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MILITARY JET FUELS, 1944 - 1987

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This report consists of a brief history of US military fuels for aircraft turbine (jet) engines and ramjet engines. The report discusses the requirements of past and current US military jet fuel specifications, when and why the specification requirements originated, and the importance of these requirements today. The purpose and origin of the various specification test methods are presented, and an extensive discussion of jet fuel additives is provided.

This report should be of value to anyone involved in research and development, logistics, and use of jet fuels. We hope that it will serve as a handy reference for the jet fuel specialist.

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SUMMARY

This report was prepared to document the history of aviation turbine (jet) fuels and their specifications' requirements and test methods. Current specifications for JP-4, JP-5, JP-7, JPTS, and JP-8 fuels contain requirements and specification limits that originated years ago. The purpose of this report is to document the reasons for these specification requirements and limits, insofar as can be determined.

A second purpose of this report is to serve as a primer for personnel newly assigned to work with jet fuels, either in research and development or in operational commands.

FOREWORD

The work reported herein was performed under Program Element 62203F, Project No. 3048, Task No. 05, Work Unit No. 91, during the period of October 1985 to October 1987. Charles R. Martel of the fuels Branch, Fuels and Lubrication Division (AFWAL/POSF), Aero Propulsion Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio 45433-6563, was the project engineer.

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INTRODUCTION

Early proponents of the aviation gas turbine (jet) engines claimed that these new engines could run on any fuel ranging from whiskey to peanut butter. Although jet engines are much more fuel tolerant than gasoline and diesel reciprocating engines, the aircraft and engine fuel system components and controls are sensitive to the physical and chemical properties of fuels. Specifications are used to limit the range of fuel properties to insure proper performance of the aircraft and engine fuel systems during all stages of flight.

In 1944, the US first published specification AN-F-32 for JP-1, a kerosine jet fuel. The first British jet fuel specification, RDE/F/KER (Provisional) was also published prior to the end of World War II. Although the first US jet engines were direct copies of early British designs, these two pioneering jet fuel specifications differed significantly in freezing point, specific gravity, sulfur, and aromatics limits. The US specification appears to have been derived from the aviation gasoline specification, while the British specification reflected the properties of illuminating kerosine, used in early British jet engines.

Since these early days, military jet fuel standardization has been obtained and maintained through the Air Standardization Coordinating Committee (ASCC), composed of the United States, United Kingdom, Canada, Australia, and New Zealand, and the North Atlantic Treaty Organization (NATO). Today the three standard NATO jet fuels are F-34 (JP-8), F-40 (JP-4), and F-44 (JP-5). The worldwide use of American, British, French, Canadian, Dutch, and other western nations' aircraft and engines has further aided the standardization of military jet fuels. The International Air Transport Association (IATA) and similar organizations have helped to standardize commercial jet fuels, which are very similar to military jet fuels.

This report discusses the requirements of US military jet fuel specifications, when and why the specifications requirements originated, and the importance of these requirements today. Information for this report has been obtained from the references listed at the back of the report, from Air Force files, and from conversations with some of the early jet fuel specialists.

SECTION II

USAF JET FUEL HISTORY

1. FIRST JET FUELS

Hans von Ohain developed the first successful aviation gas turbine (jet) engine that first flew in the Heinkel He 178 on 27 August 1939. Gasoline was the fuel used because of its ease of evaporation and known performance in aircraft fuel systems. Von Ohain has since stated that the combustor was one of the most difficult design problems encountered. Some of his early test combustors used hydrogen as the fuel because of the combustion problems encountered in using gasoline.

Across the English Channel Sir Frank Whittle also developed an aircraft gas turbine engine; both Whittle and Von Ohain were unaware of the other's work. Whittle's engine first flew in a Gloster E28/32 aircraft on 14 May 1941. The fuel used by Whittle's engine was illuminating kerosine, as gasoline was in short supply because of World War II. Diesel fuel, also considered, was not selected as it could freeze during flight.

2. USAF JET FUELS

Table 1 compares the specification requirements of US military jet fuels (see Appendix A for applicable conversion factors.) Each fuel is discussed below.

a. JP-1. The first US jet fuel, a kerosine fuel identified as JP-1 (Jet Propellant-1), had a freezing point of -60 C, the same as specified for aviation gasoline. The specification for JP-1, AN-F-32a, was first issued in 1944 and was subsequently changed to MIL-F-5616 in 1950. This specification was undoubtedly influenced by the British, as the first US jet engines were direct copies of British designs.

b. JP-2. The low freezing point and high flash point of JP-1 restricted its production to about 3 percent of the average crude oil (reference 1). To increase fuel availability, a wide-cut distillate fuel, JP-2 (specification AN-F-34) was developed in 1945. The use of JP-2 was limited to experimental testing and experimental service use and was found to have unsuitable viscosity and flammability (reference 1).

c. JP-3. The second operational fuel for US military jet aircraft was a wide-cut distillate fuel with a vapor pressure comparable to that of aviation gasoline. Specification AN-F-58 for JP-3 was issued in 1947. As jet aircraft tended to fly at higher altitudes than reciprocating engine-powered aircraft, fuel boiloff losses and vapor lock problems were encountered. However, the high vapor pressure of JP-3 aided low temperature starting and high altitude relight (references 1 and 2).

TABLE 1. Comparison of Jet Fuel Specification Requirements

SPECIFICATION REQUIREMENTS	JP-1	JP-2	JP-3	JP-4	JP-4	JP-5	JP-6	JPTS	JP-7	JP-8	RJ-1
Specification Number	AN-F-32	AN-F-3	AN-F-58	MIL-F-5624A	MIL-T-5624M	MIL-T-5624M	MIL-T-25656B	MIL-T-25524C	MIL-T-38219B	MIL-T-83133B	MIL-F-25558C
Distillation Temperature, C											
Initial Boiling Point, min	-	66	-	-	R	R	138	157	182	-	220
10 percent recovered, max	210	-	-	121	R	205	177	197 min	196 min	205	225-250
20 percent recovered, max	-	-	-	-	145	R	-	-	206 min	R	-
50 percent recovered, max	-	-	-	-	190	R	218	224	R	R	R
90 percent recovered, max	254	-	204	-	245	R	260	238	260	R	265-290
End point, max	300	260	316	288	270	290	-	260	288	300	315
Reid Vapor Pressure, lbf/in^2 at 38 C	-	2 max	5-7	2-3	2-3	-	-	-	-	-	-
Flash Point, C, min	43	-	-	-	-	60	-	43	60	38	85
Viscosity, cSt, max	10	10	-	-	-	8.5	7	12	8	8	25
at temperature C	-40	-40	-	-	-	-20	-40	-40	-20	-20	-20
Freezing point, C, max	-60	-60	-60	-60	-58	46	-54	-53	-43.3	-47	-40
Density, kg/L at 15 C											
minimum	-	-	0.728	0.747	0.751	0.788	0.780	0.767	0.779	0.775	0.842
maximum	0.850	0.850	0.802	0.825	0.802	0.845	0.840	0.797	0.806	0.840	0.863
Aromatics, vol percent, max	20	20	25	25	25	25	25	20	5	25	5
Olefins, vol percent, max	-	-	-	-	5	5	5	3	-	5	1
Bromine Number, max	3	3	30	30	-	-	-	-	-	-	-
Sulfur, wt percent, max	0.20	0.20	0.40	0.40	0.40	0.40	0.40	0.30	0.10	0.30	0.07
Mercaptan Sulfur,											
weight percent, max	-	-	0.005	0.005	0.002	0.002	0.001	0.001	0.001	0.002	0.005
Existent Gum, mg/100 mL, max	5	5	10	10	7	7	5	5	5	7	7
Accel Gum, mg/100 mL, max	8	8	20	20	-	-	10	-	-	-	14
test length, hours	16	7	16	16	-	-	16	-	-	-	16
Corrosion, copper strip, max	-	-	-	-	1b	1b	1b	1b	1b	1b	1b
Total Acid No., mg KOH/g, max	-	-	-	-	0.015	0.015	-	0.015	-	0.015	0.015
Heating Value, Btu/lb, min	-	-	18400	18400	18400	18300	18400	18400	18700	18400	18500
Smoke Point, mm, min, or	-	-	-	-	20	19	20	25	-	19	20
hydrogen Content, wt %, min	-	-	-	-	13.6	13.4	-	14.0	14.4	13.4	13.6
Thermal oxidative stability											
JFTOT test temp, C	-	-	-	-	260	260	(1)	335	355	260	-
Test length, hours	-	-	-	-	2.5	2.5		2.5	5.0	2.5	

(1) ASTM-CRC Fuel Coker, 5 h test at 425/525 F, ASTM D 1660

d. JP-4 (NATO F-40). Specification MIL-F-5624A, issued in May 1951, included Grade JP-4 fuel for the first time. With a Reid vapor pressure restricted to 2.0 to 3.0 lbf/in^2, JP-4 overcame the excessive boiloff losses encountered with JP-3 while retaining good availability and adequate low temperature starting and high-altitude relight performance. JP-4 has remained the primary jet fuel for the US Air Force to date (1987).

The MIL-F-5624A specification revision allowed the use of "cracked" materials in the formulation of JP-3 and JP-4; i.e., blending stocks that had been subjected to thermal or catalytic processes to split (crack) large molecules into smaller ones of suitable size for use in jet fuels. The specification change that allowed the addition of cracked components was the maximum allowable Bromine Number of 30.0, as compared to a Bromine number of 3.0 for JP-1 and JP-2. (A discussion of the Bromine Number follows in Section IV, paragraph 1b). Cracked products are less stable than straight distillates and can cause operational problems. In 1955 MIL-F-5624 was changed, replacing the 30.0 Bromine Number limit with a maximum olefin content of 5 percent by volume or a maximum Bromine Number of 5.0, thereby greatly reducing the amount of cracked stocks that could be used (reference 1). (The Bromine Number test was dropped from the specification in 1962.)

During the distillation of crude oil to make JP-3 or JP-4, a wide cut is taken of the distillate so as to include both the naphtha (gasoline) and kerosine fractions. JP-4 is typically composed of about 50 percent to 60 percent gasoline and the remainder is kerosine. The primary advantage of wide-cut fuels is the greatly increased availability. Reference 1 states that up to 60 percent of a barrel of crude oil could be converted into JP-3 and about 40 percent into JP-4. These estimates were based on the use of high-quality, light crude oils that are no longer available in quantity and on the inclusion of cracked components. Today (1987), cracked products (olefins) are limited to 5 percent by volume, and only heavier, lower-quality crude oils are normally available; thus, less JP-4 can be distilled from a barrel of crude oil.

e. JP-5 (NATO F-44). The first US Navy jet aircraft used aviation gasoline, but the lead in the fuel was found to attack the engine hot section components. One proposed approach was to blend the aviation gasoline with a kerosine fuel to form "Jet Mix", a product similar to JP-4. JP-5, a high flash point kerosine developed by the Navy for use in Jet Mix, was first covered by specification MIL-F-7914 dated 11 March 1952. Subsequently, JP-5 was included in MIL-F-5624B dated 7 December 1953. Although considerable work was done on Jet Mix, this product was not used operationally. The Navy found they could fly their jet aircraft using straight JP-5, which has remained the Navy's primary jet fuel.

The Navy requires a high flash point kerosine (minimum flash point of 60 C) for shipboard safety reasons. To insure adequate availability, the Navy selected a maximum freezing point of -46 C. For ship-launched aircraft this has been found to be adequate, as they fly relatively short duration missions and the ocean's thermal mass prevents the extremely low surface temperatures that may occur over land. Even with a moderately high freezing point, JP-5 has limited availability. Thus, for many years the Navy used JP-4 when operating their aircraft from land bases.

f. JP-6. JP-6 was a kerosine fuel developed in 1956 for the XB-70. Although the XB-70 was also designed to burn an exotic, boron-based fuel to give increased range, the boron-based fuel program was later cancelled because of cost and the marginal range increase obtained. JP-6 was similar to JP-5 but with a lower freeze point and improved thermal oxidative stability (see Section IV, paragraph d.) The cancellation of the XB-70 program eventually resulted in the cancellation of the JP-6 specification, MIL-J-25656, Jet Fuel, Grade JP-6.

g. JPTS. Another special purpose fuel developed in 1956 was Thermally Stable Jet Fuel (JPTS), a kerosine fuel especially designed for the high-flying U-2. JPTS featured a low freezing point and improved thermal oxidative stability. The early test fuel for the U-2 was identified as LF-1, being essentially commercial charcoal lighter fluid. JPTS, produced to specification MIL-T-25524, Turbine Fuel, Aviation, Thermally Stable, is still used in the U-2 and in the newer TR-1.

The thermal oxidative stability of early production batches of JPTS fuel often degraded during short-term storage. The degradation occurred with fuels from all but one producer, so for a short time the fuel was purchased from a single source while the problem was studied. Two changes were made to solve the problem: (1) The thermal oxidative stability requirement was increased in severity for the initial purchase of the fuel, while retaining the former thermal oxidative stability requirement as an operational use limit. (2) A proprietary additive, JFA-5 produced by the Du Pont Company, was added to all JPTS fuel (See Section V, paragraph 7.)

Mr Charles Hudson, former Chief of the Fuels and Lubrication Division of the Aero Propulsion Laboratory, tells an interesting story of the origin of the JPTS specification. He was an Air Force Captain assigned to the Fuels Branch when the U-2 was being developed under tight security restrictions. One day he was instructed to buy a tank-car load of LF-1 and have it shipped to an engine manufacturer. Not knowing what LF-1 was, he obtained a sample, had it analyzed, and determined that it was a paraffinic kerosine used as a charcoal lighter fluid (hence LF-1).

Capt Hudson was also aware of the recent crash of a classified experimental plane and of a new model of the J-57 engine with an unusually high altitude operating capability. Based on these facts, the recently acquired knowledge of the properties and cost of LF-1, and other bits of information, he concluded that a high-flying, subsonic plane was being developed by the Lockheed Company, that a special model of the Pratt Whitney J-57 engine was used, and that LF-1 was its fuel. He also knew that the Air Force was paying an excessive price for LF-1.

Capt Hudson arranged to visit an officer in the Pentagon he suspected would know about the program, if indeed it existed. He told the officer his deductions regarding the classified plane and the sources of his information. He concluded that there was a need for a military specification for a jet fuel to replace the costly LF-1. The Pentagon officer told Capt Hudson that he had an interesting theory, but that he couldn't comment on its accuracy or validity. Subsequently Capt Hudson was told to prepare the proposed specification. Capt Hudson did as he was told and heard nothing more about the matter until Gary Francis Powers' U-2 was shot down over Russia. In one of the photographs of the crashed U-2 could be seen a placard that read: "USE MIL-F-25524 JET FUEL ONLY." This was Capt Hudson's specification!

h. JP-7. The development of the SR-71 in the late 1960s required a new fuel having a low vapor pressure and excellent thermal oxidative stability, because of the very high altitude and Mach 3+ cruising speed of the SR-71. To insure adequate combustor life, the fuel was also required to have excellent combustion characteristics, initially specified in terms of Luminometer Number but later changed to hydrogen content. A high net heat of combustion was also specified. These requirements essentially limit the composition of JP-7 to paraffins and cycloparaffins. The aromatic content is typically below 3 percent by volume. This fuel composition results in a fuel with a relatively high freezing point (-43.5 C), but the SR-71 spends little time at subsonic speeds at high altitude.

