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Effect of Time in Service on the Oxidative Induction Time of Shell Rimula X Diesel Lubricating Oil

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Abstract

Problems with the auxiliary diesel engines on CF Ships, specifically carbon build-up on piston heads, resulted in a systematic study of the engines in an attempt to determine the cause. Analysis indicated that the lubricating oil was suffering from a severe fuel dilution problem. Low load engine operation was thought responsible for these problems and a number of fixes were made. These included the introduction of low load injector nozzles, increasing the engine cooling temperature, raising the charge air temperature and increasing the turbo speed. However, the carbon build-up problem persisted.

The lubricating oil used in these engines, MIL-L-9000H [1], was identified as a potential contributor to the carbon build-up. In particular, the oxidation stability of the oil was questioned. A study of the oxidative stability of the oil [2] indicated that MIL-L-9000H, the oil specified for the propulsion and auxiliary diesel engines on CF Ships, exhibited less oxidation resistance than several commercially available SAE 40 diesel lubricating oils.

In this paper the results of a study of the oxidative stability of Shell Rimula X diesel lubricating oil following service in four diesel generators on HMCS Vancouver are reported.

Introduction

Diesel lubricating oils are composed of base oils, additives and viscosity modifiers. All of these components are susceptible to oxidative degradation. The oxidative degradation process involves the formation of peroxy and alkyl radicals (see Figure 1) and will lead to the complete breakdown of the oil and subsequent equipment failure [3]. To improve stability, oxidation inhibitors, or antioxidants, are added to lubricating oils. Antioxidants work by eliminating the initiation and propagation reactions shown in Figure 1; some decompose hydroperoxides, some scavenge radicals while others deactivate the metal ions that promote hydroperoxide formation [4]. For instance, compounds such as zinc dialkyl dithiophosphates, alkylsulfides, polyalkylsulfides and metal dithiocarbamates act as hydroperoxide decomposers while arylamines and alkylphenols act as radical scavengers.

1. $RH \xrightarrow{O_2/M^{n+}} R^* + HOO^*$
2. (a) $R^* + O_2 \rightarrow ROO^*$
   (b) $ROO^* + RH \rightarrow ROOH + R^*$
3. (a) $ROO^* + HOO^* \rightarrow ROOH + O_2$
   (b) $ROO^* + R^* \rightarrow ROOR$
   (c) $R^* + R^* \rightarrow RR$

1. Initiation – formation of hydroperoxide and alkyl radicals in presence of oxygen and metal ion
2. Propagation – formation of a)alkylperoxide radical and b) regeneration of alkyl radical
3. Termination

Figure 1. Reactions involved in the oxidative degradation of hydrocarbons molecules in lubricating oils.

The operating conditions in a diesel engine, that is, the presence of oxygen and high temperatures, accelerate the oxidative degradation process. The resistance of lubricating oil to oxidative degradation is the most significant property of the oil as it defines the ability of the oil to continue to perform in-service. Two ASTM tests, ASTM D 943 Oxidation Characteristics of Inhibited Mineral Oils (TOST) [5] and ASTM D 2272 Rotating Bomb Oxidation Test (RBOT) [6], have traditionally been used to assess the oxidative stability of lubricating oils. These tests are time consuming. TOST often takes greater than 1500 hours and RBOT between 1 and 45 hours. In addition these tests require 300 mL and 30 grams of sample respectively.

Differential scanning calorimetry has been used to study the oxidative stability of oils [7-13]. An ASTM standard method, ASTM E 1858-97 Determining Oxidation Induction Time (OIT) of Hydrocarbons by Differential Scanning Calorimetry, has recently been published [14]. The advantages of this method are its precision, short analysis time (less than 2 hours) and small sample size (less than a millilitre of oil). The results of OIT testing of oils are used to rank the resistance of oils to oxidative degradation in service. That is, oils with longer OITs will have a greater resistance to oxidative degradation.

In 1999, a study of the oxidative stability of the diesel lubricating oil used in the auxiliary and propulsion diesel engines on CF Ships, MIL-L-9000H, was initiated to determine if the oxidative stability of the oil might be a contributor to carbon build-up in these engines. The results of the study [2] indicated that a number of commercially available marine diesel lubricating oils had OITs greater than MIL-L-9000H. As the engine manufacturer had suggested that the poor oxidative stability of MIL-L-9000H oil might be contributing to carbon build-up in the engines, an Operational Evaluation of Shell Rimula X, a commercial SAE 40 marine diesel lubricating oil recommended by the engine manufacturer was initiated on HMCS Vancouver.

In this paper the affect of time in service of Rimula X on OIT are reported and compared to the results for MIL-L-9000H diesel lubricating oil.

Experimental

Differential Scanning Calorimetry

All differential scanning calorimetry (DSC) was carried out on a TA Instruments Model 2910 modulated differential scanning calorimeter. A pressure cell (TA Instruments) was used for all experiments. Data acquisition and analysis was carried out using Thermal Analysis and Thermal Solutions software (TA Instruments).

The DSC was run under a dynamic atmosphere of oxygen regulated by a flow meter (Tube Cube, Matheson). The pressure cell was charged with 500 psi oxygen and the flow from the cell set at 25 mL/min. Oil samples (~3.0 mg) were analysed in aluminum pans (TA Instruments kit number T80518). The pans were cleaned according to Annex A1 in reference 14.

The temperature programs for the DSC baseline calibration, indium and tin standards and OIT runs are listed in Table 1. The DSC baseline was run without pans. The indium and tin standards were run in closed pans. The indium standard (14.75 mg) had a melt temperature of 156.60°C and a heat of fusion of 28.71 J/g. The tin standard (11.78 mg) had a melt temperature of 231.23 °C and a heat of fusion of 61.24 J/g.

The DSC cell was cleaned after every oxidation induction time run. The cleaning consisted of heating the unsealed cell to 500°C for 20 minutes. OITs were measured as described in reference 14.

