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SURVEY OF DIESEL FUELS AND AVIATION KEROSENES FROM U. S. MILITARY INSTALLATIONS

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ABSTRACT

In support of the Department of Defense goal to streamline procurements, the Army recently decided to discontinue use of VV-F-800D as the purchase specification for diesel fuel being supplied to continental United States military installations. The Army will instead issue a commercial item description for direct fuel deliveries under the Post/Camp/Station (PCS) contract bulletin program.

In parallel, the Defense Fuel Supply Center and the U.S. Army Mobility Technology Center-Belvoir (at Ft. Belvoir, VA) initiated a fuel survey with the primary objective to assess the general quality and lubricity characteristics of low sulfur diesel fuels being supplied to military installations under the PCS system. Under this project, diesel fuel delivery samples were obtained from selected military installations and analyzed according to a predetermined protocol. The results obtained from various tests show that the average, low-sulfur diesel fuel meets military requirements for DF-2 with the exception of lubricity performance. Proposed fuel lubricity requirements for military, ground-vehicle, diesel fuels are presented.

BACKGROUND AND OBJECTIVE

Effective October 1, 1993, federal regulations implemented by the Environmental Protection Agency (EPA) limited the maximum fuel sulfur content to a mass fraction of 0.05% from its previous level of 0.5%, according to ASTM D 975ⁱ. Additionally, the total aromatics content in the fuel was limited to a maximum volume fraction of 35%; or, a cetane number minimum of 40 as an alternative limit. The tendency toward more highly refined fuels, in order to meet these federal regulations, increased the potential for accelerated wear in some diesel engine fuel system components². The Army is especially vulnerable to fuel related problems for the following reasons:

- The severe operational requirements placed on Army vehicles (i.e., long periods of non-use

followed by short periods of high use levels, operation in hostile environments, including all extremes of temperature, humidity, dust, and terrain) increase the likelihood of problems in the field.

- Because non-military users buy fuel from numerous commercial sources (i.e., filling stations and truck stops), the chance of a non-military vehicle operating on only poor lubricity fuel is comparatively low. Conversely, military vehicles at any given post/camp/station are required to use fuel from a single supplier, as the minimum period for these contracts is twelve months.
- The routine military practice of slow fuel turnover allows fuels purchased in late fall and winter to be used in vehicles during spring and summer. This is a source of potential lubricity problems since winter fuels tend to be lower in density and viscosity.
- The Army/Department of Defense (DOD) has a high volume of military vehicles/equipment (V/E) with fuel sensitive pumps (e.g., rotary-type, fuel injection pumps).
- Non-military users also have the option of additizing their fuels should they feel the need exists. This solution is more difficult in the military because of additive non-availability, additive costs, and inadequate additive introduction systems.
- The changes in fuel refining/processing and distribution that were required to meet these new federal regulations also raised the question of how some other fuel properties might be affected. These properties include cloud point/freeze point/pour point, stability, and cleanliness.

As part of the overall DOD goal to streamline military procurements, the Army recently decided to discontinue use of VV-F-800D³ as the purchase specification for diesel fuel being supplied to continental United States (CONUS) military installations under the direct delivery Post-Camp-Station (PCS) contract bulletin program. This decision was made in accordance with a DOD-wide effort to reduce the number of government specifications in favor of commercial specifications. This decision was also based on the government's continuing difficulties in obtaining fuel suppliers willing to submit bids to supply fuel against the more stringent requirements of VV-F-800D. Virtually all of the fuel delivered to the Army under the PCS program is produced to meet the requirements of D 975, not the more restrictive VV-F-800D. Limited testing of the delivered fuel, after receipt by the Army, shows that the great majority meets the additional requirements of the Federal specification. As a result of the Army decision, future purchases of ground vehicle diesel

fuel will be made against the commercial specification, ASTM D 975. However, D 975 currently has no requirements for particulate contamination levels or accelerated stability. Also, the D 975 requirements for cloud point are less stringent than in VV-F-800D. Table 1 is a comparison of the requirements of these two specifications. Neither the commercial nor the military specifications contain any requirement for diesel fuel lubricity; and, since the Army is especially vulnerable to fuel lubricity problems, it was deemed very important that reliable information regarding the lubricity of these fuels be obtained.

In response, the Defense Fuel Supply Center and the U.S. Army Mobility Technology Center-Belvoir (at Ft. Belvoir, VA) initiated a fuel survey. The primary objectives of the survey were:

- 1) assess the lubricity characteristics of low sulfur diesel fuels being supplied to military installations under the PCS system, since neither the military nor the commercial specification contain a lubricity requirement;
- 2) confirm the likelihood that the currently supplied, commercial quality, fuel will meet the military requirements shown in Table 1;
- 3) provide the information to support development of a commercial item description (CID) for future diesel fuel procurements.

APPROACH

Under this project, low sulfur diesel fuel (LSDF) delivery samples were obtained from selected CONUS military installations and analyzed according to a predetermined testing protocol. The first set of samples was obtained during the summer of 1994. The second set of samples was obtained during the first three months of 1995. The fuel samples were representative of fuel deliveries to selected CONUS military facilities and were taken from delivery vehicles at the time of delivery. Each of the fuel samples was analyzed for the properties listed in Table 2.

ANALYTICAL RESULTS AND DISCUSSION

A total of 112 fuel samples were received and analyzed. Table 3 is a complete listing of the test results for these fuels. Table 4 contains descriptive statistics for each of the properties. Discussions of the results, along with frequency histograms for selected properties, follow.

Total Sulfur – Figure 1 is a frequency histogram of the total sulfur data. Nine of the samples exceeded the 0.05 mass% sulfur, maximum specification limit. The samples that failed the sulfur requirement were from installations in Alaska.

Accelerated Stability – Figure 2 is a frequency histogram of the accelerated stability data. Only two of the samples failed to meet the specification requirements for accelerated stability. This is not unexpected since the great majority of these fuels are refinery fresh or very nearly so.

Particulates – Figure 3 is a frequency histogram of the particulates data. Two of the samples failed to meet the 10 mg/L particulates requirement. Like the stability results, this very low failure rate is expected since these are refinery fresh fuels. These data also indicate that the delivery systems being used for these fuels are, in general, kept clean.

Cetane Number – Figure 4 is a frequency histogram of the cetane number data. Only two of the samples tested had cetane numbers below 40 and both of those were 39. The high value was 59 and the average was 49.

Other Properties – For several of the fuel properties, the analytical results are divided into two groups of data. These two groups of data correspond to the two fuel grades, 1 and 2, of the samples. Properties of this type include total aromatics, kinematic viscosity, cloud point, freeze point, pour point, and density.

Lubricity -- HFRR and Scuffing Load Wear Test – Figure 5 is a frequency histogram of the High Frequency Reciprocating Rig (HFRR) data. Figure 6 is a frequency histogram of the U.S. Army Scuffing Load Wear Test (SLWT) results.

Currently, the HFRR and the SLWT are the two most accepted bench tests for diesel fuel lubricity. The factors that influence the lubricity and associated fuel system component wear are numerous, and the interactions are complex. These factors include temperature, vehicle use rates, metallurgy

of fuel system components, additives, age/condition of engine, environmental conditions, and composition and properties of the fuel. Of these factors, the one that is probably least understood is fuel composition. Ongoing research has recently addressed this issue.^{4,5,6} It has been suggested that reductions in the levels of sulfur or aromatics have contributed in some way to the decreased lubricity often associated with low sulfur diesel fuel. Fuel viscosity has also been suggested as having a correlation with lubricity. Figures 7 through 12 are plots of the HFRR and SLWT data versus total sulfur, total aromatics, and viscosity. It is obvious from these plots that only the viscosity data have any apparent correlation with the lubricity tests, and this is only slight.

Figure 13 is a plot of the HFRR data versus the SLWT data. The least squares regression fit is also plotted. The correlation of these two sets of data is also low. The correlation coefficient is -0.62 .

Specific statistics as to how many of the samples failed to meet the proposed Army lubricity requirements are difficult because some of the samples were received without fuel grade information. If one makes an assumption that viscosity is a reliable indicator of fuel grade, then some general statistics are possible. There are six fuels which fall at 2.0 kg or below in the SLWT and six fall at 0.54 mm or above on the HFRR. These six fuels would be considered failed, regardless of the fuel grade, and require additive treatment. The fuels that are at or above 2.8 kg (at or below 0.34 mm for the HFRR), regardless of grade, are considered unconditional pass and may be used without concern. It is the fuels that fall between these two lines, 2.0 and 2.8 for the SLWT (0.84 and 0.38 for the HFRR), that must be evaluated according to their fuel grade. The fuels which have viscosities of less than 1.6 and scuffing loads of greater than 2.0 (less than 0.54 for the HFRR) would be considered light kerosene fuels with potentially acceptable lubricity. Fuels with viscosities of greater than 2.9 and scuffing loads of less than 2.8 (greater than 0.34 for HFRR) would be considered grade number 2 fuels with potentially unacceptable lubricity. It is recommended that the users of any fuel, with a SLWT result of less than 2.8, more closely monitor their vehicles for signs of accelerated fuel system component wear.

Approximately 10% of the fuels are in the category of unconditional fail. These fuels require additive treatment with an approved additive and monitoring vehicles for signs of abnormal wear.

Approximately 66% of the fuels are considered unconditional passes. The remaining approximately 25% would have to be considered on the basis of their fuel grade and vehicles operating on these fuels should be monitored more closely for startability, idle roughness, driveability and other symptoms that could be related to fuel injection system/component wear.

During this survey, the individual installations were asked to report instances of unusually high wear rates in fuel lubricated fuel system components or other fuel related problems. The only reports received were of apparent fuel lubricity problems. Eight installations reported this type of fuel related problem, unfortunately fuel samples were not available from all of these sites. Efforts were made to confirm the cause of the wear with mixed results. Based on the correlation to pump stand tests, resulting from the early work of the ISO/SAE task force to develop a lubricity test, it is believed that vehicles operating on less than acceptable lubricity fuel will have reduced life from fuel-lubricated components. The degree and rate of wear will depend on several factors. And even though the Army is more likely to operate any given vehicle on the same fuel for extended periods of time, Army overall use rates are relatively low. This is why it is difficult to obtain direct evidence of abnormal, wear caused by low lubricity fuel, except in the cases of extremely poor lubricity fuel. It has been the Army's experience thus far that the fuel system component wear rates are usually high enough to be noticeable only when the lubricity of the fuel is below 2.0 kg; primarily those below 1.6 kg.^{7,8}

CONCLUSIONS

- The average fuel falls within the D 975 specification limits for ASTM Grade Low Sulfur D-2.
- The samples that had sulfur levels above the EPA limit of 0.05 mass % had properties consistent with those of aviation kerosene. While it could not be confirmed, these samples may have been JP-8. Since these samples were from Alaska (Ft. Richardson and Ft. Wainwright) where kerosene fuels are used year-round, this is probably the case.
- Ft. Richardson, Ft. Wainwright, Dobbins AFB, and Malmstrom AFB appear to be receiving kerosene type fuel, even during the warmest months of the year when these samples were taken.

- The samples from Ft. Bragg and Ft. Irwin both show poor accelerated stability characteristics, and hence, would not meet the military requirements.
- Only two samples were outside the fuel particulate content limits for military use.
- It is difficult to draw specific conclusions regarding the cloud point results. Cloud point specifications are both regional and monthly; and, we cannot be certain of the actual month of purchase of the fuels. However, throughout this survey we received no reports of waxing problems. It is concluded that, in general, the fuel being delivered to U.S. military installations meets the military cloud point requirements.
- There is no apparent correlation of scuffing load from either SLWT or HFRR data with BOCLE, sulfur, aromatics, or viscosity at 40°C. This is important since it means that none of these properties can be used to estimate the scuffing load (i.e., lubricity) of a given fuel. Also, there appears to be only a minimal relationship between the SLWT and HFRR results.
- Regarding the lubricity results, approximately 10% of the fuels are in the category of unconditional fail. These fuels require additive treatment with an approved additive and monitoring vehicles for signs of abnormal wear. Approximately 66% of the fuels are considered unconditional passes. The remaining approximately 25% would have to be considered on the basis of their fuel grade and vehicles operating on these fuels should be monitored more closely for startability, idle roughness, and driveability.
- None of the JP-8 fuels met the proposed minimum scuffing load requirement of 2.8 kg for grade 2-DLS and only 3 of the fuels met the minimum SLWT of 2.0 recommended for JP-8.
- The sulfur values for the JP-8 fuels tended to be higher than those for the LSDF.
- Approximately 85% of the JP-8 fuel met the MIL-T-83133 specification requirement of 0.65 mm

maximum wear scar on the standard BOCLE, D 5001.

- All of the JP-8 fuel samples met the MIL-T-83133 specification requirement for aromatics, 25 mass % maximum.

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Table 1. Specification Requirements of VV-F-800D and D 975

Property	ASTM Method	VV-F-800D Grade DF-2	D 975 Grade Low Sulfur 2D
Visual Appearance	D 4176	Clean & Bright	Clean & Bright
Density, kg/L	D 1298	Report	NR
Flash Point, °C	D 93	52,min	52, min
Cloud Point, °C	D 2500	Local	Local
Pour Point, °C	D 97	Report	NR
K. Vis, mm/s ² at 40°C	D 445	1.9 - 4.4	1.9 - 4.1
Distillation, °C	D 86		
50% evap		Report	NR
90% evap		338,max	282 - 338
End Point		370,max	NR
Residue, vol%		3.0,max	NR
Carbon Residue, 10 % Bottoms, mass %	D 524	0.35, max	0.35, max
Sulfur, mass %	D 4294	0.5, max	0.05, max
Copper Strip Corrosion	D 130	3, max	3, max
Ash, mass %	D 482	0.01, max	0.01, max
Accelerated Stability, mg/100 mL	D 2274	1.5, max	NR
TAN, mg KOH/g	D 974	0.10,max*	NR
Particulate Contamination, mg/L	D 2276	10.0, max	NR
Cetane Number	D 613	40, min	40, min
In D 975: One of the following properties must be met: (1) Cetane Index (2) Aromaticity, % vol.	D 976 D 1319	NR NR	40, min 35, max

Table 2. Low Sulfur Diesel Fuel Analyses

Property	Units	Test Method*
Fuel Lubricity, Wear Scar Diameter	mm	High Frequency Reciprocating Rig (proposed ISO and ASTM test method)
Fuel Lubricity, Scuffing Load	kg	U.S. Army Scuffing Load Wear Test (proposed ASTM test method)
Ball-On-Cylinder Lubricity Evaluator, Wear Scar Diameter	mm	D 5001†
Sulfur	mass %	D 4294
Aromatic Hydrocarbons, mono-, di-, tri-, and total	mass %	D 5186
Kinematic Viscosity at 40°C	mm ² /sec	D 445
Cloud Point	°C	Automatic Tester
Freeze Point	°C	Automatic Tester
Pour Point	°C	D 97
Accelerated Stability, Total Insolubles	mg/100 mL	D 2274
Particulate Contamination	mg/L	Modified D 5452
Density at 15°C	g/mL	D 4052

* A more complete description of the U.S. Army Scuffing Load Wear Test is found elsewhere.⁹

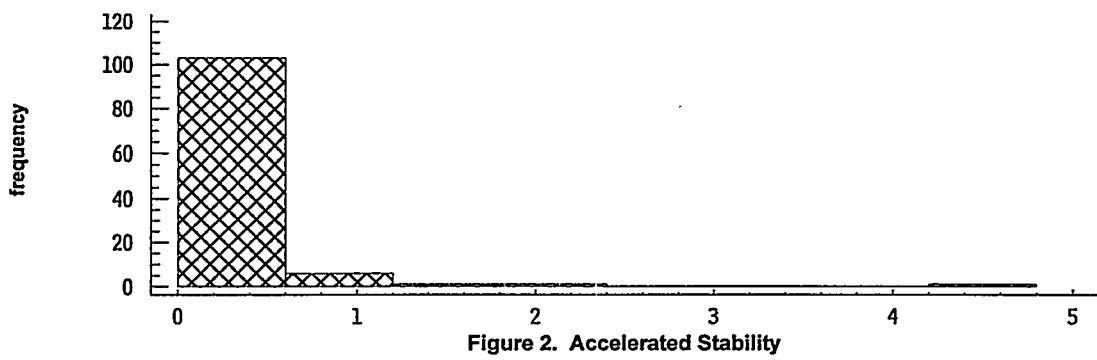
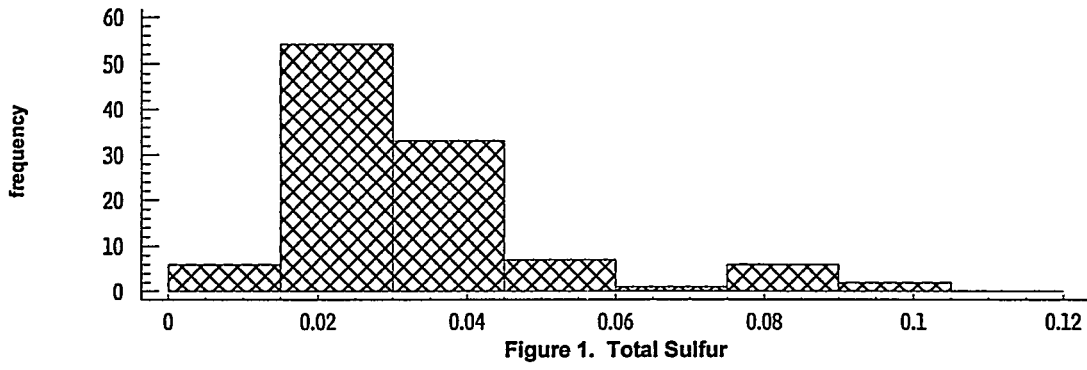
† Test methods beginning with D refer to ASTM standards found in Volume 5 of the Book of Standards.

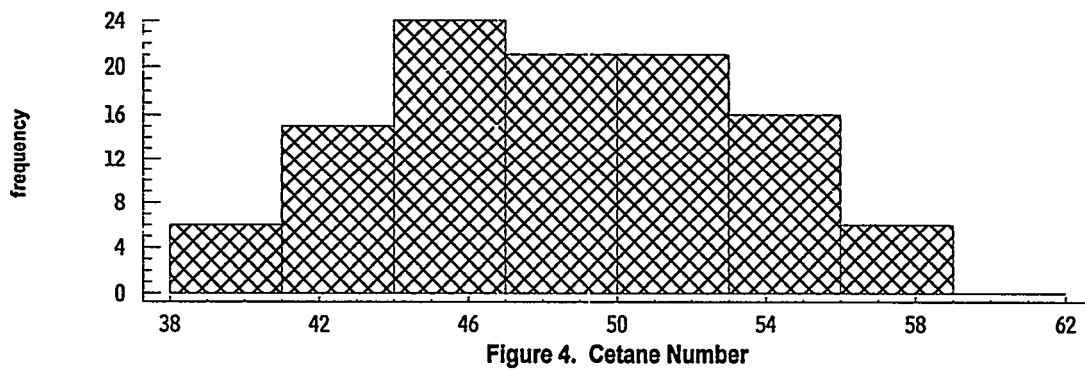
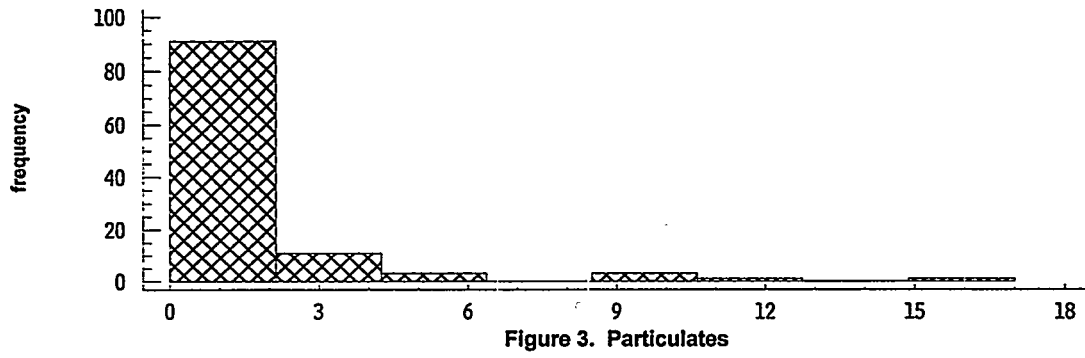
Table 3. Fuel Analysis Data

Fuel I.D.	Cetane Number	HFRR, mm	Scuff Load, g	BOCLE, mm	Sulfur, mass %	Mono-Arom	Di-Arom	Tri-Arom	Total Arom	Vis. 40C cSt.	Cloud Pt,C	Freeze Pt, C	Pour Pt, C	Acc. Stab., mg/100mL	Part. mg/L	Density D-4052
22059	50.5	0.22	2500	0.67	0.03	23.6	6.2	1.6	31.4	3.46	-8.4	-4.3	-12	0.17	9.0	0.8592
22132	56.1	0.22	3800	0.56	0.01	11.1	1.5	0.4	13.0	2.96	-13.2	-8.9	-12	0.21	4.7	0.8387
22239	58.7	0.25	4600	0.57	0.02	15.9	3.0	0.9	19.8	4.05	-2.6	-1.0	-6	0.38	1.6	0.8401
22410	50.1	0.20	4300	0.54	0.03	24.5	6.8	1.3	32.6	2.56	-12.4	-9.6	-15	0.28	1.5	0.8474
22413	42.8	0.23	3800	0.60	0.04	29.0	11.4	2.4	42.8	2.65	-19.8	-17.3	-21	1.39	1.1	0.8660
22419	57.0	0.29	3900	0.57	0.05	11.7	3.3	0.7	15.7	3.13	-4.6	1.4	-6	0.40	2.4	0.8280
22439	47.5	0.17	4000	0.60	0.04	27.6	8.2	2.2	38.0	3.16	-9.0	-5.4	-15	0.74	2.8	0.8666
22440	54.0	0.27	4300	0.54	0.02	16.5	2.8	0.9	20.2	2.55	-22.5	-19.3	-39	0.08	6.0	0.8310
22441	52.4	0.21	4600	0.52	0.03	24.6	7.2	1.3	33.1	2.60	-13.4	-9.8	-18	0.16	3.1	0.8484
22460	54.5	0.24	3000	0.66	0.03	21.6	3.9	0.7	26.2	2.34	-14.3	-9.7	-21	0.80	2.6	0.8321
22461	54.2	0.25	3500	0.56	0.04	22.5	9.0	1.5	33.0	2.51	-12.8	-10.0	-18	0.90	15.4	0.8448
22462	53.7	0.23	3100	0.60	0.03	26.2	7.6	1.2	35.0	2.81	-11.6	-7.9	-15	4.30	1.3	0.8542
22475	50.3	0.24	3600	0.59	0.04	26.8	6.2	1.7	34.7	3.19	-10.8	-7.8	-12	0.60	1.9	0.8605
22478	58.2	0.23	3600	0.56	0.01	18.4	3.3	0.9	22.6	3.15	-8.9	-3.3	-9	2.00	1.0	0.8459
22488	50.5	0.21	3200	0.57	0.04	25.4	11.1	1.7	38.2	3.00	-11.3	-10.0	-15	0.50	9.6	0.8588
22492	45.6	0.16	2800	0.64	0.03	25.0	5.2	1.2	31.4	2.86	-8.2	-4.8	-12	0.70	2.1	0.8522
22502	55.4	0.22	3200	0.48	0.02	15.0	3.0	0.8	18.8	2.47	-15.2	-11.5	-18	1.20	1.7	0.8401
22503	55.5	0.23	2500	0.53	0.02	18.6	3.6	0.8	23.0	2.57	-9.6	-7.0	-12	0.30	4.2	0.8423
22639	54.5	0.23	2400	0.58	0.02	16.1	3.2	0.9	20.2	4.02	-2.8	1.5	-6	1.10	5.7	0.8401
22641	53.3	0.15	4500	0.61	0.03	24.6	5.6	1.4	31.6	3.38	-12.3	-6.1	-12	0.30	2.6	0.8602
22698	55.0	0.25	3100	0.61	0.02	23.6	6.7	1.2	31.5	2.73	-13.7	-9.9	-17	<0.10	1.0	0.8447
22709	53.5	0.20	2500	0.60	0.03	26.3	8.5	1.8	36.6	2.95	-11.3	-6.8	-13	<0.10	1.8	0.8553
22710	49.5	0.50	1900	0.62	0.03	30.5	4.0	0.9	35.4	2.06	-18.4	-17.0	-23	0.20	2.4	0.8400
22721	50.6	0.53	3000	0.57	0.04	24.9	8.3	1.1	34.3	2.37	-15.7	-14.2	-21	0.20	2.0	0.8465
22748	54.5	0.21	2200	0.60	0.04	26.2	9.4	1.9	37.5	3.05	-11.0	-6.0	-12	0.10	1.1	0.8573
22751	46.6	0.30	2000	0.54	0.09	14.9	3.9	0.2	19.0	1.34	-52.3	-46.7	-48	<0.10	0.8	0.8115
22752	52.7	0.21	3700	0.55	0.03	23.2	5.2	1.0	29.4	2.38	-15.5	-13.0	-20	0.50	1.3	0.8417
22894	51.2	0.21	2800	0.59	0.03	25.7	11.3	2.0	39.0	3.13	-11.4	-9.9	-17	0.10	0.9	0.8613
22895	57.0	0.23	2800	0.51	0.02	15.2	2.2	0.5	17.9	2.52	-9.2	-6.6	-19	0.20	1.7	0.8380
22896	49.5	0.20	3500	0.59	0.04	26.8	8.9	1.6	37.3	2.70	-14.5	-9.7	-15	0.30	0.7	0.8552
22921	47.6	0.20	2100	0.61	0.03	30.0	6.6	1.3	37.9	3.13	-9.9	-6.9	-13	0.20	0.7	0.8652
22940	48.9	0.26	3100	0.60	0.03	27.2	8.1	1.2	36.5	2.59	-19.5	-15.5	-15	0.30	0.8	0.8516
22946	49.4	0.59	2600	0.59	0.02	18.1	2.5	0.4	21.0	1.49	-43.2	-43.4	-41	0.10	0.8	0.8118
22971	51.2	0.23	3200	0.58	0.02	23.4	4.8	1.0	29.2	3.17	-11.1	-7.4	-22	0.20	1.1	0.8536
22982	41.2	0.35	2400	0.49	0.08	19.9	3.4	0.5	23.8	1.23	-58.6	-51.7	-53	0.10	0.8	0.8125
22983	58.2	0.27	2600	0.52	0.04	12.9	4.6	0.8	18.3	2.50	1.3	6.6	-5	0.30	1.7	0.8278
23000	—	0.20	3600	0.58	0.03	25.9	8.2	2.4	36.5	2.81	-13.3	-10.1	-19	<0.10	1.2	0.8571
23009	44.7	0.71	1300	0.80	0.01	21.6	1.5	0.3	23.4	1.49	-48.6	-44.5	-43	<0.10	0.4	0.8150
23338	49.7	0.39	3800	0.62	0.04	25.6	6.9	1.4	33.9	3.41	-9.5	-5.9	-24	0.10	0.8	0.8639
23390	47.9	0.37	3600	0.61	0.04	25.5	7.9	1.3	34.7	2.66	-13.4	-10.4	-30	0.10	0.8	0.8527
23392	53.2	0.18	4200	0.54	0.05	12.7	5.0	0.4	18.1	2.60	-7.3	-3.2	-15	0.20	12.4	0.8323
23396	42.9	0.42	1800	0.55	0.10	15.7	4.0	0.1	19.8	1.32	-52.8	-46.5	-60	0.30	0.4	0.8114
23402	45.7	0.65	1700	0.65	0.03	18.4	2.5	0.1	21.0	1.53	-48.2	-43.8	-66	<0.10	0.5	0.8178
23411	42.7	0.70	1200	0.94	<0.01	18.0	0.6	<0.1	18.6	1.28	<-75	<-76	-87	<0.10	0.4	0.8069
23415	42.4	0.42	2100	0.53	0.08	20.1	3.5	0.1	23.7	1.22	-53.8	-52.0	-75	<0.10	0.5	0.8125
23437	48.7	0.46	4600	0.61	0.03	27.6	8.5	1.6	37.7	2.89	-13.3	-9.6	-24	<0.10	0.4	0.8583
23442	47.8	0.39	4600	0.61	0.03	26.5	5.0	0.8	32.3	3.02	-13.6	-10.6	-24	0.10	2.3	0.8612
23496	48.3	0.45	4300	0.61	0.03	27.1	7.9	1.4	36.4	2.86	-13.1	-9.9	-27	0.10	0.4	0.8560