The experimental fuel used in the development of the SR-71 was PF-1, procured to a specification prepared by the engine manufacturer (not to be confused with PF-1 per military specification MIL-P-87173). PF-1 was replaced by JP-7 in 1970 with the publication of specification MIL-T-38219, Turbine Fuel, Low Volatility, JP-7.

JP-7 is not a distillate fuel as are most other jet fuels but is composed of special blending stocks that have been subjected to special processes to remove aromatics. This special processing results in a very clean hydrocarbon mixture that is very low in the sulfur, nitrogen, and oxygen impurities typically found in distillate fuels. This results in a fuel that has excellent thermal oxidative stability but very poor lubricating properties. A special fuel lubricity additive, PWA-536, is used in JP-7 to prevent excessive wear of the engine fuel pump (See Section V, paragraph 4.)

i. JP-8 (NATO F-34). JP-8 is a kerosine fuel very similar to commercial Jet A-1 fuel (See Section II, paragraph 3.). Combat experience obtained during the Southeast Asian Conflict revealed that USAF aircraft using highly volatile JP-4 had higher combat losses than US Navy aircraft using low volatility JP-5. Also, crash data indicated that the probability of a postcrash fire is almost 100 percent when using JP-4; much higher than with a kerosine fuel such as JP-5 or commercial Jet A. The increased safety of kerosine fuels, as compared to wide-cut fuels such as JP-4, was also evident in the number and severity of ground handling accidents. Therefore, JP-8 was developed to give the Air Force a safer, kerosine-based jet fuel that would still have adequate availability and an acceptable freeze point (initially -50 C but recently changed to -47 C).

In 1979, JP-8 became the primary jet fuel for USAF operations in Great Britain. NATO is currently in the process of converting to JP-8 as its primary jet fuel. This conversion is to be completed in 1991.

The replacement of JP-4 with JP-8 for continental United States (CONUS) operations has been considered. Studies indicate that it would take about 2 yr for the nation's production capacity to increase sufficiently to satisfy both the Air Force's need for JP-8 and commercial aviation's need for Jet A. Also, there would be a significant cost increase with JP-8. The petroleum crude shortages caused by the oil embargo of 1973 and the Iranian revolution in 1979-80 have also discouraged the conversion to JP-8.

Because JP-8 is a kerosine-based fuel with relatively low volatility, ground starting and altitude relight performance of jet aircraft are affected. US Army helicopters have experienced significantly degraded starting performance when using JP-8. Although the technology is available to provide adequate starting/relight performance with JP-8, modification of some existing aircraft engines might be required.

The properties of JP-8 were selected to be identical to those of commercial Jet A-1, which had a freezing point of -50 C. This was done to simplify the production of JP-8. Subsequently the freezing point of Jet A-1 was raised to -47 C, and the freezing point of JP-8 has been increased accordingly. Work is continuing to determine the maximum freezing point that will just be adequate for USAF aircraft, as JP-8 availability is limited by its freeze point. For some polar locations the ground temperatures can be as low as -50 C for up to 24 h at a time, but a maximum allowable freeze point of -47 C is believed adequate for European theater flight and ground operations (reference 3.)

Although JP-8 (NATO F-34) is scheduled to become the standard NATO fuel and may eventually become the standard CONUS military fuel, JP-4 is likely to remain the standard fuel for Arctic operations. JP-4 inherently has a low freeze point, and its high volatility and low viscosity provide the excellent low temperature starting characteristics essential for Arctic operations.

j. Ramjet Fuels.

(1) RJ-1. Specification MIL-F-25558, Fuel, Ramjet Engine, Grade RJ-1, was first released in April 1956. According to available records, RJ-1 was designed for the Navaho missile, a long-range cruise missile that never became operational. RJ-1 is a high boiling range kerosine distillate fuel, and its properties are listed in Table 1. The RJ-1 specification was cancelled in March 1983, because of no existing or planned system that would use the fuel.

(2) RJ-2 and RJ-3. No information has been found on these fuels. We assume that these fuels never progressed past the development stage.

(3) RJ-4. Specification MIL-P-82522, Propellant, Jet Engine, T-H Dimer, Grade RJ-4, describes the first high density, synthetic hydrocarbon missile fuel. Developed by the US Navy, RJ-4 was used in the mid-1960s in the ramjet-powered Talos missile. The freezing point of RJ-4 is -46 C, too high for use in air launched missiles. However, RJ-4 is the primary fuel for the Ground Launched Cruise Missile. The properties and composition of RJ-4 are listed in Table 2.

(4) RJ-5. RJ-5, a proposed fuel that is a mixture of hydrogenated dimers of norbornadiene, is based on Shelldyne H technology developed by the Shell Oil Company in the 1960s. It is unusual in being a liquid hydrocarbon with a density greater than that of water. Its high freezing point, high viscosity and high cost have deterred its use in Air Force systems. See Table 2 for properties of RJ-5.

(5) RJ-6. RJ-6 is a proposed fuel consisting of a mixture of RJ-5 and JP-10 (see below). This mixture eliminates the freezing point problem and reduces the high cost and high viscosity of RJ-5, while retaining much of its high volumetric energy density. The proposed composition of RJ-6 is 60% RJ-5 and 40% JP-10. A production batch of RJ-6 has been delivered to an engine company for testing as a potential fuel for the Advanced Strategic Air Launched Missile (ASALM). See Table 2 for properties of RJ-6.

TABLE 2. Typical Properties of Liquid Hydrocarbon Missile Fuels

	RJ-4	RJ-5	RJ-6	JP-9	JP-10	PF-1
SPECIFICATION	MIL-F-82522	DRAFT	DRAFT	MIL-P-87107	MIL-P-87107	MIL-P-87173
MOLECULAR FORMULA	$C_{12}H_{20}$	$C_{14}H_{18}$	$C_{12}H_{17}$	$C_{10.2}H_{16}$	$C_{10}H_{16}$	$C_{9.6}H_{15.8}$
MOLECULAR WEIGHT	164	186	161	138.4	136	131
DENSITY @ -40 C kg/m^3	0.93	1.08	1.024	0.951	0.939	0.915
BOILING RANGE, C						
MINIMUM	207	260	182	99	181	99
MAXIMUM	221	285	285	285	183	182
FLASH PT, C	71	104	61	21	53	20
FREEZE PT, C	-46	-29	-54	-54	-90	-54
VISC, cSt @ -40C	60	2000	140	24	19	15
NET HEAT OF COMB						
MJ/m^3	39600	44900	42400	39700	39600	38400
BTU/gal	142000	161000	152000	142500	142000	138000
BTU/lb	18300	17900	18000	18000	18150	18100

k. Turbine Missile Fuels JP-9, JP-10, and PF-1. Specification MIL-P-87107, Propellant, High Density Synthetic Hydrocarbon Type, Grades JP-9 and JP-10, covers two fuels currently in use in the Air Launched Cruise Missile (ALCM). JP-9 was originally developed for use in the Subsonic Cruise Armed Decoy (SCAD) missile and later was selected as the fuel for the ALCM. JP-9 consists of a blend of RJ-5, JP-10, and methyl cyclohexane (MCH). The MCH is used to increase the volatility of the fuel to aid high altitude engine starting.

JP-10 was later selected to replace JP-9 for the ALCM. As JP-10, exo-tetrahydrodi(cyclopentadiene), does not have sufficient volatility to insure reliable high altitude engine starts, a special priming fluid, PF-1, was developed for starting and the initial operation of the engine. After the PF-1 has been consumed, the engine switches to JP-10.

Specification MIL-P-87173, Propellant, Priming Fluid, ALCM Engine, Grade PF-1, consists of JP-10 with about 10 - 12 percent MCH. The combination of PF-1 (for starting) and JP-10 gives equivalent ALCM performance as JP-9, but at a fuel costs savings of about 75 percent. Table 2 lists the composition and properties of JP-9, JP-10, and PF-1.

l. Exotic Jet Fuels. Methane has the highest energy content per unit mass (50.24 MJ/kg or 21 600 Btu/lb) of any hydrocarbon. As seen in Table 3, other elements and compounds have much higher energy contents, with hydrogen the most energetic with a heat of combustion of 120 MJ/kg (51 600 Btu/lb). Boron and its hydrides are promising fuels, with attractive energy contents per unit mass and per unit volume. Various attempts have been made to use boron and other nonhydrocarbon fuels as discussed below.

(1) SF-1. Special Fuel Number One (SF-1) was the code name for a fuel to power a high altitude, supersonic plane that was to replace the U-2. SF-1 was liquid hydrogen, a cryogenic liquid that has about 250 percent as much energy per unit mass and about 10 percent of the density of a liquid hydrocarbon fuel. When Lockheed Aircraft found a way to meet the aircraft performance requirements using a liquid hydrocarbon fuel, the SF-1 fuel/engine/airframe program was cancelled. However, much of the newly developed liquid hydrogen technology was subsequently applied to the Centaur program. The Centaur is an upper stage boost rocket that uses liquid hydrogen and liquid oxygen propellants.

(2) SF-2. In the 1950s the United States spent hundreds of millions of dollars to develop boron hydride fuels for jet aircraft. These candidate fuels promised a 40 to 50 percent increase in range as compared to conventional liquid hydrocarbon fuels.

TABLE 3. HEAT OF COMBUSTION OF VARIOUS FUELS

FUEL	MJ/kg	BTU/lb	MJ/L	BTU/gal
Liquid methane	50.0	21 600	20.80	74 700
Grade 100 AvGas	43.7	18 800	31.53	113 200
JP-4	43.5	18 700	33.06	118 700
JP-5	43.0	18 500	35.04	125 800
JP-10	42.1	18 100	39.47	141 700
Liquid Hydrogen	120.1	51 600	8.41	30 400
Diborane	73.5	31 590	32.81	117 800
Pentaborane	68.3	29 360	42.88	153 950
Carbon Black (solid)	32.8	14 090	62.3	223 400
Aluminum (solid)	31.0	13 310	83.6	300 000
Boron (solid)	57.6	24 775	134.9	483 800
JP-10/Carbon Black*	36.6	15 740	49.3	177 000
JP-10/Carbon Black**	37.4	16 100	48.9	175 500
JP-10/Aluminum*	34.5	14 830	58.6	210 800
JP-10/Boron*	44.1	18 940	68.3	245 000
JP-10/Beryllium*	57.5	24 700	76.4	275 000
HEF-2	56.5	24 300		
HiCal-3	53.2	22 860		

*43.4% Solids by Volume Slurry Fuels
**39% Solids by Volume Slurry Fuel

Specification MIL-F-26675, *Fuel, Aircraft SF-2, Grades 2, 3, and 4*, was published for fuels based on diborane (B_2H_6), pentaborane (B_5H_9), and decaborane ($B_{10}H_{14}$). Callery Chemical Company produced test quantities of HiCal-2 (based on pentaborane) for weight-limited aircraft and HiCal-3 (based on decaborane) for volume-limited aircraft. Olin Mathieson Chemical Company produced two candidate fuels; HEF-2 (n-propylpentaborane) and HEF-3 (reference 4). HiCal-3 was composed of 33 percent carbon, 51.8 percent boron, and 10.6 percent hydrogen by weight. The remainder of the material was not identified. HEF-2 was composed of 48.3 percent boron, 37.0 percent carbon, and 14.3 percent hydrogen by weight (reference 5).

The SF-2 fuels were designed for use in the XB-70 bomber. Ground tests indicated that only a 10 to 15 percent range increase would be realized, much less than the anticipated range increase of 40 to 50 percent. The incomplete combustion of boron with the formation of intermediate combustion products such as HBO_2 may have been to blame. Problems were also encountered with the deposition of boric oxide inside the engine hot section and with the poor cooling capacity of the SF-2 fuels. The extreme costs of the fuels, coupled with the marginal range increase and other technical problems, resulted in the cancellation of the SF-2 fuel program. The XB-70 development was continued for a few more years using a kerosine fuel, JP-6, but later this program was also cancelled.

(3) Slurry Fuels. By adding powdered carbon or powdered metals to a liquid hydrocarbon fuel, a slurry (or dispersed solid) fuel can be made. Special additives may be used to prevent settling of the solid phase. Research on slurry fuels goes back to at least the early 1950s, but combustion problems, fuel instability, and fuel system problems have discouraged their use. Although slurries of beryllium give the highest heating values, the toxicity of beryllium and beryllium oxide dusts have prevented any serious consideration of berrylium-based fuels.

Table 3 lists the gravimetric and volumetric heating values of several proposed slurry fuels with solids loadings of 43.4 percent by volume. Slurry fuels developed to date have had lower solids loadings so to avoid the high, non-Newtonian viscosities that result with high solids loadings. The particle sizes of the solids are also critical. Very small (submicron) particles give improved stability (i.e., less tendency for the solids to separate from the liquid carrier) but much higher viscosities.

Recently a stable, carbon-black slurry fuel, using JP-10 as the liquid carrier, was developed. High combustion efficiencies have been demonstrated in small turbine engine combustors. With a volumetric heat of combustion of 48.9 MJ/L (175 500 Btu/gal), the carbon slurry provides 15 percent more energy per unit volume than RJ-6. However, the higher density of the fuel and the need for a more complex fuel system to store, pump and meter the viscous slurry fuel, add weight to the vehicle. The actual range increase possible with carbon slurry fuel used in a turbine-powered cruise missile is only about 8 to 10 percent. This slight range increase may not justify the added cost required to use carbon slurry fuel.

Recent work on aluminum and boron slurry fuels has identified technical problems involved in their use. As conventional turbine engine combustors cannot tolerate the high flame temperatures and heat radiation involved in the combustion of these fuels, combustors made of ceramic, carbon-carbon, or other materials will be required. Fuel injector plugging problems were encountered with the candidate carbon slurry fuel, and similar problems would be expected with aluminum or boron slurry fuels.

A serious problem with boron-based fuels is the inability to completely oxidize the boron to boric oxide (B_2O_3). Intermediate combustion products such as HBO_2 cause a significant energy loss. The complete combustion of boron results in the formation of B_2O_3, a glassy solid that may deposit within the engine hot section. With aluminum slurries, the formation of aluminum oxide (Al_2O_3) may cause erosion of downstream engine components.

3. COMMERCIAL JET FUELS

Although different countries have slightly different specifications, there are three basic commercial jet fuels used in the western world. The ASTM[1] D 1655 specification designations for these three fuels are Jet A, Jet A-1, and Jet B.

Jet A and Jet A-1 are kerosine fuels, having a minimum flash point of 37.8 C and a maximum aromatics content of between 20 and 25 percent, subject to notification by the supplier. Jet A, used almost exclusively by commercial airlines operating within the continental United States, has a maximum freezing point of -40 C. Jet A-1, identical to Jet A except for having a maximum freeze point of -47 C, is used primarily by airlines operating in other countries and for transoceanic flights by US airlines.

Jet B is a wide-cut distillate fuel that is the commercial equivalent of JP-4. Jet B is not widely used as its volatility makes it less safe than Jet A and Jet A-1.

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[1] Annual Book of ASTM Standards, Volumes 05.01, 05.02 and 05.03, Petroleum Products and Lubricants, American Society for Testing and Materials, 1916 Race St., Philadelphia PA 19103.