Oil Samples

New and used samples of Rimula X SAE 40 (Shell Canada) were received from HMCS Vancouver. The used samples were from diesel generators #1, #2, #3, and #4.

The MIL-L-9000H marine diesel lubricating oils were supplied by PetroCanada.

Rotella T SAE 40 (Shell Canada), IDO Universal #40 (Irving Oil), and Duron SAE 40 (PetroCanada) were received from the Stores System, Base Halifax.

Table 1. DSC temperature programs for instrument calibration, oxidation induction time of oils, and cleaning methods.

Indium Standard: equilibrate at 120, ramp at 1°C/min to 175°C
Tin Standard: equilibrate at 200°C, ramp at 1°C/min to 250°C
DSC Baseline Calibration: Ramp at 40°C/min to 175°C, equilibrate at 175°C, isothermal for 100 minutes
Oxidation Induction Time: same as DSC Baseline but isothermal at 185°C
Clean Method: Ramp at 40°C/min to 500°C, isothermal for 20 minutes

Sample Preparation

Samples were shaken for 1-2 minutes prior to sampling. The sample (3±0.3mg) was transferred from the sample container to the DSC pan using a micropipette (50µL).

Gas Chromatography/Mass Spectrometry (GC/MS) Analysis

GC/MS analysis was carried out on a Hewlett Packard Model 6890 gas chromatograph with a Hewlett Packard Model 5973 mass selective detector (Agilent Technologies). A 30m long x 0.25 mm inside diameter DB5 (5% phenyl-95%methylsilicone stationary phase) capillary column was used for all separations. Helium at a flow rate of 1.0 mL/min was used as the carrier gas.

The GC oven was programmed to hold at 40°C for five minutes, ramp to 150°C at a rate of 8°C/min, then ramp to 300°C at a rate of 10°C/min, and finally to hold at 300°C for 15 minutes.

New and used Rimula X lubricating oil samples were diluted 1 in 250 in hexane and 1µL of the resulting solution analyzed. N-phenylnaphthalene amine was used as an internal standard for antioxidant depletion studies.

Viscosity

Kinematic viscosities of new and used Rimula X diesel lubricating oil sample were measured at 100°C.

Results and Discussion

OITs of MIL-L-9000H and Commercial Diesel Lubricating Oils

The OITs of new samples of three batches of MIL-L-9000H lubricating oils are shown in Table 2. Statistical analysis (analysis of variance [12]) indicated that differences between the OITs for samples from a particular batch of oil and the OITs for the three batches of oil were not significant.

Table 2. Oxidative Induction Times (OITs) of three batches of MIL-L-9000H diesel lubricating oils.

BATCH #/ OIT RUN	#1	#2	#3	#4	Average
Batch 981781	56.24 min	59.03	59.51		58.29
Batch 983486	57.20	57.49			57.34
Batch 991751	59.00	57.33	54.62	57.15	57.05

Analysis of variance indicated that the differences between samples from a batch and between batches were not significant.

The thermograms, that is, plots of heat flow versus time at 185 °C, for the three batches of MIL-L-9000H oils are shown in Figure 2. The thermograms of new and used MIL-L-9000H oils samples (HMCS Toronto) are shown in Figure 3. It can be seen that the OIT of the samples decreases with the number of hours in service, from 57.1 minutes for the new oil to 20.7 minutes for the oil after 377 hours.

A suggestion by the engine manufacturer that the ‘poor’ oxidative stability of MIL-L-9000H diesel lubricating oils could be contributing to the carbon build up problem led to an analysis of several commercial marine diesel lubricating oils. The results of the analysis of three commercial oils are shown in Figure 4. OIT testing indicated that the oxidative stability of the MIL-L-9000H was inferior to the commercial oils. The engine manufacturer was asked to recommend oils for an operational evaluation in the engine. One of the recommended oils was Shell Rimula X. The results of the operational evaluation of Shell Rimula X in the four diesel generators on HMCS Vancouver are reported in the next section.

Oxidative Induction Time of New and Used Shell Rimula X SAE 40 Marine Diesel Lubricating Oil Samples

The results of the OIT study of Shell Rimula X samples from diesel generators #1, #2, #3 and #4 HMCS Vancouver are shown in Table 3. Plots of the results for the four diesel generators are shown in Figures 5 through 8 respectively.

In general the OITs of the oil samples decreased with time in service. The results for the 546 hour sample from DG #2 and the 139 hour sample from #3 DG do not follow this pattern. That is the OIT for these samples is greater than for the preceding sample. Oil change logs obtained from HMCS Vancouver indicate that there was a complete oil change after 468 operating hours on DG #2. Therefore the sample marked 546 hours was only in service for 78 hours (546 – 468 hours). The oil logs do not indicate an oil change in DG #3 between 50 and 139 hours of operation. However, the OIT and other experimental data (antioxidant concentrations and viscosity) suggest that new oil had been added to this engine.

The short OITs for the 191 and 758 hour samples from DG #1, 463 hour sample for DG #2, 490 and 568 hour samples for DG #3, and the 789 hour sample for DG #4 are indicative of severe loss of oxidative stability. Although OIT has not been correlated with remaining useful life of the oil under 'normal' operating conditions, the results suggest the time that the oil will continue to perform is limited.

Figures 9 and 10 show the OIT results for 2 hour and 50 hour samples from the diesel generators. There was no 2 hour sample from DG #1. Comparison of the OITs indicates that the reduction in oxidative stability of the oil is dependent on the diesel from which it was taken. That is, the reduction in OIT depends on more than operating hours in the engine.

As noted in the Introduction, antioxidants are added to oils to enhance the oxidative stability of lubricating oils. To determine if the reduction in OIT was related to depletion of antioxidants, gas chromatography/mass spectrometry analysis of the oils was carried out.

