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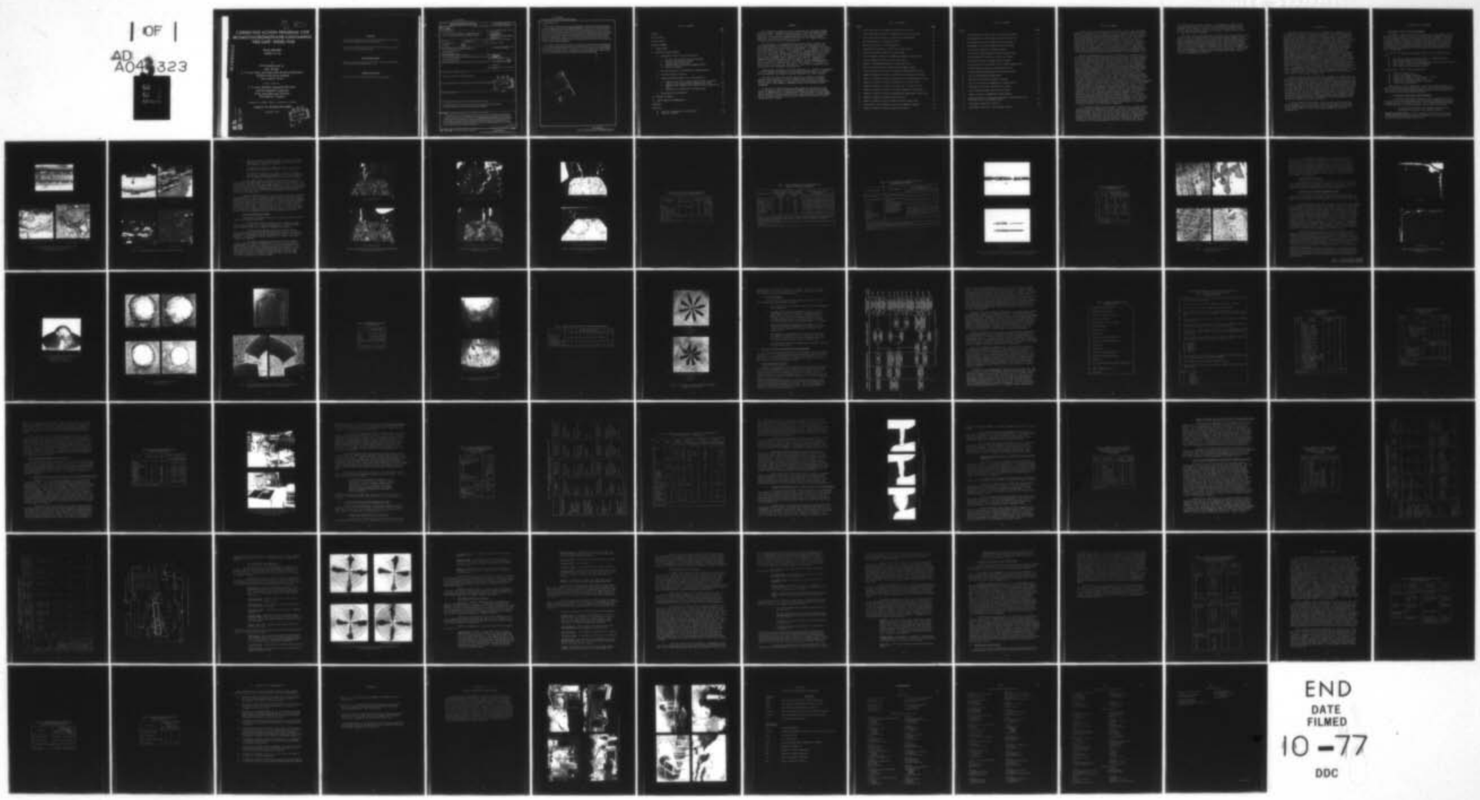

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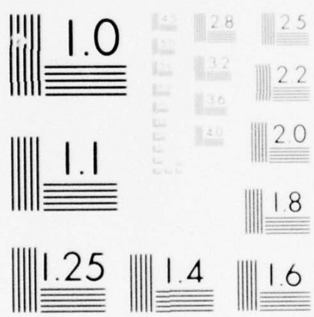

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CORRECTIVE ACTION PROGRAM FOR BROMOCHLOROMETHANE-CONTAINING "FIRE-SAFE" DIESEL FUEL

FINAL REPORT
AFLRL No. 81

by

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under contract to

U. S. Army Mobility Equipment Research and Development Command
Fuels and Lubricants Division
Fort Belvoir, Virginia

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September 1976

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20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

Following a laboratory-engine endurance test of bromochloromethane (BCM) "fire-safe fuel" (FSF) in a 12-cylinder, air-cooled, four-cycle AVDS 1790-2C diesel engine conducted by Teledyne Continental Motors, a multifaceted experimental program was originated by MERADCOM/AFLRL (Mobility Equipment Research and Development Command/Army Fuels and Lubricants Research Laboratory) to establish whether or not "fixes" could be developed to overcome the problems that caused the engine endurance test to be terminated after 150 rather than the intended 400 operating hours.

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20. ABSTRACT (Cont'd)

Recapitulation of test events, detailed post-test examinations of engine parts and used lubricant samples, and follow-through experimental studies by MERADCOM/AFLRL confirmed or indicated plausible mechanisms for the observed difficulties. First, the fuel pump plunger rod sticking problem was confirmed to have been caused by corrosion at the fuel-oil interface; second, the fuel injector valve sticking was caused by a lacquer-like deposit; third, the fuel injector nozzle holes had become substantially enlarged and elongated by predominately corrosive mechanisms; fourth, excessive distress experienced by the oil-control piston ring appeared to have resulted from combined effects of stress corrosion cracking caused by HCl and scuffing caused by inadequate lubrication; and fifth, oil filter plugging was found to have resulted from the formation of halon by-product and wear-metal-containing sludge in the lubricant.

The composite results of laboratory engine tests, corrosion tests, and other appropriate experiments with corrosion inhibitors provide only partial solutions to the problems and assure only short-term engine operation with bromochloromethane "fire-safe fuel". Accordingly, use of this fuel in combat should be only considered for limited, special, emergency operations. "No-go" positions are recommended for general combat equipment use, and no additional applied research and development is recommended for BCM FSF.

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FOREWORD

This report was prepared at the U.S. Army Fuels and Lubricants Research Laboratory (AFLRL), Southwest Research Institute, under DOD Contract Number DAAG53-76-C-0003. The project was administered by the Fuels and Lubricants Division, U.S. Army Mobility Equipment Research and Development Command (MERADCOM), Fort Belvoir, Virginia 22060, with Mr. F.W. Schaekel serving as Contracting Officer's Technical Representative.

The authors wish to acknowledge the assistance of many technical and professional members of the AFLRL staff (and other SwRI divisions) for the design and supervision of operation and maintenance of experimental apparatuses and interpretation of results. These include Messrs. J.N. Bowden, J.V. Moffitt, E.C. Owens, W.W. Wimer, and Dr. R.J. Mannheimer. Acknowledgment is also given to Mr. D.C. Babcock for producing most of the photographs used in this report and to Mr. F.W. McBryde for the installation and maintenance of electrical and electronic equipment used in support of this program. Metallurgical examinations and interpretations were provided by Mr. H.C. Burghard, Jr., and Dr. D. Davidson, assisted by Mr. J.G. Barbee. Special acknowledgment is given to Messrs. H.L. Ammlung, M.E. LePera, F.W. Schaekel, T.C. Bowen, R.D. Quillian, Jr., J.T. Gray, A.A. Johnston, S.J. Lestz and F.M. Newman for their participation, encouragement, and suggestions.

The assistance and advice of The Dow Chemical Co. is gratefully acknowledged for gratis exhaust gas analysis for halogenated substances (Dr. C.L. Putzig) and for suggestions for halogen-scavenger candidates (Dr. Randy Stauffer).

The loan of a 20mm rifle and the provision of a supply of 20mm HEIT ammunition was arranged by the Project Manager-Vehicle Rapid Fire Weapon Systems, Rock Island Arsenal at the request of the Fuels and Lubricants Division of the U.S. Army Mobility Equipment Research and Development Command (MERADCOM).

In May 1974, a steering advisory panel, headed by the Director of the Energy and Water Resources Laboratory of MERADCOM, and comprising representatives of MERADCOM, The U.S. Army Materiel Systems Analysis Activity (AMSAA), and the Ballistic Research Laboratory (BRL) was established to review progress and to coordinate activities of the various groups participating in the BCM "fire-safe fuel" program.

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EXECUTIVE SUMMARY

As part of the U.S. Army "fire-safe fuel" (FSF) research and development program, an endurance test was conducted in a new, twelve-cylinder, air-cooled, AVDS 1790-2C diesel engine by Teledyne Continental Motors. The fuel used in this test comprised 5v% bromochloromethane (BCM) in DF-2 diesel fuel (BCM FSF). The 400-hour mission profile cycle was terminated after about 150 hours of operation on BCM FSF because of repeated mechanical problems and excessive exhaust smoke production. Because of this failure, a coordinated program was initiated by the Army to establish whether or not the causes of the engine failure could be ameliorated. Priority effort was devoted to establishing viable means for implementing the use of BCM fire-safe fuel in combat situations, with the objective being to provide adequate data for developing a "go" or "no-go" position on BCM "fire-safe fuel" before the end of September 1976.

Extensive experimental data and other information was developed after the AVDS-1790-2C engine BCM FSF endurance test was terminated. The data developed by the Army Fuels and Lubricants Research Laboratory (AFLRL) included results of single-cylinder and multi-cylinder diesel engine tests, fire vulnerability tests, corrosion screening tests, and various routine laboratory and bench-scale evaluations. In addition, a metallurgical task force was organized by the U.S. Army Mobility Equipment Research and Development Command (MERADCOM) and subsequently convened at the Army Materials and Mechanics Research Center (AMMRC) to assess metallurgical aspects of the BCM FSF problems. Because of long lead-time requirements involved in developing alternate-alloy fuel injector assemblies (one year), it was not possible to even plan the testing of such injectors prior to October 1976. Hence, primary attention during this investigation was devoted to the modification of the BCM FSF formulation and/or the engine lubricant, with less emphasis being placed on the possible use of alternate corrosion-resistant alloys. An accelerated corrosion test was developed by AFLRL to provide a screening method for both approaches, and the 4-ball test (ASTM Test Method D-2266) was used for screening lubricity effects. It was soon determined that conventional corrosion inhibitors were ineffective for counteracting the harmful effects of BCM, and only one class of compounds was identified that could effectively eliminate the HCl-induced nozzle corrosion problems. This class comprises halogen-scavenger compounds containing a three-membered, carbon-carbon-oxygen ring (epoxide group). For volatility reasons, cyclohexene oxide was selected as the fuel additive to be used after brief initial successful tests were conducted with propylene oxide. For similar volatility reasons, expoxidized soybean oil was selected as a candidate crankcase lubricant halogen-scavenger. This latter material is reputed to be inactive relative to epoxide polymer formation.

The composite results of engine tests, corrosion tests, and other evaluations may be briefly summarized as follows. Of the four major problem areas encountered during the AVDS 1790-2C FSF endurance test, the injector nozzle hole enlargement, injector valve sticking, and accelerated cylinder-liner wear were successfully duplicated, but the oil-control piston ring chipping was not observed in this laboratory. The objective of eliminating or substantially reducing the injector nozzle hole enlargement was achieved by the use of cyclohexene oxide halogen-scavenger in the fuel. No additive was effective

in eliminating injector valve sticking. The accelerated cylinder liner wear was retarded briefly by the use of a low-volatility expoxide halogen scavenger in the crankcase lubricant; however, accelerated wear occurred when the halogen-scavenging capacity was consumed. Hence, the use of such oil additives is not recommended.

More than 100 hours of operation was achieved with a multi-cylinder diesel engine (V6-155) using BCM FSF plus 0.5% cyclohexene oxide; however, these results provide no assurance that the AVDS 1790-2C engine could complete the previously-sought 400-hour mission profile cycle. The results only offer promise of satisfactory short-term operation with BCM/cyclohexene oxide FSF before injector hole enlargement, injector valve sticking, or accelerated wear may cause engine failure. Accordingly, use of this fuel in combat should only be considered for limited, special, emergency operations. "No-go" positions are recommended for general combat utilization and further applied research and development on BCM FSF.

I. INTRODUCTION

When Army tactical vehicles and other equipment are subjected to incendiary ballistic attack, they are very vulnerable to fire and explosion. In the case of fires caused or intensified by fuel release, fire vulnerability reduction can be achieved by the use of fire-safety fuels. Various fire-safety fuels have been investigated by the Army and other agencies in the past, primarily for the purpose of decreasing the frequency and intensity of aircraft in-flight and post-crash fires. The approaches have included nonreversible fuel gellation, use of semi-rigid, but pumpable, fuel gels and aqueous-external-phase fuel emulsions, and use of organic-polymer antimist agents in very low concentrations. However, the Army's need for a low-vulnerability combat fuel necessitated a shift in Army R&D emphasis to investigations of diesel fuels. A candidate "fire-safe fuel" (FSF) formulation comprising 5v% bromochloromethane (BCM) in DF-2 diesel fuel (BCM FSF) demonstrated promising fire-suppression results.[1] Accordingly, a full-scale engine test was authorized by MERADCOM to be conducted by Teledyne Continental Motors (TCM) under the direction of the M60 Project Manager's Office. The objective of this test was to determine the effects of BCM FSF on the performance and endurance of a 12-cylinder, air-cooled, four-cycle diesel engine (AVDS 1790-2C) when operated in a laboratory under the 400-hour mission profile cycle. An engineering work directive was issued on 1 July 1975 by the M60 Project Manager's Office detailing the test procedures and conditions. On that date, a conference was held to review, modify, and finalize the detailed requirements for this engine endurance test.

When the engine test was initiated, the performance and exhaust emission characteristics were documented when using conventional DF-2 diesel fuel. The power curve and speed/load survey were then completed while using BCM FSF, and the engine was stopped and allowed to cool prior to conducting exhaust emission measurements. When restart was attempted, the first mechanical failure in this test was encountered. The engine would not start because the metering sleeves on both plunger rods of the fuel pump had seized. An alternate fuel pump was installed, and the test was continued, with difficulty, for a total of about 150 operating hours on BCM FSF (including the preliminary performance checks). The termination of the test in November 1975 prior to the targeted 400 hours stemmed from repeated mechanical problems which had depleted operating funds and created a potentially serious environmental pollution problem for TCM because of excessive black smoke emissions.

It is the purpose of this report to describe the activities involved in the assessment of this engine test failure, to document the corrective-action research program that followed, and to present conclusions relative to the overall efficacy of BCM FSF that were developed by the end of September 1976.

II. CORRECTIVE ACTION PROGRAM

A. Assessment of AVDS 1790-2C Failure Modes

Two members of AFLRL staff and a representative of Army Materiel Systems Analysis Activity (AMSAA) visited TCM to witness engine disassembly and perform a preliminary inspection/rating of the AVDS 1790-2C engine. Subsequent to this disassembly inspection, a meeting of the FSF Working Group was held at MERADCOM to further assess the results of the endurance test and to plan additional steps for overcoming the observed problem areas. In addition to the foregoing, the Coordinating Research Council (CRC) Army Combat Engine Fuels and Lubricants Group met at TCM and conducted another detailed inspection of engine parts.[4]

In brief, the aforementioned groups identified the following problem areas:

- Oil-control piston ring (severe chipping of chromium plating).
- Injector pump plunger rods (seizure).
- Fuel injector nozzle valve stem deposition and/or corrosion (sticking).
- Fuel injector nozzle tip holes (enlarged).
- Fuel clogging (excessive pressure drop).

Manifestations of some of these problems were:

- Excessive sludge in oil.
- Copious black smoke production.
- Tacky, sooty deposit on pistons and in oil sump.
- Substantial increase in blowby rates.
- Piston skirt scratching and metal imbedment.
- Degraded power performance.

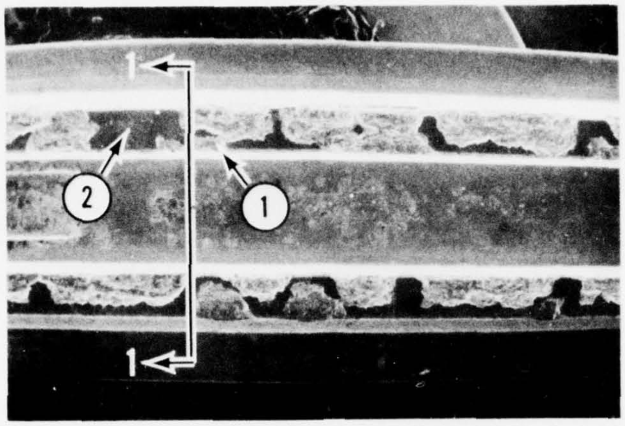
Based upon the on-site inspections, it was not possible to assess the modes by which the observed failures occurred. Hence, priorities of the AFLRL FSF research program were reoriented toward identification and amelioration of the causes of the above-described problems.

1. Oil-Control Piston Ring Failure Mechanism

A scuffing mechanism was suggested by the ring manufacturer[2] for the oil-control piston ring failure, but this does not appear to be the same mechanism for the ring examined by AFLRL. The following evidence developed by AFLRL indicates a corrosive mechanism for the piston ring failure.

a. No scuffing was evident on the chromium plating not yet chipped off of the piston ring (Figures 1 and 2)*.

*Complete hardness traverses of the chromium plating on both the "failed" and the control piston rings showed the hardness to be fairly consistent through the plating thickness of both rings.