SECTION III

FUEL PROPERTIES THAT AFFECT COMBUSTION

The combustion of jet fuel is affected by both the chemical and physical properties of the fuel. The fuel must be atomized, evaporated, intimately mixed with the combustion air, and combusted. The combustion process includes both pyrolysis and oxidation of the fuel. The pyrolysis and most of the oxidation occurs in the primary zone of the combustor, which is usually operated fuel rich. Additional air is injected into the combustor's intermediate and dilution zones to complete the oxidation of the fuel and to cool and shape the temperature pattern of the combustion gases so as to protect the turbine. The pyrolysis and combustion processes are quite complex with well over 100 different chemical reactions identified. The formation of soot during combustion is known to be affected by temperature, pressure, the local fuel/air ratio, and the fuel chemical composition, but the actual chemical reactions and soot particle growth processes are not understood.

1. ATOMIZATION

Fuel properties that affect the atomization of liquid hydrocarbon fuels include viscosity, surface tension, and density. Atomization is the breaking up of the liquid fuel into many small, discrete droplets. As the evaporation of the fuel is affected by the total surface area of the fuel exposed to the air, smaller and more numerous fuel droplets result in faster evaporation.

Current Air Force jet engines use two basic types of atomizers - pressure swirl atomizers and air-assist atomizers. The pressure swirl atomizers use high pressure to force the fuel through small orifices to form thin sheets of fuel. These sheets are unstable and breakup into ligaments which, in turn, breakup into discrete fuel droplets. The air-assist atomizers use the shearing forces generated by high velocity airflows to form the thin sheets of fuel and to help breakup the sheets of fuel into discrete droplets. Combustor design factors also affect the atomization of fuel.

2. EVAPORATION

Fuel evaporation is a function of the specific heat and latent heat of vaporization of the fuel, the distillation range of the fuel, the degree of atomization, and the combustor operating conditions including inlet air temperature, fuel/air ratio, relative fuel/air velocities, heat radiation, and the degree of fuel/air mixing. The distillation range of the fuel is the most critical fuel parameter, as most liquid hydrocarbon fuels have similar specific heats and latent heats of vaporization.

3. MIXING

The mixing of the fuel vapor and air are essentially unaffected by fuel properties, being primarily dependent upon the atomizer and combustor design factors that control the injection, atomization and mixing of the fuel with the combustion air. However, this is a critical step in the combustion of fuels, as the formation of soot is highly dependent upon the local fuel/air ratio during combustion. For example, equivalence ratios greater than about 1.3 (i.e., 30 percent more fuel than required for stoichiometric conditions) will usually result in the formation of soot. Higher equivalence ratios result in increasing quantities of soot formation.

Perfect mixing of fuel and air cannot occur if part of the fuel is still in the liquid form. The combustion of a fuel/air mixture that contains discrete liquid fuel droplets results in soot formation as the fuel/air ratio approaches infinity near the droplet surface.

4. PYROLYSIS AND OXIDATION

Hydrocarbon fuels pyrolyze (i.e., decompose at elevated temperatures) during the combustion process. The products of pyrolysis may include hydrogen, methane, ethylene, other light hydrocarbon molecules, molecule fragments, and soot. As the fuel chemistry affects the pyrolysis products formed, combustion is also affected. Normal paraffins and isoparaffins are the cleanest burning constituents of jet fuels and can be burned at equivalence ratios well above 1.3 without forming soot. Cycloparaffins are intermediate in their combustion performance and aromatics are the worst. Polycyclic aromatics have poorer combustion performance than single-ring aromatics. Thus, fuels with low concentrations of aromatics (such as JP-7) will burn much cleaner than fuels with high concentrations of aromatics (JP-5 and JP-8 often have aromatics contents as high as 22 percent by volume).

The formation of soot within gas turbine engine combustors is undesirable. Any visible smoke that is exhausted by the engine increases the probability of an aircraft being detected, and this can increase the vulnerability of the aircraft to enemy attack. Also, soot formed within the engine combustor incandesces, radiating heat to the combustor walls. This increases heat transfer to the combustor, decreasing combustor life.

The complete oxidation of hydrocarbon fuels leads to the formation of carbon dioxide and water vapor. Incomplete combustion, which results in the emission of carbon monoxide, unburned hydrocarbons, and soot, can result from the quenching of the reactions by cool combustor walls, by incomplete atomization and evaporation of the fuel, by inadequate mixing, and by inadequate combustion residence time.

Combustion efficiency is a measure of the completeness of combustion, with 100 percent efficiency occurring when all hydrocarbons are oxidized to carbon dioxide and water. Typically aircraft gas turbine engines have combustion efficiencies exceeding 99 percent at cruise and maximum power conditions. However, at low power conditions, such as during starting and at idle, the combustion efficiencies may drop significantly. Older jet engines have idle combustion efficiencies of only 60 - 70 percent, but newer jet engines have idle combustion efficiencies greater than 90 percent.

SECTION IV

SPECIFICATION REQUIREMENTS AND TEST METHODS

The various specification requirements for current USAF jet fuels are discussed in this Section. The reasons for these requirements and how the specification limits were set are discussed, where known. The specification requirements are grouped into three subsections: (1) Chemical Composition, (2) Physical Properties, and (3) Miscellaneous Requirements.

1. CHEMICAL COMPOSITION

a. Aromatics. The aromatics content of jet fuels is controlled for two basic reasons. First, aromatics have the poorest combustion performance of the four major hydrocarbon types found in jet fuels (paraffins, cycloparaffins, olefins, and aromatics). By limiting the content of aromatics, adequate combustion performance of the jet fuel can be assured. (Note that the polycyclic aromatics have much poorer combustion performance than the monocyclic aromatics.)

Second, aromatics are excellent solvents, affecting many of the elastomers used in aircraft fuel systems for sealants, gaskets, and hoses. Buna N (nitrile rubber) swells excessively and polysulfide fuel tank sealants have completely failed in fuels with high concentrations of aromatics. Fuel system elastomers are initially qualified using special test fluids having a maximum of 30 percent toluene, a monocyclic aromatic. Current jet fuel specifications limit the aromatics content to 25 percent by volume, thereby providing some margin of safety to assure adequate elastomer life.

A maximum limit on the aromatics content of fuel does not insure that fuel system elastomers will perform satisfactory. Existing fuel tank elastomers, including polysulfide sealants, fluorosilicones, fluorocarbons and nitriles, are all affected by aromatics to varying degrees. Low molecular weight alkyl benzenes (viz., benzene and toluene) appear to cause greater elastomer swell than higher molecular weight alkyl benzenes. There is evidence that polycyclic aromatics cause greater swell than alkyl benzenes. Field experience has shown that a switch from JP-4 to JP-5 or JP-8 will often result in aircraft fuel system leaks. The elastomers which have swollen with exposure to JP-4 will shrink slightly upon exposure to JP-5 or JP-8; this shrinkage is often sufficient to cause leaks.

The swell/shrink problem with fuel system elastomers can also occur with the same grade of fuel. At the end of World War II a large stock of aviation gasoline, containing significant amounts of aromatics, was on hand, so no new aviation gasoline was purchased by the military for several years. When new aviation gasoline was purchased, the refining processes had changed so that the new aviation gasoline contained essentially no aromatics. Fuel system leaks became epidemic. The immediate cure was to add toluene (an aromatic) to the aviation gasoline. The long term solution was the requirement that Grade 100/130 and 115/145 aviation gasolines contain a minimum of 5 percent aromatics. This requirement remains in Specification MIL-G-5572 for aviation gasoline. The shrink/swell leak problem can also occur with JP-4, as aromatics contents are known to vary from less than 2.5 percent to greater than 22 percent by volume.

b. Olefin Content. Olefins are the least stable of the four hydrocarbon types found in jet fuels. Olefins are similar to paraffins, but have some degree of unsaturation; i.e., some of the carbon atoms have double bonds between them. This results in molecules that are highly reactive. Petroleum products that have appreciable concentrations of olefins tend to polymerize, forming gums during storage. (Many plastics are polymers of olefins; i.e., small olefin molecules joined together to form extremely large molecules.) A maximum olefins content of 5 percent by volume is specified for most jet fuels to help prevent the formation of undesirable gums and resins.

The test method currently used to measure aromatics and olefins content is ASTM D 1319, Tests for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption. ASTM D 1319 measures the volumetric concentrations of aromatic and olefin hydrocarbons through liquid chromatography. Fluorescent dyes are added to the fuel before the fuel is injected into a glass column packed with silica gel. Alcohol is injected into the column after the fuel; this separates the hydrocarbon types within the column according to their adsorption affinities. The fluorescent dyes, preferentially adsorbed by the hydrocarbon types, enable the quantities of aromatics and olefins to be measured when the glass column is illuminated with ultra-violet light. Although quick and simple to perform, this method is not highly accurate. Also, the method does not differentiate between monocyclic and polycyclic aromatics nor among normal paraffins, isoparaffins, and cycloparaffins.

Bromine Number. Bromine readily reacts with olefins at ambient temperature, and the amount of bromine consumed is a measure of the olefin content of the fuel. The specifications for JP-1, JP-2, JP-3, and JP-4 placed an upper limit on the Bromine Number (Table 1). In 1955, the Bromine Number test became an alternative to ASTM D 1315. In 1962, the Bromine Number test was dropped altogether from the specification for JP-4 and JP-5.

Jet fuels tend to have olefin contents well below specification limits of 5 percent by volume (see Table 1). This limit of 5 percent by volume first appeared in MIL-F-25624 in May 1955 and resulted from a NATO standardization agreement that was reached at that time. The apparent purpose of this limit was to prevent the addition of "cracked" stocks to jet fuels. The cracked stocks contain olefins, unstable byproducts of catalytic and thermal cracking processes used to convert larger hydrocarbon molecules into smaller ones. To date, jet fuel production capacity has been adequate to meet US needs without using cracked products. If cracked products are eventually used in jet fuels, hydrogenation can be used to convert the unstable olefins to stable paraffins, but at an increase in cost.

c. Sulfur Content. Organic compounds containing sulfur are commonly found in crude oils, tar sands, oil shale, coal, and other fossil fuels. The total sulfur content may range from a few parts per million to several percent. The sulfur compounds present may include sulfides, disulfides, sulfones, sulfonic acids, sulfoxides, thiophenes and mercaptans. After refining, many of the sulfur compounds may still be present, as well as elemental sulfur. Some sulfur compounds are highly corrosive before combustion, but combustion converts all sulfur to sulfur dioxide. In the presence of air and moisture, sulfur dioxide reacts to form sulfuric acid, also highly corrosive under some operating conditions. Sulfur oxidation products contribute to the "acid rain" that is a problem in many parts of the world.

Military jet fuel specifications limit total sulfur content to reduce corrosion problems with jet engines. A maximum total sulfur limit of 0.4 percent by weight was selected for JP-3 and was subsequently used for JP-4 and JP-5. This limit has prevented any serious engine corrosion problems, yet the fuel producers have had no problems in meeting this limit. The commercial jet fuel specifications limit is 0.3 percent by weight, and since JP-8 was originally designed to be equivalent to Jet A-1, its specification also uses this limit. Typically, military and commercial jet fuels have total sulfur contents well below 0.1 percent by weight. As refineries convert to handle heavier, higher sulfur crude oils, increased use of sulfur removal processes may further lower the sulfur content of jet fuels.

d. Mercaptan Sulfur Content. Mercaptan sulfur compounds (mercaptans) have the general formula of R.SH and are noted for their strong, noxious odors. They may be considered to be hydrocarbon derivatives of hydrogen sulfide, which gives rotten eggs their noxious odor. The skunk's unique weapon is a mercaptan, and a mercaptan is purposely added to natural gas to give it a strong, characteristic odor, as only trace amounts are needed.

Mercaptans are present in many crude petroleums and are also formed in some refining processes. They must be removed or converted to less deleterious sulfur compounds as they are highly corrosive and degrade some aircraft fuel system elastomers. For example, polysulfide fuel tank sealants will revert to a liquid under the attack of mercaptans and trace metals solubilized by the mercaptans. The solubilizing of trace metals by mercaptans may also be a factor in the formation of gums and resins, as these reactions are catalyzed by metals.

Current jet fuel specifications limit the mercaptans content of jet fuels to 0.002 percent by weight. This limit is based on tests performed by the Wright Air Development Center in 1956, where Buna N and Thiokol (polysulfide) elastomers were exposed to JP-4 fuels containing various concentrations of mixed mercaptan sulfur compounds at 93 C (200 F). The Thiokol samples were found to deteriorate in fuels containing as little as 0.002 percent mercaptans (reference 6). Commercial jet fuel specifications allow up to 0.003 percent mercaptans by weight. Recent data indicate that trace metals (especially copper and cadmium) in conjunction with mercaptan sulfur compounds accelerate the degradation of polysulfide elastomers.

Mercaptan concentrations in jet fuels may be measured directly using ASTM D 3227, Test for Mercaptan Sulfur in Gasoline, Kerosine, Aviation Turbine and Distillate Fuels (Potentiometric Method) or indirectly through the Doctor Test, described in ASTM D 235, Standard Specification for Mineral Spirits (Petroleum Spirits)(Hydrocarbon Dry Cleaning Solvents). Appendix B provides information relating Doctor Test results to mercaptan sulfur concentrations.

e. Total Acid Number. Organic acids and traces of inorganic acids left in jet fuel following refining can corrode aircraft fuel system components. In addition, organic acids such as sulfonic acid and naphthanic acid can emulsify water in fuel and may react with dissolved metals in water bottoms to form filter-plugging precipitates (reference 7).

The Total Acid Number specification requirement resulted from an aircraft fuel system problem caused by excessive concentrations of an organic acid in the fuel. This resulted in the deposition of a soap-like material on the filter screen of fuel boost pumps. Oleic acid is believed to have been used in an oil well to control down-hole corrosion, and traces of the acid were carried over into the jet fuel during refining. The oleic acid reacted with cadmium plating used on fuel system components to form the soap-like material found on the boost pumps screens.

The specification limit of 0.015 mg KOH/g fuel is based on field data that indicated a total acid number above 0.015 mg KOH/g fuel could cause fuel system problems. The MIL-I-25017 corrosion inhibitor/lubricity additives, discussed in Section V, paragraphs 3 and 4, consist of organic acids and their derivatives, but these additives are used at concentrations well below a total acid number of 0.015 mg KOH/g.

2. PHYSICAL PROPERTIES

a. Density. Density of jet fuels is one of the key parameters that controls jet fuel composition and other physical properties. Current fuel specification density limits are based on fuels composed of about 20 to 40 percent cycloparaffins, 10 to 20 percent aromatics, and the remainder paraffins. Aromatics are the most dense, then cycloparaffins and paraffins the least dense. Thus, fuel composition changes that increase cycloparaffins or aromatics content will increase fuel density.

Fuel density must be known for the pilot to accurately calculate the mass of his fuel load, as fuel is serviced volumetrically. The engine fuel controls on older aircraft engines also meter fuel volumetrically, so the fuel control must be adjusted to compensate for fuel density changes when switching fuels. The ranges of adjustment of these older fuel controls are limited and may be inadequate to allow the use of some high density fuels now under consideration. The newest engines use digital fuel controls that automatically compensate for changes in fuel density.

Density is used in place of "specific gravity" and API Gravity where:

$$\text{API Gravity} = (141.5/\text{density}) - 131.5,$$

where density is expressed in kg/L measured at 15.6 C (60 F). Density is normally measured using ASTM D 1298, <u>Test for Density, Specific Gravity, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method.</u> (Hydrometers are calibrated floats whose displacement can be directly related to density.)

b. Volatility. Volatility is the tendency of a liquid to vaporize; i.e., to change from a liquid to a gas. For engine starting, jet fuels must be sufficiently volatile for part of the fuel to vaporize prior to ignition, as hydrocarbon fuels burn in the gaseous state only. The volatility of jet fuels is controlled in specifications by two methods: (1) distillation and (2) flash point or vapor pressure.

