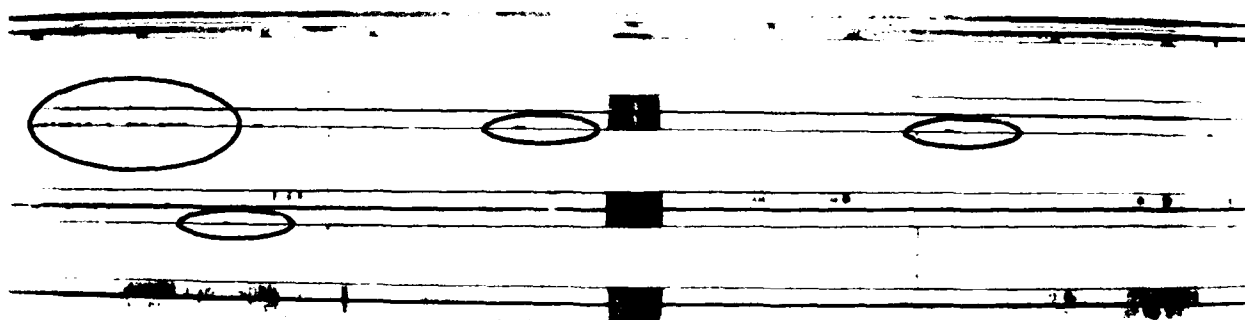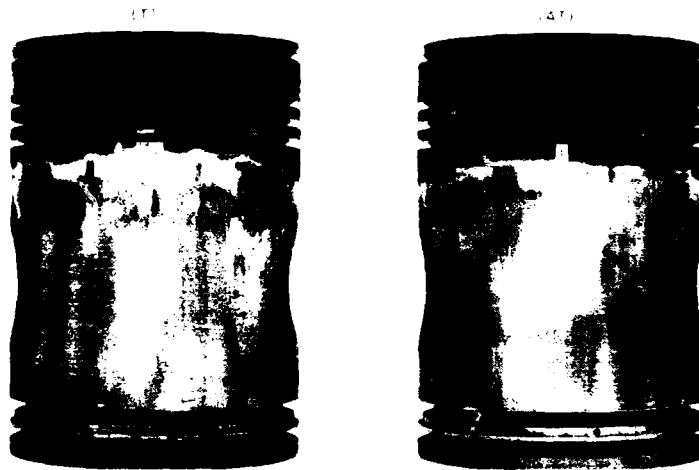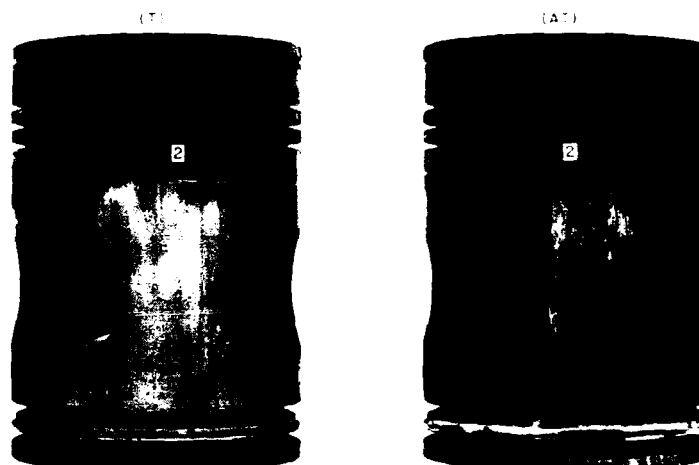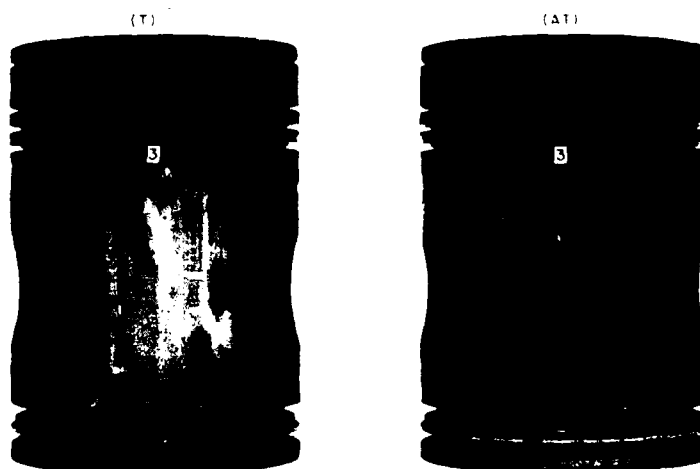Figure 9. <u>Condition of the pistons in the DD 3-53 engine</u>

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The deposit analysis given in TABLE 15 shows that the total deposit weight was about the same on each of the pistons. On piston Nos. 2 and 3, the heptane-soluble deposits seemed to be slightly higher and the DMF-soluble deposits were slightly lower than those of piston No. 1. From the appearance of the deposits on piston Nos. 2 and 3, it would seem that the DMF-soluble deposits should have been higher than those on piston No. 1. Perhaps the DMF-soluble deposits on piston Nos. 2 and 3 were less soluble and were not removed as completely as they were on piston No. 1. Fuel injector deposits were found to be quite excessive in cylinder Nos. 2 and 3. After 175 hours, the injector fouling was so severe that a power loss was noticed, and the test had to be momentarily shutdown to replace the injectors in cylinder Nos. 2 and 3.

TABLE 15. Piston Deposit Analysis

|	Piston		
	No. 1	No. 2, 3% S	No. 3, 3% S
Heptane-Soluble Piston Deposit, gm	0.1658	0.2285	0.2157
Composition, wt%			
C	ND*	ND	ND
H	ND	ND	ND
N	0.79	1.15	0.72
S	4.73	13.80	5.71
Dimethylformamide (DMF) Soluble Deposit, gm	0.6581	0.4353	0.5792
Composition, wt%			
C	56.84 ± 0.07	41.41	42.86 ± 0.16
H	6.22 ± 0.02	4.77	4.81 ± 0.07
N	2.18	1.76	1.71
S	9.81	36.40	45.90

* ND = Not Determined.

The sulfur content of the deposits formed on piston Nos. 2 and 3 was substantially greater than that found in the deposit on piston No. 1. The sulfur contents of the DMF-soluble deposits on piston Nos. 2 and 3 were unusually high; these values were double checked, but they still seemed unbelievably high. Nevertheless, the trend in the

measurements of sulfur in the deposits indicated that significantly more sulfur was incorporated into the deposits formed on piston Nos. 2 and 3 than on piston No. 1 where the only source of sulfur was the exposure to the lubricant.