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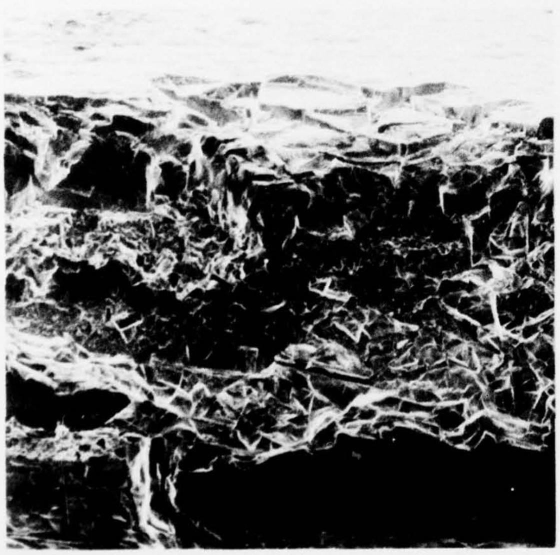
(a)



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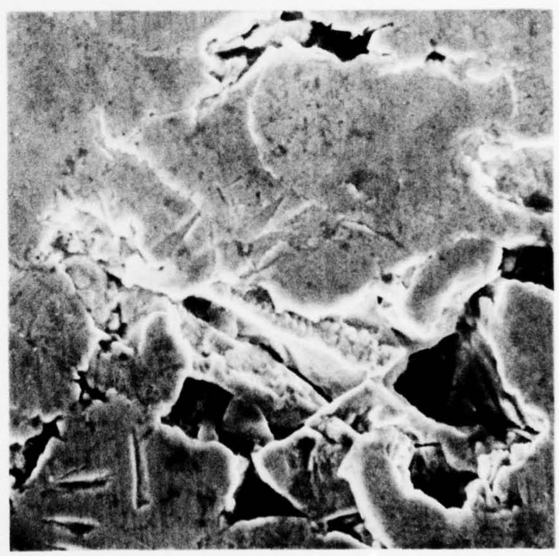
(b) Location 1 in (a)



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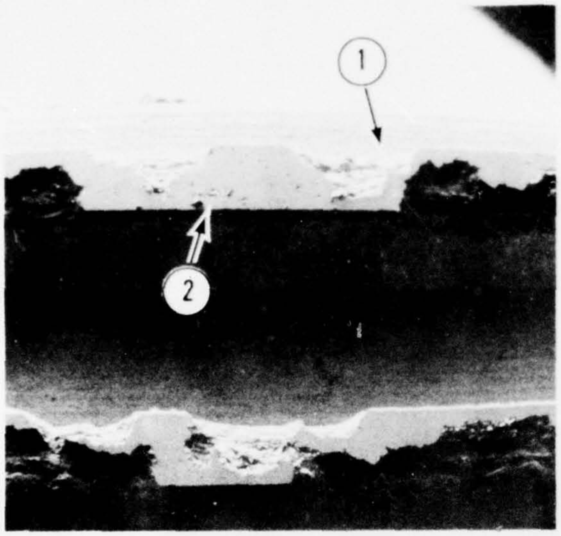
(c) Location 2 in (a)

FIGURE 1. SEM MICROGRAPHS OF WEAR SURFACE OF FAILED PISTON RING FROM TCM AVDS 1790-2C ENGINE ENDURANCE TEST WITH BCM FSF



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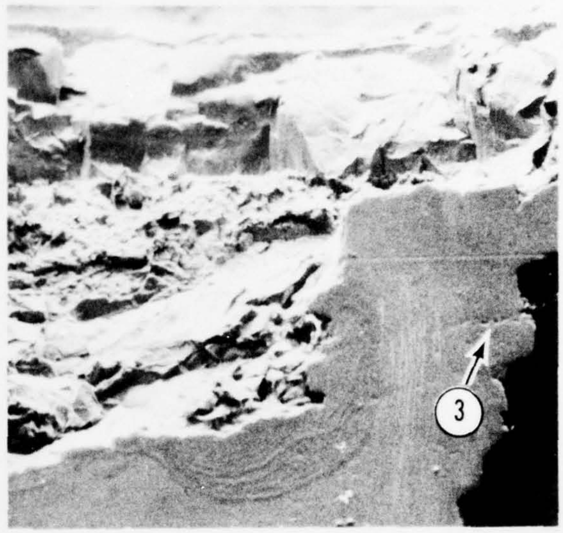
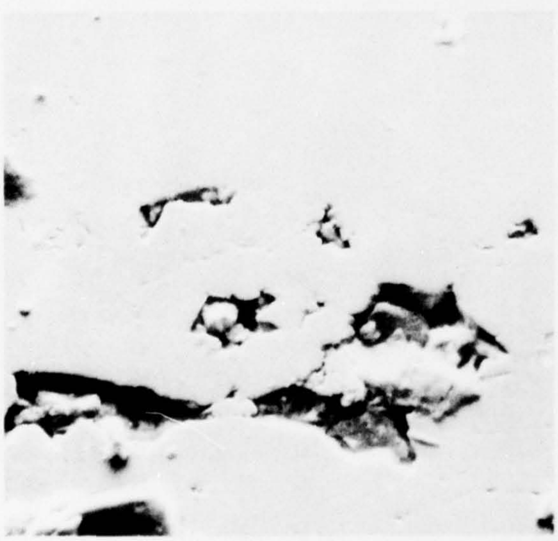
(a)



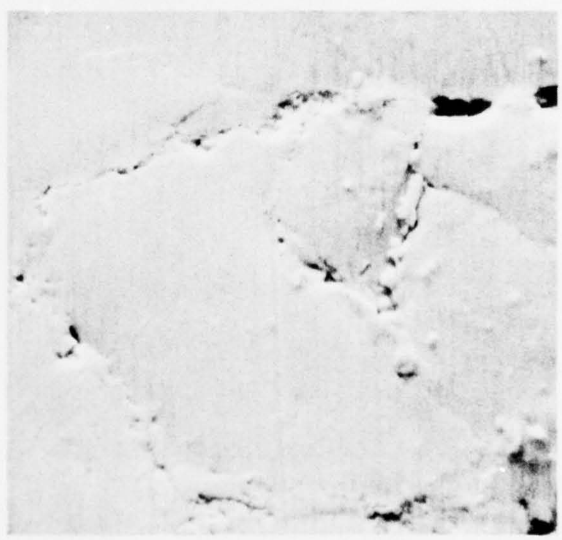
180X

(b) Location 1 in (a)



360X

(c) Location 2 in (a)



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(d) Location 3 in (b)

FIGURE 2. SEM MICROGRAPHS OF WEAR SURFACE OF FAILED PISTON RING

b. There was evidence of corrosion debris in some of the intergranular cracks in both the chromium plating and in the cast iron substrate (Figures 3, 4, and 5).

c. No significant dilution of crankcase oil with raw fuel was evident by AFLRL analysis of used oil samples (Table 1).

d. The ratio of Cl to Br in the crankcase oil was less than in the raw fuel, indicating that much of the halogen content of the oil stemmed from blowby products--not raw fuel (Table 1).

The ring manufacturer's metallurgical analyses[2] indicated that scuffing was the primary cause for the ring failure and metal transfer. This suggested that overfueling may have washed lubricant off of the cylinder walls. However, the piston ring inspected at AFLRL showed no evidence of such scuffing. In essence, however, both the manufacturer's analysis and the AFLRL analysis could be correct since the investigations used components from different cylinders of the same engine.

Subtasks conducted by AFLRL as part of this ring-failure assessment included analyses of used crankcase oil and examination of used oil filters (and analysis of the sludge contained therein). Analyses were also conducted on deposits obtained from various locations on a typical used piston from the AVDS 1790-2C engine BCM FSF endurance test. The results of these analyses, presented in Tables 2 and 3, did not provide a clear cut definition as to the failure modes stemming from the use of FSF. Due to the short term usage of the lubricant, problems, such as the asphaltic deposits, had to be attributed to the acidic components generated by the combustion of BCM FSF.

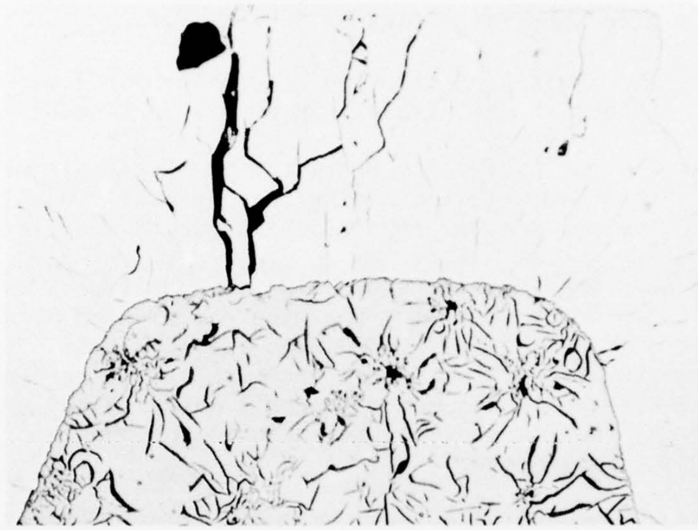
2. Injector Pump Metering Plunger

The following statements relative to the injector plunger were provided by the SwRI metallurgists:

"A discolored band was evident on the cylindrical surface of the plunger, Figure 6(a). This band consisted of a tightly adherent surface film and could not be removed by swabbing with acetone.

A qualitative microprobe analysis of the dark zones on each of the parts was performed and the results are presented in Table 4. The analyses were performed for the various elements contained in the fuel additives. In each case significant quantities of calcium, sulfur and chlorine were detected.

The surface topography of these parts was also examined in the scanning electron microscope (SEM). In the case of the pintle [Figure 6(b)], no evidence of attack of the surface was apparent in the dark zone and the microscopic features indicated the presence of a loose deposit, Figure 7(a). Distinctly different topographic features were noted between the dark zone and clean surface on the plunger as shown in Figures 7(b) and 7(c). Within the dark zone the surface was rough and pitted, suggestive of corrosive attack.



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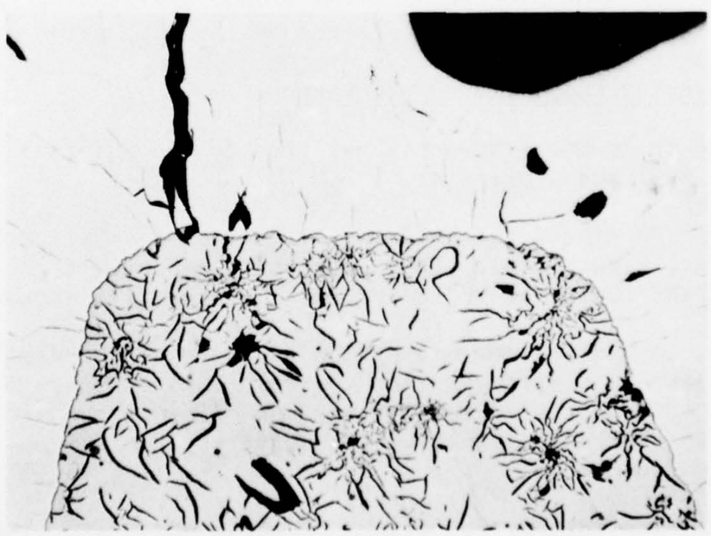
(a) Lower land in Figure 1(a)



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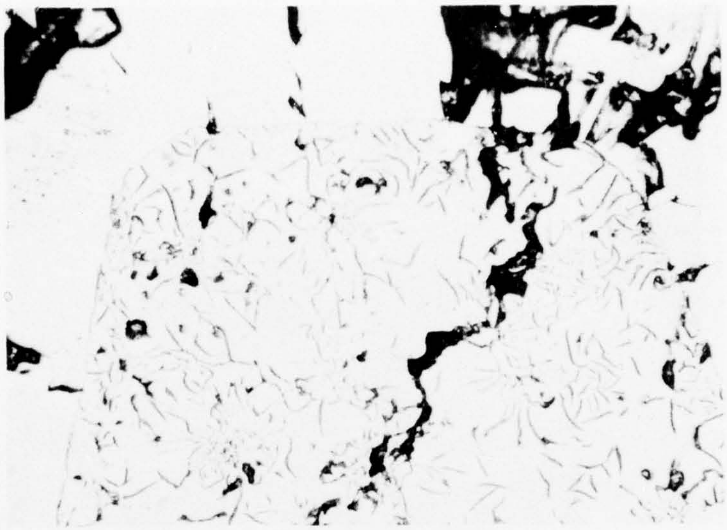
(b) Upper land in Figure 1(a)

FIGURE 3. MICROGRAPHS OF SECTION THROUGH FAILED PISTON RING
Section 1-1, Figure 1(a). Unetched.



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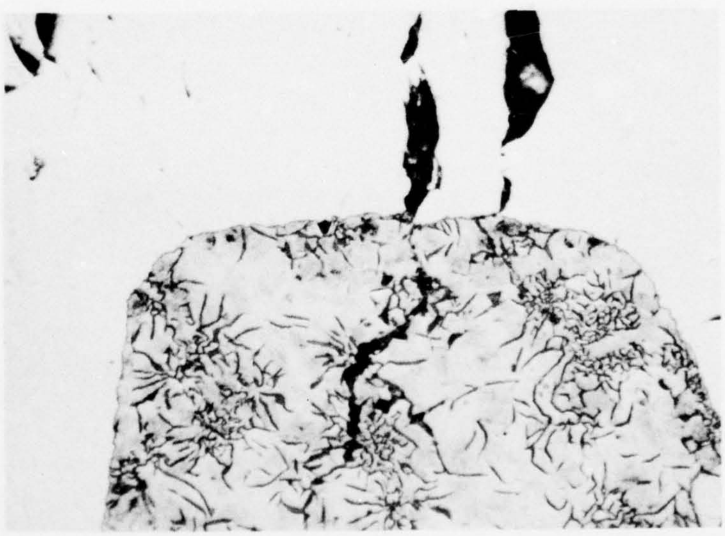
(a) Upper land 0.03 in. beyond Section 1-1, Figure 3



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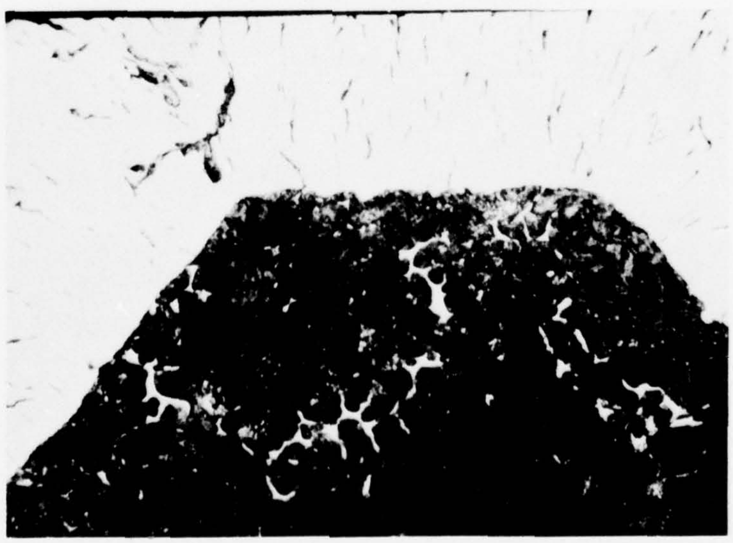
(b) Upper land 0.06 in. beyond Section 1-1, Figure 3

FIGURE 4. MICROGRAPHS OF SECTIONS THROUGH FAILED PISTON RING. Unetched.

250X

(a) Failed ring



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(b) Used ring from normal service

FIGURE 5. TYPICAL MICROSTRUCTURE OF CHROMIUM PLATING
Etchant: Electrolytic Oxalic Acid

TABLE 1. SPECIAL ANALYSES OF OIL SAMPLES FROM AVDS 1790-2C ENGINE FSF ENDURANCE TEST

Sample Designation (date)	Strong Acid No.	Total Acid No.	Fuel Dilution (% Fuel by G.C. ±0.3)	Halogen Content (wt %)	
				CL	BR
New Oil[a]	0	0.63	0.0	0.2	0.0
No. 2/(31 Oct 1975)[b]	—	—	0.4	0.5	1.5
No. 3/(6 Nov 1975)[b]	—	—	0.1	0.6	1.5
No. 4/(7 Nov 1975)[b]	—	—	0.2	0.6	1.5
Final drain/(25 Nov 1975)	1.67	9.87	0.5	0.6	1.4

[a]High Base Oil.
[b]Nos. 2, 3, and 4 from same oil fill.

TABLE 2. X-RAY FLUORESCENCE ANALYSIS OF AVDS-1790-2C
ENGINE OIL AND OIL FILTER RESIDUE

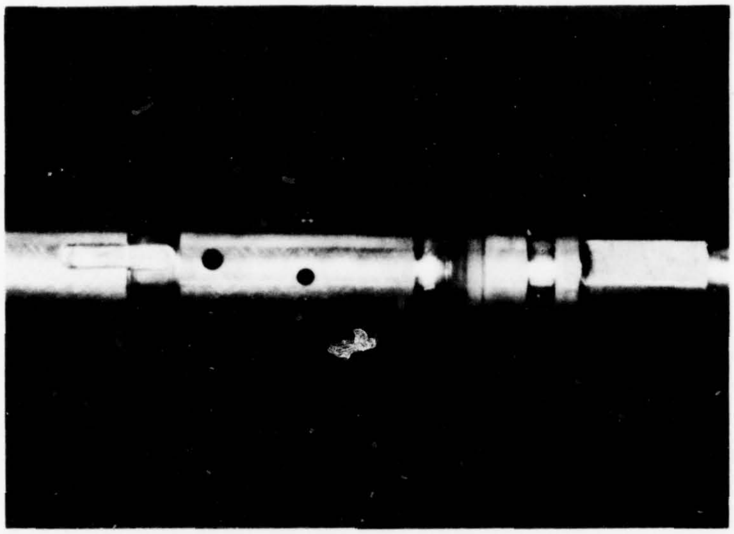
Sample Description	Duration of Exposure of Sample to FSF in Operating Engine (Hr:Min)	Duration of Engine Operation on FSF[a] (Hr:Min)	Relative Elemental Conc.[b] (Fraction of Total Peak Area)[c]						
			AL	P	S	Cl	Ca	Fe	Br
Oil Filter (10-28-75)	21:57	21:57	0.01	0.00	0.11	0.04	0.16	0.11	0.58
Oil Filter (11-17-75)	31:45	146:42	0.01	0.00	0.10	0.03	0.14	0.15	0.56
Oil Filter (11-18-75)	7:45	154:27	0.01	0.00	0.08	0.03	0.15	0.15	0.58
No. 2 Oil (10-31-75)	1:40	55:37	0.01	0.00	0.10	0.03	0.12	0.08	0.67
No. 3 Oil (11-6-75)	23:55	77:52	0.01	0.00	0.12	0.04	0.15	0.07	0.61
No. 4 Oil (11-7-75)[d]	34:50	88:47	0.01	0.00	0.10	0.04	0.13	0.08	0.64
Final Oil Drain (11-25-75)	13:35	168:02	0.01	0.00	0.12	0.04	0.14	0.07	0.62

[a]Times calculated from Log Sheet Summary in CRC Project CD-17-74 Minutes (unconfirmed) (Appendix D-1), correcting total durations for FSF operations on 17-20 October and 23 October 1975 and for operation on neat fuel on 3 November and 31 November 1975.
[b]Photos of all X-Ray spectra are on file.
[c]Values are relative peak areas and do not take into account response factors. Concentration can be compared *vertically only*, not horizontally.
[d]Nos. 2, 3, and 4 were from same oil fill.