23507	47.4	0.61	2400	0.56	0.02	18.1	2.3	0.1	20.5	1.51	-47.5	-43.6	-60	0.10	1.7	0.8138
23508	54.4	0.25	3600	0.46	0.03	13.4	3.9	0.5	17.8	2.06	-20.2	-15.8	-39	<0.10	3.6	0.8151
23509	48.5	0.40	3900	0.60	0.03	26.5	7.8	1.0	35.3	2.64	-14.5	-12.1	-24	<0.10	1.2	0.8500
23516	48.3	0.30	4400	0.61	0.03	27.1	8.7	1.7	37.5	3.09	-13.4	-10.0	-24	<0.10	0.6	0.8647
23521	51.9	0.36	2700	0.54	0.02	17.8	2.2	0.2	20.2	2.27	-8.2	-3.6	-18	0.10	1.1	0.8378
23526	53.7	0.49	2200	0.65	<0.01	17.2	3.8	0.7	21.7	3.64	-9.9	-7.3	-21	0.20	0.7	0.8428
23529	49.6	0.49	3800	0.61	0.04	25.7	10.7	1.3	37.7	3.04	-11.2	-8.3	-21	0.20	0.7	0.8577
23539	49.3	0.37	2200	0.55	0.02	15.4	3.5	<0.1	18.9	1.43	-47.9	-45.6	-60	0.10	0.4	0.8098
23540	46.0	0.49	2950	0.62	0.04	30.0	6.6	0.6	37.2	2.09	-15.8	-12.5	-27	<0.10	0.8	0.8422
23556	48.5	0.49	4250	0.63	0.03	27.7	8.6	1.4	37.7	2.76	-13.7	-10.4	-27	<0.10	1.0	0.8554
23557	53.1	0.29	2800	0.56	0.03	15.5	4.7	0.8	21.0	3.59	-20.4	-17.4	-27	0.10	0.6	0.8455
23571	50.3	0.42	4200	0.56	0.03	26.7	8.7	1.5	36.9	2.74	-12.4	-9.5	-24	<0.10	1.0	0.8550
23759	50.4	0.37	5400	0.60	0.03	25.1	4.5	0.6	30.2	3.25	-14.7	-10.0	-18	0.20	1.8	0.8578
23843	49.4	0.38	4300	0.62	0.03	24.8	5.9	0.8	31.5	3.19	-10.5	-7.6	-18	0.20	1.5	0.8553
23851	47.5	0.68	2300	0.59	0.02	19.0	2.0	<0.1	21.0	1.48	-49.3	-45.0	-63	0.10	0.5	0.8141
23984	46.4	0.72	1400	0.63	0.04	17.4	1.2	0.1	18.7	1.20	-57.5	-53.1	-75	0.10	0.6	0.7943
23988	49.6	0.74	1500	0.63	0.08	17.3	1.1	0.1	18.5	1.15	-55.4	-51.3	-72	<0.10	1.0	0.7888
23989	51.2	0.71	1600	0.60	0.04	17.3	1.1	0.1	18.5	1.20	-53.3	-53.2	-66	<0.10	0.8	0.7958
24051	50.9	0.71	1800	0.59	0.05	15.2	2.0	0.0	17.2	1.26	-46.6	-47.0	-60	0.30	0.7	0.8003
24053	46.6	0.73	1700	0.62	<0.01	18.7	1.2	0.0	19.9	1.26	-66.5	-66.1	<-78	0.10	0.8	0.8185
24093	51.5	0.68	1700	0.59	0.04	15.2	2.4	0.3	17.9	1.24	-53.3	-47.5	-69	0.30	0.8	0.7998
24095	53.6	0.34	3300	0.49	0.03	14.8	3.6	0.2	18.6	1.73	-27.7	-26.3	-42	0.20	0.5	0.8129
24103	50.9	0.71	1400	0.78	0.03	21.2	1.8	0.1	23.1	1.42	-52.8	-49.2	-60	0.20	0.4	0.8102
24134	50.6	0.71	2000	0.57	0.06	18.7	1.8	0.1	20.6	1.18	-55.9	-55.7	-72	0.20	1.5	0.7969
24143	50.1	0.47	2400	0.54	0.02	16.2	3.3	0.1	19.6	1.38	-55.3	-51.0	-66	0.10	0.7	0.8102
24147	45.7	0.48	3900	0.57	0.03	24.9	9.0	1.4	35.3	2.72	-14.8	-11.1	-24	0.10	0.9	0.8512
24253	52.6	0.28	4150	0.57	0.03	16.5	5.4	1.0	22.9	3.21	-20.3	-16.4	-30	0.20	2.0	0.8433
24260	43.9	0.26	3700	0.61	0.04	23.0	8.1	1.4	32.5	2.52	-13.7	-11.1	-24	0.20	1.1	0.8478
24282	41.3	0.19	4400	0.55	0.04	24.9	9.2	1.8	35.9	2.93	-14.5	-10.6	-24	0.20	0.3	0.8580
24284	44.6	0.71	1200	0.80	0.01	22.2	0.9	<0.1	23.2	1.29	-52.4	-54.8	-66	0.10	0.9	0.8047
24293	46.0	0.20	4400	0.55	0.04	25.2	9.1	1.8	36.1	2.93	-13.7	-9.5	-21	0.30	2.8	0.8576
24310	47.0	0.67	1900	0.57	0.04	19.8	2.5	0.1	22.4	1.37	-45.8	-37.3	-63	0.20	0.8	0.8098
24317	44.6	0.63	2600	0.51	0.03	26.5	8.9	0.9	36.3	2.80	-12.8	-11.7	-24	0.30	1.8	0.8100
24323	45.7	0.43	4550	0.57	0.03	26.1	8.8	1.5	36.4	2.74	-15.2	-27.0	-12	0.20	1.7	0.8529
24326	43.3	0.67	1950	0.57	0.05	19.7	2.5	0.1	22.3	1.37	-42.6	-30.7	-63	0.20	0.8	0.8096
24329	40.4	0.60	2050	0.70	0.03	19.6	2.9	0.1	22.6	1.58	-48.2	-57.0	-43	0.10	0.6	0.8179
24330	42.9	0.22	4250	0.51	0.04	25.1	8.3	1.8	35.2	2.95	-13.1	-9.5	-21	0.20	0.8	0.8546
24331	39.2	0.40	2700	0.54	0.09	20.4	3.8	0.1	24.3	1.22	-51.2	-51.5	-69	0.10	0.8	0.8121
24353	48.8	0.27	3500	0.57	0.04	14.4	4.8	0.7	19.9	2.72	-20.2	-15.8	-27	0.20	0.6	0.8318
24361	40.6	0.71	2200	0.55	<0.01	22.2	1.4	0.1	23.7	1.24	-44.1	-31.8	-69	0.20	0.8	0.8040
24364	43.3	0.39	3350	0.62	0.04	26.2	4.6	0.7	31.5	3.32	-13.3	-8.4	-21	0.20	1.2	0.8579
24365	44.5	0.28	3850	0.58	0.04	25.4	7.3	1.3	34.0	2.66	-13.9	-10.5	-21	0.20	1.3	0.8475
24366	—	0.21	3400	0.52	0.04	15.9	4.4	0.2	20.5	1.77	-33.7	-29.5	-42	0.20	8.9	0.8135
24367	46.5	0.67	1700	0.55	0.05	19.7	2.5	0.1	22.3	1.37	-46.0	-39.4	-63	0.20	1.0	0.8097
24368	40.6	0.23	2100	0.51	0.03	22.7	1.3	0.1	24.1	1.40	-50.2	-45.9	-60	0.20	1.2	0.8111
24369	40.6	0.36	1200	0.81	0.03	22.9	1.2	0.1	24.2	1.40	-47.9	-45.2	-57	0.20	0.6	0.8106
24371	46.5	0.59	2600	0.57	0.02	18.6	2.4	0.1	21.1	1.53	-47.7	-43.7	-57	0.20	0.7	0.8169
24373	39.3	0.43	2200	0.53	0.1	20.1	4.0	0.1	24.2	1.23	-49.0	-50.9	-66	0.10	0.2	0.8132
24375	42.9	0.66	1900	0.67	0.03	19.5	3.0	0.1	22.6	1.56	-47.4	-41.6	-54	0.10	0.0	0.8179
24376	44.0	0.64	1750	0.58	0.06	19.1	2.4	0.1	21.6	1.36	-40.5	-32.4	-63	0.20	0.8	0.8091
24378	45.2	0.32	4450	0.59	0.04	25.6	8.9	1.8	36.3	2.59	-12.0	-9.1	-27	0.20	1.0	0.8513
23244	50.3	0.65	2300	0.58	0.09	19.0	2.2	0.2	21.4	1.39	-53.0	-49.0	-63	—	—	—

24379	43.7	0.28	4500	0.58	0.04	25.8	8.2	1.7	25.7	2.77	-13.4	-10.3	-21	0.20	2.5	0.8546
24380	44.5	0.28	4250	0.56	0.03	25.2	8.5	2.1	35.8	3.05	-14.7	-10.9	-24	0.30	0.8	0.8621
24383	—	0.20	4000	0.57	0.03	16.4	5.6	1.0	23.0	3.66	-24.7	-20.4	-30	0.10	0.9	0.8496
24385	45.8	0.38	4200	0.58	0.04	26.2	12.1	1.8	40.1	2.92	-9.4	-6.7	-21	0.10	0.6	0.8579
24386	44.7	0.72	1800	0.63	0.01	21.0	2.4	0.1	23.5	1.33	-49.6	-42.3	-63	0.10	<0.1	0.8086
24387	43.4	0.31	4350	0.55	0.04	27.5	9.2	1.8	38.5	2.66	-13.3	-9.8	-24	0.10	2.0	0.8555
24388	46.6	0.67	1600	0.56	0.07	18.8	2.6	0.1	21.5	1.37	-43.5	-38.4	-60	0.10	0.9	0.8094
24391	42.5	0.45	4500	0.57	0.04	28.3	8.9	1.6	38.8	2.70	-11.8	-9.2	-21	0.10	0.7	0.8553
24393	45.7	0.60	2050	0.60	0.04	20.8	6.1	0.7	27.6	1.80	-24.0	-20.6	-42	0.10	0.3	0.8298
24405	44.9	0.68	1900	0.70	0.02	18.3	1.8	0.1	20.2	1.36	-38.5	-25.0	-60	0.20	0.8	0.8060
24431	44.8	0.39	3650	0.58	0.04	25.1	8.8	1.5	35.4	2.70	-13.4	-9.8	-21	0.10	0.7	0.8520
24459	52.8	0.21	5450	0.57	0.04	24.9	7.9	1.5	34.3	2.82	-13.2	-9.1	-21	0.20	1.3	0.8553





