FOREWORD

This report, part of the in-house research on petroleum hydrocarbon jet fuels by the Air Force Aero Propulsion Laboratory, was prepared by Mr. Herbert R. Lander, Jr.

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ABSTRACT

The Air Force has encountered problems of storing fuel for high-speed, air-breathing aircraft. The thermal stability of high-temperature, hydrocarbon jet fuels is affected by periods of storage. During storage, jet fuels must retain their physical and chemical characteristics. Eighteen JP-6 fuels and nine Thermally Stable fuels were stored for various periods of time; data are presented on the results. After only 30 weeks of ambient storage, eight JP-6 fuels failed to pass the minimum specification requirements (Specification MIL-J-25656B) for thermal stability. All of the fuels monitored passed the thermal stability requirement when procured by the Air Force. The critical period in the life of high-temperature fuels regarding thermal stability occurs in the early storage period. Handling, transfer, and fuel deterioration are cited as possible influences on this early storage degradation.

This technical documentary report has been reviewed and is approved.

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SECTION 1

INTRODUCTION

As dictated by operational as well as logistical and economical considerations, jet fuels must retain their physical and chemical characteristics during storage. Aviation turbine fuels are procured according to specifications that are essential to operate a certain system in a satisfactory manner. Both commercial and military organizations require fuels to meet these requirements at the time of procurement. In many cases, these products are not consumed immediately. Because of fluctuations in supply and demand, vast quantities of fuels must be stored for indefinite periods of time. Throughout these storage periods, the fuels must retain, to some degree, their original characteristics. As outlined in the fuel specification, this degree of retention is limited by a maximum or minimum allowable value. Most conventional fuels are not affected to any great degree by storage. Any deviations that might occur in storage are of such a degree that they are not detectable with present analytical methods.

Conventional fuels have demonstrated that basically their storage stability is excellent. Periodically contamination has caused fuel to become objectionable, but, in the majority of cases, stored fuels retain their original quality for long periods of storage.

As the speed of air-breathing aircraft increases to multi-Mach regimes, certain properties of fuel become extremely important to the proper operation of the system. One such property is thermal stability. Thermal stability is the ability of a fuel to withstand the thermal stresses to which it will be exposed in its particular mission. The high temperatures, which the fuel will experience, will result from the high surface temperatures of the airframe and the fact that the fuel will be used for cooling the airframe and engine components. Fuels are required to have high thermal stability in their application at high speeds. As the thermal stability requirement is continually increased in hydrocarbon jet fuels, the fuels become increasingly sensitive to storage and storage conditions. Most of the high temperature fuels procured by the Air Force at present are used for testing and developmental analysis. The Air Force learned that some of these fuels were failing thermal stability tests after periods of storage prior to testing.

The Air Force was first made aware of a serious "storage stability" problem when considerable quantities of JP-6 fuel failed to meet thermal stability requirements of the specification (400°F) after relatively short periods of storage. Storage under controlled laboratory conditions resulted in similar results (Reference 1). Thus field experience reinforced by laboratory determinations established the problem that the Air Force must face. Jet fuel must retain its chemical and physical properties for at least 18 months of storage.

Perhaps the storage stability problem could be solved very easily. Special processing techniques could solve the storage stability problem by removing essentially all constituents or contaminants that might affect the fuel during storage. Another approach, which might result in better storage life, would be the use of nearly pure hydrocarbons as high-temperature fuels. These two procedures might solve the operational aspect associated with the use of stored fuels; however the economical and logistical problems arising from

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these steps are not encouraging. The quantity of such fuels would definitely be limited and the cost would be high. From an economical point of view, consider the fact that a 1-cent per gallon increase in fuel costs for the supersonic transport would increase the cost per aircraft by $1,000,000 for 10,000 hours of operation (Reference 2).

The thermal stability of most jet fuels procured in the United States is measured on the ASTM-CRC Standard Fuel Coker. There is some background data relating the results of this test to the results of actual flight conditions (Reference 3). The coker test measures the tendency of fuel to cause heat-exchanger deposits or nozzle plugging. As higher thermal stability is required in fuels, certain deviations are required from the present standard coker. A high-temperature Research Coker has been developed to extend the test conditions of the standard coker. Certain modifications to standard coker equipment could also result in more severe thermal conditions. In any case, these rigs subject the fuel to temperature conditions approximating those that the fuel might encounter in its intended application. Such deleterious effects as heat exchange fouling, component deposition, manifold plugging and fuel nozzle plugging are assessed in the cokers. High-temperature cokers must take into account the effects of tank heating into their evaluation, since this heating is an additional thermal stress of high-speed flight.

At present the Air Force is procuring most of the high-temperature fuels for test purposes. These fuels are JP-6 (Specification MIL-J-25656B), Thermally Stable (Specification MIL-F-25524A), or other experimental high temperature fuels. The Air Force Aero Propulsion Laboratory of the Research and Technology Division had requested, in the Spring of 1962, that samples of all JP-6 and Thermally Stable fuels procured by the Air Force be shipped to the testing laboratories at Wright-Patterson Air Force Base. The prime objective of this program was to monitor the behavior of these fuels during storage. This program has provided considerable data not only on the behavior of these fuels during storage but also on trends of other properties.

The results obtained from analyses of 18 JP-6 fuels and 9 Thermally Stable fuels are presented in this report.

SECTION 2

TESTS AND TEST RESULTS OF JP-6 AND THERMALLY STABLE JET FUELS DURING STORAGE

PHYSICAL AND CHEMICAL CHARACTERISTICS OF FUEL

The fuels evaluated in this program are listed in Table 1. The JP-6 fuels procured by the Air Force must conform to the physical and chemical characteristics as described in Specification MIL-J-25656B. These requirements and test methods are listed in Table 2.

Prior to the Spring of 1962, the Air Force procured Thermally Stable Jet Fuel according to Specification MIL-F-25524A; the physical and chemical requirements of this specification are given in Table 3. Large quantities of this fuel, which had been shipped to various locations, were found to be unstable when tested in the fuel coker. Several instances of this apparent storage instability left the Air Force with no alternative but to obtain this fuel on a limited source procurement. In the past 2 years, the Air Force has procured Thermally Stable fuels from certain suppliers according to the vendor's specifications. The Thermally Stable fuels evaluated in this program were procured in this manner, except one, which was procured under Specification MIL-F-25524A.

TABLE 1

FUELS EVALUATED

Fuel Code	Fuel Type	Supplier
SF6-6201A	JP-6	A
SF6-6202B	JP-6	B
SF6-6203B	JP-6	B
SF6-6204C	JP-6	C
SF6-6206C	JP-6	C
SF6-6207A	JP-6	A
SF6-6208B	JP-6	B
SF6-6209A	JP-6	A
SF6-6210C	JP-6	C
SF6-6211C	JP-6	C
SF6-6212C	JP-6	C
SF6-6213A	JP-6	A
SF6-6214A	JP-6	A
SF6-6215	JP-6	blend
SF6-6217C	JP-6	C
SF6-6218C	JP-6	C
SF6-6219	JP-6	blend
SF6-6303C	JP-6	C
TSF-6201D	*TSJF	D
TSF-6203E	TSJF	E
TSF-6204E	TSJF	E
TSF-6206F	TSJF	F
TSF-6208D	TSJF	D
TSF-6305E	TSJF	E
TSF-6306D	TSJF	D
TSF-6307G	TSJF	G
TSF-6312H	TSJF	H

*TSJF = Thermally Stable Jet Fuel.

TABLE 2

CHEMICAL AND PHYSICAL REQUIREMENTS FOR JP-6 FUEL AS GIVEN IN SPECIFICATION MIL-J-25656B

Requirements	Value	Test Method	
		Fed Std No. 791	ASTM Standard
Distillation:		1001	D86
Initial boiling point (min °F)	280		
10% distillation point (max °F)	350		
50% distillation point (max °F)	425		
90% distillation point (max °F)	500		
End point (°F)	to be reported		
Sum of initial boiling point plus 50% distillation point (min °F)	600		
Residue (max vol %)	1.5		
Distillation loss (max vol %)	1.5		
Gravity (min °API)	37.0	401	D287
Gravity (max °API)	50.0	401	D287
Existent gum (max Milligrams/100 milliliters)	5.0	3302	D381
Total potential gum, 16-hr aging (max milligrams/100 milliliters)	10.0	3354	D873
Insoluble potential gum (max milligrams/100 milliliters)	to be reported	3354	D873
Sulfur, total (max % wt)	0.40	5201	D1266
Mercaptain sulfur (max % wt or	0.001	5204	D1219 or D1323
doctor test)	sweet	5203	
Freezing point (max°F)	-65	1411	D1477
Thermal value:			
Heat of combustion (min net Btu/lb or	18,400	2502	
min amline-gravity product	5,250	3601 & 401	D611 & D287
Viscosity (max centistokes at -40°F)	7	305	D445
Aromatics (max vol %)	25	3703	D1319
Olefins (max vol %)	5	3703	D1319
Smoke point (min mm)	20	2107	D1322
Corrosion, copper strip (max ASTM)	1b	5325	D130
Water reaction (max interface-rating)	1b	3251	
Aniline point (°F)	to be reported	3601	D611
Thermal stability: (425/525°F)		3464	D1660
Preheater rating (max)	3		
Filter pressure differential (max inches of Hg)	10		

TABLE 3

CHEMICAL AND PHYSICAL REQUIREMENTS FOR THERMALLY STABLE FUEL AS GIVEN IN SPECIFICATION MIL-F-25524A

Requirements	Value	Test Method	
		Fed Std No. 791	ASTM Standard
Distillation:		1001	D86
Initial boiling point	to be reported		
10% distillation point (max °F)	410		
90% distillation point (max °F)	490		
End point (max °F)	550		
Percent distilled at 400°F	to be reported		
Residue (max vol %)	1.5		
Distillation loss (max vol %)	1.5		
Gravity (min °API)	35.0	401	D287
Gravity (max °API)	50.0	401	D287
Existent gum (max milligrams/100 milliliters)	7	3302	D381
Potential gum (max milligrams/100 milliliters)	14	3354	D973
Sulfur, total (max % wt)	0.3	5201	D1266
Mercaptan sulfur (max % wt)	0.003	5204	D1219
Freezing point (max °F)	-68	1411	D1477
Thermal value:			
Heat of combustion (min net Btu/lb or	18,400	2502	
min aniline gravity product)	5,250	3601 & 401	D611 & D287
Viscosity (max centistokes at -40°F)	12.5	305	D445
Aromatics (min vol %)	5.0	3703	D1319
Aromatics (max vol %)	15.0	3703	D1319
Olefins (max vol %)	3.0	3703	D1319
Smoke point (min mm)	25.0	2107	D1322
Corrosion (max rating)	1b	5313	
Water reaction		3251	
Flash point (min °F)	110	1101	
Thermal stability: (400/500°F)		3464	D1660
Preheater rating (max)	very light tan (3)		
Filter pressure differential (max inches of Hg)	10		

TABLE 4

PHYSICAL AND CHEMICAL PROPERTIES OF JP-6 FUELS

Property	Specification Requirements	JP-6 Fuels																	
		SF6-6201A	SF6-6202B	SF6-6203B	SF6-6204C	SF6-6206C	SF6-6207A	SF6-6208B	SF6-6209A	SF6-6210C	SF6-6211C	SF6-6212C	SF6-6213A	SF6-6214A	SF6-6215	SF6-6217C	SF6-6218C	SF6-6219	SF6-6303C
Volatility																			
Distillation (°F)																			
Initial boiling point	280 min.	302	291	291	314	316	289	292	290	317	316	317	297	295	302	323	329	296	321
10% evaporated	350 max.	312	300	300	324	325	304	299	311	326	326	325	320	312	315	341	336	313	334
50% evaporated	425 max.	326	316	316	338	339	321	311	332	343	343	342	339	331	332	357	356	329	349
90% evaporated	500 max.	362	342	342	364	366	358	335	371	370	371	372	375	365	366	375	376	362	373
End point	To be reported	390	388	391	407	407	400	384	408	414	405	396	412	410	404	402	402	401	409
Residue (vol %)	1.5 max.	1.0	0.5	1.0	1.0	1.0	1.2	1.0	0.9	1.0	1.0	0.8	1.4	1.0	1.0	1.0	1.0	1.0	0.5
Loss (vol %)	1.5 max.	1.0	0.5	0.5	1.0	1.0	0.3	1.0	0.1	1.0	1.0	1.2	0.1	1.0	1.0	1.0	1.0	1.0	0.5
Sum of initial +50% point (°F)	600 min.	628	607	607	652	655	610	603	622	660	659	659	636	626	634	680	686	625	670
Freezing point (°F)	-65 max.	-65-	-65-	-65-	-65-	-65-	-65-	-65-	-65-	-65-	-65-	-65-	-65-	-65-	-65-	-65-	-65-	-65-	-65-
Viscosity (centistokes at -40°F)	7 max.	4.27	3.78	3.77	4.78	4.76	3.87	3.50	4.28	4.90	4.69	4.80	4.73	4.26	4.48	4.84	5.54	5.03	5.40
Water reaction/interface rating	1b max.	0/#1	0/#1	0/#1	0.0/#4	0.0/#4	0.5/#1	0.0/#1	0.5/#1	0.0/#2	0.0/#3	0.0/#1	0.5/#1	0.0/#1	0.0/#1B	0.0/#1	0.0/#1	0.0/#1B	0.0/#1
Sulfur content (wt %)	0.40 max.	0.023	0.022	0.025	0.016	0.0018	0.01	0.029	0.01	0.0065	0.0024	0.029	0.01	0.0139	0.008	0.032	0.023	0.022	0.019
Copper strip corrosion	1b max.	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	
Mercaptan sulfur (wt %)	0.001 max.	0.000	0.000	0.000	0.000	0.000	0.000	0.000		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		0.000
Aromatic content (vol %)	25 max.	12.3	12.5	13.2	12.5	12.9	11.7	14.5	12.9	12.3	12.6	11.6	12.5	12.3	12.5	13.6	12.9	12.1	13.3
Olefin content (vol %)	5 max.	0.5	0.5	0.2	1.8	1.8	0.7	0.5	0.5	1.1	1.1	2.2	0.8	0.6	0.8	2.8	2.9	0.7	0.8
Gravity (°API)	37-50, range	49.7	49.5	49.5	48.0	48.2	50.1	49.4	48.9	47.7	47.7	47.8	48.5	49.2	48.6	46.6	46.7	49.1	48.6
Aniline-gravity constant	5250 min.	6660	6485	6460	6480	6453	6829	6299	6523	6502	6487	6453	6567	6642	6537	6291	6473	6614	6561
Existent gum (milligrams/100 milliliters)	5.0 max.	0.0	0.4	0.4	0.2	0.0	0.2	0.4	0.2	0.0	0.0	0.4	0.2	0.0	0.4	0.2	0.8	1.0	1.8
Total potential gum (milligrams/100 milliliters)	10.0 max.	0.0	0.9	4.5	3.3	0.8	0.4	1.2	0.4	0.4	0.4	1.4	0.4	0.4	1.0	2.6	0.8		1.8
Smoke point (mm)	20.0 min.	26.5	26.5	27.5	29.0	29.0	29.6	29.5	28.7	28.0	29.5	26.0	29.2	28.5	28.5	23.0	27.0	29.5	27.0
Doctor test	sweet	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	

Tables 4 and 5 give the physical and chemical characteristics, except for thermal stability, of the JP-6 and Thermal Stability jet fuels, respectively, evaluated in this program. These characteristics were found to remain unchanged during storage; any deviation that might have occurred was of such a degree that it was not detectable with present analytical methods.

THERMAL STABILITY OF JP-6 FUEL

The Air Force specification requires the JP-6 fuel to "pass" the ASTM-CFR coker test at 425°F preheater fuel-out temperature and 525°F filter furnace temperatures. The test is run for 5 hours at a flow rate of 6 pounds per hour. Because of the lack of break point (failing conditions) data on the original fuel samples, most of the storage data were obtained on coker runs at the specification requirements (425/525°F). The effects of tank heating are not accounted for in the thermal stability requirement for JP-6.

Since most of the coker results are at one set of test conditions, provisions were incorporated for determining the effect of the test on the fuel by assigning a rating based on both the preheater rating and filter pressure results. A coker rating system was devised for this program, whereby evaluation could be made on the coker results at one set of conditions. This rating system incorporates the results of both the preheater deposit and filter pressure rise into one value that signifies the degree to which a fuel failed or passed the specification requirement. This rating is the sum of the maximum preheater tube rating plus a numerical value assigned to the pressure rise across the filter. Table 6 describes the RTD-TSR (Research and Technology Division — Thermal Stability Rating). Under this system a rating of 1 to 5 is considered acceptable while ratings of 5 to 9 denote failure with increasing numerical rating denoting increasing degradation.

All JP-6 fuels reported were stored at Wright-Patterson Air Force Base in 55-gallon supplier-furnished drums at ambient storage conditions. The drums were shielded from severe weather conditions by a roof. Several of the fuels were stored in a tropical atmosphere chamber, which subjected the fuels to a cycle of temperatures ranging from approximately 80° to 120°F daily. This latter storage was for fuels that had demonstrated good characteristics in ambient storage. The thermal stability rating of the JP-6 fuels are outlined in detail in Appendix II.

The RTD-TSR system for evaluating the coker results of the thermal stability of the fuel during storage was used to outline the storage histories of 18 JP-6 fuels in Figures I-1 through I-18. See Reference 4. The data in these figures are the results of coker data at the specification requirement (425/525°F). All of the fuels are coded according to type: SF6 (storage fuel, JP-6), year (62, 63, etc.), and number of sample (01, 02 etc.). The suppliers are desginated by capital letters according to the order of their original samples. Therefore, fuel SF6-6201A is a storage JP-6 fuel, which was the first fuel of this type received in 1962, supplied by A (Table 1).

Figure I-1 illustrates the behavior of SF6-6201A during storage at ambient conditions. This fuel rated a marginal 4 (RTD-TSR) when fresh and degraded to a 9 after only 26 weeks of summer storage. Subsequent testing on this fuel showed slight improvement after 36 weeks. Testing at 60 weeks storage gave coker results of 8. Based on Figure I-1, this fuel went from marginal to bad, back to marginal, and finally rated bad after approximately 1 year. Although this fuel rated marginal to bad throughout its history, there are indications that the same degree of failure was not realized with reversals in storage characteristics occurring during the colder winter months. Although the coker repeatability is often questioned, it is thought to be better than the differences observed during storage with this fuel.

TABLE 5

PHYSICAL AND CHEMICAL PROPERTIES OF THERMALLY STABLE JET FUELS

Property	Thermally Stable Fuels								
	TSF-62010	TSF-6203E	TSF-6204E	TSF-6206F	TSF-6208B	TSF-6305E	TSF-6306D	TSF-6307G	TSF-6312H
Volatility									
Distillation (°F)									
Initial boiling point	356	330	317	324	362	328	353	328	326
10% evaporated	368	338	333	338	372	336	362	337	339
50% evaporated	386	348	352	360	388	350	376	350	338
90% evaporated	436	368	374	399	438	372	422	370	393
End point	475	405	397	447	482	394	462	404	426
Residue (vol %)		1.0	1.0	1.0		1.0		0.5	1.0
Loss (Vol %)		1.0	1.0	1.0		1.0		0.5	1.0
% Distilled (at 400°F)		98.5	99			99			95.5
Freezing point (°F)	-69	-80	-80	-68	-72	-80	-71	-68	-68
Viscosity (centistokes at -40°F)	11.66	5.1	5.2		11.64	5.31	11.52	5.41	5.70
Water reaction/interface rating	none	1	1	1	none	1	none	1	1
Total sulfur (wt %)	0.006	0.016	0.015	0.020	0.002	0.014	0.001	0.017	0.018
Corrosion	2	1a	1a	1b	1	1a	1	neg	neg
Mercaptan sulfur (wt %)	0.0001	0.0005	0.0005	0.000	0.0001	0.0006	0.0004	0.000	0.0017
Aromatic content (vol %)		11.9	12.2	15.4	trace	11.0	trace	10.2	15.1
Olefin content, (vol %)		2.0	2.1	0.6		2.2		0.2	0.5
Gravity (°API)	51.6	47.3	47.1	47.6	51.4	47.1	51.5	49.5	46.7
Aniline — gravity constant		6433	6372	6640	8944	6415	9012	7162	
Existent gum (milligrams/ 100 milliliters	1	1.0	1.2	0.8		2.0	1	0.0	0.0
Total potential gum (milligrams/ 100 milliliters)	1	1.2	1.4		2	1.5	1	0.4	1.0
Smoke point (mm)	33	27.0	27.0	28.5	32	26.0	31.0	30.0	25.5
Doctor test		sweet	sweet	sweet		sweet		sweet	sweet
Heat of combustion, Btu/lb	18,909	18,616	18,609		18,813	18,614	18,834		
Flash point (°F)	133	112	115	114	133	116	126	116	116
Procurement specification	suppliers	suppliers	suppliers	MIL-F-25524A	suppliers	suppliers	suppliers	suppliers	suppliers

TABLE 6

RTD THERMAL STABILITY RATING SYSTEM

Coker Results	RTD-TSR System
Maximum preheater rating:	
0	0
1	1
2	2
3	3
4	4
Filter pressure rise: inches of mercury (minutes)	
0 - 0.5 (300)	1
0.6 - 1.0 (300)	2
1.1 - 10.0 (300)	3
10.1 - 25.0 (300)	4
25 (less than 300)	5

RTD-TSR is the sum of Maximum Preheater Rating Number plus Filter Pressure Rise.

Example: Fuel SF6-6201A tested on a coker at 425/525°F test conditions results in a pressure rise of 25 inches of mercury in 279 minutes and maximum preheater rating of 2. RTD-TSR is 7.

Fuel SF6-6202B (Figure I-2) gave a "good" RTD-TSR of 2 when fresh. However, sometime during transit and/or shipment to Wright-Patterson Air Force Base, this fuel dropped to a 7 rating. Coker testing at 22 weeks substantiated this rating; after 61 weeks, a maximum rating of 9 was realized.

Fuel SF6-6203B (Figure I-3) demonstrated storage characteristics similar to SF6-6202B with regard to thermal stability deterioration. These fuels were procured from the same supplier explaining to some degree their corresponding behavior during storage. At this point the possibility arose that perhaps the supplier's coker was not as severe a test as the Air Force rig. Many investigators believed this aspect to be the whole storage stability problem or at least a major portion of the problem. The Air Force requested the supplier of SF6-6203B to re-run the thermal stability test on a retained sample of this fuel. This re-run substantiated the Air Force determination for 6 weeks; thus the ability of these two rigs to reproduce the same results was demonstrated. Maximum thermal stability failure of this fuel was realized after 61 weeks of ambient storage.

Figures I-4 and I-5 present the behavior of two stored fuels from supplier C, SF6-6204C and SF6-6206C, respectively. SF6-6204C (Figure I-4) demonstrated marginal characteristics throughout 60 weeks of storage; these occurred during the winter months at 30 weeks of storage. This fuel, however, rated very good (3) after 1 year of ambient storage. Samples SF6-6204C stored in the tropical chamber rated marginal after 9 months of storage, which corresponded to the conditions of this fuel when placed in this chamber after approximately 30 weeks of ambient storage. Fuel SF6-6206C (Figure I-5) showed no effect of storage on the thermal stability required by the specification. This fuel was stored for 66 weeks.

Fuel SF6-6207A (Figure I-6) dropped in thermal stability during 54 weeks of storage. No tests were run on this fuel from between 2 weeks and 54 weeks; thus it could not be determined whether reversals occurred in this fuel similar to those of SF6-6201A, which demonstrated fluctuating behavior during storage. The only conclusion drawn on this fuel is that it appeared to lose its specified thermal stability after 54 weeks of storage.

Fuel SF6-6208B (Figure I-7) demonstrated very poor initial storage stability. This characteristic is similar to fuels SF6-6202B and SF6-6203B from the same supplier. These fuels are apparently sensitive to transit and/or handling in conjunction with storage. This fuel rated bad in storage, with a rating of 8 after 1 year of ambient storage. This fuel was not tested during the 12-53 week period, so again coker test evaluations may have fluctuated during this period.

Fuel SF6-6209A (Figure I-8) rated a marginal 4 when fresh. After only 24 weeks of storage, this fuel gave a pressure rise of 25 inches of mercury in approximately 70 minutes. Preheater ratings were not available on these runs, but at best these fuels are bad and are given ratings of 7. A rating of 7 was given to this fuel after 65 weeks of storage. This fuel is characterized by very severe filter plugging throughout its storage period.