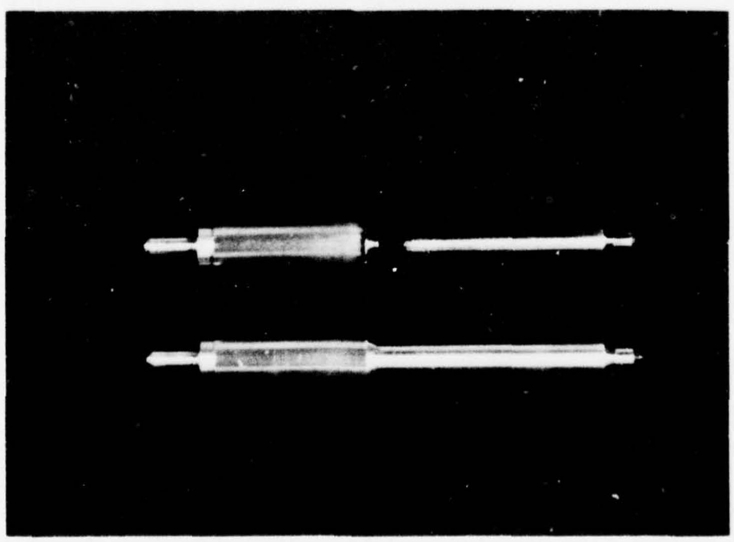
TABLE 3. X-RAY FLUORESCENCE ANALYSIS OF AVDS-1790-2C ENGINE PARTS AND RESIDUES

Sample Description	Deposit Condition	Relative Elemental Conc.[a] (Fraction of Total Peak Area)[b]						
		AL	P	S	Cl	Ca	Fe	Br
Back of Oil Ring Groove	Tacky Asphaltic-Appearing Substance	0.03	0.02	0.25	0.08	0.29	0.11	0.22
Top Side of Oil Ring Groove	Very Tacky Asphaltic Appearing Substance	0.04	0.01	0.22	0.07	0.29	0.12	0.25
Land No. 4	(Next to Oil Ring Groove) Asphaltic Appearing Substance	0.03	0.00	0.20	0.06	0.27	0.05	0.38
Land No. 3	Hard, Slightly Asphaltic Appearing Substance	0.03	0.00	0.19	0.06	0.27	0.15	0.29
Land No. 2	Hard Crystalline Substance	0.02	0.00	0.18	0.03	0.28	0.20	0.29
Land No. 1	Very Hard Substance	0.02	0.00	0.18	0.03	0.29	0.20	0.29
Piston Crown Deposit	—	0.01	0.00	0.23	0.03	0.38	0.16	0.20
Piston Undercrown	—	0.04	0.05	0.16	0.05	0.27	0.16	0.27
Oil Ring[c]	—	—	—	—	—	—	—	—

[a]Photos of all X-Ray spectra are on file.
[b]Values are relative peak areas and do not take into account response factors. Concentration can be compared *vertically only*, not horizontally. Oil filter samples can be compared to deposits on an approximate basis.
[c]Inside surfaces of ring show much higher P, Cl, S, Br, Ca compared to outside surfaces. The Cr/Fe ratio was higher on inside surfaces compared to outside.



(a) Plunger



(b) Pintle
Top: From TCM test injector
Bottom: New part

FIGURE 6. FUEL INJECTOR PUMP PLUNGER AND INJECTOR VALVE PINTLE FROM FUEL INJECTOR FROM AVDS 1790-2C ENGINE ENDURANCE TEST WITH BCM FSF

TABLE 4. MICROPROBE ANALYSIS OF PLUNGER AND PINTLE

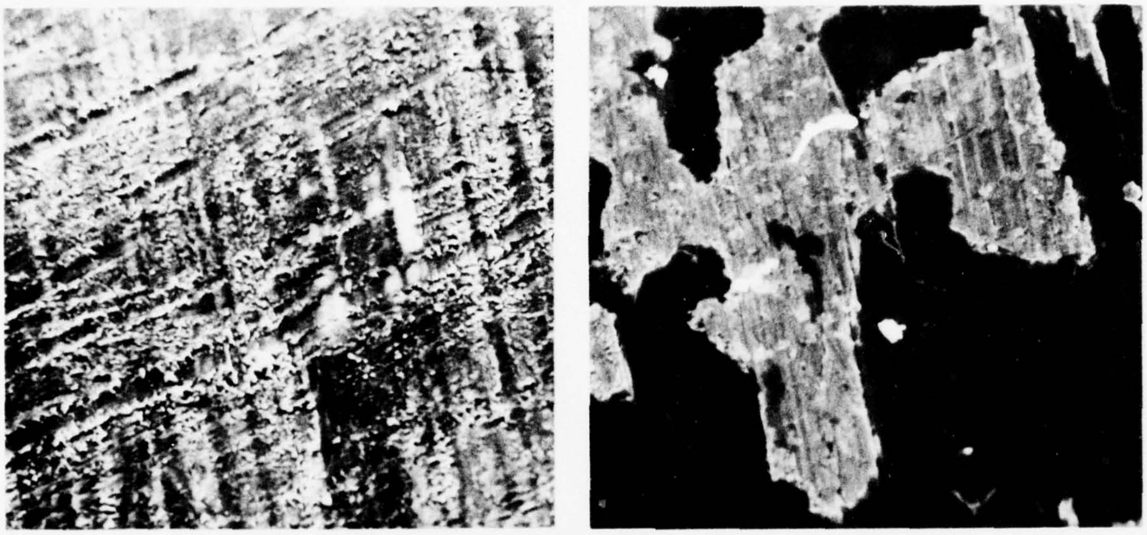
Element	Peak/Background[a]		
	Pintle Tip	Deposit on Pintle Body	Dark Band on Plunger
Mg	ND[b]	ND	c
Ba	ND	ND	ND
Zn	ND	ND	ND
Ca	1600/1250	5300/3550	3900/1430
S	750/235	1136/240	160/107
P	ND	ND	71/56
Br	ND	ND	ND
Cl	566/214	5000/375	1010/170

Notes:

[a]Counts in 30 sec., $i = 0.5 \times 10^{-7}$ amps.

[b]ND–Not detected.

[c]Mg preferentially located within pits P/B = 360/93 for reduced area scan.



880X 880X

(a) Locations in dark zone of pintle

880X

(b) Clean zone on plunger

880X

(c) Dark zone on plunger

FIGURE 7. SEM MICROGRAPHS OF SURFACES OF PINTLE AND PLUNGER

A longitudinal metallographic section was taken through the dark zone of the plunger. Examination of this section revealed definite pitting of the surface within the dark zone, while the surface profile at the clean zone was extremely flat and smooth (see Figure 8). These metallographic features together with the fine-scale topography observed in the SEM examination are definite evidence that the dark band on the plunger is the result of corrosive attack. It should be noted that both sulfur and chlorine were present in significant amounts within this zone of the plunger. Either of these elements could cause corrosive attack of the plunger."

3. Injector Nozzle Valve Stem

The dark area on the pintle was found to be acetone soluble, and SwRI metallurgists saw no evidence of corrosion [Figure 6(b)]. As in the case of the previously discussed engine parts, significant quantities of chlorine were present in dark zone on the pintle (see Table 4).

4. Injector Nozzle Tip Hole Enlargement Effects

All of the eight holes in each of the two injector nozzles examined by SwRI metallurgists showed diameter increases, ranging from two holes with a 25% increase, to two holes with a 117% increase (Figures 9 and 10).

Photomicrographs of the cross-section of the largest versus smallest hole in a used nozzle revealed intriguing patterns (Figure 11). Both showed no enlargement of the hole entrance. The largest demonstrated a "belling" shape similar to that which is characteristic of a trumpet. However, the smallest indicated only slight enlargement of the hole outlet, but substantial enlargement between the inlet and outlet. A second nozzle was examined in the same manner to confirm the generality of these observations. Significant quantities of chlorine-containing deposits were present within the nozzle tip holes (Table 5). Such debris is visible in Figure 12. Microhardness traverses of the tip, and the wall of the two nozzles showed the hardnesses of each to be approximately the same. However, the microstructures of the two were different. Since analyses showed the compositions to be about the same (Table 6), these microstructural differences probably stemmed from differing thermal histories of the two nozzles.

Rather than only attributing the previously-mentioned excessive smoke emissions to overfueling because of nozzle hole enlargement, an alternate explanation could lie in the influences of the nonuniform nozzle injector tip hole enlargement on spray density and distribution. Figure 13 illustrates changes that occurred in the spray patterns* of a typical nozzle from the AVDS 1790-2C engine FSF endurance test after about 30 hours exposure to BCM FSF (with overnight shutdowns). These reveal substantial decreases in spray penetration with attendant increases in spray-droplet

*Taken using the AFLRL liquid injection technique. This method of spray analysis utilizes a clear liquid, such as kerosene, as the injection media rather than a compressed gas, thus eliminating the resultant fuel fog. It has been proven effective as a means of observing relative differences in spray patterns.

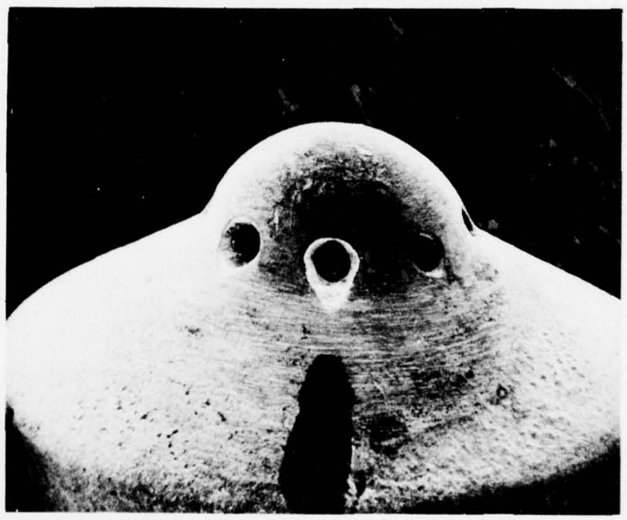
750X

(a) At dark zone

750X

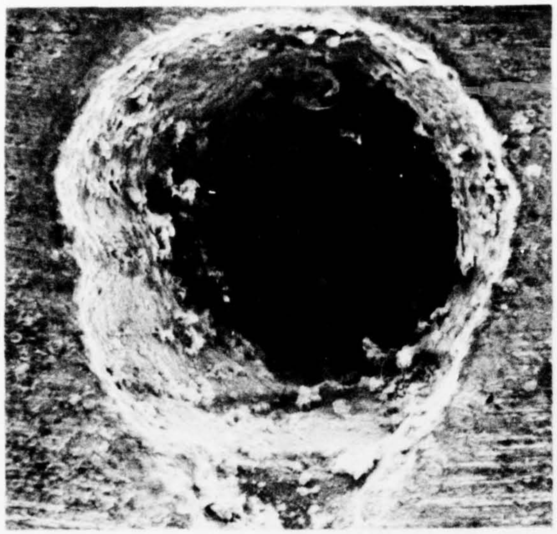
(b) At clean surface

FIGURE 8. MICROGRAPH OF SECTION THROUGH INJECTOR PLUNGER. Unetched.



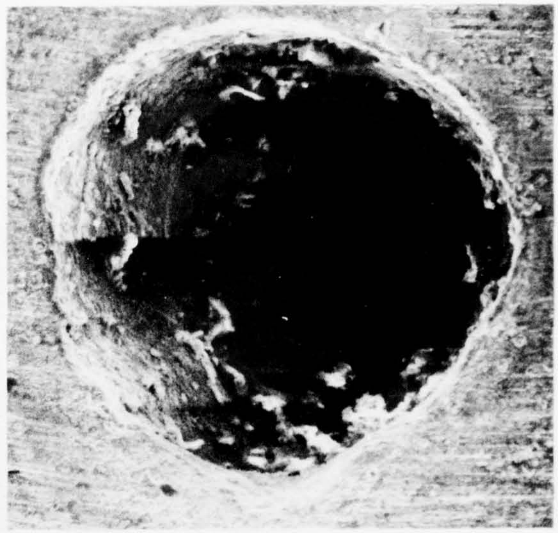
12X

FIGURE 9. FAILED INJECTOR TIP (CENTER HOLE IN MICROGRAPH DESIGNATED AS NO. 1) FROM AVDS 1790-2C ENGINE ENDURANCE TEST WITH BCM FSF



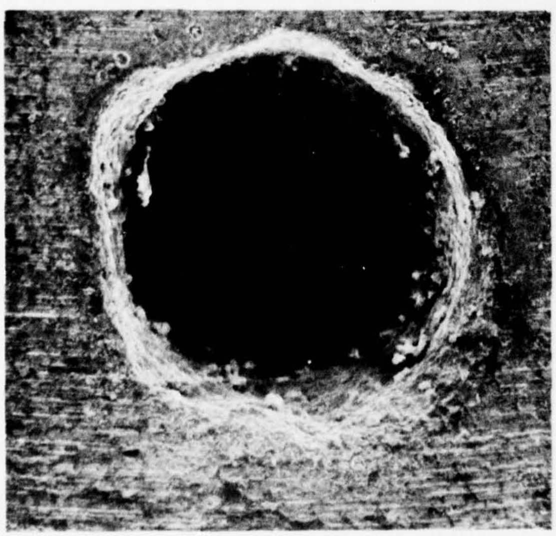
100X

Hole No. 1



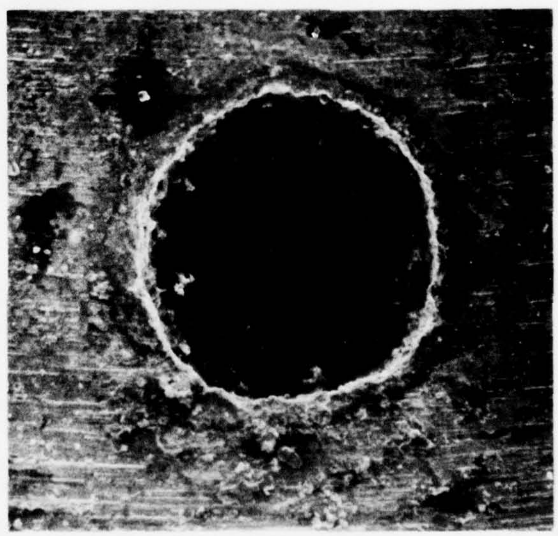
100X

Hole No. 2



100X

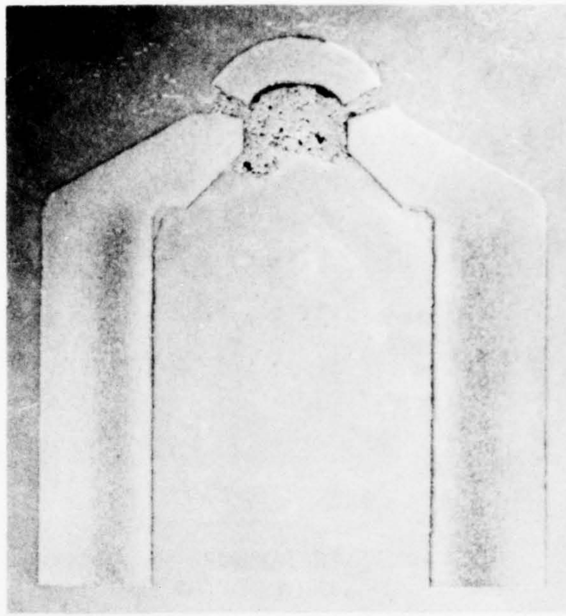
Hole No. 3



100X

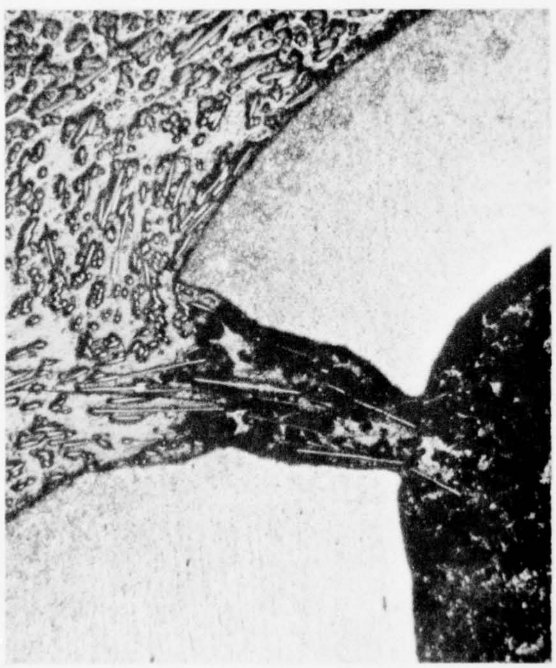
Hole No. 4

FIGURE 10. SEM MICROGRAPHS OF HOLES IN FAILED INJECTOR TIP



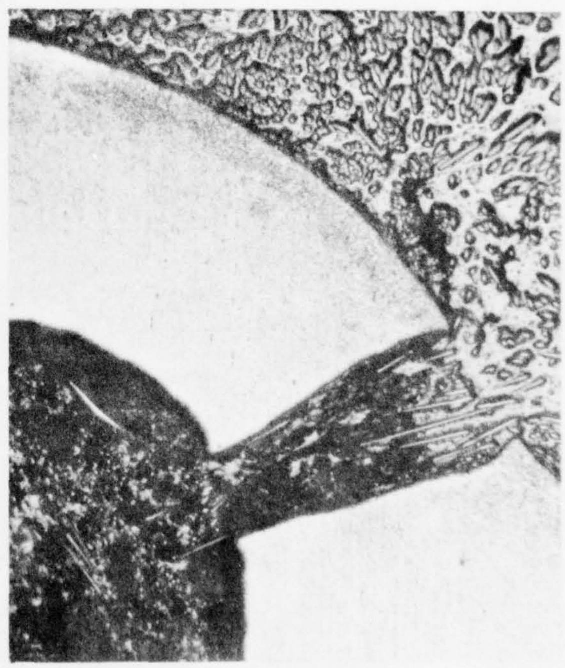
8X

(a) Used



50X

(b) "Used" Hole 1



50X

(c) "Used" Hole 5

FIGURE 11. SECTIONED SPECIMEN REVEALING CROSS-SECTIONS OF LARGEST AND SMALLEST HOLE IN FAILED AVDS 1790-2C INJECTOR NOZZLE

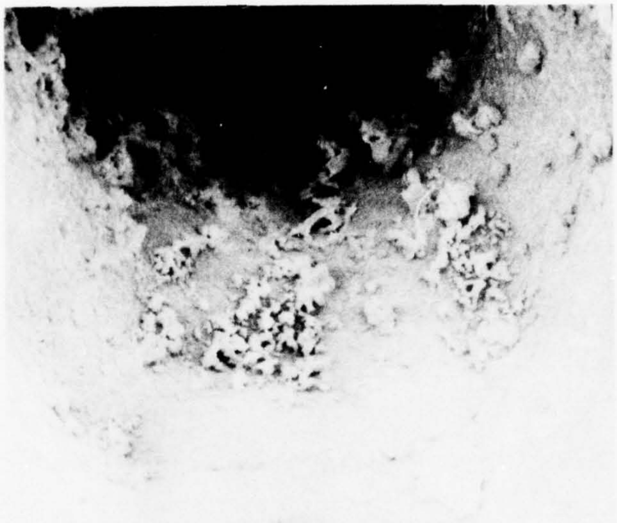
TABLE 5. MICROPROBE ANALYSIS OF FUEL INJECTOR TIP

Location[a]	Peak/Background[b]	
	Cl	Br
Area 1	469/52	Not detected
Area 2	283/48	Not detected
Area 3	42/10	Not detected
Conical Surface	500/85	1350/1200

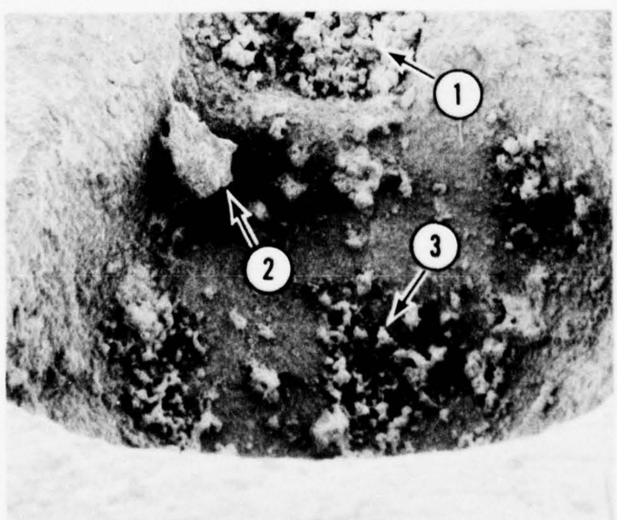
Notes:

[a]See Figure 12 for location of areas examined.