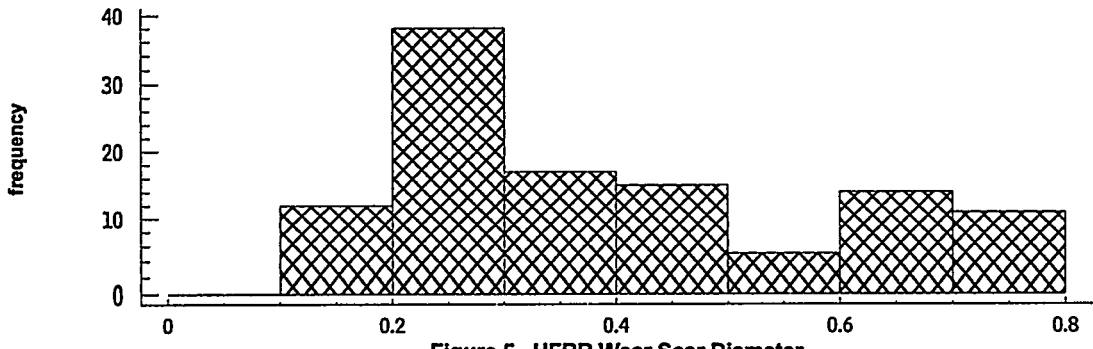


Figure 5. HFRR Wear Scar Diameter

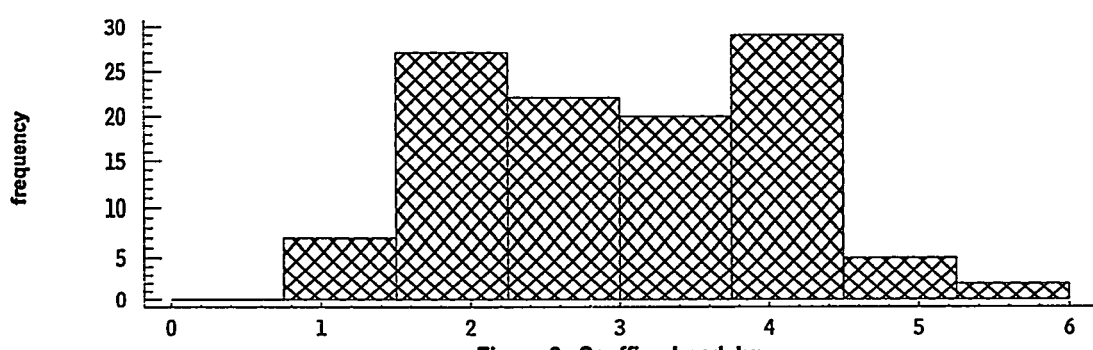


Figure 6. Scuffing Load, kg

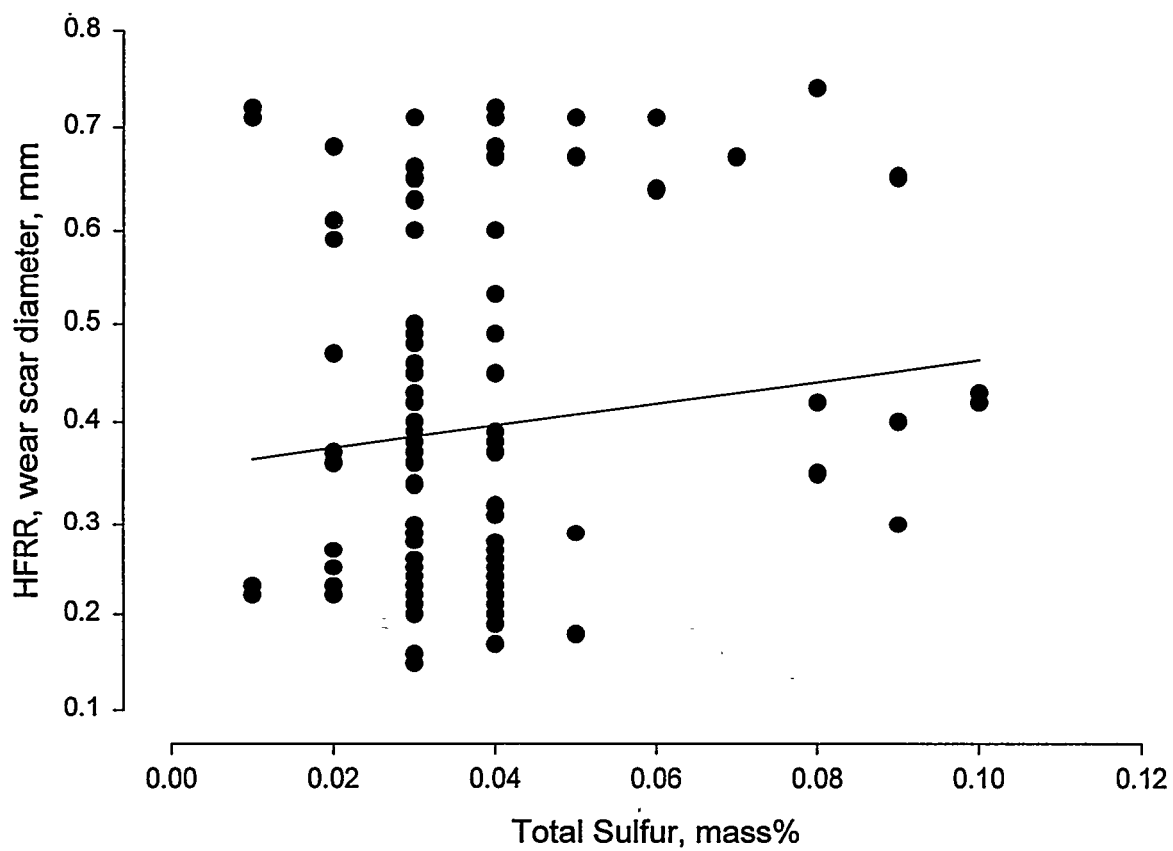


Figure 7. HFRR vs Total Sulfur

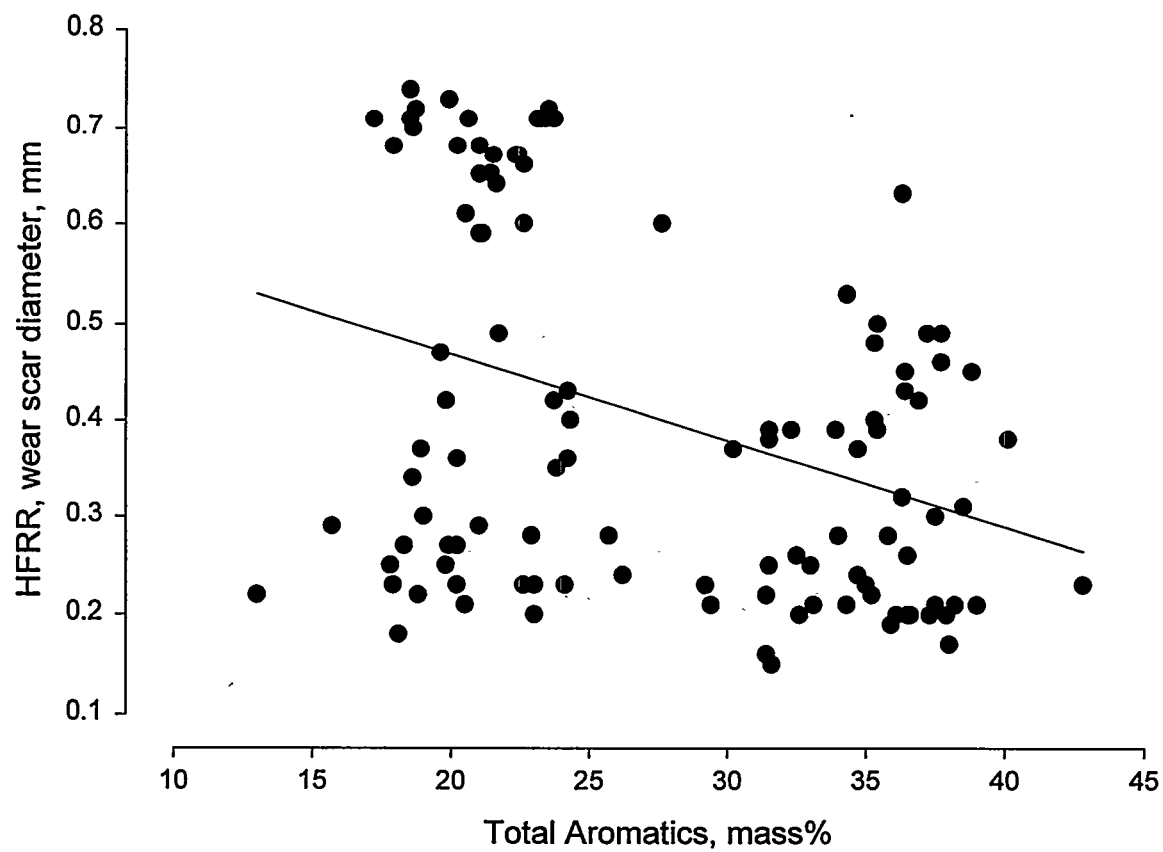


Figure 8. HFRR vs Total Aromatics

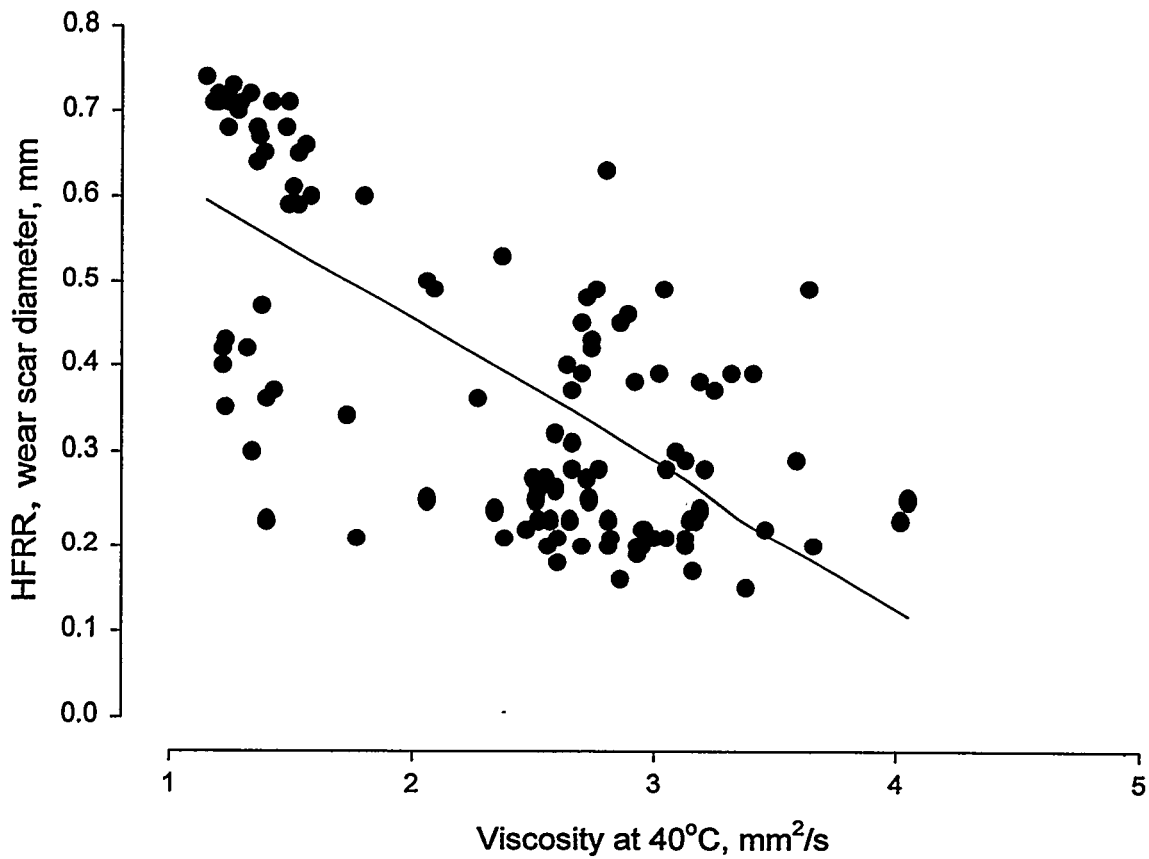


Figure 9. HFRR vs Viscosity at 40°C

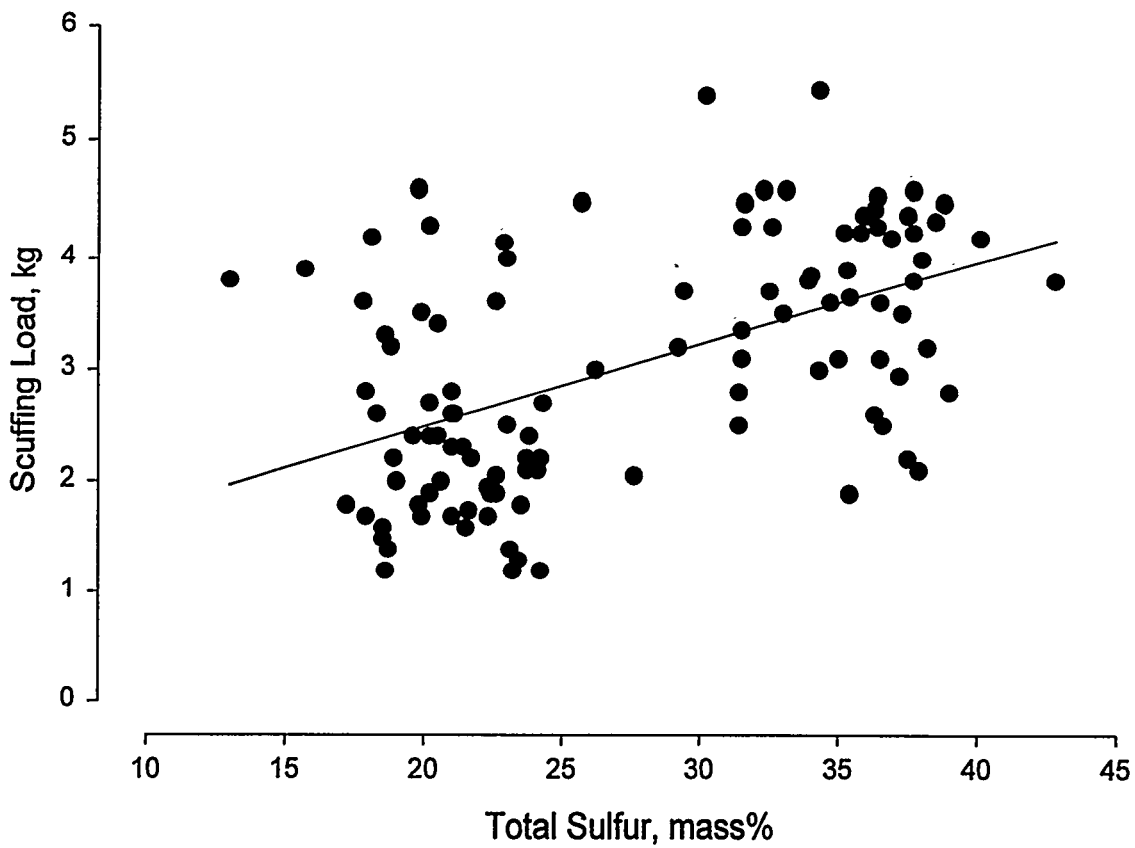


Figure 10. Scuffing Load vs Total Sulfur

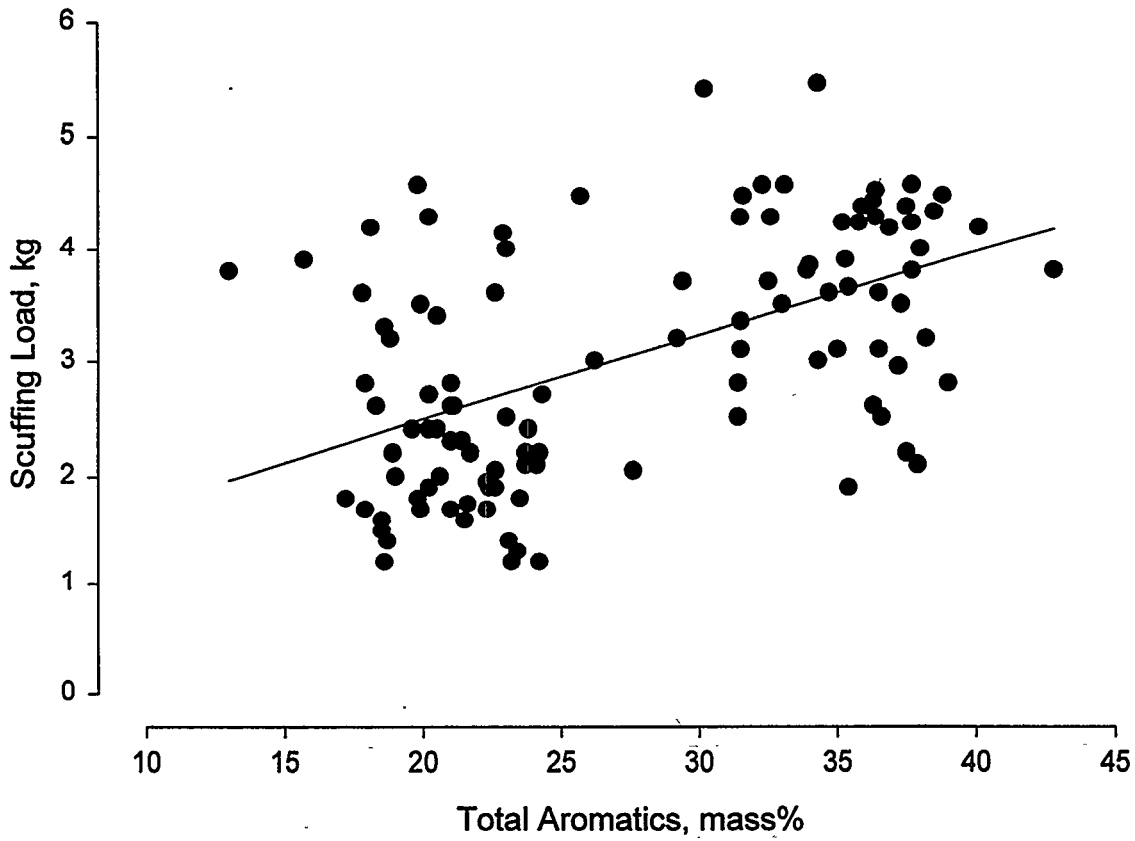


Figure 11. Scuffing Load vs Total Aromatics

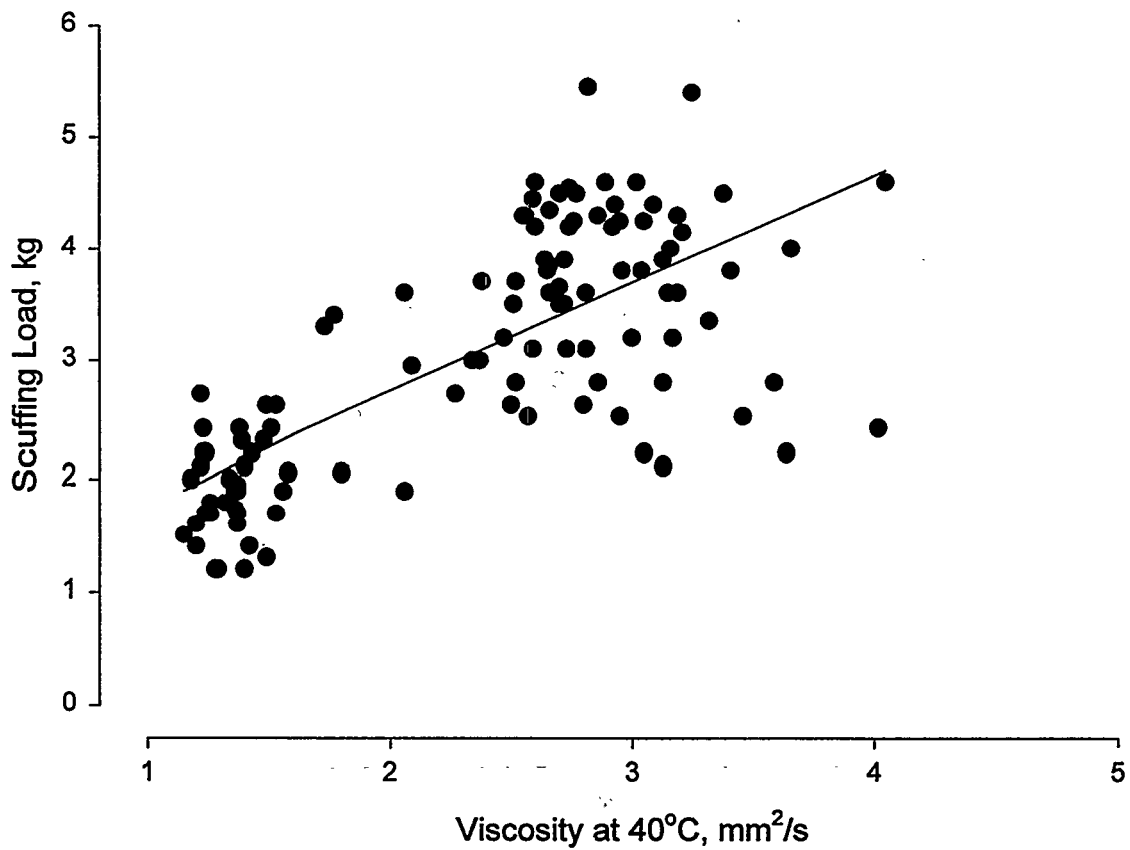


Figure 12. Scuffing Load vs Viscosity at 40°C

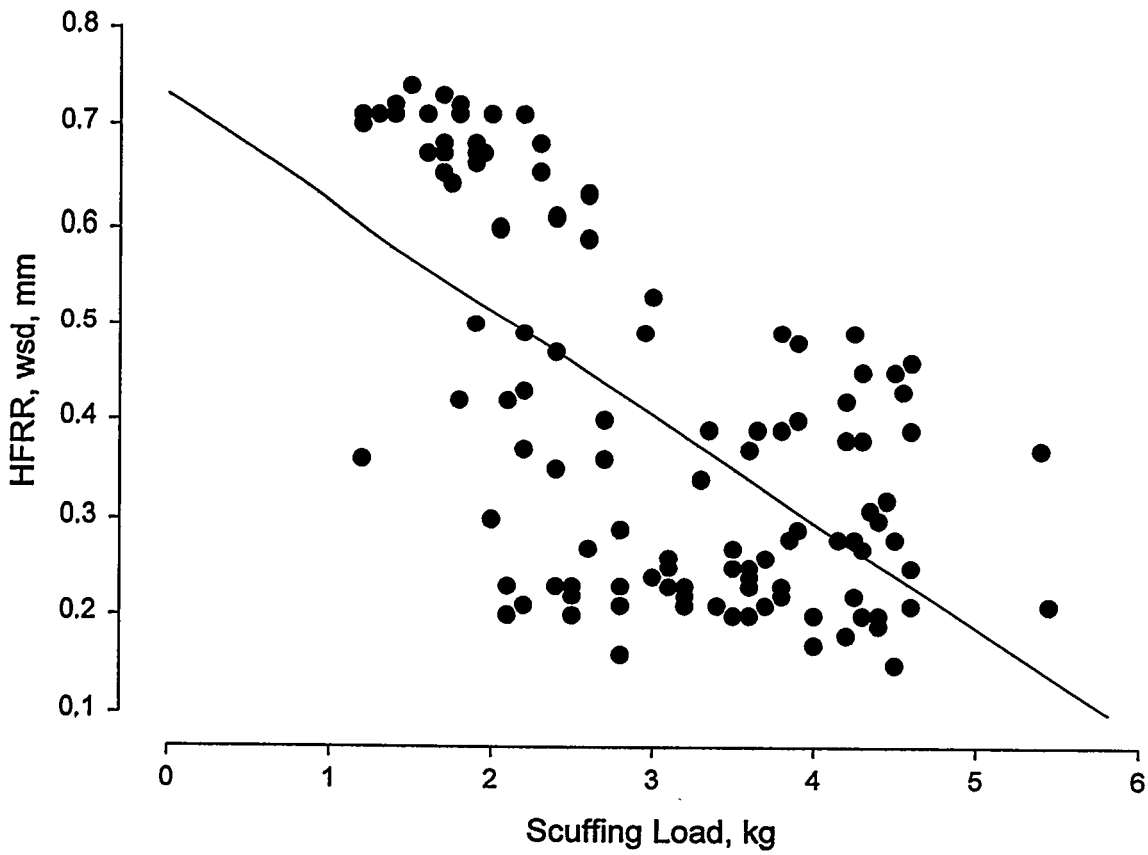
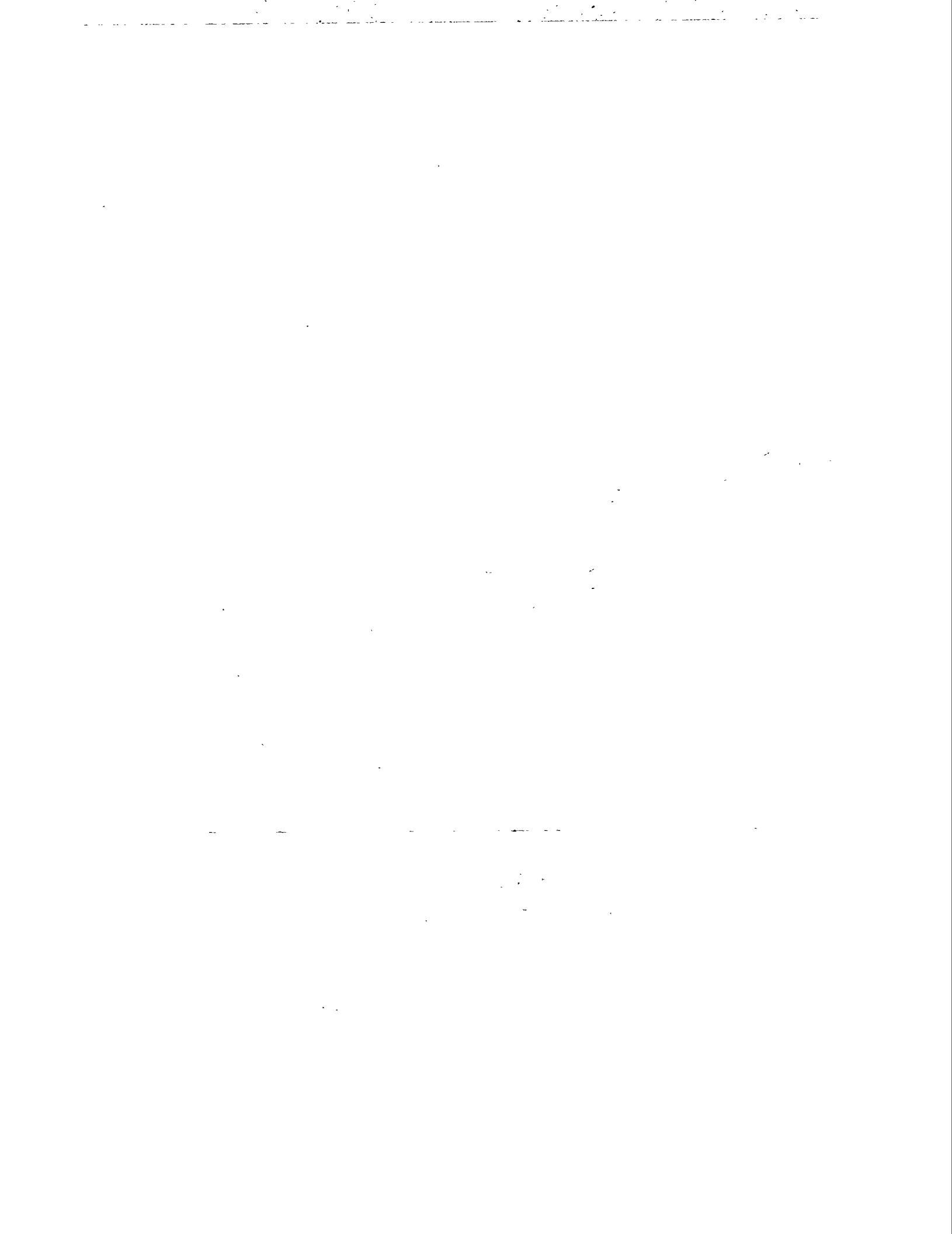


Figure 13. HFRR vs Scuffing Load



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on Stability and Handling of Liquid Fuels***

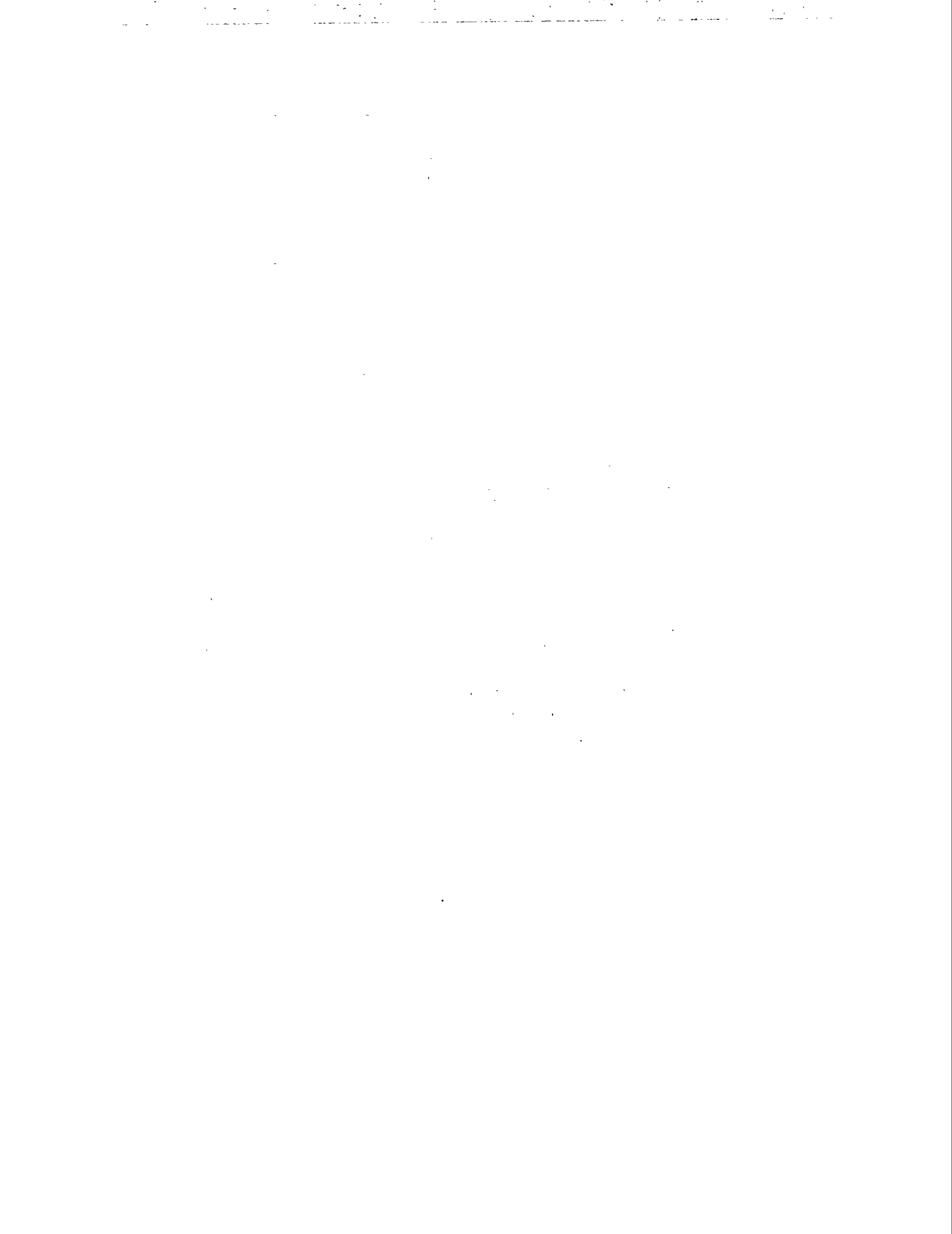
Vancouver, B. C., Canada
October 12-17, 1997

**RECENT DEVELOPMENTS IN THE PRODUCTION OF STABLE FUEL OIL FROM H-OIL
PROCESS BOTTOMS**

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The H-Oil Process, a commercial ebullated-bed process licensed by HRI, Inc a subsidiary of IFP Enterprises, is used to convert and upgrade heavy petroleum residue. In the H-Oil Process, typically 50 to 75 percent of the vacuum residue in the feedstock is converted to distillates. The remaining, unconverted atmospheric or vacuum residue can be utilized in traditional bottoms outlets such as coker feed, resid FCCU feed, feed to a hydrogen generation unit or fluxed with distillates and sold as a No. 6 fuel oil. Many new H-Oil Licensees, with existing markets for fuel oil, have designated that the unconverted bottoms be used to produce a heavy fuel oil product. The use of heavier, more sour crudes, coupled with more stringent specifications for saleable fuel oil has made the production of stable, high quality fuel oil a difficult challenge. With six operating or planned commercial H-Oil Plants producing heavy fuel oil from the unconverted bottoms, HRI/IFP has taken the lead and initiated a high level of research and development in the area of fuel oil blending. The results of this R&D are discussed in this paper and have greatly increased the understanding of and subsequent utility of the blended fuel oil product from the H-Oil Process.



6th International Conference
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THE ELIMINATION OF COLOR IN KEROSENE FRACTION DERIVED FROM DURI AND
MINAS CRUDE OIL MIXTURE BY EXPOSURE TO LIGHT

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ABSTRACT

Kerosene derived from a mixture of Duri and Minas crude oils 70:30 changes color during storage. The color develops rapidly, few hours after distillation.

Ageing of distillates obtained by a narrow cut TBP distillation of the crude mixture in the range of kerosene showed that the color precursors in the kerosene were distributed in all the distillates.

Sun light treatment on the colored kerosene showed that the treatment can eliminate or reduce the color considerably. Sun light treatment on the fresh kerosene developed color at the beginning, but then after reaching peak the color began to disappear. Light treatment using an incandescent lamp showed similar results, but the effect occurred more slowly.

It seems that the colorless color precursors in the fresh kerosene distillate changes into colored compounds during the storage which is then converted into colorless compounds after being exposed to light.

Apart from the change or the elimination of the color, the data of the kerosene characteristics showed that most of the properties of the untreated and treated kerosene were very similar.

INTRODUCTION

The consumption of kerosene in Indonesia tends to increase every year. To meet the need for kerosene in particular and fuels in general, one of the policies taken by the Indonesian Government is to increase the production capacity of the existing refineries and to construct new refineries. Balongan Refinery of Unit Pengolahan VI Pertamina is one of the new refineries. The refinery is designed for a feed comprising Duri crude oil and Minas crude oil, with a ratio of 80:20 by volume.

Duri crude oil is a heavy crude with API gravity of 21.4 and classified as naphthenic-

intermediate having a pour point of 70°F. Minas crude is a medium crude with API gravity of 35.5 and classified as paraffinic-intermediate having a pour point of 100°F¹.

The kerosene produced by this refinery is a combination of a kerosene stream coming from a crude distilling unit and a kerosene stream coming from a hydrogen cracking unit. In general, the properties of the kerosene produced by Balongan Refinery meet the kerosene specification issued by the Indonesian Directorate General of Oil and Gas², but viewed from the point of view of color, the kerosene is not stable and does not meet the criteria. The instability of the kerosene, the change of the appearance from colorless to colored, takes place rapidly during storage. The color of the kerosene, measured by Lovibond cell 18", may go beyond 2.50.

Visual observation of the kerosene derived from Duri-Minas crude oil showed that it was the kerosene stream coming from the crude distilling unit that underwent colorization to become yellow to greenish-yellow in few hours after distillation. The kerosene stream coming from the hydrogenation cracking unit, on the other hand, is colorless and relatively stable.

Some of the common methods used to eliminate color, or to increase the stability of fuels to resist the formation of color, include acid washing³ and zeolite absorption⁴. The method used at present by Balongan Refinery to increase the stability of the kerosene towards color formation is to pass the kerosene into a column packed with clay. The treatment is sufficiently effective, where the treated kerosene has very good stability. But the use of the clay brings about a problem, because the clay has to be replaced every 12 days, leading to the accumulation of spent clay which can cause pollution.

The observation of the kerosene stored for a long time showed that the fresh colorless kerosene became colored and reached a peak rapidly and then gradually lost color very slowly over a long time. Storage in a room in a condition that illuminated by a light seems to accelerate the color reducing process.

Due to the tendency to change color from colorless into colored and then back to colorless or to a considerably reduced level of color, a study was carried out to see the effect of light treatment on the kerosene to accelerate these processes.

EXPERIMENTAL

Storage of kerosene samples

The kerosene samples were put into 500 mL transparent blue cap bottles. The bottles intended for dark storage were wrapped with Al-foil, while the bottles intended for light storage were not. For room storage at ambient temperature, the samples were allowed to stand for the desired period. For storage under the sun light exposure, the samples were allowed to stand directly under light outdoor for the desired period. For storage under incandescent light, the samples stood under the light of an incandescent lamp for the desired period.

The separation of color from the colored kerosene

The extraction of color with sulfuric acid was carried out by mixing 100 mL of colored kerosene with 10 mL H_2SO_4 (70%). The acid layer was separated and added with 40 mL of H_2O and was extracted with 20 mL dichloromethane. The addition of water and dichloromethane was repeated until the acid layer was colorless. Dichloromethane extract was then washed with water to remove residual acid and dried with $CaCl_2$. The dichloromethane was then removed by evaporation.

The extraction of color with methanol was carried out by mixing 40 mL of colored kerosene with 20 mL methanol. The methanol layer was separated and the methanol was evaporated.

The extraction of color with clay was carried out by the addition of 0.8 g clay into 200 mL colored kerosene. The clay was separated and washed with 2 x 5 mL hexane to remove residual kerosene. The clay was then extracted with dichloromethane and methanol.

Kerosene specification measurement

The measurement of kerosene specification was based on kerosene specification issued by Indonesian Directorate General of Oil and Gas², including properties such as specific gravity (ASTM D1298), Lovibond color (IP-17), smoke point (ASTM D1322), distillation (ASTM D86), Flash point Abel (IP-170) and Copper strip (ASTM-D130). Nitrogen and sulphur measurement were carried out by Dhorman (ASTM D4629) and sulphur X-ray analysis (ASTM D4294) respectively.

RESULT AND DISCUSSION

Visual observation on the kerosene samples at ambient storage

Visual observation of the change of the color of kerosene derived from the distillation of the 70:30 Duri-Minas crude oil mixture stored in the blue cap bottles wrapped with Al-foil at ambient temperature showed that the colorless fresh kerosene underwent colorization to become yellow in one day after distillation. The color developed further on standing to a greenish yellow.

From Table 1, it can be seen a comparison of the Lovibond color scale of a stable commercial kerosene and a Duri-Minas kerosene which has been stored for a month in Al-foil wrapped blue cap bottles. It can be seen that the commercial kerosene has the color scale 1 while the Duri-Minas kerosene has a color scale >4.

Further observation on the change of the color of Duri-Minas kerosene kept in transparent blue cap bottles and stored in a room at ambient temperature showed that the fresh kerosene which was initially colorless changed into colored, which then slowly lost the color again.

From Table 1, it can also be seen the difference of the Lovibond color scale between a Duri-Minas kerosene kept in a transparent blue cap bottle and a Duri-Minas kerosene kept in a blue cap bottles wrapped with Al-foil, stored for a month in a room under light exposure. It can be seen that the Duri-Minas kerosene exposed to light has a color scale of 1 while the Duri-kerosene wrapped in Al-foil has a color scale >4.

Observation of the color formation in several Duri-Minas crude oil mixtures

Minas crude oil has been known to have good stability. To see the extent of the effect on the change of the color for the addition of Duri crude oil to Minas crude oil, an observation of the color on various Duri-Minas crude oil mixtures was made. The kerosene samples were kept in Al-foil wrapped blue cap bottles stored in a room at ambient temperature. The results are shown in Table 2. It can be seen that the content of 10% Duri in the mixture has an effect on the color. On the first day the Lovibond color scale reaches 3.5 and decreases to 2.5 on the second day and decrease to L2,5 on the third day and stays at scale L2,5 until the fourteenth day. On the mixture with 20% Duri, the color scale decreases to 2.5 on the fifth day and to L2,5 on the seventh day, while for the mixture with 70% Duri, the color stays at 3.5 until the fourteenth day. It is evident that the more

Duri crude oil in the mixture the longer the duration of the presence of color in excess of the specification limit.

Storage of distillate fractions of Duri-Minas kerosene

Ten distillates obtained by a narrow cut TBP distillation of the crude mixture in the range of kerosene, which are all colorless, were stored without exposure to light. The storage of the distillates showed that all the distillates (Table 3) underwent color change after one day storage at ambient temperature. This indicates that color precursors are present in the whole boiling point curvature of the kerosene.

The combination of all the colored distillate fractions back into one kerosene fraction, followed by a distillation in accordance with the ASTM D86 method showed that the color remains as a residue in the last distillate fraction. This gives an indication that the color precursors, which are initially colorless and are present in the whole boiling point curvature plot, after being colored, have higher boiling points. The change of the boiling point is possibly caused by such a reaction as polymerization or condensation leading to the formation of higher molecular weight molecules, or the occurrence of the rearrangement of atoms in the molecules leading to the formation of molecules having higher boiling points.

Direct exposure of kerosene to light

Visual observation on the change of color of the kerosene stored in transparent blue cap bottles under direct exposure to sun light outdoor (Table 4) showed that the kerosene, which initially had a Lovibond color scale of 1, rapidly reached a color scale of more than 4 after five minutes and the color then decreased again to color scale 4 after fifty-five minutes. It then gradually decreased to 1 after about three hours. The same thing happened to fresh colorless kerosene. The kerosene started to become yellow after two minutes and reached greenish yellow in about a quarter of an hour; the color then disappeared or become considerably reduced after three hours.

Visual observation on the change of the color of colored kerosene stored in transparent blue cap bottles under direct exposure to the light of incandescent lamps (Table 5) showed that exposure under 40 and 25 watt incandescent lamps has the effect of eliminating or reducing color, but this effect took place more slowly than exposure to direct sunlight. A kerosene sample which initially has

a Lovibond cell 10mm color scale of about 0.75, decreased to 0.25 after eight days exposure to a 40 watt incandescent lamp and to 0.25 after nine days exposure to a 25 watt incandescent lamp. Exposure of the kerosene samples under 15 and 10 watt incandescent lamps up to sixteen days reduced the color only to the color scale of 0.5.

It can be seen that the storage of fresh kerosene which is colorless initially (condition A) will undergo a change of color into greenish yellow (condition B) which further undergoes the elimination or the reduction of the color (condition C). The colorization-decolorization process is accelerated by light.

The change of color caused by the exposure to light is presumed to be the result of a photochemical reaction of sequence of reactions. The change from colorless color precursors (condition A) into colored compounds (condition B) and back to considerably colorless compounds (condition C) indicated that the colorless color precursors at condition A is not identical with the colorless compounds at condition C, because the colorless compounds at condition C are relatively stable, while the colored compounds at condition B are intermediate compounds linking the change of the colorless color precursors at condition A into colorless compounds at condition C. The mechanism of the colorization-decolorization possibly covers the rearrangement of the molecule and/or such a reaction leading to the formation of other compounds having higher molecular weight.