The results suggest that the wear and deposit formation in cylinder Nos. 2 and 3 were much greater because the partial pressure of sulfur dioxide was much higher in those cylinders. Not only was the sulfur dioxide concentration higher because it was formed in the cylinder, its partial pressure was also very much higher than it would have been anywhere else in the engine because the combustion gases within the cylinder were highly compressed. The fact that the concentrations of SO_2 in the cylinder are relatively high seems to best explain the results obtained on cylinder bore and ring wear. Piston deposit composition seemed to also be influenced by the concentration of sulfur dioxide in the combustion gases, but the level of contamination of sulfur in the lubricant seemed to play a role as well. In the course of the DD 3-53 engine test, the lubricant contained a relatively high concentration (0.24 wt%) of sulfur. In other engines where much lower levels of sulfur are found in the lubricant, one might expect the deposit formation to be more dependent on the composition of the combustion gases within the cylinder.

E.   Corrosion Chemistry

The corrosion of metals by acids is a well-known process. Acids react with metals by two mechanisms; the most elementary of these processes is the displacement of hydrogen (8), such as

$$Fe + H_2SO_4 = H_2 + FeSO_4$$
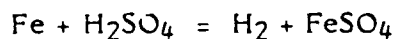
The displacement reaction is a slow reaction compared to the electrochemical effect that acids have on the oxidation of metals. Basically, rust forms when iron is in the presence of oxygen, water, and an acidic electrolyte.(9) To understand this mechanism, it is helpful to envision a multitude of cathodes and anodes arbitrarily assigned to the surface of the metal. Oxygen is reduced at the cathode

$$1/2 \, O_2 + H_2O + 2 \, electrons = 2OH^-$$
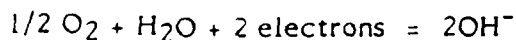
and iron is oxidized at the anode

$$Fe - 2\ electrons = Fe^{++}$$

This corrosion process does not occur unless an electrolyte such as sulfuric acid is present. When sulfuric acid is the electrolyte, the OH^- ions combine with H^+ ions to make water, and Fe^{++} ions combine with $SO_4^=$ to make iron sulfate. As the corrosion process proceeds, the H ions are consumed and the pH of the solution increases towards neutrality.

At first glance, it might be assumed that the oxidation mechanism described above is solely responsible for corrosive wear of the cylinder bores and rings in diesel engines, and it may also be conceivable that sulfurous acid entrapped by the lubricant would have an effect similar to that of sulfuric acid. In aqueous medium, SO_2 forms an acidic solution that is sometimes called sulfurous acid, even though, in the strict sense of the word, that chemical structure is thought not to exist. Nevertheless, aqueous solutions of SO_2 may be very acidic and, depending on the concentration, the pH can be as low as 1.6. In that sense, the corrosion chemistry described above for sulfuric acid is equally as possible for sulfurous acid.

Actually, the strength of the acid does not seem to be that important in cylinder bore and ring wear. It has been shown that formic acid is primarily responsible for the cylinder bore and ring wear in methanol-fueled spark ignition engines.(10-12) On an equal concentration basis, sulfurous acid is much stronger than formic acid. Since SO_2 comprises more than 99 percent of the sulfur oxides formed within the cylinder of a diesel engine, the concentration of sulfurous acid could easily be more than two orders of magnitude greater than the amount of sulfuric acid dissolved in the lubricant. In that light, sulfuric acid should only play a minor role in the corrosion process.

Experiments were carried out to determine the reactivity of sulfurous acid with iron. These experiments were first performed by placing iron coupons in relatively dilute aqueous solutions of sulfur dioxide. The test tube was nearly completely filled with the solution and tightly capped to prevent oxygen from diffusing into the solution. In a 0.1-percent aqueous solution of SO_2, the reaction with the iron coupon did not behave anything like the acid-metal reactions described above. Instead of erosion of the metal

by the acid, the iron coupon turned black in a few minutes, and the solution became hazy with what appeared to be a white insoluble substance. The white haze in the solution did not precipitate, but gradually cleared in about 5 minutes. After about 10 minutes, the reaction appeared to be complete, and the iron coupon was coated with a black reaction product. Some of the black product had flaked off the coupon and appeared as a precipitate at the bottom of the sealed test tube.

The illustration in Fig. 10 shows a striking comparison of a new polished steel ball bearing with one that was immersed in a 0.1-percent aqueous solution of SO_2. The black coating on the ball bearing resembles the iron sulfide coating that is formed in the bluing of a gun barrel.

Figure 10. Comparison of a virgin steel ball bearing (left) with one that has been immersed in a 0.1-percent aqueous solution of sulfuric acid

A pH probe inserted into the sulfurous acid solution before the iron coupon was immersed gave a relatively strong acid pH of 1.7; after the coupon was immersed in the solution and the reaction was complete, the pH rose to 5.5. It was concluded that the acid had been consumed and that the solution was essentially neutral.

The coupon was removed from the solution and analyzed for sulfur by X-ray fluorescence in the Scanning Electron Microscope (SEM). When it was discovered that the black reaction product contained sulfur, chemical tests were performed to determine the oxidation state of the sulfur. It seemed reasonably certain that the product was neither iron sulfite nor iron sulfate, because these salts are relatively soluble in water and the ferrous forms are colorless except for a slight green tint. Apparently the product was a sulfide since it was insoluble in water and black in color. The test for sulfide was performed; a drop of hydrochloric acid was placed on the black deposit, and a piece of moistened lead acetate paper was held above the coupon to detect effervescent hydrogen

sulfide. When a positive test for hydrogen sulfide was found, it was confirmed that iron sulfide was present in the reaction product.

Continued experimentation was carried out employing gravimetric analytical techniques to determine more about the composition of the corrosion product. In preliminary experiments, several samples were examined to gain some insight into the development of an analytical approach and to determine what measurements needed to be made. TABLE 16 shows the final result of the gravimetric analysis of two samples of the corrosion product.

TABLE 16. Gravimetric Analysis of Iron Coupon

Sample	A*	B	C	A-C	B-C
1	4.6366	4.6241	4.5693	0.0673	0.0548
2	5.3426	5.3330	5.2723	0.0703	0.0607

* A = initial coupon weight, grams; B = coupon weight, grams, after reaction with SO_2; and C = coupon weight, grams, after corrosion product was removed by light sanding.

The results in TABLE 16 show that the coupon weight, B, only decreased slightly after reaction with SO_2. Since C is the weight of the coupon after the corrosion product is removed, the value, A-C, is the weight of the iron oxidized by the SO_2 solution. The value, B-C, is the weight of the corrosion product adhering to the metal coupon. The remainder of the corrosion product is the insoluble material that flaked off and became a precipitate at the bottom of the reaction vessel. Additional information given in TABLE 17 for samples 1 and 2 include the concentrations of sulfur and iron in solution and the weight of the precipitated corrosion product.

