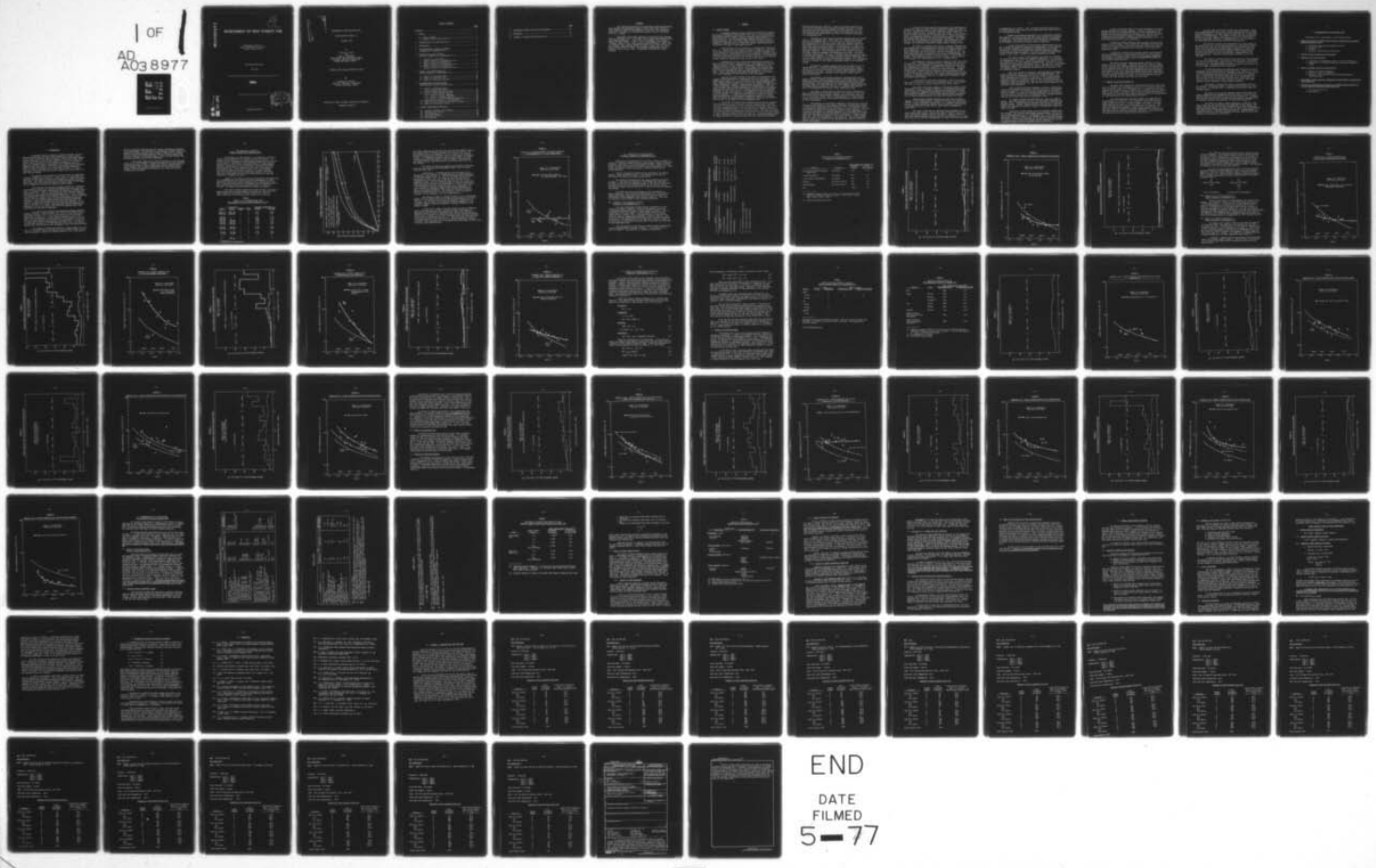
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DEVELOPMENT OF HIGH STABILITY FUEL

DEPARTMENT OF THE NAVY
NAVAL AIR PROPULSION TEST CENTER
CONTRACT N00140-74-C-0618

FINAL REPORT FOR PHASE III

DEC., 1976

Exxon Research and Engineering Company, Government Research Laboratory, Linden, N. J.

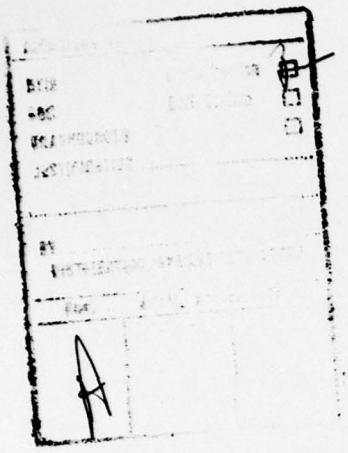
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DEVELOPMENT OF HIGH STABILITY FUEL

FINAL REPORT FOR PHASE III

December 1976

by

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Prepared Under Contract N00140-74-C-0618

For

Department of the Navy
Naval Air Propulsion Test Center
Trenton, New Jersey 08628

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FOREWARD

This report was prepared by the Government Research Laboratories, Exxon Research and Engineering Company, Linden, New Jersey, under Contract N00140-74-C-0618 for the Department of the Navy. The program was monitored by the Naval Air Propulsion Test Center, Trenton, New Jersey, by Mr. C. J. Nowack.

This report covers work conducted in the period from 8 January, 1976, to 8 November, 1976. Prior work on this program was conducted under the following contracts: 1 July, 1974 to 31 December, 1974, Contract N00140-74-C-0618, Phase I; 1 April, 1975 to 30 November, 1975, Phase II; 7 October, 1972 to 7 July, 1974, Contract N00140-73-C-0547; 5 April, 1973 to 6 October, 1973, Contract N00140-72-C-6892; 5 April, 1971 to 5 April, 1972, Contract N0019-71-C-0463. The principal investigators were Dr. William J. Taylor and Dr. John W. Frankenfeld assisted by Mr. Robert Bruncati.

1. SUMMARY

1.1 Overall Summary

An extended program has been completed which meets the original objective of developing a High Stability JP-5 fuel. This fuel exhibits the markedly improved thermal stability characteristics required for high speed aircraft and yet retains the general physical characteristics of present day JP-5. This development makes possible the design of an improved performance Mach 4 to 5 speed range aircraft without resorting to cryogenic or specialty fuels and simplifies logistic problems because of its ability to be used in lower speed aircraft.

High Stability JP-5 is achieved via a combination of deoxygenation, i.e., removal and/or exclusion of molecular oxygen (O_2), and control of the type and level of trace impurity sulfur, nitrogen and oxygen compound and olefins. High Stability JP-5 can be produced by catalytic hydrotreating of petroleum fractions using current technology. The development of this technology and the results of the other work carried out under the overall program is summarized in this section of the report.