Kerosene specification tests on the kerosene samples

The result of specification tests carried out on the kerosene samples comprising clay treated kerosene, colored kerosene, and the colored kerosene after being exposed to the sun light until its color considerably reduced is shown in Table 6.

From Table 6, it can be seen that generally, apart from the color, all three kerosenes meet the criteria of kerosene specification. Viewed from the color, the use of light to overcome the color problem in kerosene then offers a much cheaper treatment which at the same time ecologically friendly.

The separation of color from kerosene

Treatment with sulfuric acid, 70% by weight, on both the fresh and colored Duri-Minas kerosene can extract the color. Treatment with the acid reduces the color very well, from >4.0 to

1.0 in Lovibond 18" scale . Fraytet³, in his experiment on a jet fuel sample reported that treatment with sulfuric acid could eliminate and stabilize the color and could separate about 90% of nitrogen compounds. The determination of nitrogen and sulfur content on the fresh Duri-Minas kerosene in this experiment showed that the kerosene contained about 21 ppm nitrogen and 178 ppm sulfur, while the determination of the nitrogen and sulfur content on the colored kerosene after treatment with clay showed that the kerosene contained about 7 ppm nitrogen and 165 ppm sulfur. There were about 14 ppm nitrogen and 13 ppm sulfur lost together with the color being separated from the colored kerosene.

Basic treatment with NaOH to separate the color compounds from the colored kerosene did not work well. The treatment is carried out by mixing 100 mL colored kerosene sample with 10 mL NaOH, 7.1M. This experiment indicated that the colored compounds are not acids.

Treatment with methanol on the colored Duri-Minas kerosene could also extract the color. The treatment also reduced the color very well. Sharma and Agrawal⁵ in his experiment on middle distillate samples also reported that treatment with methanol reduced color.

The separation of the color with acid and methanol gives an indication that the color in the colored kerosene is both basic and polar.

Conclusion

The change of the color in Duri-Minas kerosene derived from a crude distilling unit is not constant. The change from colorless kerosene into colored kerosene takes place very quickly, while the change from colored kerosene into colorless or less colored kerosene takes place more slowly. For a colored mixture of Duri-Minas, 70:30, the presence of color with the Lovibond scale in excess of the criteria of the specification stays longer than for mixtures containing a higher proportion of Minas. The change from colored kerosene into colorless or less colored kerosene can be accelerated by light.

Storage of ten distillates obtained by a narrow cut TBP distillation of the Minas crude oil mixture in the range of kerosene showed that the color precursors are present in all fractions. The combination of all the colored distillates into one kerosene fraction followed by the redistillation of the fraction showed that the color remained in the residue.

The color in the kerosene can be separated by extraction with acid, extraction with methanol and absorption with clay. Extraction with acid and methanol showed that the color compounds are basic and polar. The determination of nitrogen and sulphur content in the fresh kerosene and colored kerosene after being treated with clay to eliminate the color from the kerosene showed that about two thirds of the nitrogen content present in the kerosene and about one tenth of sulphur content present in the kerosene took part in the formation of the color.

Apart from the change or the elimination of the color, the data of the kerosene characteristics showed that most of the properties of the untreated and treated kerosene are considerably the same.

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2. Direktorat Jenderal minyak dan gas bumi-DPE, Data dan Informasi Minyak, Gas dan Panas Bumi 1985-1990, Edisi pertama, Jakarta, 1991.
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4. Ellis, J., Korth, J., Removal of Nitrogen Compounds for Hydrotreated Shale Oil by Adsorption on Zeolite, *Fuel*, **73**, 10, 1569-1573, 1994.
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Table 1: Room storage at ambient temperature for 1 month

No.	Sample	Storage condition	Color (Lovibond cell 18")
1	Commercial kerosene	Wrapped with Al-foil	0.75
2	Duri-Minas Kerosene	Wrapped with Al-foil	> 4
3	Duri-Minas Kerosene	Not wrapped with Al-foil	1.00

Table 2: The effect of crude oil composition on the change of the color of kerosene stored in a room at ambient temperature in blue cap bottles wrapped with Al-foil

Day	Composition of crude oil (Duri:Minas)				
	10:90	20:80	30:70	50:50	70:30
1	3.5	3.5	3.5	3.5	3.5
2	2.5	3.5	3.5	3.5	3.5
3	L2.5	3	3.5	3.5	3.5
4	L2.5	3	3.5	3.5	3.5
5	L2.5	2.5	3	3.5	3.5
6	L2.5	2.5	3	3.5	3.5
7	L2.5	L2.5	2.5	3.5	3.5
8	L2.5	L2.5	2.5	3.5	3.5
9	L2.5	L2.5	2.5	3	3.5
10	L2.5	L2.5	L2.5	3	3.5
11	L2.5	L2.5	L2.5	3	3.5
12	L2.5	L2.5	L2.5	2.5	3.5
13	L2.5	L2.5	L2.5	2.5	3.5
14	L2.5	L2.5	L2.5	2.5	3.5

Table 3: The color of distillate fractions derived from a colorless fresh kerosene and a colored kerosene one day after storage

Fraction	Cutting temperature (°C)	Colorless fresh kerosene	Colored kerosene
1	164-176	Colored	Colorless
2	176-181	Colored	Colorless
3	181-185	Colored	Colorless
4	185-190	Colored	Colorless
5	190-196	Colored	Colorless
6	196-200	Colored	Colorless
7	200-205	Colored	Colorless
8	205-212	Colored	Colorless
9	212-220	Colored	Colorless
10	220-227	Colored	Colored

Table 4: The change of the color of Duri-Minas (70:30) kerosene on the exposure to sun light

No.	Duration of exposure (minutes)	Color (Lovibond cell 18")
1	0	1
2	5	4
3	10	>4
4	55	>4
5	60	4
6	90	3
7	140	2
8	180	1

Table 5: The change of the color of Duri-Minas (70:30) kerosene on the exposure to the light of incandescent lamps

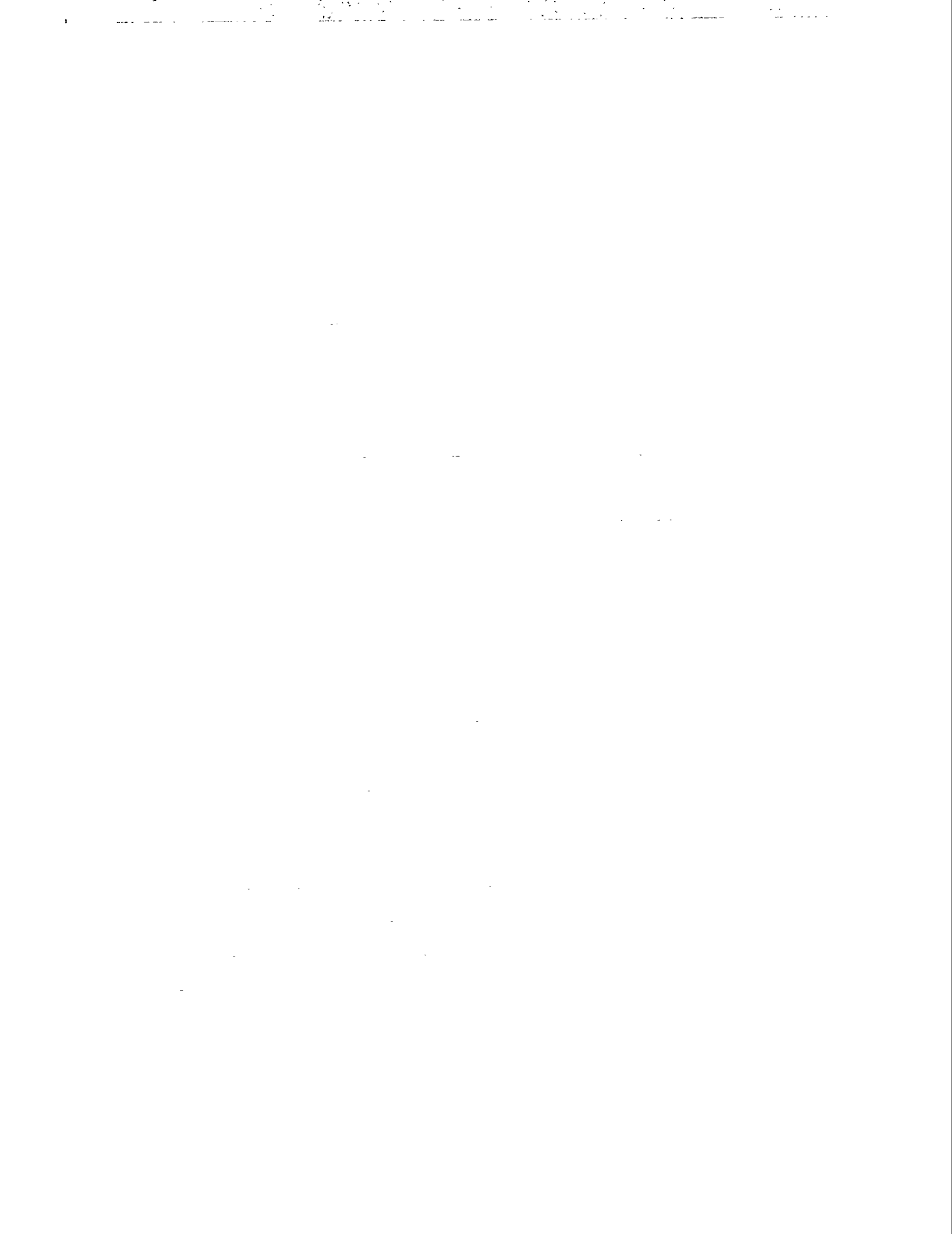
No.	Time (Day)	Color (Lovibond cell 10mm)			
		40 watt	25 watt	15 watt	10 watt
1	0	0.75	0.75	0.75	0.75
2	1	L0.75	L0.75	L0.75	L0.75
3	2	0.5	L0.75	L0.75	L0.75
4	5	L0.5	0.5	0.5	0.5
5	6	L0.5	L0.5	0.5	0.5
6	8	0.25	L0.5	0.5	0.5
7	9	0.25	0.25	0.5	0.5
8	16	0.25	0.25	0.5	0.5

Table 6: Specification test on Duri-Minas kerosene

Properties	specification		Kerosene sample		
	Minimum	Maximum	KAC	KB	KC
Specificgravity 60/60°F	-	0.835	0.8056	0.8066	0.8036
Color Lovibond cell 18"	-	2.50	0.75	>4.00	1.00
Smoke point mm	16	-	23	23	22
Distillation					
distillate at 200°C % vol.	18	-	55	55	60
Final boiling point, °C	-	310	245	244.5	243
Flash point Abel	100	-	120.5	124	123
Sulphur content % wt.	-	0.20			
Copper strip (2 hours/100°C)	-	1	1a	1a	1a

KAC = kerosene after clay treatment; KB = colored kerosene

KC = kerosene after being exposed to sun light



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on Stability and Handling of Liquid Fuels
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**DEVELOPMENT OF FIELD ANALYTICAL PROCEDURES FOR
BETZDEARBORN SPEC•AID™ 8Q462, A JET FUEL THERMAL STABILITY
ADDITIVE**

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Abstract:

The United States Air Force proposes to change the specification for jet fuels to include a thermal stability additive. This change in specification requires a method for rapid determination of the presence of the additives. Field usable analytical procedures to determine the presence of the additive above a threshold concentration and others capable of providing semi-quantitative determination of the concentration of BetzDearborn's SPEC•AID™ 8Q462 have been developed and will be discussed.

Introduction:

Modern jet fuels are formulated to meet differing fuel specifications. A given base fuel may be modified with additive package to meet the different fuel specifications, (e.g., Jet A, JP5 or JP8). The JP8 +100 program is designed to extend the thermal stability of the fuel meeting the JP8 specification. Field testing of the JP8+100 jet fuel has pointed out its effectiveness as a fuel, but has also pointed at difficulties in handling the fuel with the existing fuel delivery system. The special handling requirements and the need to control the evaluation have created a demand for analytical procedures to determine the presence of the +100 thermal stability additive, SPEC•AID 8Q462, in jet fuels. The objective of the test development program is to develop a field test procedure that is at least capable of determining if the concentration of SPEC•AID 8Q462 in jet fuel is above 10 ppm. Ideally, the test procedure will provide quantitation within 10 ppm. The

test procedure should be viable in a field environment, and be simple enough to be performed by inexperienced personnel. Any instrumentation required for the test should be commercially available at a modest cost. The target analyte is a mixture of several surface and chemically active components dissolved in a hydrocarbon solvent. The JP8+100 stability additive qualification procedure is lengthy and expensive, which ruled out simple fixes such as adding a unique dye to the formulation.

A chemical analyst would begin the search for a new analytical procedure by analyzing the novelty of the analyte. For the SPEC•AID 8Q462, one would ascertain if there was chemical functionality that could be distinguished from the fuel matrix. This chemical functionality might be chemical functional groups, or it might be overall elemental composition. The active ingredient that imparts the +100 thermal stability to JP8 is a proprietary surfactant¹. For purposes of illustration, we may use the soap pictured in Figure 1. The important features of the soap are the existence of a polar headgroup and a hydrocarbon tail. The hydrocarbon tail is essentially indistinguishable from the fuel matrix, so the analyst is left with the polar headgroup as the analytical tag. Even this can be problematic in that a modern aviation fuel contains several surface active agents which may contain functional groups similar to that found in the analyte. This is not the case for the thermal stability additive in SPEC•AID 8Q462, but the polar headgroup does represent a minor part of the molecule. An analytical technique targeting the unique constitution of the polar headgroup must therefore be extremely sensitive in order to achieve the target product detection limits. Workers at Pratt & Whitney² have developed an ICP method for determining the concentration of SPEC•AID 8Q462 in jet fuel. The method requires expensive instrumentation and skilled operators to achieve a detection limit of 30 ppm. The method is not suitable for field use and would be difficult to locate outside an analytical laboratory environment.

An alternative approach to chemical analysis has been suggested by BetzDearborn's professional analytical staff³, (*i.e.*, to focus on the nature of the hydrocarbon tail of the surfactant). The hydrocarbon tail doesn't include unusual bonds or heteroatoms, but it is based on a man made polymer. The products of the pyrolytic degradation of the hydrocarbon tail rarely form in the pyrolysis of naturally occurring

organic compounds. The main pyrolyzate is isobutylene, which is detected by gas chromatography. The detection limit of the method is determined by the amount of isobutylene produced from pyrolysis of the base fuel; sample chromatograms are seen in Figure 2. Detection limits using this technology are ca. 15 ppm SPEC•AID 8Q462, but optimization of the technique should be able to improve the limits of detection. This technique is in principle field portable, though it requires a trained and competent analyst. This technique probably is useful as a reference technique, but not as a field technique. An alternative strategy for evaluating the concentration of an analyte in a fluid is to determine the concentration response of a property imparted to the fluid by the additive. The downside of this approach is that there may be other materials which can affect the response of this property and, therefore, the analytical test may not be as selective as one would desire. An obvious choice for a thermal stability additive, such as SPEC•AID 8Q462, would be to measure the thermal stability of the fuel. We did not deem this a practical choice because the apparatus and time involved (hours) would be inappropriate for a field test. We chose to focus on the surfactant properties of SPEC•AID 8Q462. Several of the problems associated with the handling of the JP8+100 fuel are direct consequences of the powerful surfactancy of the additive (*e.g.*, interference with the test for undissolved water in aviation turbine fuel (ASTM D-3240) and disarming of the water coalescer). Further, it is well known that small concentrations of surfactant materials can dramatically change the surface related properties of fluids⁴. The surfactant is a very good dispersant, and is particularly effective at dispersing metal oxides. We chose optical scattering as a probe of dispersion, and measured it using a simple hand-held, single-beam fixed wavelength instrument⁵. Even after deciding on a strategy, there are many technical obstacles which must be overcome, before the technique can be deployed to the field.

Experimental Section:

The +100 additive, SPEC•AID 8Q462, is a powerful dispersant. We propose to use this dispersancy to indirectly detect the additive. Our strategy is to add a small

amount (100mg/14mL of fluid) of a solid, jet fuel insoluble material to the jet fuel, mix to generate a dispersion, separate the poorly dispersed solid by centrifugation, and then to use optical absorption measurements on the fluid portion to measure turbidity. In this test, turbidity is related to the concentration of SPEC•AID 8Q462. It was discovered during the development of the test procedure, that a second reagent, acetone, was necessary to counteract the dispersant properties of extraneous surfactants present in the jet fuels. The required quantity of the second reagent varied with jet fuel performance specification.

The experimental protocol for preparing the dispersion and then settling the non-dispersed particles is extremely important to the test procedure. Great care was exercised in design of an experimental protocol that could be largely instrumented so that the actual operator has little effect on the outcome of the test. The dispersion is reproducibly created by using a timed (5 minutes) Speco rotator, and both the speed (850 rpm) and time (5 minutes) of centrifugation is controlled. A Hach pocket digital colorimeter, with a fixed wavelength of 528 nm which has been modified to read in raw counts, is used to make the optical loss measurement. Because optical scattering is the actual physical measurement, the physical characteristics of the dispersed medium are extremely important and are tightly controlled. Further reagents, tube sizes and types are all specified in the protocol, which is graphically presented in Figure 3.

Discussion:

The first important task was to find a good metal oxide to use as a dispersible reagent. The wide variety of clays and aluminosilicates was the focus of our early work. Unfortunately we discovered that dispersion of the clays afforded little discrimination between the surfactant of interest and the other surfactants present in the fuel. This was not the case however for iron oxide (Fe_2O_3). Iron oxide was relatively poorly dispersed in fuel containing all of the additive package except the +100 additive and there was a marked change in the optical density as a function of additive concentration. The change was distinct enough that it was visible to the naked eye, Figure 4. Unfortunately, more results quickly showed just how sensitive the test results were to small changes in the test

procedure. We found that even with timed mixing in a shaker box and a standardized centrifugation procedure, we had significant variability between test sets. Our centrifuge had six positions for tubes, so a test set consisted of six concentrations of additive in fuel from a given source. We observed significant variability on a given fuel, Figure 5, and even more of a variation between fuels, Figure 6. The variation could not be accounted for with the mass of iron oxide used in a given test. Further, if the same samples were repeatedly cycled through the protocol, the measured optical density steadily increased (Figure 7). The increased optical density observed with repeated cycling of a given sample through the test correlated very highly with mixing severity (either time of mixing or mixing method), higher optical densities were also obtained in single tests when smaller iron oxide particle sizes were used. We concluded that part of the problem was the friability of the iron oxide particles. When the mixing was replaced with a very gentle mixing protocol, a much improved reproducibility within a given fuel sample was obtained (the change in mixing protocol also required a change in the centrifugation procedure).

The variability between fuels was a more complex issue. Protocol changes, which improved the reproducibility within a fuel, only served to refine the basic difference between fuels of the same specification but from different sources. Significantly, fuel from a given source had a different response curve that depended on the additive package (Jet A, JP5 or JP8) present in the fuel sample. We concluded that the interaction between the surface active agents in the fuels (naturally occurring or from the additive package) were interfering with the measurement. There were two possible approaches, a) renew our search for a dispersed material that was uniquely dispersed by our analyte, or find a second reagent that would modify the surfactant tendencies of the fuel/additive combination, so that the contribution of the extraneous (for our purposes) surface active agents would be masked. A second reagent was found, which reduced the variability between fuels significantly. JP5 and JP8 fuels responded nearly the same after addition of the second reagent, but the Jet A fuel packages require a separate response curve (Figures 8,9).

It was hypothesized that the nature of this test would be strongly affected by temperature. Toward that end, experiments were performed at higher and lower temperatures. Our low temperature experiments were performed at a temperature of 30 °F and the initial high temperature measurements were performed at 100 °F outside in the heat and humidity of Houston, Texas. The results are presented in Figure 10. The low temperature experiments had a different response curve, but the high temperature experiment showed uniform results at all additive concentrations. Test results did not vary when the reagents were returned to the laboratory environment and allowed to cool.

When fresh reagents were used, test results were within normal variation. An experiment was performed in an environmental chamber at an elevated temperature, but at controlled humidity. These results are presented in Figure 10. Temperature does appear to affect the test results, but apparently high humidity can seriously invalidate the test.

Conclusions:

A simple technique has been developed to determine the concentration of SPEC•AID 8Q462 in jet fuel. Under laboratory conditions it appears capable of detecting the thermal stability additive down to a concentration of 25 ppm (as SPEC•AID 8Q462). There are several possible problems with this field analysis technique:

- 1) It is indirect and may be fooled.
- 2) High relative humidity seems to invalidate the test.
- 3) The ability of a vendor to supply consistent quality reagent packages has yet to be verified.
- 4) As currently constituted it does not meet the original detection limit target.

The technique also offers several advantages:

- 1) It is inexpensive.
- 2) Under appropriate environmental conditions it can be used in the field.
- 3) It is rapid.

- 4) It requires very little specially constructed equipment.
- 5) The operator does not require extensive training.

Several military laboratories are set to evaluate the method. Feedback from this evaluation will be used to move this test to the field.

Acknowledgements:

We would like to acknowledge W. John Delaney, of BetzDearborn Inc., for allowing us to include a discussion of his work. We would also like to acknowledge D. P. Jaquay for his work on this project which was interrupted by his untimely death. We would also like to thank Steve Anderson of the Aero Propulsion and Power Directory at Wright Laboratories for acquiring the jet fuels used in this work. We thank the Hach Corporation for generously providing the pocket digital colorimeter used in this work.

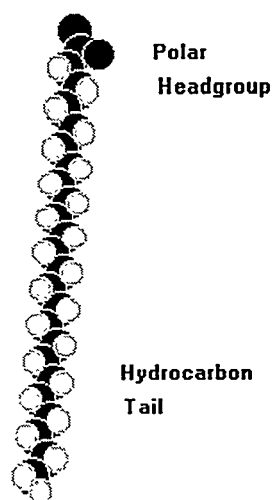


Figure 1. A soap as a model surfactant

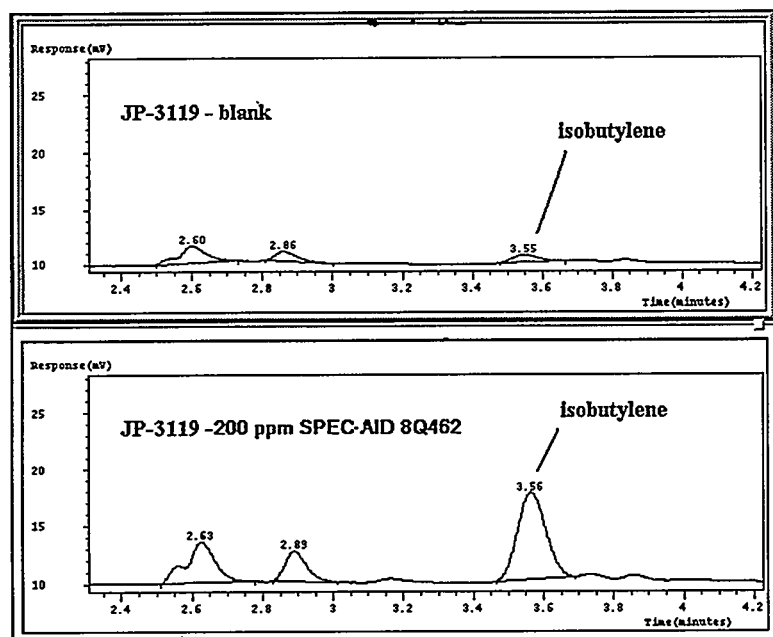



Figure 2. Sample results from the GC/Pyrolysis method

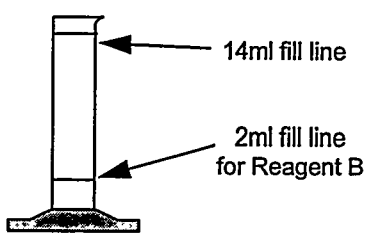
Instructions for the +100 Residual Test in JP8 and JP-5 Jet Fuel

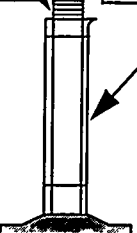
Step 1

15 ml test tube



Marked Cylinder

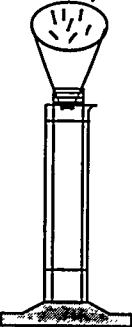




Put test tube inside specially marked cylinder

Step 2

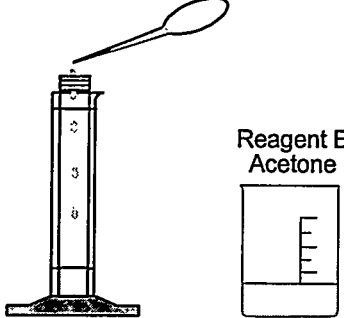
Reagent A
Fe2O3



- Place funnel in test tube
- Tear open Reagent A packet (Fe2O3)
- Tap funnel to get powder down into test tube.

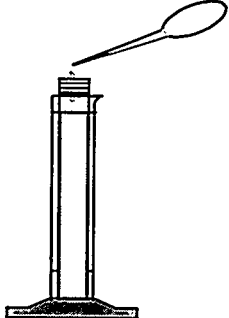
Step 3

Using dropper in Reagent B bottle, add reagent to bottom line on cylinder




Step 4

Fill cylinder to top line with fuel being tested using disposable pipet from kit.



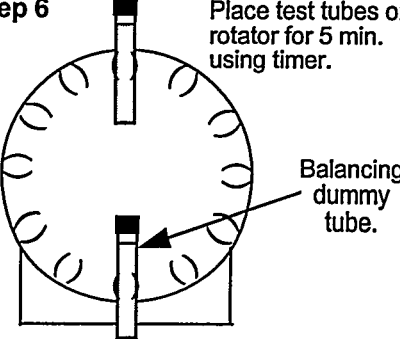
Step 5

Cap tightly.



Step 6

Place test tubes on rotator for 5 min. using timer.

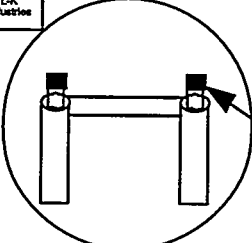


Balancing dummy tube.

Step 7

Immediately after rotator stops, place in centrifuge. Be sure to balance with a dummy tube if necessary.

L-K Industries



Centrifuge should have mark for setting of 850 rpm. Set timer for 5 mins.

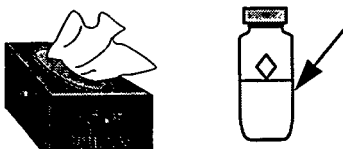
Balancing dummy tube.

BETZDEARBORN HYDROCARBON PROCESS GROUP INC. 997 (POWERNTLABUP8.PPT)

Instructions for the +100 Residual Test in JP8 and JP-5 Jet Fuel (Cont'd)

Step 8
Zero the Colorimeter

8a) Fill Color Cell with fuel being tested. (but does not have Reagents in it.)



10ml Color Cell

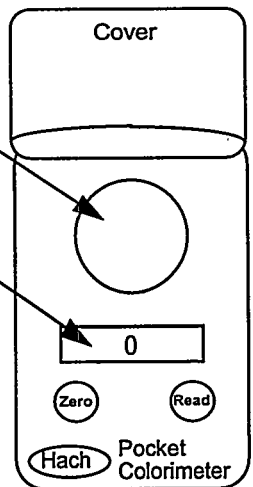
8b) Wipe outside surface of color cell with lens wipe.

8c) Place Color Cell in holder with diamond in front.

8d) Replace cover.

8e) Press zero button. 0 will appear in digital display

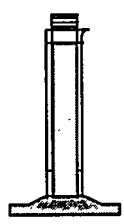
8f) Dispose of sample per site requirements.