From the data in TABLES 16 and 17, the weights of iron and sulfur and the total weight of the insoluble corrosion product can be determined. The weight of iron in the corrosion product is the difference between A-C and the iron in the solution. The weight of sulfur in the corrosion product is the difference in the weight of sulfur in solution before the coupon was immersed, and the weight of sulfur remaining in solution after the reaction with the coupon was complete. The total weight of the corrosion product is B-C plus the weight of the precipitate.

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TABLE 17. Chemical Analysis of Products in Solution and Weight of Precipitated Corrosion Product

Sample	S Solution, wt%	Wt of S Solution, g	Fe Solution, ppm	Wt of Fe Solution, g	Wt of Precipitate, g
1	0.15	0.012	848	0.00678	0.0604
1*	0.26	0.0208	0	0	0
2	0.14	0.0112	793	0.00634	0.061
2*	0.25	0.020	0	0	0

* Same sulfurous acid solution, but without the iron coupon.

Based on the data in TABLES 16 and 17, the corrosion product contains 52.55-percent iron and 7.45-percent sulfur, with the remainder consisting of oxygen and water of hydration. Based on that composition, the best fit for the empirical formula appears to be $FeS \cdot FeO \cdot Fe_2O_3 \cdot 6H_2O$ where the theoretical percentages of iron and sulfur are 52.26 and 7.49, respectively.

The reaction of iron with SO_2 in aqueous solution appears to be an oxidation-reduction process. In Schilling's (4) review of the literature on sulfur-related corrosion, he gives mention of some French work by Leboucher (13) and some Russian work by Iofa and Besproskurnov (14) on the reaction of sulfurous acid with iron. They made observations similar to those reported above, i.e., the reaction involves an oxidation-reduction process, and they proposed the following overall reaction:

$$SO_2 + 2H_2O + 3Fe = FeS + 2Fe(OH)_2$$
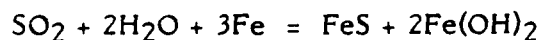
Based on the composition of the corrosion product as determined in the present study, the reaction above seems to be highly probable.

In addition to examining the reaction of SO_2 with iron in aqueous solution, iron coupons were also immersed in 100-neutral mineral oil containing about 0.1-percent SO_2 and 200 ppm of water. The coupons from these tests were compared with similar coupons that had been placed in the crankcase of the Petter diesel engine when it was operated on sulfur-containing fuels and when air containing SO_2 was inducted. The coupons were

examined with a scanning electron microscope equipped with X-ray fluorescence detection. In the electron micrographs shown in Fig. 11, the light cottonball-like structures on the surfaces of both coupons represent nonconducting substances that are most probably metal oxides and sulfides. The X-ray spectrum of these structures showed the presence of sulfur; the instrument was not capable of detecting oxygen.

Comparing the coupons in Fig. 11 is somewhat confusing because of the factor of 2.5 difference in the magnification of the images, but similarity in the corrosion sites seems to be reasonably evident.

It may not be that surprising that the appearance of the corrosion sites on the coupon from the engine are similar to those on the coupon from the bench test. The evidence given earlier in this report strongly favors SO_2 as the principal sulfur oxide in the exhaust gas. Undoubtedly, SO_2 is equally prominent in the blowby gases that enter the crankcase of the engine. In the cylinder of the engine, the partial pressure of SO_2 can be more than an order of magnitude greater than in the exhaust or blowby; it might be imagined that corrosion on ring and cylinder wall surfaces would be substantially greater than on the coupon placed in the crankcase of the engine.

F.   Wear Tests

In most tribological studies, it has been generally agreed that sulfuric acid is the main cause of corrosive attack of cylinder bore and ring surfaces in diesel engines that burn fuels containing sulfur. Examples of these studies include the recent works of Yahagi, et al. (15) and Lane, et al. (16). Both workers employed relatively advanced reciprocating wear rigs to examine the effects of sulfuric acid contamination in lubricants on corrosive wear. Only a few studies, such as the work of Desportes, et al. (17), considered the possibility that contamination of the lubricant with sulfurous acid (H_2O + SO_2) could be important in the corrosion process. Although Desportes, et al. considered sulfurous acid, they still hold the accepted view that sulfuric acid is the prominent cause of corrosive wear in diesel engines that combust fuel-bound sulfur.

In the present work, the results suggest strongly that sulfurous acid plays a much more important role in the corrosion process than has been previously acknowledged. To further appraise this theory, the change in wear caused by contaminating a lubricant

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a. Iron coupon from crankcase of Petter engine
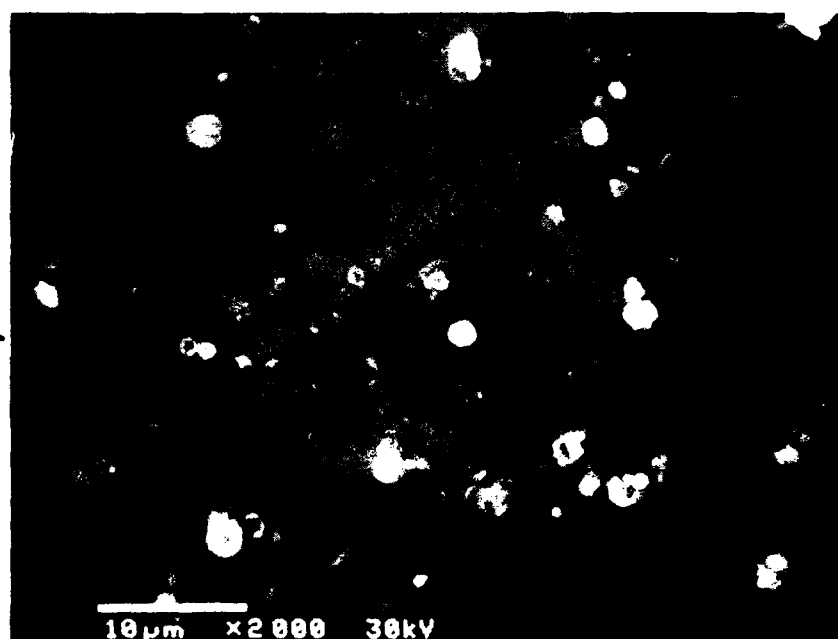
b. Iron coupon exposed to 100-neutral oil containing water and SO_2

Figure 11. <u>Electron micrographs</u>

with sulfur dioxide and water was investigated using a Ball-on-Cylinder Lubricity Evaluator (BOCLE). The BOCLE employs a steel ball that rides on a rotating cylinder. Wear is induced by increasing the load (force) of the ball on the cylinde.. The lubricity of a lubricant is measured by the diameter of the wear scar that is produced on the ball. Normally, oil samples are purged with air before the test is begun because dissolved oxygen increases the wear rate. In effect, the BOCLE measures both abrasive and corrosive wear. Studies have shown that oxidation of the oil and the metal at the wear site is an important aspect of the wear mechanism.(18) It has been found that there is a significant decrease in the wear rate when all traces of oxygen are removed from the oil. In the present study, air purging was used in tests of the base oil, but it was not performed on the oil samples contaminated with SO_2 and water. There were two reasons for this: 1) air purging could drive off part of the dissolved SO_2, and 2) it might result in increased oxidation of SO_2 to sulfuric acid.