(1) Distillation is a method of separating a mixture of liquids by their boiling points. The distillation characteristics of a fuel are determined by evaporating the fuel and recondensing the fuel in a graduate, while simultaneously measuring the fuel vapor temperature and volume of condensate recovered. By plotting the vapor temperature versus percent condensate recovered, a distillation curve similar to those seen in Figure 1 is produced.

Control of fuel volatility is achieved by limiting the fuel vapor temperatures at various percentages of condensate recovered. For example, JPTS (Table 1) requires a minimum initial boiling point of 157 C and a minimum 10 percent recovered temperature of 196 C. These minimum recovered temperatures insure that the fuel is not too volatile, thereby providing a high flash point and minimizing fuel boiloff losses at high altitudes. Maximum recovered temperatures are imposed at the 50 percent, 90 percent, and end point to insure that all of the fuel will evaporate within the engine combustor's primary zone, thereby avoiding excessive soot formation and carbon deposits within the combustor.

The lower distillation range (initial boiling point and 10 percent and 20 percent recovered) is indirectly limited by either the flash point or the vapor pressure (see below). The upper distillation range (90 percent recovered and the end point) may be indirectly controlled by the specified freezing point of the fuel. Distillation test methods include ASTM D 86, Test for Distillation of Petroleum Products, and ASTM D 2887, Test for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography.

(2) Vapor Pressure. The vapor pressure of jet fuel is a direct method for specifying volatility. ASTM D 323, Vapor Pressure of Petroleum Products, Reid Method, or ASTM D 2551, Test for Vapor Pressure of Petroleum Products (Micromethod), are specified for use with JP-4. In these methods a specified amount of the fuel is placed in a pressure container having a fixed vapor/liquid ratio. The container and contents are heated to 37.8 C and the pressure rise recorded; this pressure rise is the Reid Vapor Pressure. The true vapor pressure is slightly higher than the Reid Vapor Pressure, as errors result from the air trapped in the pressure container and because of the vapor space above the fuel.

(3) Flash Point. As kerosine fuels such as JP-5 and JP-8 have vapor pressures an order of magnitude below that of

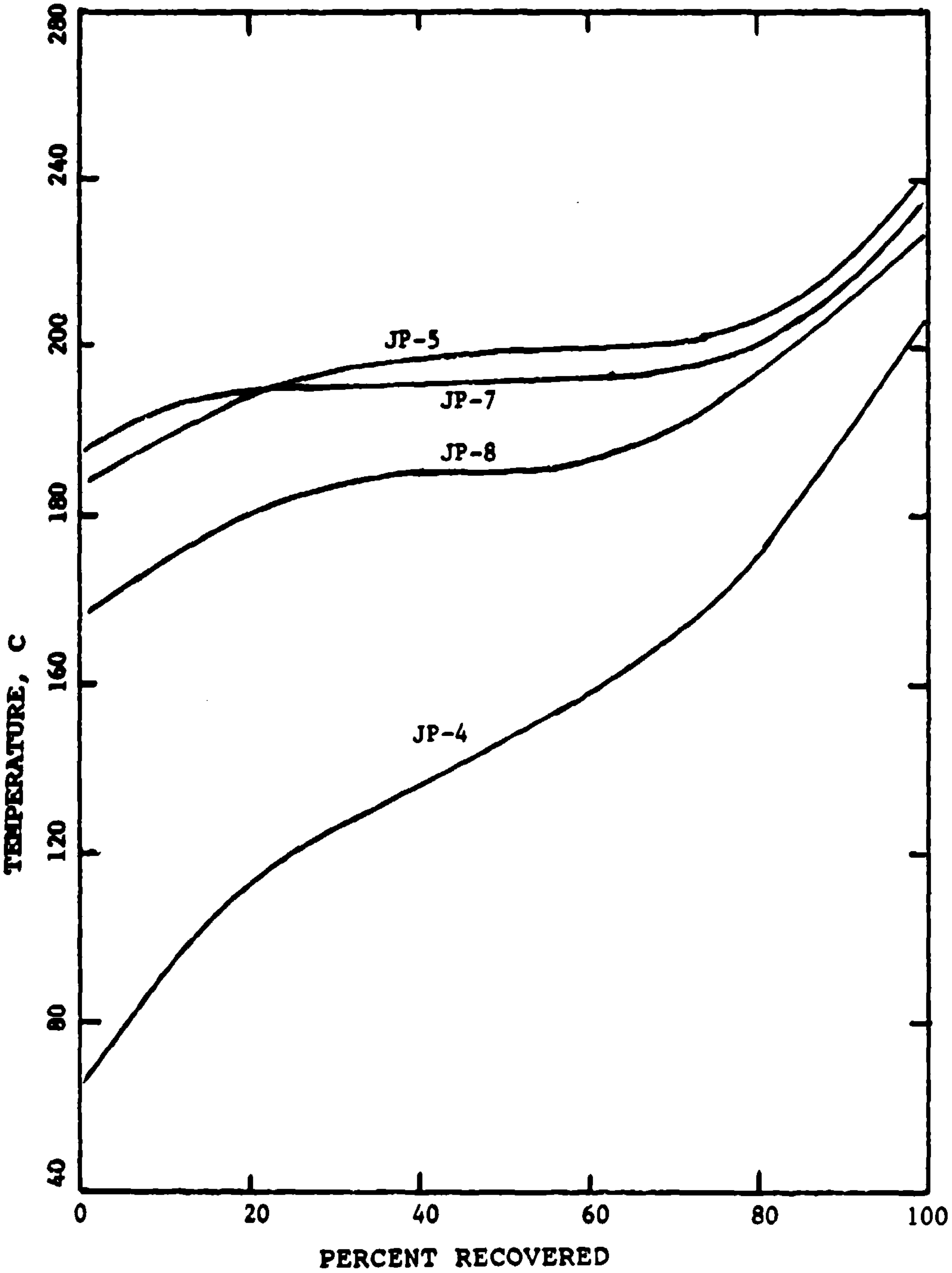

Figure 1. Typical distillation curves for jet fuels

JP-4, simple vapor pressure tests are not suitable. By heating a volume of the fuel within a closed cup and testing the flammability of the vapor space within the closed cup at regular temperature intervals, a temperature is found at which the fuel just produces sufficient vapor to flash (burn). As the amount of fuel vaporized is directly related to its vapor pressure, the flash point is an indirect measure of the volatility of a fuel.

The flash point of liquid petroleum products is widely used as an indicator of flammability. Federal and state safety regulations classify the hazards associated with liquid hydrocarbons by their flash points. Volatile fuels such as JP-4 and gasoline seldom have their flash points measured, as their flash points are below most ambient temperatures.

Flash point test methods commonly specified include: ASTM D 56, Test for Flash Point by Tag Closed Tester; ASTM D 93, Flash Point by Pensky-Martens Closed Tester; and ASTM D 3243, Test for Flash Point of Aviation Fuels by Setaflash Closed Tester. Differences in the procedures and test apparatus of these test methods result in flash point differences of up to 3 C.

(4) Boiloff Losses. When aircraft climb rapidly to high altitudes, air dissolved in the fuel is released. Also, rapid evaporation of the volatile fractions of the fuel may cause the fuel to boil. These processes can cause significant quantities of liquid fuel to be carried out of the tank vents along with the released air and fuel vapor. The development of JP-4 was partially a result of the excessive boiloff losses experienced with the more volatile JP-3 (Section II, paragraph 2c).

All USAF jet aircraft, except for the U-2, SR-71, and XB-70, operate on JP-4. The U-2 was designed to operate at very high altitudes where the atmospheric pressure is quite low. To avoid excessive fuel boiloff losses, a kerosine fuel (JPTS) was selected. The XB-70 (JP-6) and SR-71 (JP-7) aircraft combine high altitude operation with supersonic speed, subjecting their fuels to low ambient pressures and high temperatures. Thus, JP-6 and JP-7 are also kerosene fuels with low vapor pressures. Although boiloff losses can also be controlled by fuel tank pressurization, this requires stronger, heavier fuel tanks that penalize aircraft performance.

c. Viscosity. Viscosity is a measure of the resistance to flow of a fluid. Aircraft and engine fuel systems are designed to operate with liquid fuels having a specified range of viscosities so that fuel lines, valves, and pumps of minimum size and weight can be used. As the viscosity of jet fuels is strongly temperature dependent, the viscosity of the fuel at its minimum operating temperature must be known.

Also of importance is the effect of viscosity on fuel atomization. The performance of pressure atomizers and air-assist atomizers is strongly dependent upon fuel viscosity. The subsequent evaporation of the fuel and the mixing of the fuel with air to form a combustible mixture are highly dependent upon the fuel nozzle performance. Engine manufacturers specify a maximum fuel viscosity of 12 centistokes for reliable engine starting performance; this would limit engine starting to temperatures of -20 to -30 C when using JP-5, JP-8, Jet A, or Jet A-1 kerosine fuels.

Kinematic viscosity is determined by measuring the time required for a fixed volume of fuel at a prescribed temperature to flow through a calibrated capillary tube. The viscosity is calculated from the flow time and the capillary tube diameter and length. In the 1940s and 1950s, the standard viscosity test temperature was -40 C, but in recent years international standardization agencies have settled on a test temperature of -4 C. The standard viscosity test method is ASTM D 445, Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosities).

d. Freezing Point. The freezing point of jet fuel must be below the coldest temperature reached within aircraft fuel systems, else the fuel may solidify and stop fuel flow to the engine. As seen in Table 1, early jet fuel specifications required freezing points of -60 C or below. These extremely low freeze point requirements limited fuel availability and are now known to be quite conservative. Perhaps the most severe environment likely to be encountered by USAF aircraft is at Eielson AFB, Alaska, where ground temperatures as low as -50 C have occurred for periods as long as 24 h. Although temperatures aloft may be lower than -50 C, aerodynamic heating of the aircraft moderate these temperatures significantly.

For the European theatre a maximum freezing point of -47 to -50 C should be adequate. A freezing point only slightly below -50 C should be adequate for any aircraft operating anywhere in the world (reference 3).

The freezing point test method, ASTM D 2386, Test for Freezing Point of Aviation Fuels, is conservative in that the temperature measured is that at which the last crystal of fuel melts. More accurate results are obtained by measuring melting points than initial freezing points, as supercooling is avoided. The minimum temperature at which fuel will still flow is anywhere from 1 to 10 C below the measured freezing point. Efforts are underway to evaluate test methods for measuring the minimum fuel flow temperature as possible replacements for freezing point.

3. MISCELLANEOUS SPECIFICATION REQUIREMENTS

a. Combustion Performance. The combustion performance of jet fuels includes two different aspects. These are discussed below.

(1) Net Heat of Combustion. The Net Heat of Combustion is the lower heating value of the fuel; this assumes that the water formed through combustion remains in the vapor form. In English units the heat of combustion is in Btu/lb and in SI units in MJ/kg where 1 MJ/kg = 42.99 Btu/lb. Direct methods for determining the net heat of combustion include ASTM D 240, Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter, and ASTM D 2382, Test for Heat of Combustion of Hydrocarbon Fuels by Bomb Calorimeter (High-Precision Method). Also used are estimation methods including ASTM D 1405, Method for Estimation of Net Heat of Combustion of Aviation Fuels (Aniline-Gravity), and ASTM D 3338, Method for Estimation of Heat of Combustion of Aviation Fuels. The latter method uses a correlation based on the density, distillation temperatures, and volume percent of aromatics.

The minimum net heat of combustion specified for JP-4, JP-5, JPTS, and JP-8 are seldom, if ever, approached. Other fuel property limits including density, volatility, and Smoke Number or Hydrogen Content are more restrictive.

(2) Burning Quality. Specifications for JP-1, JP-2, JP-3, and initially for JP-4 did not include any combustion quality requirement. However, early jet engines had severe exhaust smoke and carbon deposition problems, leading to the recognition of the importance of fuel combustion performance. Fuel combustion performance methods used in fuel specifications have included Smoke Point, Smoke Volatility Index (a calculation using Smoke Point and the volume percent of fuel that evaporates below 204 C), and Luminometer Number (essentially an automated Smoke Point method).

Combustion research work conducted in the 1950s and 1960s showed a close correlation between the combustion performance of a fuel and its hydrogen/carbon ratio or hydrogen content. Recently, US military jet fuel specifications were revised to specify a minimum hydrogen content or Smoke Point as the combustion performance parameter. There is still some contention as to the accuracy of hydrogen content as a fuel combustion parameter, and commercial jet fuel specifications continue to rely on the Smoke Point and Luminometer Number methods.

ASTM D 1322, Test for Smoke Point of Aviation Turbine Fuels, consists of burning the fuel sample in a wick lamp and measuring the height of a flame that can be obtained without soot forming at the flame tip. Although originally developed for illuminating kerosines, this simple test has proven to be quite suitable for jet fuels. ASTM D 1740, Luminometer Numbers of Aviation Turbine Fuels, is still used in commercial jet fuel specifications but not in military jet fuels. This test is essentially an automated Smoke Point method. A new smoke point test apparatus is under development that eliminates the viscosity and volatility effects inherent in the wick lamp used with the Smoke Point apparatus.

To measure the hydrogen content of fuel, the preferred test method is ASTM D 3701, Hydrogen Content of Aviation Turbine Fuels by Low Resolution Nuclear Magnetic Resonance Spectrometry. Methods formerly used include ASTM D 1018, Test for Hydrogen in Petroleum Fractions (a combustion method) and ASTM D 3343, Method for Estimation of Hydrogen Content of Aviation Fuels (based on correlations involving fuel density, distillation temperatures, and volume percent aromatics.)

b. Corrosivity. Aircraft fuel systems include many different metals of construction, and the corrosion of these metals by the fuel must be avoided. As some of the sulfur compounds present in fuel are corrosive, a corrosion test is incorporated in jet fuel specifications. ASTM D 130, Test Method for Detection of Copper Corrosion From Petroleum Products by the Copper Strip Tarnish Test, is included in current jet fuel specifications. In this test a polished copper strip is exposed to the fuel under controlled conditions and subsequently examined for corrosion. Virtual absence of elemental sulfur or other corrosive sulfur compounds is assured when there is no more than a slight tarnish (reference 8).

Some British jet fuel specifications include a more sensitive corrosion test that uses a silver strip. They found this was necessary as some British aircraft use a fuel pump that uses silver plating as a bearing material. Any sulfur attack of the silver plating greatly decreases the life of the pump.

c. Fuel Cleanliness. Jet fuel must be clean and dry to insure that the flow of metered fuel to the aircraft engine is not interrupted and that the fuel system functions properly and reliably. Fuel contaminants generally fall into two basic categories: undissolved or free water and solid particulates.

(1) Water Contamination. The most common and potentially serious jet fuel contaminant is water. Water can contaminate jet fuel at many locations, beginning at the refinery, during fuel storage, transport, and servicing. If present in significant quantities, water may be pumped to the engine rather than fuel, causing engine flameout. Water can also freeze within the aircraft fuel system, blocking fuel flow to the engine. Water also promotes the growth of microorganisms within fuel systems, leading to filter plugging and corrosion problems.