Deoxygenation was one of the major modifications planned for High Stability JP-5 fuel. Deoxygenation of a fresh Humble JP-5 fuel was found to increase its fuel stability "breakpoint" temperature in the Advanced Fuel Unit to 1100°F, which is 550°F higher than the same fuel exhibited on an air saturated basis. Deoxygenation of an aged (5 years old) JP-5 fuel increased its fuel stability "breakpoint" by 230°F to 800°F. These results demonstrated that deoxygenation has the potential for a major improvement in the stability of JP-5 type fuels.

Data has also been obtained on the effect of deoxygenation with a group of fuels representing a spectrum of fuel sta bility levels. Two highly refined fuels, i.e., JP-7 and P&W 523, and two intermediate quality fuels showed significant reductions in the rate of deposit formation at higher temperatures. However, a poor quality fuel prepared in 1963 failed to show a reduction in deposit formation with deoxygenation. These results indicated that although deoxygenation has the potential for markedly improving fuel stability, it is not a "magic cure-all" for the stability problems of a fuel of any quality. Fuel composition must be controlled to insure that the full potential of deoxygenation to improve thermal stability is achieved. In order to develop rational criteria for setting these specifications, an experimental program was carried out to determine the effects of certain classes of compounds, present as trace impurities in JP-5, on the stability of the deoxygenated fuel.

The effect of various sulfur compound types on deposit formation was investigated at levels within present day specifications (4,000 PPM level S) in a deoxygenated JP-5 fuel. Results indicated that trace levels of sulfur compounds can have a very strong effect on stability even in a rigorously deoxygenated fuel (i.e., less than 1 PPM). Moreover, the different classes of sulfur compounds which can be present in JP-5 fuel were found to have a markedly different effect on stability. Of the three major classes of sulfur compounds found in the parent crude oil, condensed thiophenes had no deleterious effect on stability, whereas a thiol and various sulfides

markedly decreased fuel stability. Thiols are currently restricted in JP-5 (10 ppm S maximum) and if sweetening processes are used to achieve this level, then two additional classes of sulfur compounds, i.e., disulfides and possibly polysulfides, could be introduced into the fuel. Both disulfides and polysulfides were found to be extremely deleterious in a deoxygenated fuel.

The effect of trace impurity nitrogen compounds was also investigated in a deoxygenated fuel. Since there is no current specification limiting the nitrogen level in JP-5, the effect of nitrogen compounds was investigated at the 100 ppm N level, which was judged to be the probable upper limit for total nitrogen in the majority of JP-5 fuels obtained from present petroleum sources. A wide spectrum of nitrogen compound types which are representative of those potentially present in jet fuels were evaluated. These nitrogen compound types included pyrroles, pyridines, amines, non-aromatic heterocyclics and an amide. The effect of nitrogen compound level was also investigated with both a pyrrole and a pyridine type compound. In general, nitrogen compounds per se were found not to be highly deleterious in a deoxygenated JP-5 fuel. This lack of a strong adverse effect on stability of nitrogen compounds in a deoxygenated fuel is in contrast to their highly deleterious nature in air saturated systems.

The effects of oxygen compounds were also evaluated in JP-5 at the 100 ppm level. No direct specification limits the organic oxygen content of JP-5 fuel, although the total acidity specification controls the carboxylic acid level. Classes of organic oxygen compounds investigated included peroxides, carboxylic acids, phenols, furans, esters, alcohols and ketones.

The presence of peroxides resulted in extremely high rates of deposit formation, producing deposit formation levels equivalent to highly deleterious species such as disulfides even though present at much lower concentrations. Thus, peroxides must be removed and hydrocarbon hydroperoxide formation in High Stability JP-5 (for example, during long periods of storage) must be prevented if the fuel is to exhibit high stability when it is deoxygenated and exposed to high temperature stress.

The effect of the presence of carboxylic acids on deposit formation varied widely with the acid employed. At the 100 ppm O level two carboxylic acids increased deposits, whereas other carboxylic acids did not. At the 10 ppm O level, which is representative of a level required to meet the present military total acidity specification, decanoic acid was still deleterious.

The presence of most phenolic compounds at the 100 ppm O level had relatively little effect on total deposit formation, although some increase in local deposit formation rate was observed. Even at the 1000 ppm O level the presence of dimethylphenol had little effect on total deposits. This lack of an inhibiting effect on a deoxygenated system at high temperature is in contrast to the behavior of phenolic compounds in air saturated fuels at ambient conditions where they are employed as an additive to enhance storage stability. One phenolic compound, 2,6-di-t-butyl phenol, a common antioxidant, was found to be deleterious to fuel stability. This was discovered during a study of its effects on fuel additives, the results of which are given in this report.

The effect of furan compounds was evaluated uing benzofuran and dibenzofuran, which are typical of furan compounds potentially present in jet fuel. The presence of these furan compounds in deoxygenated JP-5 fuel did not increase the level of deposits which were formed. Some representative esters, alcohols and ketones, were also studied at the 100 ppm O level. The naphthenic compounds, cyclohexylformate, methylcyclohexanol and methylcyclohexanone did not increase deposit formation. The aromatic and straight chain aliphatic analogs, however, were somewhat more deleterious. Thus, methylbenzoate, phenylformate, dodecyl alcohol and 5-nonanone all contributed to moderately higher deposit formation rates.

The effects of representative olefins on deposit formation were investigated using a deoxygenated pure compound blend which simulates jet fuel compositions. It was necessary to use the pure compound blend to avoid interference from other olefins, naturally occurring in JP-5. The blend consisted of 24% of n-dodecane, 24% of 2,2,5-trimethylhexane, 30% of isopropylcyclohexane and 20% of sec-butylbenzene (all percentages by weight). The olefins were added at the 2 wt. % level. This is well below the present JP-5 specification of 5 vol. % maximum olefins.

The influence of olefins on deposit formation varies with chemical structure. Aliphatic monoolefins such as 1-dodecene have little or no effect on deposit formation in deoxygenated fuel while certain alicyclic (naphthenic) and aromatic monoolefins were deleterious. Diolefins also showed varying influences depending on their structure. Aliphatic diolefins with conjugated double bonds were relatively harmless while, in the aromatic series, those with double bonds conjugated with the ring proved to be the most deleterious. Most olefins studied promoted deposit formation at temperatures below 700°F, a range where deoxygenated fuels are normally quite stable.

A representative acetylenic hydrocarbon, 1-decyne, was evaluated, also at the 2 wt. % level in the 4-compound blend. This compound was found to be among the most deleterious of all those studied.

The effect of the major classes of hydrocarbons found in petroleum derived jet fuel on deposit formation in a deoxygenated system was investigated. Hydrocarbon compound classes investigated included paraffins, n-paraffins, naphthenes (cycloparaffins) and aromatics. Starting with paraffinic compounds, a series of pure compound blends representative of typical petroleum derived jet fuels were prepared and tested.