In performing these tests, it was important to choose a base lubricant that would not react with sulfur dioxide. Experiments were carried out on the thermal stability of various fuels and lubricants contaminated with sulfur dioxide. These tests, described in the thermal stability section of this report, showed that a 100-neutral oil gave no evidence of reaction with SO_2 and did not form deposits. The 100-neutral oil was an ideal base lubricant because it was also free of additives that might otherwise compensate for the effects of dissolved water and sulfur dioxide on wear.

To simulate the composition of the lubricant in a diesel engine, small amounts of SO_2 and water were added to the base oil. In preparation for the BOCLE tests, a volume of base oil large enough for several tests was saturated with water. The oil saturated with water was allowed to equilibrate for a few days to precipitate possible excess water. Then the oil/water mixture was decanted from the vessel and stored for future use. The water content of the oil was determined by Karl-Fischer analysis. When an oil sample containing a lower concentration of water was desired, a portion of the saturated batch was blended with dry base oil.

The BOCLE tests were done in a timely fashion to prevent unnecessary oxidation of the dissolved SO_2. Also, for this same reason, the SO_2 was added to the oil just prior to the test. A small portion of the test oil blend was used for sulfur analysis by X-ray fluorescence.

TABLE 18 shows the test results obtained with the BOCLE.

TABLE 18. BOCLE Test Results of Sulfur and Water Contents of Base Oil

Run No.	Sulfur, wt%	Water, wt%	Wear-Scar Dia., mm	Test Duration, minutes	Load, grams
1	0.0	0	0.227	30	1000
2	0.125	382	0.390	30	1000
3	0.125	382	0.385	240	500
4	0.0	0	0.200	240	500
5	0.39	78	0.270	30	1000
6	0.43	518*	0.300	30	1000
7	0.21	259	0.280	30	1000
8	0.0	282	0.235	30	1000
9	0.075	282	0.360	30	1000
10	0.075	282	0.345	30	1000
11	0.070	282	0.325	30	1000
12	0.080	282	0.295	30	1000
13	0.085	282	0.290	30	1000

* Water content was above the saturation level.

The test results for Run Nos. 1 through 7 were performed using the same BOCLE cylinder, and they were scheduled in the order given in TABLE 18. The most striking differences between the contaminated oil and the dry-base oil was observed in the first four runs. Run Nos. 1 and 2 were done with a load of 1000 grams and Run Nos. 3 and 4 with a load of 500 grams to test for variation in the wear mechanism with load. Since the wear rate is proportional to the cube of the load, the test durations of Run Nos. 3 and 4 were increased from 30 to 240 minutes. This correlation appeared to agree surprisingly well with theory and did not indicate any abnormalities in the wear process because the wear scars obtained in Run Nos. 1 and 2 were almost identical with the respective values for Run Nos. 3 and 4.

Comparing Run Nos. 1 and 2 and 3 and 4 shows that the additions of sulfur dioxide and water increased the wear scar diameter an average of 82.2 percent of the base oil value.

This increase in the wear scar is attributed primarily to sulfur dioxide in the oil since water by itself appeared to have only a small effect on wear-scar diameter; compare Run Nos. 1 and 4 with Run No. 8. Desportes, et al. (17) made similar measurements with a Pin-on-Disc Friction instrument and found an increase of 25 percent in the wear-scar diameter when SO_2 was added to n-dodecane containing the antiwear additive ZDDP, water, and a succinamide emulsifier. The antiwear additive ZDDP used in their experiments may have mitigated the effect of SO_2 on the wear process, but nonetheless, their results generally agree with the present study.

Run Nos. 5, 6, and 7 were made to determine more about the dependence of sulfur dioxide and water concentration on the wear-scar diameter. It was expected that increasing the sulfur dioxide concentration would increase the wear-scar diameter. Contrarily, Run Nos. 5 and 6 seemed to indicate that higher concentrations of sulfur dioxide decrease the wear scar diameter. This decrease suggests that there may be a maximum wear scar at some intermediate concentration of sulfur dioxide. An intermediate concentration of sulfur dioxide was tried in Run No. 7. The result, given in TABLE 18, clearly shows that there was no marked increase in the wear-scar diameter. Instead, it appears from the results of Run Nos. 5, 6, and 7 that the wear-scar diameter became relatively independent of the sulfur dioxide concentration; of course, this assumes that there is at least some sulfur dioxide in the oil.