[b]Counts in 30 sec., $i = 0.2 \times 10^{-7}$ amps.



200X

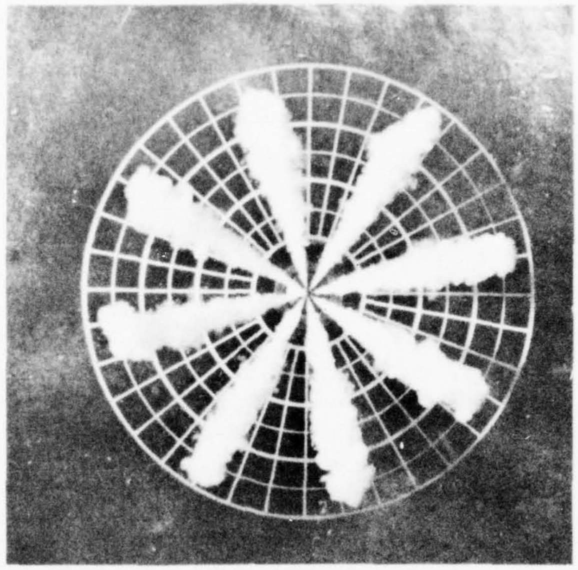


180X

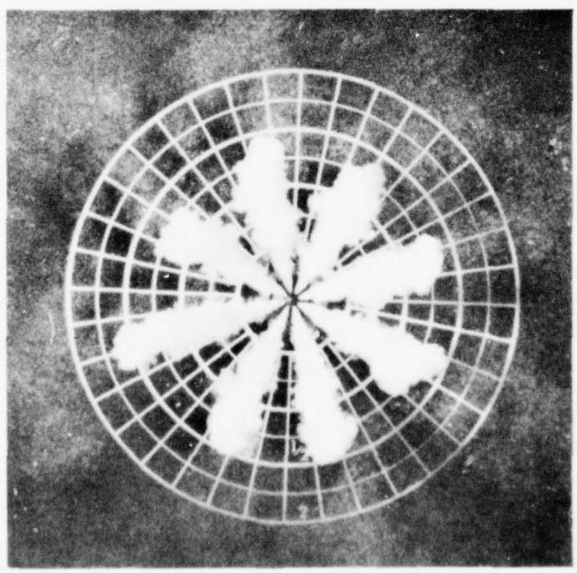
FIGURE 12. AREAS OF SEM MICROPROBE EXAMINATION – FAILED INJECTOR TIP. Hole No. 1.

TABLE 6. COMPOSITION OF USED AVDS 1790-2C DIESEL ENGINE NOZZLES

	Tip Alloy Composition, wt %						
	C	Mn	Si	Cr	Ni	Mo	V
Alby Specification (AISI E 9317)	0.15-0.20	0.45-0.65	0.20-0.35	1.0-1.4	3.0-3.5	0.08-0.15	–
No. A Nozzle Used with BCM FSF by TCM	0.62	0.53	0.28	1.25	3.29	0.10	<0.01
No. B Nozzle Used with BCM FSF by TCM	0.53	0.51	0.28	1.30	3.05	0.10	<0.01



(New)
7.5° After SOI
26.5° Duration
1200 RPM



(Used 145 hr with Diesel Fuel + BCM)
7.5° After SOI
21.5° Duration
1200 RPM

FIGURE 13. NEAT DIESEL FUEL SPRAY PATTERNS FOR NOZZLES FROM AVDS 1790-2C ENGINE

concentrations in the near-vicinity of the nozzle. These effects alone could result in poorer fuel-air mixing, diminished combustion efficiency, and substantially increased smoke emissions.

5. Overall Assessment

The conclusions drawn by the SwRI metallurgists on the basis of these observations are summarized as follows:

a. The failure of the piston ring was associated with no inherent plating defects.

b. Failure of the piston ring provided to AFLRL occurred by intergranular cracking of the chromium plating and subsequent loss of chips of the plating. The metallographic features of the cracking are compatible with failure due to inadequate lubrication, but the possibility of stress-corrosion cracking due to a contaminant cannot be discounted.

c. Significant amounts of chlorine were present in the dark zones on the injector pump plunger and injector pintle and in the deposits present in the injector tip holes (see Tables 4 and 5).

d. The mechanism of enlargement of the injector tip holes was not definitely identified, but it is most likely that the metal loss occurred as the result of corrosion rather than by erosion, possibly during engine shut-down periods.

e. The dark band on the injector pump plunger definitely resulted from corrosive attack.

B. Plan for Correction of Hardware-Fuel Incompatibility

The flow chart presented in Figure 14 was developed to place the various aspects of the AVDS 1790-2C hardware-fuel incompatibility problem in proper perspective. For the MERADCOM/AFLRL corrective action program, tasks 5-9 and 11-12 were selected for investigation (where the numbers correspond to those shown in Figure 14 under "Task No.").*

C. Corrosion/Lubricity Studies

Because of the identified role of corrosion in the failure of the AVDS 1790-2C engine endurance test, an accelerated corrosion test was developed to facilitate screening of corrosion inhibitors and alloys. This was in agreement with one of the recommendations made by the Army Scientific Advisory Panel Ad Hoc Group on Fire-Safe Fuels.[3] This laboratory test procedure utilized the glassware specified for ASTM D943, an oxidation test for

*Task No. 4 was not selected because it was learned that the AVDS 1790-2C nozzle vendor conducts proof-tests of nozzles at twice the maximum rated flow rate without seeing evidence of corrosion. This is hydrodynamically equivalent to doubling the fuel density; hence, erosion should not be expected because of the more dense fuel.

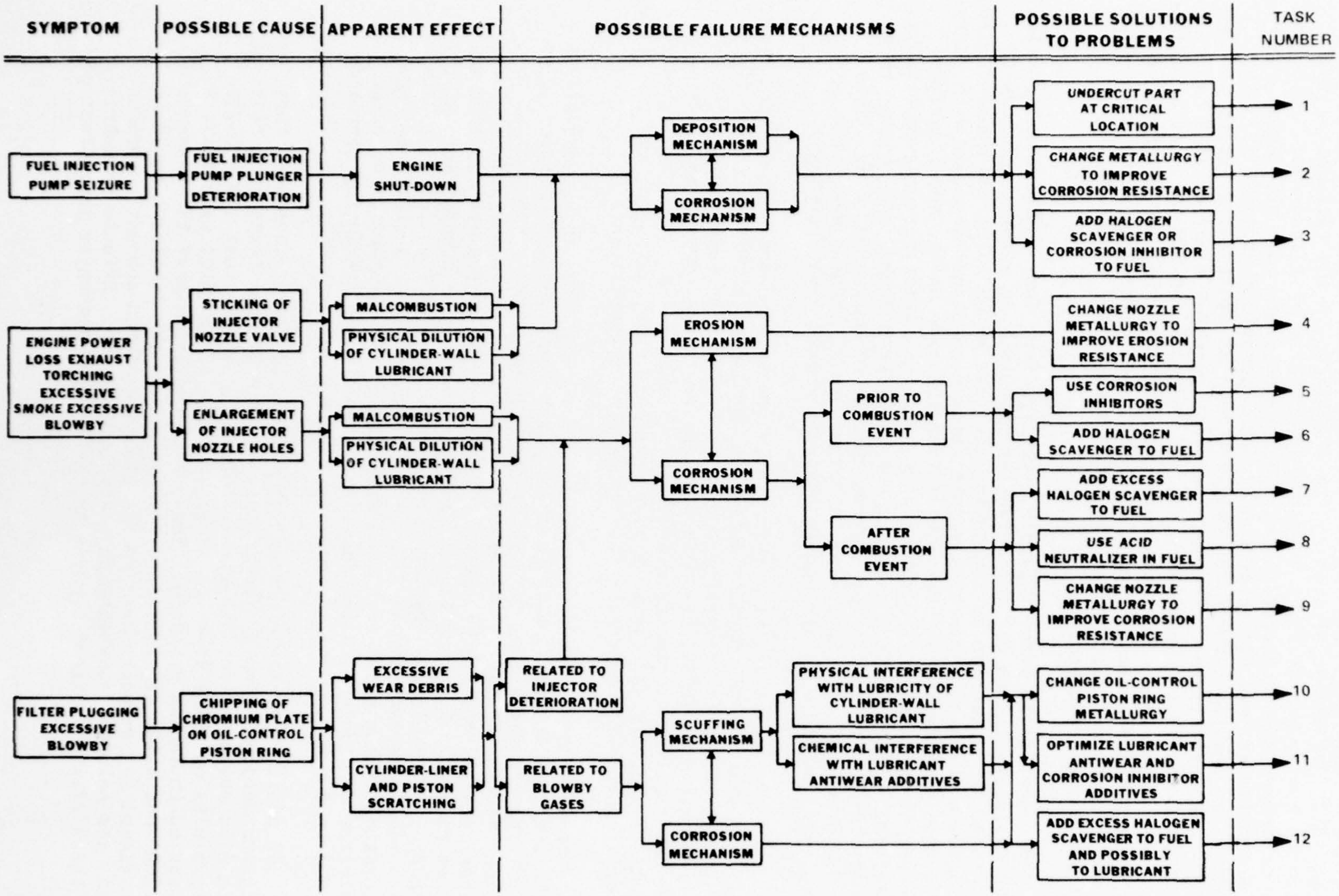


FIGURE 14. PLAN FOR CORRECTION OF HARDWARE–FUEL INCOMPATIBILITY AVDS 1790-2C/BCM FSF

turbine oils, but the procedure was modified to emphasize corrosion conditions. A 300 ml sample of fuel or oil was placed in the test cell which contained a nitrogen delivery tube and was covered by a condenser. The test coupon washers were attached to the nitrogen delivery tube with nylon string. The assembly then was placed in an oil bath controlled at 135°C (275°F). Nitrogen was bubbled through the delivery tube at about 3-1/2 liters per hour to keep the fuel stirred. The test was continued for a period of 5 hours, after which the test coupons were removed and examined for evidence of corrosion. The above test conditions were developed by trial and error until differences between diesel fuel and BCM "fire-safe fuel" could be observed. For more pronounced distinction, 50 ppm HCl was added to the fuel or oil that was being evaluated.

Four test cells were available, enabling four fuel and/or metal samples to be evaluated in one day for corrosion effects. An attempt was made to quantitate the corrosive action during the test by weighing the coupons before and after each test. Normally, weight gains were observed (along with corrosion) resulting from the formation of iron chloride on the metal surface; however, these very small weight changes were not quantitatively repeatable. Therefore, weighing of the test coupons was discontinued, and results were reported as "no corrosion" or various degrees of corrosion, i.e., light, medium, or heavy corrosion. In some cases, only staining was observed which, upon exposure to air, could become a rusted area overnight.

Extensive screening with this procedure revealed that many substances, including conventional fuel or lubricant corrosion inhibitors (Table 7), were ineffective for preventing corrosion by BCM FSF containing traces of hydrochloric acid (HCl). Results of these tests are summarized in Table 8. Although the list of candidate inhibitors shown in Table 7 does not indicate it, many suppliers and users of such materials were canvassed, and the listed materials generally represent "best-choice" recommendations.

One class of compounds, namely epoxides, was found to be generally effective as HCl corrosion inhibitors. Such compounds are believed to be so effective because they form chlorohydrins and thereby consume HCl without forming a salt. An inhibitor candidate from another class of compounds referred to as substituted imidazolines, appeared promising at low concentrations. However, it was found that at higher concentrations, this compound (Amine-O) promoted corrosion even when no HCl was added to BCM FSF. (This observation was also encountered in the ER-3 single-cylinder laboratory engine tests discussed elsewhere in this report.) No other inhibitor candidates studied showed any promise for preventing corrosion by HCl in BCM FSF.

In addition to the aforementioned corrosion test procedure, fuel, new oil, and used oil samples from Cummins engine 80-hour tests (not filtered) were also evaluated for "lubricity" using the 4-ball test (ASTM D-2266). The results of these steel-on-steel (E-52100 grade 25EP) wear tests are presented in Tables 9 and 10. These data indicated that the presence of cyclohexene oxide or epoxidized soybean oil in the lubricant could be beneficial for reducing wear in the presence of BCM combustion products until its halogen scavenging capacity is depleted. Effects on lubricity of the additive designed for use as the halogen-scavenger ingredient of

TABLE 7. ADDITIVES SCREENED IN BCM FSF CORROSION STUDY

1.	High MW substituted imidazoline.
2.	High MW substituted imidazoline.
3.	3(2-xenoxy) 1,2 expoxy propane (3-2X).
4.	Amino surface-active agent.
5.	Epoxidized soybean oil from three suppliers.
6.	Epoxidized linseed oil.
7.	Cyclohexene oxide.
8.	Propylene oxide.
9.	Approved corrosion inhibitor MIL-I-25017.
10.	Approved corrosion inhibitor MIL-I-25017.
11.	Tributyl amine.
12.	Ethylene diamine.
13.	Approved corrosion inhibitor MIL-I-25017.
14.	Approved corrosion inhibitor MIL-I-25017.
15.	Epoxide type.
16.	A zonc-salicylate-base-inhibitor for MIL-L-21260B preservative oil.
17.	MIL-L-21260B preservative oil.
18.	Benzotriazole.

TABLE 8. PARTIAL SUMMARY OF RESULTS OF AFLRL ACCELERATED CORROSION TESTS OF ALLOYS[a] AND CANDIDATE CORROSION INHIBITORS

- Alloys A, B, 1, 2, 3, 4, and 5 are not affected by 5% BCM FSF or by engine lubricating oil (Texaco Ursa LA-3, SAE-30) containing 5% BCM.
- Alloys A, B, 2, 3, 4, and 5 are attacked by 5% BCM FSF containing 50, 100, or 200 ppm HCl.
- Alloy 1 shows no-to-slight attack by 5% BCM FSF containing 50 or 100 ppm HCl.
- Alloys A and B are protected from attack by 50 ppm HCl in 5% BCM FSF containing 0.1% and 0.3% Amine-O but are vulnerable to attack in 5% BCM FSF containing 0.5% Amine-O and 0 to 200 ppm HCl.
- Alloys 2 and 3 (1, 4, and 5 not tested) are protected from attack by 50 ppm HCl in 5% BCM FSF containing 1% Amine-O.
- Alloys A and B are not protected from attack by 50 ppm HCl in 5% BCM FSF containing 0.3% tributylamine, and copious quantities of black, water-soluble deposits are formed.
- Alloys A, B, 1, 2, 3, 4, and 5 are protected from attack by up to at least 400 ppm HCl in 5% BCM FSF containing 1% cyclohexene oxide (up to at least 50 ppm HCl in 5% BCM FSF containing 0.1% cyclohexene oxide).
- Alloys A and B are not protected from attack by 50 ppm HCl in 5% BCM FSF containing the following commercially-available corrosion inhibitors at a concentration of 0.5%.
    - TOLAD 245
    - TOLAD 246
    - UNICOR J
    - HITEC E-515
    - HITEC E-580
    - L-1161
- Alloys A and B are not protected from attack by 50 ppm HCl in 5% BCM FSF saturated with benzotriazole (this compound is essentially insoluble in BCM FSF).
- Alloys A and B are attacked by 50 ppm HCl in 5% BCM in lubricating oil.
- Alloys A and B are protected from attack by 50 ppm HCl in 5% BCM in lubricating oil containing 2% cyclohexene oxide.

[a]Alloy Code	Alloy
A	M-2 Steel
B	52100 Steel
1	Hastelloy X
2	Hastelloy No. C-276
3	Haynes No. 25
4	Haynes No. 188
5	Haynes No. 6B

TABLE 9. PARTIAL SUMMARY OF RESULTS OF
4-BALL WEAR TESTS
(ASTM D-2266)

Sample No.	Sample (Unfiltered)	Total Acid No., mg KOH/g	Scar Diameter, mm
1	New Oil[a]	1.8	0.45
2	New Oil + 50 ppm HCl	2.2	0.45
3	New Oil + 0.5% CHO	1.4	0.43
4	New Oil + 0.5% Amine-O	1.0	0.42
5	Cummins No. 1 Drain Oil	13.7	0.84
6	Cummins No. 2 Drain Oil	16.4	0.94
7	Cummins No. 2 Drain Oil +50 ppm HCl	17.4	0.87
8	Cummins No. 2 Drain Oil +2.0% Molyvan	18.2	0.92
9	Cummins No. 2 Drain Oil + 0.5% CHO	13.0	0.76
10	Cummins No. 2 Drain Oil + 2.0% CHO	8.9	0.67
11	Cummins No. 2 Drain Oil + 0.5% Amine-O	15.4	0.93
12	Cummins No. 3 Drain	16.5	0.91
13	Cummins No. 3 Drain + 2% CHO	–	0.74
14	MIL-L-21260B (Preservative Oil)	–	0.51
15	MIL-L-21260B (Preservative Oil) + 100 ppm HCl	–	0.52
16	Cummins No. 3 Drain + 2.5% Lubrizol 1161	15.3	0.76
17	Cummins No. 3 Drain + 5% Lubrizol 1161	15.5	0.88

[a]MIL-L-2104C SAE 30.

TABLE 10. SUMMARY OF EPOXIDIZED SOYBEAN OIL 4-BALL WEAR TESTS (ASTM D-2266)

Sample No.	Fluid	Viscosity	Scar Diameter (mm)
New Oil			
1[a]	New Oil[b]	133	0.46
2[a]	New Oil + 5% PX-800 (ESO)[c]	132	0.37
3[a]	New Oil + 5% PX-800 (ESO) + 50 ppm HCl	133	0.38
4[a]	New Oil + 5% PX-800 (ESO) + 100 ppm HCl	133	0.37
Used Oil			
		Total Acid Number mg KOH/g	Scar Diameter, mm
5	Cummins No. 3 Drain	16.5	0.91
6	Cummins No. 3 Drain + 5% PX-800 (ESO)	9.8	0.62
7	Cummins No. 3 Drain + 5% Kronox-S (ESO)	9.6	0.65

[a]Samples 1-4 run in corrosion rig at 135°C (275°F) for 5 hours prior to viscosity and lubricity tests.
[b]MIL-L-2104C, SAE 30.
[c]Epoxidized soybean oil (ESO).