Representative compounds evaluated in this study included n-dodecane, 2,2,4-trimethylpentane, isopropylcyclohexane, sec-butylbenzene, tetralin, indene, naphthalene and decalin. In a vigorously deoxygenated system, the major hydrocarbon compound classes (excluding olefins) found in petroleum derived jet fuels are all quite stable at temperatures below 1000°F.

The effect of pressure, an important design parameter for advance engines, was studied. Results show that the effect of total pressure on the deposit formation process is complex. However, results do show that deposit formation rates at 1000 psig are equivalent to, or less than, rates at 250 psig with deoxygenated JP-5 fuels (both fresh and aged)

at temperatures up to 1000°F. Thus, the higher pressures required by a high speed aircraft fuel system are not deleterious toward fuel stability in a deoxygenated system.

Studies of the physical properties of the carbonaceous deposits were conducted in order to learn more about their character and mechanism of formation. Both chemical analyses and scanning electron micrographs have been made. The results show that both the chemistry and morphology of the deposits varies with the oxygen content of the fuel.

A study of the effects of interactions between olefins and sulfur, nitrogen and oxygenated compounds in deoxygenated JP-5 was conducted. This study was designed to determine what compound types can undergo interactions in this system and whether innocuous species may interact to form deleterious reaction products. The first interactions studied were between certain sulfur, nitrogen and oxygen compounds and olefins.

The typical olefin, α-methylstyrene, was chosen as a standard of comparison for all olefin-N,S,O compound interactions. The fuel used was deoxygenated Jumble JP-5. The olefin, α-methylstyrene, had previously been tested only in a four component standard blend. As a result, a new standard run, incorporating the olefin, in JP-5, was required. Surprisingly, the deposit formation was significantly lower in the case of JP-5 than in the synthetic blend. The difference was particularly noteworthy in the low temperature regimes.

Two sulfur containing compounds, dibenzothiophene and phenyl-n-propyl sulfide were studied in conjunction with α-methylstyrene. The olefin was added to deoxygenated JP-5 at the 2 weight % level and the sulfur compounds were at a level of 3,000 ppm S. The thiophene-olefin combination showed no interaction while the olefin-sulfide exhibited a moderately "negative" interaction. That is, the total deposits from the combination were significantly less than the sum of those produced by two components tested separately.

Three nitrogen-containing compounds, a pyrrole, a substituted aniline and a pyridine were tested at the 100 ppm N level with α-methylstyrene (2 weight %). The aniline and pyridiene showed no interaction with the olefin but the pyrrole interacted moderately with the olefin in a positive manner; deposits with the combination were noticeably greater than the sum of those from the two interactants alone.

Six oxygen-containing compounds were run, each with α-methylstyrene. The olefin was added at 2 wt. % and the oxygen compounds at the 100 ppm O level. Dibenzofuran and n-decanoic acid did not interact with α-methyl styrene. However, dodecyl alcohol, methyl benzoate, trimethylphenol and 5-nonanone all exhibited "negative" interactions ranging from slight to strong.

Interaction studies between sulfur and nitrogen compounds were also studied. Two runs were made between dibenzothiophene (3,000 ppm S) and 2,5-dimethylpyrrole and 2,4,6-trimethylpyridine. Both nitrogen compounds were added at 100 ppm N. The thiophene and the pyridine showed no interaction. However, the thiophene and the pyrrole interacted strongly in a positive way to afford much greater deposit formation than the sum of deposits formed by the two components when studied alone.

A series of runs were made to study the interactions of various nitrogen and oxygen-containing compounds. "Negative" interactions were observed between 2,4,6-trimethylpyridine and 2,4,6-trimethylphenol and between 2,4,6-trimethylpyridine and n-decanoic acid. However, "positive" interactions were encountered between 2,5-dimethylpyrrole and 2,4,6-trimethylphenol and between 2,5-dimethylpyrrole and n-decanoic acid. The latter was a particularly strong interaction.

Interactions between different types of oxygen-containing compounds were also studied. These included the combination of an acid and a phenol, acid and a ketone, acid and a furan and an ester and a phenol. In all cases, negative interactions were observed. These ranged from moderate to strong.

A noteworthy interaction was observed between 2,5-dimethylpyrrole and n-decanoic acid. These materials produced a visible sludge in deoxygenated JP-5 even when mixed in low levels at ambient temperature. This suggests a potential storage stability problem for jet fuels containing these trace impurities.

The effects of metal surfaces on deposit formation in deoxygenated JP-5 was investigated. Tubes made of Inconel, titanium, copper-nickel, aluminum and a titanium-aluminum-vanadium alloy were substituted for the stainless steel 304 tube which was employed in all previous runs in the Advanced Fuel Unit. The usual temperature zones from 700-1000°F were employed in all cases except with aluminum where lower temperatures were used. Significantly higher deposits were found with all the new materials except the Ti-3Al-2.5 V alloy. Use of this material resulted in about 10% lower deposits than with the SS-304 tube.

1.2 Summary of Work During Phase III

The major effort during the first half of Phase III of this contract was devoted to an investigation of the effects of current fuel additives on deposit formation in deoxygenated JP-5. In addition, the room temperature interaction between a pyrrole and a carboxylic acid was investigated in more detail. The second half of Phase III was concerned with an investigation of dissolved metal effects and with drawing up recommendations for fuel specifications and manufacturing processes.

The room temperature interaction between 2,5-dimethylpyrrole and n-decanoic acid was found to be influenced by both light and the oxygen content of the fuel. In some instances, the amount of sediment formed exceeded the quantity of pyrrole added to the fuel. This suggests other molecules are being incorporated into the sediment. The rates of formation and appearance of the sediments suggest that the mechanism of deposit formation at ambient temperature is different from that which obtains under high temperature conditions. This interaction has implications for the storage of high stability fuel.

The fuel additives studied included three antioxidants, di-sec-butyl-p-phenylenediamine (Dupont #22), 2,6-di-t-butylphenol and 2,6-di-t-butyl-4-methylphenol; a corrosion inhibitor, Hitec-515; and an anti-icing additive, 2-methoxyethanol. The purpose of these tests was to determine whether any of these commonly used additives would prove deleterious to the high temperature stability of deoxygenated JP-5. All were added at the prescribed levels according to military specifications.

The additives studied varied significantly in their effects on the stability of JP-5. Two of the antioxidants, 2,6-di-t-butyl-4-methylphenol and Dupont #22 were not deleterious to fuel stability while the third, 2,6-di-t-butylphenol increased deposit formation by nearly 500%. The corrosion inhibitor, Hitec-115, promoted slightly higher deposit formation (18%) while the anti-icing additive, 2-methoxyethanol, was highly deleterious. The latter caused deposit formation to rise more than 250%.