Fuel SF6-6210C (Figure I-9) showed very little deterioration during storage. Marginal quality was detected during early storage, but 60 weeks testing indicated very good storage stability. This fuel was stored under tropical conditions for 9 months and tested; these tests also resulted in good thermal stability results.

Fuel SF6-6211C (Figure I-10) remained thermally stable throughout 60 weeks of storage (ambient and tropical conditions). This fuel demonstrated a definite period during early storage when apparent thermal deterioration was beginning. However, further storage resulted in a good rating of 2 for 29 weeks and an additional 9 months at tropical conditions.

Fuel SF6-6212C (Figure I-11) demonstrated storage characteristics similar to SF6-6211C. This fuel also demonstrated a period of apparent degradation with regard to thermal stability. However, again, this apparent start of deterioration was not continued but resulted in "fresh condition" ratings after longer periods of storage even under "tropical storage" conditions.

Fuel SF6-6213A (Figure I-12) again demonstrates the failure of fuel during transit from the supplier and/or initial storage. This fuel rated 3 at the refinery but rated from 6 to 8 after 6 weeks. After 46 weeks of ambient storage, this fuel rated 6. Most fuels seem to be sensitive to initial storage, which perhaps indicates transit and excessive handling problems and a need for better housekeeping procedures.

The initial effects of the combination of handling, transit, and storage are dramatically illustrated for SF6-6214A in Figure I-13. In 4 weeks of storage, this fuel went from an RTD-TSR of 1 to an 8. After 42 weeks of ambient storage, this fuel again rated "very good" with a 3 RTD-TSR. This fuel illustrates one of the largest reversals uncovered during this program.

Fuel SF6-6215 (Figure I-14) was blended from 50% SF6-6201A fuel and 50% SF6-6212C fuel. This blend was of marginal thermal stability quality when fresh and showed improvement after 46 weeks of storage at both ambient and tropical conditions.

Fuel SF6-6217C (Figure I-15) showed no deterioration in thermal stability after 50 weeks of ambient and tropical storage conditions. Fuel SF6-6218C (Figure I-16) remained thermally stable for 15 weeks.

Fuel SF6-6219 was blended from 70% (volume) fuel SF6-6201A and 30% (volume) SF6-6206C and demonstrated good storage stability during 53 weeks at both tropic and ambient conditions.

Fuel SF6-6303C (Figure I-18) after 30 weeks of ambient storage showed a slight improvement in thermal stability.

THERMAL STABILITY OF THERMALLY STABLE FUEL

Prior to the Spring of 1962, the Air Force procured Thermally Stable Jet Fuel according to Specification MIL-F-25524A. Large quantities of this fuel, which had been shipped to various locations, were found to be unstable when tested in the fuel coker. Several instances of this storage instability left the Air Force with no alternative but to obtain this fuel on a limited source procurement. In the past 2 years, the Air Force has procured Thermally Stable Jet Fuel from two suppliers according to the vendor's specifications.

Thermally Stable Jet Fuel is required to pass the ASTM-CFR standard fuel coker, which is continuously operated for 5 hours at a preheater temperature of 400°F and a filter temperature of 500°F and a fuel flow of 6 pounds per hour. The pressure drop across the filter should not be greater than 10 inches of mercury and the maximum preheater deposit should be very light tan in color or a Code 3. This thermal stability requirement, as given in Specification MIL-F-25524A, remains a qualification on Thermally Stable Jet Fuel procured to the vendor's specification. Limited procurement has resolved the storage stability problem associated with Thermally Stable Jet Fuel, but this type of action is undesirous for various apparent reasons.

Thermally Stable fuels tested in this program include not only fuels from the two suppliers but several experimental fuels submitted to the Air Force for evaluation. These experimental fuels were submitted, in the hope that they would demonstrate good storage behavior, perhaps qualifying the supplier as a future Air Force supplier.

All of the Thermally Stable jet fuels reported, were stored at Wright-Patterson Air Force Base in 55-gallon supplier-furnished drums at ambient storage conditions. The storage drums were shielded from severe weather conditions by a roof. Appendix III presents the detailed thermal stability history of the stored, Thermally Stable jet fuels.

The RTD-TSR system for evaluating the coker results of the thermal stability of fuel during storage was used to outline the storage histories of nine, Thermally Stable jet fuels in Figures I-19 through I-27. The data in these figures are the results of coker data at the MIL-F-25524A requirement of 400/500°F. All of the fuels are coded according to type: TSF (Thermally Stable Fuel), year (62, 63, etc.), and number of sample (01, 02 etc.). The suppliers are designated by capital letters according to the order of their original samples. Therefore, fuel TSF-6201D is a Thermally Stable Fuel, which was the first such fuel received in 1962; it was supplied by D.

Figure I-19 illustrates the behavior of TSF-6201D during storage at ambient conditions. This fuel retained its ability to pass the coker at 400/500°F through 75 weeks of storage. The Supplier's data on this fuel indicated marginal filter pressure rise of 4.8 inches of mercury at the refinery; however this figure did not indicate eventual fuel failure as might be expected. Subsequent coker tests during storage gave filter plugging of less degree.

TSF-6203E (Figure I-20) rated 2 when procured by the Air Force and deteriorated to a rating of 4 to 5 after approximately 10 weeks of storage. However, after 78 weeks of storage, this fuel rated a very good 1 or 2. This fuel, like several of the JP-6 fuels, showed tendencies to deviate from the specification early in storage but upon further storage passed the thermal stability requirement.

TSF-6204E (Figure I-21) from the same supplier as TSF-6203E remained thermally stable through 60 weeks of ambient storage. Periodically during storage, this fuel demonstrated tendencies to plug the filter; these tendencies failed to become worse upon further storage.

TSF-6206F (Figure I-22) is the only fuel reported that was procured according to the Air Force Specification MIL-F-25524A. This fuel was obtained by RTD after it had failed the thermal stability test during storage. This fuel was received at RTD on 12 July 1962, tested, and stored. As indicated in Figure I-22, TSF-6206F was marginal upon its arrival and remained in this state after 29 weeks of storage. However, after 1 year of ambient storage, this fuel caused severe filter plugging, which resulted in a maximum failure of 9. Filter plugging failure was detected in this fuel even at 375/475°F coker conditions after 1 year of storage.

Fuel TSF-6208D (Figure I-23) retained its good thermal stability through 68 weeks of ambient storage. This fuel was not tested between initial conditions and 68 weeks storage at 400/500°F standard coker conditions. This fuel, however, passed coker analysis at 20 and 28 weeks at more severe test conditions of 425/525 and 450/550°F.

Fuel TSF-6305E (Figure I-24) was stored for 34 weeks at ambient conditions and retained its thermal stability, based on analysis at specification requirements. This fuel deteriorated slightly during the first 8 weeks of transit and/or storage, but not enough to fail the coker. This fuel, like TSF-6208D, passed the coker test at conditions of 450/550°F during storage. It is doubtful that this fuel would drop from 450/550°F to 400/500°F during storage for only 34 weeks.

TSF-6306D (Figure I-25) retained its thermal stability for 33 weeks of ambient storage. Again this fuel had good thermal stability, in excess of 450/550°F, which is one reason why this fuel did not fail specification requirements after only 33 weeks.

Experimental fuel TSF-6307G (Figure I-26) was supplied to the Air Force to meet Specification MIL-F-25524A. This fuel was marginal when it arrived at RTD but did not deteriorate further in 20 weeks of ambient storage. Storage will be continued on this fuel to determine if improvement or failure will be realized.

Experimental fuel TSF-6312H (Figure I-27) was also supplied to the Air Force to meet the MIL-F-25524A specification. This fuel was very bad in thermal stability and rated 9 on arrival at RTD. After 17 weeks of storage, this fuel was showing slight improvement; however filter plugging was still bad and ratings of 6 to 7 were determined. This fuel will be studied for storage tendencies at longer periods of storage.

SECTION 3

DISCUSSION OF TEST RESULTS

Thermal stability is required in high-temperature, hydrocarbon jet fuels, if advanced air-breathing turbojet systems are to operate at optimum efficiency. The Air Force feels that its jet fuel should remain thermally stable for at least 18 months of ambient storage.

Eighteen JP-6 fuels were evaluated in this program; eight of these fuels rated from marginal to bad in thermal stability after approximately 30 weeks of storage. These results are based on coker tests run at the present requirement of 425/525°F in Specification MIL-J-25656B. As indicated, many of these fuels were of marginal thermal stability shortly after procurement perhaps indicating deficiencies in handling. In many of the fuels, initial storage resulted in immediate deterioration of thermal stability; in some cases, this initial trend leveled off and the fuel retained its passing quality; in still other instances, this initial degradation was only compounded in further storage.

Table 7 lists the JP-6 fuels into two groups based on 30 weeks of ambient storage. This table indicates whether a fuel passed the thermal stability requirement after 30 weeks of storage. This table illustrates the main reason why JP-6 was procured sole source for the last year; the only vendor able to supply fuel with at least 30 weeks of storage stability was Supplier C. Suppliers A and B failed to furnish a single fuel that passed the coker requirement after the 30 weeks. Fuel SF6-6214A degraded badly during initial storage (in transit) from a 1 to an 8; however after 42 weeks at ambient storage this fuel rated a passing 2, so conceivably this fuel may have been passed at 30 weeks.

Nine, Thermally Stable jet fuels were evaluated in this program; three of these fuels were marginal to bad in thermal stability when entered into the program, based on coker analysis at 400/500°F.

Table 8 lists the "good" and "bad" fuels based on coker analysis for only 20 weeks of storage. Six of the fuels passed the thermal stability test when fresh, after 20 weeks storage, and longer in some cases.

No Thermally Stable Jet Fuel evaluated went unstable during storage; fuels that rated "failing" initially are the only ones rated "failing" during storage. Many of the Thermally Stable fuels evaluated not only passed the specification requirement for thermal stability, but could not be failed at conditions considered to be the limit on the standard coker. This statement holds for several of the "passing" JP-fuels also.

The chemical and physical specification tests on the storage test fuels failed to indicate any storage trends uncovered by the coker analysis. The principal objective of the Air Force is to put a test in the military specification to guarantee storage stability. Current investigations are aimed at this goal.

TABLE 7

THERMAL STABILITY OF JP-6 FUELS DURING STORAGE (Based on Coker Analysis at 425/525°F Test Conditions During Ambient Storage)

Storage Life	
Less than 30 weeks	No Failure
SF6-6201A	SF6-6204C (52)*
SF6-6202B	SF6-6206C (66)
SF6-6203B	SF6-6210C (60)
SF6-6207A	SF6-6211C (66)
SF6-6208B	SF6-6212C (60)
SF6-6209A	SF6-6215 (48)
SF6-6213A	SF6-6217C (49)
**SF6-6214A	SF6-6218C (18)
	SF6-6219 (53)
	SF6-6303C (29)

*Numbers in parentheses indicate weeks of storage without thermal stability failure

**Initially appeared to have failed in less than 30 weeks; however after 42 weeks it passed the thermal stability tests.

TABLE 8

THERMAL STABILITY OF THERMALLY STABLE JET FUELS DURING STORAGE (Based on Coker Analysis at 400/500°F Test Conditions During Ambient Storage)

Storage Life	
Less than 20 weeks	No Failure
TSF-6206F	TSF-6201D (75)*
TSF-6307G	TSF-6203E (78)
TSF-6312H	TSF-6204E (60)
	TSF-6208D (68)
	TSF-6305E (34)
	TSF-6306D (33)

*Numbers in parentheses indicate weeks of storage without thermal stability failure.

SECTION 4

CONCLUSIONS

Thermal stability of high-temperature, hydrocarbon jet fuels is affected by periods of storage. Storage can be broken down into a number of aspects; these would include treatment, handling, transportation, and physical storage. Any one or all of these aspects could affect the thermal stability of a fuel especially when these stability requirements are in the region of 400°F and above. The storage stability problem at this point becomes very complex. It involves a great many variables. The first of these variables begins to appear the moment a fuel is processed at the refinery, while the last is presented at the use point. These include all of the testing, handling, transportation, and environmental conditions encountered by the fuel on its journey to the actual storage facilities. The physical storage of a fuel is very important and consists of many variables also. These would include testing; container characteristics; geographic location; cleanliness of transporting, transferring, and storage facilities; and many others that might arise in individual instances. In other words, once a fuel finally reaches its point of use it has run the gamut; it has passed over or through many types of materials; it has been stored for varying lengths of time in a variety of equipment; and it has, in some cases, been exposed to varying climatic conditions. This list could go on for a considerable length of time, with individual fuels adding certain irregularities that might arise in their particular path from refinery to use point. These variables, be what they are, combined with actual thermal deterioration of the fuel caused by the reaction of components of the fuel within themselves or caused by contaminants introduced in the past history of the fuel, are principles that must be considered when attempting to solve the problem of storage stability.

Most of the fuels tested by the Air Force demonstrated thermal stability deterioration during the initial period of storage. All of the fuels passed the thermal stability requirements at the refinery; the break points of these fuels were not determined. Had the failure conditions of these fuels been determined at the refinery, considerable information could have been uncovered concerning the actual drop in thermal stability as determined by drop in break point. Indications are that several of the fuels were processed to pass the thermal stability requirement with no "cushion" to withstand slight deterioration in storage. In spite of this fact, several of the fuels had break points of 50-75°F lower than the specification requirements after approximately 1 year storage. If thermal stability cushions are to be built into fuels prior to storage, limits will have to be raised to 75°F above present specifications in order to guarantee quality fuel after 1 year of storage. Since cushions of this nature are out of the question, a more practical solution to the problem is desired.

Although it is not clear exactly what constituents in jet fuel degrade thermal stability during storage, trends have been uncovered, which have opened new areas for research. Many of these areas are now being investigated by the Air Force and its contractors. Present Air Force contractual efforts are outlined as follows:

Contractor: Southwest Research Institute
Contract: AF 33(657)-11246
Objective: Investigate the influence of additives on the storage stability of high temperature fuels.

Contractor: Phillips Petroleum Company
Contract: AF 33(657)-10639
Objectives:

1. Investigate the storage stability of high-temperature, hydrocarbon fuels to determine the factors contributing to instability in storage;

2. Develop an accelerated storage test, which will predict the storage life of fuels;

3. Evaluate a small scale technique to evaluate thermal stability of fuels.

Contractor: Bureau of Mines
Contract: DO 33(615)-64-1009
Objective: Application of radioisotope tracer techniques to investigate the influence of fuel constituents on the storage stability of high temperature fuels.

SECTION 5

REFERENCES

1. G. D. Kittredge, Thermal Stability of Hydrocarbon Fuels, ASD-TDR-61-238, Part II, prepared by Phillips Petroleum Company on Contract AF 33(616)-7241, Aeronautical Systems Division, Wright-Patterson AF Base, Ohio, July 1962.

2. R. C. Sheard, SST Fuels and Lubricants, presentation at the 66th Annual Meeting of the American Society for Testing and Materials at Atlantic City, New Jersey, June 23-28, 1963.

3. D. A. Randal, Flight Tests to Determine the Thermal Stability of Five JP-4 Fuels Under Simulated B-52 Cruise Conditions in an F-100C Aircraft, WADC-TN-58-327, Wright Air Development Center, Wright-Patterson AF Base, Ohio, January 1959.

4. H. R. Lander, Storage Behavior of High Temperature Fuels, presentation at the Society of Automotive Engineers (Mid-Continent Section) and Society of Professional Engineers and Scientists of Tinker Air Force Base at Oklahoma City, Oklahoma, February 21, 1964.

APPENDIX I

ILLUSTRATIONS ON THERMAL STABILITY OF FUELS DURING STORAGE

In Figures I-1 through I-18, coker conditions were at 425/525°F as required in Specification MIL-J-25656B.

In Figures I-19 through I-27, coker conditions were at 400/500°F as required in Specification MIL-F-25524A.