Examination of the BOCLE cylinder used in the test revealed that it had a brown tarnished appearance. This brown tarnished appearance of the iron surfaces was also observed by Desportes, et al. (17) in the Pin-on-Disc Friction test. It appeared that corrosion products such as iron sulfide had formed on the BOCLE cylinder and that this had the effect of increasing the lubricity. This hypothesis seems to agree with the results from Run Nos. 8 through 13 shown in Fig. 12 where the wear-scar diameter is plotted versus the run number. It is shown in TABLE 18 that the water contents of the blends tested in Run Nos. 8 through 13 were each 282 ppm. The oil used in Run No. 8 did not contain any sulfur dioxide, but each of the subsequent oil samples in Run Nos. 9 through 13 contained about the same amount (0.08 percent) of sulfur in the form of added sulfur dioxide. Run Nos. 8 through 13 were scheduled in numerical order and they were started with a new cylinder in the BOCLE. Fig. 12 shows that when the oil is contaminated with sulfur dioxide, there is a significant enhancement of the wear-scar diameter, but repeated tests of the same contaminated oil samples tends to decrease the
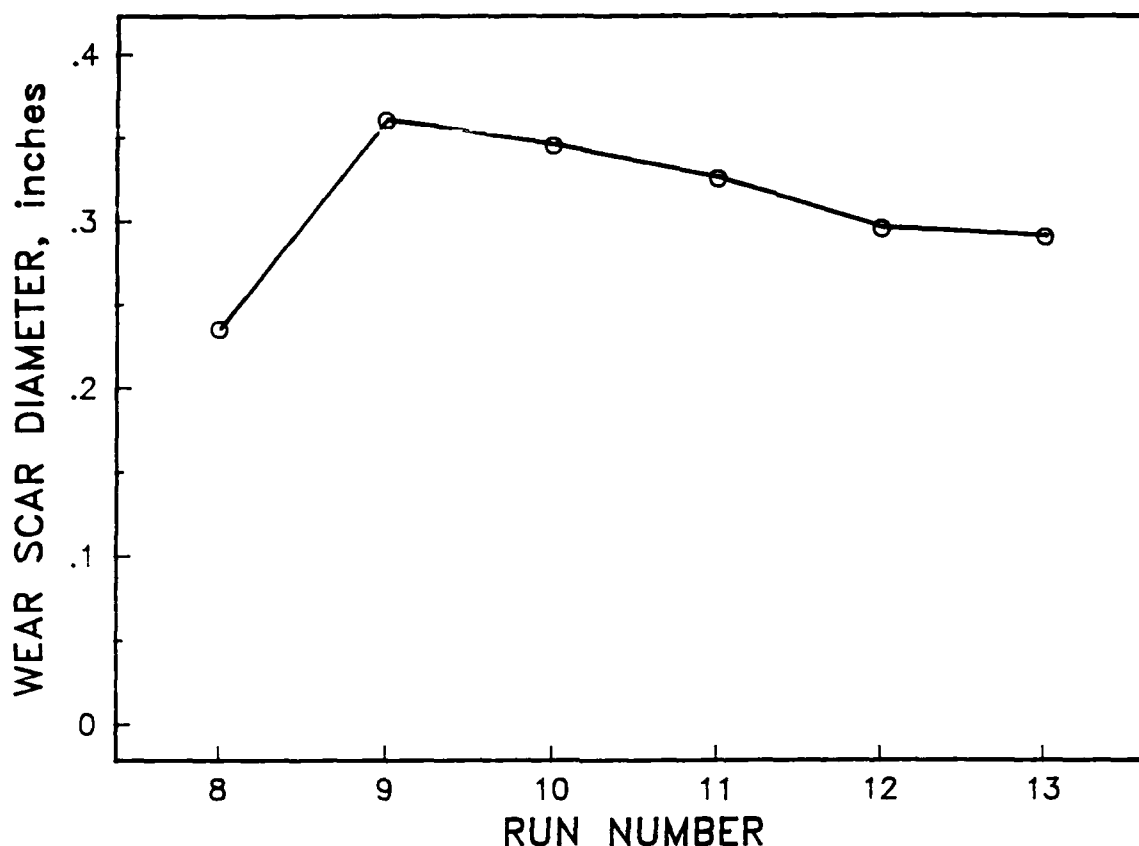
Figure 12. Wear-scar diameters plotted for Run Nos. 8 through 13
(Data given in TABLE 18; Run No. 8 = base oil; Run Nos. 9 through
13 = oil is contaminated with the same amounts of SO_2 and water)

wear-scar diameter. This suggests, as mentioned above, that the corrosion products tend to improve the lubricity. Metal sulfides, such as MoS_2, are noted for their lubrication properties; perhaps these properties are also shared to some extent by iron sulfide.

G. Effects of Sulfur Dioxide on Lubricants

It has been well established that fuel-bound sulfur and nitrogen tend to enhance the formation of piston deposits in diesel engines. The recent work of Frame (1) showed that sulfur contributed more to deposit formation than nitrogen. Deposit formation was strongly dependent on the concentration of fuel-bound sulfur, but it did not seem to be greatly influenced by the molecular structure of sulfur compounds. Several sulfur compounds were examined, and only one showed a significant deviation from the average; the disulfide-type sulfur tended to produce more deposits.

In the combustion of diesel fuel, all sulfur compounds are rapidly oxidized to sulfur dioxide. Since this oxidation is not influenced to any extent by the molecular structure of the fuel-bound sulfur, and in view of the fact that sulfur dioxide spends more time in the cylinder than any other known form of sulfur, it would not be surprising to find that sulfur dioxide is an important precursor to deposit formation. The question of whether or not sulfur dioxide is important in deposit formation is addressed in this report. The results discussed below have to do with effects of sulfur dioxide on the deposit-forming tendencies of diesel engine lubricants.

H.   Solubility

The solubility of gases such as oxygen, nitrogen, and hydrogen in hydrocarbons is very low.   For example, only about 100 ppm of oxygen will dissolve in mineral oil at atmospheric conditions.   It may be of some surprise then to find that the solubility of sulfur dioxide in lubricants is several orders of magnitude greater than that of oxygen. Although the solubility of SO_2 in lubricants is not thoroughly addressed in the literature, Schilling (4) tacitly mentions that as much as 2-percent sulfur in the form of SO_2 can dissolve in the oil.   Since this statement was not referenced and documented, some approximate measurements of solubilities were made in four oils.   The oils examined included 100-neutral mineral oil (MO), a polyalphaolefin (PAO), both free of additives, and two formulated diesel engine lubricants (FL1 and FL2).

The solubilities were determined by purging the oil samples with pure sulfur dioxide gas for a period of about 5 minutes.   While the samples were being purged, they were exposed to a sulfur dioxide pressure of one atmosphere.   TABLE 19 gives the results obtained for the PAO, FL1, and FL2 oil samples.   These measurements show that sulfur dioxide is exceedingly soluble in oils.

The formulated lubricants tend to have a greater capacity for sulfur dioxide, probably because the additive package contains alkali compounds that neutralize and absorb acidic substances.

A second method was also used to measure the solubility of sulfur dioxide in oils.   Oil samples were placed in 50-mL flasks and weighed.   The oil samples in the flasks were purged with about 300 cm^3 of sulfur dioxide.   They were then weighed again, and the

TABLE 19. Solubility of SO$_2$ in Oils

Test Oil	Purged with SO$_2$	Sulfur, wt%	Dissolved SO$_2$, wt%
PAO	No	0.01	0.0
PAO	Yes	0.78	1.54
FL1	No	0.47	0.0
FL1	Yes	1.40	1.86
FL2	No	0.55	0.0
FL2	Yes	1.73	2.36

weight gain was taken as the amount of sulfur dioxide dissolved in the oil. The results of these measurements are given below in TABLE 20.

TABLE 20. Dissolution of SO$_2$ in Oils

Test Oil	Dissolved SO$_2$, wt%
Polyalphaolefin	0.68
Mineral Oil	0.59
Formulated Oil	0.67

The concentrations found in the second method were lower than those given in TABLE 19 because the samples were purged with less sulfur dioxide gas, and it was not possible to ensure a sulfur dioxide partial pressure of one atmosphere during the purging process.

From the results of the solubility measurements given in TABLES 19 and 20, it may be concluded that diesel engine lubricants could absorb as much as 2-percent sulfur dioxide if their partial pressure were one atmosphere. Based on this 2-percent estimate, it is possible to calculate the approximate amount of sulfur dioxide that could be absorbed by the lubricant on the cylinder wall of a diesel engine. If the sulfur content of the fuel is

2 percent and the compression ratio of the diesel engine is 15 to 1, the calculated partial pressure of sulfur dioxide in the burned gas with the piston at top dead center is 9.3 mm of Hg.