The effects of dissolved metals on the stability of deoxygenated JP-5 was also investigated. The metals studied were copper (100-200 ppb) iron (10 and 100 ppb) and vanadium (10 ppb). In addition, the effect of benzotriazole, a recommended metal deactivator, and an acid boiling in the jet fuel range, n-decanoic acid were evaluated.

The dissolved metals were generally less deleterious in the deoxygenated fuel as compared with air saturated JP-5. Copper, at a level of 100 ppb, produced about 30% more carbonaceous deposits relative to controls in deoxygenated systems and nearly 80% more in an air saturated fuel. Iron was more deleterious than copper in the deoxygenated fuel. The fuel with 10 ppb iron had about 90% more total carbon relative to controls while at the 10 ppb level, deposits increased by about 160%. Vanadium actually appeared to inhibit deposit formation.

The presence of n-decanoic acid had no observable effect on the tendency for dissolved copper to promote deposit formation in deoxygenated fuel. Benzotriazole had, if anything, a deleterious effect in the same system.

The effects of the various compound classes studied during the overall program have been summarized and their effects on possible new specifications for high stability JP-5 have been pointed out. It appears that new specifications will be needed and new analytical techniques will be required to monitor the quantities of certain trace impurities.

The effects of various refining processes on producing a thermally stable fuel were reviewed and are summarized in this report. Particular attention was paid to those processes such as doctor sweetening, which may produce harmful impurities as well as those, such as hydrofining, which should serve to minimize deleterious species. Recommendations of a general nature as to the last processes were also drawn up and are presented at the conclusion of this report.

2. RECOMMENDATIONS FOR ADDITIONAL WORK

Additional work is recommended in the following areas:

A. Quantitative Work on Compound Types and Trace Impurities to Determine Maximum Tolerable Levels.

- Unsaturated hydrocarbons especially olefins
- Carboxylic acids
- Peroxides
- Sulfides, disulfides and polysulfides

B. Continued Work on Deleterious Interactions

C. Effects of Jet Fuel Additives

- Confirmation of deleterious effects of certain additives
- Compatibility of different additives under high temperature stress

D. Study of Storage Stability of New Synfuels

- Effects of nitrogen compounds
- Effects of light and temperature
- Effects of other compound types including predominant hydrocarbon types

E. Development of New Analytical Techniques for Measurement of Deleterious Trace Impurities

F. Evaluation of Manufacturing Processes to Determine Effectiveness and Cost of Removing Deleterious Trace Impurities

- Petroleum derived JP-5
- New synfuels

3. INTRODUCTION

As the Mach number of supersonic aircraft increases, the airframe skin temperature and engine inlet temperature increase rapidly. The net result is that the fuel is exposed to greater and greater thermal stress as the speed of the aircraft increases. If the fuel fails under thermal stress the aircraft can be rendered inoperable in a variety of ways, e.g., degraded fuel can form deposits and sediments which can markedly lower heat transfer coefficients in key areas and/or plug narrow tolerance parts and filters. For a high speed airplane operating at Mach 4.5, ram air temperatures are in the range of 1400°F. In such situations, the fuel is the only material present which can be used as a heat sink for cooling.

The question of the stability of the fuel used in a high speed aircraft is complex for two reasons. First, there is a large number of potential problem areas in which it can be exposed to a severe but different stress. And, second, the chemical reactions and physical processes which occur during fuel degradation which ultimately result in the formation of sediment and deposits are themselves quite complex.

Exxon Research and Engineering Company carried out a comprehensive analysis for the Navy of the fuel requirements for high speed aircraft in a program entitled "Investigation and Analysis of Advanced Hydrocarbon Fluids" (1). Inputs to this analytical study included extensive conversations with engine-airframe manufacturers and both open literature and in-house Exxon Research fuel stability information. Factors considered include trade-offs between engine-airframe design parameters and fuel properties. Also tradeoffs among various fuel properties themselves involved in various fuel modification approaches were analyzed. This analysis concluded that presently used JP-5 fuel was inadequate for aircraft in the Mach 4 to 5 range. High temperature thermal stability was determined to be the key problem and led to the conclusion that "High Stability JP-5" fuel must be developed.

As a result, Exxon Research and Engineering Company proposed a program to develop a "High Stability JP-5" fuel for high speed aircraft. This "High Stability JP-5" is to have essentially the same hydrocarbon composition as present JP-5. Thus, physical properties such as volumetric heat of combustion, boiling range and freezing point will be the same, and "High Stability JP-5" fuel will have the capability to be used in lower speed aircraft interchangeably with regular JP-5. In addition, the intrinsic availability of "High Stability JP-5" will be the same as present JP-5, and its cost will be considerably lower than specialty fuels.

The program to develop High Stability JP-5 was framed in the context of an extended effort involving bench scale studies of fuel modifications necessary to improve the thermal stability of JP-5 type fuels so

that fuel production specifications and storage and handling techniques can be established. Fuel modifications investigated included removal and exclusion of molecular oxygen (O_2), control of trace levels of organic sulfur, nitrogen and oxygen compounds, control of olefin compound type and level, reduction of dissolved metals, control of metal surface type contacting the fuel, and the use of additives.

This report summarizes the results obtained in the final phase (Phase III) of this program. Included are effects of jet fuel additives and dissolved metals. Finally, taking into account findings from the entire program, some general recommendations for fuel specification changes, preferred manufacturing processes, and storage and handling techniques are presented.

4. ROOM TEMPERATURE INTERACTION BETWEEN A PYRROLE AND A CARBOXYLIC ACID

During Phase II of this contract a room temperature interaction between 2,5-dimethylpyrrole and n-decanoic acid was reported (2). It was observed that when these two compounds were mixed at levels of 100 ppm (N and O basis) in deoxygenated JP-5 an immediate darkening of the fuel resulted and, in a short time, a flocculent sediment or sludge appeared. Although a darkening of the fuel was observed if the pyrrole was added alone, the rate at which it occurred was lower than in the presence of the carboxylic acid. Neither the base fuel nor the fuel containing the acid alone showed any tendency to darken or to produce sediment. Since these observations have significance with respect to the storage stability of high stability fuels it was deemed advisable to study the interaction in somewhat more detail.

Samples of JP-5 (500 g) containing various amounts and combinations of 2,5-dimethylpyrrole and n-decanoic acid were deoxygenated by helium sparging and then stored in glass containers both in sunlight and in the dark. Corresponding solutions of air-saturated fuel were handled similarly. The containers were removed from storage periodically, filtered and replaced. The sediment recovered was dried, weighed and examined.