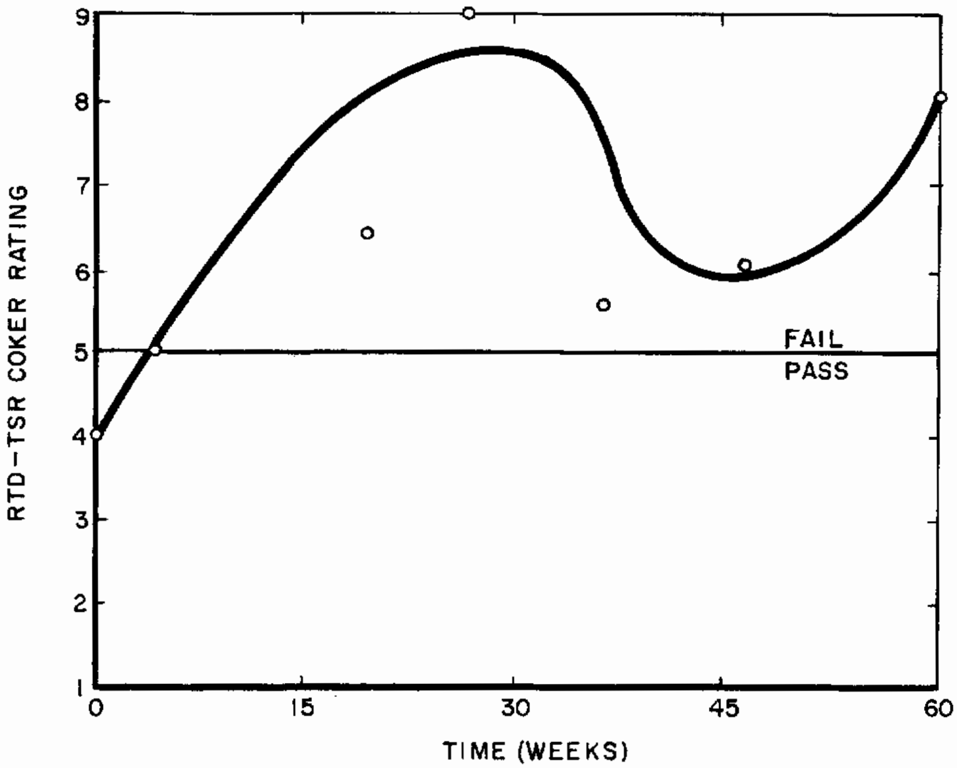

Figure I-1. Thermal Stability of SF6-6201A Fuel During Storage

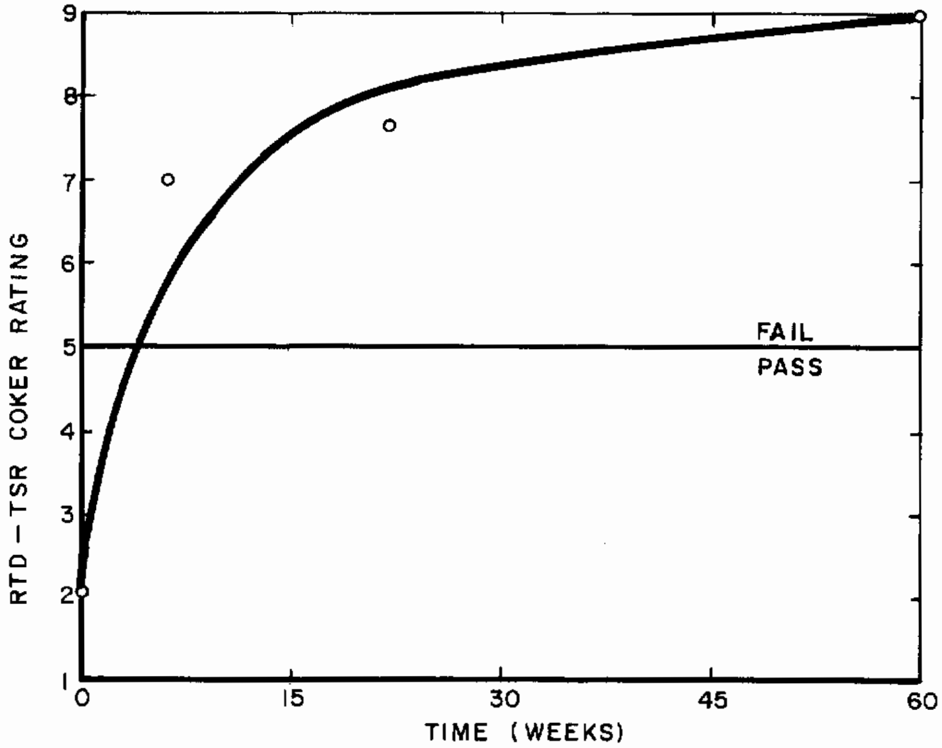

Figure I-2. Thermal Stability of SF6-6202B Fuel During Storage

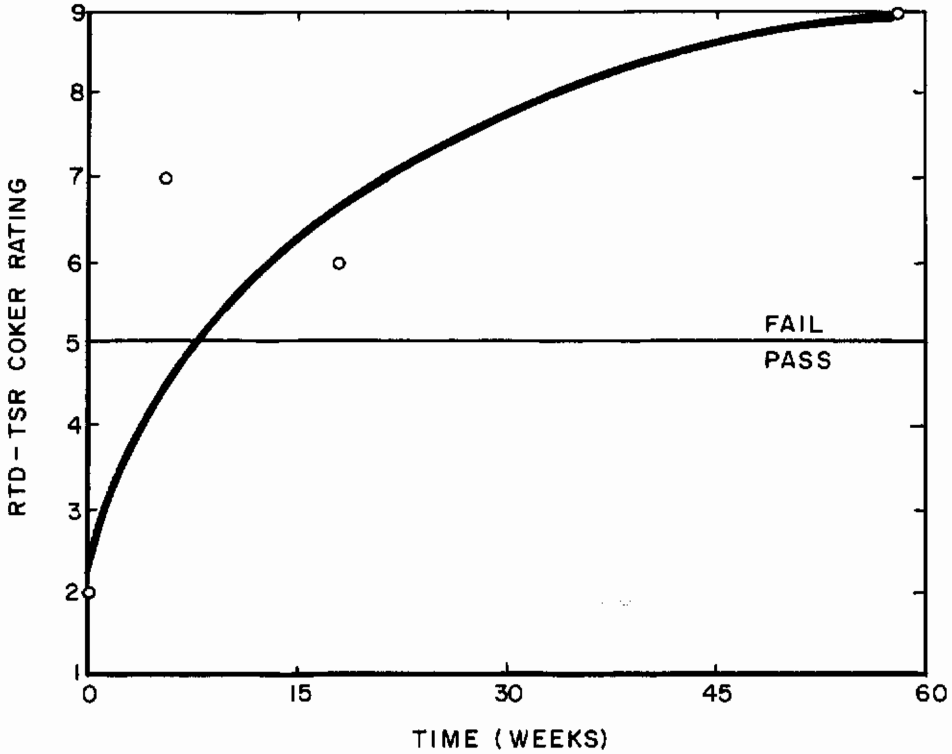

Figure I-3. Thermal Stability of SF6-6203B Fuel During Storage

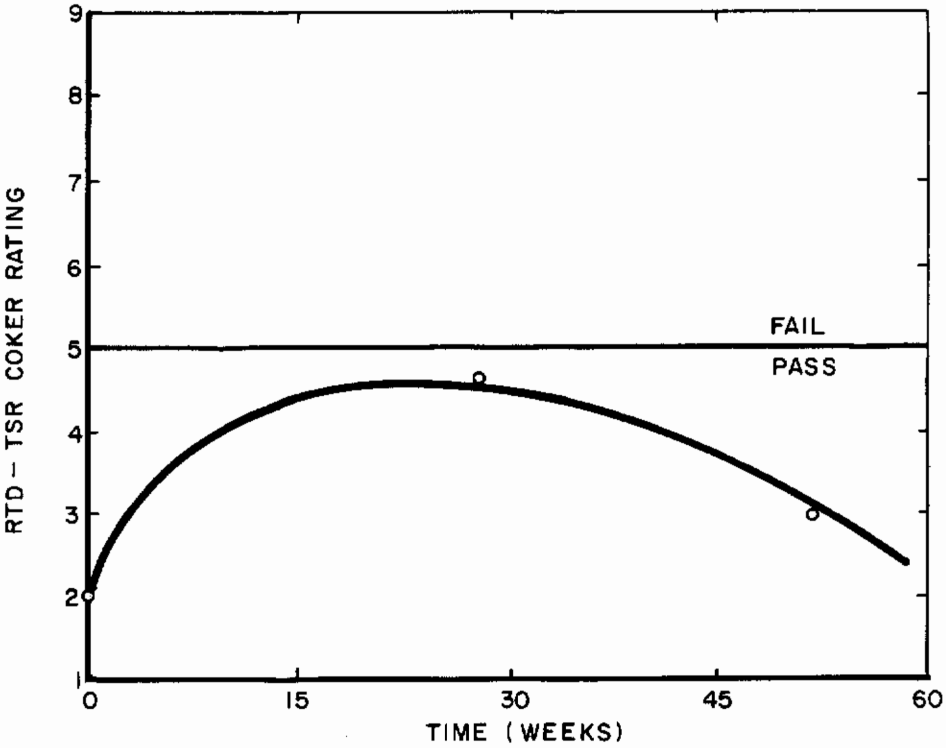

Figure I-4. Thermal Stability of SF6-6204C Fuel During Storage

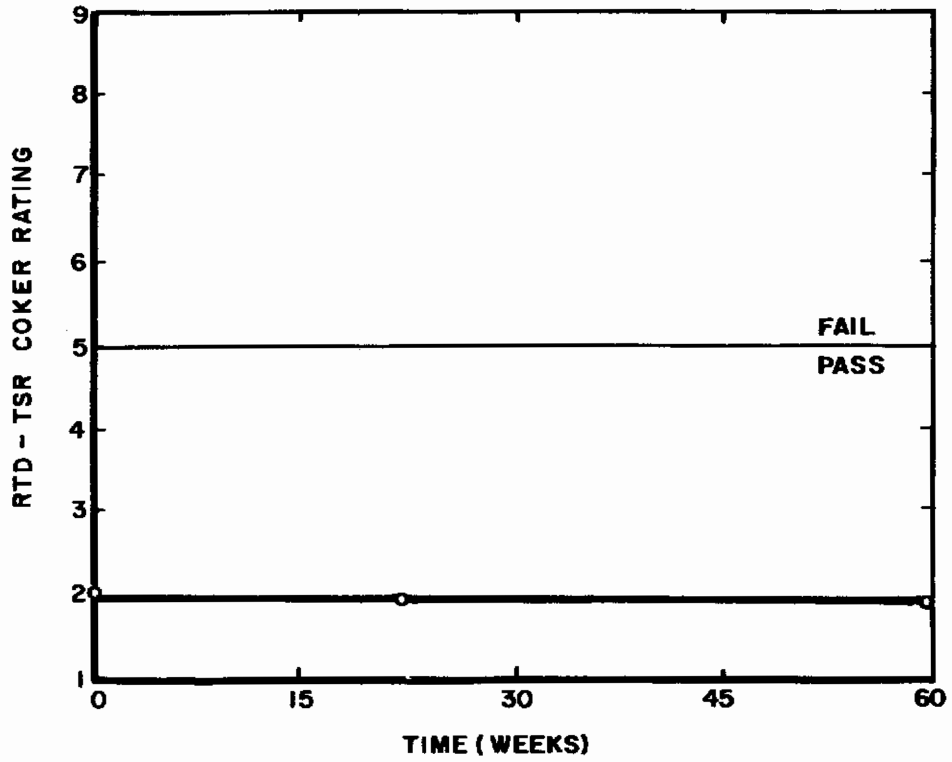

Figure I-5. Thermal Stability of SF6-6206C Fuel During Storage

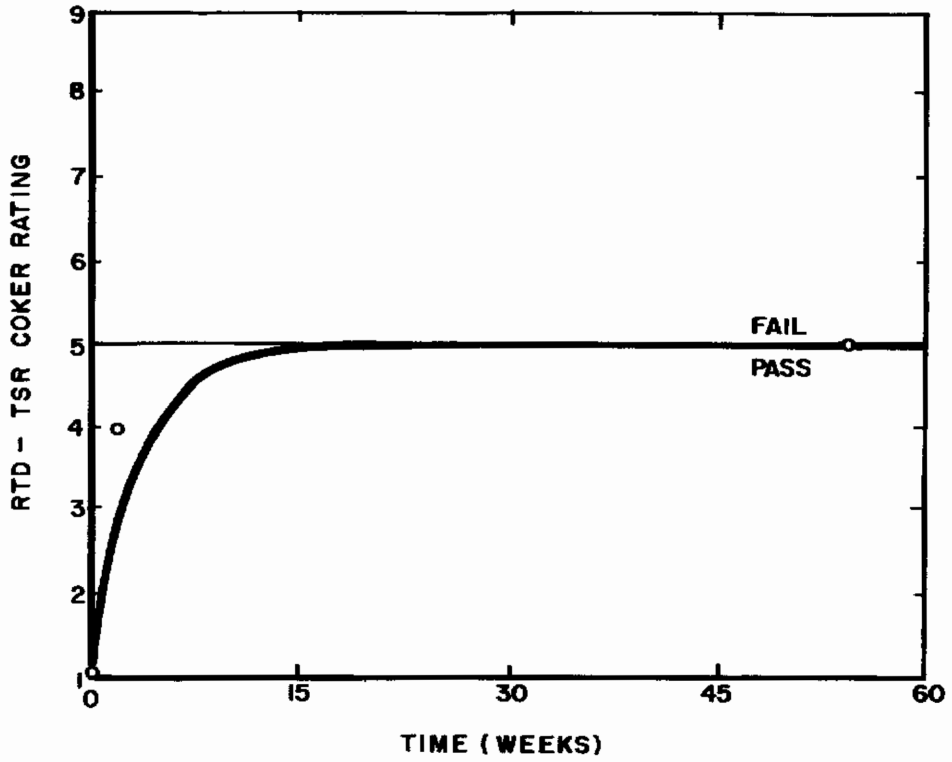

Figure I-6. Thermal Stability of SF6-6207A Fuel During Storage

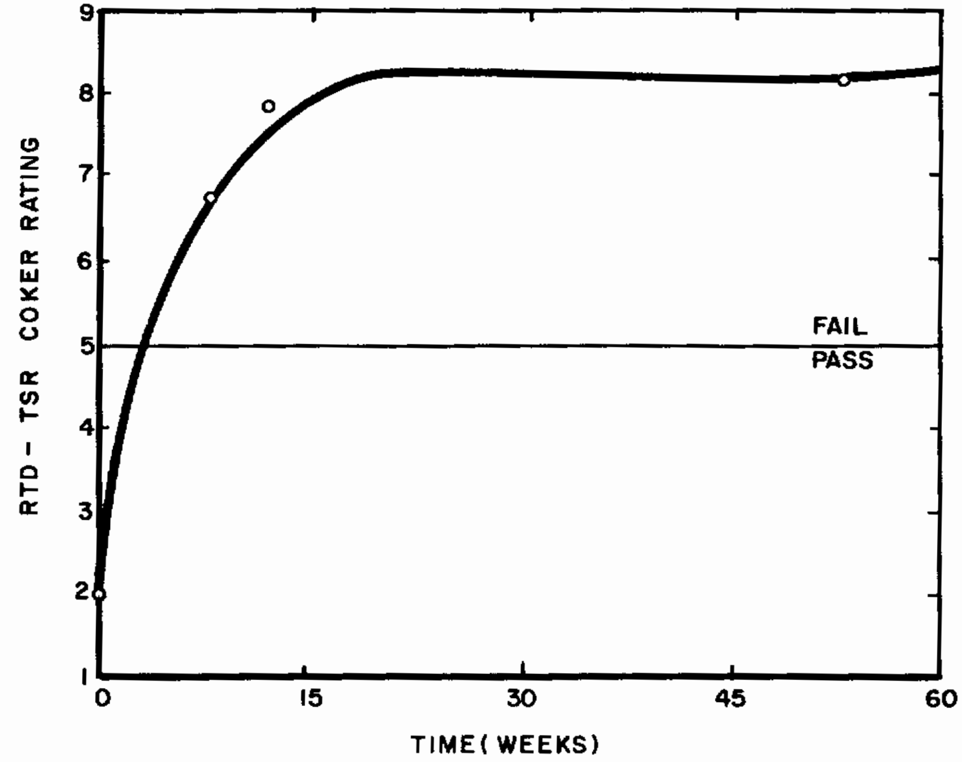

Figure I-7. Thermal Stability of SF6-6208B Fuel During Storage

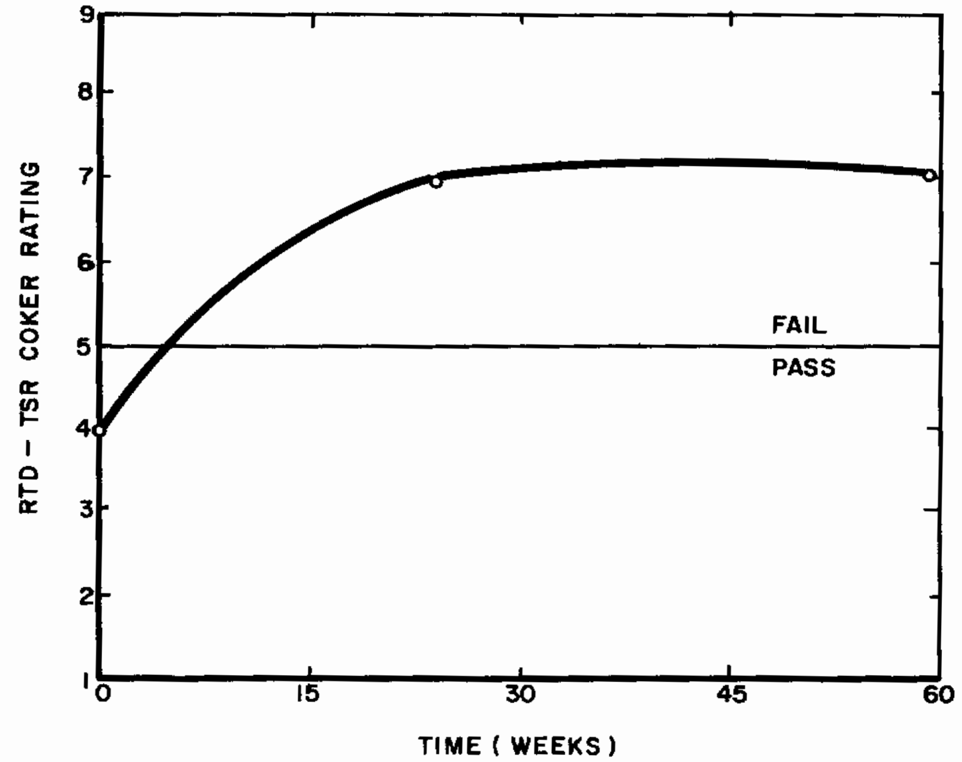

Figure I-8. Thermal Stability of SF6-6209A Fuel During Storage

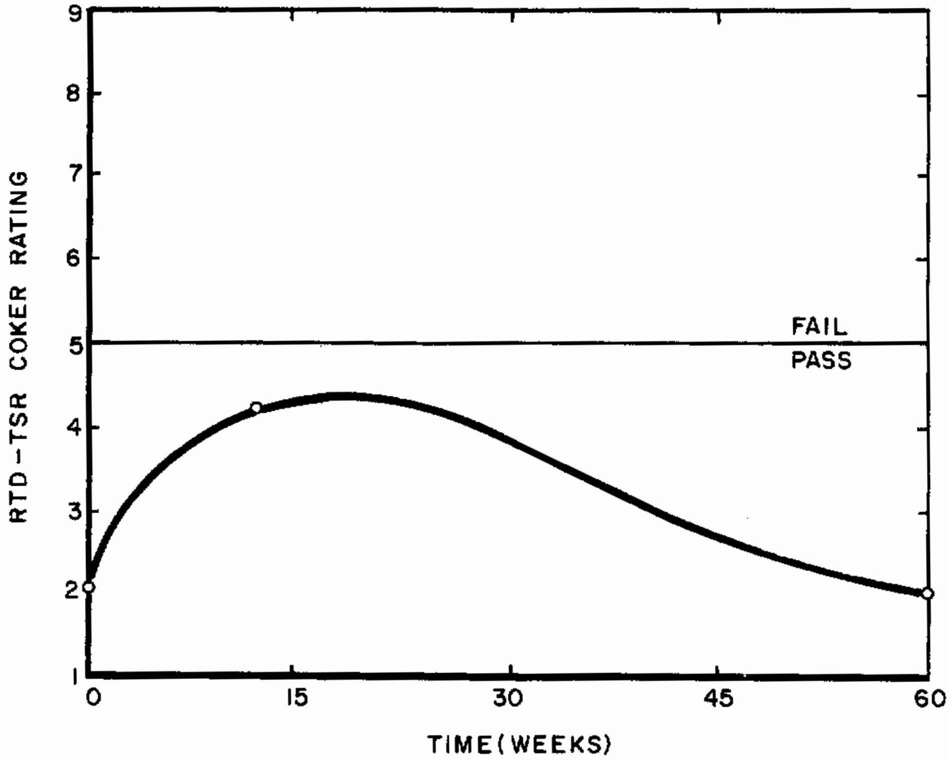

Figure I-9. Thermal Stability of SF6-6210C Fuel During Storage

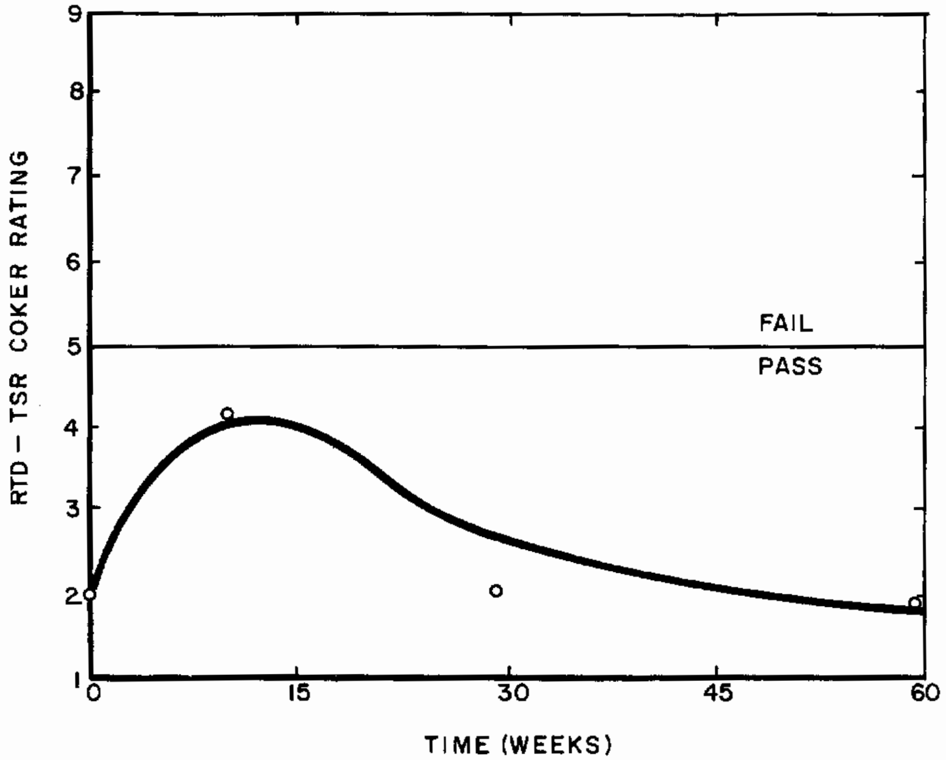

Figure I-10. Thermal Stability of SF6-6211C Fuel During Storage

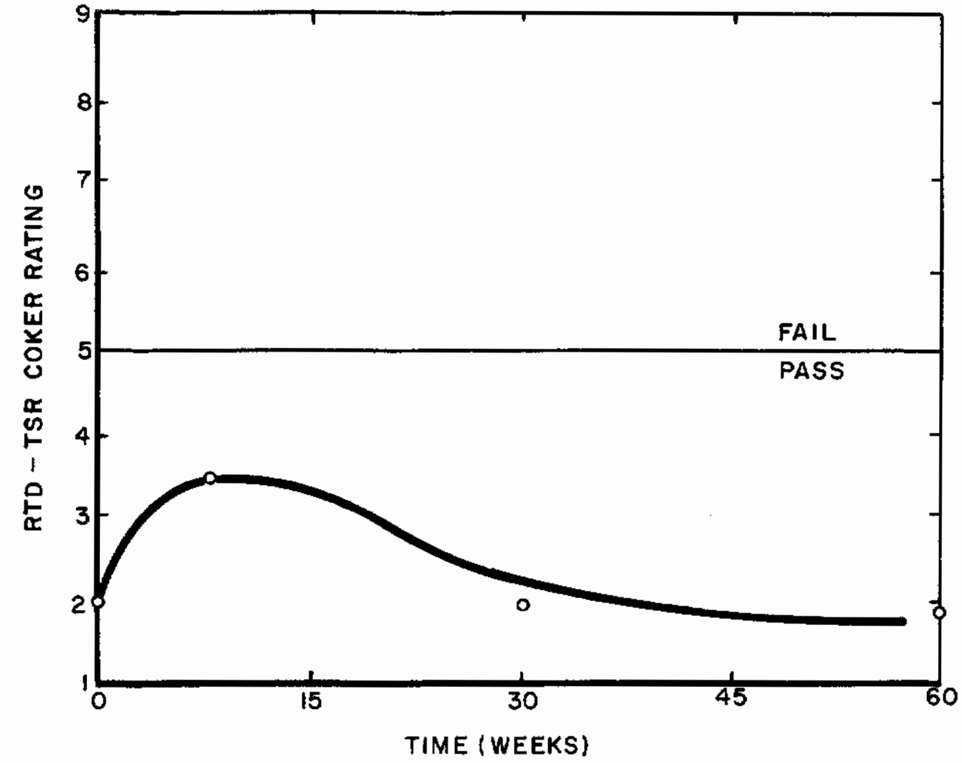

Figure I-11. Thermal Stability of SF6-6212C Fuel During Storage

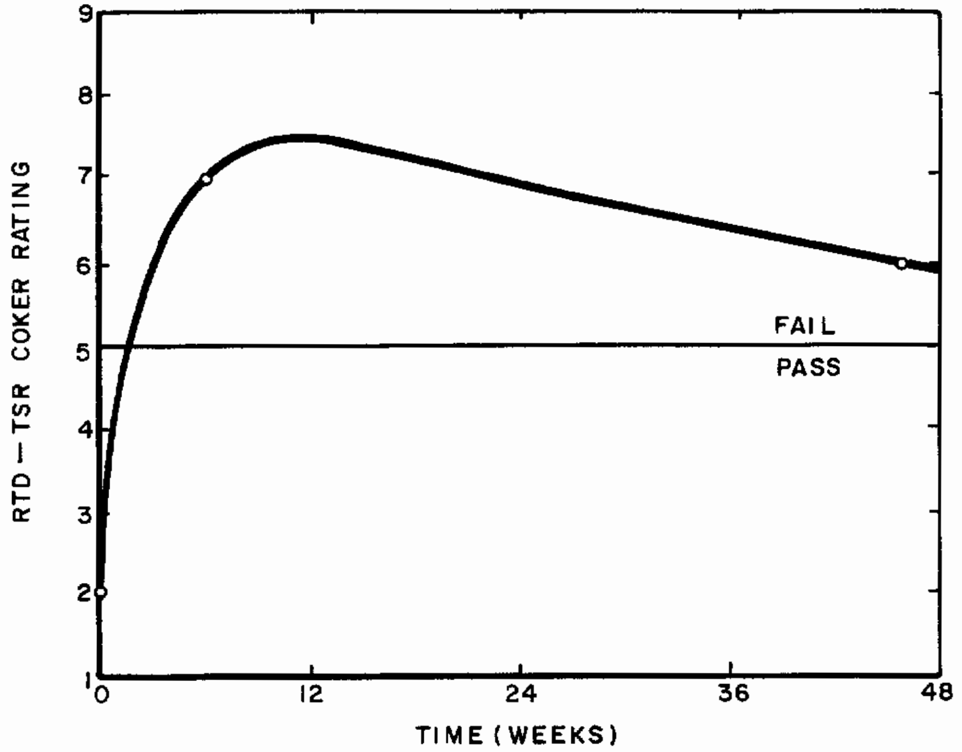

Figure I-12. Thermal Stability of SF6-6213A Fuel During Storage

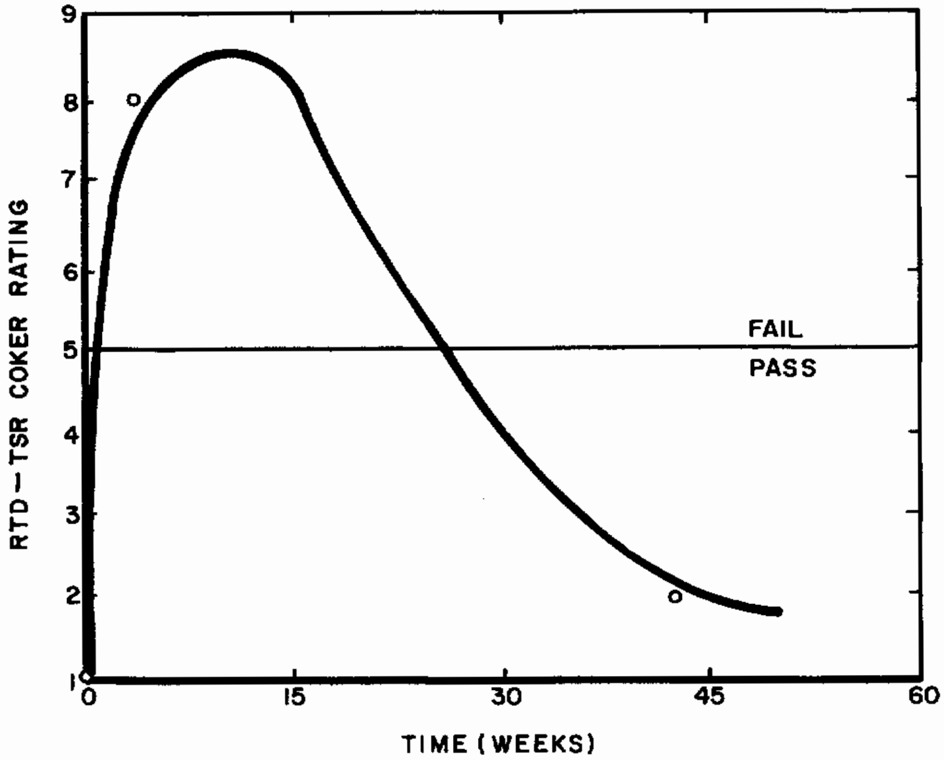

Figure I-13. Thermal Stability of SF6-6214A Fuel During Storage

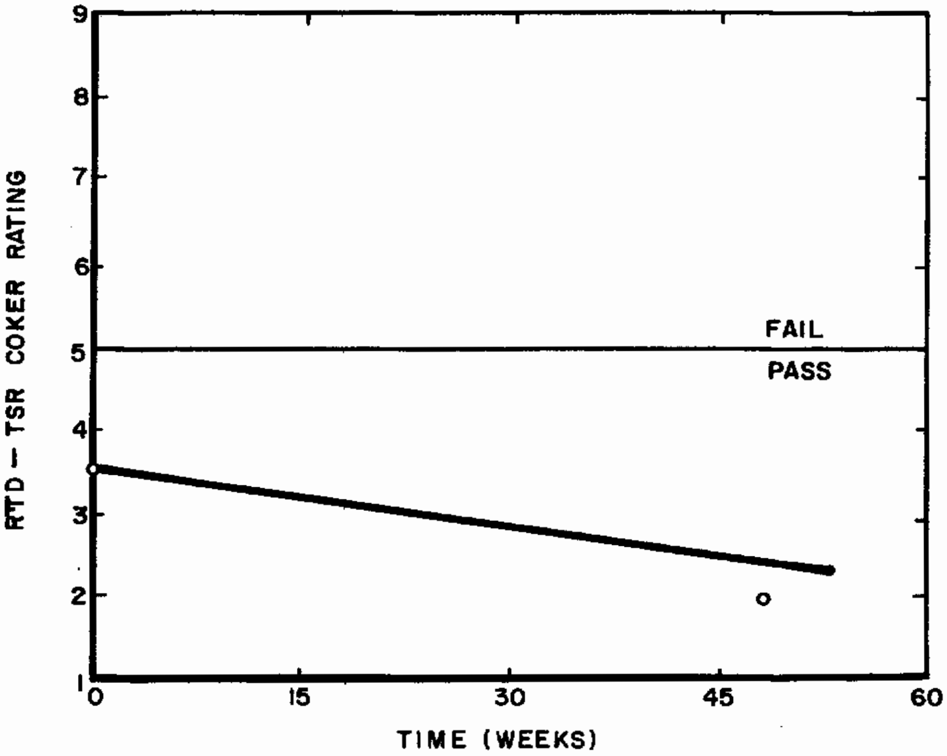

Figure I-14. Thermal Stability of SF6-6215 Fuel During Storage

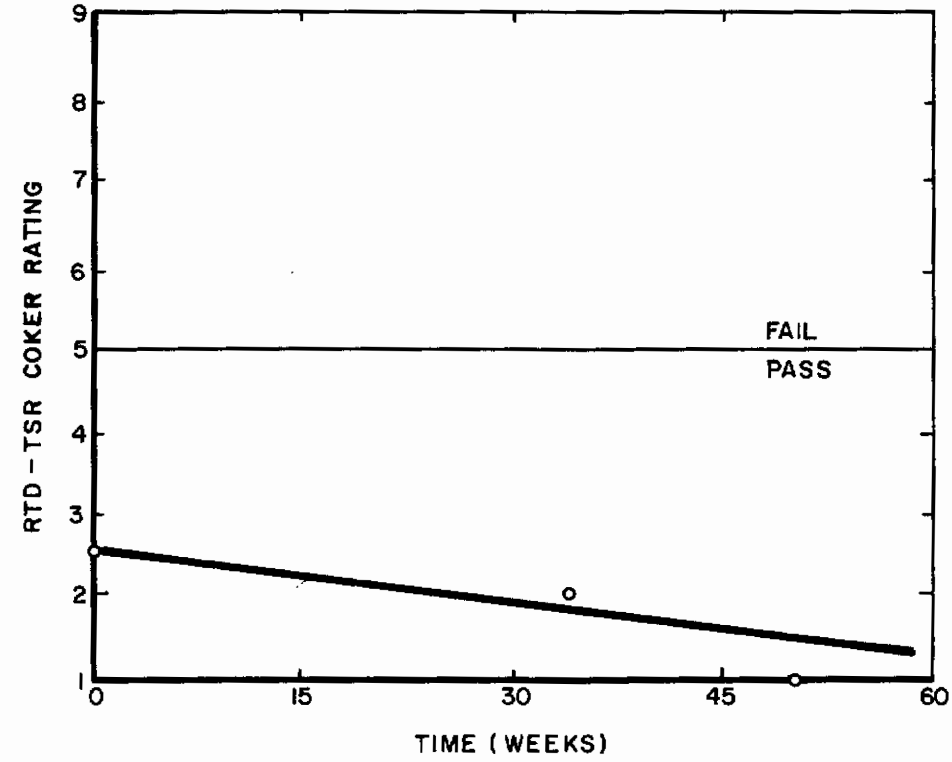

Figure I-15. Thermal Stability of SF6-6217C Fuel During Storage

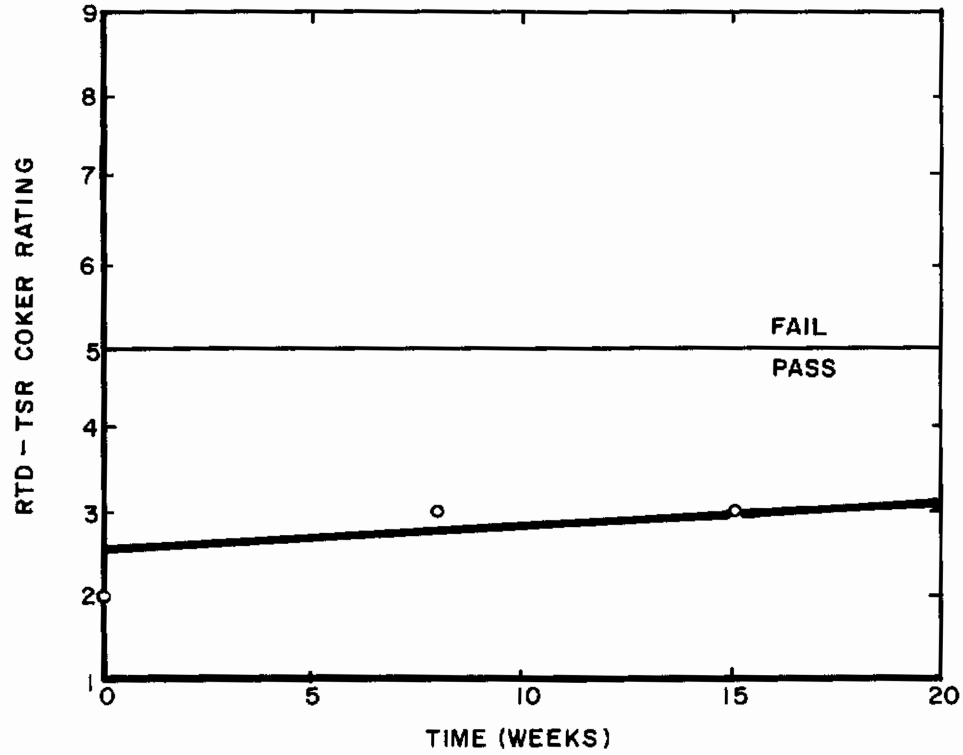

Figure I-16. Thermal Stability of SF6-6218C Fuel During Storage

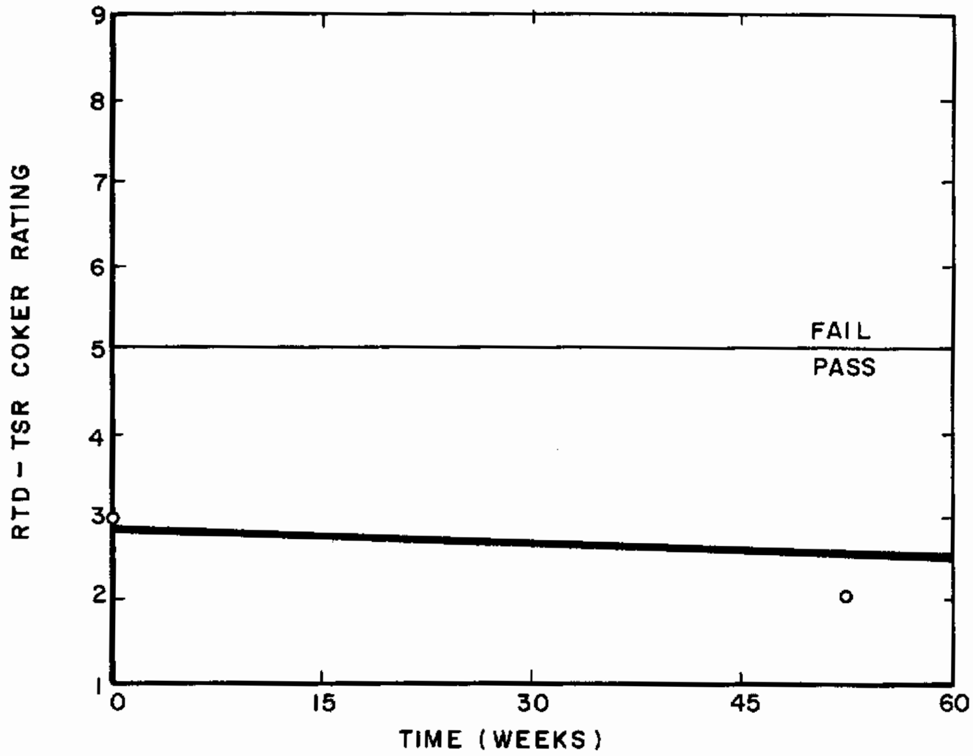

Figure I-17. Thermal Stability of SF6-6219 Fuel During Storage

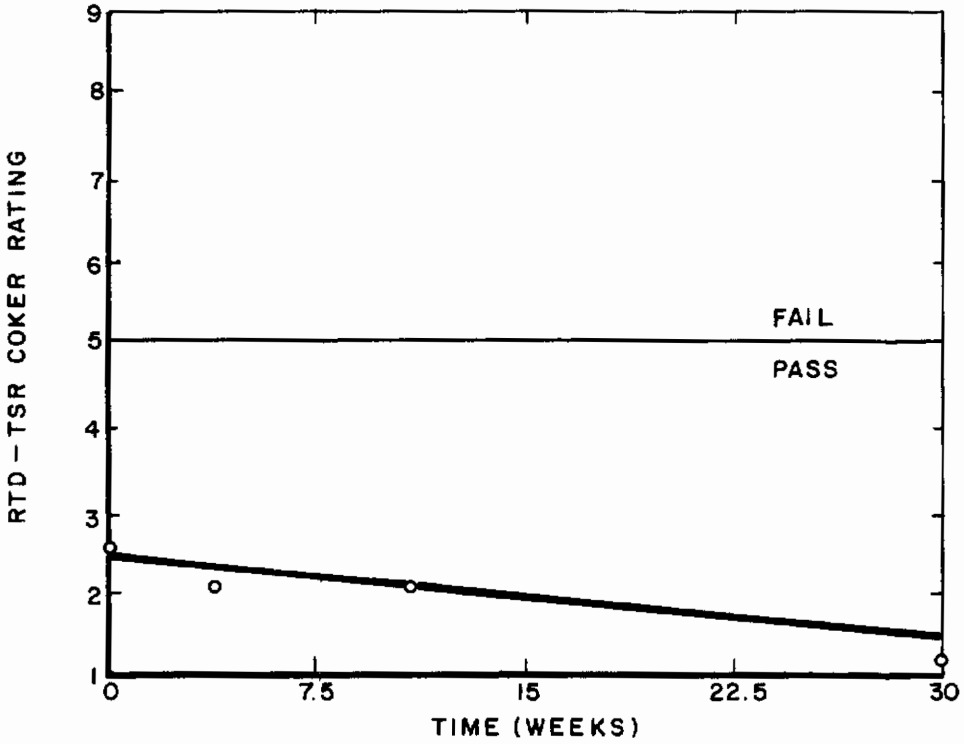

Figure I-18. Thermal Stability of SF6-6303C Fuel During Storage

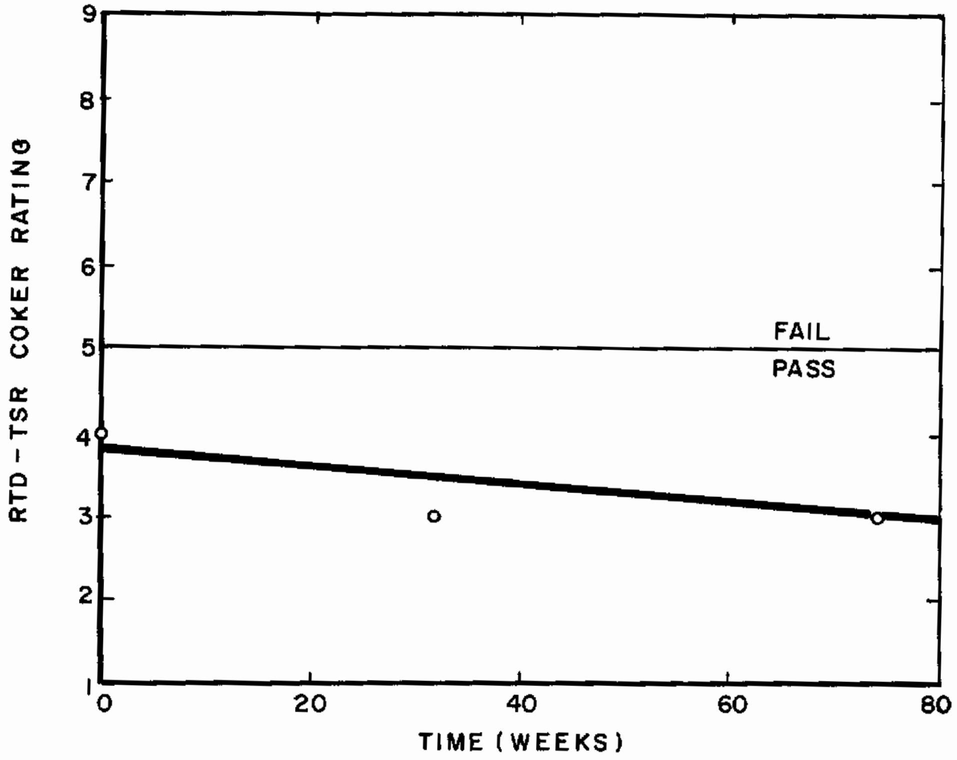

Figure I-19. Thermal Stability of TSF-6201D Fuel During Storage

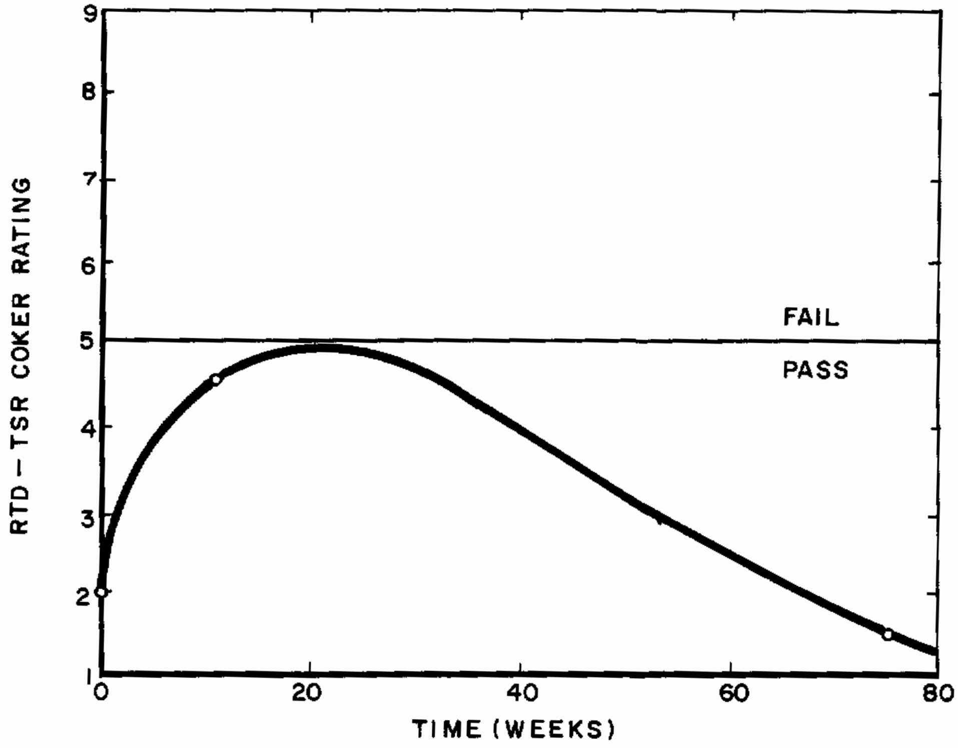

Figure I- 20. Thermal Stability of TSF-6203E Fuel During Storage

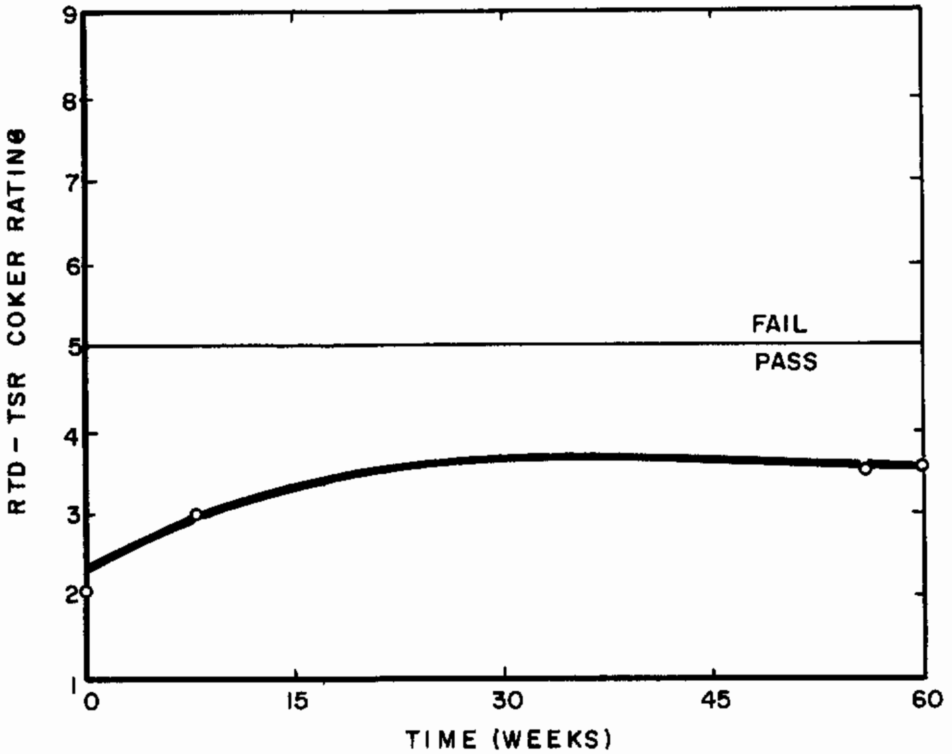

Figure I-21. Thermal Stability of TSF-6204E Fuel During Storage

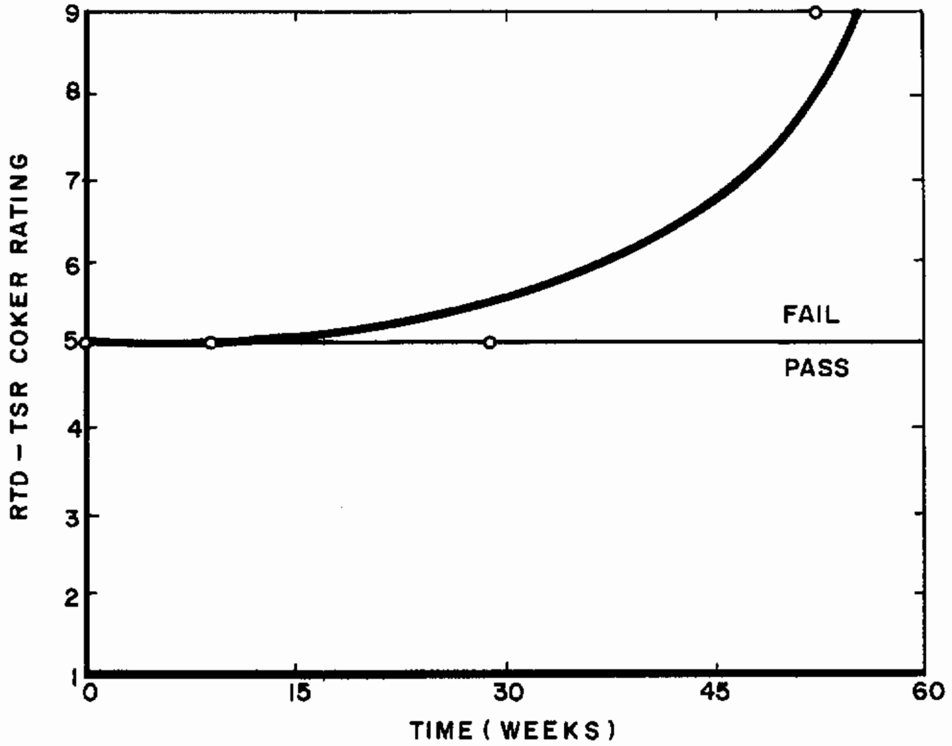

Figure I-22. Thermal Stability of TSF-6206F Fuel During Storage

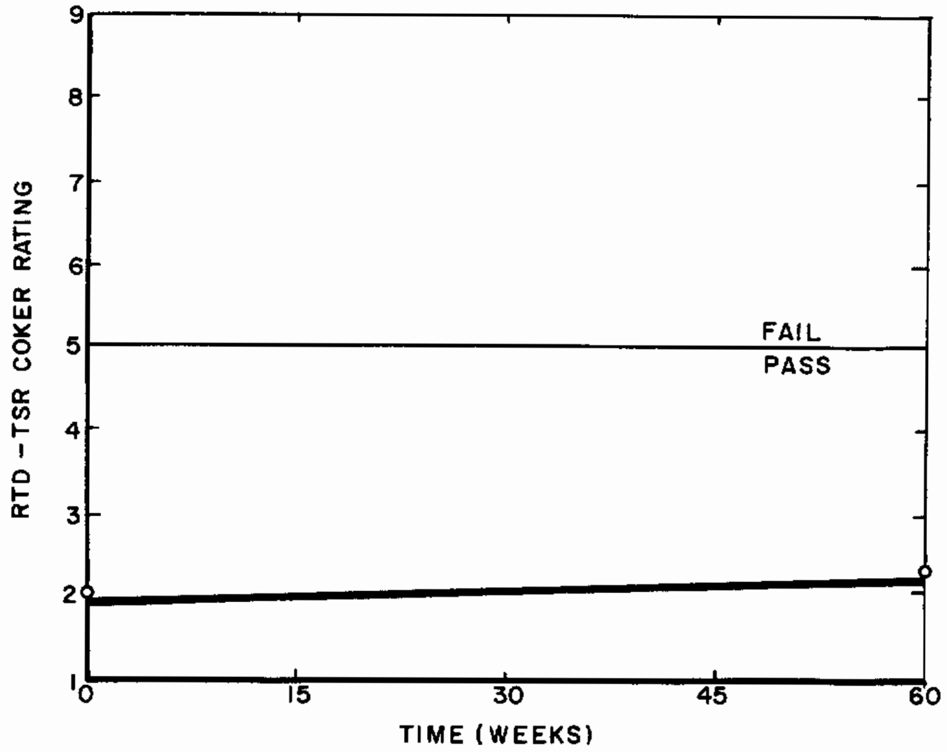

Figure I-23. Thermal Stability of TSF-6208D Fuel During Storage

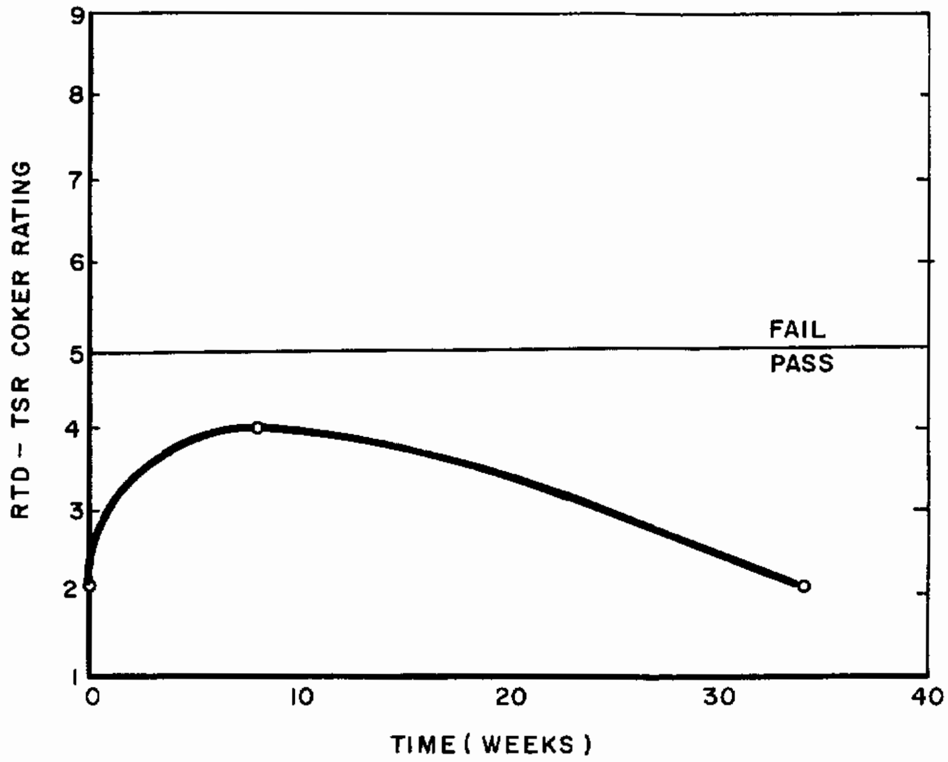

Figure I-24. Thermal Stability of TSF-6305E Fuel During Storage

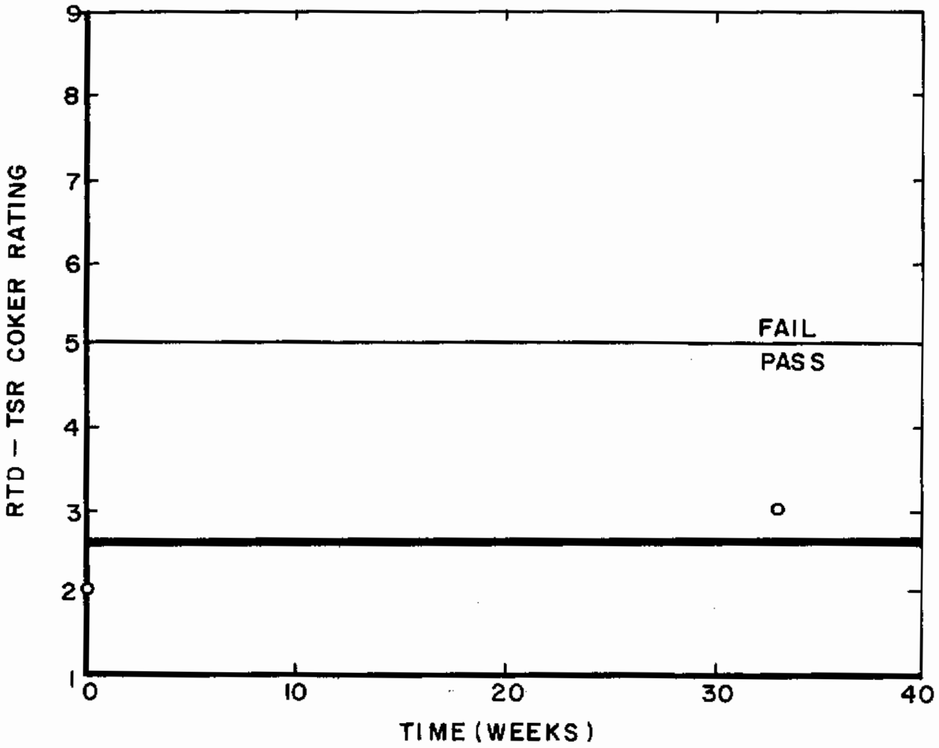

Figure I-25. Thermal Stability of TSF-6306D Fuel During Storage

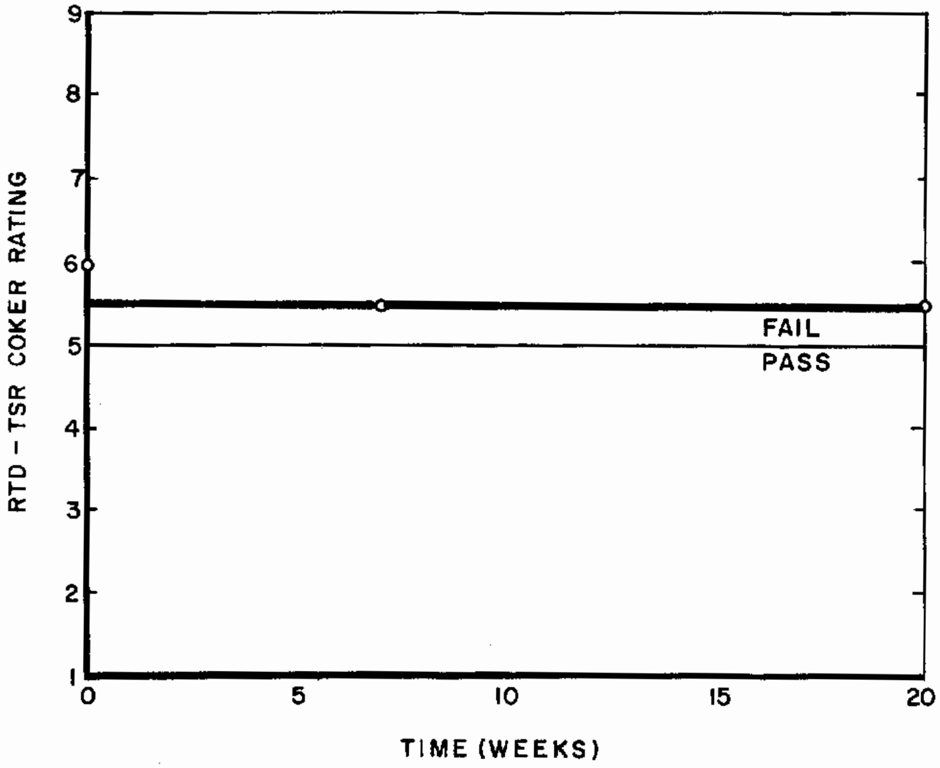

Figure I-26. Thermal Stability of TSF-6307G Fuel During Storage

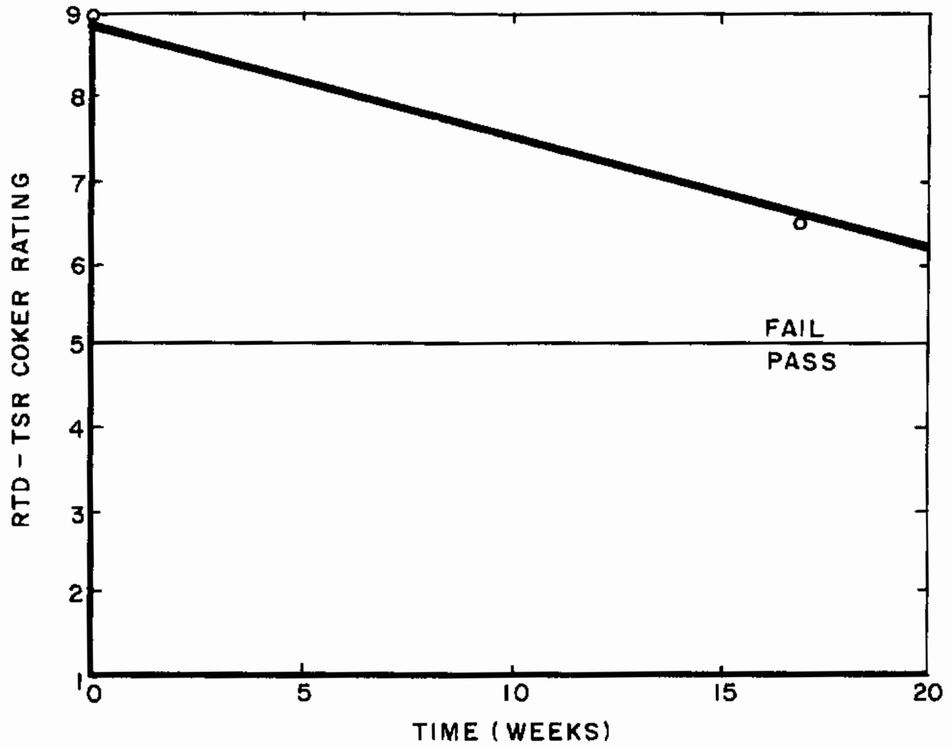

Figure I-27. Thermal Stability of TSF-6312H Fuel During Storage

APPENDIX II

THERMAL STABILITY RATINGS OF JP-6 FUELS DURING STORAGE

Note: A standard ASTM-CFR coker was used in all of the thermal stability tests. The equipment and operating procedures were in accordance with Method 3464 of Federal Test Method Standard No. 791 (ASTM Method D1660). No deviation from this method was allowed. The tests were continually operated for 5 hours at preheater and filter temperatures indicated and at a fuel flow of 6 pounds per hour.

FUEL SF6-6201

Date received at RTD: 7 June 1962 Supplier A

Date	Storage Time (Weeks)	Test Conditions (°F)	Test Results Pressure Differential in Inches of Hg (minutes)	Test Results Maximum Preheater Rating
14 May 62	–	425/525	6.9 (300)	1
7 Jun 62	4	425/525	9.1 (300)	2
20 Sep 62	18	425/525	25.0 (300)	2
21 Sep 62	18	425/525	25.0 (279)	2
25 Sep 62	19	425/525	25.0 (193)	2
26 Sep 62	19	425/525	24.3 (300)	2
16 Nov 62	26	425/525	25.0 (81)	4
19 Nov 62	26	400/500	25.0 (183)	3
20 Nov 62	26	375/475	25.0 (231)	2
17 Jan 63	36	425/525	5.7 (300)	2
17 Jan 63	36	425/525	25.0 (300)	2
25 Mar 63	46	425/525	14.6 (300)	2
1 Jul 63	60	425/525	17.5 (300)	4
1 Jul 63	60	400/500	0.2 (300)	1
25 Jul 63	63	400/500	0.7 (300)	1

FUEL SF6-6202

Date received at RTD: 8 June 1962 Supplier B

Date	Storage Time (Weeks)	Test Conditions (°F)	Pressure Differential in Inches of Hg (minutes)	Maximum Preheater Rating
27 Apr 62	–	425/525	0.3 (300)	1
11 Jan 62	6	425/525	12.9 (300)	3
27 Sep 62	22	425/525	12.0 (300)	3
27 Sep 62	22	425/525	25.0 (286)	3
2 Jul 63	61	425/525	25.0 (188)	4
2 Jul 63	61	400/500	25.0 (280)	3
22 Jul 63	64	375/475	8.8 (300)	1

FUEL SF6-6203

Date received at RTD: 22 June 1962 Supplier B

Date	Storage Time (Weeks)	Test Conditions (°F)	Test Results	
			Pressure Differential in Inches of Hg (minutes)	Maximum Preheater Rating
22 May 62	—	425/525	0.3 (300)	1
3 Jul 62	6	425/525	2.7 (300)	4
27 Sep 62	18	425/525	3.9 (300)	3
27 Sep 62	18	425/525	5.3 (300)	3
3 Jul 63	58	425/525	25.0 (234)	4
3 Jul 63	58	400/500	25.0 (249)	3
23 Jul 63	61	375/475	3.4 (300)	2

FUEL SF6-6204

Date received at RTD: 10 July 1962 Supplier C

3 Jul 62	—	425/525	0.0 (300)	1
5 Dec 62	22	425/525	0.0 (300)	3
7 Dec 62	22	400/500	0.0 (300)	2
8 Dec 62	27	425/525	0.0 (300)	4
14 Jan 63	28	400/500	0.0 (300)	4
5 Jul 63	52	400/500	0.0 (300)	1
5 Jul 63	52	425/525	0.0 (300)	2
1 Oct 63	tropic room since 31 Dec 62	425/525	0.0 (300)	4