MIL-L-21260B "operational-preservative" lubricant were evaluated (as were those of the preservative oil itself). These conventional corrosion inhibitor fluids did not significantly influence the wear scar. Although it is recognized that the wear scar cannot be related directly to observed wear in an engine, it was felt that the test might satisfactorily indicate trends.

Table 10 shows the effect of epoxidized soybean oil (ESO). Such substances are used commercially as halogen scavengers in plastic manufacturing processes. The upper portion of the table shows the results obtained when ESO is added to a new crankcase lubricant. These particular samples had been previously subjected to the AFLRL accelerated corrosion test (i.e., heated at 135°C (275°F) for 5 hours) to determine whether they would cause corrosion or produce deleterious lubricant effects, such as an increase in viscosity or increase in wear. The results show no change in viscosity and some slight increase in lubricity. It should be noted that ESO reduced the acid number of the used oil and significantly reduced the wear observed in the 4-ball test with the used oil.

D. Engine Performance/Compatibility Investigation

A series of engine tests was conducted to evaluate the "fixes" that were developed for the problem areas that surfaced during the AVDS 1790-2C engine endurance test. However, prior to these performance tests, a brief test was conducted to measure the halogen-containing constituents of the exhaust from a multi-cylinder engine, and these results are presented in Table 11. The test procedure and analytical techniques are discussed more completely in subsequent sections.

1. Cummins V6-155 Engine Exhaust Emission Test on 5% BCM "Fire-Safe Fuel"

A Cummins V6-155 diesel engine, procured in 1972 for use in an evaluation of diesel fuel containing dibromomethane, was selected as the initial engine to be used in the diesel fuel/bromochloromethane exhaust gas analysis project. The engine was disassembled, inspected for signs of corrosion which may have taken place during storage (4 years), and all critical parts were cleaned. New rings and injectors were installed, the valves cleaned and reseated, a pressure pickup was installed in one cylinder, and the engine reassembled. Since the engine was to be operated at a remote site, a skid-mounted package containing an engine radiator, the V6-155, and a power-absorbing water-brake dynamometer was assembled (Figure 15). A control console and associated hardware permitting temperature, pressure, load-control, and oscilloscope (combustion pressure traces) data to be recorded and monitored, was assembled.

Engine power curves were developed for comparison with the manufacturer's data with no major problems being encountered. The analysis of the exhaust for Br_2 and Cl_2 from diesel fuel containing bromochloromethane was accomplished using bubbler solutions containing carbon tetrachloride. Thirty liters of exhaust gas were bubbled through the solution and aqueous potassium iodide was added to an aliquot. If a purple color appeared in the lower carbon tetrachloride layer, then free chlorine, free bromine, or

TABLE 11. BCM FSF EXHAUST EMISSION TEST
WITH V6-155 CUMMINS ENGINE

Fuel	Engine Load, lb	Engine Speed, rpm	Exhaust Gas Composition, ppm			
			Cl_2	Br_2	HCl	HBr
BCM FSF	5	300	7	None	70	None
BCM FSF + 0.5% cyclohexene oxide	4	788	3	None	79	None
BCM FSF	120	2000	3	None	116	None
BCM FSF	120	2000	3	None	95	None
BCM FSF	149	2400	None	None	214	None
BCM FSF	112	2400	–	None	158	None
BCM FSF	135	2800	–	None	652	None
BCM FSF + 0.5% cyclohexene oxide	138	2800	6	None	a	None
BCM FSF	100	2800	–	None	337	None

[a]Engine exhaust system not thermally equilibrated.

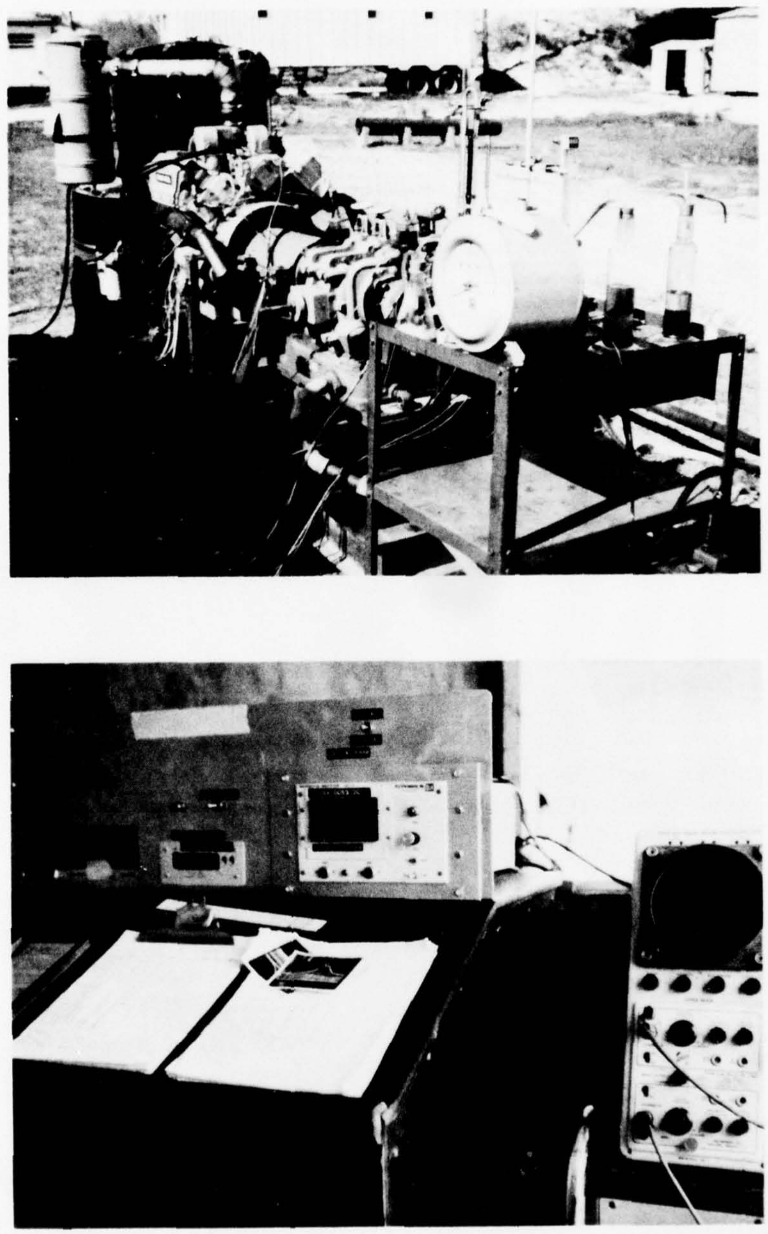


FIGURE 15. PHOTOGRAPHS OF PORTABLE LABORATORY TEST STAND AND CONTROL CONSOLE FOR CUMMINS V6-155 ENGINE AT REMOTE SITE

both, were present. To determine which halogens were present, the potassium iodide solution was analyzed by X-ray fluorescence spectrophotometry (XRF). Standards of potassium chloride and potassium bromide in aqueous potassium iodide were prepared for quantitative results.

The analysis for hydrogen chloride and hydrogen bromide was accomplished using a dual (in series) bubbler system. The first was a bubbler, containing carbon tetrachloride which was used to trap any organic halogens or any free halogens present. The second was a bubbler containing 0.1 N NaOH with a phenolphthalien indicator. A total volume of 30 liters was bubbled through the solutions. After sampling, all of the lines to the 0.1 N NaOH bubbler were rinsed into the bubbler solution to catch any acids remaining in these lines. The NaOH solution was then analyzed by X-Ray fluorescence. Standards of sodium chloride and potassium bromide in 0.1 N NaOH were also prepared.

The organic halogens were sampled with adsorption tubes provided by Dow Chemical Co. These samples were taken further down the exhaust line to get a cooler sample. A total of 2 liters of exhaust gas was pulled through each tube. There was one sample tube for each organic halogen sampling. Organic halogens, collected in these tubes, were measured by Dow Chemical Co. Incidentally, samples of the exhaust gas generated when the engine was operated on fuel containing BCM and cyclohexene oxide also were shown to contain no harmful chemical species that were not found when fuel and BCM alone were used.

The results provided by Dow Chemical Co. did not differ substantially from single-cylinder results previously observed by AFLRL. The new results are summarized as follows:

> No BR_2 or HBr was detected, but traces of Cl_2 were present in some of the gas samples (<10 ppm). Significant traces of brominated organics were also present in all of the samples (<10 ppm). These compounds included unburned BCM, dibromomethane, brominated aromatics, and brominated light hydrocarbons.

Selected properties of the base fuel, base fuel plus 5% (liq. vol.) BCM (BCM FSF), and BCM FSF plus 0.3% (wt) cyclohexene oxide are presented in Table 12.

2. Cummins V6-155 Engine BCM FSF Compatibility Tests

A series of four engine tests was conducted, three of 80 hours duration and one of 114 hours duration. The mechanical effects observed after each of these tests are summarized in Table 13. Effects of each of these tests on the lubricants are summarized in Table 14.

a. Eighty-Hour Cummins Test No. 1 with BCM FSF

Following the previously-described exhaust emissions tests, the Cummins V6-155 diesel engine was disassembled, inspected for deposits

TABLE 12. TYPICAL ANALYSES OF FSF BASE FUEL AND SELECTED PROPERTIES OF BASE FUEL, BCM FSF, AND BCM FSF PLUS 0.3% CHO

Fluid Property	Value
Base Fuel Gravity, °API (g/ml)	37.3 (0.84)
Base Fuel Distillation, %:	
IBP, °C (°F)	177 (350)
10	223 (434)
50	251 (483)
80	286 (547)
95	341 (646)
EP	360 (680)
Sulfur, wt %	0.04
Viscosity at °C (100°F), cSt	3.4
Flash Point, °C (°F)	62 (144)

Fuel	Total Acid No.	Density at 15°C (gm/ml)
Base Fuel (DF-2)	0.02	0.860
BCM FSF	0.01	0.908
BCM FSF plus 0.3% (wt) cyclohexene oxide	0.03	—

TABLE 13. SUMMARY OF MECHANICAL EFFECTS OF BCM FSF COMPATIBILITY TESTS WITH CUMMINS V6-155 DIESEL ENGINE

	80-Hour, Cummins No. 1 (BCM FSF)	80-Hour, Cummins No. 2 (BCM FSF plus 0.5% Cyclohexene Oxide)	80-Hour, Cummins No. 3 (BCM FSF plus 1% Cyclohexene Oxide)	114-Hour, Cummins No. 4 (BCM FSF plus 1.5% Cyclohexene Oxide)
Piston Condition After Test:				
Crown and Fire Land	Partial replica of irregular spray pattern on piston crown	Partial replica of uniform spray pattern on piston crown	Partial replica of uniform spray pattern on piston crown	Partial replica of uniform spray pattern on piston crown
Skirt	Clean	Very black	Tarnished	Tarnished
Top Piston Ring:				
Original End Gap, μm (in.)	500 (0.020)[a]	750 (0.030)[a]	~750 (~0.030)[a]	~650 (~0.025)[a]
End Gap Increase, %	60[a]	100[a]	~100[a]	~250
Chromium Plating	No distress	Worn through completely on 2 rings (partially on others)	Worn through completely on 2 rings (partially on others)	Worn through completely on 6 rings
Oil Control Piston Ring:				
End Gap Increase, %	Not measured	Not measured	Not measured	~220
Chromium Plating	No distress	No distress	No distress	No distress
Cylinder Liner Condition:				
Before Test	Like new	Honed because of previously-developed wear step	New	New
After Test	~100 μm (0.004 in.) wear step developed at top-ring top dead center	~75 μm (0.003 in.) wear step developed at top-ring top dead center	~100 μm (0.004 in.) wear step developed at top-ring, dead center	~100 μm (0.004 in.) wear step developed at top-ring dead center
Fuel Injector Condition After Test:				
Pintle	Like new	Light deposition on upper end	Light deposition on upper end	Light deposition on upper end
Nozzle Tip Holes	Hole enlargement ranged from none to about 400%	A few holes enlarged about 80% at exit only; others appeared unchanged	A few holes enlarged about 50% at exit only; some appeared unchanged	A few holes enlarged about 50% at exit only; some appeared unchanged
Engine Condition Below Ring Belt	Rust-like color	Very black	Slightly black	Slightly black
Max. Power Loss, %	11	2	2	5

[a]In worn cylinder at top-ring top-dead-center position.

TABLE 14. SUMMARY OF LUBRICANT EFFECTS DURING BCM FSF COMPATIBILITY TESTS WITH CUMMINS V6-155 DIESEL ENGINE

Property	Original Oil	Cummins No. 1 BCM FSF		Cummins No. 2 BCM FSF to .5% Cyclohexane Oxide		Cummins No. 3 BCM FSF + 1% Cyclohexane Oxide	Cummins No. 4 BCM FSF + 1.5% Cyclohexane Oxide	
		40 Hr	76 Hr	76 Hr	76 Hr	80 Hr	50 Hr	114 Hr
Metals, %								
Ca	0.37	0.31	0.28	0.26	—	0.26	—	0.27
Cr	—	0.004	0.004	0.19	0.17	0.035	—	0.007
Fe	—	0.019	0.07	0.23	0.20	0.197	—	0.157
Cu	—	0	0.007	0.06	0.06	0.051	—	0.10
Zn	0.10	0.08	0.07	0.06	—	0.06	—	0.07
Ba	0.06	0.05	0.05	0.06	—	0.05	—	0.05
Pb	—	—	—	0.014	—	0	—	0
Nonmetals, %								
S	0.58	—	—	9.43	—	0.46	—	0.38
Cl	0.017	0.15	0.15	0.16	—	0.14	—	0.17
Br	0	0.80	1.04	1.37	—	1.5	—	1.4
Total Acid No., mg KOH/g	1.83	10.1	13.7	16.6	—	16.4	14.6	13.6
Total Base No., mg KOH/g	12.5	4.4	3.3	4.1	—	3.6	2.8	2.8
Acid Content, meq/l	—	—	0.08	—	—	—	—	—
Viscosity, cSt								
38°C (100°F)	131.1	138.4	153.0	210.8	—	212.53	117.9	175.4
100°C (212°F)	12.7	13.3	15.4	21.0	—	21.22	18.1	16.8
Pentane Insolubles, wt % with coagulant	—	4.01	7.3	8.8	—	6.5	5.9	6.2
Benzene Insolubles, wt % with coagulant	—	1.4	3.6	3.0	—	1.0	0.8	1.0
Fuel Content of Used Oil, %	—	—	<0.5	—	—	—	—	—

[a]MIL-L-2104C, SAE 30.

and corrosion, the cylinders were honed, new piston rings were installed, all valves were reseated, and the engine reassembled. The injectors that were installed were inspected for evidence of enlargement of the injection holes since they had been briefly used in the previously reported BCM exhaust emissions test. They were found to show no enlargement and appeared in satisfactory condition for addititional service. After installation on the previously-described portable dynamometer test stand, the engine was run under varying load conditions to assure performance acceptable to the manufacturer's new equipment requirements.

Following this checkout and a break-in run, the first in the series of tests was conducted at a remote site using BCM FSF. The test cycle consisted of 8 hours running at 3/4 load - 2400 rpm, followed by an overnight (16-hour) shutdown. This cycle was performed five working days with a 48-hour shutdown on weekends. Each evening before shutdown, a full-power check was made to determine if performance deterioration had occurred.

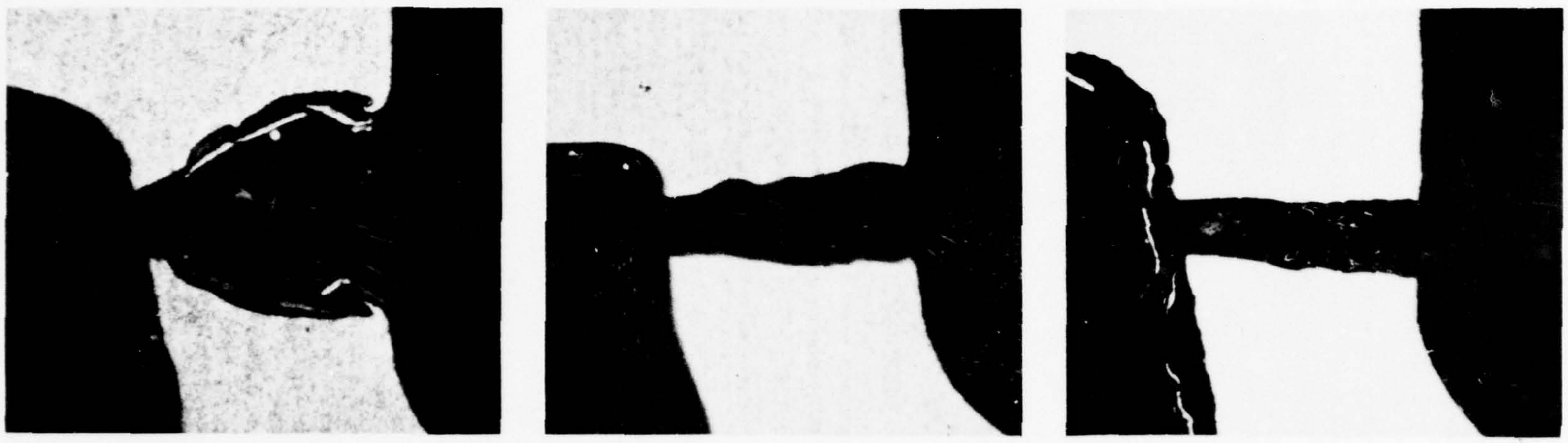
The initial 80-hour endurance test was completed in this engine using BCM FSF and a MIL-L-2104C engine lubricant. The engine was disassembled and inspected, with the following distress noted: (1) significant injector tip orifice hole enlargement, which was random in specific hole location, (2) excessive cylinder bore wear, as evidenced by the wear step at top-dead center, and (3) significant piston ring end-gap change (0.010-0.012 inch) as measured in the cylinder bore--suggesting high liner/ring wear. There was no visible distress of the chromium-plated ring faces. The maximum power that could be developed by the engine decreased more than 10% during the 80-hour test. Conversely, the fuel consumption rate at the constant operating load increased more than 10% during the test.

Some of the seven holes in each injector nozzle tip exhibited diameter increases of about 400%. Sectioned specimens (typified by that shown in Figure 16a) indicated no change in the hole-inlet diameter for a typical enlarged hole (as appeared to have been the case with AVDS 1790-2C injector tips from the TCM test with BCM FSF). The cavity formed by the drastically enlarged injector hole-outlet appeared to be nearly hemispherical.

b. Eighty-Hour Cummins Test No. 2 with BCM Plus 0.5% Cyclohexene Oxide

A second run was completed in this engine with 0.5v% cyclohexene oxide added to the BCM FSF. Prior to this run, new piston rings were installed, all valves were reseated, and the cylinder liners were honed to eliminate the wear step that developed during the previous run. Because of this honing, the piston rings were looser than in the previous test; however, this rebuilt engine developed about 4% more power during break-in on neat fuel than it did in the previous test.