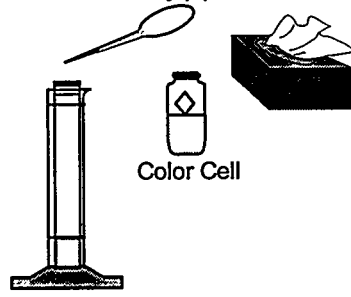
Hach Pocket Colorimeter

Step 9

9a) Uncap tube and place in cylinder.



9b) Pipet down to 2ml line on cylinder & put in Color Cell. Wipe outside of cell with wipe. Throw away pipet.



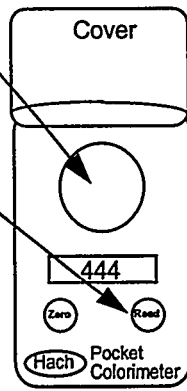
Color Cell

9c) Place Color Cell in holder with diamond in front.

9d) Replace cover.

9e) Press "read" button and digital number appears. Find this color number on the reference chart below. Example: 444 is ~50ppm.

9f) After proper sample disposal, clean cell with a few drops of Reagent B.



Hach Pocket Colorimeter

Chart for Determining Concentration of Additive			
SPEC-AID 8Q462	Range of Color Readings from Hach		
0 ppm	140	to	221
25 ppm	209	to	366
50 ppm	309	to	575
100 ppm	517	to	833
200 ppm	941	to	990



Figure 3. Pictorial description of the test protocol.

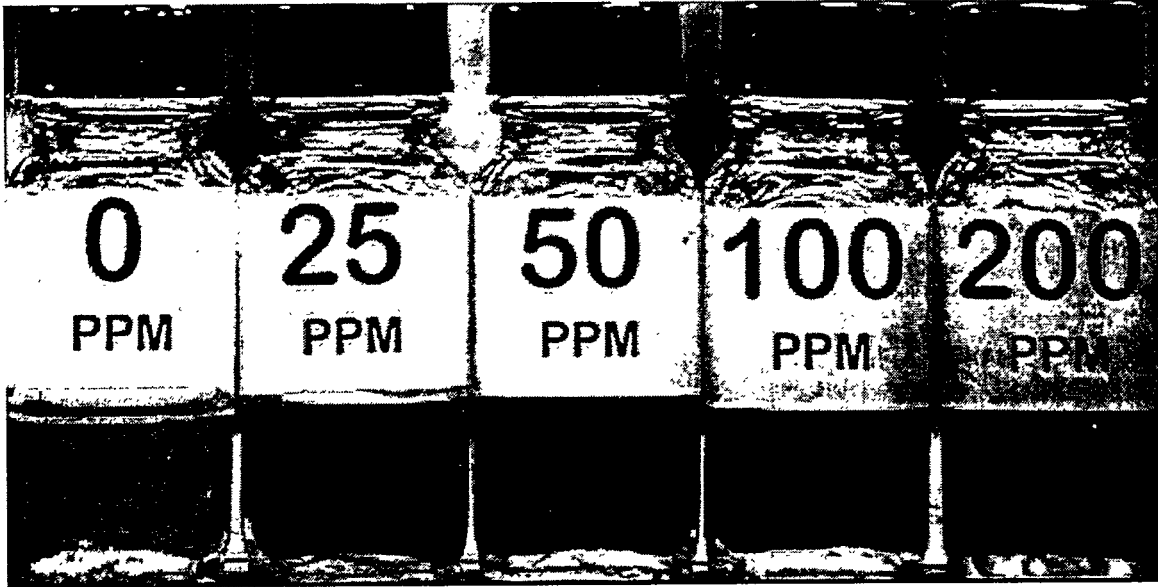


Figure 4. Visual Evidence of Iron Oxide Dispersability

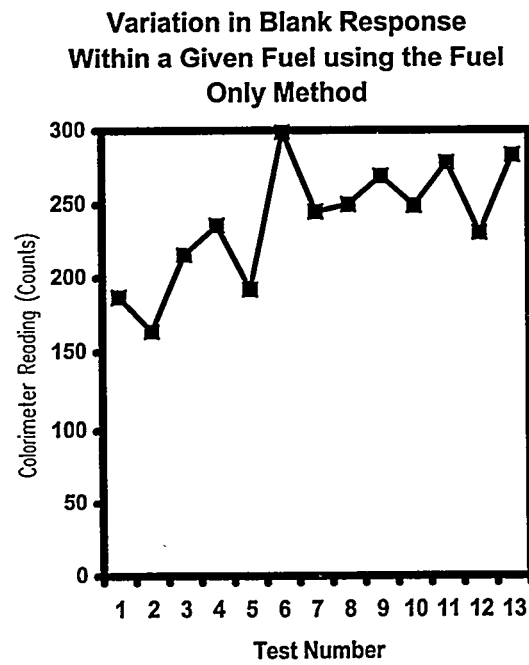
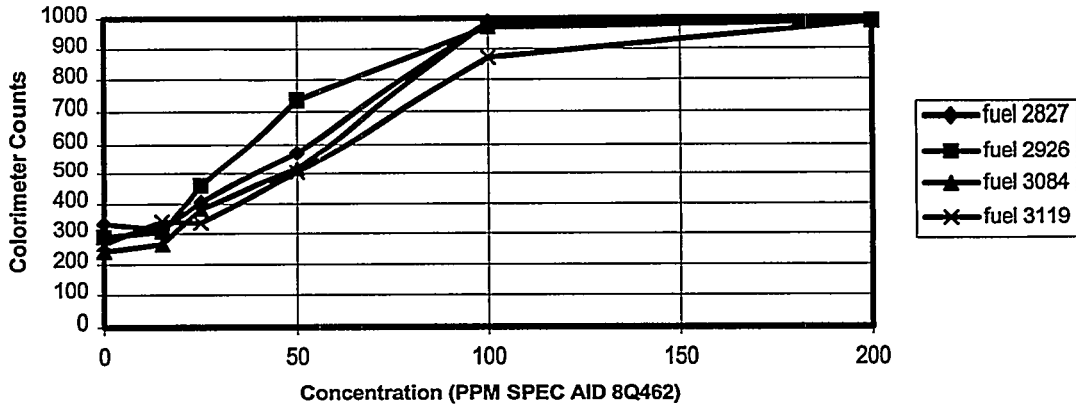


Figure 5. Reproducibility of the one reagent test with a given fuel.

Variation Between Fuels of a Given Specification (Fuel Only Method)



Fuel Variability (Two Reagent Method)

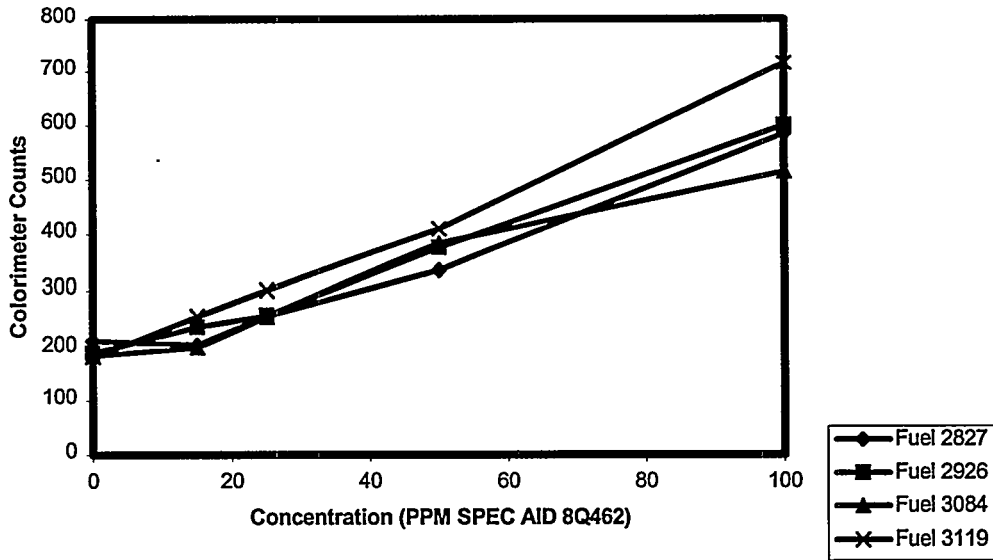


Figure 6. Variation between fuels in the tests.

**Increase in Response for Residual Test as a Function of
number of Cycles Through the Protocol**

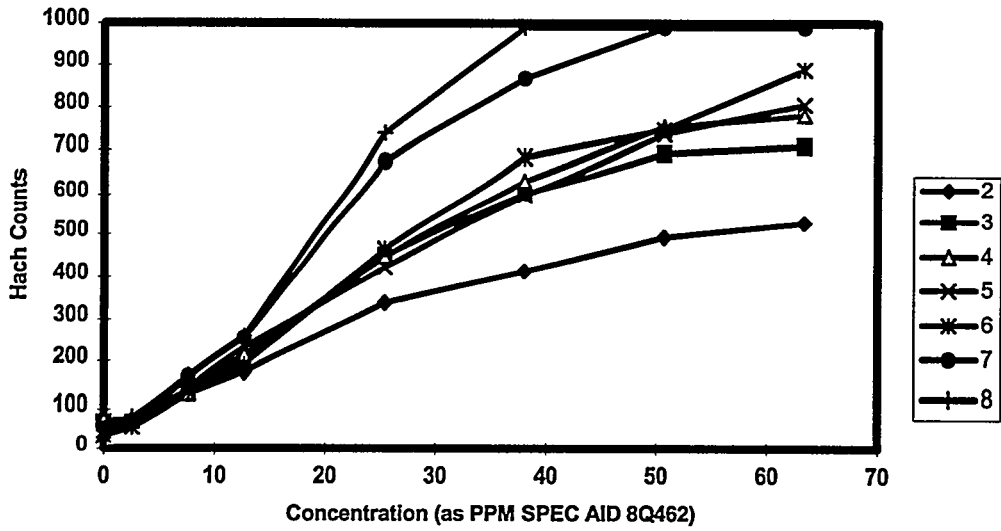


Figure 7. Increase in optical density for a given fuel, when the sample is subjected to multiple test cycles.

Comparison of JP5 and JP8 Fuel Response in the Residual Test

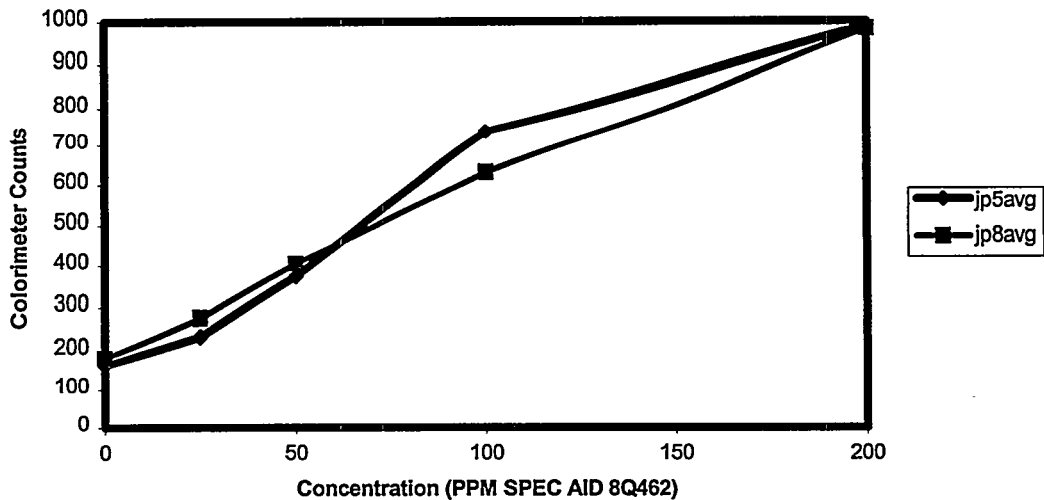


Figure 8. Comparison of the response of JP5 and JP8 fuels to the two reagent residual test.

Results of Residual Test Method For Jet A Fuels

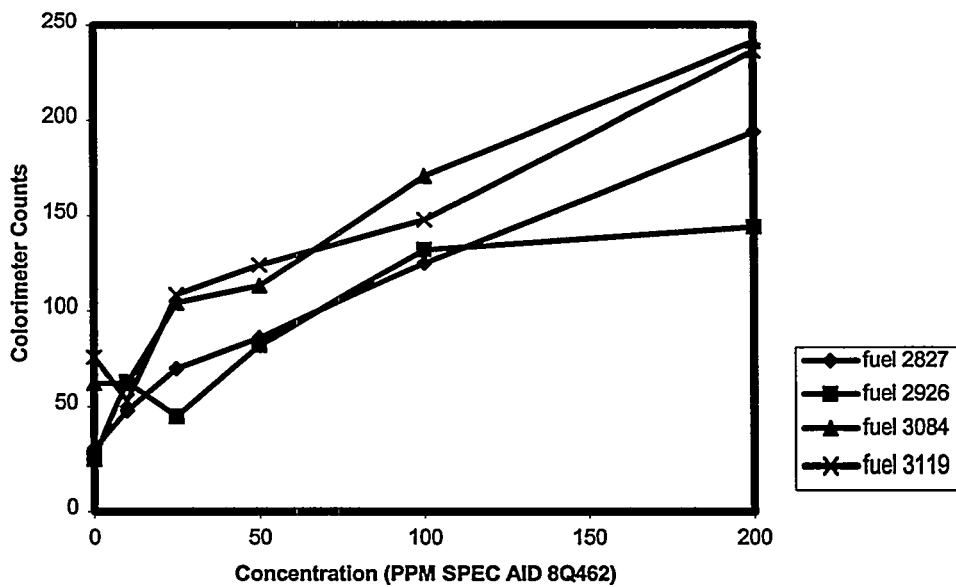
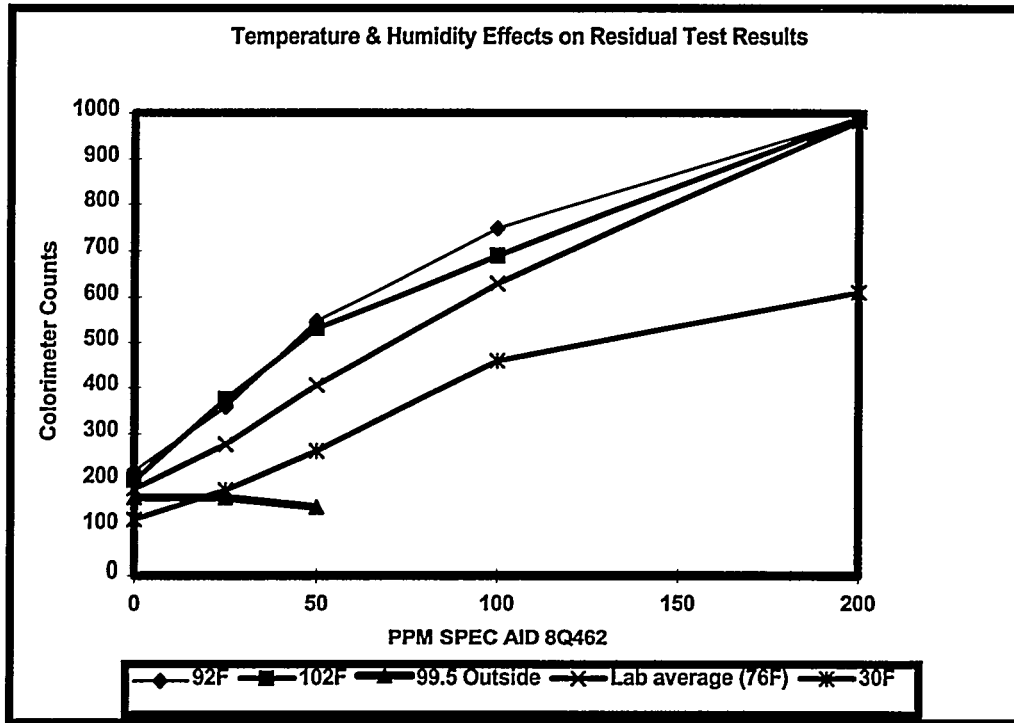


Figure 9. Response of Jet A fuels to the two reagent residual test.



Figure

10. Comparison of results from the residual test as a function of temperature and humidity. Tests run at 92F and 102F were performed in an oven under low humidity conditions.

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³ W. John Delaney

⁴ K. J. Lissant **Demulsification Industrial Applications** , Marcel Dekker, Inc. New York, 1983

⁵ G.W. Ewing, **Instrumental Methods of Chemical Analysis**, McGraw-Hill New York, 1975 pp136-140

*6th International Conference
On Stability And Handling Of Liquid Fuels
Vancouver, B.C., Canada
October 13-17, 1997*

**A COMPARISON OF JET FUEL THERMAL OXIDATION TEST VISUAL
TUBE RATINGS WITH DEPOSIT MEASUREMENT BY ELLIPSOMETRY**

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Abstract

A new analytical technique for measuring deposit thickness and/or volume on JFTOT tubes, called Ellipsometric Tube Analysis, has been developed. A study of over 500 samples, produced by testing operational fuels from a range of sources world-wide, has identified the representative deposit volume and thickness conditions corresponding to VTRs 0→3. The results suggest that ellipsometry has the potential to be used in the jet fuel specification for rating JFTOT tubes. Detailed analysis shows that abnormal deposits are no thicker than normal ones of a similar visual rating and the work calls into question the need for aviation turbine fuels producing abnormal JFTOT tube ratings to be automatic specification failures. This type of evaluation now allows JFTOT break points to be correlated with a quantitative measurement of deposition.

Introduction

The thermal stability of jet fuel is measured by the Jet Fuel Thermal Oxidation Tester⁽¹⁾ (JFTOT) for specification purposes. In this test, fuel is passed over a heated aluminium test piece for 2½ hours at a temperature of 260 °C. At the end of the test, the colour of the deposit on the test piece is compared visually with a set of colour standards numbered 0→4 which define the Visual Tube Rating (VTR). If the colour does not match any of the standards then the tube is rated as “abnormal”. In the jet fuel specification, all ratings of 3 or greater and all abnormal deposits are failures.

Conventional thinking is that the darker the deposit, the thicker it is. Little information has been available about the thickness of abnormal deposits. For aircraft fuel system performance, however, deposit thickness and volume are more meaningful than

colour. Accurate non destructive measurements of deposit thickness have been impossible until now.

Thin films on reflective surfaces, such as JFTOT tubes, change the polarisation of light passing through them. These changes can be measured using ellipsometry, and the resulting data converted into film thickness or volume using a single layer model for the deposit on the substrate metal. In this work an Ellipsometric Tube Analyser (ETA), developed by BP Oil International and Plasmos GmbH, and combining the ellipsometric principles with specific JFTOT tube handling has been used to quantify the deposits generated by the JFTOT test. More than 500 JFTOT tubes generated from a world-wide selection of operational jet fuels have been analysed so far.

Experimental

All the jet fuel samples sent to the MoD's Fuels Laboratory at DERA Pyestock from February to September 1997 were tested for thermal stability by JFTOT at the standard 260 °C and the VTR assigned. ETA was used to measure the deposit thickness at 1200 points on each tube and a profile built up. An example of this can be seen at Figure 1. Maximum thickness and total volume of the deposit were determined from the profile.

To assess the effect of varying JFTOT test temperatures on deposit thickness, four fuels were tested over a range of temperatures.

Results and Discussion

The data on maximum thickness and total deposit volume are plotted against VTR for each tube and shown in Figures 2 and 3. For each VTR between 0 and <4 the thicknesses or volumes fall within the ranges 0 to 230 nm and 0 to $2.85 \times 10^{-5} \text{ cm}^3$ respectively. The trend is for increasing deposit thicknesses and volumes with increasing VTR. Above VTR 4 the spread of results becomes much wider. The relatively narrow range for VTR<4 is not surprising since the VTR system, which is

based on visual detection and comparison, is designed to focus on the critical region which defines JFTOT pass or fail. The data set also demonstrates the influence of subtle changes in deposit colour produced by different fuels. This explains the range of thickness/volume data for any given VTR. On this basis, if we consider a given fuel however, and vary the JFTOT temperature, the thickness/volume and VTR should be more consistent.

Conventionally the break point is defined as the highest temperature which the fuel has a pass rating. From Figure 4 it is also possible to define the break point as either the temperature where the deposit exceeded a certain thickness or volume, for example, 100 nm or $2.0 \times 10^{-5} \text{ cm}^3$ respectively, or at the point of change of gradient of the curve. An example, for three different fuels, can be seen in figure 4. The break point determined by ETA will often be higher than that determined by VTR because many VTR failures are caused by abnormal deposits. Sample RD97143, shown in Figure 5, was a good example of this. The break point was 180°C by VTR. The ETA break point was around 245 °C.

Out of a total of 207 JFTOT failures seen in the Fuels Laboratory during this period of work, 141 were due to abnormal deposits. There was no evidence from the ETA results that the presence of abnormal deposits was related to an increase in the maximum thickness or volume for a particular visual rating. These findings suggest that abnormal deposits may represent no increased threat to aircraft operation.

The use of ETA to measure deposit thickness or volume would permit the development of a precision statement for the JFTOT method. The subjective nature of the deposit rating has been one of the drawbacks of the test since its introduction into specifications in the 1970s and has been the subject of discussions at most standardisation meetings since then. After evidence was presented to ASTM, in the early 1990s, on the poor repeatability and reproducibility of JFTOT results, the Coordinating Research Council (CRC) was tasked in 1993 to “expedite their effort to obtain an instrumental method of rating tube deposits”. ETA appears to have the potential to fulfil this goal.

Conclusions

A large data set has been gathered on JFTOT tube deposit measurements using ETA. The technique showed itself to be a useful tool for measuring deposit thickness or volume on JFTOT tubes.

Consideration should be given to permitting the use of ETA in the jet fuel specification as a method for rating JFTOT tubes. A tube deposit thickness of about 100 nm or volume of about $2.0 \times 10^{-5} \text{ cm}^3$ could be set as a tentative pass/fail level for the jet fuel specification derived from this sample set.

A precision statement for ASTM D3241 has long been sought after. ETA has the potential to provide this.

Consideration should be given to removing from the jet fuel specification the abnormal deposits classification as a mode of failure.

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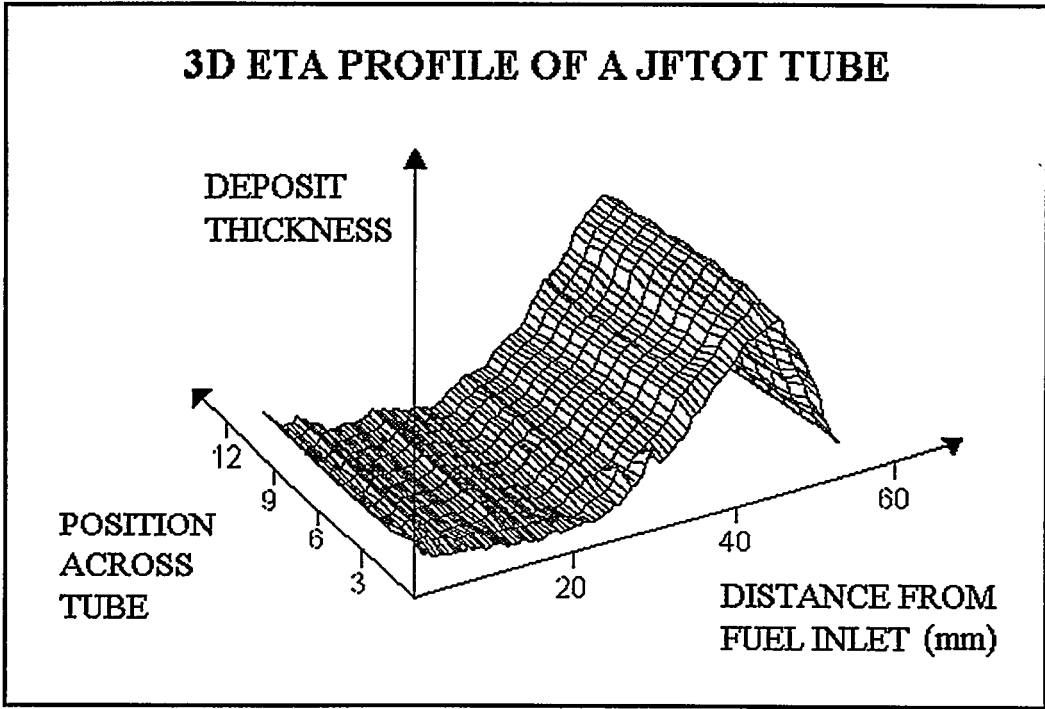