Antioxidant Depletion

Chromatograms, that is,GC/MS traces, of new and used oil samples from DG #1 and DG #2 HMCS Vancouver are shown in Figures 11 and 12. Analysis of the chromatograms indicated that presence of two hindered phenol-based antioxidants; 2,6-di-tert-butylphenol with a retention time of 4.3 minutes and 4,4'-methylenebis(2,6-di-tert-butylphenol) with a retention time of 20.1 minutes. The peak with a retention time of 14.7 minutes is due to n-phenylnaphthalene amine, which was added as an internal standard to each of the samples.

Table 3. OITs, antioxidant concentrations, and viscosities of Rimula X samples from #1, #2, #3, and #4 diesel generators HMCS Vancouver.

Sample	Time in use hours	OIT minutes	Antioxidant mg/L***	Viscosity cSt
New	0.0	77.3	20.2/2.1	14.9
#1 DG	0.09	71.8	20.2/2.6	14.8
#1 DG	50.0	51.3	3.8/2.3	14.8
#1 DG	121.0	42.8	2 2/1 7	14 6
#1 DG	191.0	11.4	0.2/0.0	17.6
#1 DG	758 0	8.2	0.2/0.0	18.3
New (#2 DG)	0 0	76.6	24 2/2.4	14 8
#2 DG	2.0	73.3	18.8/2.5	14.9
#2 DG	50.0	55.5	3.3/2.4	14.6
#2 DG	463.0	14.6	0.0/0.0	15.3
#2 DG	546.0	45.4*	4.6/2.2	14 5
#2 DG	583.0	30.8	0.2/1.2	14.8
#3 DG	2.0	49.5	20.1/3 1	14.7
#3 DG	50.0	41.6	4.5/2.8	14.9
#3 DG	139 0	72 1**	17.8/3.0	14 8
#3 DG	490.0	8.8	0.7/0 0	17.1
#3 DG	568.0	8.5	0.4/0 0	17 3
#4 DG	2 0	57.8	11.6/2.5	14.8
#4 DG	50.0	49.8	4.8/2.7	14.8
#4 DG	789.0	7.9	0 3/0 0	18 9

*Oil change at 468 hours
**Results suggest oil change prior to sampling
***First number refers to concentration of 2,6-di-tert-butyl phenol and the second number the concentration of 4,4'-methylenebis(2,6-di-tert-butyl phenol).

The depletion of these two antioxidants was followed by comparıng the area under their peaks to the area under the internal standard peak. The results of the antioxidant depletion study for DGs #1, #2, #3, and #4 are shown in Table 3.

In general, the area under the antioxidant peaks decreased with the time the oil was in service. However, for the 546 hour sample in DG #2 the concentration of the antioxidants increased relative to the 463 hour sample (see Figure 10). This anomalous behavior was also observed in the OIT analysis. As was noted in the OIT discussion, the oil log for the engine indicated that there had been a complete oil change after 468 hours. Therefore the 546 hour sample had only been in service for approximately 78 hours. The results for the 139 hour sample from DG #3 are also anomalous. However, the result is consistent with the OIT results. That is, an increase in antioxidant concentration should correspond to an increase in OIT.

Viscosity

Several factors can affect the viscosity of lubricating oils including oxidative degradation, fuel dilution, and carbon build-up. The OIT results indicate that oxidative stability of the oil is decreasing with time in service. As oxidative degradation increases, reactions, such as the R* + R* termination reaction shown in Figure 1, can produce higher molecular weight hydrocarbons and a concomitant increase in the viscosity of the fluid. Suspended solids, such as carbon, also increase the viscosity of lubricating oils. In contrast to this, fuel dilution reduces the viscosity of SAE 40 lubricating oils.

The kinematic viscosities of the new and used Rimula X samples are shown in Table 3. The viscosity of the used oils remains constant or decreases slightly and then increases with time in service. For instance, the viscosity of the oil in DG #1 decreased from 14.9 cSt (new) to 14.6 cSt (121 hours) and then increased to 17.6 cSt (191 hours) and 18.3 cSt (758 hours). The decrease is due to fuel dilution of the oil. The increase in fuel dilution of the oil can be seen in Figure 9. The fuel peaks are located between 6 minutes and 16 minutes. As the time in service increases the viscosity increase related to carbon build up or oxidative degradation over rides the decrease due to fuel dilution.

As was observed for the OIT and antioxidant depletion results, viscosity measurement also reflected the change in oil in DG #2 at 468 hours. That is, the viscosity of the 546 hour sample was less than the 463 hour sample.

Conclusions

The OIT of Shell Rimula X diesel lubricating oil is greater than MIL-L-9000 H diesel lubricating. This suggests that under a given set of operating conditions that Rimula X will have superior oxidation resistance compared to MIL-L-9000H oils.

The OIT of Rimula X decreases with the time in service. This reduction has been related to the depletion of antioxidants in the oil.

Fuel dilution and carbon build-up have significant affects on the viscosity of the oil. Fuel dilution leads to a decrease in the viscosity for shorter in service times while carbon build-up leads to an increase in the viscosity of the oil at longer in service times.

The presence of fuel and carbon in the used Rimula X oil suggest that the source of the carbon in the oil is the incomplete combustion of fuel in the engine.