Jet fuel can hold up to 70 p/m (parts per million) at 25 C. When the fuel is exposed to low temperatures, such as occurs during high altitude flight, much of the dissolved water condenses. With aviation gasoline, any suspended water rapidly settles to the bottom of the tank where it can be drained. As jet fuels are more dense and viscous than gasoline, suspended water (and solid particulates) do not settle nearly as fast. If surfactants (i.e., surface-active agents such as soaps and detergents) are also present, fuel-water emulsions may form and prevent the water from separating from the fuel by gravity.

In addition to the removal of suspended water from fuel by gravity, filter-water separators (filter-separators) are used to remove solid particulates and undissolved (free) water from fuel during ground transfer and servicing. Filter-separators consist of a depth filter, a coalescence media, and a hydrophobic membrane installed within a pressure vessel. However, the surfactants that can prevent gravitational separation of water from fuel can also interfere with filtration, coalescence and water separation.

In 1954, the Air Force began to use fuel corrosion inhibitor additives to control corrosion of pipelines and storage tanks. These additives function by depositing layers of molecules on metal surfaces to protect the metal from oxygen and moisture. For these additives to function, they must be surface-active, plating out on metal surfaces and at interfaces (such as fuel-water interfaces.) Although corrosion inhibitor additives greatly reduce the contamination of jet fuel by iron oxide corrosion products, they can exacerbate the water contamination problem.

In 1958, a B-52 bomber crashed after five of its eight engines flamed out during final approach. Examination of the wreckage revealed large quantities of water in the fuel tanks. Reasoning was that this water caused the flameout of the engines. Many other accidents and incidents during this time period were also blamed on water in fuel.

Also during this time period, many USAF aircraft fuel tanks were found to be infested with microorganisms (fungi and bacteria). Moderate to severe corrosion of integral fuel tanks was found in some of the infested tanks. Liquid water appeared to be needed for the growth of the microorganisms. Consequently, a massive research and development program was initiated to solve the water-related problems. Improved filter-separators, new test methods for the water separation characteristics of fuels and fuel additives, a fuel additive to serve as an antifreeze agent for water in aircraft fuel system, and means of controlling microorganisms in aircraft fuel systems were sought.

Specification test methods used to control water contamination of jet fuels include:

(a) Water Tolerance Test, a test developed for aviation gasoline to determine if alcohols or other water soluble agents were present, was modified for jet fuels. In this test 20 mL of distilled water are added to 80 mL of fuel, the mixture is shaken for 2 min and then allowed to settle. Any increase in volume of the water bottoms indicates that some water-soluble material from the fuel was extracted. Bubbles or "lace" at the fuel/water interface indicate the presence of surfactants that may interfere with the separation of water from the fuel. This test method, ASTM D 1094, Test for Water Reaction of Aviation Fuels, is specified in jet fuel specifications, as it is easily conducted in the field with a minimum of equipment.

(b) Water Separometer Index (WSI). Another fuel/water separation characteristics test is the Water Separometer. In the late 1950s, Dr. John Krynitski of the Naval Research Laboratory developed a miniature coalescer test device. Water is added to the test fuel, the fuel/water mixture emulsified, the emulsion pumped through coalescence media, and the degree of fuel/water separation is measured using a transmissometer. This device was found to be quite sensitive to the presence of surfactants in fuel, and a variation of the device became ASTM D 2550, Test for Water Separation Characteristics of Aviation Turbine Fuels. This test method became a jet fuel specification requirement in 1964.

In March 1969, the Water Separometer Index, Modified (WSIM) replaced the WSI method. One significant use of the WSI and WSIM was to screen the MIL-I-25017 corrosion inhibitors for their effects on coalescence. The corrosion inhibitors that seriously degraded the WSI or WSIM ratings were removed from the qualified products list (QPL-25017). Their removal from jet fuels helped to alleviate the water-in-fuel contamination problem.

Neither the Water Reaction Test nor the WSIM test give good correlations with actual field performance of filter-separators. The performance of the filter-separators may only gradually degrade over months of service as thousands of gallons of different batches of fuel are filtered. The Water Reaction Test and the WSIM are only run on a single fuel, and the tests last for only a few minutes. Never-the-less, these tests have helped to reduce the water contamination problems that plagued the Air Force in the late 1950s and early 1960s. For jet fuels to pass the Water Tolerance and the WSIM tests, fuel producers must insure that the fuel contains a minimum of surfactants. As most jet fuel is not accepted by the Air Force until delivered, the fuel transport agencies must also maintain the fuel clean and dry.

Further developments of the Water Separometer have lead to a new device called the MicroSep, ASTM D 3602, Field Test for Water Separation Characteristics of Aviation Turbine Fuels. The MicroSep is much faster and cheaper to run than the WSIM and is expected to replace it in a few years.

(c) Fuel System Icing Inhibitor (FSII). The specification requirement for a minimum FSII concentration in the fuel indirectly assists in maintaining clean, dry fuel. The jet fuel additive, Fuel System Icing Inhibitor (FSII), is added to and dissolves in the fuel. If free water is present, part of the FSII migrates to the water. Specifications require that FSII be maintained at a concentration of 0.08 to 0.15 percent by volume. Failure to keep fuel systems dry results in the loss of FSII to tank water bottoms, and additional FSII may have to be added. To avoid this extra work, fuel handling personnel are more conscientious about the regular draining of fuel tank sumps.

(2) Solid Particulates. Specifications for JP-1, JP-2, JP-3, and JP-4 did not include limits on solid particulate contaminants. The first jet fuel storage and handling systems were converted from aviation gasoline use and were not noted for delivering clean, dry fuel. The use of fuel-soluble corrosion inhibitors was begun in 1954 to prevent the internal corrosion of ferrous tanks and pipelines, major sources of particulates (rust). Also, as new fuel systems have been built, improved materials and designs have been used to reduce corrosion and to aid in the removal of contaminants.

Improved fuel storage, handling and servicing systems led to the revision of MIL-T-5624 in 1965 to limit the mass of solid particulates in the fuel. Present fuel specifications require that the fuel delivered to the Government have not more than 0.5 to 1.0 mg/L of solids. The more stringent limits are for JPTS and JP-7 fuels. These specification limits evolved with time and represent compromises of what is obtainable with reasonable effort and what is needed to protect critical engine components.

The test method used for measuring solid particulates is ASTM D 2276, Test for Particulate Contaminant in Aviation Turbine Fuels. This method consists of filtering a prescribed quantity of test fuel through a preweighed, membrane filter and measuring the increase in filter weight caused by the contaminants. This test may be combined with the Filtration-Time test described below.

(3) Fuel Filterability. The 1973 revision Jof specification MIL-T-5624 included a Filtration Time test as a new fuel quality control requirement. This test measures the time required to pass fuel through a filter under controlled conditions. A high filtration time is indicative of a fuel containing materials that may rapidly plug filter-water separators and aircraft filters. This requirement was added to eliminate jet fuel filterability problems that have intermittently occurred since the 1950s.

A filter-plugging precipitate can be formed by reactions involving MIL-I-25017 corrosion inhibitor/lubricity improver additive and water containing trace metals. The fatty acids in the corrosion inhibitor apparently react with the trace metals to form a gelatinous precipitate (reference 9). Fuel that has been transported by barge or sea-going tanker is likely to have poor filterability unless care has been taken to insure that the fuel remains dry.

Smith (reference 4) reported a filter plugging problem that occurred with Viscount aircraft operating out of London. Investigation revealed that a significant quantity of copper was in the fuel, carried over from a copper-sweetening process. The copper was chelated by the metal deactivator, NN'-disalicylidene ethylene- diamine, added to the fuel to prevent fuel stability problems caused by the copper. However, the solubility of the copper chelate in jet fuels was found to be inadequate at low temperatures, and the copper chelate was being deposited on the filters. By replacing the NN'-disalicylidene ethylenediamine metal deactivator with one whose metal chelates are more soluble in fuel, the problem was solved. (See Section V, paragraph 2.)

Smith (reference 4) also reported another filter plugging problem that began to occur in many parts of the world in the late 1950s. Colonies of microorganisms were found growing in the water bottoms of ground and aircraft fuel tanks. These microorganisms could form thick, spongy masses that could plug filters and cause corrosion problems. (See Section V, paragraph 5.)

d. Thermal Oxidative Stability. During the development of the Pratt Whitney J-57 turbojet engine in the early 1950s, fuel atomizer nozzle fouling was encountered. The severity of the problem was found to vary with different batches of fuel (reference 10). The ability of a fuel to resist the formation of these deposits is called thermal oxidative stability or thermal stability. The immediate solution to the J-57 problem was a redesign of the fuel manifold and nozzles to reduce fuel heating. However, the need to control the tendency of fuels to form deposits when exposed to high temperatures was recognized, and studies of the problem were initiated.

Despite intensive studies, the chemistry involved in the formation of fuel deposits formed at elevated temperatures is not well understood. Analyses of the deposits have revealed the presence of high concentrations of metals, sulfur, nitrogen, and oxygen compounds. Metals such as copper, iron, lead, and zinc have been shown to accelerate the formation of deposits at high temperatures. Copper, for example, only needs to be present at concentrations of about 10 to 20 p/b (parts per billion) to degrade the thermal oxidative stability of a fuel.

When various static tests were found to be inadequate, a dynamic test device was developed (reference 11, 12.) This device, later to become known as the ASTM-CRC Fuel Coker, simulated the engine fuel system by flowing the fuel across a heated tube and then through a heated filter (the filter simulated the atomizer nozzle.) An increase in pressure drop as the fuel flowed through the filter was indicative of inadequate thermal stability. Subsequently, the amount of deposit formed on the heater tube was also found to be indicative of fuel thermal instability. The Coker evolved into a standard test method, ASTM D 1660, which was used in jet fuel specifications for many years.

In 1966, the Coordinating Research Council initiated the development of an improved thermal oxidative stability test method (reference 9). This culminated in ASTM D 3241, Test for Thermal Oxidative Stability of Aviation Turbine Fuels (JFTOT Procedure). The JFTOT is essentially a miniaturized, automated version of the Fuel Coker, requiring less test time, less test fuel, and less manpower.

One major problem with the Coker and the JFTOT is the lack of a good method for rating the amount of deposits that form on polished aluminum heater tubes. A visual comparison of the deposit color to color standards is used for the Coker and the JFTOT. The Alcor Corporation, developer of the JFTOT, developed a Tube Deposit Rater (TDR) that measures the change in heater tube reflectivity caused by the deposits. An unresolved controversy exists as to the use of the TDR, as the visual rating and the TDR often give conflicting results. However, there has always been a problem with the visual rating method, as some deposits are of different colors than the color standards, and deposits may be dull or glossy. Other tube deposit rating techniques under consideration include beta-ray backscatter, light interference, voltage breakdown through the deposit, and deposit burnoff.

For JPTS and JP-7 fuels the JFTOT test method and the Alcor TDR deposit rating method are specified. To further improve the tube deposit rating procedure, the JFTOT heater tube is rated both before and after the test, and the maximum increase in the TDR rating caused by deposits is the criterion used. This method has shown good precision and removes the subjectivity of the visual rating method.

One basic problem that occurs with the use of simulative tests such as the Coker and the JFTOT is the need to increase test severity so as to shorten test length. In a jet engine, fuels with poor thermal stability may foul the atomizer only after hundreds of hours of operation. For quality control testing, the tendency of the fuel to form deposits must be determined using a test that can be run in a few hours. Thus, test temperature is increased to reduce test length. This approach is valid if the reaction rates and not the reactions change with temperature. We have only limited evidence to validate this assumption (reference 13).

e. Color. The color of a petroleum product can often reveal the presence of contaminants and possibly the identity of the material. Dyes are used to identify petroleum products and to indicate the presence of tetraethyl lead in gasolines. For example, MIL-H-5606 hydraulic fluid is dyed red, Grade 100 Low Lead aviation gasoline is dyed blue, and Grade 100 aviation gasoline is dyed green. A sample of jet fuel that has a red, blue, or green color would be suspected of being contaminated with one of these other products.

Jet fuels are not dyed (except for aiding in the detection of fuel system leaks, see Section V, paragraph 8), and their natural color ranges from water white to straw. Although some military jet fuel specifications require that the fuel color be reported, no current specification places limits on color.

ASTM D 156, Saybolt Color of Petroleum Products (Saybolt Chromometer Method), is the test method normally specified. The Saybolt color is related to the depth of a column of fuel sample, the color of which is compared with specified standards. The greater the number (between +30 and -16), the lighter the color (reference 8).

f. Existent Gum. Hydrocarbon fuels slowly oxidize during storage to produce soluble and insoluble gums or resins. Soluble gums will leave deposits upon evaporation. For example, gums in gasoline deposit within intake manifolds and on intake valves of reciprocating engines.

The existent gum test method, ASTM D 381, Test for Existent Gum in Fuels by Jet Evaporation, consists of evaporating a known quantity of fuel and measuring the weight of the residue remaining. Either a heated air jet or a steam jet is used to speed the evaporation of the fuel.

Although the first jet fuel specifications limited existent gum, the effects of gum in turbine fuels were not known. It was assumed that insoluble gums could affect fuel metering pumps, fuel valves, and fuel filters (reference 1). We believe that the existent gum requirement in jet fuel specifications was carried over from the aviation gasoline fuel specifications just in case the gums might cause problems in turbine engines.

Mr Charles Hudson (see Section II, paragraph 2g) describes a test conducted to determine the importance of existent gums in aviation turbine fuels. This test was run about 1950 at Wright-Patterson AFB on a J-65 turbojet. The J-65 turbojet engine, used in the Martin B-57 Canberra bomber and in the F-84F fighter, used vaporizer tubes for fuel injection and atomization. The vaporizer tubes were candy-cane-shaped tubes through which a portion of the combustion air and all of the fuel passed before entering the combustor. The vaporizer tubes extended into the combustion chamber where heat from the burning fuel helped to vaporize the fuel. The fuel and air then exited the vaporizer tube near the dome of the combustor. As the vaporizer tubes in the J-65 were subject to burnout, fuel gum was suspected to be a factor. Tests were conducted with a J-65 using fuel that had been doped with different quantities of roofing tar, used to simulate gum. The tests showed that existent gum contents in excess of 20 mg/100 mL caused premature burnout of the vaporizer tubes. Therefore, a maximum allowable existent gum content of 10 mg/100 mL was selected for jet fuel specifications.

The existent gum test method of 1950 used a heated air jet to evaporate the jet fuel. Subsequent to the J-65 test, the existent gum test was modified to allow the use of a higher temperature steam jet. With the more effective steam jet, a fuel with an existent gum content of 10 mg/100 mL, using the air jet, would only have about 7 mg/100 mL of gum. The specifications were amended to place a 7 mg/100 mL limit on jet fuel when tested with the steam jet. This limit has remained in effect since about 1952.

Although the J-65 engine is no longer in the Air Force inventory, the US Marine Corps AV-8 Harrier aircraft's Pegasus engine and several other British aircraft engines use vaporizer tubes for fuel injection and atomization. Also, existent gums may affect other parts of aircraft fuel systems. For example, we suspect that existent gums may contribute to the deposits formed when fuel is subjected to high temperatures. (See Section IV, paragraph 3d.)

g. Electrical Conductivity. Hydrocarbon fuels are excellent electrical insulators, and electrostatic charging occurs as jet fuel flows through fuel system components. This electrical charge can accumulate and produce incendiary spark discharges; many aircraft fuel system fires have resulted. Static dissipator fuel additives, that increase the electrical conductivity of fuel, have proven effective in suppressing electrostatic spark discharges in conventional aircraft fuel systems. However, some tactical aircraft use an open-pore, urethane foam in their fuel tanks to suppress fires and explosions. This foam has created a severe electrostatic problem that was not corrected by the use of fuel static dissipator additives. Section V, paragraph 6, discusses this problem and static dissipator additives in greater detail.