Figure 1

Breakpoint Determination of a Selection of Aviation Turbine Fuels

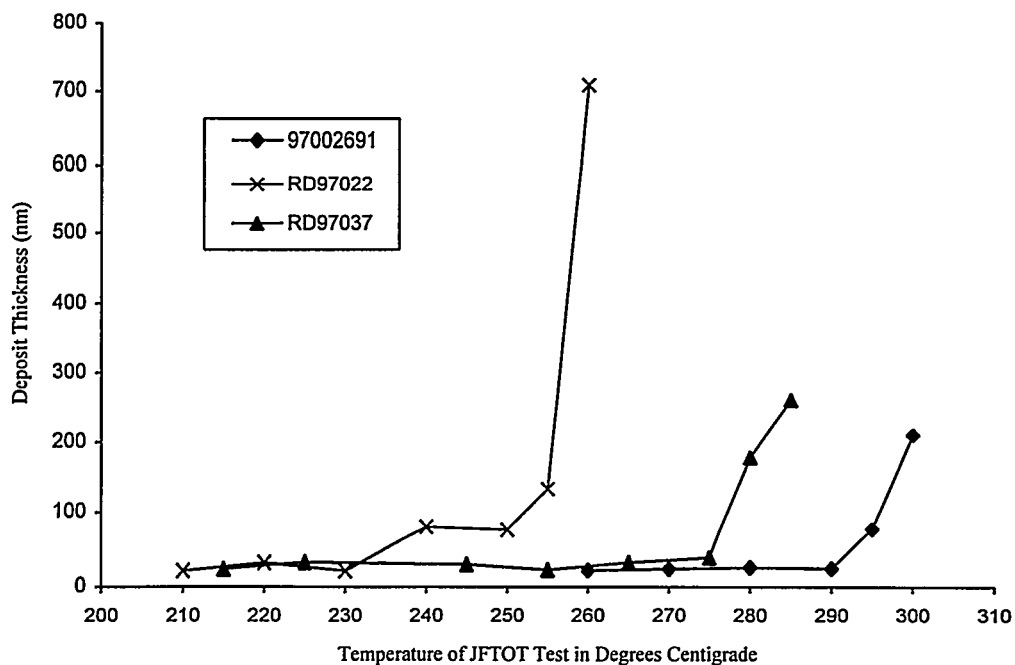


Figure 4

Breakpoint Determination of Sample RD97143

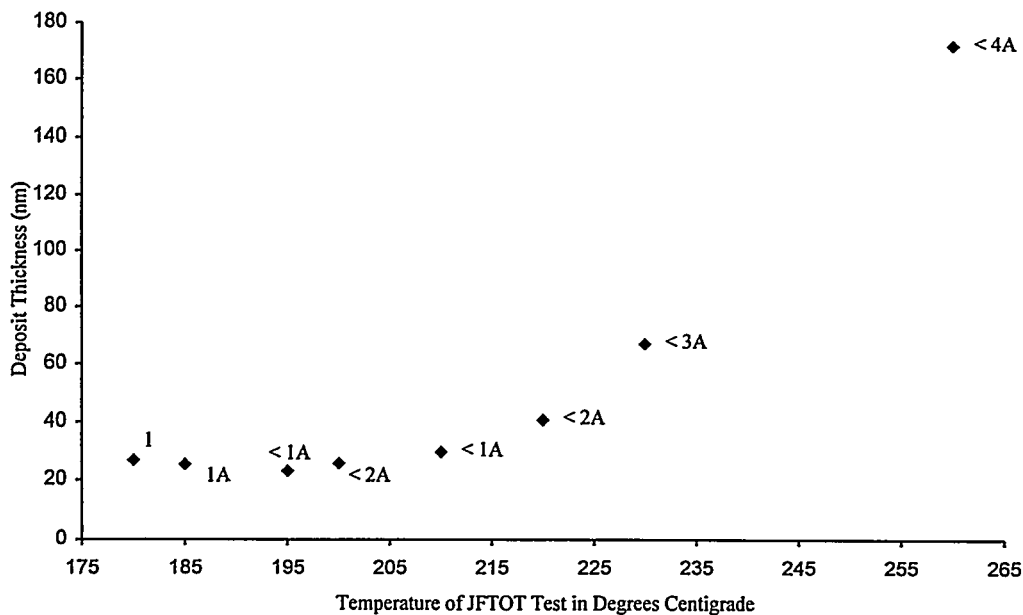
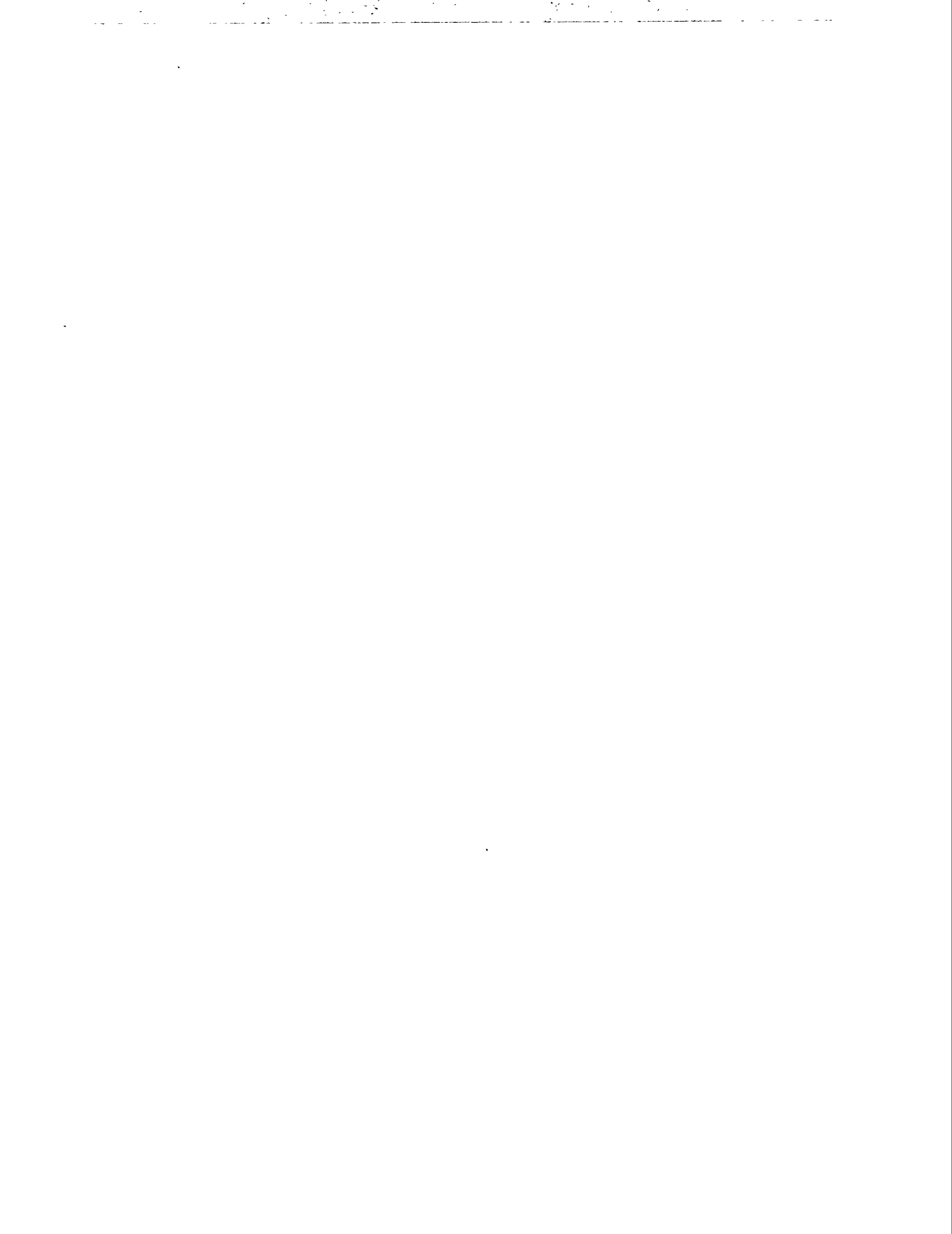


Figure 5



*6th International Conference
on Stability and Handling of Liquid Fuels*
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DEVELOPMENT OF AN ELLIPSOMETRIC JFTOT TUBE ANALYSER (ETA)

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Abstract

Problems associated with the current visual rating of JFTOT tube deposits used for specification purposes are well known. The method suffers from operator subjectivity, the main cause of differences in visual rating of tubes between laboratories. The visual rating method also provides no information on the thickness and volume of deposit which are far more meaningful for characterising fuels, especially for aircraft and engine manufacturers. Ellipsometry was identified in the BP Oil laboratories as a suitable technique for measuring accurately the thickness/volume of JFTOT tube deposits (as described at the 5th International Conference on the Stability and Handling of Liquid Fuels). A dedicated ellipsometric JFTOT tube analyser (ETA) has now been developed through collaborations between BP, the UK MOD and the Munich-based company Plasmos GmbH, who built the instrument. The strengths of ETA lie in the ease of the measurement, and the fact that *absolute* measurements are produced, without the need for calibration. Three-dimensional deposit profiles along and around the whole length of the JFTOT tube test section can be generated giving information on deposit thickness and total deposit volume. ETA thus provides the capability to provide a more meaningful interpretation of deposit assessment for research and quality assurance purposes.

Introduction

Problems associated with the current visual rating of JFTOT tube deposits used for specification testing of aviation kerosine fuels are well known. The method suffers from operator subjectivity, which is the main cause of differences in visual rating of tubes between laboratories¹, and colour standards vary between laboratories, exacerbating the situation. In addition, borderline and abnormal deposits are difficult to rate, and the nature of the visual rating procedure means that no precision statement can be ascribed to ASTM D3241. At ASTM's behest, the Co-ordinating Research Council were set the task a number of years ago to identify an instrumental method of rating tube deposits to overcome these problems. The visual rating method also provides no information on the thickness and volume of deposit, which are far more meaningful for characterising fuels, especially for aircraft and engine manufacturers. At the 5th International Conference on Stability and Handling of Fuels², it was

reported that ellipsometry had been identified and developed in the BP Oil Sunbury laboratories as a suitable technique for measuring the thickness and volume of JFTOT tube deposits. A dedicated ellipsometric JFTOT tube analyser (ETA) has since been developed through collaborations between BP, the UK MOD and the Munich-based company Plasmos GmbH, who built the instrument.

Features of ETA

The original project had as its goal to develop an instrument capable of providing a non-subjective measurement of the thickness of deposits on JFTOT tubes. The essential features of ETA are a polarised laser beam, produced by a low power 1.55 micron laser, an optical detector system and a specially designed tube handling system. The laser provides a “footprint” on the tube surface of the order of 50 microns, and the tube handling assembly allows for a resolution along the length of the tube of approximately 0.5 mm, see Figure 1. The ellipsometric measurement is based on the change in the state of polarisation of light reflected from a surface and is dependent on the substrate (the JFTOT tube) refractive index and absorption coefficient, and the film (the tube deposit) absorption coefficient, refractive index and thickness. Details of the principles of the approach are given elsewhere.² Pictures of the ETA instrument and the tube handling system are shown in Figures 2 and 3.

The strengths of ETA lie in the ease of the measurement, and the fact that absolute measurements are produced, without the need for calibration. Three-dimensional deposit profiles along and around the whole length of the JFTOT tube test section can be generated giving information on maximum deposit thickness and total deposit volume, see Figure 4. Up to 1200 points (100 points by 12 slices around the tube) can be measured in *ca* 35 minutes. The data can be presented in topographic, isometric or 3D format.

Data verification

In order to confirm the accuracy of the ETA measurements, deposits were examined with known thickness. JFTOT tubes were prepared using Langmuir-Blodgett (LB) controlled deposition techniques, such that monomolecular films of cadmium behenate (a C₂₂ carboxylic acid) were deposited onto the surface of new aluminium tubes. The thickness of the

monomolecular film can be determined by X-ray diffraction and the value quoted in the literature is 3.0nm.³ A series of multiple films of known thickness, increasing from 0 to 100nm were produced and examined by ETA; the thickness profile is shown in Figure 5. Knowing the number of molecular layers deposited allows the thickness of the films to be calculated and the results shown confirm the accuracy of the ETA measurement.

Comparison with visual ratings

More than 300 JFTOT tubes have been examined by ETA in the BP Sunbury laboratory. For a given fuel generating normal deposits, *ie* with colours which match the coloured standards in the visual rating procedure, thickness of deposits increases with increasing visual rating. Some “peacock” and most “abnormal” deposits, which are automatic failures under the current rating system, are thin and might be acceptable from an engine operational point of view. Within each visual rated category, there is evidence for considerable variation in deposit thickness and volume, suggesting that the role of visual ratings for tube deposit assessment is questionable. ETA thus provides the capability to provide a more meaningful interpretation of deposit assessment for both research and jet fuel specification uses. Streak and spot deposits can be handled with ease. Detailed information on the relationship between deposit thickness/volume and visual rating was presented by UK MOD at the 6th IASH Conference⁴.

Conclusions

ETA provides the capability to:

- satisfy the aviation industry needs for a non-subjective instrumental method for rating JFTOT tube deposits, in particular, removing the problems associated with rating abnormal and borderline deposits
- enable a precision statement to be developed for ASTM D3241
- rate aluminium, stainless steel and coated tubes
- define a JFTOT specification limit and breakpoint temperature in terms of deposit volume.

Acknowledgements

This project was funded by UK Ministry of Defence and Air BP. The authors would like to acknowledge the efforts of the team at Plasmos who contributed to the design and completion of ETA. The authors are grateful for the financial support from Air BP and Plasmos towards the cost of manufacture of the ETA prototype.

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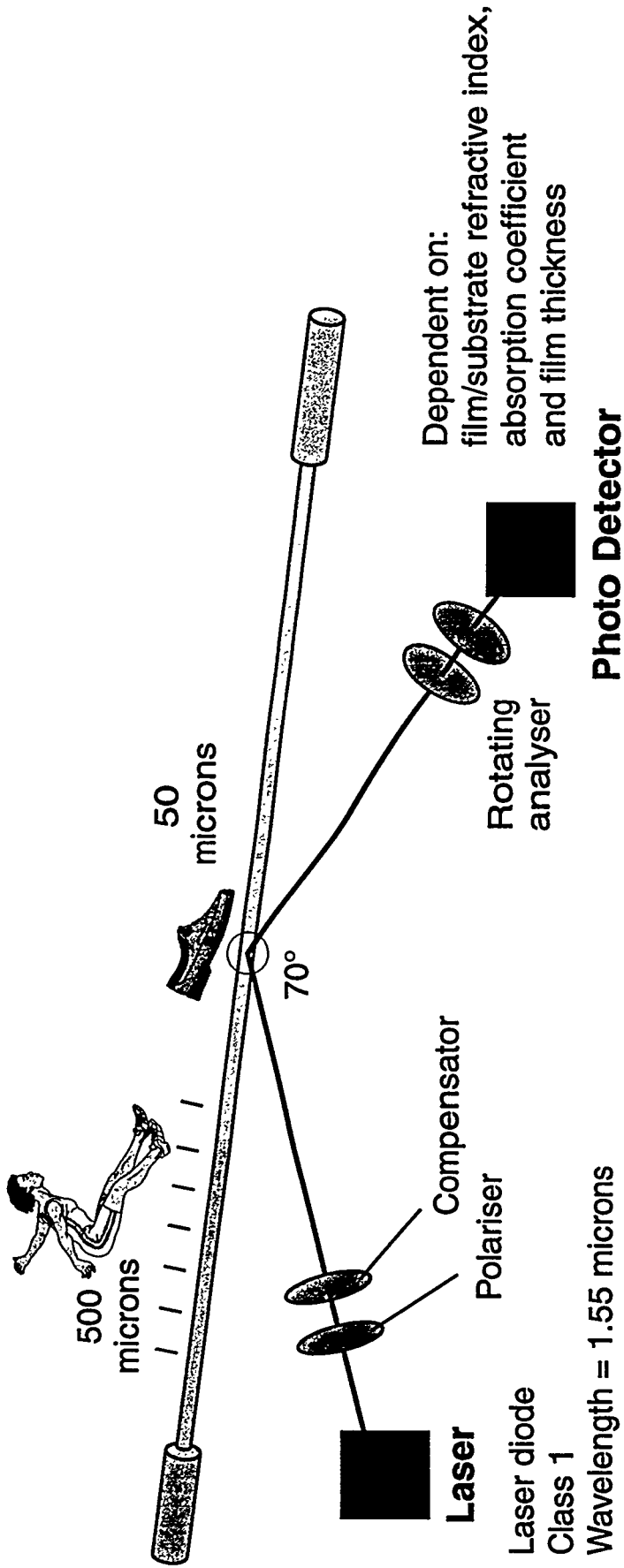


Figure 1. ETA configuration

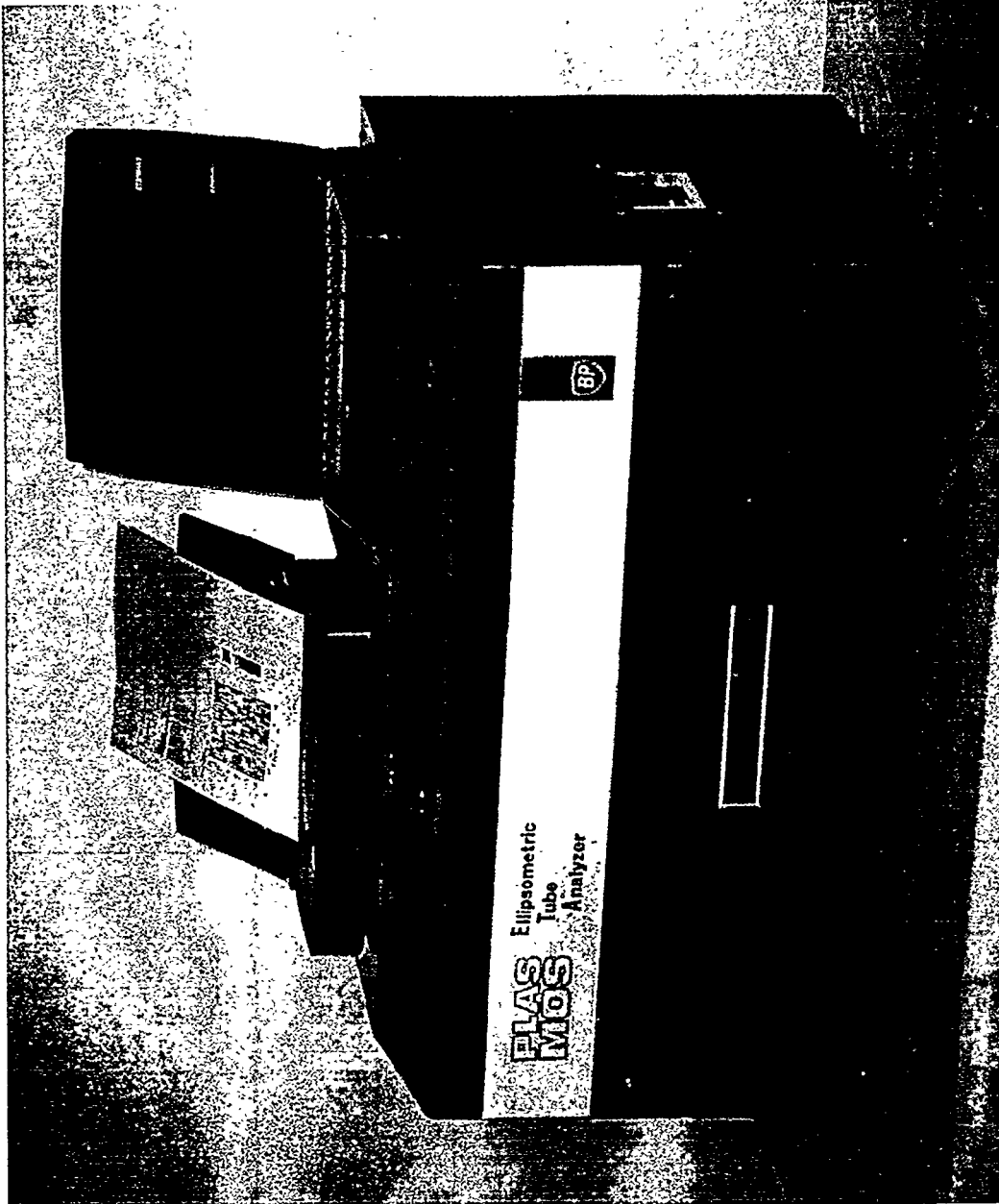


Figure 2. ETA

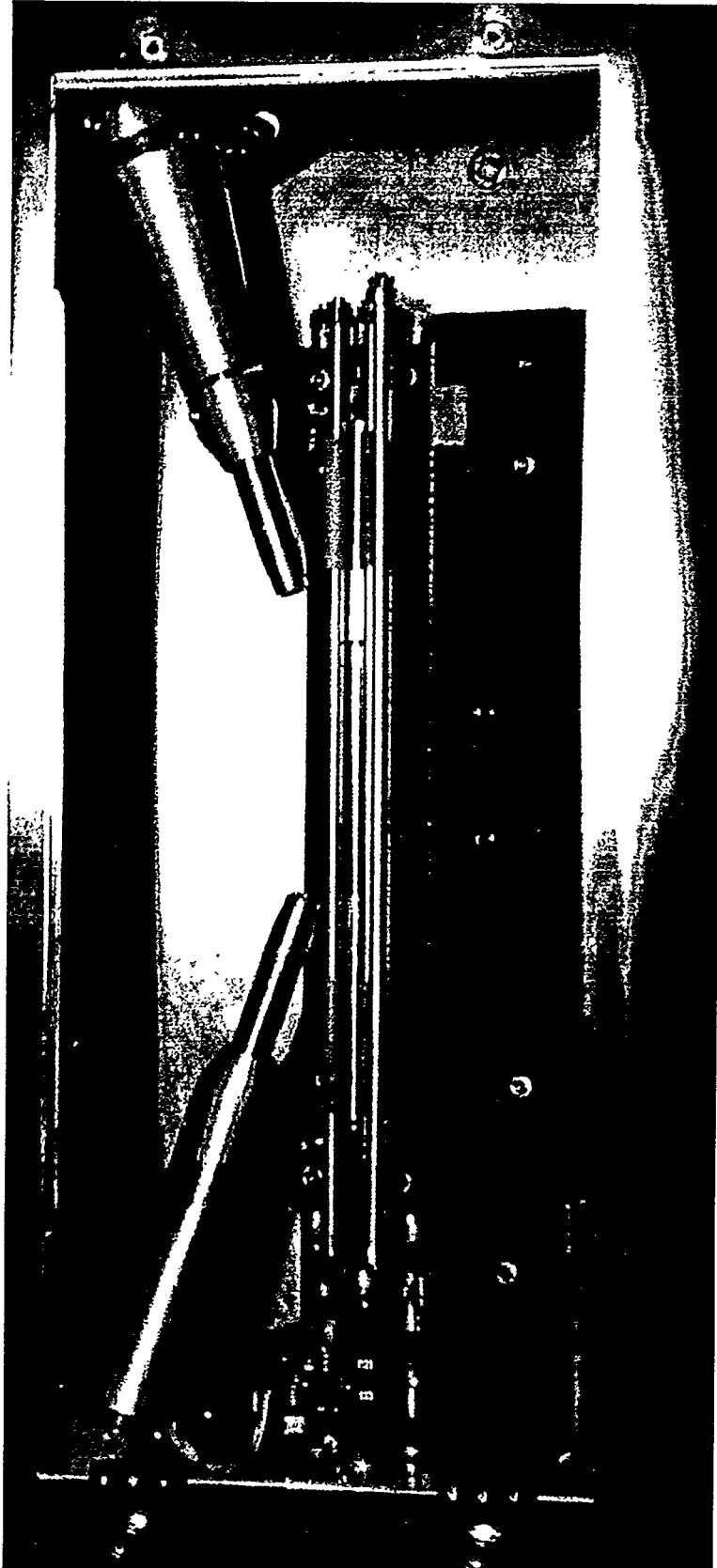


Figure 3. Tube handling system

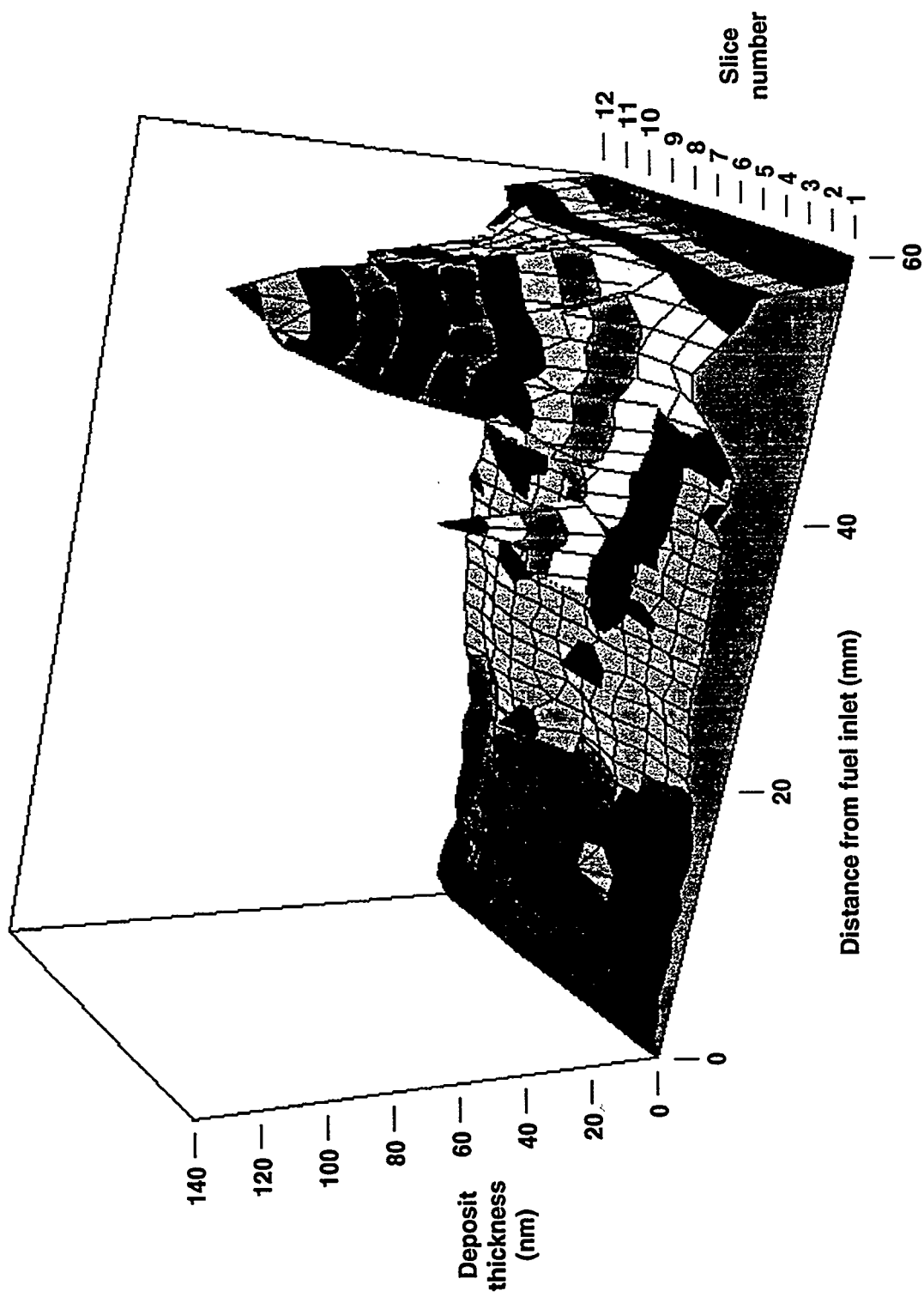
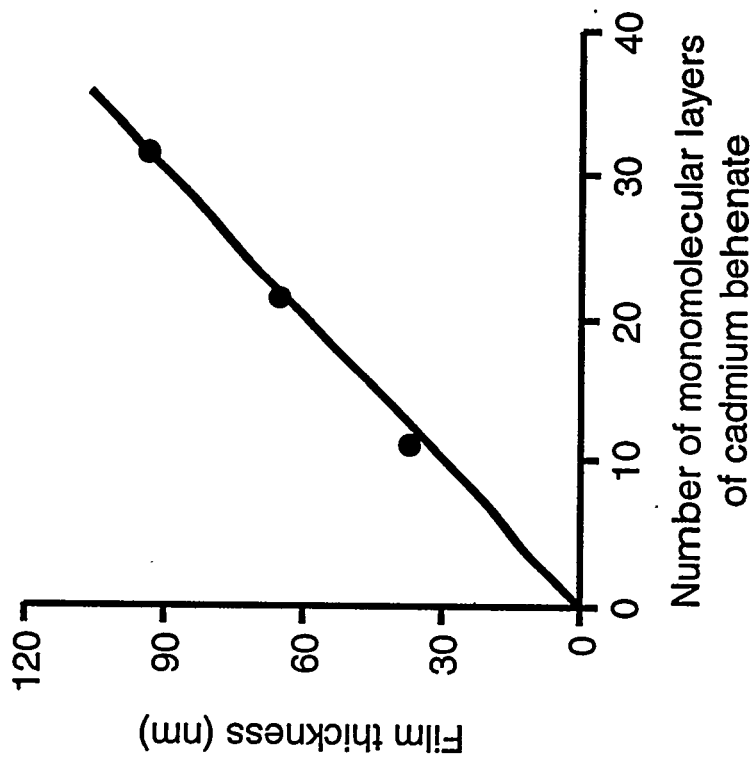
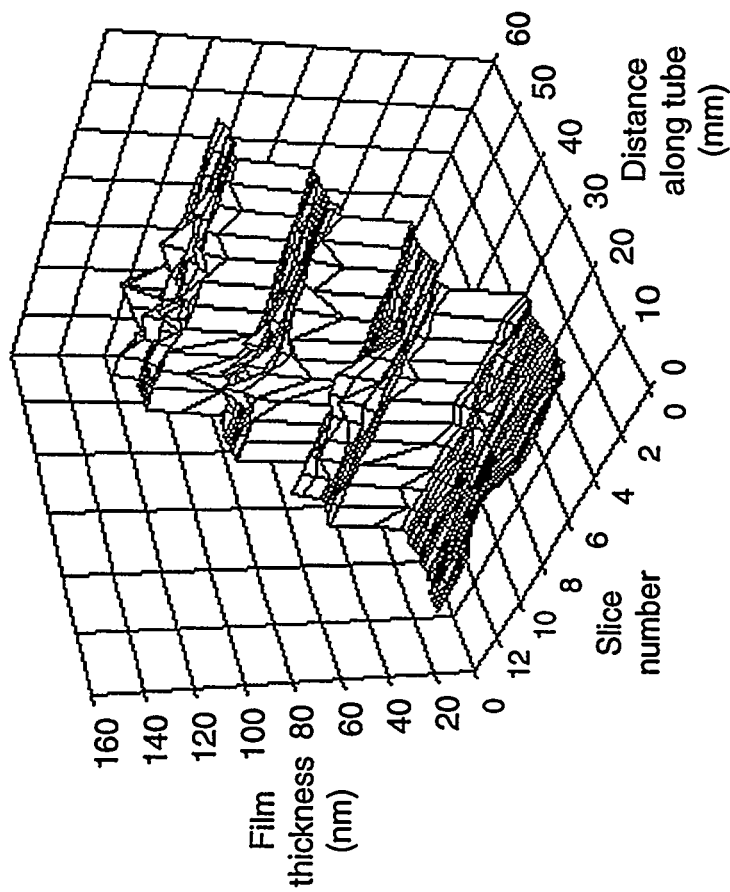


Figure 4. 3-D deposit profile



- 'Clean' steps
- Film dimensions agree with molecular size
– chain length of behenic acid = 3.0nm

Figure 5. L-B film-coated tubes



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THE AUTOXIDATION OF PHENALENE

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It is generally agreed that the "Pedley mechanism" (J. F. Pedley, R. W. Hiley, and R. A. Hancock, *Fuel*, **68**: 27, 1989) is an excellent hypothesis which can partially rationalize the oxidative degradation of many diesel fuels. The first step of the Pedley mechanism involves the autoxidation of phenalene to form phenalenone. In this paper we will report our mechanistic investigation into the details of this process and comment on the importance of our results with respect to understanding the oxidative degradation of middle distillates in general.