The results of these experiments are shown in Table 1 and Figure 1. Rapid darkening and significant amounts of sediment were obtained in all samples containing the pyrrole on the pyrrole plus acid. The fuel with no additives or with the acid alone, afforded no sediment and

TABLE 1

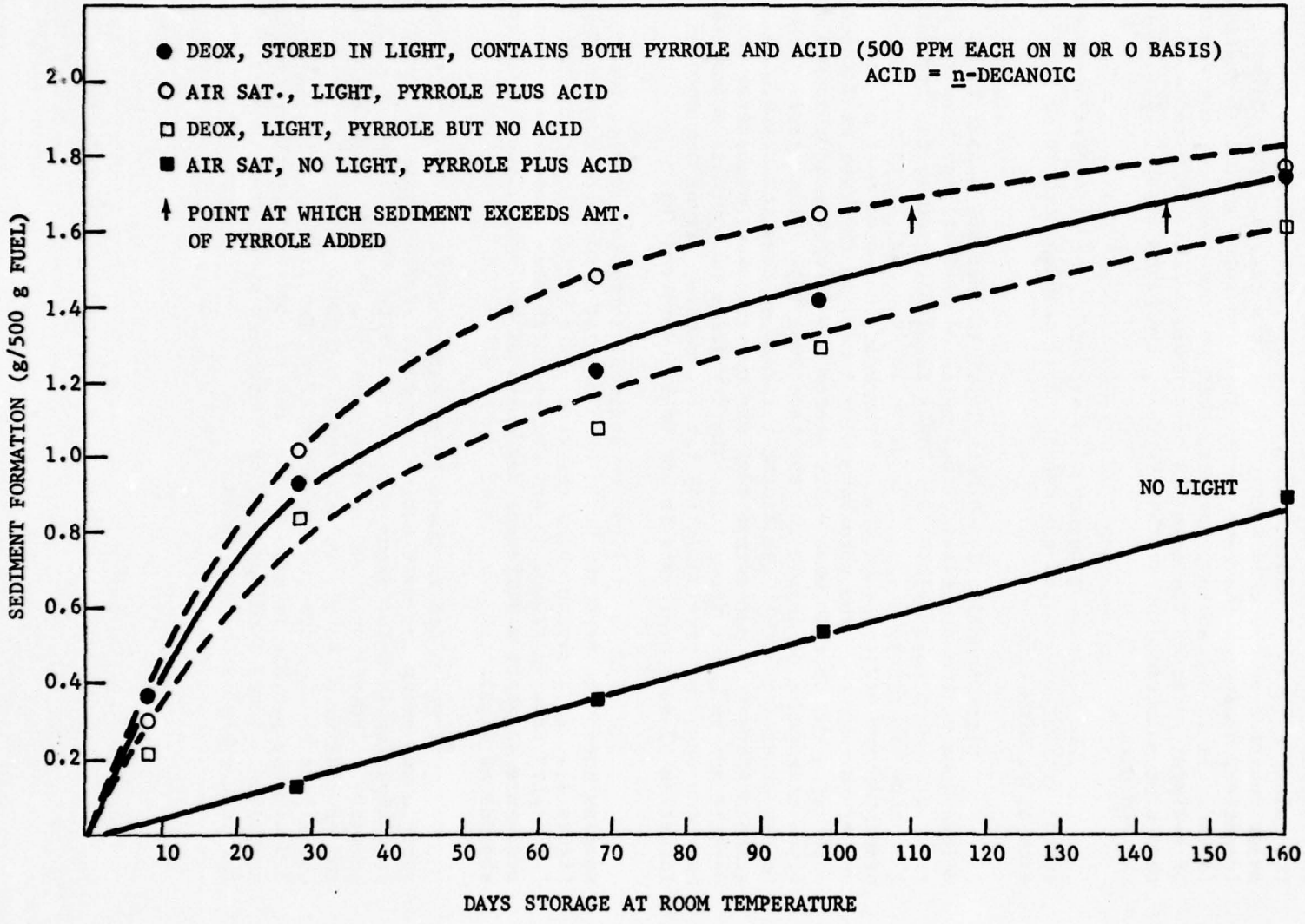
EFFECTS OF 2,5-DIMETHYLPYRROLE (DMP) AND n-DECANOIC ACID ON SEDIMENT FORMATION IN JP-5*

Presence Of				Sediment (g/500g Fuel) At	
DMP	Acid	Oxygen	Light	28 Days	160 Days
2000 ppm	2000 ppm	-	+	2.61	4.07
2000 ppm	2000 ppm	+	+	3.43	5.39
500 ppm	---	-	+	0.81	1.62
500 ppm	---	+	-	0.98	1.73
500 ppm	500 ppm	-	+	0.92	1.75
500 ppm	500 ppm	+	+	1.10	1.74
500 ppm	500 ppm	-	-	0.38	0.92
100 ppm	100 ppm	-	+	0.30	0.31
100 ppm	100 ppm	+	+	0.28	0.28
50 ppm	50 ppm	-	+	0.14	0.15
50 ppm	50 ppm	+	+	0.18	0.20
---	---	+	+	--	--
---	500 ppm	+	+	--	--

* Stored at room temperature.

FIGURE 1

SEDIMENT FORMATION IN JP-5 UNDER INFLUENCE OF DIMETHYLPYRROLE



only slight darkening was observed even after 160 days storage (Table 1). The relative rates of sediment formation are shown in Figure 1. The major function of the acid appears to be as a catalyst for sediment formation, enhancing the rate rather than the total amount of sediment formed. It is noteworthy, however, that in some instances the amount of sediment exceeded the quantity of pyrrole added. This indicates that some molecules, other than pyrrole, are being incorporated into the sediment.

The effects of oxygen also appears to be catalytic since the curves for the oxygenated and deoxygenated samples tend to approach each other with time.