The electrical conductivity of fuel is measured by subjecting the fuel to a known voltage potential and measuring the resulting current flow. This allows the resistivity of the fuel to be calculated, and conductivity is simply the reciprocal of resistivity. The electrical conductivity of fuel is normally specified in units of picoSiemens per meter (pS/m), where a Siemens is a reciprocal ohm. Test methods in use include ASTM D 2624, Test for Electrical Conductivity of Aviation and Distillate Fuels Containing a Static Dissipator Additive, and ASTM D 4308, Standard Test for Electrical Conductivity of Liquid Hydrocarbon Fuels by Precision Meter.

SECTION V

FUEL ADDITIVES

Fuel additives are special chemicals added to fuels to impart specific properties or to counter the effects of fuel contaminants. The following classes of fuel additives are or have been used in jet fuels.

1. ANTIOXIDANTS

Antioxidant additives are added to jet fuels and other petroleum products to prevent the formation of gums and peroxides during storage. Antioxidants function by reducing or preventing the formation of free radicals in the fuel that lead to the formation of gums and peroxides. Normal antioxidant concentrations in jet fuels range from 0 to 14 mg/L.

During prolonged fuel storage in the presence of oxygen, peroxides can form in jet fuels. Peroxides are deleterious to the thermal stability of jet fuels, possibly being the precursors of deposits (reference 14). As antioxidants are effective in preventing peroxide formation, they help to maintain the thermal stability of fuels (reference 15).

Peroxides also attack fuel tank polysulfide sealants and other fuel system elastomers. In 1976, a US Navy A-7 aircraft crashed due to the failure of a fuel control diaphragm. Peroxides in the fuel were found to have attacked the neoprene rubber diaphragm and caused its failure. Through extensive laboratory tests, the Navy demonstrated the ability of antioxidants to prevent peroxidation of jet fuels. As a result of this work, antioxidants are now required in all JP-5 fuel (see MIL-T-5624M.) Smith (reference 4) has also reported peroxide attack of neoprene and nitrile rubber fuel hoses, sealing rings, and diaphragms.

The two basic types of antioxidants used in jet fuels have been phenyl diamines and hindered phenols. The phenyl diamines are no longer used in military jet fuels because they degrade the thermal stability of the fuel (reference 7). The hindered phenols have no negative effects on thermal stability, and at very high concentrations (about 5000 p/m) have been reported to slightly improve jet fuel thermal stability (reference 15).

Currently, jet fuel antioxidants have no specified qualification or approval procedures. Recent additions to the list of approved antioxidants (see MIL-T-5624M) have been based on the demonstrated equivalent performance of candidate antioxidants as compared to approved antioxidants. The two test methods usually used for demonstrating the effectiveness of antioxidants are ASTM D 525, Oxidative Stability of Gasoline (Induction Period Method), and ASTM D 873, Oxidation Stability of Aviation Fuels (Potential Residue Method). In these test methods the candidate antioxidant is added to a fuel which is then pressurized with oxygen and heated to 100 C. The ASTM D 525 test method measures the induction time required for the oxygen uptake to reach a prescribed rate. The ASTM D 873 test method measures the amount of residue (gum) formed after a fixed period of time.

Candidate antioxidants are also tested using ASTM D 3241, Thermal Oxidation Stability of Turbine Fuels (JFTOT Procedure), to insure that the antioxidant does not degrade the jet fuel's thermal stability.

A standardized procedure for the qualification of antioxidants for jet fuels is needed. The importance and use of antioxidants is increasing, as the use of hydrotreating and hydrocracking processes to produce jet fuels increases. Jet fuels that have been subjected to severe hydrogenation processes lose their natural antioxidants and are subject to rapid peroxidation. Hydrotreated jet fuels must have antioxidants added before the fuel is exposed to oxygen (i.e., the atmosphere), as antioxidants do not reverse oxidation reactions that have previously occurred.

2. METAL DEACTIVATOR ADDITIVES

Metal deactivator additives (MDA) were initially added to gasolines that had been treated using the copper sweetening process (a method to convert mercaptan sulfur compounds to less noxious sulfur compounds). The MDA was used to deactivate any traces of copper left in the fuel, as copper will catalyze oxidation reactions that form gums. Copper and some other metals will also degrade the thermal oxidative stability of jet fuels. (See Section IV, paragraph 3d.)

MDAs function by forming a chelate with the metal. The chelate effectively isolates the metal from the fuel. Three MDAs have been used in jet fuels:

(1) N,N'-disalicylidene-1,2,-propanediamine
(2) N,N'-disalicylidene-1,2,-cyclohexanediamine
(3) N,N'-disalicylidene-1,2,-ethylenediamine

The third MDA shown above is no longer used as it forms chelates that are relatively insoluble in jet fuels and can plug filters. (See Section IV, paragraph 3c(3) and reference 4.) The other two MDAs are currently approved for use in military jet fuels at concentrations ranging from 0 to 6 mg/L.

MDAs are optional additives, used at the discretion of the fuel producer. They are likely to be used when contamination of the fuel by trace metals, especially copper, has occurred or is suspected. Although developed primarily for use with copper, the MDAs are also effective with other metals such as lead. Navy studies with jet mix (two parts JP-5 and one part aviation gasoline) showed excessive gum formation unless either a MDA was added or the tetraethyllead additive was removed from the gasoline (reference 16).

The addition of MDA appears to improve the thermal oxidative stability of fuels, as measured using the Coker or the JFTOT. In one case the addition of MDA to a fuel reduced filter plugging during a thermal stability Coker test but had no significant effect on tube deposit ratings. However, there is limited evidence that the MDA only delays the formation of a deposit on a Coker or JFTOT tube by passivating the metal surface. MDA is not a cure-all for thermal instability; Leas reported on a JP-6 fuel that became thermally unstable, although it contained both an antioxidant and a metal deactivator (reference 17).

Another type of metal deactivator that has been tested, but not used operationally, is benzotriazole. The US Navy demonstrated the effectiveness of benzotriazole in reducing copper pickup by JP-5 stored in a copper-alloy fuel system. Also, a fuel that had been contaminated with up to 1200 p/b of copper was restored to its original thermal stability after the addition of benzotriazole (reference 18, 19).

3. CORROSION INHIBITORS

Specification MIL-I-25017, Inhibitor, Corrosion, Fuel Soluble, was issued in 1954 when corrosion inhibitors were first added to jet fuels to protect commercial pipelines. In 1955, Specification MIL-F-5624 was modified to require the mandatory use of corrosion inhibitors in JP-3, JP-4, and JP-5 jet fuels. However, fuel-water separation problems associated with the use of the corrosion inhibitors resulted in the removal of the corrosion inhibitors from these fuels in March 1960.

In September 1962 the corrosion inhibitors were again made a mandatory requirement, but only after the corrosion inhibitor specification had been revised (MIL-I-25017A) to require a minimum Water Separation Index rating for jet fuels containing the corrosion inhibitors. This new requirement resulted in the removal of several inhibitors from the qualified products list (QPL).

In November 1965, the corrosion inhibitors were again removed from jet fuels, but within a few weeks aircraft engine fuel control malfunctions began to occur. These field problems led to the discovery that the corrosion inhibitors significantly improve the lubricating properties of fuels. To solve the fuel control problems, the mandatory use of corrosion inhibitors in JP-4 was again required in November 1966. The Navy, which has a more difficult fuel-water separation problem with JP-5, did not use corrosion inhibitors in JP-5 again until 1979, when fuel lubricity problems became acute. The mandatory use of the corrosion inhibitors in JP-5 has been required since then.

Currently, Specification MIL-I-25017D requires the inhibitors to be compatible with each other and with other fuel additives. Other requirements include fuel-water separation performance, effectiveness in preventing corrosion, storage stability, and minimal effect on jet fuel properties. A Qualified Products List (QPL-25017) is maintained that lists the approved inhibitors, their use limits, and selected properties for quality assurance checks. Work is presently underway to add a lubricity test using the Ball-On-Cylinder Lubricity Evaluator apparatus.

The currently approved corrosion inhibitors are primarily composed of organic fatty acids or their derivatives. Their normal use concentrations range from 6 to 31.5 mg/L.

4. LUBRICITY ADDITIVES

Smith (reference 4) states that the viscosity of wide-cut fuels and some kerosines is inadequate to provide the hydrodynamic film needed to prevent metal-to-metal contact in fuel controls and pumps. Thus, boundary lubricants are needed to provide a tenacious film that prevents or minimizes metal-to-metal contact.

Distillate jet fuels contain sulfur, nitrogen, and oxygen impurities that are effective boundary lubricants. However, when jet fuels are hydrotreated, the naturally-occuring boundary lubricants are removed or destroyed, and severe wear and failure of fuel controls and fuel pumps can occur within a few hours of operation.

As discussed in Section V, paragraph 3. above, MIL-I-25017 corrosion inhibitors were found to improve jet fuel lubricity. These additives inhibit corrosion by migrating to surfaces, plating out and forming a protective film. This film, which prevents oxygen from reaching the surface to cause corrosion, also acts as a boundary lubricant. Appledorn et al (reference 20) found that the abrasive wear that can occur in fuel pumps is corrosion related. The metal surfaces corrode and the corrosion products act as abrasives. As the corrosion inhibitors prevent the formation of the abrasive corrosion products, abrasive wear is also eliminated. Another form of wear is scuffing, wherein metal surfaces contact each other, weld together, and are then broken apart. The protective film formed by the corrosion inhibitors prevents or minimizes the metal-to-metal contact that can lead to scuffing.

The Air Force has had few documented fuel lubricity problems since requiring the mandatory addition of the corrosion inhibitors to all JP-4 beginning in November 1966. These few incidents, manifested by fuel pump wear problems at specific Air Force Bases, were caused by the inadequate addition of the corrosion inhibitor/lubricity improver additive to the fuel. The injection of additional additive into the fuel always resolved the problem.

Another lubricity problem occurred during the accelerated mission testing of a F100 engine using JP-4 derived from cil shale. As this fuel had been severely hydrotreated during processing, 18 mg/L of an approved MIL-I-25017 corrosion inhibitor was to be added to the fuel prior to its shipment from Colorado to West Palm Beach, FL. During the accelerated mission testing, two different pumps experienced severe wear. Subsequently, Ball-On-Cylinder Lubricity Tests were conducted on retained samples of the test fuel. These tests indicated that some batches of the fuel had marginal lubricity (i.e., ball wear scars in excess of 0.35 mm diameter.) Some batches of the fuel are believed to have not injected with the mandated corrosion inhibitor additive.

A subsequent accelerated mission testing of a TF30 engine was performed using the same shale-derived JP-4. For the TF30 test each batch of fuel was tested for lubricity, and additional corrosion inhibitor was added if needed to maintain a Ball-On-Cylinder wear scar of 0.35 mm or lower. No fuel pump wear problems were encountered.

The commercial airlines and other military services have demonstrated the effectiveness of the MIL-I-250177 inhibitors as lubricity additives, as they have used the inhibitors to solve fuel lubricity problems identified with specific fuels.

One other fuel lubricity additive is PWA-536, a proprietary additive procured to a Pratt Whitney Aircraft specification. This additive is used in JP-7 jet fuel at a concentration of 200 to 250 p/m by weight. The effectiveness of PWA-526 was based on fuel pump endurance tests conducted at 149 C.

The Ball-On-Cylinder Lubricity Tester was first used with jet fuels by Esso Research and Engineering Company in the mid-1960s (reference 20). Although several of these devices were built over the next 15 to 20 yr, they were not identical, and a standard test procedure was never approved. Round-robin tests with these early devices indicated poor reproducibility. In 1984, the InterAv Corporation developed an improved Ball-On-Cylinder Lubricity Tester and have now produced over thirty of these devices Also, Falex outer bearing rings are used in lieu of the steel cylinders. Round-robin tests using these new, identical testers with the Falex ring have been completed. Preliminary test results indicate significantly improved test precision. Another effect of the Falex bearing ring is that the wear scars are about 50 percent larger than those obtained with the steel cylinders. A standardized fuel lubricity test method based on the InterAv device should be available within the next two or three yr.

5. FUEL SYSTEM ICING INHIBITORS

Water contamination in aviation fuels has always been a serious problem. In liquid form water can cause temporary engine flameout, but in solid form (ice) can block filters and fuel lines and completely stop fuel flow to engines. In the 1940s and 1950s, free, undissolved water in fuel was suspected to have caused many in-flight incidents and accidents. The crash of a B-52 in 1958 revealed the magnitude of the problem, as sheets of ice were found inside the wrecked aircraft's fuel tanks. The ice had blocked the flow of fuel to five of the eight engines causing the plane to crash.

A major research and development program to solve the water-in-fuel problem was initiated as a result of the B-52 crash in 1958. One objective was the development of a fuel system icing inhibitor (FSII). The FSII was to be added to the fuel but would preferentially migrate to any free water present and act as an antifreeze. The Phillips Petroleum Company developed a proprietary FSII known as Phillips 55MB that was subsequently tested and accepted for use in Air Force fuels beginning in 1962. This FSII consisted of 87.3 percent ethylene glycol monomethyl ether (EGME) and 12.7 percent glycerol. Although EGME and glycerol will dissolve in the fuel, they are much more soluble in water. The freezing point of the water-FSII solution is about -50 C.