Assuming that Henry's Law holds, and it is a fact that the lubricant is able to absorb up to 2-percent sulfur dioxide with a partial pressure of 760 mm of Hg, the lubricant on the cylinder wall could absorb as much as 244 ppm of sulfur dioxide gas from the combustion gases. Although this result is ideal in that it assumes an infinite amount of time for the absorption of gas to take place, it demonstrates, nevertheless, that there is a definite potential for the absorption of sulfur dioxide by the lubricant on the cylinder wall of a diesel engine.

I.   Reactivity

While examining the solubility of sulfur dioxide in lubricants, it was soon realized that the additive-free polyalphaolefin oil began to change from a clear to a completely opaque liquid with a black precipitate. The 100-neutral oil and the formulated lubricants did not give any visible evidence of chemical reaction. Subsequent experiments with the polyalphaolefin showed that as little as 0.1-percent sulfur dioxide caused dramatic changes in the appearance of the oil. Fig. 13 shows the result obtained when a 0.11-percent blend of sulfur dioxide in polyalphaolefin was heat stressed at $100^\circ C$ for a period of 24 hours. The difference between the neat oil and the one treated with sulfur dioxide is most enlightening in that this seems to be related to deposit formation in diesel engines.

To investigate the nature of this reaction, some simple experiments were performed to determine the reactivity of sulfur dioxide with pure organic compounds. The substances selected for study included decane, 1-decene, and cumene. Experiments were performed in the short term by purging the hydrocarbon with sulfur dioxide and looking for an immediate change, and in the long term by capping the vessels and heat stressing them at $100^\circ C$ for several days. In the short term, there was no visible evidence of reaction in the decane and cumene samples. These samples absorbed only about 0.2-percent sulfur dioxide, which was the amount that might be expected to dissolve. To the contrary, 1-decene absorbed about 5-percent sulfur dioxide, and it turned to an opaque reddish-brown liquid. In comparing the infrared spectra of pure 1-decene with that of the reddish-
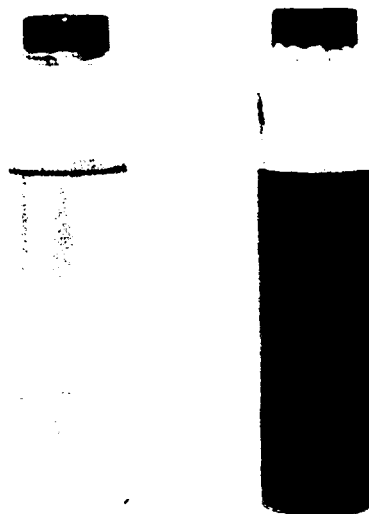
Figure 13. Samples of neat polyalphaolefin oil
(The sample on the left is neat polyalphaolefin oil. On the
right, the same oil is treated with 0.11-percent SO_2. Both
samples were heat stressed at 100°C for 24 hours.)

brown reaction product, it was very apparent that two new absorption bands appeared at 1121 and 1343 cm^{-1}. Bands in this region of the spectrum reflect the presence of sulfones.(19) Weaker bands at 500, 1185, and 1378 cm^{-1} were also new, giving further support that chemical bond formation had occurred between 1-decene and sulfur dioxide. A strong shift from 1704 cm^{-1} to 1735 cm^{-1} appeared to occur in the 1-decene spectrum after it had reacted with sulfur dioxide. This shift also indicated that a significant chemical change had occurred in the molecule.

Heat stressing of the 1-decene sample seemed to enhance the reaction that had already occurred with the sulfur dioxide. In addition to the opaque reddish-brown liquid, a black gummy deposit was found precipitated in the vessel.

The results show explicitly that the reaction of alkenes with sulfur dioxide was substantial. This substantial reaction is most probably why the polyalphaolefin oil reacted with sulfur dioxide. It is highly probable that the polyalphaolefin oil contained some residual molecules with double bonds because it was a polymer of 1-decene.

In the long-term heat stress tests, small amounts of black deposit were found on the vessel wall of the decane sample. An infrared spectrum of the deposit was obtained using the KBr-pellet technique. The spectrum suggested that the deposit must have been formed by the reaction of sulfur dioxide with an impurity in the decane because there were very few absorption bands that were similar to the spectrum of decane. Note the infrared spectra of 1-decene and the reaction product with sulfur dioxide were very similar except for the few new bands that were attributed to reaction products.

The heat-stressed cumene sample turned a light-brownish tint, and no formation of gum or deposit was apparent until after the sample had been in storage for several weeks. Traces of gum-type deposit precipitated on the the walls of the vessel several weeks after the heat-stressing period was over.

J.   Thermal Stability

The instability of a fuel or oil generally refers to the gums, sediments, or deposits that can form as the result of a set of complex chemical reactions when hydrocarbon fluids are stored for a long time at ambient conditions, or when they are thermally stressed inside an engine.(20) This form of instability generally results from the partial oxidation of hydrocarbons. However, in the present study, the concern was that sulfur dioxide may also react with hydrocarbons in the lubricant to form deleterious deposits.   To investigate deposit formation from the aspect of thermal stability, various fuels and oils were treated with sulfur dioxide and examined in the Jet Fuel Thermal Oxidation Tester (JFTOT) procedure, ASTM D 3241. In the conventional JFTOT procedure, the test oil is aerated and then passed over a heated tube to induce oxidation reactions and deposit formation. Normally, the tube is heated to $500^{\circ}F$ ($260^{\circ}C$) and the test duration is 150 minutes. In the present study, aeration was performed on the neat fuels and lubricants used to establish baseline data. However, when the fuels and lubricants were treated with sulfur dioxide, the tests were performed without aeration. This procedure was used because there was concern that air purging would change the concentration of sulfur dioxide in the test fluid.

Preliminary experiments were carried out at a temperature of $500^{\circ}F$ ($260^{\circ}C$) on a relatively stable JP-5 jet fuel. A conventional JFTOT test on this fuel showed that it was very stable; the tube deposit rating was a Code 1, indicating that there was no

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visible deposit present on the tube. Note the deposit rating of a JFTOT tube can range from Code 1 to Code 4; the greater the deposit the higher the code number. In addition to the tube deposit rating, there is a filter in the line after the fluid passed over the hot tube. Sometimes solid matter is formed in the decomposed fluid that does not adhere to the tube surface and form the deposit that is potentially possible. In that case, the pressure drop across the filter may be used as an indicator of thermal instability.

When the JP-5 fuel was treated with about 0.1-percent sulfur in the form of sulfur dioxide, the deposit rating increased to a Code 3; that is, change in the fuel's tendency to form deposits that could be interpreted as a significant decrease in its thermal stability.

Subsequent tests were carried out on 100-neutral mineral oil, decalin, and the polyalpha-olefin oil. The results of these tests are given in TABLE 21.