2 Oct 63		425/525	0.0 (300)	4

FUEL SF6-6206

Date received at RTD: 10 July 1962 Supplier C

3 Jul 62	—	425/525	0.3 (300)	1
3 Dec 62	22	425/525	0.0 (300)	1
4 Dec 62	22	425/525	0.3 (300)	1
6 Dec 62	22	450/550	0.0 (300)	1
3 Oct 63	66	425/525	0.0 (300)	1
4 Oct 63	66	425/525	0.0 (300)	1

FUEL SF6-6207

Date received at RTD: 11 July 1962 Supplier A

22 Jun 62	—	425/525	0.1 (300)	0
11 Jul 62	2	425/525	0.8 (300)	2
8 Jul 63	54	425/525	25.0 (300)	1
8 Jul 63	54	400/500	1.7 (300)	3
23 Jul 63	56	375/475	1.7 (300)	2

FUEL SF6-6208

Date received at RTD: 25 July 1962 Supplier B

Date	Storage Time (Weeks)	Test Conditions (°F)	Test Results	
			Pressure Differential in Inches of Hg (minutes)	Maximum Preheater Rating
3 Jul 62	—	425/525	0.1 (300)	1
23 Aug 62	7	425/525	25.0 (300)	3
24 Aug 62	7	425/525	25.0 (160)	3
27 Aug 62	7	425/525	25.0 (200)	2
29 Aug 62	8	425/525	25.0 (191)	2
10 Sep 62	10	425/525	25.0 (163)	3
20 Sep 62	11	425/525	25.0 (241)	3
24 Sep 62	12	425/525	25.0 (173)	3
25 Sep 62	12	425/525	25.0 (193)	2
9 Jul 63	53	425/525	25.0 (178)	3
9 Jul 63	53	400/500	14.8 (300)	3
23 Jul 63	55	375/475	9.1 (300)	2

FUEL SF6-6209

Date received at RTD: 10 August 1962 Supplier A

12 Apr 62	—	425/525	2.75 (300)	1
28 Sep 62	24	425/525	25.0 (73)	—
28 Sep 62	24	425/525	25.0 (52)	—
10 Jul 63	65	425/525	25.0 (68)	2
10 Jul 63	65	400/500	25.0 (198)	4
24 Jul 63	67	375/475	6.2 (300)	2

FUEL SF6-6210

Date received at RTD: 5 September 1962 Supplier C

24 Aug 62	—	425/525	0.1 (300)	1
9 Nov 62	11	425/525	0.5 (300)	3
9 Nov 62	11	425/525	0.0 (300)	2
14 Nov 62	12	425/525	0.2 (300)	2
15 Nov 62	12	450/550	0.3 (300)	3
19 Nov 62	12	425/525	0.1 (300)	1
27 Nov 62	13	450/550	0.4 (300)	3
7 Oct 63	tropic room since 8 Jan 63	425/525	0.0 (300)	1
7 Oct 63		425/525	0.0 (300)	1
15 Oct 63	60	425/525	0.0 (300)	1
16 Oct 63	60	425/525	0.0 (300)	1

FUEL SF6-6211

Date received at RTD: 5 September 1962 Supplier C

Date	Storage Time (Weeks)	Test Conditions (°F)	Test Results	
			Pressure Differential in Inches of Hg (minutes)	Maximum Preheater Rating
24 Aug 62	–	425/525	0.2 (300)	1
5 Nov 62	10	425/525	0.3 (300)	2
6 Nov 62	10	450/550	1.6 (300)	3
7 Nov 63	11	425/525	2.5 (300)	2
21 Nov 63	13	450/550	10.2 (300)	3
19 Mar 63	29	425/525	0.0 (300)	1
7 Oct 63	tropic room since 8 Jan 63	425/525	0.0 (300)	1
8 Oct 63		425/525	0.0 (300)	1

FUEL SF6-6212

Date received at RTD: 5 September 1962 Supplier C

24 Aug 62	–	425/525	0,0 (300)	1
11 Oct 62	7	425/525	0.7 (300)	2
11 Oct 62	7	425/525	0.0 (300)	2
15 Oct 62	8	425/525	0.0 (300)	2
16 Oct 62	8	450/550	0.9 (300)	2
29 Oct 62	10	450/550	0.7 (300)	3
21 Mar 63	30	425/525	0.0 (300)	1
10 Oct 63	tropic room since 8 Jan 63	425/525	0.0 (300)	1
10 Oct 63		425/525	0.0 (300)	1

FUEL SF6-6213

Date received at RTD: 13 September 1962 Supplier A

22 Aug 62	–	425/525	0.3 (300)	1
1 Oct 62	6	425/525	25.0 (217)	3
1 Oct 62	6	425/525	15.1 (300)	2
5 Oct 62	6	425/525	13.2 (300)	3
5 Oct 62	6	425/525	17.9 (300)	3
11 Jul 63	46	425/525	14.2 (300)	2
11 Jul 63	46	400/500	6.7 (300)	1
24 Jul 63	48	400/500	1.1 (300)	1

FUEL SF6-6214

Date received at RTD: 10 October 1962 Supplier A

Date	Storage Time (Weeks)	Test Conditions (°F)	Test Results: Pressure Differential in Inches of Hg (minutes)	Test Results: Maximum Preheater Rating
28 Sep 62	–	425/525	0.0 (300)	0
26 Oct 62	4	425/525	25.0 (253)	4
29 Oct 62	4	400/500	0.2 (300)	2
29 Oct 62	4	375/475	0.8 (300)	1
30 Oct 62	4	425/525	2.7 (300)	4
12 Jul 63	42	425/525	0.4 (300)	1
12 Jul 63	42	400/500	0.5 (300)	1
17 Sep 63	51	450/550	25.0 (277)	4

FUEL SF6-6215

Date received at RTD: 19 November 1962 Supplier: 50% - A, 50% - C
(SF6-6201 (SF6-6212)

20 Nov 62	–	425/525	0.0 (300)	3
21 Nov 62	–	425/525	0.5 (300)	3
28 Nov 62	1	425/525	0.2 (300)	1
29 Nov 62	1	450/550	25.0 (300)	3
17 Dec 62	4	450/550	0.6 (300)	4
8 Oct 63	tropic room since 8 Jan 63	425/525	0.0 (300)	0
8 Oct 63		425/525	0.0 (300)	0
18 Oct 63	48	425/525	0.0 (300)	1
18 Oct 63	48	425/525	0.0 (300)	1

FUEL SF6-6217

Date received at RTD: 20 November 1962 Supplier C

25 Oct 62	–	425/525	0.0 (300)	1
27 Oct 62	–	400/500	0.3 (300)	1
28 Oct 62	–	425/525	0.4 (300)	1
29 Oct 62	–	450/550	0.2 (300)	2
29 Oct 62	–	475/575	0.2 (300)	3
24 Jun 63	34	450/550	0.1 (300)	1
24 Jun 63	34	425/525	0.0 (300)	1
25 Jun 63	34	450/550	0.1 (300)	4
11 Oct 63	tropic room since 8 Jan 63	425/525	0.0 (300)	0
11 Oct 63		425/525	0.0 (300)	0

FUEL SF6-6218

Date received at RTD: 20 November 1962 Supplier C

Date	Storage Time (Weeks)	Test Conditions (°F)	Test Results	
			Pressure Differential in Inches of Hg (minutes)	Maximum Preheater Rating
30 Oct 62	—	425/525	0.1 (300)	1
1 Nov 62	—	400/500	0.0 (300)	1
2 Nov 62	—	450/550	0.3 (300)	2
6 Nov 62	—	475/575	0.2 (300)	3
2 Jan 63	8	425/525	0.2 (300)	2
3 Jan 63	8	425/525	0.2 (300)	2
21 Jan 63	11	450/550	0.2 (300)	2
18 Feb 63	15	450/550	0.2 (300)	4
20 Feb 63	15	425/525	0.0 (300)	2
20 Feb 63	15	450/550	0.0 (300)	4
21 Feb 63	15	450/550	0.3 (300)	3
13 Mar 63	18	450/550	0.1 (300)	2

FUEL SF6-6219

Date received at RTD: 14 December 1962 Supplier: 70% - A, 30% - C
(SF6-6201) (SF6-6206)

17 Dec 62	—	425/525	0.04 (300)	2
17 Dec 62	—	425/525	0.0 (300)	2
18 Dec 62	—	450/550	0.1 (300)	2
18 Dec 62	—	425/525	0.1 (300)	1
19 Dec 62	—	450/550	0.57 (300)	4
9 Oct 63	tropic room since 8 Jan 63	425/525	0.0 (300)	1