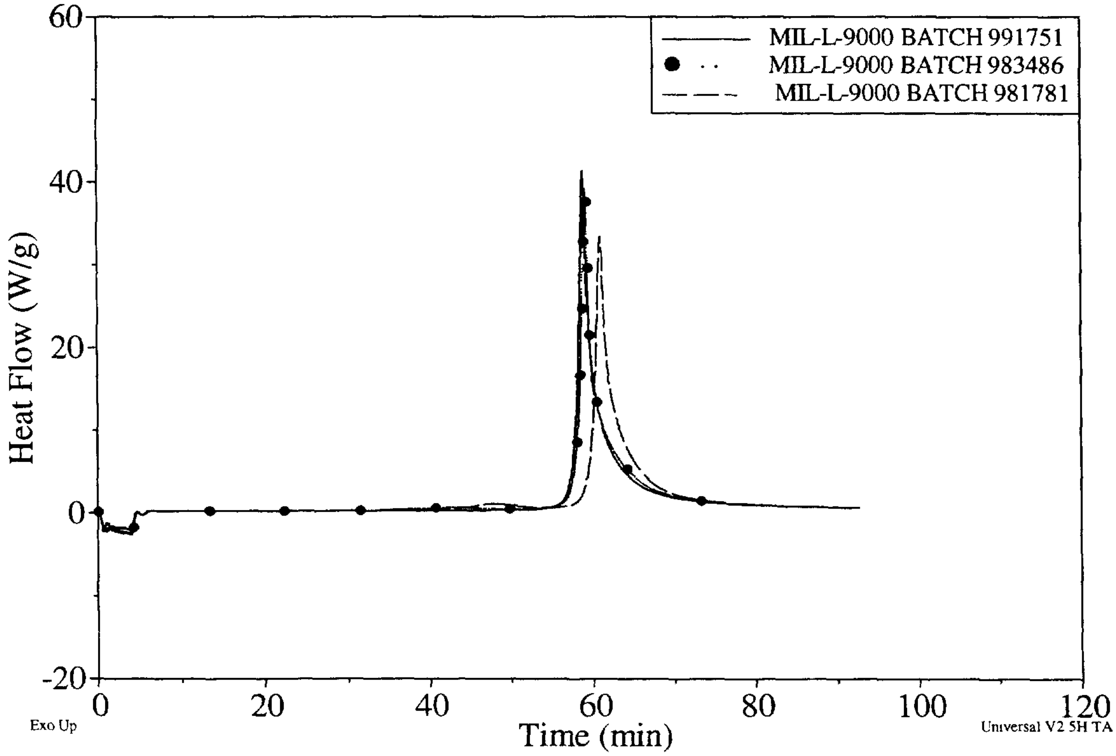

Figure 2. Thermograms of three batches of MIL-L-9000H diesel lubricating oil.

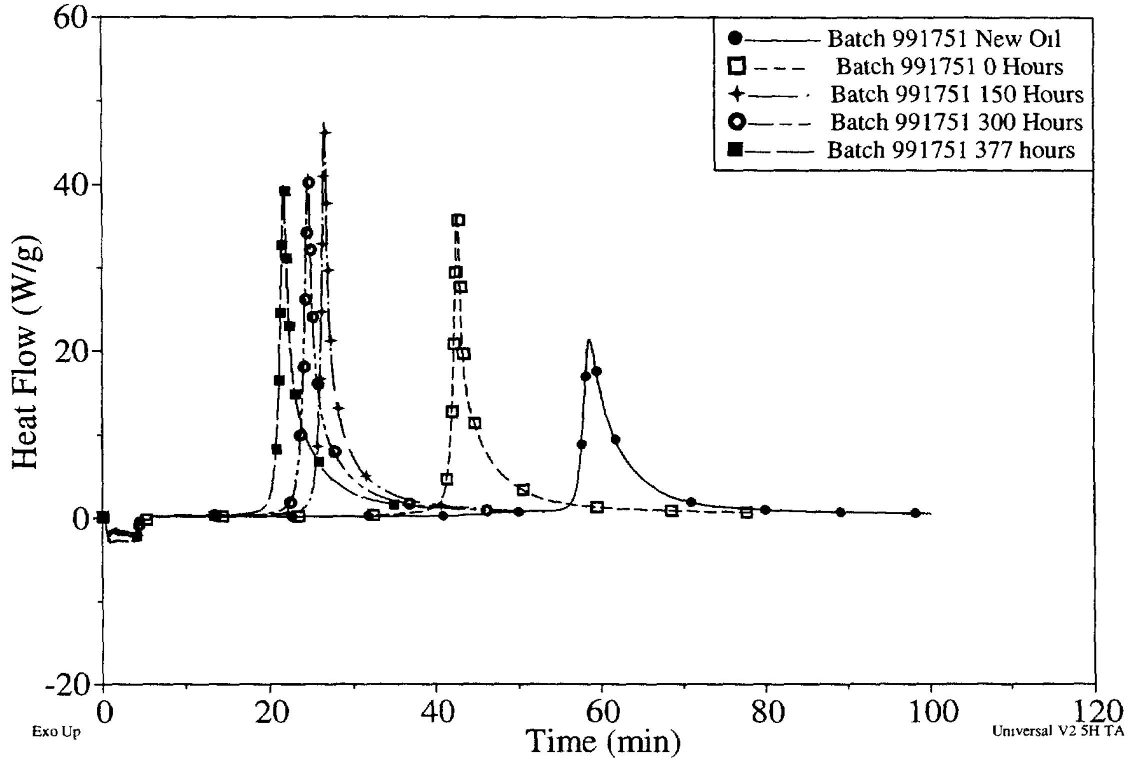

Figure 3. Thermograms of new MIL-L-9000H and MIL-L-9000H after 0, 150, 300, and 3777 hours in #4 DG HMCS Toronto.