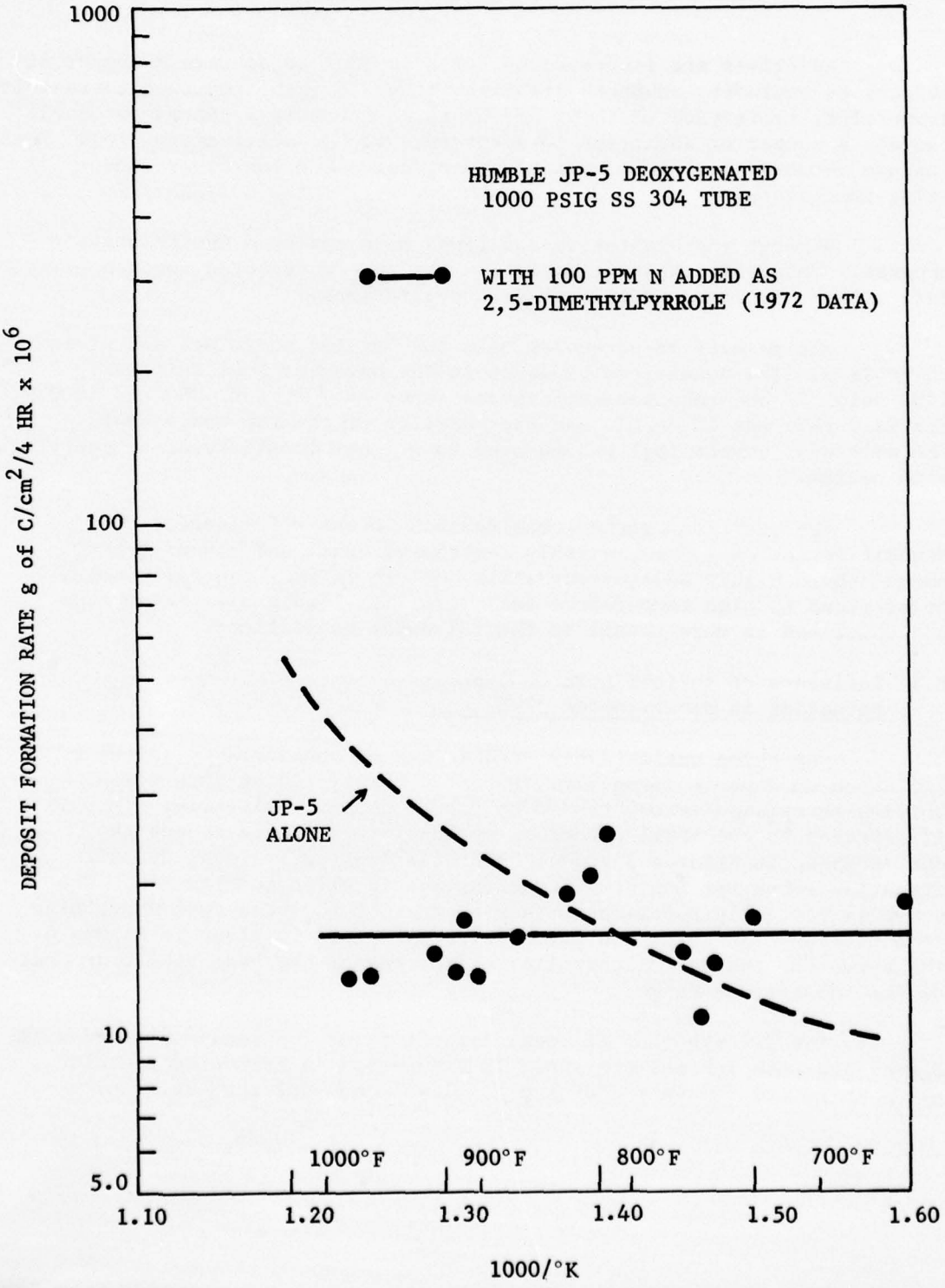
Significantly, 2,5-dimethylpyrrole does not appear to be deleterious to the stability of deoxygenated JP-5 at high temperatures at least when present alone (3). This is illustrated by the Arrhenius plot shown in Figure 2 (3). The curve for the fuel containing 2,5-dimethylpyrrole lies below that of the base fuel over most of the temperature range. The total deposits formed in the case of the fuel doped with the pyrrole were 1,310 micrograms of carbon as compared with 1,485 micrograms of carbon for the base fuel (3). This result, added to the observation that the sediment formed at room temperature is quite different in appearance suggests two different mechanisms for deposit and sediment formation. The formation of pyrrolic sediments has been observed previously (4) but the nature, extent and mode of formation of such sediments is not well understood (4).

The effects of light on sediment formation is also interesting. Samples stored in darkness build up sludge at a much lower rate (Table 1, Figure 1). In addition, both the rate of formation (straight line for "no light" case in Figure 1) and different physical appearance of the sediments suggests a different mechanism of sediment formation in the absence of light.

It was noted in Phase II of this project (2) that 2,5-dimethylpyrrole was among the most active compounds studied with respect to participating in deleterious interactions with other trace impurities. Moderate to strong positive interactions were observed between the pyrrole and an olefin, a phenol, an acid and a thiophene under the high temperature conditions of the Advanced Fuel Unit (2). The present data indicate that 2,5-dimethylpyrrole is also deleterious to ambient temperature storage stability. These findings must be considered when establishing specifications for future high stability fuels.

FIGURE 2

EFFECT OF 2,5-DIMETHYLPYRROLE ON DEPOSIT FORMATION IN DEOXYGENATED JP-5 AT HIGH TEMPERATURES



5. EFFECTS OF JET FUEL ADDITIVES ON DEPOSIT FORMATION IN DEOXYGENATED JP-5

Additives are incorporated into jet fuel to achieve a number of objectives including enhanced stability toward oxygen, improved corrosivity properties, resistance to icing and improved lubricity. Naval jet fuels contain a number of additives in accordance with specifications (5). These include antioxidants, metal deactivators, corrosion inhibitors and icing inhibitors.

Several representative additives were employed in the present program. These are shown in Table 2. The levels selected for use fall within the range of allowable concentrations.

The results of screening with the various additives are given in Table 3. The conditions employed in the Advanced Fuel Unit were 1000 psig, SS 304 tube and temperature zones at 700, 800, 900 and 1000°F. The feed rate was 10 cc/min and the duration of the run was 4 hours. The molecular oxygen (O_2) was reduced to <1 ppm in all cases by sparging with helium.

The additives varied considerably in their influences on deposit formation. Some, notably 2-methoxyethanol and 2,6-di-t-butylphenol where highly deleterious while the others were generally not deleterious to high temperature fuel stability (Table 3). These runs are described in more detail in the following subsections.

5.1 Influence of Antioxidants on Deposit Formation in Deoxygenated JP-5

The three antioxidants studied varied considerably in their influence on deposit formation. Dupont #22 antioxidant (N,N-di-s-butyl-p-phenylenediamine) tended to reduce deposits slightly. This is illustrated by the total amount of carbon formed (Table 3) and the curves shown in Figures 3 and 4. The distribution of local deposit formation rates for Dupont #22 antioxidant is given in Figure 3. The curve is virtually superimposable with that of the base fuel containing no additives. An Arrhenius plot of the same data is given in Figure 4. The curve for the antioxidant lies below that of the base fuel over most of the temperature range.

The distribution of local deposit formation rates obtained with 2,6-di-t-4-methylphenol are shown in Figure 5. An Arrhenius plot is given in Figure 6. This additive is clearly non-deleterious.