9 Oct 63		425/525	0.0 (300)	1
17 Oct 63	53	425/525	0.3 (300)	1
17 Oct 63	53	425/525	0.0 (300)	2

FUEL SF6-6303

Date received at RTD: 2 April 1963 Supplier C

3 Apr 63	—	400/500	0.0 (300)	2
3 Apr 63	—	425/525	0.1 (300)	1
3 Apr 63	—	450/550	0.1 (300)	3
5 Apr 63	—	450/550	0.0 (300)	3
12 Apr 63	1	425/525	0.0 (300)	2
12 Apr 63	1	450/550	0.2 (300)	3
22 Apr 63	3	425/525	0.0 (300)	1
22 Apr 63	3	425/525	0.0 (300)	3
29 Apr 63	4	450/550	0.0 (300)	3
30 Apr 63	4	425/525	0.0 (300)	1
16 Jul 63	11	425/525	0.1 (300)	1
16 Jul 63	11	450/550	0.0 (300)	4
12 Nov 63	29	425/525	0.0 (300)	0
12 Nov 63	29	425/525	0.0 (300)	0

APPENDIX III

THERMAL STABILITY RATINGS OF THERMALLY STABLE FUELS DURING STORAGE

Note: A standard ASTM-CFR coker was used in all of the thermal stability tests. The equipment and operating procedures were in accordance with Method 3464 of Federal Test Method Standard No.791 (ASTM Method D1660). No deviation from this method was allowed. The tests were continually operated for 5 hours at preheater and filter temperatures indicated and a fuel flow of 6 pounds per hour.

FUEL TSF-6201

Date received at RTD: 1 June 1962 Supplier D

Date	Storage Time (Weeks)	Test Conditions (°F)	Test Results	
			Pressure Differential in Inches of Hg (minutes)	Maximum Preheater Rating
18 May 62	—	400/500	4.8 (300)	1
8 Jun 62	3	400/500	1.7 (300)	2
27 Dec 62	32	400/500	0.1 (300)	2
24 Oct 63	75	400/500	0.7 (300)	0
25 Oct 63	75	400/500	1.2 (300)	1

FUEL TSF-6203

Date received at RTD: 14 June 1962 Supplier E

19 Apr 62	—	400/500	0.1 (300)	1
25 Jun 62	9	400/500	0.9 (300)	4
12 Jul 62	11	400/500	0.0 (300)	3
19 Jul 62	12	400/500	0.5 (300)	2
28 Oct 63	78	400/500	0.3 (300)	0
29 Oct 63	78	400/500	0.2 (300)	1

FUEL TSF-6204

Date received at RTD: 14 June 1962 Supplier E

27 Apr 62	—	400/500	0.2 (300)	1
26 Jun 62	8	400/500	0.0 (300)	2
20 May 63	56	400/500	2.4 (300)	1
20 May 63	56	425/525	25.0 (297)	4
27 May 63	57	400/500	0.7 (300)	1
27 May 63	57	425/525	0.2 (300)	2
5 Jun 63	58	425/525	5.5 (300)	3
18 Jun 63	60	400/500	0.3 (300)	0
18 Jun 63	60	400/500	1.5 (300)	3

FUEL TSF-6206

Date received at RTD: 12 July 1962 Supplier F

Date	Storage Time (Weeks)	Test Conditions (°F)	Test Results	
			Pressure Differential in Inches of Hg (minutes)	Maximum Preheater Rating
12 Jul 62	—	400/500	0.0 (300)	4
13 Jul 62	—	350/450	0.0 (300)	2
21 Aug 62	6	400/500	0.7 (300)	3
17 Sep 62	9	400/500	0.2 (300)	3
30 Jan 63	29	400/500	0.9 (300)	3
30 Jan 63	29	400/500	0.6 (300)	3
12 Feb 63	31	400/500	0.4 (300)	3
12 Feb 63	31	400/500	0.5 (300)	4
15 Feb 63	31	400/500	0.1 (300)	4
25 Feb 63	32	400/500	0.1 (300)	2
15 Jul 63	52	400/500	25.0 (181)	4
15 Jul 63	52	425/525	25.0 (191)	4
24 Jul 63	53	375/475	25.0 (200)	1

FUEL TSF-6208

Date received at RTD: 21 August 1962 Supplier D

13 Jul 62	—	400/500	0.8 (300)	0
27 Nov 62	20	425/525	0.2 (300)	2
28 Nov 62	20	450/550	0.3 (300)	3
29 Jan 63	28	450/550	0.4 (300)	2
29 Jan 63	28	450/550	0.3 (300)	2
30 Oct 63	68	400/550	0.1 (300)	1
31 Oct 63	68	400/500	0.1 (300)	2

FUEL TSF-6305

Date received at RTD: 29 March 1963 Supplier E

27 Feb 63	—	400/500	0.0 (300)	1
28 Feb 63	—	425/525	0.0 (300)	1
2 Mar 63	—	450/550	0.0 (300)	1
3 Mar 63	—	475/575	0.0 (300)	1
25 Apr 63	8	400/500	0.5 (300)	2
24 Apr 63	8	425/525	3.6 (300)	1
24 Apr 63	8	450/550	2.6 (300)	2
29 Apr 63	8	450/550	0.8 (300)	2
28 Jun 63	16	450/550	0.9 (300)	2
1 Nov 63	34	400/500	0.4 (300)	0
4 Nov 63	34	400/500	0.5 (300)	1

FUEL TSF-6306

Date received at RTD: 4 April 1963 Supplier D

Date	Storage Time (Weeks)	Test Conditions (°F)	Test Results	
			Pressure Differential in Inches of Hg (minutes)	Maximum Preheater Rating
11 Mar 63	—	400/500	0.7 (300)	0
13 May 63	8	425/525	0.5 (300)	1
13 May 63	8	450/550	0.2 (300)	1
17 Jul 63	17	450/550	3.4 (300)	1
5 Nov 63	33	400/500	1.9 (300)	1
6 Nov 63	33	400/500	0.2 (300)	1

FUEL TSF-6307

Date received at RTD: 4 June 1963 Supplier G

10 Jun 63	—	425/525	17.4 (300)	2
10 Jun 63	—	450/550	3.2 (300)	3
17 Jun 63	1	400/500	3.3 (300)	4
17 Jun 63	1	400/500	7.7 (300)	4
21 Jun 63	2	400/500	3.9 (300)	2
21 Jun 63	2	400/500	2.2 (300)	3
5 Aug 63	7	400/500	3.9 (300)	2
5 Aug 63	7	400/500	18.1 (300)	2
7 Nov 63	20	400/500	7.4 (300)	3
8 Nov 63	20	400/500	10.0 (300)	1

FUEL TSF-6312

Date received at RTD: 26 June 1963 Supplier H

18 Jul 63	—	400/500	25.0 (260)	4
18 Jul 63	—	400/500	25.0 (235)	4
22 Jul 63	—	375/475	23.6 (300)	1
25 Jul 63	—	375/475	11.6 (300)	1
14 Nov 63	17	400/500	25.0 (291)	2
15 Nov 63	17	400/500	23.0 (300)	1

APPENDIX IV

RECLAMATION OF DEGRADED JET FUELS

The Ashland Oil and Refining Co., Inc., had developed, independently and upon its own initiative, a process for rehabilitating fuels that had degraded in storage. This process had demonstrated over the last 5 years its ability to rehabilitate fuels that had degraded in transit or storage. In an effort to determine whether such a process could be applied to its serious storage problem, the Air Force contracted Ashland to evaluate its process on several Air Force degraded storage fuels. This effort was performed under Air Force Contract AF 33(657)-11097. The results of the entire program are reported in APL TDR 64-74, "Reclamation of JP-6 Type Jet Fuels Which Became Thermally Unstable During Storage."