TABLE 21. JFTOT Test Results

Test Fluid	Temperature, °F (°C)	Sulfur, wt%	Deposit Rating	Filter Plugging
100-Neutral Mineral Oil	500 (260)	0.0	Code 1	No
100-Neutral Mineral Oil	500 (260)	0.11	Code 1	No
100-Neutral Mineral Oil	600 (316)	0.0	Code 1	No
100-Neutral Mineral Oil	600 (316)	0.12	Code 2	No
Decalin	500 (260)	0.0	Code 1	No
Decalin	500 (260)	0.13	Code 2	Yes
Polyalphaolefin	500 (260)	0.0	Code 1	No
Polyalphaolefin	500 (260)	0.12	Code 3	Yes

The 100-neutral mineral oil was found to be very stable and resistant to attack by sulfur dioxide. Only at 600°F (316°C) did sulfur dioxide affect the stability of this oil. This reaction was the opposite of that found for decalin and the polyalphaolefin oil; their stabilities were greatly reduced by the sulfur-dioxide treatment. This is shown in TABLE 21 by the increase in the deposit rating and by the fact that the fluids containing sulfur dioxide plugged the filter. For the sulfur dioxide-treated fluids, the filter plugging occurred in 90 minutes with decalin and in 50 minutes with the polyalphaolefin oil.

The results of the work show that sulfur dioxide formed in the combustion of sulfur-containing fuels most probably plays a major role in the formation of deposits in diesel engines.

V. SUMMARY AND CONCLUSIONS

To gain a better understanding of the role of fuel sulfur in deposit formation and cylinder bore and ring wear, several bench-scale experiments and full-scale engine tests were performed. Particular emphasis was placed on determining the importance of sulfuric acid in the wear mechanism. Thermodynamic and kinetic arguments did not support the formation of sulfuric acid within the combustion chamber. Hence, one of the main objectives of this work was to determine experimentally if sulfuric acid is formed in the diesel combustion process. Also, it was of interest to determine which fuel sulfur constituents formed in the combustion process cause increased deposit formation in diesel engines.

A method of analysis was developed to measure the concentrations of sulfur dioxide and sulfuric acid mist in the exhaust. In developing this analysis technique, a great effort was made to prevent the oxidation of sulfurous acid, which would lead to a falsely high concentration of sulfuric acid in the exhaust gases.

Since sulfuric acid has a high probability of being formed in the exhaust line because temperatures are relatively low, and there is also a possible effect of wall catalysis on sulfur-dioxide oxidation, gas samples were taken as closely as possible to the exhaust port of a Petter single-cylinder diesel engine operating on a blend of JP-7 fuel and tert-butyldisulfide. The analysis showed that very little, if any, sulfuric acid was present in

the exhaust; the measurements showed that less than 0.3 percent of the sulfur dioxide formed in the combustion process was converted to sulfuric acid. It was thus concluded that sulfuric acid was relatively unimportant, and that sulfur dioxide formed quantitatively from the combustion of fuel sulfur was the principal cause of cylinder bore and ring wear in diesel engines.

Two full-scale engine tests were completed. In the first test, SO_2 gas was injected into the air intake of a Petter engine at a concentration equivalent to that experienced when operating the engine on a fuel containing 2-percent sulfur. Exhaust gas analysis showed that less than 0.4 percent of the sulfur dioxide was converted to sulfuric acid during the combustion process. The test showed that SO_2 was responsible for the formation of deposits in the engine, but was only accountable for about 51 percent of the wear observed in similar tests using fuel-bound sulfur. This difference in wear is not understood, but it is speculated that it might result from the difference between a homogeneous and a stratified SO_2 concentration in the combustion chamber.

The second test was performed in a three-cylinder DD 3-53 engine equipped with individual fuel injection pump systems for each cylinder. In this test, a neat Jet A fuel was used in the first cylinder, and a Jet A fuel containing 3-percent sulfur was used in the other two cylinders. The results of this test showed that even though the three cylinders shared the same lubricant, the cylinders burning the high-sulfur fuel experienced considerably more wear and deposit formation than the cylinder operated on neat fuel.

An oxidation-reduction reaction was found to take place between iron and sulfurous acid. The corrosion products appeared to consist of a mixture of iron sulfide and iron hydroxide. Based on its iron and sulfur contents, the corrosion product matched most closely the empirical formula, $FeS \cdot FeO \cdot Fe_2O_3 \cdot 6H_2O$. Considering the fact that the concentration of sulfuric acid in the cylinder of a diesel engine is negligible, it is concluded that sulfur dioxide, which is relatively abundant, is the primary cause of cylinder bore and ring wear.

A BOCLE was used to determine the effects of sulfur dioxide on lubricity. The results showed that the contamination of a 100-neutral mineral oil-based lubricant with as little as 0.05 percent of sulfur dioxide and about 200 ppm of water caused the wear to increase

more than 50 percent above the neat base lubricant. It was very evident from these results that corrosive wear was greatly enhanced by the presence of sulfur dioxide in the lubricant.

The solubility of sulfur dioxide in lubricants was examined. With a partial pressure of sulfur dioxide of one atmosphere, the concentration of sulfur dioxide in various lubricants was found to be in the neighborhood of 2 percent. For a diesel engine with a compression ratio of 15:1, operating on a fuel containing 2-percent sulfur, the partial pressure of sulfur dioxide in the combustion chamber, with the piston positioned at top dead center, is 9.3 mm of Hg. According to Henry's Law, the concentration of sulfur dioxide absorbed by the lubricant film on the cylinder wall could be as high as 250 ppm. By combining the dissolved SO_2 with the water that is present in the lubricant, a highly corrosive medium is produced at the surface of the cylinder wall.

Experiments were performed to determine the reactivity of sulfur dioxide with hydrocarbons. Olefins were found to be very reactive, forming black insoluble tarlike products; aliphatics and aromatics were found to be relatively stable in the presence of sulfur dioxide. The results suggest that hydrotreatment of lubricant base stocks may help to remove olefinic structures that react with sulfur dioxide and tend to form harmful deposits.

The JFTOT apparatus was used to determine the effect of sulfur dioxide on the thermal stability of lubricants. Small additions of sulfur dioxide to a polyalphaolefin oil, which otherwise had a high thermal stability rating, greatly depressed the oil's thermal stability and caused considerable insoluble matter to be formed. Similar effects of sulfur dioxide were observed in experiments with JP-5 fuel and pure compounds such as decalin. The results of these bench-scale experiments were substantiated in the full-scale engine tests in which sulfur dioxide was introduced into the air intake of the Petter single-cylinder diesel engine. In that test, it was shown that the increase in the engine deposits attributed to sulfur in the fuel was the same as that observed when sulfur dioxide was added to the air intake. The conclusion is that sulfur dioxide, formed by the combustion of fuel sulfur, plays a major role in the formation of deposits in diesel engines.