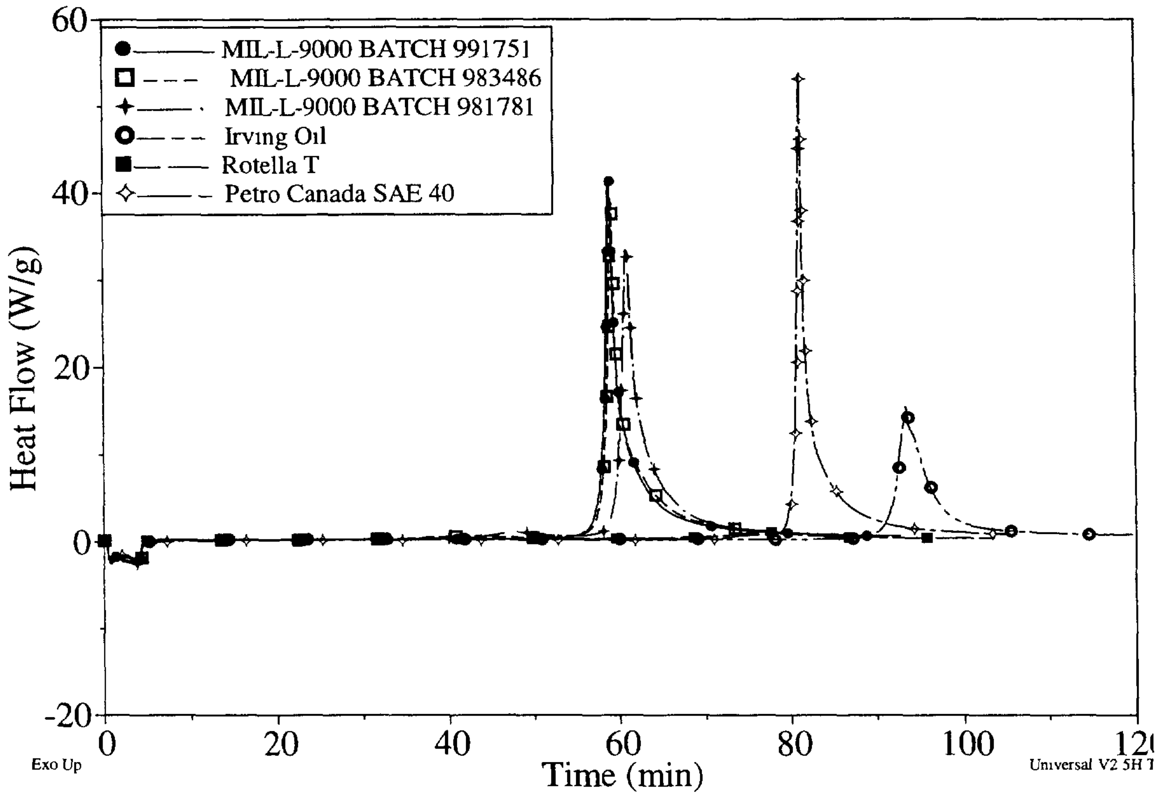

Figure 4. Thermograms of three batches of MIL-L-9000H, Irving Oil IDO Universal #40, Shell Rotella T, and PetroCanada Duron SAE 40 diesel lubricating oils.

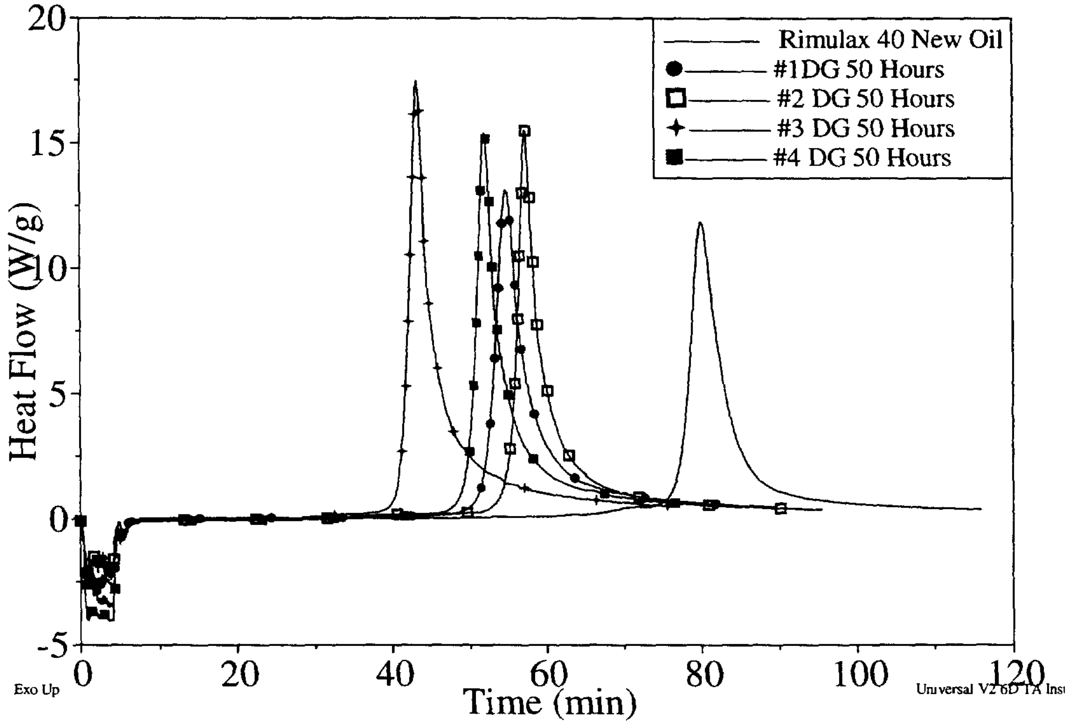

Figure 5. Thermograms of new and used Rimula X diesel lubricating oil samples from DG #1 HMCS Vancouver.