Ten of the JP-6 type fuels that had degraded in the present program were supplied to Ashland for treatment in their process. The thermal stability break points of the degraded fuels are shown in Table IV-1. Ashland checked the degraded fuels on the standard ASTM-CFR Fuel Coker at 450/550°F test conditions and then processed the fuels in the reclamation unit; after being processed, these fuels were again run on the standard coker at 450/550°F test conditions. The fuels were then stored for 6 months at ambient conditions after which the thermal stability determinations at 450/550°F were repeated. This information is tabulated in Table IV-2. The degraded fuels were rehabilitated to passing the standard coker preheater at 450°F fuel out temperature. This higher level of thermal stability was retained in the additional 6 months of ambient storage. Storage tests are continuing of the reclaimed fuels to determine their life. These tests are being completed in-house by the Air Force at Wright-Patterson Air Force Base.

Analytical tests were run on the reclaimed fuels before and after treatment. A list of these tests and procedures are tabulated in Table IV-3. The results of these tests on the before and after treatment fuels are listed in Tables IV-4 through IV-13.

TABLE IV-1

THERMAL STABILITY BREAK POINTS ON THE DEGRADED AIR FORCE FUELS AS DETERMINED BY THE ASTM-CFR STANDARD FUEL COKER

Fuel	1963 Date	Test Conditions (°F)	Pressure Differential in Inches of Hg (minutes)	Total Preheater Ratings (13 stations)												
				1	2	3	4	5	6	7	8	9	10	11	12	13
SF6-6201A	1 Jul	400/500	0.2 (300)	1	1	1	1	1	1	1	1	1	1	1	1	1
	25 Jul	400/500	0.7 (300)	1	1	1	1	1	1	1	1	1	1	1	1	1
	1 Jul	425/525	17.5 (300)	1	1	1	1	1	1	1	1	1	1	1	4	3
SF6-6202B	22 Jul	375/475	8.8 (300)	1	1	1	1	1	1	1	1	1	1	1	1	1
	2 Jul	400/500	25.0 (280)	2	2	2	2	2	2	2	2	2	2	3	3	3
	2 Jul	425/525	25.0 (188)	1	1	1	1	1	1	1	1	1	2	4	3	3
SF6-6203B	23 Jul	375/475	3.4 (300)	1	1	1	1	1	1	2	2	1	1	1	1	1
	3 Jul	400/500	25.0 (249)	3	3	3	3	3	3	3	3	1	1	3	3	3
	3 Jul	425/525	25.0 (234)	1	1	2	3	3	3	1	1	1	1	3	4	3
TSF-6206F	24 Jul	375/475	25.0 (300)	1	1	1	1	1	1	1	1	1	1	1	1	1
	15 Jul	400/500	25.0 (128)	0	0	0	0	0	0	1	1	3	4	4	4	1
	15 Jul	425/525	25.0 (191)	1	1	1	1	1	1	1	1	1	4	4	4	3
SF6-6207A	23 Jul	375/475	1.7 (300)	1	1	1	1	1	1	1	1	2	2	2	2	2
	8 Jul	400/500	1.7 (300)	1	1	1	1	1	1	1	1	1	1	3	2	2
	8 Jul	425/525	25.0 (300)	1	1	1	1	1	1	1	1	1	1	1	1	1
SF6-6208B	23 Jul	375/475	9.1 (300)	1	1	1	1	1	1	1	2	2	2	2	2	1
	9 Jul	400/500	14.8 (300)	2	2	2	2	2	2	2	2	2	2	3	3	2
	9 Jul	425/525	25.0 (178)	1	1	1	1	1	3	3	2	1	1	1	1	1
SF6-6209A	24 Jul	375/475	6.2 (300)	1	1	1	1	1	1	1	1	1	1	1	1	2
	10 Jul	400/500	25.0 (198)	1	1	1	1	1	1	1	2	2	4	3	3	2
	10 Jul	425/525	25.0 (68)	1	1	1	1	1	1	1	1	1	1	2	2	1
SF6-6213A	11 Jul	400/500	6.7 (300)	1	1	1	1	1	1	1	1	1	1	1	1	1
	24 Jul	400/500	1.1 (300)	1	1	1	1	1	1	1	1	1	1	1	1	1
	11 Jul	400/500	14.2 (300)	1	1	1	1	1	1	1	1	1	1	1	2	2
SF6-6214A	12 Jul	400/500	0.5 (300)	1	1	1	1	1	1	1	1	1	1	1	1	1
	12 Jul	425/525	0.4 (300)	1	1	1	1	1	1	1	1	1	1	1	1	1
	17 Sep	450/550	25.0 (277)	1	1	1	1	1	1	1	1	1	4	4	4	4
TSF-6312H	22 Jul	375/475	23.6 (300)	1	1	1	1	1	1	1	1	1	1	1	1	1
	25 Jul	375/475	11.6 (300)	1	1	1	1	1	1	1	1	1	1	1	1	1
	18 Jul	400/500	25.0 (260)	1	1	1	1	1	1	1	1	1	2	4	4	1
	18 Jul	400/500	25.0 (235)	1	1	1	1	1	1	1	1	2	4	4	4	2

TABLE IV-2

THERMAL STABILITY PREHEATER RATINGS ON ASHLAND RECLAIMED FUELS

Fuel	Total Preheater Ratings		
	Before Treatment	After Treatment	Treated and 6 Months Storage
SF6-6201A	1111234444444	1111111111111	1111111111111
SF6-6202B	1111111113334	1111111111111	1111111112221
SF6-6203B	1112223444444	1111111111111	1111111111111
TSF-6206F	1111114444443	1111111111111	1111111111111
SF6-6207A	1111111144444	1111111111111	1111111111111
SF6-6208B	1111111133332	1111111111111	1111111111111
SF6-6209A	1111111111444	1111111111111	1111111111111
SF6-6213A	1111111444444	1111111111111	1111111111111
SF6-6214A	1111111134444	1111111111111	1111111111111
TSF-6312H	1112344444444	1111111111222	1111111111111

NOTE: Fuels were analyzed on the ASTM-CFR Fuel Coker at 450/500°F test conditions.

TABLE IV-3

ANALYTICAL PROCEDURES AND METHODS ON THE RECLAIMED FUELS

Test	Procedure Reference
Aromatics (vol %)	ASTM D1319
Olefins (vol %)	ASTM D1319
Pyrrole nitrogen (ppm)	Analytical Chemistry, 30 p 259, 1958
Basic nitrogen (ppm)	Phillips Method 142-57R
Polycyclic aromatics (wt %)	ASTM D1840
Bromine number	ASTM D1159-61
Copper (ppb)	Air Force Method, see Appendix IX
Iron (ppb)	Air Force Method, see Appendix VII
Phenols (ppm)	Universal Oil Products Method 262-59
Indenes (ppm)	Air Force Method, see Appendix VIII

ppm = parts per million
ppb = parts per billion

TABLE IV-4

EFFECT OF RECLAMATION ON TOTAL AROMATIC CONTENT USING ASTM D1319 METHOD

Fuel	Volume (percent)	
	Before Treatment	After Treatment
SF6-6201A	12.3	9.5
SF6-6202B	12.5	8.2
SF6-6203B	13.2	10.5
TSF-6206F	15.4	11.7
SF6-6207A	11.7	9.4
SF6-6208B	14.5	12.1
SF6-6209A	12.9	11.6
SF6-6213A	12.5	11.1
SF6-6214A	12.3	11.4
TSF-6312H	15.1	12.8

TABLE IV-5

EFFECT OF RECLAMATION ON TOTAL OLEFIN CONTENT USING ASTM D1319 METHOD

Fuel	Volume (percent)	
	Before Treatment	After Treatment
SF6-6201A	0.5	0.9
SF6-6202B	0.5	3.1
SF6-6203B	0.2	1.2
TSF-6206F	0.6	0.6
SF6-6207A	0.7	0.8
SF6-6208B	0.5	0.5
SF6-6209A	0.5	0.6
SF6-6213A	0.8	0.7
SF6-6214A	0.6	0.9
TSF-6312H	0.5	0.8

TABLE IV-6

EFFECT OF RECLAMATION ON PYRROLE NITROGEN CONTENT USING PROCEDURE IN ANALYTICAL CHEMISTRY, 30, p 259, 1958

Fuel	Parts per Million	
	Before Treatment	After Treatment
SF6-6201A	0.3	0.1
SF6-6202B	0.2	0.1
SF6-6203B	0.2	0.2
TSF-6206F	0.5	0.1
SF6-6207A	0.3	0.1
SF6-6208B	0.2	0.1
SF6-6209A	0.2	0.1
SF6-6213A	0.3	0.1
SF6-6214A	0.3	0.1
TSF-6312H	0.2	0.1

TABLE IV-7

EFFECT OF RECLAMATION ON BASIC NITROGEN CONTENT USING PHILLIPS METHOD 142-57R

Fuel	Parts per Million	
	Before Treatment	After Treatment
SF6-6201A	2.1	1.4
SF6-6202B	0.7	1.4
SF6-6203B	1.1	1.3
TSF-6206F	5.0	1.5
SF-6207A	1.6	1.3
SF6-6208B	1.1	1.4
SF6-6209A	1.7	1.3
SF6-6213A	1.9	1.3
SF6-6214A	2.1	1.4
TSF-6312H	0.5	1.7

TABLE IV-8

EFFECT OF RECLAMATION ON POLYCYCLIC AROMATIC CONTENT USING ASTM D1840 METHOD

Fuel	Weight (percent)	
	Before Treatment	After Treatment
SF6-6201A	0.25	0.19
SF6-6202B	0.07	0.07
SF6-6203B	0.14	0.07
TSF-6206F	0.23	0.74
SF6-6207A	0.19	0.19
SF6-6208B	0.12	0.04
SF6-6209A	0.39	0.30
SF6-6313A	0.42	0.36
SF6-6214A	0.29	0.30
TSF-6312H	0.81	0.79

TABLE IV-9

EFFECT OF RECLAMATION ON BROMINE NUMBER USING ASTM D1159-61 METHOD

Fuel	Before Treatment	After Treatment
SF6-6201A	0.99	0.64
SF6-6202B	0.31	0.32
SF6-6203B	0.28	0.32
TSF-6206F	0.39	0.54
SF6-6207A	0.68	0.64
SF6-6208B	0.29	0.32
SF6-6209A	0.67	0.64
SF6-6213A	0.80	0.77
SF6-6214A	1.06	1.01
TSF-6312H	0.70	0.68

TABLE IV-10

EFFECT OF RECLAMATION ON COPPER CONTENTS USING AIR FORCE METHOD (APPENDIX IX)

Fuel	Parts per Billion	
	Before Treatment	After Treatment
SF6-6201A	35	3
SF6-6202B	33	1
SF6-6203B	26	2
TSF-6206F	10	2
SF6-6207A	137	2
SF6-6208B	15	0
SF6-6209A	146	2
SF6-6213A	49	4
SF6-6214A	48	1
TSF-6312H	13	1

TABLE IV-11

EFFECT OF RECLAMATION ON IRON CONTENTS USING AIR FORCE METHOD (APPENDIX VII)

Fuel	Parts per Billion	
	Before Treatment	After Treatment
SF6-6201A	28	23
SF6-6202B	17	20
SF6-6203B	18	13
TSF-6206F	—	10
SF6-6207A	56	15
SF6-6208B	178	10
SF6-6209A	128	15
SF6-6213A	262	12
SF6-6214A	90	14
TSF-6312H	59	12

TABLE IV-12

EFFECT OF RECLAMATION ON PHENOL CONTENT USING
UNIVERSAL OIL PRODUCTS METHOD 262-59

Fuel	Parts per Million	
	Before Treatment	After Treatment
SF6-6201A	135	10
SF6-6202B	26	10
SF6-6203B	27	10
TSF-6206F	—	10
SF6-6207A	209	10
SF6-6208B	44	10
SF6-6209A	215	10
SF6-6213A	206	10
SF6-6214A	185	10
TSF-6312H	188	10

TABLE IV-13

EFFECT OF RECLAMATION ON INDENE CONTENT USING
AIR FORCE METHOD (APPENDIX VIII)

Fuel	Parts per Million	
	Before Treatment	After Treatment
SF6-6201A	135	1.7
SF6-6202B	26	8.9
SF6-6203B	227	3.4
TSF-6206F*	—	0.5
SF6-6207A	209	0.5
SF6-6208B	44	9.4
SF6-6209A	215	2.8
SF6-6213A	206	2.0
SF6-6214A	184	0.5
TSF-6312H	188	10

APPENDIX V

SELECTED PROPERTIES OF JP-6 FUELS

DIELECTRIC CONSTANT*

Fuel	Temperature (°F)	Dielectric Constant at Various Frequencies				
		100 cycles/sec.	400 cycles/sec.	1 kilocycle/sec.	10 kilocycles/sec.	100 kilocycles/sec.
SF6-6201	68			2.078	2.075	
	100			2.054	2.052	
	150			2.020	2.018	
	200			1.984	1.983	
SF6-6202	68			2.080	2.079	
	100			2.056	2.054	
	150	2.024		2.022	2.019	
	200			1.984	1.982	
SF6-6203	68			2.074	2.072	
	100			2.051	2.048	
	150			2.016	2.013	
	200			1.980	1.979	
SF6-6204	68		2.091	2.091	2.088	
	100		2.072	2.072	2.069	2.076
	150		2.034	2.034	2.031	2.039
	200		1.997	1.995	1.993	2.001
SF6-6206	68			2.091	2.089	
	100			2.070	2.069	
	150			2.034	2.031	
	200			1.996	1.994	
SF6-6208	68			2.083	2.082	
	100			2.060	2.057	
	150			2.025	2.023	
	200			1.986	1.984	
SF6-6210	68			2.091	2.089	
	100			2.066	2.064	
	150			2.031	2.029	
	200			1.993	1.991	
SF6-6211	68			2.090	2.088	
	100			2.068	2.066	
	150			2.033	2.031	
	200			1.996	1.993	
SF6-6212	68			2.083	2.081	
	100			2.059	2.057	
	150			2.026	2.024	
	200			1.990	1.998	

*Determined by Monsanto Research Corp. under Contract No. AF33(657)-8193.

Fuel	Temperature (°F)	Dielectric Constant at Various Frequencies				
		100 cycles/sec.	400 cycles/sec.	1 kilocycle/sec.	10 kilocycles/sec.	100 kilocycles/sec.
SF6-6215	68			2.086	2.084	
	100			2.064	2.063	
	150			2.027	2.024	
	200			1.990	1.987	
SF6-6219	68			2.081	2.079	
	150			2.023	2.020	
TSF-6203	68			2.096	2.094	
	100	2.076		2.073	2.072	2.076
	150			2.040	2.038	
	200			2.003	2.001	
TSF-6204	68			2.086	2.084	
	100			2.061	2.059	
	150			2.026	2.024	
	200			1.991	1.989	
TSF-6205	68			2.091	2.088	
	100			2.069	2.068	
	150			2.035	2.033	
	200			1.998	1.997	
TSF-6208	68			2.051	2.049	
	100			2.028	2.027	
	150			1.999	1.997	
	200			1.962	1.960	

DISSIPATION FACTOR*

The dissipation factors of the SF6 and TSF fuels were calculated by the equations given below. The equations were taken from the operating instructions for the Balsbaugh cells and from a journal article by L. J. Berberich, Analytical Chemistry 17, 582 (1945). The symbols in the two references are not alike so a completely different set of symbols was used in the equation found below.

The calculated dissipation factors are fractional units and not percents as is sometimes used.

The dissipation factor of the leads, D_L, is required and is given by the following equation to calculate the dissipation factor of the sample:

$$D_L = \left(\frac{C_a}{C_L} + 1\right) D_{T_a} \qquad \text{(V-1)}$$

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*Determined by Monsanto Research Corporation under Contract No. AF 33(657)-8193.

When this is known for the temperatures and frequencies used, the dissipation factor of the sample, D_x, can be calculated by the equation

$$D_x = \frac{C_{T_x} D_{T_x} - C_L D_L}{C_x} \tag{V-2}$$

where the symbols have these meanings:

D_L = dissipation factor of the leads, which includes the part of the measuring cell between the cylindrical electodes and its terminals as well as that of the coaxial cable from the cell to the capacitance measuring bridge

C_a = cell constant = capacitance of the cylindrical electrodes filled with (or separated by) air

C_L = capacitance of the lead cable and that part of the cell between the electrodes and the terminals

D_{T_a} = the total dissipation factor of the leads and the cell filled with air

D_x = the true dissipation factor of the electrodes filled with the unknown sample

C_{T_x} = drum corrected total capacitance of leads and cell filled with an unknown liquid

D_{T_x} = total dissipation factor of leads and cell filled with unknown liquid

C_x = capacitance of the cylindrical electrodes filled with the unknown liquid

D_{T_a} was a measured value made on the empty cell. Temperature has a small effect on the value while frequency has a much greater effect. C_a and C_L were calculated from measurements on the cell filled with a standard liquid and are nearly constant. Since D_{T_a} is a variable quantity, D_L also changes. Hence, the quantity $C_L D_L$ was calculated for each temperature and frequency. T_x and D_{T_x} are measured values made on the unknown sample. From these, one can calculate the capacitance of the sample, C_x, the dielectric constant, K_x, and dissipation factor, D_x. The dissipation factors on fuels are given as follows:

Fuel	Temperature (°F)	Dissipation Factor at Various Frequencies				
		100 cycles/sec.	400 cycles/sec.	1 kilocycle/sec.	10 kilocycles/sec.	100 kilocycles/sec.
SF6-6201	68			0.00025	0.00021	
	100			0.00024	0.00018	
	150			0.00022	0.00022	
	200			0.00024	0.00020	
SF6-6202	68			0.00030	0.00023	
	100			0.00024	0.00018	
	150	0.00029		0.00022	0.00022	
	200			0.00027	0.00023	
SF6-6203	68			0.00030	0.00021	
	100			0.00026	0.00023	
	150			0.00022	0.00022	
	200			0.00024	0.00020	
SF6-6204	68		0.00426	0.00189	0.00018	
	100		0.00674	0.00281	0.00031	*
	150		1.303	0.00519	0.00057	*
	200		2.258	0.00920	0.00098	*
SF6-6206	68			0.00089	0.00023	
	100			0.00150	0.00031	
	150			0.00225	0.00038	
	200			0.00428	0.00058	
SF6-6208	68			0.00027	0.00021	
	100			0.00027	0.00021	
	150			0.00022	0.00017	
	200		0.00047	0.00024	0.00018	0.00019
SF6-6210	68			0.00079	0.00023	
	100			0.00237	0.00036	
	150			0.00412	0.00051	
	200			0.0150	0.0016	
SF6-6211	68			0.00076	0.00023	
	100			0.00258	0.00041	
	150			0.00535	0.00064	
	200			0.01502	0.00164	
SF6-6212	68			0.00064	0.00021	
	100			0.00180	0.00034	
	150			0.00304	0.00051	
	200			0.01119	0.00133	
SF6-6215	68			0.00097	0.00023	
	100			0.00201	0.00036	
	150			0.00294	0.00043	
	200			0.00701	0.00082	

*$C_L D_L$ greater than C_{T_x} D_{T_x} and D_x cannot be calculated.

Fuel	Temperature (°F)	Dissipation Factor at Various Frequencies				
		100 cycles/sec.	400 cycles/sec.	1 kilocycle/sec.	10 kilocycles/sec.	100 kilocycles/sec.
SF6-6219	68			0.00177	0.00031	
	100					
	150			0.00547	0.00072	
	200					
TSF-6203	68			0.00040	0.00021	
	100	0.00050		0.00034	0.00021	0.00010
	150			0.00054	0.00022	
	200			0.00035	0.00020	
TSF-6204	68			0.00043	0.00023	
	100			0.00042	0.00021	
	150			0.00065	0.00022	
	200			0.00064	0.00023	
TSF-6205	68			0.00032	0.00018	
	100			0.00027	0.00018	
	150			0.00038	0.00017	
	200			0.00040	0.00018	
TSF-6208	68			0.00024	0.00018	
	100			0.00021	0.00015	
	150			0.00019	0.00019	
	200			0.00024	0.00017	

THERMAL CONDUCTIVITY AND SPECIFIC HEAT

Fuel	Thermal Conductivity at Various Temperatures Btu/(hr) (sq ft) (°F/ft)			Specific Heat at Various Temperatures Btu/(lb) (°F)		
	145°F	219°F	334°F	104°F	212°F	302°F
SF6-6201	0.0631	0.0611	—	0.553	0.585	—
SF6-6202	0.0622	0.0599	—	0.534	0.570	—
SF6-6203	0.0628	0.0605	—	0.528	0.566	—
SF6-6204	0.0654	0.0645	0.0627	0.465	0.563	0.645
SF6-6206	0.0646	0.0638	0.0617	0.478	0.537	0.597
SF6-6208	0.0633	0.0612	—	0.514	0.565	—
SF6-6210	0.0649	0.0624	0.0620	0.482	0.541	0.594
SF6-6211	0.0657	0.0648	0.0631	0.468	0.546	0.615
SF6-6212	0.0638	0.0602	0.0616	0.527	0.564	0.606
SF6-6215	0.0634	0.0611	0.0606	0.508	0.569	0.630
SF6-6219	0.0630	0.0633	0.0624	0.438	0.498	—
TSF-6203	0.0657	0.0627	0.0620	0.541	0.595	0.645
TSF-6204	0.0642	0.0621	0.0625	0.491	0.543	0.595
TSF-6205	0.0642	0.0620	0.0601	0.479	0.537	0.583
TSF-6208	0.0628	0.0597	0.0614	0.540	0.586	0.627

VAPOR PRESSURE

Because of various problems associated with laboratory vapor-pressure devices at high temperatures and pressures, correlation techniques are presently considered best for determining the vapor pressure of hydrocarbon fuels. See Reference V-1. The calculation technique developed by British Petroleum (Reference V-2) for determining the vapor pressure of hydrocarbons was used in determining the vapor pressure of fuel SF6-6209A. The vapor pressure of this fuel is plotted in Figure V-1 versus 1000/°R. Data from this figure are presented in Table V-1. This fuel is thought to be representative of a typical JP-6 with regard to distillation range and volatility.

REFERENCES

V-1 A. E. Zengel, H. R. Lander, W. G. Scribner, and J. H. Warren, An Examination of Methods for Calculating Vapor Pressure of Petroleum Hydrogen, APL-TDR-64-37, Research and Technology Division, Wright-Patterson AF Base, Ohio, March 1964.