After the test, the engine was disassembled and inspected, with the following effects noted: (1) substantial reduction in injector tip hole enlargement, (2) increased cylinder liner wear, (3) increased piston ring end-gap change (approximately 0.030 inch), and (4) extreme blackening of all engine parts below the ring belt. The black color seemed to be caused by a thin layer of lacquer-like carbonaceous substance containing bromine and iron in



(a) 5% BCM FSF *(b) 5% BCM FSF + 0.5% CHO* *(c) 5% BCM FSF + 1.0% CHO*

FIGURE 16. SECTION THROUGH LARGEST HOLE IN V6-155 ENGINE FUEL INJECTOR NOZZLE AFTER 80 HOURS OPERATION

addition to other trace metals. It could be removed by rubbing with a pencil eraser.

There was visible wear on the chromium-plated piston ring faces (some rings had lost all of the chromium plating). The maximum power that could be developed by the engine decreased by less than about 4% during the 80-hour test. Conversely, the fuel consumption rate at the constant operating load increased less than 4% during the test.

One or two holes in each fuel injector nozzle tip exhibited diameter increases of about 70%; however, most of the hole sizes were essentially unchanged. Sectioned specimens (typified by that shown in Figure 16b) indicated no change in the hole-inlet diameter for a typical enlarged hole. The hole enlargement was greatest at the outlet, with a nearly straight smooth transition to the zero-enlargement at the inlet.

c. Eighty-Hour Cummins Test No. 3 with BCM FSF Plus 1.0% Cyclohexene Oxide:

A third 80-hour test was completed with a *new* Cummins V6-155 diesel engine using 1.0v% cyclohexene oxide (CHO) as the halogen scavenger in BCM FSF. Results are summarized in Tables 13-15. One piston was removed from each side of the new engine and inspected prior to the test in order to confirm the types (and condition) of piston rings used in the engine. The initial oil charge contained 2v% CHO; however, gas-chromatographic analyses revealed that the oil no longer contained CHO (or the CHO-HCl reaction product) after 8 hours of operation.

Oil samples were withdrawn daily and evaluated for wear metal content and acid buildup, and the results are presented in Tables 14 and 15.

Following this engine test, the engine was disassembled and inspected, with the following effects noted: (1) further reduction in injector nozzle hole enlargement, (2) about the same amount of cylinder liner wear, (3) about the same top piston ring end-gap change, and (4) reduced blackening of engine parts below the ring belt, all relative to the previous run with 0.5% CHO.

There was visible wear on the chromium-plated piston ring faces (some rings had lost all of the chromium plating). The maximum power that could be developed by the engine decreased by less than about 2% during the 80-hour test. Conversely, the fuel consumption rate at the constant operating load increased less than 2% during the test.

Many of the fuel injector nozzle tip holes appeared to be about the same diameter as those in the original nozzle. One or two holes on each injector exhibited diameter increases of about 50%. Sectioned specimens (typified by that shown in Figure 16c) indicated no change in the hole-inlet diameter for a typical enlarged hole. As in the preceding test, the enlargement was greatest at the hole outlet, but with a nearly straight transition to zero-enlargement at the hole outlet.

TABLE 15. SUMMARY OF ANALYSES OF USED OIL FROM CUMMINS V6-155 ENGINE OPERATING ON BCM FSF CONTAINING 1.0% CYCLOHEXENE OXIDE

Operating Hours	Wear Metals, %			Total Acid Number, mg KOH/g	Total Base Number, mg KOH/g
	Fe	Cr	Cu		
0[a]	0	0	0	1.83	12.50
8	0.003	0	0	4.24	10.65
16	0.010	0	0	5.34	8.78
24	0.022	0.007	0	7.05	6.91
32	0.022	0.008	0	7.55	5.04
40	0.035	0.015	0	9.58	3.18
48	0.052	0.022	0	10.69	3.18
56	0.081	0.025	0	12.23	3.03
64	0.117	0.030	0.007	14.46	3.31
72	0.130	0.029	0.014	14.56	4.15
80	0.197	0.035	0.051	16.40	3.55

[a]MIL-L-2104C, SAE 30.

d. Cummins Endurance Test with BCM FSF Plus 1.5% Cyclohexene Oxide:

A fourth test was completed with a *new* Cummins V6-155 diesel engine using 1.5v% cyclohexene oxide (CHO) in the BCM FSF. This test was intended to be an endurance test terminating at the end of 400 hours of service. The 1.5% CHO concentration was chosen because of the progressively decreasing hole enlargement observed with 0, 0.5, and 1.0% CHO (Figure 16). Unfortunately, at the end of 114 hours the engine began to lose oil pressure and the power output dropped off, thus the test was terminated. Subsequent inspection of the disassembled engine parts revealed the cause for the oil pressure decrease was probably the excessive in-service wear of most bearing surfaces in the engine. Inspection of the injector holes showed enlargement up to approximately 50% on a few holes but the majority were unchanged or only slightly altered. The enlargement occurred at the hole outlet and was similar to that observed in earlier inspections on previous engine tests.

Eight-hour oil samples were drawn daily from the engine and evaluated for wear metal content and acid build-up, and the results, summarized in Table 16, show that the wear metals were excessive and the acid number was extremely high, thus providing an environment conducive to excessive wear and/or corrosion, leading to probable catastrophic failure.

3. Single-Cylinder TARADCOM ER-3 Engine BCM FSF Compatibility Tests

A series of six 40- to 80-hour tests was conducted with the TARADCOM ER-3, single-cylinder, four-stroke cycle, diesel engine. The study was conducted to evaluate the effects on fuel injector nozzle tip hole enlargement and piston ring distress of using BCM FSF with and without halogen scavenger in the fuel and/or lubricant. The mechanical effects observed after these tests are summarized in Table 17, and the results of the lubricant analyses are detailed in Table 18. For each test in this series, the ER-3 engine was (a) rebuilt to include new bearings, a new cylinder sleeve, and a new piston/ring assembly, (b) installed on a laboratory dynamometer test bed, and (c) given a standard break-in using neat CAT 1-G/1-H reference fuel and the same MIL-L-2104C lubricant as that used in the multicylinder tests. Also, to prevent contamination of the laboratory and/or its exhaust dilution system when operating the engine on BCM FSF, a commercial exhaust scrubbing device, having a maximum gas flow capacity of 2.27 m^3/min (80 cfm), was inserted in the engine exhaust line. During the test series, this device required extensive modification to maintain its reliability and efficacy. The final version of the ER-3 exhaust system is illustrated in Figure 17.

Because of the vulnerability of the exhaust scrubber to high gas temperature and pressure, it was impossible, when selecting the constant operating conditions for the two TARADCOM ER-3 tests, to duplicate or even simulate, those of either the AVDS 1790-2C or Cummins V6-155 engine tests on BCM FSF. Thus, in order to meet the scrubber requirements and yet provide a reasonable fuel input rate and low smoke, the nominal operating conditions selected for both of the TARADCOM ER-3 tests were: speed, 2200 rpm; fuel rate, 4.3 kg/h (9.5 lb/h); jacket temperature, 85°C (185°F); sump oil

TABLE 16. SUMMARY OF ANALYSIS OF USED OIL FROM CUMMINS V6-155 ENGINE OPERATING ON BCM FSF CONTAINING 1.5% CYCLO-HEXENE OXIDE

Operating Hours	Wear Metals, %			Total Acid Number, mg KOH/g
	Fe	Cr	Cu	
8[a]	0.006	–	–	4.42
16[a]	0.006	–	–	5.44
31[a]	0.005	–	–	–
36	0.007	–	–	–
46	0.012	–	0.006	7.19
55	0.026	–	0.018	9.03
63	0.048	0.0095	0.008	10.41
69	0.088	0.059	0.011	11.98
77	0.131	0.123	0.016	13.40
84[a]	0.055	0.047	0.015	–
92	0.055	0.020	0.008	8.44
100	0.079	0.044	0.006	10.96
108	0.12	0.088	0.006	14.46
114	0.157	0.10	0.007	13.6

[a]Indicates time of oil change.

TABLE 17. SUMMARY OF MECHANICAL EFFECTS OF BCM FSF COMPATIBILITY TESTS WITH TARADCOM ER-3 SINGLE-CYLINDER DIESEL ENGINE

	60-Hour TARADCOM No. 1 (BCM-FSF)	80-Hour TARADCOM No. 2 (BCM FSF Plus 0.5% Cyclohexene Oxide)	40-Hour TARADCOM No. 3 (BCM FSF Plus 0.5% Amine-O)	55-Hour TARADCOM No. 4 (BCM FSF Plus 1% Amine-O)	40-Hour TARADCOM No. 5 (BCM FSF)	80-Hour TARADCOM No. 6 BCM FSF Plus 0.5% CHO and Ref. Oil Plus 5% ESO
Piston Condition After Test:						
Crown and Fire Land	Heavy black deposits	Heavy black deposits	Heavy black deposits	Heavy black deposits	Heavy black deposits	Heavy black deposits
Skirt	Clean	Slight lacquer on one side	Clean	Clean	Clean	Varnish on both sides
Top Piston Ring:						
Original End Gap, μm (in.)	400 (0.016)[a]	560 (0.022)[a]	640 (0.025)[a]	560 (0.022)[a]	~560 (0.022)[a]	460 (0.018)[a]
End Gap Increase, %	88[a]	9[a]	28[a]	36[a]	9[a]	94[a]
Chromium Plating	Discolored (Possible light deposit)	Discolored (Possible light deposit)	Clean	Clean	Slight wear, no corrosion	Badly worn
Oil Control Piston Ring:						
Eng Gap Increase, %	3	3	0	4	0	9
Chromium Plating	No distress	No distress	No distress	No distress	No distress	No distress
Cylinder Liner Condition:						
Before Test	New	New	New	New	New	New
After Test						
Wear step at top-ring top dead center, μm (in.)	~150 (0.006)	~100 (0.004)	~145 (0.006)	~130 (0.005)	~100 (0.004)	~200 (0.008)
Fuel Injector Condition After Test:						
Pintle	Etched area on upper surface	Etched area on upper surface	Bright upper surface. Slight corrosion on lower stem. Lacquered tip.	Bright upper surface. Increased corrosion on lower stem. Clean tip.	Bright upper surface. Varnish-like deposit ring on lower stem just above needle tip. Clean tip.	(At 40 hours) stuck in tip body. Etched area on upper surface. Corrosion and tacky deposit on lower stem and needle tip.
Nozzle Tip Holes	Shallow craters around all holes. No ID changes. 30% less spray penetration.	Slight cratering at one hole. No ID changes. No significant difference in spray penetration from new condition.	Three holes like new. One hole had off-set crater possibly caused by a flaw in metal. Spray penetration ranged from 50 to 25 to 100% of normal	All holes like new. No significant difference in spray penetration from new condition.	All holes like new. Spray penetration from one hole about 95% of normal and from adjacent hole about 85%. Other two holes showed normal spray penetration.	All holes like new. Spray pattern test obviated by stuck pintle.
Engine Condition Below Ring Belt:	Clean	Clean	Clean	Clean	Clean	Clean
Max. Power Loss, %	30	27	26	22	37	42

[a]In calibrated gauge block.

TABLE 18. SUMMARY OF LUBRICANT EFFECTS DURING BCM FSF COMPATIBILITY TESTS WITH TARADCOM ER-3 SINGLE-CYLINDER DIESEL ENGINE

Property	Original Oil[a]	TARADCOM No. 1 BCM FSF		TARADCOM No. 2 BCM FSF + 0.5% Cyclohexene Oxide		TARADCOM No. 3 BCM FSF + 0.5% Amine-O	TARADCOM No. 4 BCM FSF + 1% Amine-O	TARADCOM No. 5 BCM FSF	TARADCOM No. 6 BCM FSF + 0.5% CHO + 5.0% ESO
		40 Hr	60 Hr	40 Hr	80 Hr	40 Hr	55 Hr	40 Hr	80 Hr
Metals, %									
Ca	0.37	—	—	0.4	0.4	0.34	0.25	0.39	0.23
Cr	—	0.0002	0.0003	<0.0001	0.0003	0	0	0	0
Fe	—	0.03	0.04	0.023	0.068	0.058	0.021	0.049	0.055
Cu	—	0.003	0.004	<0.0001	0.0002	0	0	0.002	0.005
Zn	0.10	—	—	0.09	0.09	0.09	0.09	0.10	0.06
Ba	0.06	—	—	0.05	0.04	0.03	0.046	0.03	0.02
Pb	—	—	—	<0.0001	<0.0001	0	0	0	0
Nonmetals, %									
S	0.58	—	—	—	—	—	0.57	0.58	0.16
Cl	0.017	—	0.16	0.18	0.23	0.16	0.11	0.18	0.067
Br	0	—	—	0.55	0.83	0.75	—	0.82	0.95
Total Acid No., mg KOH/g	1.83	6.9	8.5	6.3	8.3	8.0	5.3	8.0	6.5
Total Base No., mg KOH/g	12.5	7.3	5.2	8.7	6.0	6.7	8.8	6.7	4.1
Acid Content, meq/l	—	—	—	—	—	—	—	—	—
Viscosity, cSt									
38°C (100°F)	131.1	132.5	133.4	136.0	146.0	138.8	105.1	145.5	155.8
100°C (212°F)	12.7	12.9	13.1	13.1	13.8	13.4	11.3	13.8	14.2
Pentane Insolubles, wt % with coagulant	—	1.4	2.7	1.2	2.8	2.23	1.5	1.7	1.7
Benzene Insolubles, wt % with coagulant	—	0.9	1.1	0.8	1.3	1.0	0.6	1.2	0.9
Fuel Content of Used Oil, %	—	—	—	—	—	—	—	—	—

[a]MIL-L-2104C, SAE 30.

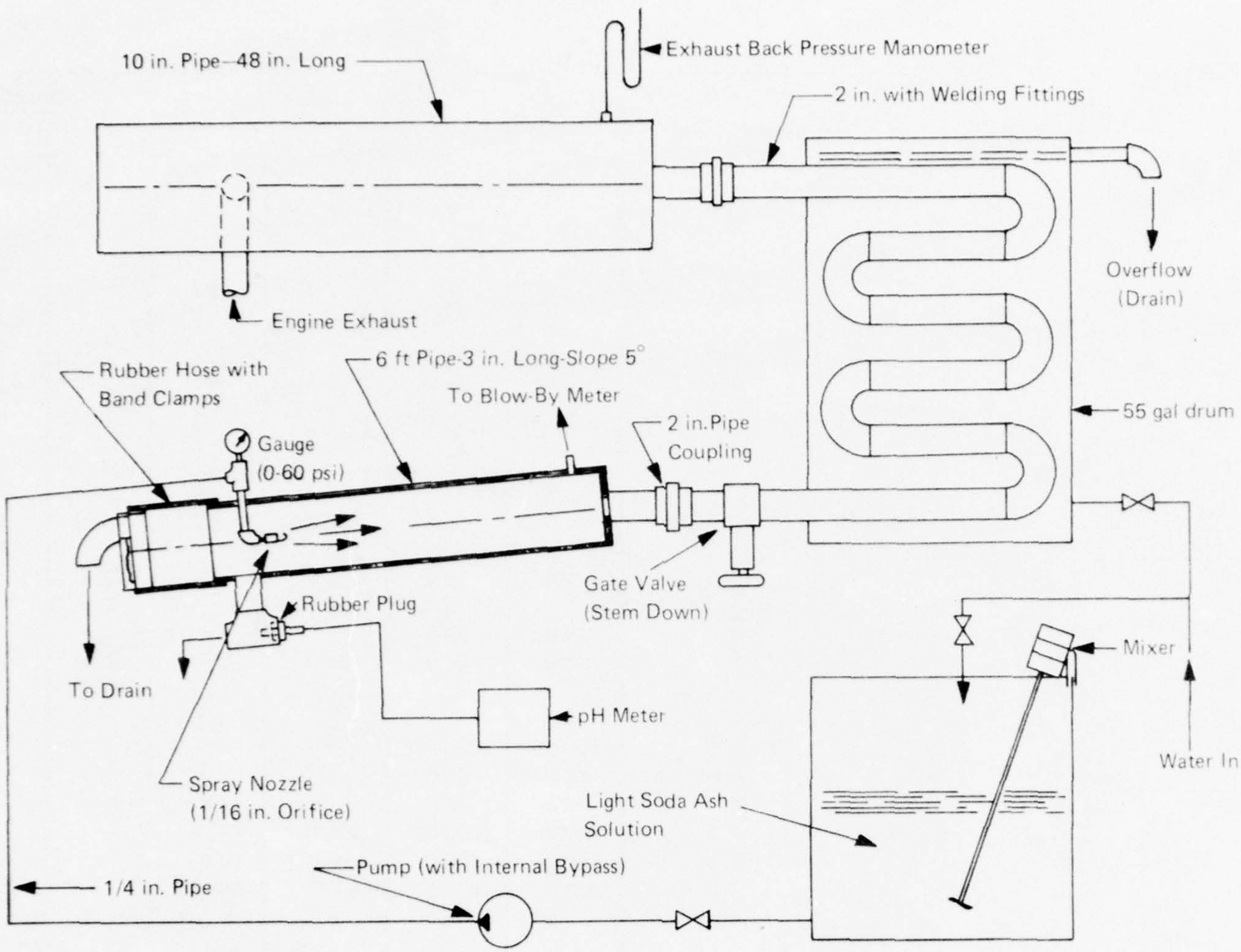


FIGURE 17. EXHAUST SYSTEM FOR TARADCOM ER-3 DIESEL ENGINE

temperature, 85°C (185°F); intake air temperature, 52°C (125°F); absolute intake air pressure, 3.1 kPa (80.0 in. Hg); and exhaust back pressure, minimum.

a. ER-3 Engine Tests No. 1 and No. 2:

The first test was conducted primarily to determine the effects of BCM FSF on injector tip hole enlargement and distress of the chromium plating on the top compression- and oil-control piston rings. The second test was similar to the first test, but with 0.5v% CHO added as a halogen scavenger.

Although the duration of each ER-3 test was scheduled for 80 hours, the first one, which involved the use of BCM FSF without CHO, was terminated at 60 hours due to the gradual development of a 30% power loss. Parts inspection after the first test showed the following:

Injector Tip - Most holes had shallow cratering at the exit, but the minimum ID's of all holes were the same as new. Spray pattern (liquid injection technique) showed about 30% less penetration from two holes than when new (Figure 18).

Injector Pintle - Evidence of presumed corrosion over a small area of the upper surface.

Top Piston Ring - 87.5% increase in end-gap and possible film deposit on chromed face.

Oil Control Ring - 3% increase in end-gap but no chromium distress.

Cylinder Liner - Bore wear over top ring travel ranged from 0.1422 mm (0.0056 in.) at top to 0.0559 mm (0.0022 in.) at bottom. Heavy black deposit covered entire area above top ring travel.