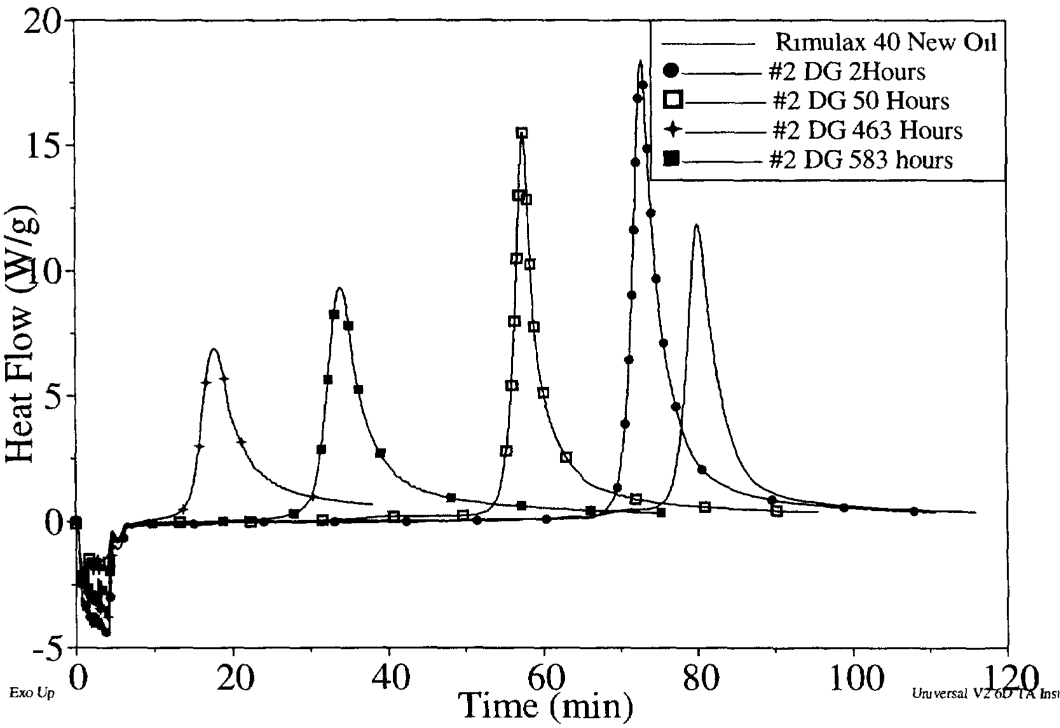

Figure 6. Thermograms of new and used Rimula X diesel lubricating oil samples from DG #2 HMCS Vancouver.

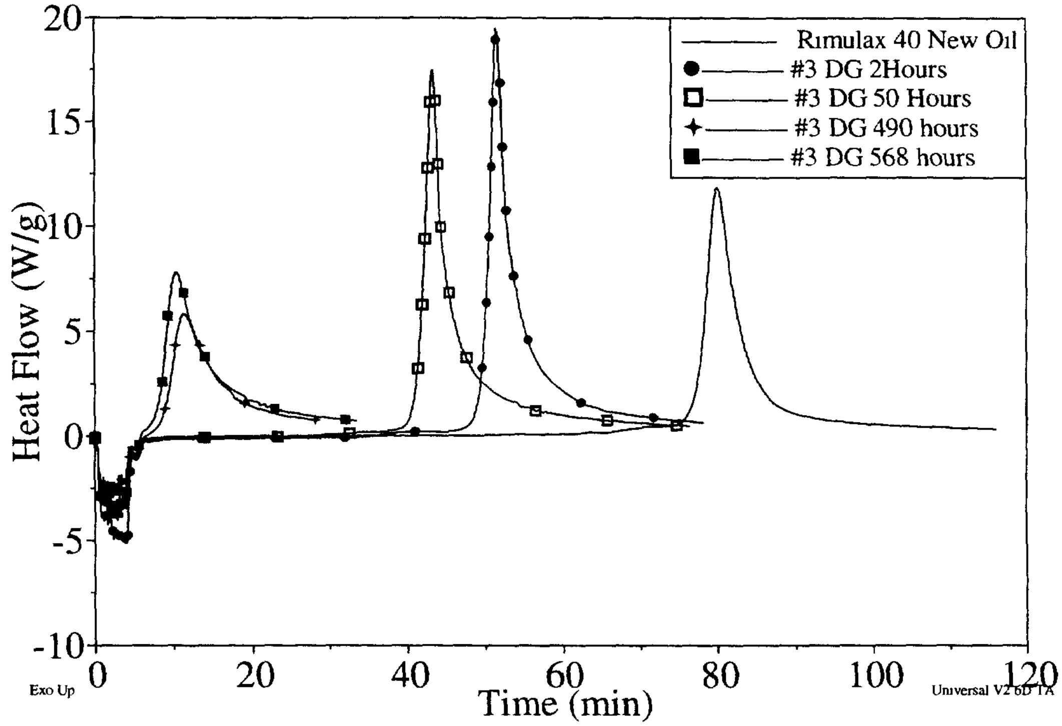

Figure 7. Thermograms of new and used Rimula X diesel lubricating oil samples from DG #3 HMCS Vancouver.