**6th International Conference
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**FOLLOW-UP STUDY OF AN OCCUPATIONAL HEALTH PROBLEM WHEN
HANDLING JET FUEL AFTER INITIATE ACTIONS**

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ABSTRACT

In connection with the Swedish Air Force fuel change in 1991-1992 from Rb77 (JP-4) to Ff75 (JP-8), occupational health problems in the form of unpleasant odour, fatigue, headaches, irritated, blocked or stuffed nose and skin irritations increased.

A previous study revealed that there was a connection between these health problems and certain sulfur-organic compounds in the jet fuel. Measures have now been taken to reduce such compounds. The occupational health problems have now been studied and the results show a significant decrease concerning such problems though a high frequency of occupational health problems still remains, among them fatigue, irritated, blocked or stuffed nose and skin irritation.

Preliminary international reports draw attention to liver changes in connection with the handling of jet fuel, resulting in uneasiness among personnel who handle such daily over a long period of time.

Exposed and unexposed groups from our previous study have now undergone blood tests to ascertain possible liver changes. Preliminary results show liver changes in the exposed group. Measured exposure to Ff75 indicates low levels, considerably under the occupational exposure limit.

INTRODUCTION

When the Swedish Air Force changed fuel from Rb 77 (JP-4) to Ff75 (JP-8) during 1991-1992, occupational health problems were reported from the military air force bases. The symptoms were headache, dizziness, fatigue and unpleasant odour. This problem arose from some batches of the new jet fuel. An investigation was instigated in 1993 for the purpose of defining the source of the occupational health problems. A questionnaire and measured exposure study were executed and a further study that revealed a connection between these health problems and certain sulfur-organic compounds in the jet fuel (1). After reducing the latter compounds, the problems decreased.

Because there were still some occupational health problems despite the above measures, another questionnaire study was executed in 1996. Elevated liver function test results at an airbase in Norway was also reported (7). They changed jet fuel from F40 (JP-4) to F34 (JP-8) in 1988-1991. After these observations, liver-tests were also performed in Sweden.

MATERIALS AND METHODS

Questionnaire studies

In the previous study (1) a performed questionnaire (2) was used to collect subjective occupational health problems among personnel exposed in their work to jet fuel. Totally 78 persons answered the questionnaire, which corresponds to a reply frequency of 97%. After initiate actions where sulfur-organic compounds were reduced, the occupational health problems were followed up in the same group and with the same questionnaire. 76 persons answered the questionnaire, which corresponds to a reply frequency of 97%.

The frequency of collecting occupational health problems in the exposed group before and after initiate actions was compared to an unexposed control group of 42 persons, which was matched to sex, age and employment time. Smoking, consumption of medicine and alcohol rates were controlled in the two groups.

Exposure measurements

Exposure measurements were performed on 12 persons, divided in three groups, jet fuel handling group (N=3), work shop service group (N=3) and flight service group (N=6). Sampling was performed with diffusion samples (Tenax TA), which were placed in the breathing zone during a normal working-day, and analyzed by thermal desorption (ATD-400, Perkin-Elmer) followed by gas chromatographic separation in high resolution capillary column. Detection was done with a mass selective detector (ITD 800, Finnigan). Calculation of jet fuel as the total concentration of volatile organic compounds (TVOC) was done according to the Air Profile Model (3).

Liver function test

All persons in the exposed and unexposed group underwent blood tests in order to analyse liver-associated enzymes, aspartate aminotransferase (ASAT) and alanine aminotransferase (ALAT). If increasing levels were revealed, new blood tests were taken later on, after a talk with a doctor about living habits and history of illness.

RESULTS

Results from the first questionnaire study (fig 1) indicated a high frequency of occupational health problems compared to the control group. The dominating symptoms being fatigue, irritated-blocked or stuffed nose, headache, heavy headedness, irritated-dry throat and skin irritation. In order to complete the picture in the presented figures, a simple mathematical calculation model has been used (4). The quotient (RB) between experienced occupational health symptoms among the exposed group and the control group (unexposed) has been calculated. A calculated quota of 1,0 corresponds to the

control group and their answer based on occupational health symptoms. At the first questionnaire study the calculated RB-value was 4,0.

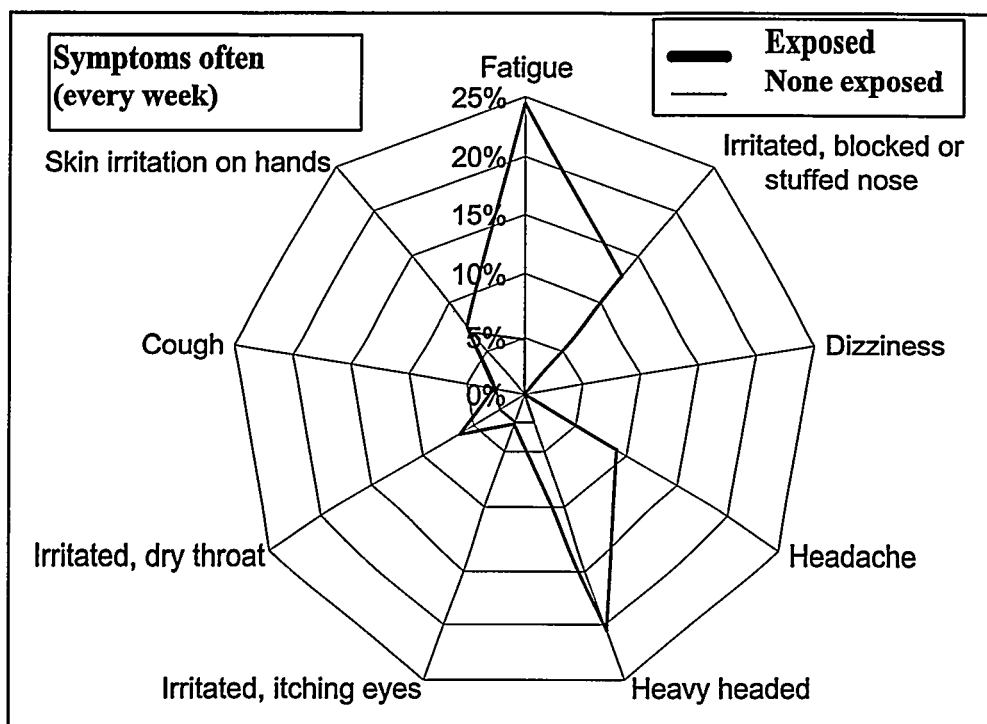


Figure 1 Before reducing sulfur-organic compounds, RB=4,0

Results from the follow-up questionnaire study, after measures taken to reduce certain sulfur-organic compounds are shown in fig. 2. Totally, occupational health problems have decreased, but are significantly higher compared to the control group. Calculated RB-value is 2,9. Skin irritation on hands and irritated, blocked or stuffed nose symptoms have increased compared to the situation prior to measures taken.

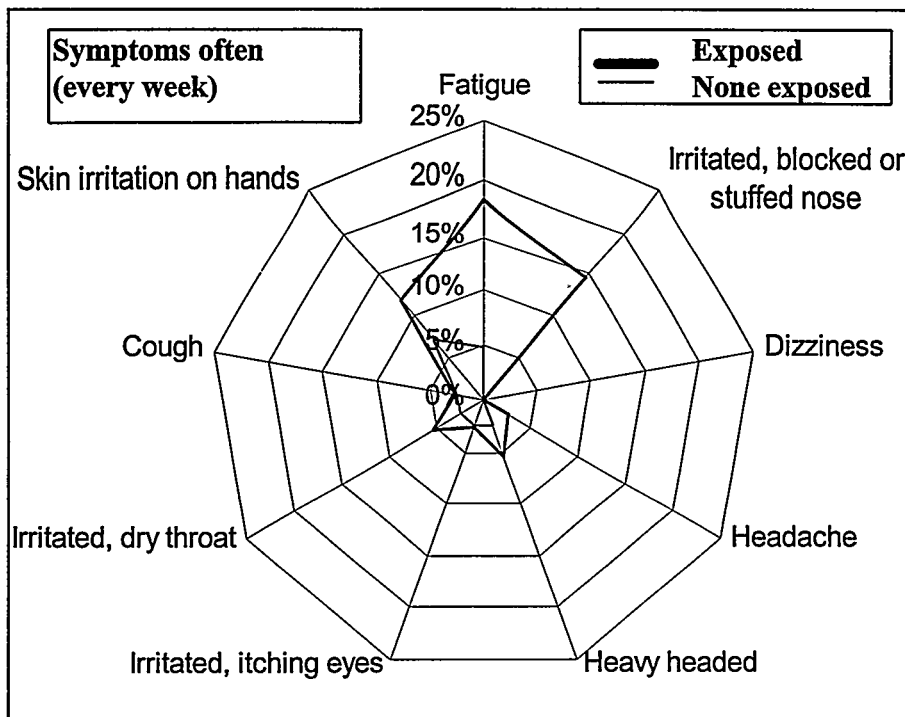


Figure 2 After reducing sulfur-organic compounds, RB=2,9

The frequency of occupational health problems from the control group (N=42) is shown in figure 3.

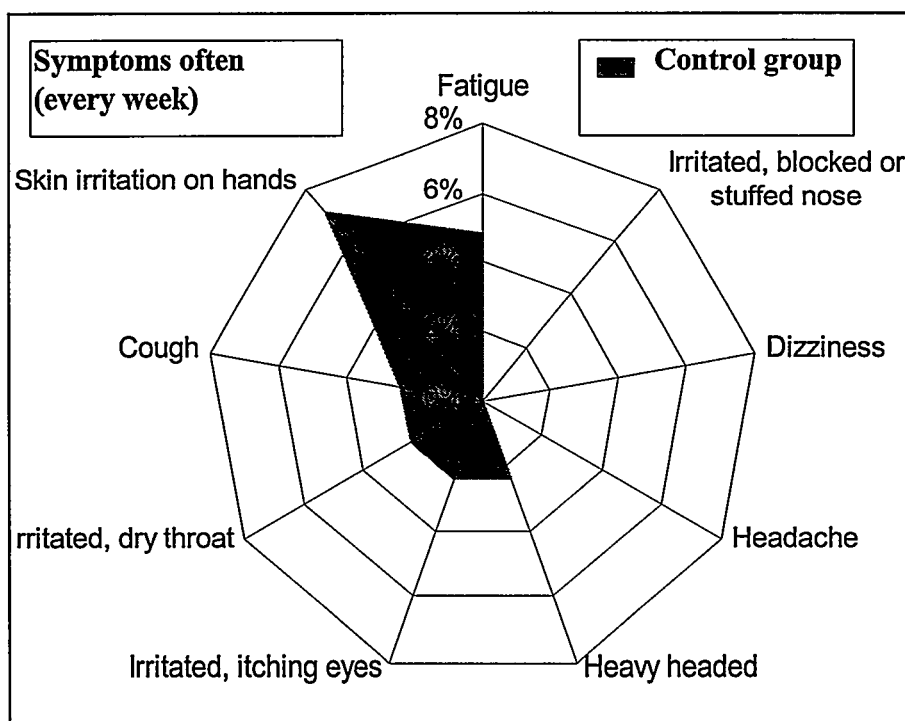


Figure 3 Control group, RB=1,0

Measured exposure in the three groups is shown in fig 4. The present Swedish occupational exposure limit (OEL) for jet fuel is 350 mg/m^3 (1996) for the time-weighted average (TWA) concentration for a whole workday (8 h) and 500 mg/m^3 for the short-time exposure limit (STEL) time weighted over 15 min (5). The measured levels of jet fuel are considerably under the occupational exposure limit (0,5-4,8% of OEL). The highest exposure level was measured in the jet fuel handling group ($46,8 \text{ mg/m}^3$, 13,4 % of OEL), while the flight service group have the lowest exposure.

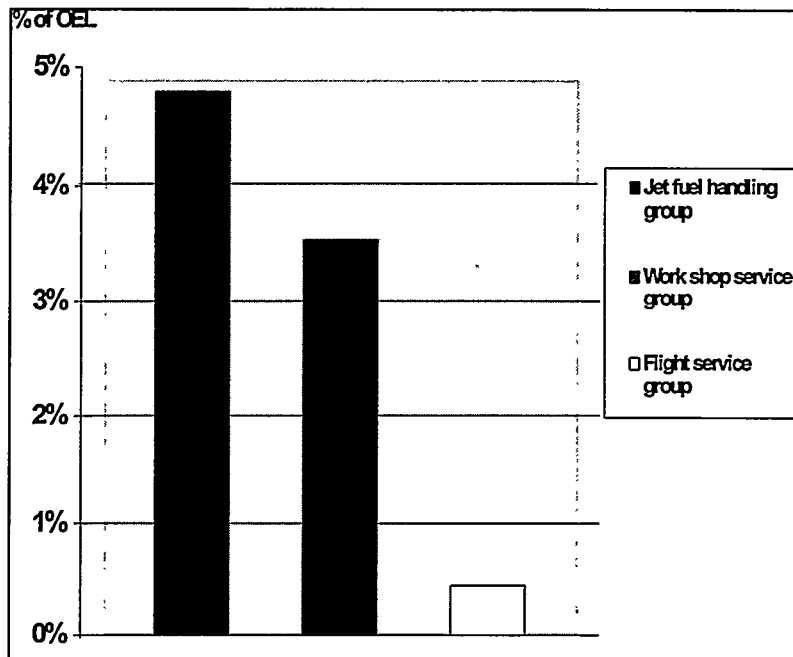


Figure 4 Exposure measurements

Results from the exposed group and control group blood tests show increasing levels of liver-enzymes (ASAT, ALAT) in the exposed group (10,5 %). The corresponding result in the control group was 2,4%. Control of living habits in the form of consumption of alcohols and medicines, revealed a much higher frequency in the control group compared to the exposed group.

DISCUSSION

The frequency of occupational health problems decreased after actions to reduce sulfur-organic compounds, but are still too high, compared to the control group. Symptoms that have increased after measures are skin irritation, and irritated, blocked or stuffed nose. The highest frequency of decrease are headache and heavy headedness.

Measured exposure to jet fuel indicates very low levels, in all the cases under the occupational exposure limit (OEL). A previous study at the Swedish Air Force has also shown low levels (6). Measured exposure to jet fuel in Norway has been carried out with similar results (7). A recently published study has revealed CNS-effect (Central Nervous System) at low level exposure to jet fuel (8).

The vapour phase from the jet fuel has been measured. Any aerosol phase has not been collected at these measurements. Sweden and Norway have reported considerable oil-layer on surfaces like window-panes in houses and cars, in the area of airports. These oil-layers can come from jet fuel and the problem is considerable during the cold time of year. The influence of this aerosol phase is very difficult to estimate because no measurements have been carried out in this field.

There are many factors, that can cause increasing levels of liver-enzymes in the exposed group compared to the control group, for example overweight and increased levels of blood-fat. The difference cannot be explained from differences in habits of living such as taking alcohols and medicines, since such is much more frequent in the control group compared to the exposed group. Effects from jet fuel as a contribution factor to these increased levels of liver-enzymes cannot be excluded in this connection seeing that the effect and dimension of the occurring aerosol phase is unknown. Further research is required to elucidate the presence of aerosols and their effect to exposure upon inhaling and skin absorption.

CONCLUSION

- By reducing the sulfur-organic compounds in the jet fuel, the previous occupational health problems decreased. But there are still a high frequency of occupational health problems compared to a control group.
- Despite low levels of measured exposure when handling jet fuel, a high frequency of occupational health problems still remains.
- Despite low levels of measured exposure when handling jet fuel, there are increased levels of liver-enzymes in the exposed group compared to the unexposed group (control group).
- Further research is required to elucidate the presence of aerosols and their effect at exposure upon inhaling and skin absorption.

Acknowledgements

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***IASH '97, the 6th International Conference
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**MICROBIAL SUCCESSION AND ITS IMPACT ON OXYGENATED GASOLINE
IN LABORATORY MICROCOSMS**

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Abstract

Fuel biodeterioration costs are not well quantified. Incidents of serious biodeterioration are generally considered to be rare. Based on numerous field observations the authors had reason to believe that the actual incidences of gasoline and gasoline-system biodeterioration exceeds the recognized and reported incident rates substantially. The first step in improved biodeterioration diagnostics is a clear definition of the commercial impact of uncontrolled microbial contamination in gasoline over water. In this presentation, the authors describe a series of microcosm studies designed to evaluate the impact of a contaminant microbial community on fuel and bottom-water properties in replicate microcosms. Triplicate challenged and unchallenged microcosms were run, using oxygenated, regular unleaded gasoline over water supplemented with a commercial sea-salt preparation (3 ppt). Microbial activity in the challenged microcosms mediated a number of significant gross, physical and chemical fuel and bottom-water property changes relative to unchallenged microcosms. Most noteworthy was the average 67-% loss of oxygenates and the marked shift from isoparaffin and normal paraffin hydrocarbons to and alkyl isoparaffins. Moreover, mild-steel corrosion rates, and filter plugging occurred at least twice as fast, in challenged microcosms were four to five times greater than rates in unchallenged microcosms.



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KIT FOR DETERMINATION OF HYDROGEN SULFIDE IN LIQUIDS

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ABSTRACT

A recently patented test kit has been successfully used for the determination of hydrogen sulfide concentrations in a variety of oils or aqueous liquids. The kit consists of a sample bottle provided with a screw cap carrying a colorimetric hydrogen sulfide indicator. The indicator is protected from contact with the liquid sample by a vapor-permeable silicone membrane. After a few minutes shaking of the sample in a closed bottle, the hydrogen sulfide content is estimated by comparison of the indicator color with a set of standard colors. The method is remarkably free of interferences from other constituents in the liquid sample. Examples of the use of this method for analysis of hydrogen sulfide in crude petroleum and aqueous solutions of surfactants are presented.

INTRODUCTION

Hydrogen sulfide is a corrosive, highly toxic gas which is found in crude petroleum and in a variety of aqueous liquids where stagnant, anoxic conditions have allowed sulfate-reducing bacteria to proliferate, e.g. in water bottoms of fuel storage tanks, oily waste storage, bilge water, and in water distribution systems and sewage treatment facilities. It is frequently desirable to be able to determine the presence and concentration of hydrogen sulfide in the field in order to assess hazard to personnel and the need for subsequent treatment. While kits for this purpose exist, there appear to be none that are directly applicable to a variety of liquids using a simple, single procedure.

This report summarizes the results of work done to develop such a kit. The success of the approach taken here depends on the high permeability of silicone resin films to gases, particularly hydrogen sulfide, and an impermeability to liquid oil or water. This makes it

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possible to use a silicone barrier membrane to separate a hydrogen sulfide detector from a liquid sample containing dissolved hydrogen sulfide. Colorimetric detectors such as salts of lead, copper or other metals are convenient for field use as they undergo marked visual color changes when they react with hydrogen sulfide. Such an indicator detector may be incorporated in a silicone resin matrix or impregnated in a porous support separated from the liquid sample by a silicone barrier membrane. The concentration of hydrogen sulfide may be judged by the degree of color change produced in a certain contact time with the liquid when compared to a set of standard colors.

Because of the wide range of concentrations of hydrogen sulfide encountered and the different nature of liquid samples, it has been necessary to devise different versions of the detection kit. For crude petroleum, an oil-resistant silicone resin was required and for covering the wide range of concentrations encountered, the rate of diffusion of hydrogen sulfide across the membrane must be adjusted by changing the thickness of the silicone membrane. For highest sensitivity with aqueous solutions, the sensor material was incorporated directly in a silicone resin with high permeability to hydrogen sulfide.

PREPARATION OF KITS

KITS FOR OILS

Silicone barrier membrane: An oil-resistant, fluorinated silicone resin solution was spread with a doctor blade on a flat, non-stick, surface. For additional strength, a thin mono-filament nylon mesh was incorporated in a bi-layer resin film. The thickness of the membrane was controlled by the doctor blade setting. After curing, the film was cut into circles to fit across the inside of bottle caps provided with septum holes and cemented in place.

The thickness of the barrier membrane for kits intended for high concentrations of hydrogen sulfide (30-300 ppm) was 0.33 mm; for low concentrations (3-50 ppm) the thickness was 0.14 mm.

Sensors for hydrogen sulfide in oil: White 0.8 micron nylon filters were soaked in 10 percent lead acetate solution, drained and allowed to dry. For kits intended for low concentrations of

hydrogen sulfide, the sensitivity was increased by addition of five percent glycerol to the soaking solution. The dry filters were cut into circles 2 cm in diameter and each circle was mounted in the middle of a 2.3 cm square plastic microscope cover slip.

A cover slip with attached nylon filter sensor was centered sensor side down over the septum hole in a bottle cap provided with a barrier membrane. A piece of duct tape about 2.8 cm square was placed over the cover slip and pressed down firmly around the edges to bring the sensor in good contact with the top of the cap surface.

KITS FOR AQUEOUS MEDIA

The procedure given is for preparing kits to determine hydrogen sulfide at low concentration (0.25-8 ppm) in water. Lead acetate is dispersed in finely divided form directly in a silicone resin with high permeability to hydrogen sulfide.

A silicone resin/sensor suspension was prepared by dissolving 0.10 gm lead acetate in 1.7 mL methanol to which was added 7 mL xylene with rapid mixing followed by 2.7 gm silicone resin. The suspension was dispensed in 0.06 mL portions in the center of white, polyethylene foam liners in plastic bottle caps. The deposit was spread evenly in a circular area 1.5 cm in diameter and allowed to cure for a day or more in a horizontal position.

ANALYTICAL PROCEDURE

To make an analysis, 100 mL of oil or water was placed in a high-density, polyethylene sample bottle (HDPE) with as little exposure and mixing with air as possible. To assure that hydrogen sulfide was in the un-ionized form in aqueous samples, about 0.1 gm of citric acid was added. The bottle was immediately closed with a bottle cap carrying the appropriate sensor, inverted and swirled with occasional reinversions to assure good mixing. After 5.0 minutes, the cap was removed in the case of aqueous samples or the tape holding the sensor lifted in the case of the oil sample so that the sensor could be inspected and matched with an appropriate set of standards to assess the concentration of hydrogen sulfide in the sample.

RESULTS

The kit has been used in an ongoing monitoring program of hydrogen sulfide in crude petroleum stored in salt dome caverns of the U. S. Department of Energy's Strategic Petroleum Reserve. The hydrogen sulfide concentration in these crudes varied widely from less than 5 ppm to over 300 ppm.

The agreement between the on-site determination with the kits and those obtained in a laboratory using a conventional method (2) on carefully preserved samples was good (Table 1). Mercaptans do not interfere with the kit sensor.

Kits for aqueous solutions have been used extensively in a study of hydrogen sulfide generation in naval ship piping systems containing a solution of seawater and a foaming agent for fighting fires. Table 2 shows typical values. Considerable variation in hydrogen sulfide concentration existed in different sections of the system on the same ship. Appearance of black particulate matter and a foul odor in the sample did not necessarily mean that hydrogen sulfide was present.

In the course of these studies it became clear that, unless stringent precautions were taken to avoid exposure of a sample to air, considerable hydrogen sulfide could be lost in the process of storing and transporting the samples to a laboratory analysis site. Thus the kits described here may not only give an immediate on-site estimation of hydrogen sulfide concentration in a sample, but may also give a more accurate determination than a delayed laboratory analysis.

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Table 1. Hydrogen Sulfide in Crude Oil Stored in the Strategic Petroleum Reserve

	<u>Hydrogen Sulfide Concentration (ppm)</u>	
	<u>Cavern</u>	<u>Lab Determination</u> <u>Kit Determination</u>
BC19	25.7	30-40
BC 101B	15.4	20-30
BH107B	32.3	40-50
BH108B	50.4	40
BH109B	6.0	10
BM110B	54.2	50-60

Table 2. Hydrogen Sulfide in Fire Mains on Naval Ships

<u>Ship</u>	<u>Location</u>	<u>H₂S Concentration (ppm)</u>
LHD-2	HR 17	0.25
	HR-18	>16
	HR-19	ND*
	HR-30	ND
	HR-33	>16
LHD-4	HR-38	0.25
	HR-52	ND
	Zone 6	ND

*ND- Not detectable



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LIQUID-PHASE OXIDATION KINETICS FOR A PARAFFIN BLEND

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ABSTRACT

Kinetics of O₂ depletion in an air-saturated (74.7 ppm O₂) paraffin blend (Exxsol D-80) were conducted with a Near-Isothermal Flowing Test Rig (NIFTR) using passivated heat-exchanger tubing over the range 408 - 438 K. Hydroperoxide formation was monitored by cyclic voltammetry. Autoxidation data are consistent with an initiation mechanism involving hydroperoxide dissociation; the kinetic data are independent of the initial O₂ concentration. Data analysis yielded the following rate parameters: $\log(k_i/s^{-1}) = (15.2 \pm 1.6) - (33.1 \pm 3.1)/\theta$, $\log[k_{iv}(k_i/2k_v)^{1/2}/M^{-1/2}s^{-1/2}] = (9.5 \pm 0.2) - (26.3 \pm 0.4)/\theta$, and $\log[(k_{iv}/2k_v)^{1/2}/M^{-1/2}s^{-1/2}] = (3.3 \pm 1.3) - (12.5 \pm 2.6)/\theta$ (where k_i , k_{iv} , and k_v are rate constants for initiation, propagation, and termination, respectively, $\theta = 2.303RT \text{ kcal mol}^{-1}$, R is the ideal-gas-law constant, and T is absolute temperature). Results are discussed with reference to kinetic parameters reported for conventional aviation fuels and normal paraffins.