V-2 The Calculation of the Vapour Pressures of Aviation Fuels, Technical Memorandum No. 110.040, The British Petroleum Company Limited, BP Research Center, Petroleum Division, Sunbury-On-Thames, 20 June 1960.

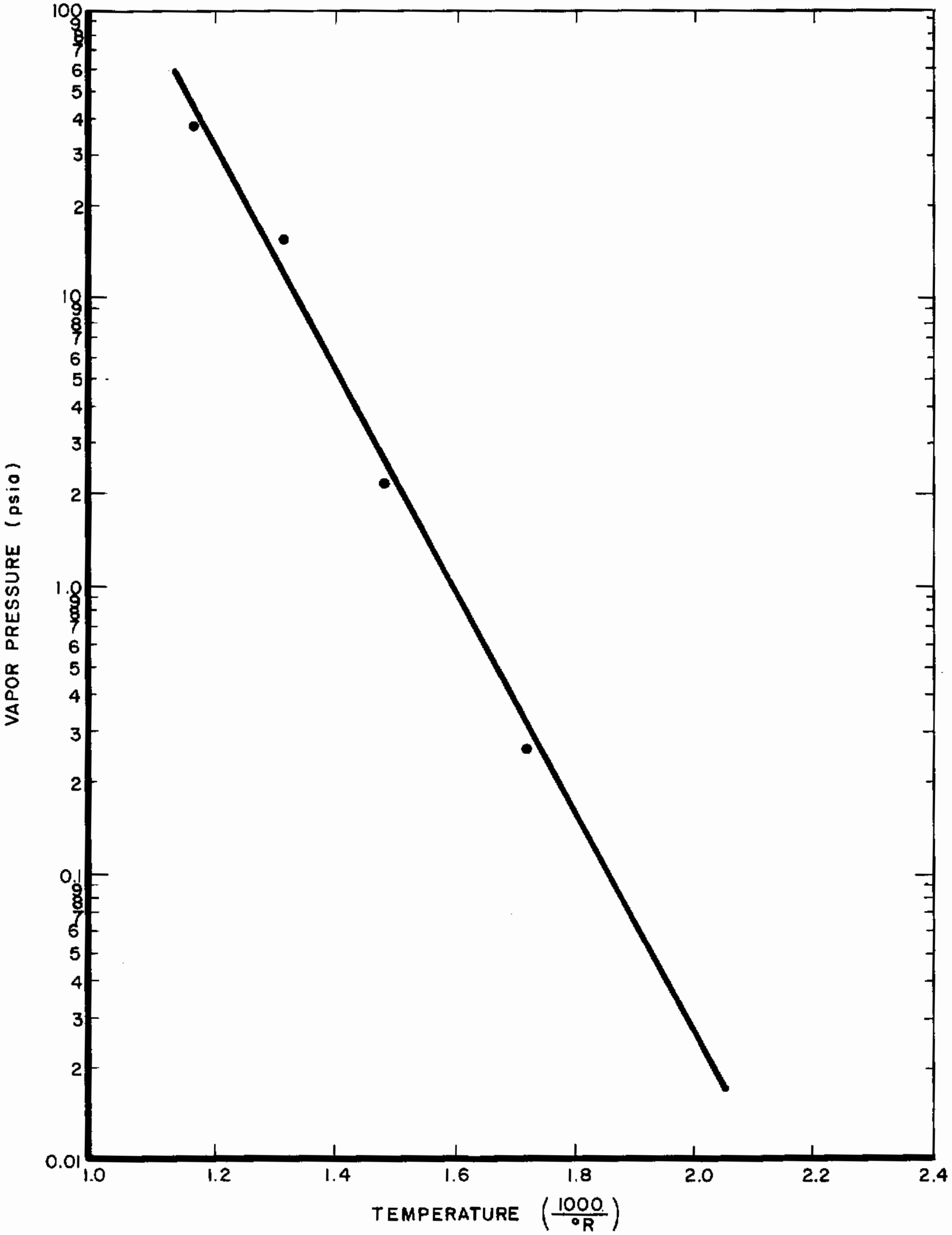

Figure V-1. Calculated Vapor Pressure of SF6-6209A Fuel

TABLE V-1

VAPOR PRESSURE DATA ON SF6-6209A FUEL

Temperature (°F)	Vapor Pressure (psia)
50	0.032
100	0.16
150	0.60
200	1.75
250	4.8
300	10.6
350	24.0
400	45.0

APPENDIX VI

TEST PROCEDURES FOR DETERMINING PPB ZINC IN JET FUELS

(Procedures developed by Monsanto Research Corporation under
Contract No. AF 33(657)-8193; reported by Dr. W. G. Scribner)

A. INTRODUCTION

The method described here for the determination of zinc in JP-6 fuels is based on the dithizone mixed-color method described by Sandell (Reference VI-1).

B. SUMMARY

Zinc is extracted from the fuel sample by shaking with 0.01N hydrochloric acid. Any fuel-water emulsion or undissolved zinc in the aqueous extract is taken care of by heating the extract to the boiling point. A suitably sized aliquot is buffered to pH ca 4.75 by sodium acetate-acetic acid buffer, and most interfering substances are reduced by the addition of 25% aqueous sodium thiosulfate. The zinc ions are reacted with and extracted from the aliquot by a 0.001% solution of dithizone in carbon tetrachloride. The intensity of the resulting color is measured spectrophotometrically, and the zinc content of the color solution is determined from a standard curve.

The lower limit of detection for zinc is about 3 ppb. The upper limit is 21 ppm. The spectrophotometric sensitivity of the dithizone test for zinc is about 5.4 μg of zinc per absorbance unit.

It has been shown that the presence of Tenamene-2, DuPont metal deactivator (disalicylal propylenediamene), and moderate amounts of stannous and stannic ions do not interfere with the accuracy of the method.

C. PROCEDURE

1. Extraction of Zinc From Fuel

a. Pipet 150 ml of fuel sample (2 x 75 ml) into a clean (zinc-free) 16-ounce, Boston Round bottle with a 28-mm polyseal cap. A smaller sample (as low as 50 ml) may be used if a very high concentration of zinc is suspected in the sample.

b. Add by pipet 30 to 150 ml of 0.01N HC1 (depending upon zinc content of sample).

c. Seal bottle tightly with polyseal cap and place securely on its side on floor of platform rocker (Eberback). Shake on platform rocker at a setting of 85 for 15 minutes.

d. Remove bottle from rocker and let stand until phases separate (minimum time--10 minutes).

e. Decant off most of fuel layer into waste fuel container.

f. Remove remainder of fuel layer by suction via water aspirator. Leave any emulsion on scum in water layer.

g. Transfer water layer (acid extract) to clean (zinc-free) appropriately sized beaker. Place beaker on hot plate and bring to boiling point. If any scum or emulsion is present, boil contents of beaker gently until scum or emulsion either disappears or rises to top to form a fuel layer.

h. Cool; remove any fuel layer by suction as before. If extract is to stand over night, transfer to a clean (zinc-free) 2-ounce Boston Round bottle with cap.

2. Analysis of Acid Extract

a. If further dilution of the extract is necessary due to a very high zinc content, transfer a suitable aliquot of the extract to a clean (zinc-free) volumetric flask of appropriate size and dilute to mark with 0.01N HCl.

b. Add by pipet to a clean (zinc-free) 125 ml separatory funnel (with Teflon stopcock and Ŧ stopper) a 10-ml aliquot of either the extract or its dilution (if a dilution has been prepared).

c. Add by pipet 5.0 ml of acetate buffer. Swirl gently to mix.

d. Add by pipet 1.0 ml of sodium thiosulfate reagent. Swirl gently to mix.

e. Add by pipet 5.0 ml of 0.001% dithizone in CCl_4 reagent.

f. Stopper the funnel and shake funnel and contents vigorously by hand for 2 minutes.

g. Let stand two minutes for layers to separate.

h. Drain part of lower, colored layer into a 1-cm spectrophotometer cell.

i. Read absorbance at 535 mµ with carbon tetrachloride as a reference. Make cell corrections.

j. Run a blank by adding 10 ml of 0.01N HCl to separatory funnel in Step 2b and carrying it through the rest of the procedure.

k. Determine the µg of zinc in the aliquot taken in Step 2b from the net absorbance (absorbance of sample less absorbance of blank) and a fairly recent calibration curve. If the µg of zinc exceeds 5.0, re-run a smaller aliquot of the extract or dilution.

3. Calculations

$$\text{ppb zinc} = \frac{(\mu\text{g of zinc in aliquot})\ (\text{ml total acid extract})\ (\text{ml extract dilution})\ (1000)}{(\text{wt of sample in grams})\ (\text{ml aliquot of total extract})\ (\text{ml aliquot of extract dilution})}$$

NOTE: The weight of sample in grams may be determined by multiplying the volume (ml) taken by the density of the sample (grams/ml).

D. PREPARATION OF CALIBRATION CURVE

NOTE: A new calibration curve should be determined whenever a new batch of color reagent (0.001%) is prepared or 30 days has elapsed since a curve has been determined on the batch of color reagent in use.

1. Prepare fresh zinc standard solutions D, E, F, and G (Section F).*

2. Into 125-ml separatory funnels add by pipet the following:

a. 10 ml of standard E (equivalent to 1 μg of zinc).

b. 5 ml of standard G (equivalent to 2 μg of zinc) and 5 ml of 0.01N hydrochloric acid.

c. 10 ml of standard F (equivalent to 3 μg of zinc).

d. 10 ml of standard G (equivalent to 4 μg of zinc).

e. 5 ml of standard D (equivalent to 5 μg of zinc) and 5 ml of 0.01N hydrochloric acid.

f. 10 ml of 0.01N hydrochloric acid (blank).

3. Carry all six funnels through procedure (Section C, Part 2 Steps c through i).

4. Determine the net absorbances of the standards by subtracting the absorbance of the blank.

5. Plot the net absorbances of the standards (ordinate) vs the μg of zinc in the standards (abscissa).

6. The resulting curve will not be a straight line; thus,

a. The curve must be used at all times when determining the zinc content of fuel samples--no factor can be used to convert absorbance units to micrograms of zinc;

b. No values above 5 micrograms of zinc should be extrapolated when running fuel samples.

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*Although there is no procedural requirement demanding strict adherence to this method of preparing a calibration curve (i.e., the use of five different standard zinc solutions), its use may result in a more reproducible curve than would result from using 1.0, 2.0, 3.0 ml, etc. of one solution only (D).

E. CLEANING GLASSWARE

1. To remove all organic matter and metals

a. Fill glassware with chromic-sulfuric acid glass cleaning solution

b. Let stand for 30 minutes

c. Rinse thoroughly with tap water

d. Rinse three times with distilled water

e. Rinse three times with triple glass distilled water

f. Rinse three times with reagent grade acetone

g. Dry with dry nitrogen gas

2. To remove zinc only

a. Rinse with a mixture of 5 ml of acetate buffer, 5 ml of 0.01% dithizone in carbon tetrachloride, and 10 ml of zinc-free water

b. Rinse three times with acetone

c. Rinse three times with hot tap water

d. to g. (as in Paragraph E1).

F. REAGENTS

1. Zinc Standard A, 1000 μg/ml, 0.0153OM

a. Treat reagent grade zinc shot for 2 or 3 minutes with 100 ml of 0.5% sulfuric acid to remove superficial oxide coating.

b. Rinse bright, unpitted shots well with distilled water, reagent grade acetone, and finally ethyl alcohol. Remove excess alcohol with a stream of nitrogen.

c. Weigh into a 150-ml beaker 0.9999 to 1.0004 grams (or as near the upper limit as possible) of the clean, dried zinc shot to the nearest tenth of a milligram.

d. Cover the shot with 2 ml of distilled water and add 6 ml of 1:1 nitric acid in two 3-ml portions. Add the second portion only after the first violent action subsides.

e. Add an additional 1 ml of concentrated nitric acid and warm to dissolve the remaining zinc..

f. Finally, heat to boiling to expel oxides of nitrogen.

g. Cool and quantitatively transfer to a 1-liter volumetric flask. Dilute to the mark with zinc-free water and shake well to mix thoroughly.

h. If the amount of zinc weighed out in Steps c was not in the range prescribed, calculate the molarity of Standard Solution A:

$$\text{M of A} = \frac{\text{grams of zinc}}{65.37}$$

i. Store in polyethylene or other zinc-free container.

2. Zinc Standard B, 100 μg/ml, 1.530 x 10^{-3}M

a. Add by pipet 50 ml of Solution A to a 500-ml volumetric flask. If the molarity of Solution A was calculated to be less than 0.015295M or more than 0.015304M, add, instead, by buret, the proper amount of Solution A calculated to produce a 1.530 x 10^{-3}M solution when diluted to 500 ml:

$$\text{ml of A to be added} = \frac{0.7650}{\text{M of A}}$$

b. Dilute to mark with zinc-free water. Shake well to mix thoroughly.

c. Store in polyethylene bottle.

3. Zinc Standard C, 10 μg/ml

a. Add by pipet 50 ml of Solution B to a 500-ml volumetric flask.

b. Add 350 ml of zinc-free water. Swirl to mix well.

c. Add 4 ml of concentrated hydrochloric acid in two 2-ml portions, swirling to mix well after each addition.

d. Dilute to mark with zinc-free water. Shake well to mix thoroughly.

e. Store in polyethylene bottle.

4. Zinc Standard D, 1 μg/ml: Dilute 10 ml of Solution C to 100 ml in a volumetric flask with 0.01N hydrochloric acid. Discard after using.

5. Zinc Standard E, 0.1 μg/ml: Dilute 10 ml of Solution D to 100 ml in a volumetric flask with 0.01N hydrochloric acid. Discard after using.

6. Zinc Standard F, 0.3 μg/ml: Dilute 30 ml of Solution D to 100 ml in a volumetric flask with 0.01N hydrochloric acid. Discard after using.

7. Zinc Standard G, 0.4 μg/ml: Dilute 40 ml of Solution D to 100 ml in a volumetric flask with 0.01N hydrochloric acid. Discard after using.

8. Hydrochloric Acid, 0.1N: Add 17 ml of concentrated hydrochloric acid to 2 liters of zinc-free water, slowly with stirring.

9. Hydrochloric Acid, 0.01N: Add 200 ml of 0.1N hydrochloric acid to 1800 ml of zinc-free water, slowly with stirring.

10. Acetate Buffer, pH ca 4.75

a. Make up 200 ml of a 2N solution of acetic acid: Add 23 ml of glacial acetic acid to 177 ml of zinc-free water slowly while stirring.

b. Make up 200 ml of 2N solution sodium acetate: Dissolve 32.8 grams of reagent grade anhydrous sodium acetate in 100 ml of zinc-free water. Dilute to 200 ml with more zinc-free water.

c. Mix the above solutions in a 32-oz zinc-free Boston Round glass bottle.

d. Add 10 ml of 0.01% dithizone in carbon tetrachloride; seal bottle well with polyseal cap.

e. Shake on platform rocker in horizontal position for 10 minutes at full speed.

f. Let stand 10 minutes for layers to separate.

g. Filter through S&S597 filter paper into polyethylene bottle.

11. Color Reagents

a. Dithizone in carbon tetrachloride 0.01% (w/v): Dissolve 0.0200 grams of dithizone, purified by method of Welcher (Reference VI-2) in 200 ml of reagent grade carbon tetrachloride. Store in polyethylene in refrigerator.

b. Dithizone in carbon tetrachloride, 0.001% (w/v): Dilute 20 ml of the above dithizone solution to 200 ml with more carbon tetrachloride. Store in polyethylene in refrigerator.

12. Sodium Thiosulfate, 25%: Dissolve 50 grams of sodium thiosulfate pentahydrate in 200 ml of zinc-free water. Store in polyethylene bottle.

13. Zinc-Free Water: Use triple glass-distilled water.

G. EQUIPMENT

1. Boston Round glass bottles: 16-oz, 32-oz, and 2-oz.

2. Pipets, class A: 1, 5, 10, 20, 30, 50, and 75 ml.

3. Buret, class A, with Teflon stopcock: 50 ml.

4. Eberbach Platform Rocker.

5. Separatory funnels, Squibb-type, with Ultramax (Teflon) stopcocks and stoppers: 125 ml.

6. Spectrophotomeric cells, pyrex, 1-cm rectangular.

7. Spectrophotometer: Beckman Model B or suitable substitute.

H. REFERENCES

VI-1. E. G. Sandell, Colorimetric Determination of Traces of Metals, Third Edition, Interscience Publishers, New York, N. Y. 1959.

VI-2. F. J. Welcher, Organic Analytical Reagents, Volume III, page 466, D. Van Nostrand Co., Inc., New York, N. Y. 1947.

APPENDIX VII

TEST PROCEDURES FOR DETERMINING PPB IRON IN JET FUELS

(Procedures developed by Monsanto Research Corporation under
Contract No. AF 33(657)-8193; reported by Dr. W. G. Scribner)

A. INTRODUCTION

This method for the determination of iron is based on the use of bathophenanthroline (Reference VII-1) and its adaptation for the determination of traces of iron in JP-6 fuels.

B. SUMMARY

Particulate iron is dissolved by thoroughly heating the measured samples to 82°C and performing the subsequent extraction steps while the samples are still hot. Iron is extracted by shaking with 1N hydrochloric acid. A second extraction is performed on the warm sample with water added to the aqueous layer. All iron is reduced to the ferrous state by the addition of hydroxylamine hydrochloride to a suitably sized aliquot of the aqueous extract. The aliquot is buffered to pH4 by addition of 10% aqueous sodium acetate, and the ferrous ions are reacted with aqueous bathophenanthroline solution to produce a red color. The color is extracted from the aqueous layer with isoamyl alcohol. The colored isoamyl alcohol layer is diluted to volume with absolute ethanol, and the color intensity is measured spectrophotometrically.

Under the conditions of this analysis, the captions Li, Na, K, Be, Mg, Ca, Sr, Ba, Ce(IV), Ce(III), Pr(III), rare earths in general, Th, Ti, Zr, Vanadate and Vanadyl, Cr(III), W, U, Mn, Fe(III), Ru(III), Os, Ni, Pd, Pt, Ag, Zn, Cd, Hg(I), Hg(II), B, Al, Ga, Tl(I), Sn(II), Sn(IV), also Te, Se, and Co do not interfere. Up to 250 micrograms of Cu can be present in the color solution without altering the results in the determination of iron. The common anions, chloride, sulfate, iodide, thiosulfate, cyanide, thiocyanate, sulfide, phosphate, nitrate, acetate, and perchlorate will not interfere. Tenamene-2 is destroyed by allowing the fuel to stand over-night acidified with hydrochloric acid.

On the recommended size sample, the lower limit of detection is 4 ppb (20 ml aliquot of extract), and the upper limit is 1500 ppb (5 ml aliquot). Higher concentrations of iron can be detected in smaller samples and/or larger quantities of acid extract.

C. PROCEDURE

1. Extraction and Dissolution of Iron

a. Pipet 250 ml of fuel into a clean 16 oz Boston Round glass bottle supplied with clean neoprene rubber stopper. Polyethylene lined screw caps should not be used because the polyethylene dissolves in hot JP-6 fuels.

b. Add 2 ml 1N hydrochloric acid (iron-free) to each bottle of jet fuel.

c. Stopper bottle and secure with copper wire and place in oven at 82°C for 1 to 2 hours.

d. Remove bottle from oven and shake for 5 minutes horizontally on a platform rocker at setting "85." Do not allow bottle to cool before it is shaken.

e. Return bottle to oven at 82°C for another period of 1 to 2 hours (or for remainder of work day).

f. Remove bottle from oven and let stand at room temperature overnight.

g. Place bottle back in oven next morning for at least 1 hour.

h. Remove bottle from oven and shake for 5 minutes horizontally on a platform rocker. Do not allow bottle to cool before it is shaken.

i. Remove bottle and stopper; add 28 ml re-distilled (iron-free) water (buret). Stopper and re-wire.

j. Place bottle back in oven for at least 1 hour.

k. Remove bottle from oven and shake for 10 minutes horizontally on a platform rocker set at "85."

2. Determination of Iron

a. Permit fuel to cool to room temperature. During this time interval (approximately 1 hour), the water extract will separate from the fuel.

b. Decant off most of fuel layer into waste fuel container. Remove rest of fuel layer by suction from water aspirator.

c. Transfer 20 ml aliquot of extract from bottle to 125-ml separatory funnel by means of pipet.

d. Add 10 ml re-distilled water to extract in 125-ml separatory funnel.

e. Pipet 2.0 ml of 10% iron-free hydroxylamine into 250-ml separatory funnel with water extract. Shake briefly to mix.

f. Pipet 4.0 ml of 10% iron-free sodium acetate into same 250-ml separatory funnel. Shake briefly to mix.

g. Pipet 4.0 ml of 0.001M bathophenanthroline into extract. Shake briefly to mix.

h. Add 6.0 ml of isoamyl alcohol.

i. Shake vigorously for 1 minute.

j. Let stand at least 5 minutes.

k. Drain off lower water layer.

l. Collect upper colored layer into clean 10-ml volumetric flask. Rinse separatory with 2 ml of ethanol and drain into volumetric. Bring volume up to 10-ml mark with more ethanol.

m. Read absorbance on Beckman Spectrophotometer at 533 mμ in 1-cm rectangular cells with 4:6 ethanol-isoamyl alcohol mixture as reference.

n. If iron content is excessive (i.e., absorbance greater than 2.0), repeat from Step c using 5.0 ml of extract and 25 ml of iron-free water. If iron content is still excessive, repeat entire analysis using smaller sample and/or larger quantities of acid and water in extraction step.

o. Run blank without fuel, using 30 ml of iron-free water and same amount of reagents. This measures amount of iron present as a contaminant in the reagents.

3. Calculation

$$\text{ppb iron} = \frac{(\text{net absorbance})\ (25\ \mu\text{g/A})\ (30)\ (1000)}{(\text{wt of sample in grams})\ (\text{ml of aliquot})}$$

Note: Weight of sample in grams is obtained by multiplying the sample volume (ml) by its density (grams/ml).

Net absorbance is obtained by subtracting the absorbance of the blank from the absorbance of the sample and applying the necessary cell corrections.

D. PREPARATION OF CALIBRATION CURVE

Note: Once a calibration curve has been established, further standards need not be run except as on occasional check.

1. Add by pipet 1.0, 2.0, 5.0, 10.0, and 15.0 ml aliquots of the standard iron solution (containing 1.00 μg of iron per ml, and corresponding to 1.00, 2.00, 5.00, 10.0, and 15.0 μg of iron) to separate 125-ml separatory funnels.

2. To the contents of the funnels add sufficient iron-free distilled water to make 30 ml.

3. Carry the contents of each funnel through Steps a through i and k of Section 2 of the Procedure section. Run blank on 30 ml of iron-free water and all reagents.

4. Plot net absorbances of standards (ordinate) versus micrograms of iron (abscissa).

5. Determine average slope of curve (A units/μg of iron) utilizing the data secured for each standard and its reciprocal (μg of iron/A unit). An avergage slope of 0.0400 A units per microgram of iron should be obtained by a valid curve. The reciprocal of this ratio is 25.0 μg/A unit, the factor by which the net absorbance of the sample should be multiplied to obtain the micrograms of iron in the aliquot of sample. Any experimental curve that is not a straight line or does not have the aforementioned slope should be regarded as suspect.

E. CLEANING GLASSWARE

Rinse separatory funnel, pipets, and bottles already cleaned by conventional methods with chromic-sulfuric acid glass cleaning solution or 1N hot hydrochloric acid followed by additional rinses with tap water, distilled water, then triple glass distilled water; and then dry with reagent grade acetone rinses and remove acetone by applying dry air or nitrogen.

F. REAGENTS

1. Bathophenanthroline solution, 0.001M in 50% ethanol: Dissolve 0.0668 grams of bathophenanthroline (4, 7-diphenyl-1, 10-phenanthroline, G. Frederick Smith Chemical Co., Catalog Item No. 108) in 100 ml of ethyl alcohol and dilute with 100 ml of iron-free water. Store in polyethylene bottle with polyethylene cap.