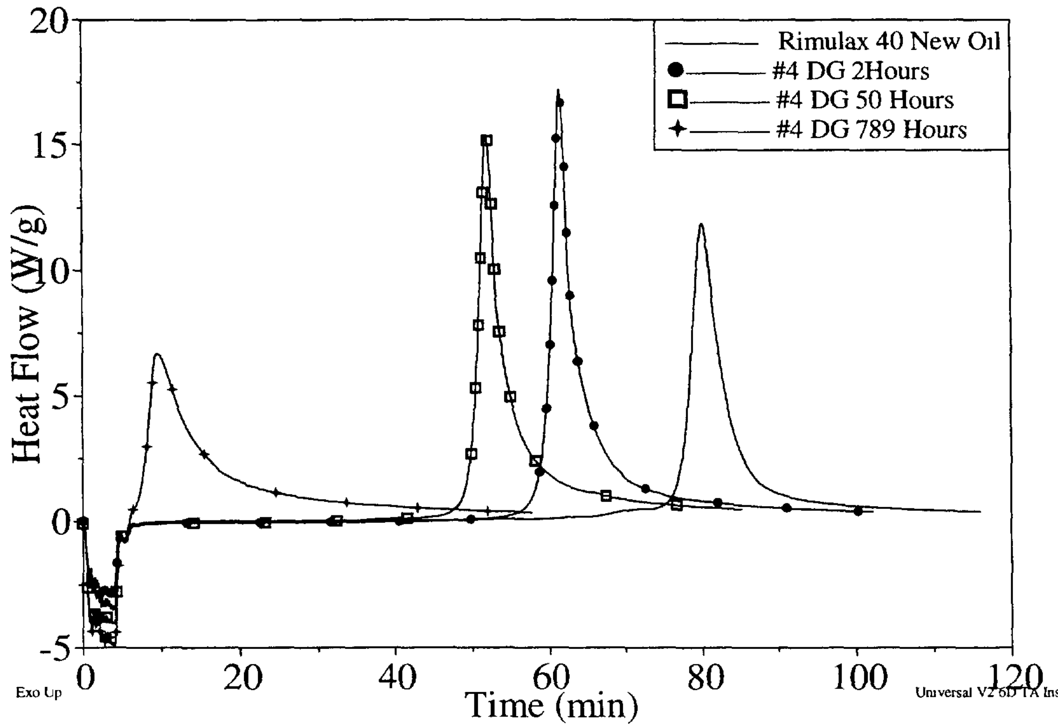

Figure 8. Thermograms of new and used Rimula X diesel lubricating oil samples from DG #4 HMCS Vancouver.

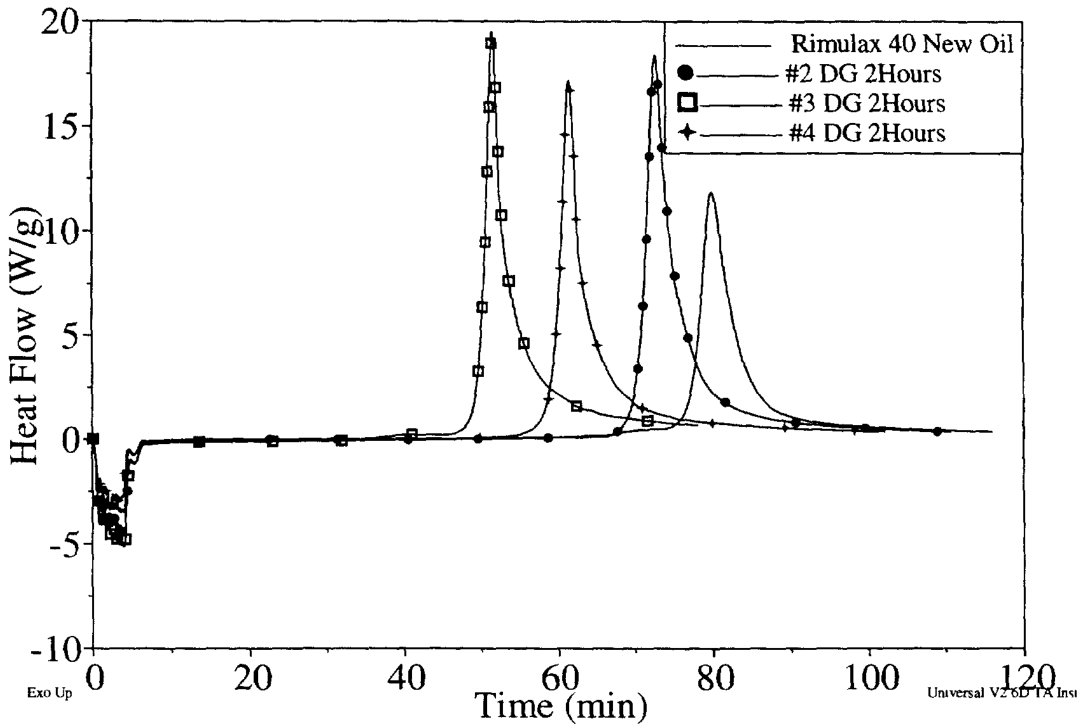

Figure 9. Thermograms of new and 2 h Rimula X diesel lubricating oil samples from DG #2, DG #3, and DG #4 HMCS Vancouver.

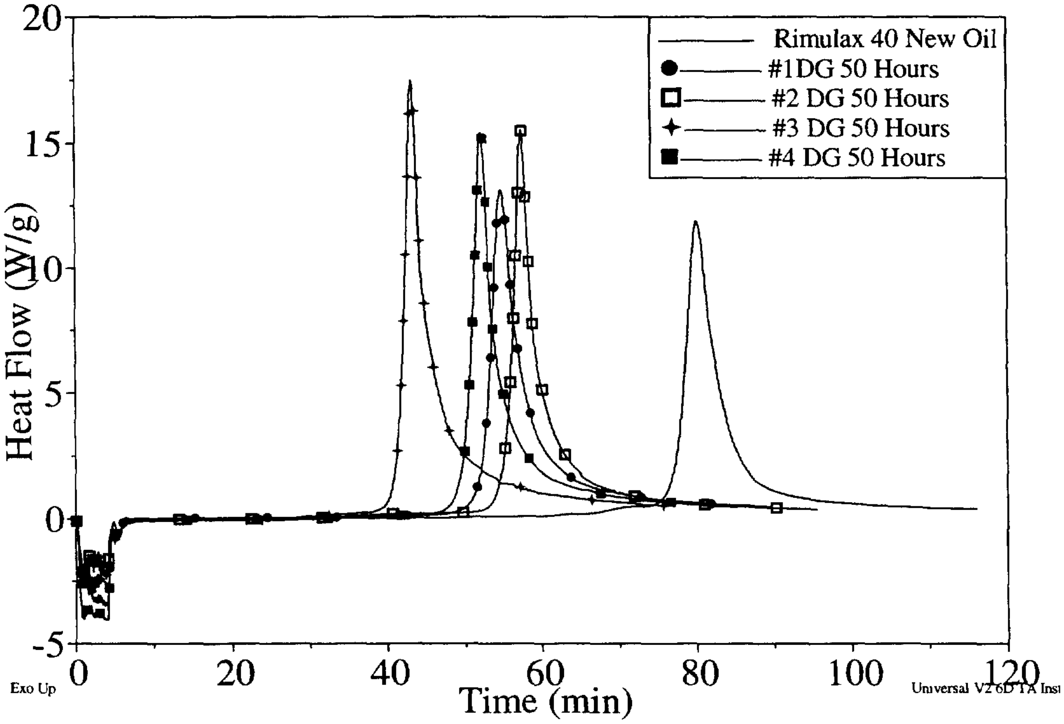

Figure10. Thermograms of new and 50 h Rimula X diesel lubricating oil samples from DG #1, DG #2, DG #3, and DG #4 HMCS Vancouver.