The results of this study support a new theory that SO_2 is the principal cause of fuel sulfur induced wear and deposit formation in diesel engines. It should be recognized in

future work that corrosion by sulfurous acid is a major process affecting cylinder bore and ring wear in diesel engines operating on high-sulfur fuels.

The results of the present work show that the mechanism of iron corrosion by sulfurous acid (H_2SO_3) involves an oxidation reduction mechanism, whereas sulfuric acid (H_2SO_4) simply behaves as an acid, causing galvanic corrosion. These differences in the mechanism may suggest new approaches to inhibiting the corrosion process, e.g., new possibilities may emerge in additives and metallurgy that would not have been considered if the current belief that sulfuric acid was the principal cause of corrosion continued to prevail.

The role of fuel-bound sulfur in the formation of deposits has been an important concern, but the complexity of the problem has suppressed major efforts to investigate the mechanism. The results of the present study indicate that the problem of deposit formation may be limited to reactions of sulfur dioxide with the lubricant. With that in mind, it may be possible to test lubricants based on their reactivity with sulfur dioxide and, perhaps, reactive components in the oil could be removed by the manufacturer in the processing stage.

VI. RECOMMENDATIONS

Several studies have examined the effect of fuel sulfur concentration on wear and deposit formation. It has been shown that the wear rate is proportional to $(sulfur)n$, where n is greater than unity. It is recommended that future work should include experiments to determine the effect of sulfur-dioxide concentration in the inlet air on wear and deposit formation. If sulfur dioxide is solely responsible for wear and deposit formation, the dependence on sulfur-dioxide concentration should be the same as that found for fuel sulfur content.

The reaction of sulfurous acid with iron metal is not well understood. The products of this oxidation-reduction reaction appear to be FeS and $Fe(OH)_2$, but little is known about the mechanism. Future work should include experiments to determine the effects of temperature and sulfurous acid concentration on the rate of the reaction with an iron metal surface. The results of such a study may be helpful in explaining the dependence of fuel sulfur on the cylinder bore and ring wear observed in diesel engines.

Further work is recommended on determining the effects of both sulfuric acid and sulfurous acid on wear. A more quantitative investigation needs to be made to compare the corrosive wear of lubricants containing equal concentrations of sulfur in the forms of sulfuric and sulfurous acid.

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APPENDIX

**Wheeled-Vehicle Test Procedure for the
DD 3-53 Engine**

WHEELED-VEHICLE TEST PROCEDURE FOR THE DD 3-53 ENGINE

Instructions

1. **Pretest Preparations.**

1.1 **Filter Elements.** Install new element in oil filter and change oil in air filter bath (using test oil).

1.2 **Sump Oil Charge.** Charge engine sump to full mark on dipstick with test oil (AL-16237-L). Close filler cap and motor engine for 1 minute at low speed (about 500 rpm) to fill oil cooler, filter, and internal oil passages. Recheck level and add to full mark again (should be about 25 lb).

1.3 **Priming Fuel System.** After changing over to test fuel and flushing fuel lines, remove the Allen plug from top of primary fuel filter and fill the filter with fuel, then reinstall plug.

1.4 **Break-In Procedure.** Set jacket coolant-out temperature controller at 205°F. Start engine and idle at 650 rpm for 5 minutes, then warm up at about 1000 to 1200 rpm for 10 minutes. If no engine malfunctions or leakages occur, conduct the following break-in and record complete log sheet readings at end of each setting. Calculate: BHP, Torque, BSFC, and BMEP.

Time, minutes	Speed, rpm	Idle, lb	Jacket-Out Temperature, °F
30	1800	25	160
30	2100	55	160
30	2300	70	160
30	2400	80	160

1.5 **Full-Load Performance Test.** Following the break-in run, conduct a full-load performance test run at the following conditions. Allow conditions to stabilize at each speed, then record complete log sheet readings at end of each setting. Calculate BHP, Torque, BSFC, and BMEP.

Speed rpm	Jacket-Out Temperature, °F
1400	160
1600	160
1800	160
2000	160
2200	160
2400	160
2600	160

1.6 <u>Valve Clearance Check.</u> Upon completing the full-load performance test, stop engine and <u>immediately</u> check the <u>hot</u> clearance of the exhaust valves. Adjust clearances to 0.023 to 0.025 in., also check injector height per gauge.

1.7 <u>Oil and Fuel Change-Over.</u> Upon completing valve clearance check, drain oil sump and filter. Discard drain and oil filter element. Weigh and record (on oil consumption log) a new oil filter element. Install new oil filter and then charge system with full charge of test oil (AL-16237-L) as in Item 1.2. Record weight of total charge. Change-over to test fuel (AL-16127-F) and flush fuel lines. Replace both fuel filter elements and prime as in Item 1.3. Weigh oil blowby can and record (oil consumption log).

1.8 <u>Full-Load Performance Test.</u> Following fuel change-over, run full-load performance test as in Item 1.5.

<u>Check and adjust oil level before starting test.</u>

2. <u>Test.</u>

2.1 <u>Warm-Up.</u> At the start of each day--idle for 5 minutes, then start test cycle at 2400 rpm.

2.2 <u>Test Conditions.</u> After warm-up, the following test cycle conditions are followed:

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Test Cycle for 15 Days

Period	Time, hr	Load, %	rpm	Coolant Temperature, °F
1	2	100	2400 ± 20	160
2	1	0	1500 ± 25	100 ± 2
3	2	100	2400	160
4	1	0	1500	100
5	2	100	2400	160
6	1	0	1500	100
7	2	100	2400	160
8	1	0	1500	100
9	2	100	2400	160
10	10	------------------Shutdown------------------		

Operate at test conditions 14 hours/day for a total of 210 hours. Complete log sheet readings at end of each period. Calculate: BHP, Torque, BSFC, and BMEP.

2.3 Daily Cool-Down. After the last test hour each day, reduce the speed to idle (600 to 650 rpm) for 5 minutes (without resetting coolant controller), then stop engine.

2.4 Used Oil Samples. Flush oil filter tap, and withdraw a used oil sample during daily 5-minute cool-down (Item 2.3) according to the Oil Consumption Log schedule and record sample weight.

Identify each sample as to Test Hours, Test No., and Oil Code (AL-16237-L). Take: 1-oz sample every 7 hours, except at 70 and 140 hours, take 12-oz sample. At end of test, take 16-oz sample. Take daily oil samples to Chem Lab for elemental analyses by XRF.

2.5 Oil Additions. New test oil additions, if required, are to be made at the end of each day after shutdown. Allow 5 minutes for oil to drain back to sump. Add weighed new oil to restore sump level to full by dipstick. Record weight of add-on oil consumption log.

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2.6 <u>Final Oil Drain.</u>   Upon completion of post-test power curves and while engine is warm, drain the sump, saving one gallon of used oil in clean can. Tag can, showing Test No., Oil Code, Date, and Test Hour. Also remove oil filter element, weigh, and record.

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