INTRODUCTION

Aviation fuels, which are a complex mixture of normal and cyclic paraffins, aromatics, and heteroatomic compounds, may be subjected to severe thermal oxidative stress because of their application as a heat sink in modern aircraft.¹ Surface fouling resulting from this use can be reduced by utilizing highly refined fuels. For example, mild hydrotreatment lowers the concentration of metals and O-, S-, and N-heteroatom-containing species implicated² in reduced thermal stability. More severe hydrotreatment can reduce the total aromatic content.³ Certain high-performance military aircraft such as the SR-71 require specialty JP-7 fuels having low vapor pressure, high thermal oxidative stability, high heats of combustion, and very low concentration of heteroatoms. These requirements can be met by mixing blends

of paraffin and cycloparaffin stocks having very low aromatic content and by introducing a lubricity additive.⁴ The commercial solvent blend Exxsol D-80, manufactured by Exxon for use as a reactive diluent, possesses some desirable characteristics as a model fuel. Comprised of a blend of normal and cyclic paraffins having an aromatic content of < 1%, it is precisely a JP-7 fuel without lubricity additive. It is also representative of severely hydrotreated fuels having reduced aromatic content. Furthermore, since it contains neither synthetic antioxidant nor dissolved metals, it provides an ideal model system for studying autoxidation without added inhibition or metal-catalyzed initiation. In this study, we report the liquid-phase oxidation kinetics measured for air-saturated Exxsol D-80 with the Near-Isothermal Flowing Test Rig (NIFTR).

EXPERIMENTAL

Exxsol D-80 is a solvent blend having an approximate composition of 41% cycloparaffins, 58% paraffins, and 0.8% aromatics. The chain length is 12, and the specific gravity is 0.8072. All experiments were conducted in a single-reaction phase at a system pressure of 2.3 MPa using the NIFTR apparatus that has been described in detail elsewhere.⁵ Reaction occurred as the fuel was pumped slowly through 0.318-cm-o.d., 0.216-cm-i.d. tubing passivated by the Silcosteel⁶ process and clamped tightly within an 81.3-cm heated-Cu-block (40 kg) heat exchanger. Stress duration--the residence time within the heated tube--was varied by changing the fuel flowrate and was calculated based on plug flow. Relative dissolved O₂ concentrations of unstressed and stressed fuel were measured using the high-pressure GC sampling method of Rubey.⁷ Calibration based on an independent GC-MS measurement⁸ of 74.7 ppm (w/w) for air-saturated JP-7 yields an equivalent molarity of 1.88×10^{-3} at 298 K.

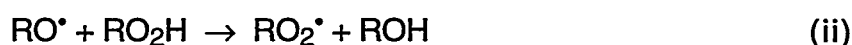
Depletion experiments for a ten-fold variation in the initial [O₂] (10 - 100% O₂ saturation) were conducted at 413 K for assessing the O₂ dependence of the reaction rate. Depletion of O₂ in air-saturated Exxsol D-80 was monitored over the temperature range 408 - 437 K. Oxygen-depletion data expressed as %O₂ were converted to units of moles per liter (M) from the fuel density within the specified temperature range.

Hydroperoxide formation was monitored from 413 to 428 K using cyclic voltammetry⁹ for samples corresponding to 21% O₂ saturation. Hydroperoxide data were expressed in units of moles per liter (M). Measurements at ambient temperature indicated an initial hydroperoxide concentration of $< 10^{-5}$ M.

RESULTS AND DISCUSSION

Data. Oxygen depletion versus time plots at 413 K for a ten-fold variation in the initial $[O_2]$ are illustrated in Figure 1. Figure 2 shows the temperature dependence for O_2 depletion for air-saturated Exxsol D-80 from 408 to 437 K. Figure 3 demonstrates the change in hydroperoxide content from 413 to 433 K for air-saturated fuel and at 413 K for O_2 -saturated blends, respectively. The O_2 -depletion data given in Figure 1 indicates that initial rates are independent of O_2 ; at longer times the global rate increases with time.

Reaction Mechanism. The lack of an O_2 dependence for the initial rates, the acceleration at longer time, and the hydroperoxide data are indications that initiation involves trace quantities of hydroperoxide. Thus, the oxidation mechanism may be expressed as



where RO_2H is hydroperoxide, RH is the paraffinic blend, R^\bullet is a radical, RO_2^\bullet is the peroxy radical, and P_1 and P_2 are molecular products. Reaction i is the major initiation reaction. Reactions iii - iv are propagation steps, and reaction v is the primary termination pathway since $[RO_2^\bullet] > [R^\bullet]$ and $k_{iii} \gg k_{iv}$ at steady state.

Application of the steady-state principle to the proposed mechanism yields

$$\frac{-d[O_2]}{dt} = k_v \left[\frac{k_i}{2k_v} \right]^{1/2} \left(2[RO_2H] \right)^{1/2} [RH] \quad (1)$$

With the assumptions $[O_2] = [O_2]_0(1-\alpha)$, $[RO_2H] = \alpha[O_2]_0$, $[RH] = [RH]_0(1-\lambda\alpha)$ (where α is the extent of reaction, λ is $[O_2]_0/[RH]_0$, and $[O_2]_0$ and $[RH]_0$ are initial concentrations), Equation (1) may be rearranged to obtain

$$\frac{d\alpha}{dt} = 2^{1/2}k_{iv} \left[\frac{k_i}{2k_v} \right]^{1/2} \frac{[RH]_0}{[O_2]_0^{1/2}} \alpha^{1/2}(1 - \lambda\alpha) \quad (2)$$

For hydroperoxide formation the steady-state hypothesis coupled with the assumption $[RH] \approx [RH]_0$ yields

$$\frac{d[RO_2H]}{dt} = k_{iv} \left[\frac{k_i}{2k_v} \right]^{1/2} [RH]_0 [RO_2H]^{1/2} - k_i [RO_2H] \quad (3)$$

Integration of Equations (2) and (3) yields (4) and (5), where $k_{ap} = k_{iv}(k_i/2k_v)^{1/2}$, $a = 2^{-1/2}k_{iv}(k_i/2k_v)^{1/2}[RH]_0$, and $b = k_i/2$.

$$[O_2] = [O_2]_0 \left[1 - \lambda^{-1} \left(\frac{e^{k_{ap}(2[RH]_0)^{1/2}t} - 1}{e^{k_{ap}(2[RH]_0)^{1/2}t} + 1} \right)^2 \right] \quad (4)$$

$$[RO_2H] = \left[\frac{a - (a - b)[RO_2H]_0^{1/2} e^{-bt}}{b} \right]^2 \quad (5)$$

Values of k_{ap} were evaluated from nonlinear least-squares fits according to Equation (4) using the O_2 -loss data at each temperature given in Figure 1 and a constant value of λ . At 413 K, $[O_2]_0 = 1.69 \times 10^{-3}$ M and $[RH]_0 = 3.93$ M, yielding $\lambda = 4.3 \times 10^{-4}$. The $[RO_2H]$ data were insensitive to $[RO_2H]_0$; therefore, the data in Figure 3 were fitted to Equation (5) with the assumption $[RO_2H]_0 \approx 10^{-7}$ M. Values for the composite rate coefficients (a and b) were solved simultaneously to obtain values for k_i and $k_{iv}/(2k_v)^{1/2}$.

Arrhenius plots are illustrated in Figure 4. A least-squares analysis for $k_{iv}(k_i/2k_v)^{1/2}$, $k_{iv}/(2k_v)^{1/2}$, and k_i yielded Equations (6) - (8)

$$\log\left(k_{iv}(k_i/2k_v)^{1/2}/M^{-1/2} \text{ s}^{-1}\right) = (9.5 \pm 0.2) - \frac{(26.3 \pm 0.4)}{\theta} \quad (6)$$

$$\log\left(k_{iv}/(2k_v)^{1/2}/M^{-1/2} \text{ s}^{-1/2}\right) = (3.3 \pm 1.3) - \frac{(12.5 \pm 2.6)}{\theta} \quad (7)$$

$$\log(k_i/\text{s}^{-1}) = (15.2 \pm 1.6) - \frac{(33.1 \pm 1.6)}{\theta} \quad (8)$$

Error estimates for activation parameters in Equations (6) - (8) are one standard deviation, $\theta = 2.303RT \text{ kcal mol}^{-1}$, R is the ideal-gas-law constant, and T is absolute temperature. The solid lines in Figures 1 and 2 illustrate the fits obtained from the average rate parameters summarized in Equation (6).

Discussion. All of the plots in Figures 1 and 2 exhibit an O_2 dependence that is independent of $[\text{O}_2]_0$ and that accelerates with increasing time. This behavior is expected for autoxidation initiated by trace quantities of hydroperoxide; such behavior is consistent with the observations of Fodor et al.¹⁰ for a series of conventional aviation fuels subjected to thermal stress over the range 316 - 393 K. The calculated O_2 depletion indicated by the solid lines in Figures 1 and 2 is in excellent agreement with the experimental data. The O_2 -depletion data have a much greater precision than the hydroperoxide data, as evidenced by the standard errors obtained for $k_{iv}(k_i/2k_v)^{1/2}$ and k_i summarized in Equations (6) and (8).

A major objective of the present work was to determine whether Exxsol D-80 would be useful as a model compound for comparison with conventional fuels. If compared to conventional aviation fuels, Exxsol D-80 should closely resemble an additive-free hydrotreated kerosine having a low aromatic content. Fodor et al.¹⁰ reported data for formation of hydroperoxides in a straight-run, additive-free kerosine with an apparent rate constant $\log(k/\text{s}^{-1}) = 10.2 - 19.4/\theta$. For Fodor's data, the apparent pre-exponential factor is expressed as $\log(A_{iv}(A_i/2A_v)^{1/2}[\text{RH}])$. At the average temperature (423 K) for data reported in the present paper, $[\text{RH}] = 3.89$. This may be combined with the pre-exponential summarized in Equation (10) to obtain $\log(A_{iv}(A_i/2A_v)^{1/2}[\text{RH}]) = 10.1 \pm 0.2$ which is in good agreement with Fodor's results¹⁰ for an additive-free kerosine. Unfortunately, the associated activation energy for Exxsol D-80 differs from that for the additive-free kerosine by 7 kcal mol^{-1} .

The benchmark for comparison of the unimolecular dissociation rate constants for RO₂H decomposition is based on the selection of Benson¹¹ for t-butyl hydroperoxide with $\log(k_i/s^{-1}) = (16.1 \pm 1) - (43 \pm 1)/\theta$. For Exxsol D-80 $E_i = 33.1 \pm 3.1$ kcal mol⁻¹ is lower than the value of 42 ± 1 kcal mol⁻¹ proposed by Benson.¹¹ Anomalies such as this are not uncommon for hydroperoxide decomposition; numerous studies^{10,12,13} have shown that the Arrhenius parameters for hydroperoxide homolysis in the condensed phase vary widely. If induced decomposition is the predominant pathway for a particular RO₂H decomposition, this should be manifested by the observed pre-exponential factor. Dissociation of RO₂H formed in the autoxidation of Exxsol D-80 exhibits $\log(A_i/s^{-1}) = 15.2 \pm 1.6$ which is within the uncertainty of the preferred value expected for t-butyl hydroperoxide. This supports our assertions that the decomposition of RO₂H formed in the autoxidation of Exxsol D-80 is truly unimolecular and that Exxsol D-80 is an excellent candidate for modeling the behavior of aviation fuels.

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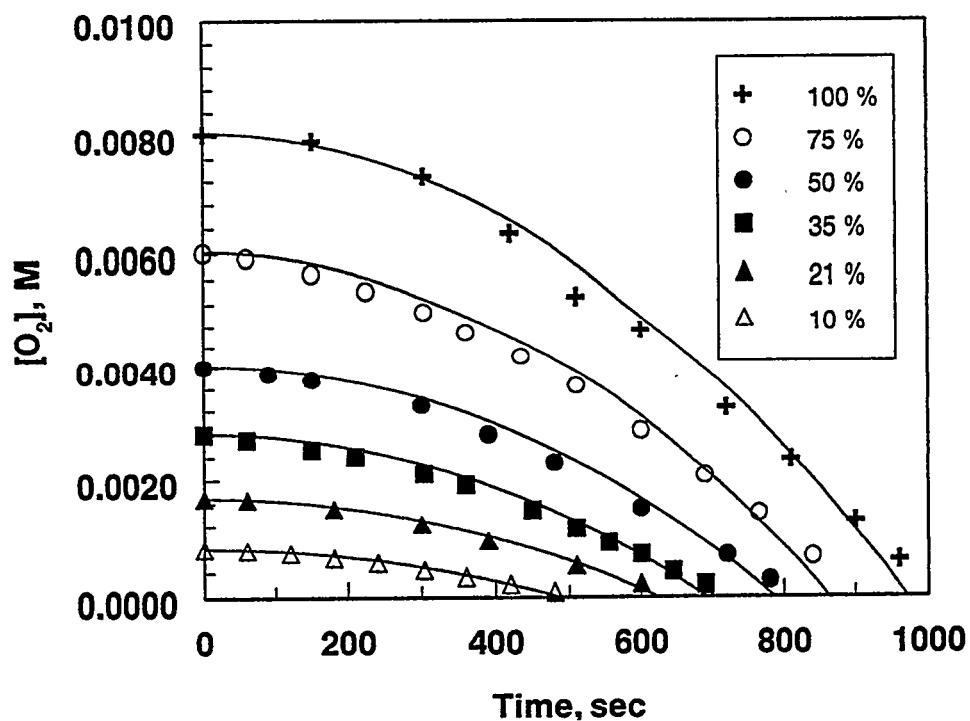


Figure 1. Influence of Dilution on O_2 Depletion at 413 K.

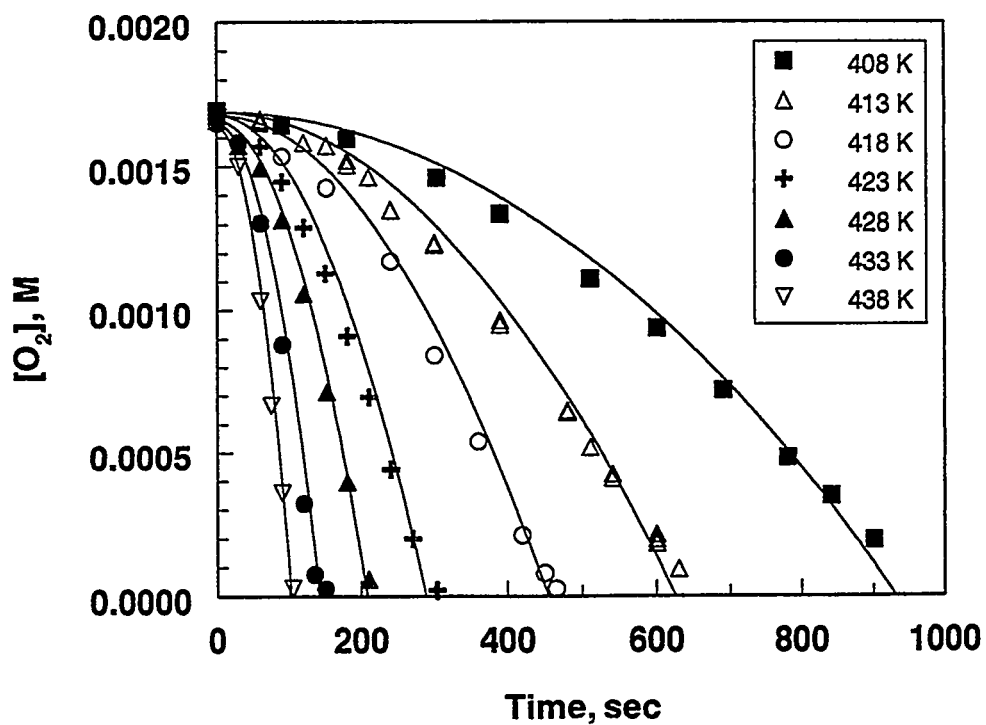


Figure 2. Influence of Temperature on O_2 Depletion for Air-Saturated Exxsol D-80 from 408 to 438 K.

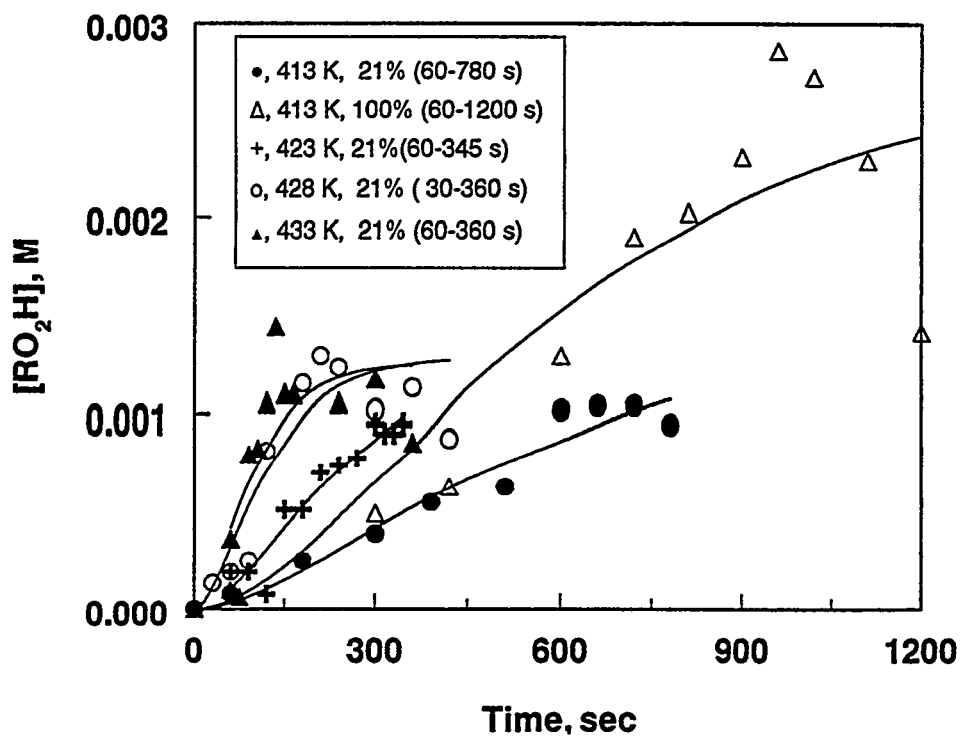


Figure 3. Variation of RO_2H from 413 to 433 K for Air-Saturated Exxsol D-80 and at 413 K for O_2 -Saturated Exxsol D-80.

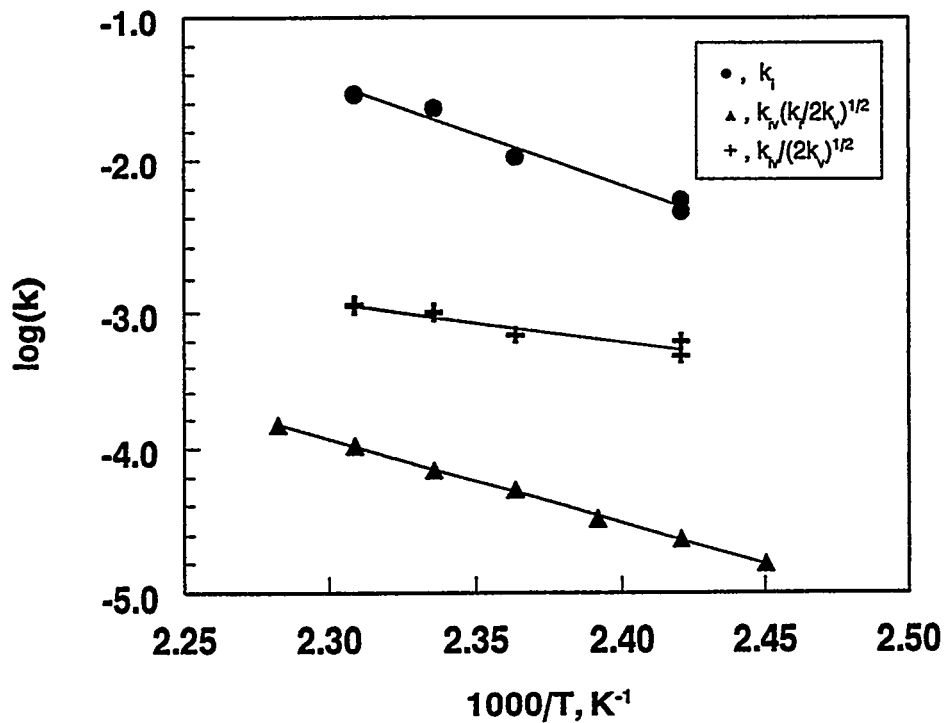


Figure 4. Arrhenius Plot for Exxsol D-80 Oxidation from 408 to 438 K and RO_2H Formation from 413 to 433 K.



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EXPERIENCE IN USE OF AUTOMATIC HEAVY FUEL OIL STABILITY ANALYZER

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INTRODUCTION

Stability or long term storage life is an important factor demanding of heavy fuel oils refined in the thermal cracking/visbreaking production units. The stability figure for heavy fuel oils indicates the precipitation tendency of asphaltene molecules in the oil.

The stability figure is usually determined by the manual precipitation spot test method using visual detection. However, this manual method is tedious and takes up to an hour to perform. An automatic stability analyzer performs the same stability procedure as the manual method only in few minutes.

In this study we compared nearly one hundred stability figures of visbreaker products determined both manually and automatically. The results obtained by the analyzer correlated well with the those by the manual method.

RESULTS

The stability figures of Visbreaker tar (Vistar) production process were monitored during nine months by PORLA automatic stability laboratory analyzer. Figure 1 shows the stability figures obtained by PORLA and the deviations from the manual method during the monitoring period. Figure 2 illustrates the correlation between P value and operating temperature of visbreaker unit.

CONCLUSIONS

- PORLA is a fast and accurate analyzer for handling of product quality and process control of heavy oil production.
- PORLA can be used for optimization of thermal cracking units.
- PORLA is much faster than the manual method.
- PORLA is easy to handle.

FIG 1: STABILITY FIGURES BY PORLA AND DEVIATIONS FROM MANUAL VALUES

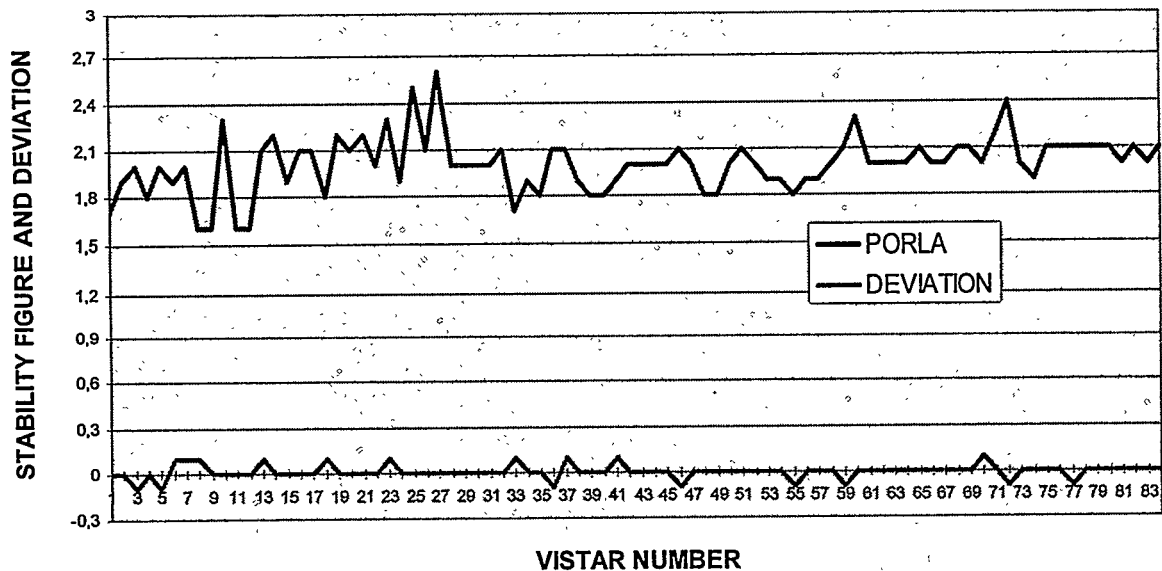
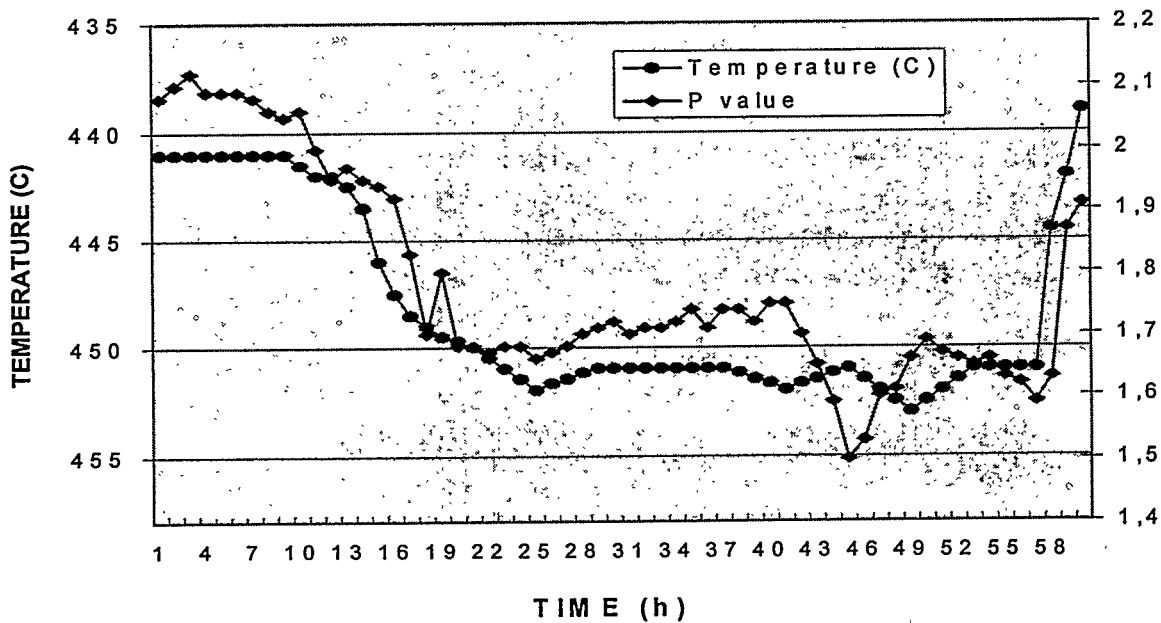


FIG 2: CORRELATION OF STABILITY AND TEMPERATURE IN THERMAL CRACKING PROCESS



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**TESTS TO EVALUATE AND PREDICT DIESEL AND GASOLINE ENGINE FUEL SYSTEM
DEPOSITS**

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Diesel and gasoline fuels have varying degrees of depositing potential in engines. Some additives have the ability to reduce deposit potential to acceptable levels. The current fuel deposit related engine and laboratory test techniques are briefly reviewed in this paper. Data developed with deposit enhancing additives to demonstrate deposit control is also presented. Approaches for relative ranking of additive deposit controlling properties of gasolines are demonstrated.

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**THE MEASUREMENT OF ANTIOXIDANT PERFORMANCE IN AVIATION TURBINE FUEL
USING THE QUARTZ CRYSTAL MICROBALANCE AND NEAR ISOTHERMAL FLOWING
TEST RIG**

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Antioxidants are widely used in aviation turbine fuel to inhibit hydrocarbon oxidation during transport and storage. However, the approved antioxidant formulations vary among the major turbine fuel specifications. In an attempt to rationalize the antioxidant formulations and establish a common list based on efficacy, the performance of currently approved antioxidants was measured using the Quartz Crystal Microbalance (QCM) and the Near Isothermal Flowing Test Rig (NIFTR). The QCM is a static system that employs a polarographic oxygen probe to measure the depletion of headspace oxygen in real time. The NIFTR employs a gas chromatographic technique to measure the dissolved oxygen concentration in the fuel as it passes through a heated tube. The ability of an antioxidant to delay oxygen consumption is a measure of performance. Results for the various hindered phenolic and amine antioxidants will be presented.