TABLE 2

JP-5 ADDITIVES EMPLOYED IN ADVANCED FUEL UNIT STABILITY TESTS

Additive	Function	Concentration Range Permitted (a)	Level Used in Test
N,N-Di-s-butyl-p-phenylenediamine (Dupont #22)	Antioxidant	up to 31 ppm (b)	20 ppm
2,6-Di-t-butylphenol	Antioxidant	up to 31 ppm (b)	20 ppm
2,6-Di-t-butyl-4-methylphenol	Antioxidant	up to 31 ppm (b)	20 ppm
Hitec-515 (Monsanto Chem. Co.)	Corrosion Inhibitor	18-57 ppm (c)	45 ppm
2-Methoxyethanol	Anti-icing Additive	up to 0.15 Vol. % (b)	0.124 Vol. %

(a) Concentrations on a weight basis

(b) According to MIL-T-5624K

(c) According to QPL-20517-E

TABLE 3

EFFECTS OF JET FUEL ADDITIVES ON DEPOSIT FORMATION IN DEOXYGENATED JP-5

Additive	Function	Total Carbonaceous Deposits (a)	
		Micrograms Carbon	As ppm Based on Fuel
N,N-Di-s-butyl-p-phenylenediamine (Dupont #22)	Antioxidant	1271	.66
2,6-Di-t-butylphenol	Antioxidant	8493	4.40
2,6-Di-t-butyl-4-methylphenol	Antioxidant	1465	.76
Hitec-515	Corrosion Inhibitor	1747	.91
2-Methoxyethanol	Anti-icing Additive	5468	2.84
None		1485 (b)	.77

(a) Cummulative deposits formed in a 4 hour run in the Advanced Fuel Unit. Conditions: 1000 psig, SS 304 tube, Zone 1 - 700°F, Zone 2 - 800°F, Zone 3 - 900°F, Zone 4 - 1000°F.

(b) Adjusted for missing rate value.