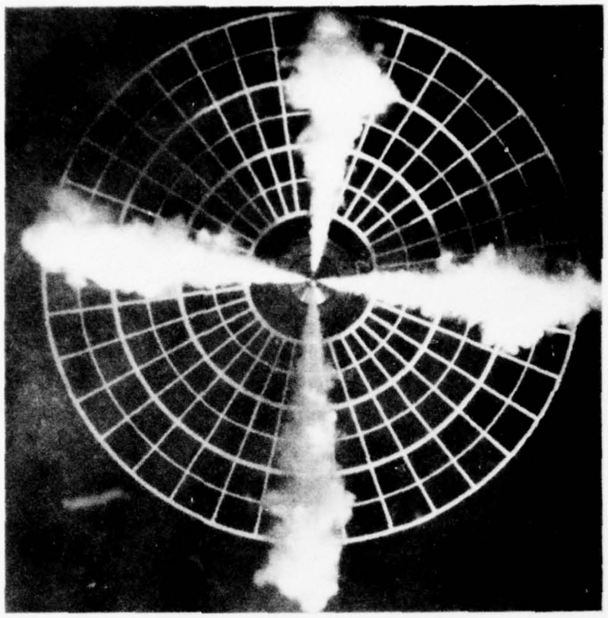
Piston - Heavy black deposit covered entire fire land, but skirt was clean.

Inspection of parts after the ER-3 80-hour test of BCM FSF containing CHO (test No. 2) revealed the following:

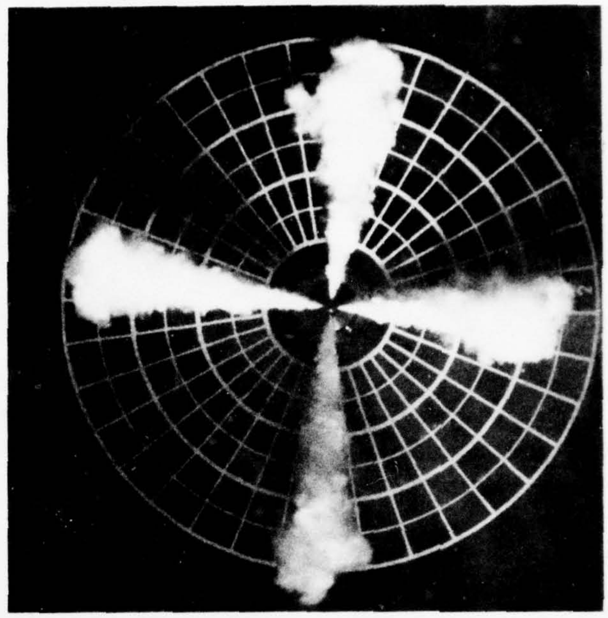
Injector Tip - Only one hole had slight cratering at the exit, but the minimum ID's of all holes were equal and as new. Spray pattern (liquid injection technique) showed no significant change in penetration (Figure 18).

Injector Pintle - Same distress as noted in test without CHO.

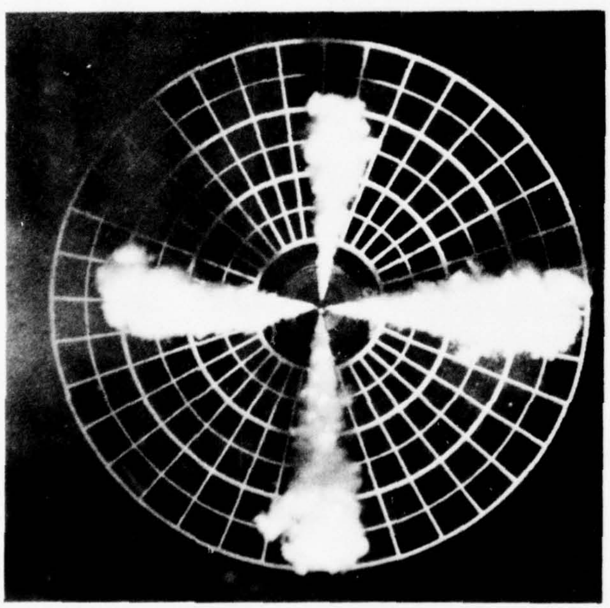
Top Piston Ring - 9% increase in end gap and possible film deposit on chromed face.



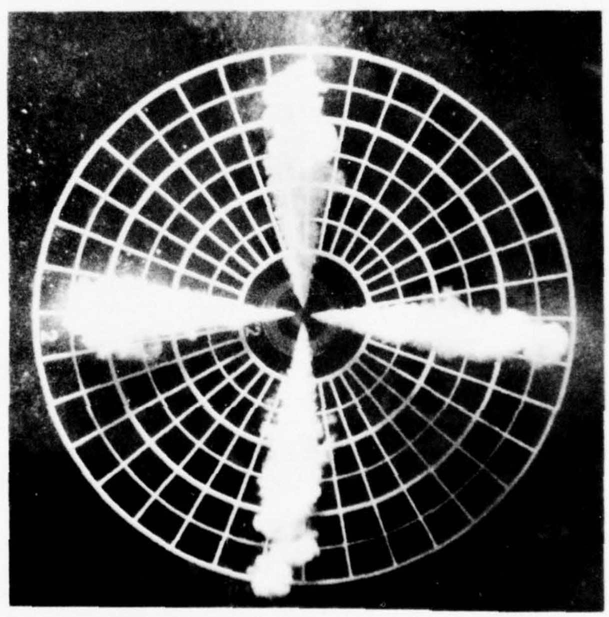
NEW NOZZLE



120 HOURS–BASE FUEL



60 HOURS–BCM FSF



80 HOURS–BCM FSF + CHO

FIGURE 18. SPRAY PATTERNS FOR A NEW NOZZLE AND NOZZLES USED WITH NEAT DF-2 PLUS BCM, AND DR-2 PLUS CHO

Oil Control Ring - 3% increase in end gap and no chromium distress.

Cylinder Liner - Bore wear over top ring travel ranged from 0.1067 mm (0.0042 in.) at top to 0.0127 mm (0.0005 in.) at bottom. Heavy black deposit covered entire area above top ring travel.

Piston - Heavy black deposit covered entire fire land, and antithrust side of skirt had some light lacquer (about 9.0-9.5 CRC merits).

Spray pattern tests (liquid technique) illustrated in Figure 18 indicated deteriorated spray distribution and penetration relative to those of a typical new injector after the first test (BCM FSF). The spray patterns obtained after the second test (BCM FSF plus 0.5% CHO) indicated that the spray distribution and penetration were almost equivalent to those of a typical new injector.

Based on the above data, it is evident that the addition of 0.5v% CHO to the BCM FSF reduced injector tip hole cratering, improved the final fuel spray pattern, and reduced cylinder and piston ring wear in the TARADCOM ER-3 engine when used under these test conditions.

b. ER-3 Engine Tests No. 3 and No. 4:

Tests No. 3 and No. 4 were conducted to investigate an alternate halogen-scavenger. Test No. 3 used BCM FSF containing 0.5v% Amine-O, a halogen scavenger representative of a class of heterocyclic amines referred to as substituted imidazolines. The primary objective of the test was to evaluate the anti-corrosion potential of the Amine-O with respect to the fuel injection nozzle tip and the chromium-plated top and oil control piston rings. Results are summarized in Tables 17 and 18.

Originally, the duration of this run was intended to be 80 hours; however, when periodic analyses (by XRF) of used oil samples indicated that the iron content had increased from zero to 580 ppm in 40 hours, the test was terminated at that point.

Post-test inspection of engine parts revealed the following for test No. 3:

Injector Tip - One hole had irregular, off-set cratering which may have been due to a flaw in the metal rather than to a fuel corrosion mechanism. The three other holes were not distressed at the exit, and the minimum ID's of all four holes were equal and the same as new. Spray pattern (liquid injection technique) showed penetration from distressed hole was about 25% less than normal and from each of the two adjacent holes about 50% of normal. Penetration from the fourth hole appeared normal.

Injector Pintle - No mechanical distress was evident, but the lower stem had slight corrosion. Also, the discharge tip had a dark lacquer-type deposit.

Top Piston Ring - 28% increase in end-gap, but no corrosion.

2nd Comp. Ring - 25% cold-stuck.

Oil Control Ring - No increase in end-gap and no corrosion.

Cylinder Liner - Bore wear over top ring travel ranged from 0.45 mm (0.006 in.) at top to 0.028 mm (0.001 in.) at bottom. Heavy black deposit covered entire area above top ring travel.

Piston - No mechanical distress, but heavy black deposit covered entire side area above third compression ring.

Since it was uncertain whether the cratering of the single hole of the injector tip in the 40-hour test with BCM FSF containing 0.5v% Amine-O was due to corrosion distress or to a manufacturing flaw (although the latter was strongly suspected), it was decided to conduct another ER-3 engine test with the BCM FSF, but this time with 1.0v% Amine-O instead of a 0.5v% added to the fuel. Again, the duration of test was scheduled for 80 hours.

From the outset, this evaluation of BCM FSF with the higher dosage of Amine-O was characterized by abnormal oil consumption and generally higher than usual blowby rates. For these reasons, which suggested high wear of the cylinder liner and/or piston rings, the test was terminated at 55 hours.

Post-test inspection of engine parts showed the following:

Injector Tip - No cratering or "bell-mouthing" of any of the four holes, the minimum inside diameters of which were equal and the same as when new. Spray pattern (liquid injection technique) was essentially uniform and normal with respect to penetration and plume intensity.

Injector Pintle - More corrosion on lower stem than with 0.5v% Amine-O, but no lacquering of discharge tip.

Top Piston Ring - 36% increase in end-gap, but no corrosion.

Oil Control Ring - 4% increase in end-gap, but no corrosion.

Cylinder Liner - Bore wear at T.D.C. position of top ring was 0.117 mm (0.005 in.). Heavy black deposit covered the entire area above top ring travel.

Piston - No mechanical distress, but heavy black deposit covered entire side area above third compression ring.

Further inspection of parts revealed that the valve stem-to-guide clearances were within allowable limits; however, it was observed that a groove in the crankshaft on the line of contact with the lip of the rear main seal had deepened significantly during the course of this series of BCM FSF evaluations. It was concluded, therefore, that the abnormally high oil consumption during the test with BCM plus 1.0v% Amine-O had been largely due to leakage caused by excessive crankshaft-seal groove enlargement.

c. <u>ER-3 Engine Tests No. 5 and No. 6:</u>

A repeat test involving the use of BCM FSF *without* the addition of halogen scavenger was conducted in the TARADCOM ER-3 single-cylinder diesel engine. This repeat test was intended to either verify or refute the results obtained in the initial ER-3 engine evaluation of this fuel. It may be recalled that the first run had been characterized by numerous and lengthy unscheduled shutdowns because of exhaust gas scrubber malfunctions, and it was felt that those interruptions might have affected the end results of that test. In view of the fact that the scrubber problems were subsequently resolved, a reevaluation of the straight BCM FSF under the same test conditions was considered necessary and appropriate.

The scheduled duration of this test, like that of each of the single-cylinder BCM FSF evaluations in this series, was 80 hours. However, at 20 hours the engine gradually began to lose power, so that by 40 hours the loss was about 37%. The test was terminated at that point because the engine speed (2200 rpm) could no longer be maintained due to the drag imposed by the cooling water in the wet gap of the dynamometer.

Since neither the blowby nor oil consumption rates had been excessive, it was suspected that a change, such as hole enlargement, had developed in the fuel nozzle tip to deleteriously alter the spray pattern and consequently reduce the power output of the engine. Thus, after stopping the engine, the nozzle tip was removed, soft-wiped to remove carbon, and visually inspected. The exit diameters of all holes appeared normal. Since the possibility remained that the tip had experienced *internal* distress, a tip having a known, normal spray pattern was substituted, and, the engine was restarted (while still warm) and brought up to test conditions. The resultant brake power was only 7% less than that obtained with the original tip at the start of the 40-hour test. Immediately after stopping the engine, the original nozzle tip was reinstalled and the engine was then brought up to the same test conditions again. This time, the brake power was about 18 percent less than that at the start of the 40-hour test. Despite the renewed ability to maintain speed by virtue of a reduction in brake power loss (i.e., from 37% to 18%), it was concluded that the flow characteristics of that tip *had* deteriorated since new and that continuation of the BCM FSF test would shortly result in further loss of power and speed.

Using the liquid injection technique, a photograph was then taken of the spray pattern of the fuel nozzle tip from the 40-hour BCM FSF test. This picture showed essentially equal plume intensity from all holes, but the spray penetration from one hole was about 85% of normal, about 95% of normal from an adjacent hole, and normal from the remaining two holes. Subsequently, the tip and pintle were examined under a microscope. This inspection revealed that the exit diameters of all tip holes and the surfaces of the pintle were as new. The nozzle tip was then sectioned on the longitudinal centerline of the hole that gave the least spray penetration, and photomicrographed. This detailed picture showed the hole was tapered to a slightly larger entrance diameter.

The ER-3 engine was disassembled for inspection of parts which showed the following:

Top Piston Ring - 9% increase in end-gap. Also, slight chrome face wear but no corrosion.

Oil Control Ring - No increase in end-gap and no chrome distress.

Cylinder Liner - Bore wear at top of ring travel was 0.0889 mm (0.0035 in.). Also, heavy black deposit covered entire area above top of ring travel.

Piston - Heavy black deposit covered entire side area above third compression ring; otherwise, the piston skirt was clean.

When the results of this 40-hour ER-3 evaluation of straight BCM FSF were compared to those of the initial 60-hour, interrupted test with the same fuel, the data from the current run differed in that,

a. The overall average brake horsepower output level was about 8% less,

b. No signs of injector tip hole cratering were evident, and the post-test spray pattern was more nearly normal from all holes,

c. No corrosion or other distress of the injector pintle was found, and

d. Cylinder and piston ring wear was less, but disproportionally so.

Following this second aborted run on straight BCM FSF, an 80-hour test (No. 6) was initiated in the ER-3 engine using BCM FSF containing 0.5v% cyclohexene oxide (CHO) and a MIL-L-2104C, SAE 30 lubricant containing 5.0v% epoxidized soybean oil (ESO). Addition of a material having a flash point of approximately 316°C (600°F) and reactive with HCl seemed to be a viable solution for reducing the acid build-up in the engine lubricant.

The operating schedule for this test consisted of 16 consecutive hours per day starting at 8:00 AM at which time new oil was added, if needed, to restore the initial charge level. Each day a hot used oil sample was withdrawn from the engine gallery at about 3:00 PM and just before shutdown. These samples were analyzed for TAN, TBN, and wear metals content by X-Ray fluorescence.

By the end of 40 hours of test, the engine's brake horsepower output had dropped to 58% of its initial level and speed could no longer be maintained. Since in other respects, the operating conditions appeared normal, it was suspected that a problem had developed in the fuel injection nozzle. Thus, after withdrawing a used oil sample for analysis, the engine was stopped and the nozzle was removed for inspection. It was found that the pintle had seized in the tip body, but the tip exit holes did not appear to be blocked or enlarged. Upon freeing the pintle, small areas of corrosion were evident on both the upper and lower portions of the pintle as well as tacky lacquer-like deposits on the needle and lower stem areas.

Since the primary purpose of this test was to evaluate the efficacy of the ESO in the lubricant, a new nozzle tip assembly was installed to permit continuation of the test to 80 hours. Meanwhile, a microscope examination of the removed tip confirmed no enlargement of the fuel exit holes and no other exterior distress. Upon resuming the test with this new injector tip, the power output was found to be restored to its original level.

Although the operating conditions were maintained throughout the remaining 40 hours, excessive oil consumption. to the extent of losing over 20% main oil pressure, and requiring the total additions of 2.9 kg (6.3 lb) new makeup oil to restore the standard 5.9 kg (13.0 lb) charge, was experienced during that period. These oil makeups, amounting to 0.7 kg (1.5 lb) at 48 hours, 1.4 kg (3.0 lb) at 63 hours, and 0.8 kg (1.8 lb) at 74 hours, created a "sawtooth" effect on time plots of TAN and TBN values for the two-a-day used oil samples, thereby obscuring the influence of ESO on TAN increase and TBN decrease. Disassembly of the engine after test revealed the following:

Deposits - More than usual granular carbonaceous deposits were found on valve deck and rocker cover. Hard carbon deposits had formed on valve springs, rocker components, piston fire land and cylinder area above top ring travel. Varnish spots were present on both sides of piston skirt. Carbon deposits were present in all piston ring grooves and on all lands. The second and third compression rings were sluggish in their grooves.

Chromed Rings - No corrosion was apparent on top ring but chromed face was badly worn. No corrosion or other distress of chromed rails of oil control ring occurred.

Other Rings - The second and third compression rings were worn.

Injector (No. 2) - The pintle of the replacement tip was corroded on the upper stem about the same as the first, but corrosion of the lower stem and needle areas was considerably less than the first.

4. Discussion of Cummins and ER-3 Engine Tests

Exhaust emissions tests did not indicate any substantial differences in the nature of the brominated organic constituents from single-cylinder versus multi-cylinder engines (CLR vs. Cummins) operating on BCM FSF.

Eighty-hour tests conducted at a remote site with BCM FSF in a multi-cylinder engine (Cummins V6-155) reproduced the power loss and fuel injector nozzle hole enlargement problems (but not the oil-control piston ring chipping or the fuel injector valve sticking phenomena) that had been observed in the AVDS 1790-2C endurance test.

Subsequent engine tests using 0.5% and 1.0% CHO added to the BCM FSF demonstrated essentially no power loss and substantially reduced injector hole enlargement, with the 1% CHO test producing less enlargement than the 0.5% CHO test. However, each of the BCM/CHO tests resulted in wrist pin bushing wear and somewhat more piston ring wear than did the 5% BCM FSF test. A fourth test was conducted with this multi-cylinder engine with 1.5% CHO in the BCM FSF, and this was intended to be an endurance test. At 80 hours, the developed power was about the same as at the beginning of the test, and other measures of performance looked good. However, at 114 hours, the oil pressure was decreasing rapidly and became too low to allow continued running. Post-test inspection revealed severe wrist pin bushing wear and also substantially more piston ring wear than that observed with the shorter 0.5% or 1.0% CHO tests. In effect, for this multi-cylinder engine test, the CHO additive appears to have served its intended function of protecting fuel injector nozzle holes from corrosive enlargement, but at the same time, it appears to have created an accelerated-wear-conducive environment.

Simultaneous 80-hour (or less) tests conducted in the laboratory with the single-cylinder TARADCOM ER-3 diesel engine produced results somewhat contradictory to those observed during the multi-cylinder engine tests. It was not unexpected that results obtained with the single-cylinder engine would be different from those generated by the multi-cylinder engine because the engine parts were made of different alloys, and engine operating conditions were different. This test series did reproduce the fuel injector valve sticking problem, but did not reproduce the fuel-injector-nozzle hole enlargement or oil-control piston ring chipping phenomena observed in the AVDS 1790-2C endurance test. The addition of 0.5% CHO to the BCM FSF significantly reduced the amount of piston ring/liner wear, in contrast with the multi-cylinder engine tests where the opposite effect was observed. However, the fuel injector valve sticking problem was not alleviated by the presence of CHO.