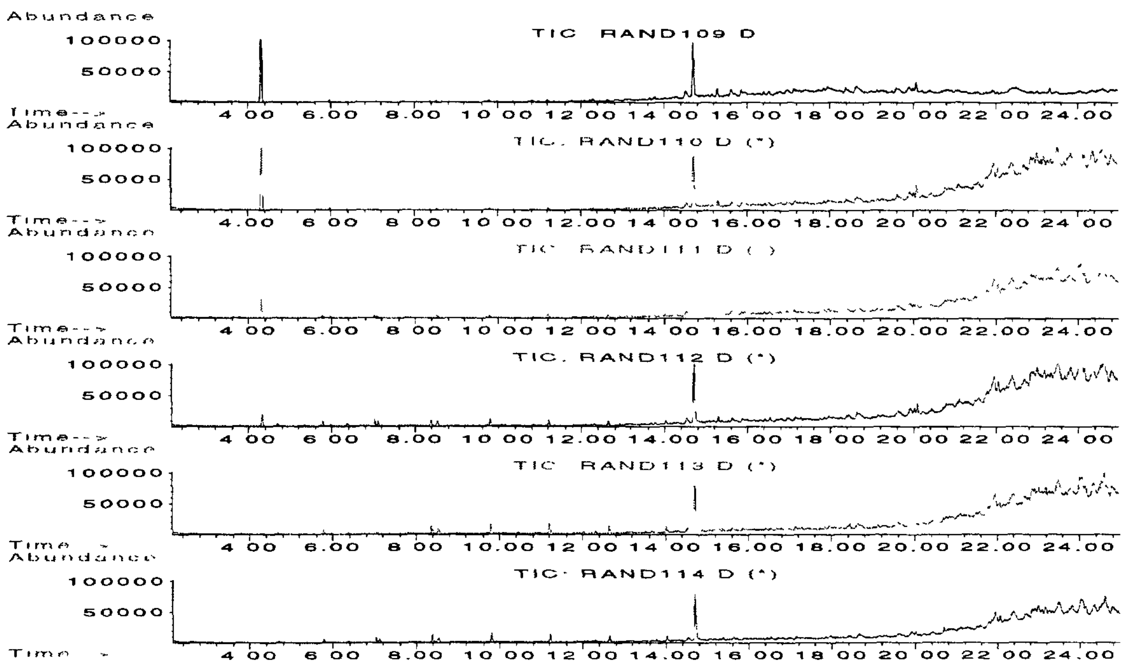

Figure 11. Chromatograms of new and used Rimula X oils samples from DG #1 HMCS Vancouver. From top; new oil, and used oil samples after 0.09 , 50 h, 121 h, 191h, and 758 h in the engine.

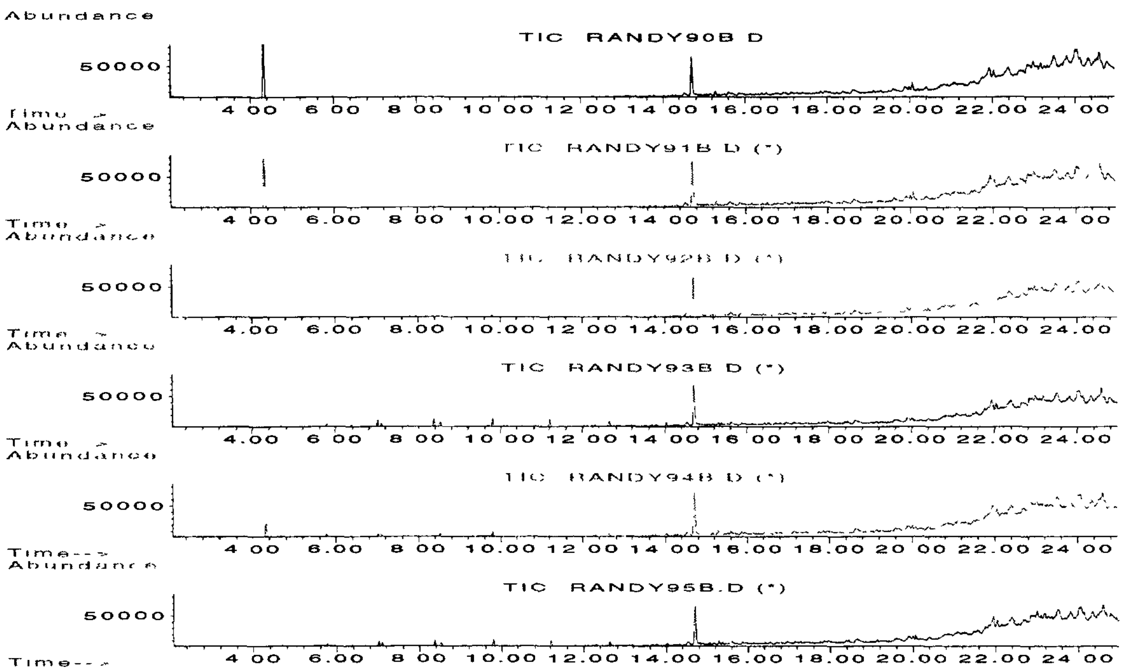

Figure12. Chromatograms of new and used Rimula X oils samples from DG #2 HMCS Vancouver. From top; new oil, and used oil samples after 2 h, 50 h, 463 h, 546 h, 583 h in the engine.

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