The addition of 0.04 percent of FSII to jet fuel was found to completely eliminate the formation of ice in aircraft fuel systems that contained small quantities of free water. To provide a margin of safety, a minimum of 0.08 percent FSII was required in the fuel delivered to aircraft. Military jet fuel specifications were modified to require 0.10 to 0.15 percent of FSII in the fuel delivered to the Air Force. Figure 2 shows the effectiveness of Phillips 55MB in depressing the freezing point of water in the

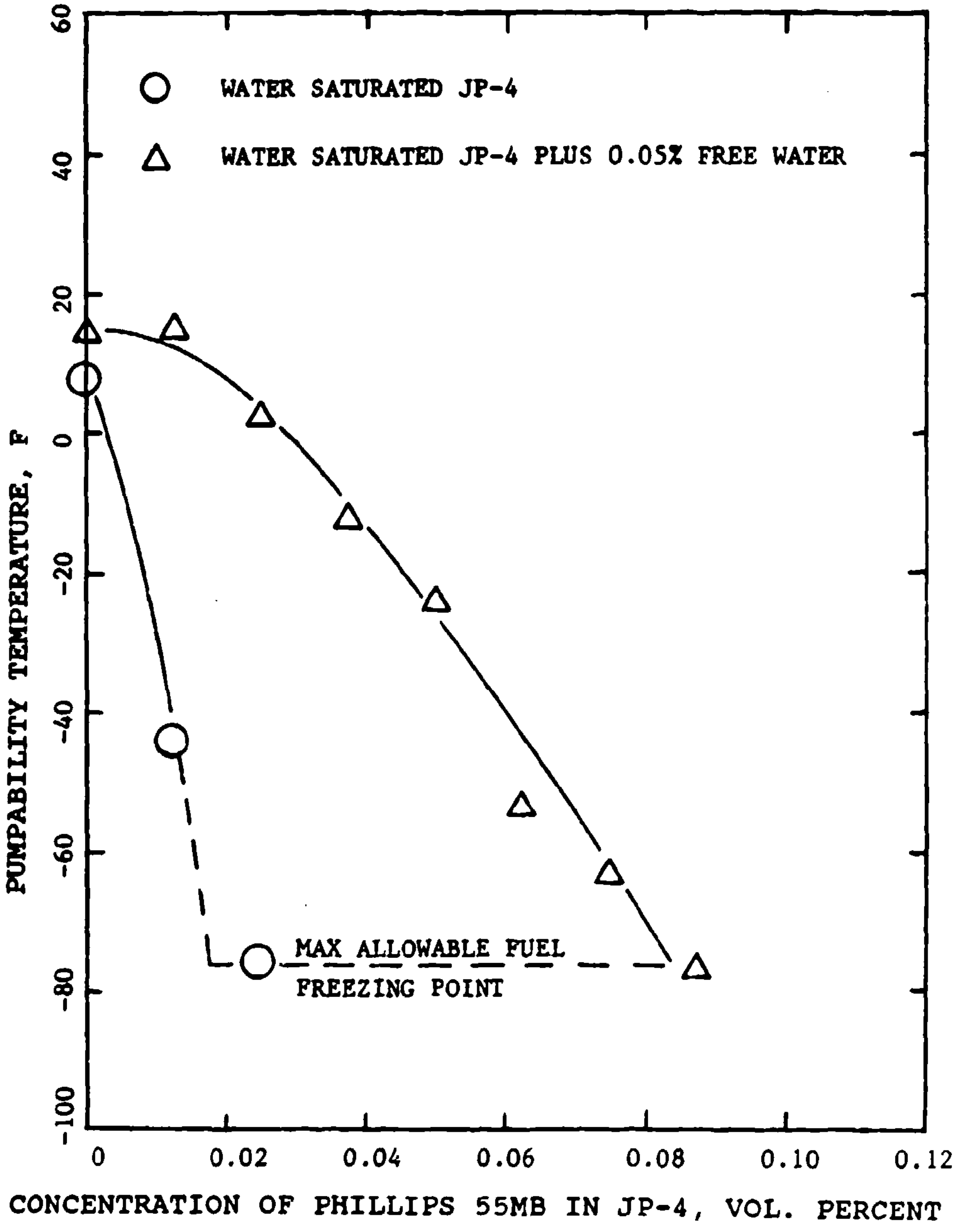

Figure 2. Effectiveness of fuel system icing inhibitor in preventing filter plugging

fuel. As the fuel temperature is reduced, dissolved water comes out of solution and will plug the filter if the water droplets freeze. With sufficient FSII present, the fuel will continue to flow through the filter at subfreezing temperatures (reference 21).

Specification MIL-I-27686, Inhibitor, Icing, Fuel System, was first published in September 1961 for the Phillips 55MB formulation. Subsequent field experience indicated that the glycerol was not completely dissolving in the fuel and was causing problems. Consequently, the specification was changed in September 1962 and again in August 1963 to reduce the glycerol concentrations to 2.6 percent and then to 0.4 percent. In March 1970, specification MIL-I-27686 was revised to completely remove the glycerol, leaving only ethylene glycol momomethyl ether. Problems with the stability of the EGME during storage later resulted in a specification amendment to allow the use of an antioxidant at concentrations up to 150 p/m.

The initial FSII formulation included glycerol to protect fuel tank sealants and coatings from attack by the EGME, as initial compatibility tests had indicated a softening of the materials in the presence of EGME. Subsequent tests, including a field test conducted by the Navy, indicated that the glycerol was not needed. However, the EGME must be completely dissolved in the fuel or in the water phase, as pure EGME will attack many elastomers. Thus, the EGME is normally added to the fuel before the fuel is delivered to the Air Force to insure that the EGME is completely dissolved before the fuel is serviced to aircraft.

For the few commercial jet aircraft that require FSII, the FSII is added during fuel servicing, using aerosol cans of FSII. Unconfirmed reports have been received of damage to aircraft fuel tanks by the FSII that was not adequately mixed with the fuel.

The US Navy used MIL-I-27686 FSII (EGME) in JP-5 until about 1984. The EGME was found to lower the flash point of the JP-5 by up to 3 C, reducing the availability of JP-5. Therefore, the Navy developed a new FSII, diethylene glycol monomethyl ether (DGME), covered by Specification MIL-I-85470. As DGME is slightly less effective than EGME, a concentration of 0.15 to 0.20 percent by volume of DGME is specified by MIL-T-5624L for JP-5.

One of the benefits that resulted from the use of FSII was that the aircraft fuel tank sumps and ground storage tank sumps could be drained all year. Previously, water that collected in the sumps would freeze during the winter and prevent draining until the spring thaw.

An unexpected benefit of using FSII in jet fuel was the elimination of the "microorganisms in fuel" problem. (See Section IV, paragraph 3c.) In the late 1950s, aircraft fuel tanks (and ground storage tanks) often became infested with microorganisms and could suffer severe corrosion. Fungi and bacteria would grow at the fuel-water interface, using the fuel as a source of carbon. Evidently, their waste products can be corrosive. Extensive investigation of the problem was made, but the problem disappeared when FSII began to be used. Smith (reference 4) claims that the EGME has no appreciable biocide effect at normal use concentrations, but this statement does not agree with field experience. Since the use of FSII in JP-4 began in 1962, microorganisms have not caused the US Air Force any known problems. The commercial airlines, which do not use FSII, continue to be plagued by microorganisms and must periodically treat their aircraft fuel systems with biocides.

<u>NOTE:</u> EGME and other glycol ethers have been identified as being hazardous if inhaled or adsorbed through the skin. In laboratory animal studies, birth defects and adverse effects on pregnancy have been observed. Also, prolonged and repeated exposure has caused damage to male reproductive organs.

6. STATIC DISSIPATOR ADDITIVES

Pure hydrocarbon liquids are excellent electrical insulators. When jet fuels and other hydrocarbons flow through pipes and filters, trace contaminants may ionize and charge separation occur (i.e., the charges of one sign are adsorbed onto surfaces while the charges of the opposite sign remain with the flowing fuel). This results in a net electrical charge build-up in the fuel and in the fuel system. Fuel system components are electrically bonded to the airframe, and any charge present will safely bleed to ground. However, the charge in the fuel dissipates very slowly. Under some conditions sufficient charge may accumulate in the fuel to produce incendiary spark discharges. If the fuel/air mixture is flammable, a fire or explosion results.

In the 1960s the Air Force experienced only one or two static-initiated fuel system fires per year, usually with ground servicing equipment such as refuelers. However, in the late 1960s, the fuel tanks of some tactical aircraft were equipped with a polyester-urethane, open-pore foam to suppress fires and explosions. The foam proved to be very effective as a fire and explosion suppression system, saving many aircraft and their crews during combat operations in the Southeast Asian conflict. In the mid-1970s, many of the foam-equipped aircraft were returned to the United States, and fuel tank fires began to occur with these aircraft. Although the fuel tank fires were always minor (as the foam effectively suppressed the fire), these incidents caused much consternation.

Tests revealed that high electrostatic potentials were generated when fuel flowed through the foam. To eliminate this static-induced problem, static dissipator additives (SDA) were added to the fuel. These additives increase the electrical conductivity of the fuel by several orders of magnitude and allow any charge in the fuel to bleed rapidly and safely to ground.

The electrical conductivity of fuel is strongly affected by temperature, with a temperature decrease of 20 to 40 C reducing fuel conductivity by 50 percent. Laboratory tests indicated that the conductivity of the fuel should be between 100 and 700 pS/m. The fuel specifications were therefore revised to require that the fuel be delivered to the Air Force with a conductivity between 200 and 600 pS/m; this would permit significant fuel temperature changes without exceeding fuel conductivity limits.

A service test of two candidate static dissipator additives, Shell ASA-3 and DuPont Statis 450, was conducted in 1978 (reference 22). Sufficient amounts of these additives were used to increase the conductivity of the fuel to between 200 and 600 pS/m. This required between 0.5 and 2.0 p/m of ASA-3 or Stadis 450, as variations in fuel composition and trace impurities affect the quantity of SDA required.

Shell ASA-3 SDA has been used in turbine fuel by other countries in both military and commercial aircraft since 1962. It is composed of Aerosol OT (a dispersant) and chromium and calcium salts. In all previous experience with ASA-3 in turbine fuels, a minimum fuel conductivity of only 50 pS/m was adequate to prevent incendiary spark discharges. This normally required only about 0.5 p/m of ASA-3. DuPont Stadis 450 had not previously been used in jet fuels. However, it contained no metals and appeared to have less of an effect on fuel-water separation characteristics than did ASA-3. Therefore, Stadis 450 was included in the service test to insure two sources of supply (reference 22).

The service test and subsequent field experience with JP-4 containing the SDAs was disappointing; the increased fuel conductivity did not eliminate static-initiated fires in aircraft whose fuel tanks contained the polyester-urethane foam. This failure is believed due to the excellent electrical insulation characteristics of the foam, and the fuel's SDA does not significantly increase the electrical conductivity of the foam. A polyether-urethane foam with improved life was introduced in the early 1970s. This new foam was found to generate even more static charge than the older polyester-urethane foam, increasing the number of fuel tank fires.

Consideration was given to increasing the conductivity of the fuel to much higher levels, although fires have occurred with fuels having conductivities at least as high as 250 pS/m. However, fuel tank gauging systems on older aircraft are affected by fuels with high conductivities. For example, the KC-135 uses a 400 Hz ac capacitance gauging system that loses accuracy when fuel conductivities exceed 500 pS/m. Newer aircraft such as the F-15 and F-16 use a 6000 Hz pulsed dc capacitance gauging system that is unaffected by fuels having conductivities as high as 5000 pS/m (reference 23).

The service test indicated that ASA-3, Stadis 450 or a mixture of the two could be used in military jet fuels without causing any serious problems. One of the major concerns with the SDAs was the degradation of the fuel-water separation characteristics of the fuel. Before and during the service test of the two additives, single filter-separator elements were removed from service and checked for their ability to remove water from fuel. The exposure of the elements to fuel containing the SDAs was found to have only a minor effect on the water removal performance of the elements (reference 22).

The major jet engine manufacturers have approved the use of ASA-3 and Stadis 450 in their engines. However, these approvals are for additive concentrations of 1.0 p/m of less, well below the concentrations actually being used in some JP-4 and JP-8 fuels. To date we have no reports that indicate these higher concentrations of SDA have caused any engine problems.

Work is currently under way by various agencies to solve the static-charging problem. Electrically conductive foam is one promising approach (reference 24). A recent service test demonstrated the effectiveness of electrically conductive foams in eliminating static hazards within aircraft fuel tanks.

7. THERMAL OXIDATIVE STABILITY ADDITIVES

DuPont Jet Fuel Additive Number 5 (JFA-5) is the only jet fuel additive used in military jet fuels for improving fuel thermal oxidative stability. This proprietary additive has been required in Thermally Stable Jet Fuel (JPTS) since March 1970 (MIL-T-25524B). The concentration of JFA-5 used in JPTS is 3 to 4 lb/1000 bbl (about 9 to 12 mg/L), but Pratt Whitney Aircraft has approved the use of JFA-5 in commercial jet fuel at concentrations up to 30 lb/1000 bbl.

JFA-5 is an ashless mixture of polymers, organic amines, and amides in kerosine (reference 25), and is compatible with other fuel additives. One problem that results from the dispersive effects of JFA-5, however, is the low Water Separation Index, Modified, (WSIM) ratings. The addition of 3 to 4 lb/1000 bbl of JFA-5 in JPTS fuel typically gives WSIM ratings in the 50 to 60 range. However, with the new MicroSeparometer (ASTM D 3602), ratings are typically in the high 80s to low 90s.

The effectiveness of JFA-5 in improving the thermal stability of jet fuels has been well documented in small scale test devices. Fuel Coker tests with eight jet fuels indicated that the addition of JFA-5 significantly reduced Coker tube deposit ratings, filter pressure differentials, or both (reference 26). The Air Force has obtained similar results using both the Fuel Coker and the JFTOT. The effectiveness of JFA-5 is believed to be partially due to its dispersive qualities, preventing fuel degradation products from agglomerating together into particles large enough to plug filters or to deposit onto surfaces.

Another method for improving the thermal stability of jet fuels is to remove the dissolved oxygen from the fuel. Beneficial results are seen with most fuels when dissolved oxygen concentrations are reduced to below 30 p/m, but to obtain the maximum benefit the dissolved oxygen must be reduced to below 1 p/m (referemce 27).

8. DYES

Liquid red and yellow dyes procured to specification MIL-D-81298, Dye, Liquid, for the Detection of Leaks in Aircraft Fuel Systems, may be added to JP-4, JP-5, or JP-8 to aid in the detection of fuel system leaks. The dyes must be predissolved in the fuel prior to servicing, as the concentrated dyes may damage fuel system elastomers. Only the yellow dye may be used for flight tests, as the red dye has a high level of particulates which could potentially create a flight safety problem. The red dyed fuel may used by aircraft only after dilution with 10 parts of undyed fuel to 1 part of dyed fuel. In 1987 the specification was revised to include the a green dye that fluoresces when illuminated by ultraviolet light.

The Tactical Air Command requested fuel dyes to help detect fuel leaks that were causing in-flight fires and explosions with the F-105 aircraft. Dyed fuel is used in static engine runups or flight tests, and the fuel system is then inspected for traces of dye, deposited wherever fuel has leaked and evaporated. Red and yellow dyes were found to be suitable, but as hydraulic fluid is dyed red, yellow was selected as the preferred color. Colors such as blue, green, and purple were found to completely mask the fuel, hiding any suspended solids or water that might be present.

9. SMOKE SUPPRESSANT ADDITIVES

Although the black, smoky exhausts of jet aircraft create an aesthetic problem, the military disadvantage of the smoky jet exhaust became fully apparent during the Southeast Asian conflict. The smoky exhaust plume greatly increased aircraft visibility, providing additional time for the enemy to initiate defensive measures. In the late 1960s the US Navy modified combat aircraft to inject a smoke suppressant additive into the fuel during combat operations. The additive used was CI-2 (methylcyclopentadienyl manganese tricarbonyl), manufactured by the Ethyl Corporation. Although effective in reducing the opacity of the exhaust plume, the use of CI-2 was discontinued because of its toxicity and damage to the engine hot section components (reference 28).

The passage of the Clean Air Act and the increasing sensitivity of the American public to air pollution resulted in a Naval Air Rework Facility in California being cited for excessive exhaust smoke issuing from jet engine test stands (reference 29). The use of smoke suppressant fuel additives was one of several methods investigated to resolve the test cell smoke problem. (The test cells are classified as "stationary sources" and must meet more stringent emission requirements than do jet aircraft.) Some of the commercial airlines use CI-2 (manganese) or Apollo DGT-2 (barium and manganese) additives for their test stand operations (reference 28). Tests conducted by the Navy and others resulted in the selection of Arapahoe Ferrocene (dicyclopentadienyl iron) as an effective smoke suppressant fuel additive. Ferrocene is only used during the test stand operation of jet engines that are the worst "smokers" (reference 29). Recently (1986), cerium octoate was found to be superior to ferrocene, and testing is underway to approve the use ofcerium octoate in specific engines during test stand operation.