E. Metallurgical Considerations

Several organizations knowledgeable of the metallurgical aspects of corrosion/erosion phenomena were consulted during the early phase of this corrective-action program. The assistance of AMMRC was formally requested by MERADCOM, and other organizations were contacted by AFLRL. These included Frankford Arsenal, American Bosch, an independent consultant, and TARADCOM. Following meetings of these groups at MERADCOM and at AMMRC, the consensus was: (1) material screening tests and material acceptance criteria should be developed as soon as possible, (2) corrosion bench testing of candidate materials should commence as soon as possible, and (3) as likely injector candidate materials appear, they should be provided to American Bosch for initial engineering evaluation and ultimate fabrication for the AVDS 1790-2C engine family. However, initial injector tip evaluations, using improved corrosion-resistant tip materials, would be conducted at AFLRL in the TARADCOM ER-3 high-output single-cylinder diesel engine. Because of a one-year development period required by American Bosch, it would not be possible to complete such tests until some time during FY77. Demonstration of improved injector tip performance in this engine would provide added confidence that such materials would function acceptably in the AVDS 1790-2C engine.

Each of the nozzle suppliers (American Bosch and Cummins) furnished the basic alloy composition currently used in his injector tips. Further, each stated that he would cooperate in improving the corrosion resistance of his injection equipment. For reference purposes, the identify and nominal composition (where available to AFLRL) of the various alloys included in fuel injectors of immediate interest to the BCM FSF research program are summarized in Table 19.

TABLE 19. SUMMARY OF IDENTITY AND COMPOSITION OF ALLOYS USED IN FUEL INJECTORS INVOLVED IN BCM FSF RESEARCH PROGRAM

	Injector Nozzle Tip	Injector Pintle	Fuel Pump Plunger Rod
Cummins V6-155 Engine			
Alloy Designation	AISI 8630 H Steel	—	D4 Tool Steel
Composition, %			
C	0.28–0.33	—	2.25
Mn	0.70–0.90	—	—
P	0.040 max	—	—
S	0.040 max	—	—
Si	0.20–0.35	—	—
Ni	0.40–0.70	—	—
Cr	0.40–0.60	—	12.00
Al	—	—	—
Mo	0.15–0.25	—	1.00
Heat Treatment and	Quench and Temper to 40–45R_c	—	62–64R_c
Surface Treatment	—	—	Oxide Penetrant
AVDS 1790-2C Engine			
Alloy Designation	AISI E9317 Steel	M-2 Steel	AISI 52100 Steel
Composition, %			
C	0.15–0.20	0.85	0.95–1.10
Mn	0.45–0.65	—	0.25–0.45
P	0.025 max	—	0.025 max
S	0.025 max	—	0.025 max
Si	0.20–0.35	—	0.20–0.35
Ni	3.00–3.50	—	—
Cr	1.00–1.40	4.0	1.30–1.60
Al	—	—	—
Mo	0.08–0.15	5.0	—
V	—	2.0	—
W	—	6.25	—
TARADCOM ER-3 Engine			
Alloy Designation			
Analysis of Nozzle, %			
C	0.19	—	—
Mn	0.39	—	—
Si	0.27	—	—
Cr	1.82	—	—
Ni	1.85	—	—
Mo	0.18	—	—
V	<0.01	—	—

III. SUMMARY OF RESULTS

The composite results of the foregoing research program are summarized in Tables 20, 21, and 22. Each figure itemizes the four problem areas: injector nozzle hole enlargement, injector valve sticking, oil-control piston ring chipping, and accelerated wear. Table 20 shows the fuel and/or lubricant modification investigated for alleviating each problem area, the observed effects related to the problem area, and finally, any secondary effects. For injector-nozzle hole enlargement, propylene oxide halogen-scavenger was found to be effective for removing hydrocloric acid from vapor in the developed corrosion test; however, it proved to be too volatile to use as a diesel fuel additive. Consequently, cyclohexene oxide halogen scavenger was selected as the fuel additive and was found to substantially reduce nozzle hole enlargement in engine tests; however, it produced accelerated wear of engine parts. The injector valve sticking problem observed with the ER-3 engine was attacked by the use of cyclohexene oxide halogen scavenger in the fuel. However, this additive had no effect on this problem. Oil-control piston ring chipping was not observed in any of these engine tests. Alleviation of accelerated wear was approached by employing epoxidized soybean oil in the lubricant. During initial stages of the engine test in which this additive was employed, increase in acid number of the lubricant was retarded by the presence of the additive. However, subsequently, the acid number increased at an accelerated rate relative to tests in which the epoxidized soybean oil was not utilized. This lubricant additive produced accelerated wear in the ER-3 engine.

Table 21 summarizes the maximum number of operating hours that can be assured based upon the results observed with laboratory engines for the same four problem areas itemized in Figure 21. The injector hole enlargement with bromochloromethane fire-safe fuel caused engine shutdown with the ER-3 after 60 operating hours, but when 0.5% cyclohexene oxide was included in the fuel, the Cummins engine had suffered no power loss due to injector nozzle hole enlargement at 110 hours of operation. Significant power loss apparently because of injector valve sticking was encountered with the ER-3 engine at 40 to 80 hours, both with and without 0.5% CHO in the BCM FSF. As mentioned previously, oil-control piston ring chipping was not encountered in any of the engine tests. Accelerated wear was not encountered in the ER-3 with BCM alone during 60 hours of operation. However, the multi-cylinder engine did experience a shutdown because of accelerated wear with the use of 1.5% CHO after about 110 hours of operation.

Table 22 relates these four problem areas to whether or not 5% BCM plus 0.5% CHO would be satisfactory for engine use on short-term or long-term bases. In the case of the injector hole enlargement, the FSF possibly would be adequate for short-term use, but its suitability for long-term use is unknown. For injector valve sticking, its suitability is unknown for either short-term or long-term use. The oil-control piston ring resistance to chipping would probably be satisfactory in short-term use, but is unknown for long-term use. Accelerated wear would not be a problem with short-term use; however, it could become a serious problem for long-term use.

TABLE 20. SUMMARY OF ADDITIVE EFFECTS ON BCM FSF ENGINE PROBLEM AREAS

Problem Area	Fuel and/or Lubricant Modification Investigated	Effects Related to Problem Area	Secondary Effects
Injector Nozzle Hole Enlargement	Propylene oxide halogen scavenger in fuel	Removed HCl from vapor in corrosion test	Too volatile
	Cyclohexene oxide halogen scavenger in fuel	Substantially reduced nozzle hole enlargement in engine tests	Accelerated wear of V6-155 engine parts
Injector Valve Sticking	Cyclohexene oxide halogen scavenger in fuel	None	Reduced wear of ER-3 engine parts
Oil Control Piston Ring Chipping	None	Chipping not observed	—
Accelerated Wear	Epoxidized soybean oil in lubricant	Initial retardation of acid number increase, subsequent acceleration of acid number increase	Accelerated wear of ER-3 engine parts

TABLE 21. MAXIMUM HOURS OF FSF OPERATION ASSURED IN LABORATORY ENGINES

Problem Area	Operating Hours with FSF Containing:	
	BCM Only	BCM Plus 0.5% CHO
Injector Hole Enlargement	60 (ER-3)	> 114 (V6-155)
Injector Valve Sticking	40-80 (ER-3)	40-80 (ER-3)
Oil-Control Piston Ring Chipping	>80 (V6-155)	> 114 (V6-155)
Accelerated Wear	>60 (ER-3)	114 (V6-155)

TABLE 22. SUMMARY OF BCM FSF LABORATORY ENGINE TEST RESULTS

Problem Area	5% BCM Plus 0.5% CHO Satisfactory for Engine Use	
	Short Term	Long Term
Injector Hole Enlargement	Yes	?
Injector Valve Sticking	?	?
Oil-Control Piston Ring Chipping	Yes	?
Accelerated Wear	Yes	No

IV. CONCLUSIONS AND RECOMMENDATIONS

This corrective-action program developed information that provides a substantitive basis for the following conclusions and recommendations.

- Problems stemming from diesel fuel injector nozzle hole enlargement during engine operation with BCM FSF are alleviated by the presence of cyclohexene oxide in the fuel.
- The injector valve sticking problem observed during diesel engine operation with BCM FSF was not alleviated by the presence of cyclohexene oxide in the fuel.
- Chipping of the chromium plating on the oil-control piston ring, such as that encountered during the earlier AVDS 1790-2C diesel engine endurance test with BCM FSF, was not encountered during engine tests conducted as part of this study.
- Accelerated wear effects observed during diesel engine operation with BCM FSF are aggravated by the presence of cyclohexene oxide in the fuel.
- Accelerated wear caused by BCM FSF is mitigated by the presence of epoxidized soybean oil in the crankcase lubricant until the halogen scavenging capacity of the epoxy group is consumed, after which, lubricant deterioration and accelerated wear effects are promoted, relative to the absence of epoxidized soybean oil.
- Conventional corrosion inhibitors and lubricant acid scavengers are ineffective for preventing fuel injector hole enlargement or accelerated engine wear.
- Diesel engines in Army mobility equipment could probable operate satisfactorily during limited, short-term emergency use, i.e., less than about one hundred hours of service.
- Long-term utilization of BCM FSF is not a viable consideration on the basis of present knowledge.
- No additional applied research and development should be devoted to the use of BCM as a fire-vulnerability-reduction fuel additive.

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APPENDIX A

BALLISTIC EVALUATION OF FIRE-SAFE FUEL

A series of replicated ballistic tests was conducted by AFLRL to tentatively establish the efficacy of 5% BCM FSF at a realistic maximum fuel tank temperature of 77°C (170°F) (Figures 19 and 20). These tests comprised the firing of 20 mm HEIT rounds horizontally into 76 liters (20 gal.) of fuel contained in a 114-liter (30 gal.) horizontally-mounted drum. A tilted (45°) aluminum plate was mounted 30 cm (1 ft.) in front of the drum face so that the 1000 m/s projectile would penetrate its center and become actuated before striking the center of the drum face below the liquid level. The results of these tests indicated that BCM FSF [5% (liq. vol.) BCM in a 63°C (145°F) flash point diesel fuel] did not experience sustained ground fires, but did exhibit flash fireball effects. The test results also demonstrated that the presence of 1% cyclohexene oxide (candidate halogen scavenger) in the BCM FSF did not adversely affect the ground-fire flammability resistance of BCM FSF.

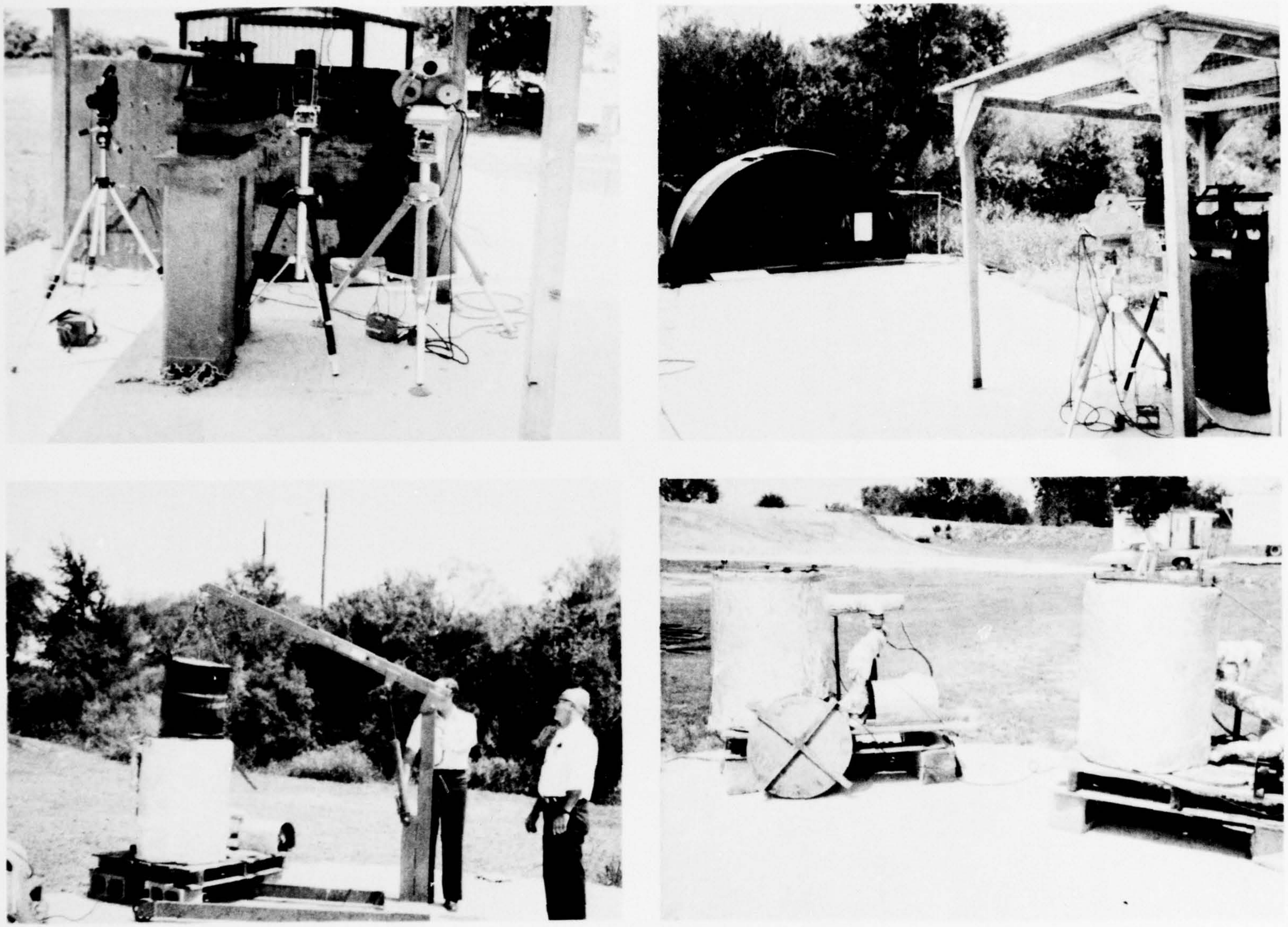

FIGURE 19. PHOTOGRAPHS OF BALLISTIC FACILITY

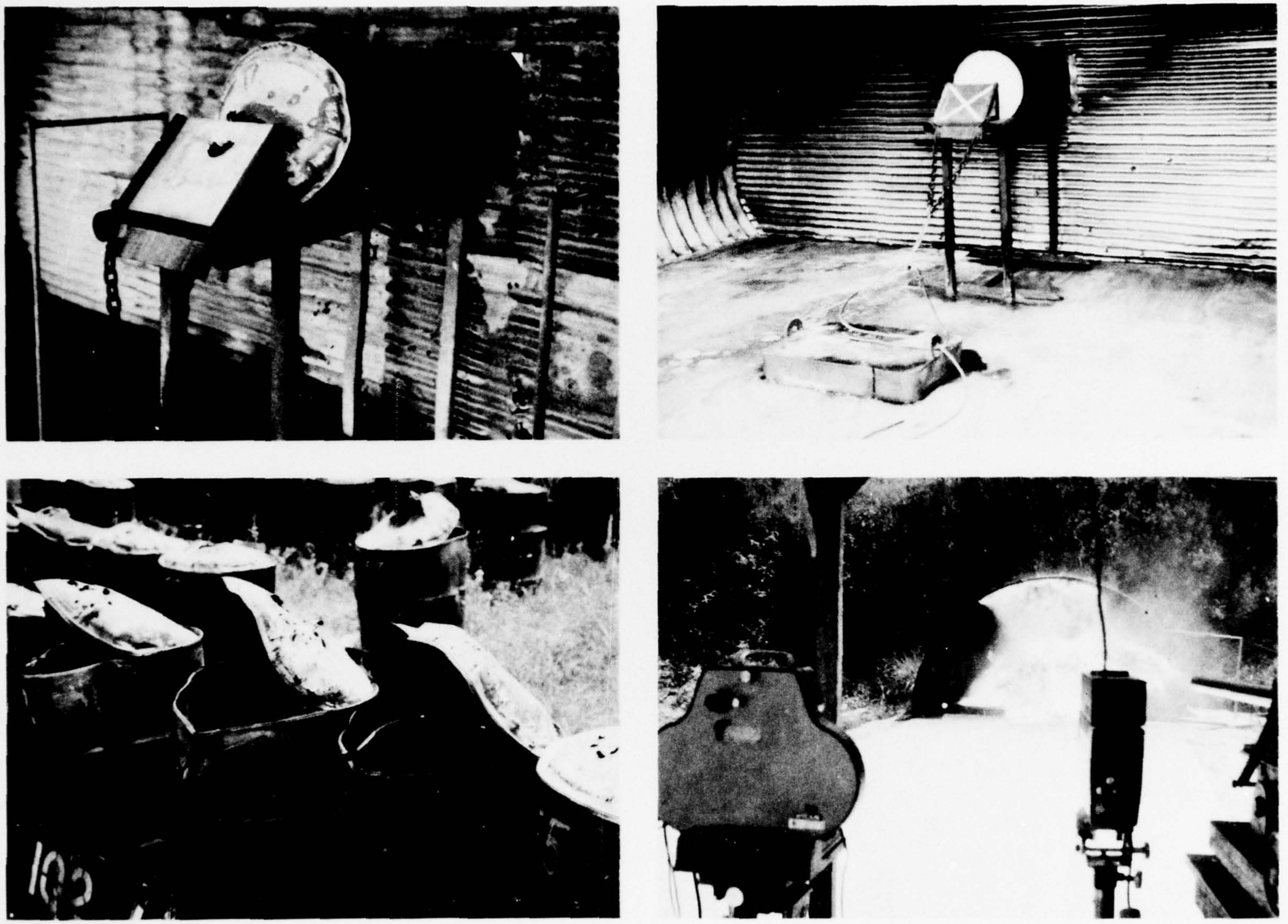

FIGURE 20. PHOTOGRAPHS OF BALLISTIC TEST AND SPENT TARGETS

APPENDIX B

GLOSSARY OF ACRONYMS AND ABBREVIATIONS

Acronym	Definition
AFLRL	Army Fuels and Lubricants Research Laboratory
AMMRC	Army Materials and Mechanics Research Center
AMSAA	Army Materiel Systems Analysis Activity
MERADCOM	Mobility Equipment Research and Development Command
TARADCOM	Tank Automotive Research and Development Command
TCM	Teledyne Continental Motors

Abbreviation	
BCM	bromochloromethane
BCM FSF	bromochloromethane fire-safe fuel [5% (liq. vol.) in DF-2]
CHO	cyclohexene oxide
DF-2	No. 2 diesel fuel
ER-3	single-cylinder engine developed by TARADCOM
ESO	epoxidized soybean oil
SAN	strong acid number (ASTM D664)
SEM	scanning electron microscope
TAN	total acid number (ASTM D664)
XRF	X-Ray fluorescence analysis

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