2. Hydroxylamine hydrochloride, 10% aqueous solution, iron-free: Dissolve 20 grams of hydroxylamine hydrochloride in 200 ml of iron-free water in a clean, iron-free 16-oz Boston Round glass bottle with "Polyseal" cap. Add 8 ml of 0.001M bathophenanthroline; shake well to mix thoroughly. Add 40 ml of isoamyl alcohol and shake horizontally on an Eberbach platform rocker at a setting of "85" for 10 minutes. Let stand 5 minutes for layers to separate. Draw off top layer by suction from water aspirator. Add 2 ml of 0.001M bathophenanthroline, mix well, and add 20 ml of isoamyl alcohol. Shake on platform rocker as before. Let stand 5 minutes and draw off top layer as before. Store in polyethylene bottle with polyethylene cap.

3. Sodium acetate, 10% aqueous solution, iron-free: Dissolve 20 grams of sodium acetate, anhydrous in 200 ml of iron-free water in a 16-oz Boston Round glass bottle with "Polyseal" cap. Add 6 to 8 ml of 0.001M bathophenanthroline and 4 ml of 10% hydroxylamine hydrochloride. Shake well to mix thoroughly. Add 40 ml of isoamyl alcohol and shake horizontally on an Eberbach platform rocker at a setting of "85" for 10 minutes. Let stand 5 minutes; then draw off top layer by suction from water aspirator. Repeat addition of reagents and extraction as before; then draw off top layer as before. Transfer to polyethylene bottle with polyethylene cap.

4. Isoamyl alcohol, reagent grade.

5. Ethanol, absolute.

6. Iron-free water: Use triple, glass distilled water.

7. Standard iron solution, 1.00 microgram of iron per ml: Weigh carefully 0.0702 grams of ferrous ammonium sulfate hexahydrate or 0.0684 grams of ferrous ethylenediammonium sulfate tetrahydrate (G. Frederick Smith Chemical Co., Catalog Item No. 41) to a 1-liter volumetric flask. Add iron-free water to dissolve the salt; add 2.5 ml of concentrated sulfuric acid; mix well. Dilute to mark with iron-free water and mix well. Pipet 100 ml of this solution into another 1-liter volumetric flask; add 2.5 ml of concentrated sulfuric acid; mix well. Dilute to the mark with iron-free water, and mix well. The first flask contains 10.0 micrograms of iron per ml; the second, 1.00 micrograms of iron per ml.

8. Hydrochloric acid, 6N, iron-free: Slowly and cautiously add 150 ml of concentrated hydrochloric acid to 150 ml of iron-free water while stirring. Let cool to room temperature and transfer to a 32-oz Boston Round glass bottle with "Polyseal" cap.

Add 40 ml of diethyl ether and extract by shaking horizontally on platform rocker for 10 minutes at a setting of "85." Let stand 5 minutes; draw off top layer by suction from water aspirator. Repeat extraction two more times. Store in polyethylene bottle with polyethylene cap or other suitable iron-free container.

9. Hydrochloric acid, 1N, iron-free: Slowly and cautiously add 35 ml of hydrochloric acid, 6N, iron-free, to 175 ml of iron-free water while stirring. Cool to room temperature. Store in polyethylene bottle with polyethylene cap.

10. Isoamyl alcohol-ethanol mixture, 6:4: Mix 40 ml of absolute ethanol with 40 ml of isoamyl alcohol.

11. Chromic-sulfuric acid glass cleaning solution.

12. Acetone, reagent grade.

G. EQUIPMENT

1. Boston Round bottles, 16-oz, 32-oz.

2. Stoppers, "neoprene" or rubber, No. 3.

3. Wire, copper, No. 18B+S.

4. Pipets, transfer, class A: 1, 2, 3, 4, 5, 6, 10, 15, 20, 50, 100, and 200 ml.

5. Separatory funnels, Squibb-type, with "Ultramax" ("Teflon") stopcocks and ST stoppers: 125 ml.

6. Volumetric flasks, class A: 1 liter.

7. Buret, class A, with "Teflon" stopcock: 50 ml.

8. Spectrophotometric cells, 1 cm, rectangular, "Pyrex."

9. Platform rocker, Eberbach.

10. Oven, any type, capable of maintaining 82°C and holding sufficient 16-oz Boston Round bottles.

11. Spectrophotometer, Beckman, Model B, or other suitable instrument.

H. REFERENCES

VII-1. H. Diehl and G. F. Smith, The Iron Reagents: Bathophenanthroline; 2,4,6-Tripyridyl-S-Triazine; Phenyl-2-Pyridyl Ketoxime. The G. Fredrick Smith Chemical Company, 867 McKinley Avenue, Columbus, Ohio. 1960.

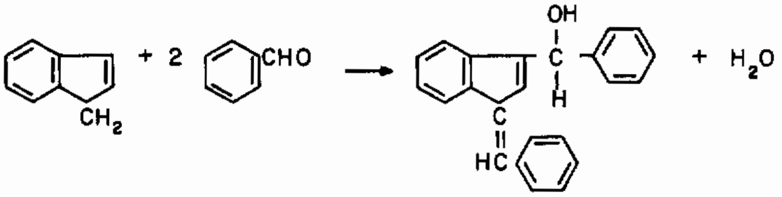
APPENDIX VIII

TEST PROCEDURES FOR DETERMINING PPM INDENES IN JET FUELS

(Procedures developed by Monsanto Research Corporation under
Contract No. AF 33(657)-8193; reported by Dr. W. G. Scribner)

INTRODUCTION

The procedure for the determination of indenes in JP-6 fuel is an adaptation of a method of Skoog and DuBois (Reference VIII-1). Their method is based on the reaction of indene and benzaldehyde to form a yellow compound, 1-(α-hydroxybenzyl)-3-benzalindene:



Their method called for the heating at reflux temperature of a mixture of the sample, 20 ml of 2% benzaldehyde in 95% ethanol, and 5 ml of 3% methanolic potassium hydroxide. After 10 minutes, the solution is cooled, acidified with 1 ml of glacial acetic acid and diluted to 50 ml with 95% ethanol. Absorbance is read at 420 mμ using 1-cm cells vs 95% ethanol. Under these conditions a 20-gram fuel sample containing 100 ppm indenes would give a net absorbance of only 0.23 unit. Furthermore, clear solutions did not result upon dilution to 50 ml because of the lack of mutual solubility of JP-6 and 95% ethanol. Consequently, it was necessary to scale up the fuel sample size and to find a means of coupling fuel and 95% ethanol.

It was found after some experimentation that a turbid mixture of 30 ml JP-6, 20 ml benzene, 10 ml methanolic potassium hydroxide, 20% of 4% benzaldehyde in 95% ethanol, and 10 ml of 95% ethanol could be rendered perfectly clear by the addition of 10 ml of dioxane. At this dilution, the absorbance due to 100 ppm indene (30 ml fuel sample) would be about 0.800 when measured in 5.00-cm cells.

The published procedure provided the option of heating the fuel-reagent mixture for color development, or for overnight color development. Initial experiments were performed with color development produced by heating. A calibration curve was prepared using 0, 1, 2, 3, 4, and 5 ml of an indene standard solution (0.492 mg/ml in benzene) by adding 20 ml of benzene, 20 ml of benzaldehyde solution, 10 ml of methanolic potassium hydroxide. The mixture was heated to near boiling, cooled, acidified with 2 ml of acetate acid and diluted to 100 ml with 95% ethanol.

The absorbance readings were obtained at 420 mμ in 5.00-cm cells versus ethanol. See Table VIII-1.

TABLE VIII-1

INDENE ABSORBANCE READINGS

mg Indene	Gross Absorbance	Net Absorbance
0.0	0.034	—
0.492	0.166	0.132
0.984	0.305	0.271
1.476	0.439	0.405
1.968	0.574	0.540
2.460	0.719	0.685

A plot of these data yielded a straight line. It was soon discovered that commercial dioxane might be contaminated with substances that interfere, and subsequent work was performed using re-distilled dioxane. It was also observed that some samples appeared to contain Tenamene-2. This became apparent when samples after color development were treated with acetic acid prior to measurement.

A fuel sample SF6-6306 was found to contain 5 ppm indene with no evidence of Tenamene-2. This fuel was doped to contain 60 ppm of fresh Tenamene-2, and, when again analyzed for indene, the absorbance measurement yielded an apparent indene content of 70 ppm.

Because of the interference of Tenamene-2 and because of erratic data on other samples, it was felt desirable to investigate the overnight color development and also to refrain from acidification prior to absorbance measurements.

Skoog and DuBois reported an increase in the slope of a calibration curve obtained via overnight color development when compared with a calibration curve obtained on heated samples. We also observed this (0.329 A/mg vs 0.274 A/mg). Blanks, although higher, were quite reproducible (0.073, 0.073, 0.076, 0.074). 2.47 mg indene standards run on successive days were also quite reproducible (0.818, 0.804, 0.817, 0.814, 0.814 net absorbance units).

The sample of SF6-6306 doped with 60 ppm Tenamene-2 was analyzed by the modified procedure. An apparent indene content of 21 ppm was found, which is considerably lower than the value, 70 ppm, found by the first procedure. Because this fuel was doped with twice the maximum allowable concentration of Tenamene-2 and yielded a positive error of only 15 ppm, it was felt that the modified method could be reliably applied for the analysis of indenes in JP-6 fuels. Further justification for this was based on additional experiments with this fuel.

SF6-6303 was doped with 87 ppm indene and extracted with dilute hydrochloric acid. Analysis for indene indicated no loss of indene via hydrochloric acid extraction. This fuel was then doped with both indene and Tenamene-2, and a portion was extracted with hydrochloric acid. Analysis for indene on extracted and unextracted portions yielded no significant difference in ppm indene found. This provides additional proof for the non-interference of Tenamene-2.

Fuel SF6-6303 was analyzed repeatedly. Values of 59, 56, 61, and 62 ppm indene were found. The fuel was doped with an additional 102-ppm indene and an experimental value of 162 ppm resulted.

The method is probably reliable to at least within ±10% of the observed value from 10 to 100 ppm and to within ±20% from 1 to 10 ppm. The actual procedure follows.

PROCEDURE

Solutions

1. Indene Standard A, 20 mg/ml

Pipet 5.00 ml of indene into a 250-ml volumetric flask and dilute to the mark with benzene. Pipet another 5.00 ml indene into a tared, stoppered weighting bottle and weigh to the nearest 0.001 gram. Calculate the strength of the indene solution in mg/ml.

2. Indene Standard B, 0.5 mg/ml

Pipet 5.00 ml of solution A into a 200-ml volumetric flask and dilute to the mark with benzene. Calculate the concentration of indene in mg/ml from the known strength of solution A.

3. Benzaldehyde Solution

Dissolve 10 ml of benzaldehyde in 95% ethanol and dilute to 250 ml (graduate). Prepare fresh daily.

4. Alcoholic KOH

Dissolve 6 grams of reagent grade potassium hydroxide in 200 ml of methanol and mix well.

5. Dioxane, Redistilled

6. Benzene, Reagent Grade

Analysis of Samples

1. Into clean, dry, 100-ml volumetric flasks add 30.0 ml of sample (pipet), 20 ml of benzene, 20 ml of benzaldehyde solution, 10 ml of dioxane, and 10 ml of 3% potassium hydroxide. Mix well and allow to stand overnight. Protect from light.

2. Simultaneously run two blanks and two or three standards (5.00 ml of indene-B).

3. On the following morning, dilute to the mark with 95% ethanol and mix well. If a faint turbidity due to crystalline material (benzoic acid?) is observed, allow the solution to stand for a while prior to filling curvettes.

4. Measure the absorbance at 420 mμ in 5.00-cm cells vs 95% ethanol in the reference cells.

5. Correct absorbance readings for cell differences.

Calculations

1. Calculate net absorbances by subtracting the average blank from all other readings.

2. Calculate the factor, f, milligrams of indene per absorbance unit by dividing the milligrams of indene taken by the net absorbance for each standard. Average the factors. The average will probably fall between 3.00 and 3.10.

3. Calculate the ppm indene in the sample from the equation:

$$\text{ppm indene} = \frac{(A)\,(f)\,1000}{(\text{ml sample})\,(\text{density of sample})}$$

where A is the net absorbance of the sample.

Clean Up

Clean volumetric flasks and cells by thorough rinsing with warm tap water, acetone, distilled water, and acetone, in that order. Dry with nitrogen or air. Do not allow cells containing the samples or standards to stand for an appreciable time because the glass might be attacked by the alcoholic base.

REFERENCE

VIII-1 D. Skoog, and H. DuBois, Anal. Chem. 21, 1528, 1949.

APPENDIX IX

TEST PROCEDURES FOR DETERMINING PPB COPPER IN JET FUELS

(Procedure developed by Monsanto Research Corporation under
Contract No. AF 33(657)-8193; reported by Dr. H. C. Eyster)

INTRODUCTION

The method for the determination of copper in JP-6 fuels is based on the procedure outlined by Arlis Wheeler, Monsanto Chemical Company, Research Center Analytical Section (Reference IX-1) and modified to make possible the use of 250-ml samples of JP-6 fuel.

REAGENTS

1. Sodium Hypochlorite Solution - 5% solution, reagent grade.

2. 4N Redistilled Hydrobromic Acid. It is important that this reagent be redistilled because it is likely to contain considerable copper.

3. Chloroform - Reagent grade.

4. Hydroxylamine Hydrochloride - 10% solution.

5. Carbon Tetrachloride - Reagent grade.

6. Zinc Salt of Dibenzyldithiocarbamic Acid - 0.01% solution in carbon tetrachloride. Filter and store in a brown bottle in a cool dark place.

7. Dilute Sulfruic Acid (1:3)

8. Copper Sulfate Solution - Prepare by accurate dilution of a stock solution containing exactly 1.571 grams of copper sulfate, 5-hydrate ($CuSO_4.5\ H_2O$) per liter of solution. Dilute exactly 25 ml of the stock solution to 2 liters in a volumetric flask to give a working solution containing 5 micrograms copper per ml. The copper sulfate solutions should be freshly prepared at monthly intervals and stored in polyethylene bottles.

9. Water - Triple distilled in glass still. Use for preparation of reagents.

10. Copper-free Glassware - Add about 15 ml triple distilled water, 3 ml dilute sulfuric acid, and 5 ml of the carbon tetrachloride solution of zinc dibenzyldithiocarbamate. Shake thoroughly, drain, and then dry glassware with reagent grade acetone and a stream of dry nitrogen gas. All glassware should be super clean to avoid faulty results due to contamination.

PREPARATION OF CALIBRATION CURVE

This procedure is based on the method of Stone, Ettinger, and Gantz (Reference IX-2) with some modification.

1. Pipet 0, 1, 2, 5, 10, and 15 ml, respectively, of the 5 μg copper/ml solution of copper sulfate into six 50-ml clean bottles. The one with 0-ml copper is the blank.

2. Add 15, 14, 13, 10, 5, and 0 ml, respectively, of triple distilled water to equalize the volumes.

3. Add 3 ml dilute (1:3) sulfuric acid and 10 ml carbon tetrachloride solution of zinc dibenzyldithiocarbamate to each. Shake each bottle thoroughly four times with 30 seconds rapid shaking each time.

4. Pipet lower colored carbon tetrachloride solutions into separate 1-cm spectrophotometer cells and read absorbance in Beckman Model B Spectrophotometer at 435 mμ, using carbon tetrachloride as the reference fluid.

5. Plot a graph of the net absorbance values (gross absorbance minus absorbance of blank). From the graph find the amount of copper that produces an absorbance of 1.000. Use this value (amount of copper) as a conversion factor.

6. Convert absorbance of unknown sample into μg copper by simply multiplying the net absorbance by the conversion factor. (We found this conversion factor to be 40.7. See Figure IX-1.)

Table IX-1 gives the data obtained for the preparation of the calibration curve in Figure IX-1.

TABLE IX-1

COPPER ABSORBANCE READINGS

Amount of Copper	Gross Absorbance*	Net Absorbance
Zero copper (blank)	0.026	—
5 μg copper (1 ml)	0.149	0.123
10 μg copper (2 ml)	0.283	0.257
25 μg copper (5 ml)	0.636	0.615
50 μg copper (10 ml)	1.261	1.235
75 μg copper (15 ml)	1.900	1.874

*Slit width = 0.33 mm.

ADAPTING THE PROCEDURE TO JP-6 FUELS

Extraction of Copper

There is the problem of being sure that the copper is completely extracted from the fuel. The reaction of hydrobromic acid with soidum hypochlorite produces bromine which brominates the fuel sample and is effective in the extraction of copper. The color of bromine should not fade completely. Most fuel samples require extra bromine. This is insured by adding 40 ml of 5% sodium hypochlorite instead of the recommended 10 ml, and neutralizing the alkalinity by an additional 5 ml redistilled hydrobromic acid. At least one JP-6 fuel required 50 ml 5% sodium hypochlorite to prevent complete bleaching to colorless.

The original Arlis Wheeler method prescribes 10 ml 5% sodium hypochlorite (0.007 mole) and 15 ml 4N re-distilled hydrobromic acid (0.06 mole). The additional sodium hypochlorite and hydrobromic acid causes a change in the blank absorbance value from 0.024 to 0.073. Most of the contaminating copper is present in the purchased sodium hypochlorite solution, the quality of which could be improved by having a sodium hypochlorite solution prepared with triple distilled water.

Validity of Method

An isooctane solution of copper naphthenate of known strength was analyzed by the method. Found, 1.8 μg/ml; expected, 1.96 μg/ml; recovery, 92%.

JP-6 fuel (TSF-6208) was doped with an additional 50 ppb copper by adding 1 ml copper napthenate solution, 1.96 μg/ml, to 39.5 grams of fuel. Analyses showed the fuel to have 11 ppb copper and the same fuel doped with an additional 50 ppb copper to have 53 ppb copper. (Expected 61 ppb copper, recovery 87%.)

PROCEDURE

Fuel Sample

Pipet 250 ml of cold fuel into a clean 500 ml separatory funnel. Convert fuel volume into fuel weight with appropriate conversion data.

Extraction and Analysis

1. Add 10 ml of 5% sodium hypochlorite. Shake 15 minutes.

2. Add 15 ml of 4N redistilled hydrobromic acid. Shake vigorously for 15 minutes.

3. If fuels bleach to colorless in Step 2, add 30 ml additional 5% sodium hypochlorite and 5 ml additional redistilled hydrobromic acid to neutralize the extra hypochlorite. Add these additional amounts of reagent as soon as Step 2 becomes colorless. The total shaking time in Steps 2 and 3 should be 15 minutes.

4. Let stand 5 minutes, then drain lower water extract into clean bottle.

5. Pipet an aliquot into a clean 500-ml separatory funnel. An aliquot sample size of 20 ml is appropriate for fuels requiring only 10 ml of 5% sodium hypochlorite and 15 ml of 4N redistilled hydrobromic acid, and 50 ml for fuels requiring 40 ml of 5% sodium hypochlorite and 20 ml of 4N redistilled hydrobromic acid.

6. Add triple distilled water to aliquot, 68 ml when aliquot is 20 ml and 170 ml when aliquot is 50 ml. Shake briefly to mix.

7. Add 20 ml chloroform (graduate) and shake for 2 minutes. Discard the lower chloroform layer.

8. Repeat Step 7.

9. Add 10 ml of 10% hydroxylamine hydrochloride to separatory funnel and shake to mix.

10. Add 20 ml of carbon tetrachloride (graduate) and shake for 2 minutes. Discard the lower carbon tetrachloride layer.

11. Add (with pipet) 10 ml of 0.01% solution of zinc dibenzyldithiocarbamate in carbon tetrachloride. Shake for 5 minutes. Allow to stand for 2 minutes.

12. Drain the lower carbon tetrachloride layer through a plug of sterile absorbent cotton into a clean 50-ml bottle.

13. Transfer the filtrate to a 1-cm spectrophotometer cell and read absorbance at 435 mμ on a Beckman Model B Spectrophotometer with carbon tetrachloride as the reference solution.

14. Run a blank for each variation of the procedure.

Calculations

$$\frac{\begin{pmatrix}\text{ml aqueous phase,} \\ \text{Steps 1, 2, 3}\end{pmatrix}\begin{pmatrix}\text{absorbance sample - blank}\end{pmatrix}\begin{pmatrix}\text{factor} \\ \text{of 40.7}\end{pmatrix}}{(\text{ml of aliquot, Step 5})} = \mu\text{g copper}$$

$$\frac{\mu\text{g copper x 1000}}{\text{wt of fuel in grams}} = \text{ppb copper}$$

REFERENCES

IX-1. A. Wheeler, private communication.

IX-2. I. Stone, R. Ettinger, and C. Gantz, "Non-Ashing Technique for Determination of Traces of Copper in Malt Beverages," Analytical Chemistry 25, pp 893-895, 1953.

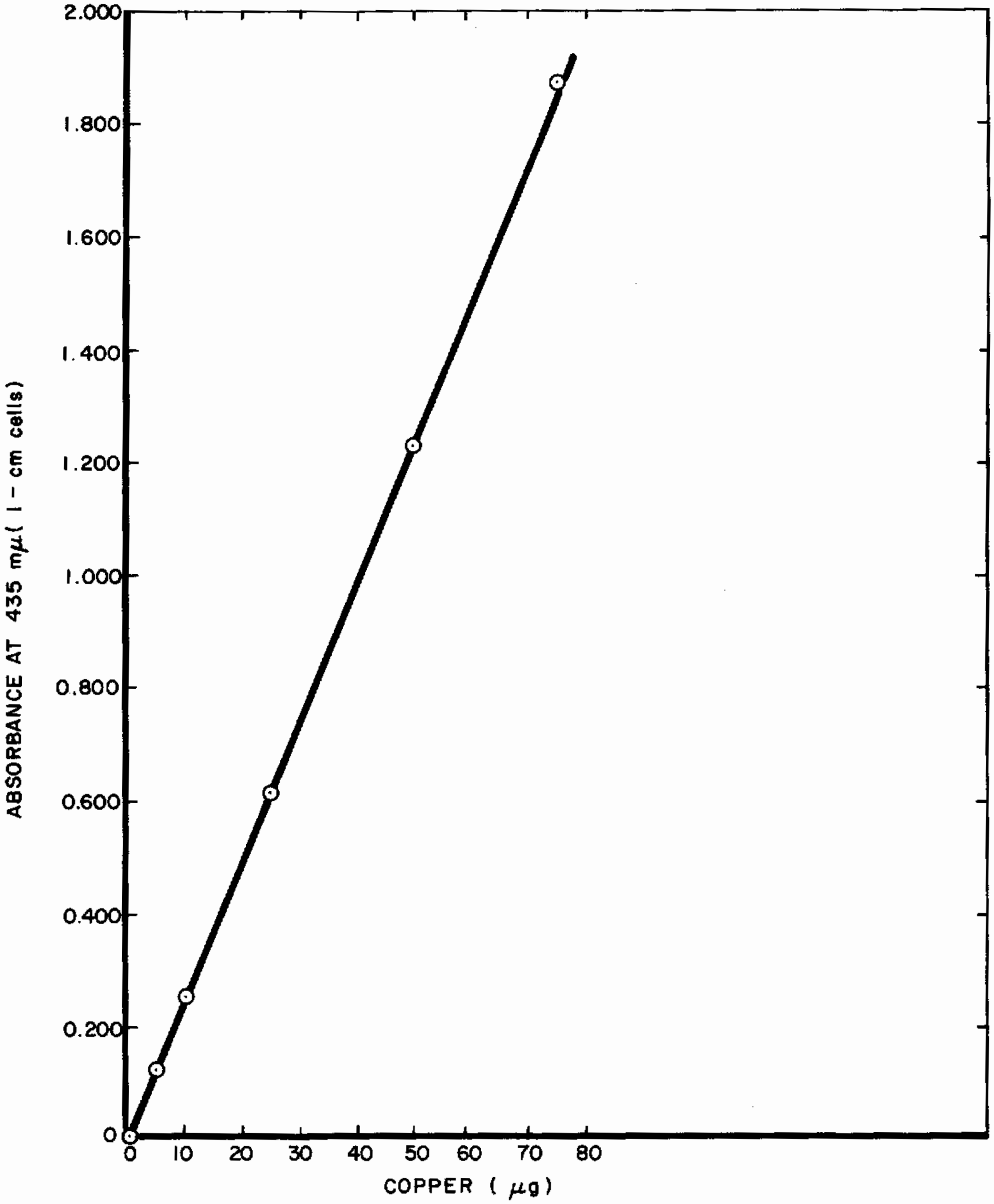


Figure IX-1. Absorbance Versus Weight of Copper (Using 10 ml zinc Dibenzyldithiocarbamate in CCl_4)