Ferrocene was chosen by the US Navy (and subsequently the US Air Force) as the preferred smoke suppressant additive because it and its combustion products are nontoxic, it is cost effective, and causes no long term damage to the engines. However, to reduce the amount of additive used to a minimum, the US Navy developed an Automated Smoke Abatement System that monitors the opacity of the test stand exhaust plume and controls the additive injection rate to just keep the plume within legal limits. Although the combustion of ferrocene produces iron oxide products that deposit within the engine hot section, the deposits are soft and blow out of the engine during subsequent engine operation. As some engines suffer temporary performance degradation after only a few minutes of operation because of the iron oxide deposits, the use of ferrocene is restricted to short periods of time (reference 29).

The use of ferrocene as a smoke suppressant additive during flight was never seriously considered. The ferrocene degrades the thermal oxidative stability of the fuel, and this can cause premature plugging of fuel nozzles and afterburner spraybars.

The mechanisms by which the smoke suppressant additives reduce exhaust smoke are not clearly understood. Howard and Kausch (reference 30) give a good review of the mechanisms believed responsible.

10. HALONS

Halons are the generic names of halogenated hydrocarbons, and are widely used as fire extinguishing and cleaning agents. Freon is a registered trade name for Halons. Although halons are not normally used in jet fuels as additives, we find situations where they may be present. For example, some commercial airliners are equipped with fuel tank explosion suppression systems that quickly flood the tank ullage space with halon, when activated by a fire or explosion detector. Fires and incipient explosions are thereby suppressed. Similarly, the fuel tanks of the F-16 aircraft can be flooded with Halon 1301 (bromotrifluoromethane) to provide fire and explosion protection during combat. Part of the Halon 1301 dissolves into the fuel and is carried throughout the aircraft and engine fuel system.

Prior to the use of Halon 1301 in F-16 aircraft fuel systems, extensive tests were performed to insure that the Halon would cause no performance or life problems with the F-16 aircraft and its F100 engine. Pratt and Whitney Aircraft, Government Products Division, concurred with the use of Halon 1301 in fuel supplied to the F100 engine with the following provisions: (1) The fuel may contain no more than 0.5 percent by weight maximum. (2) There will be only limited use of fuel containing the Halon 1301. The test results that supported this approval were reported in Bendix Report ECD 863-19057R, CECO Report R-856, and an unknown Pratt & Whitney report.

Another potential use of Halons in jet fuel is as a fuel tank leak tracer compound. A program is currently underway to evaluate a tank leak detection method wherein Halon(s) are added to jet fuel at concentrations of about 1 p/m. Any leakage of the fuel from the tank can be detected using special sensors. Initial tests indicate that this method may be suitable for monitoring underground fuel tanks for fuel leaks.

11. PIPELINE FRICTION REDUCER ADDITIVES

Very high molecular weight polymer additives are in everyday use to reduce the friction of crude oils and other petroleum products pumped through pipelines. These proprietary additives are added at concentrations of 10 to 100 p/m by volume. They reduce pipeline friction by suppressing turbulence, causing the fluid to flow in the plug flow mode. These additives are also being considered for use in jet fuels to increase the flow capacity of jet fuel pipelines.

Similar additives have also been tested as antimisting additives to reduce the formation of flammable mists in the event of an aircraft crash landing. However, concentrations as high as 0.3 percent by volume are needed to obtain antimisting performance. Extensive tests, including aircraft crash tests, have been conducted with these additives.

Both pipeline friction reducing additives and antimisting additives degrade under high shear stresses, as the long molecular chains of the polymers are broken or cut. Special additive injection systems are required to prevent high shear conditions. Additive reinjection may be required after fuel flow through a high speed centrifugal pump or other high shear device.

Jet fuels containing friction reducing additives or antimisting additives may be difficult to filter, because of the presence of the very high molecular weight polymers. These polymers also give high existent gum readings. Combustion tests of fuels containing these additives have indicated little or no problems, as the high shear forces encountered by the fuel during pumping and metering degrade the polymers.

12. SNAKE OILS

Snake oils are the slang name given to fuel additives that are claimed to improve combustion performance, reduce fuel consumption and friction, and possibly other good things. Snake oils are usually proprietary and promoted using endorsements by "satisfied users" rather than backed by extensive test data. Without knowledge of composition and accurate test data, the positive (or negative) effect of any additive cannot be determined. Thus, the only safe and conservative thing to do is to not use it. Aviation turbine engines are very expensive to replace and their malfunction during flight can be disastrous.

Often a snake oil is claimed to significantly improve combustion efficiency or to reduce fuel consumption. As aircraft turbine engines have combustion efficiencies exceeding 99 percent at cruise and maximum power conditions, such a claim would be invalid. Only during startup and at idle do combustion efficiencies drop much below 99 percent.

Apparently harmless fuel additives used in diesel fuels or gasolines could have serious consequences if used in jet fuels. For example, additives that contain metallic compounds could attack engine hot section components such as the combustor and turbine. Solvents and other potential additive constituents could attack elastomers, cause corrosion of close-fitting components of fuel pumps and fuel controls, or degrade the thermal oxidative stability of the fuel, resulting in deposits that could foul heat exchangers or plug fuel spray nozzles. A partially plugged fuel nozzle can distort the fuel spray pattern, creating a local hot spot that can damage or destroy the turbine, the single most expensive component of a turbine engine.

SECTION VI

FUTURE JET FUELS

1. CHANGES TO CRUDE OILS

During the first three decades of jet-propelled aircraft, jet fuels have primarily been distillates derived from high quality, light crude oils. These light crudes, such as Light Arabian Crude, are high in paraffins and low in aromatics and sulfur. Distillates of these crudes produce high-quality jet fuels with a minimum of processing. Beginning in the 1970s, the increasing demand for crude oil, coupled with the declining production of high-quality light crudes, resulted in the increasing use of heavier, lower-quality crudes for the production of jet fuels. Distillates from these lower-quality crudes require additional processing to produce acceptable jet fuels. Even heaver, lower quality crude oils are now being produced; crudes so heavy and viscous that they must be heated or diluted before then can be produced. Processes that "crack" the heavy molecules into smaller molecules are required to produce jet fuels from these crude oils.

In the late 1970s, considerable interest was generated in the production of synthetic crudes (syncrudes) from oil shale, tar sands, coal, and biomass. At that time the prediction was that by the year 2000, a large portion of our domestic fossil fuel production would be from syncrudes. Now (1987) we see that the US production of the syncrudes will be of no consequence by the year 2000. Although Canada produces about 200,000 bbls/d of syncrude from tar sands, only a few pilot plants and demonstration plants have produced syncrudes in the US.

The Air Force has extensively tested and flight qualified jet fuel derived from oil shale, but problems in producing shale syncrudes and the recent decreases in the cost of petroleum will likely delay the operational use of shale derived jet fuels for many years. Similar programs produced test quantities of jet fuels from tar sands and from coal for laboratory testing and evaluation, but flight testing and qualification of these fuels in Air Force aircraft was not completed. These and related programs have provided information that will eventually result in broadened jet fuel specifications that will increase availability and reduce the costs of future jet fuels.

As the heavier petroleum crudes replace the lighter crudes, refinery processes changes are required. The heavier crudes often contain significant quantities of sulfur and nitrogen, and hydrotreating is used to remove these contaminants. Hydrotreated fuels, although having improved combustion performance, tend to be deficient in lubricity and unstable in storage. Thus, jet fuels containing hydrotreated feedstocks must contain antioxidant and corrosion inhibitor/lubricity improver additives. Increased concentrations of these additives may be required in future jet fuels to insure adequate fuel lubricity and storage stability.

Other refinery processing changes have resulted from the decrease in markets for residual fuels (i.e., the heavy portion of crude oil that cannot be distilled). Refineries use thermal or catalytic cracking processes to make lighter products from the residual fuels. Unless stabilized by hydrotreating, cracked products will contain highly reactive, unstable olefins. Naphtha and kerosine fractions of cracked products are beginning to be blended into jet fuels in small amounts, but the severity of resulting fuel stability problems is not yet apparent.

2. HIGH DENSITY JET FUELS

Korosi and Rubin (reference 31) demonstrated that light pyrolysis fuel oil, a cracked gas oil byproduct, can be converted into a jet fuel that meets all applicable specification requirements except for a higher density and possibly a higher viscosity. Catalytic cycle oils (byproducts of catalytic cracking processes), light pyrolysis fuel oils (byproducts from steam cracking), and similar refinery byproducts have little value other than as boiler fuels. These cracked byproducts consist primarily of single-ring and polycyclic aromatics. Hydrotreating these cracked byproducts to saturate the aromatic rings produces fuels composed of alkylcyclohexanes and alkyldecalins. Jet fuels produced from these products have higher densities, lower freezing points, and higher viscosities and surface tensions than conventional jet fuels.

In addition to being a potential, substantial new source of jet fuels, these high-density, naphthenic jet fuels significantly increase the range of volume-limited aircraft such as tactical fighters. (A volume-limited aircraft is one that can takeoff and fly at a heavier weight than can be carried because of volume limitations.) The increased density of naphthenic fuels results in a volumetric heat content about 15 percent greater than for conventional jet fuels. Much of this additional energy can be translated into increased aircraft range. For weight-limited aircraft such as cargo aircraft, a range penalty of a few percent will result when using high-density, naphthenic jet fuels. (JP-9 and JP-10 fuels, used in volume-limited cruise missiles, are examples of high-density jet fuels.)

The increasing use of heavier crude oils, which have higher concentrations of naphthenes and aromatics, is already resulting in jet fuels becoming slightly more dense. Thus, the proposed development of high-density jet fuels may merely accelerate a long term trend.

3. ENDOTHERMIC JET FUELS

In the 1960s research was conducted on hydrocarbon jet fuels that could be catalytically dehydrogenated prior to combustion. The endothermic dehydrogenation reaction significantly increases the available heat sink of liquid hydrocarbon fuels, permitting their use in Mach 3 - 6+ hypersonic aircraft. The problems involved in using cryogens such as liquid methane or liquid hydrogen would thereby be avoided.

The revived interest in hypersonic aircraft and missiles has also revived interest in endothermic fuels. It is fortuitous that the most promising endothermic fuels are naphthenic; i.e., similar in structure to candidate high-density fuels already under development. Research work is underway to examine candidate high-density fuels as endothermic fuels.

4. CRYOGENIC JET FUELS

Liquid hydrogen, first test flow as a jet fuel by the NACA in 1955, was seriously considered as a jet fuel in the 1950's. (See Section II, paragraph 21(1).) Liquid hydrogen is an excellent jet fuel with a heat of combustion about 2-1/2 times higher than for JP-4 and with excellent combustion characteristics. Its serious disadvantages include very low density (about 10 percent of that of JP-4), its cryogenic nature (which requires expensive storage, transport, and transfer systems), and high cost. Despite these drawbacks considerable enthusiasm has been shown for aircraft fueled by liquid hydrogen. For Mach 6 plus speeds, supersonic combustion is required, and liquid hydrogen is the most promising fuel for supersonic combustion.

Liquid hydrogen is already used as a rocket fuel, but at only a few launch sites. Thus, the costs of producing, storing, transporting, and transferring liquid hydrogen are much less than if hydrogen-fueled aircraft were operating from multiple bases.

Liquid methane is another candidate jet fuel. It is considerably more dense than liquid hydrogen, has a lower heat of combustion, but has the same disadvantages of any cryogen. However, it is much cheaper to produce than liquid hydrogen.

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APPENDIX A

CONVERSION FACTORS

1 USA Barrel (bbl)(petroleum) = 42 gallons (gal)(US)

1 gallon (US) = 3.785 Liters (L)

1 pound/1000 bbl (lb/Kbbl) = 2.856 grams/cubic meter (g/m^3)

1 British thermal unit/pound (Btu/lb) = 0.002326 megaJoule/kilogram (MJ/kg)

1 Imperial gallon (Igal) = 4.55 Liters (L)

1 Btu/gal = 2.7856×10^{-4} megaJoule/Liter (MJ/L)

Fahrenheit (F) = 1.8 X Celsius (C) + 32

10^{-12} Ohm^{-1} Meter^{-1} = picoSiemens per meter (pS/m)

APPENDIX B

MERCAPTAN SULFUR LEVELS VS DOCTOR TEST

Listed below are summaries of information concerning mercaptan sulfur levels versus doctor test results:

(1) Mr Roger Organ of the Caltex Corporation, Dallas, TX, provided data dating from 1963 that showed that:

(a) Doctor negative results are obtained with mercaptan sulfur levels below 0.0004 wt percent.

(b) Doctor tests are usually positive but can be negative where high molecular weight mercaptans predominate for mercaptan sulfur levels between 0.0004 to 0.0008 wt percent.

(c) Doctor tests are positive for mercaptan sulfur levels greater than 0.0008 wt percent.

(2) Mr Lou Thomason, Refinery Associates, Inc., San Antonio TX, provided test results for mercaptans and Doctor test on eleven cargos of JP-8 (F-34) loaded at Lagoven, as follows:

% Mercaptans	Doctor Test
0.00017	Negative
0.00038	Positive
0.00019	Negative
0.00018	Positive
0.00032	Positive
0.00045	Positive
0.00029	Positive
0.00018	Negative
0.00012	Negative
0.00032	Positive
0.00030	Positive

Mr Thomason concluded by stating that "These tests indicate anything above approximately 2 ppm (0.0002%) mercaptan will result in a positive Doctor test. We are not sure why we are getting positive Doctor test with such a low mercaptan. Normally a mercptan content of about 10 ppm or less would result in a negative Doctor test. As you can see, the Lagoven JP-8 (F-34) will not meet you current requirement of Doctor negative. We are asking Lagoven to re-evaluate their test procedure and will notify you of the results as soon as possible."

(3) The following data were obtained from "Jet Fuel Treatment", by K. M. Brown, UOP Process Division, Universal Oil

Products Company, 23 Sept 1971. For the Doctor test to be negative (i.e., sweet), the mercaptan present must not exceed the following concentration:

Mercaptan Compound	Concentration
Methyl mercaptan	0.002%
Ethyl mercaptan	0.0006%
Propyl mercaptan	0.0009%
2-methyl-2 propanethiol	0.0004%
3-methyl-1 butanethiol	0.0003%
Heptanethiol	0.0001%
Mercapto benzene	0.002%

Based on the boiling ranges of typical jet fuels and the different mercaptans, JP-4 (F-40) would could contain ethyl mercaptan, propyl mercaptan (propanethiols), butanethiols, and higher molecular weight mercaptans. JP-8 (F-34) and JP-5 (F-44) fuels could contain hexanethiol and heavier mercaptans. Mercapto benzene could be expected to be found in JP-4, JP-5, and JP-8 fuels.

(4) A survey was undertaken in the 1957-58 time period to compare the Doctor test with measured quantities of mercaptans. The results were found in a letter dated 5 Nov 1958 signed by Mr Leo J. Conlon, Chief Petroleum and Chemicals Laboratory of the Directorate of AF Petroleum. The results given in the letter were:

No. Samples	Doctor Test	Mercaptans
222	Negative	Less Than 0.001%
1	Negative	0.0015%
90	Positive	Less Than 0.001%
85	Positive	0.0012 to 0.0048%

(5) In conclusion it appears that fuels with mercaptan sulfur levels less than 0.001 wt percent may give positive Doctor test results.

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