FIGURE 3

DEPOSIT FORMATION WITH DUPONT #22 ANTIOXIDANT

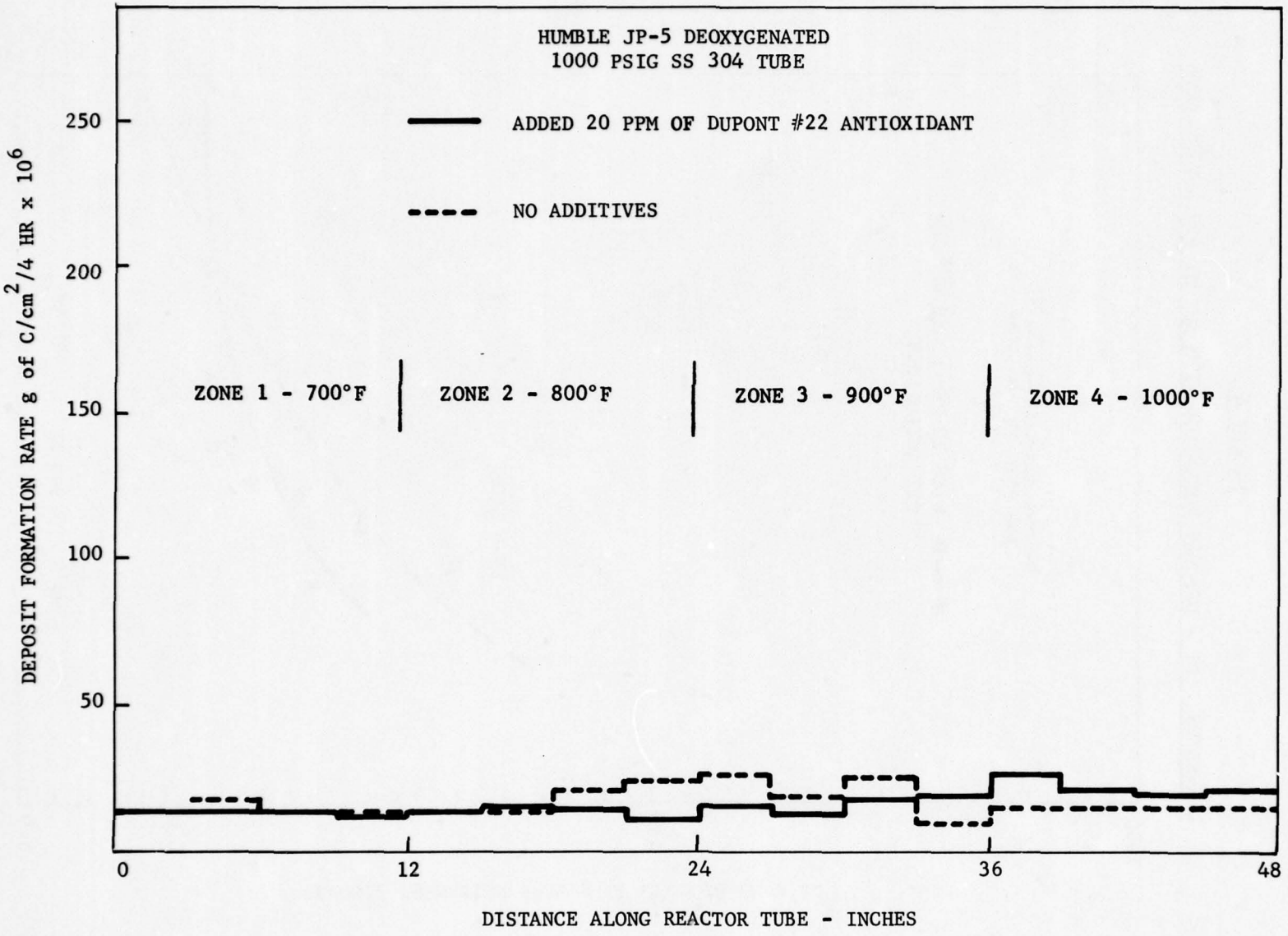


FIGURE 4

ARRHENIUS PLOT - DEPOSIT FORMATION WITH DUPONT #22 ANTIOXIDANT

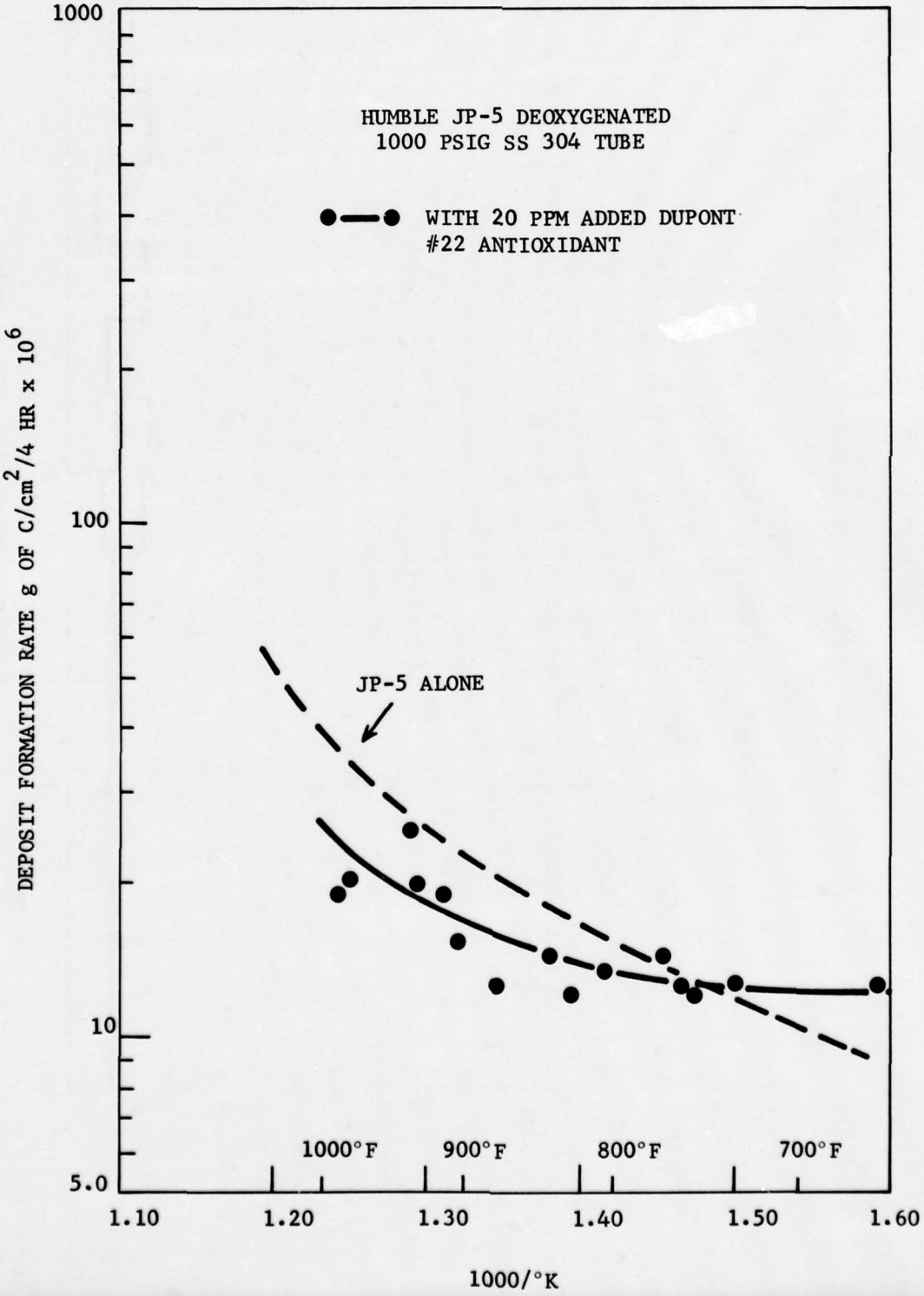
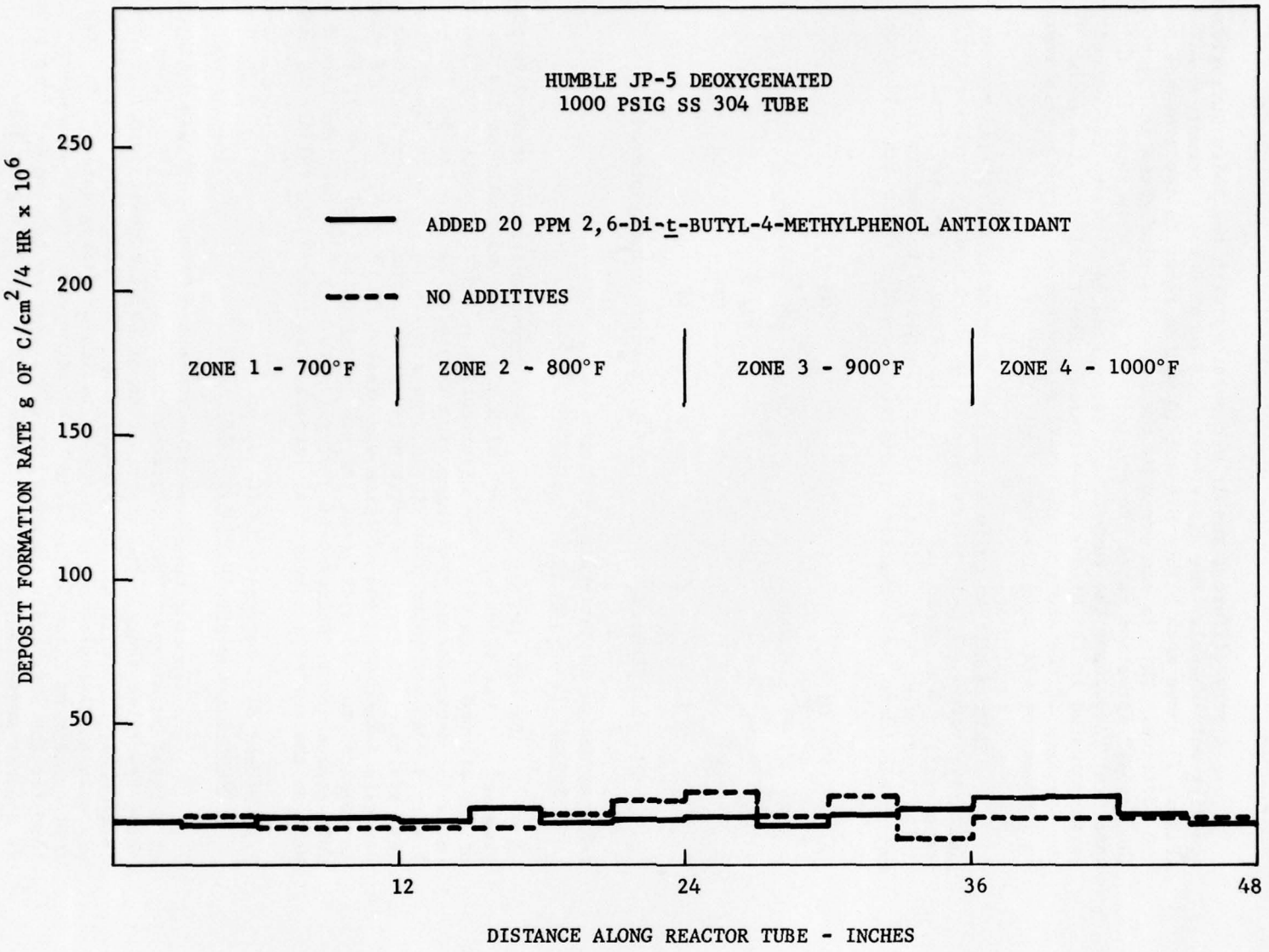


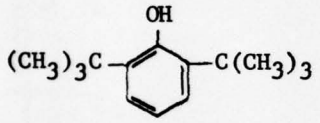
FIGURE 5

DEPOSIT FORMATION WITH 2,6-Di-t-BUTYL-4-METHYLPHENOL ANTIOXIDANT



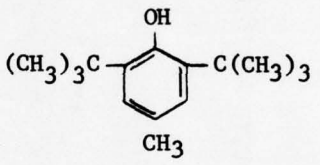
A very different result was obtained with the third antioxidant, 2,6-di-t-butylphenol. The distribution of local deposit formation rates (Figure 7) shows much higher deposit formation rates in the presence of the additive. This is confirmed by the Arrhenius plot given in Figure 8. The deposit formation rates are considerably higher than those for the base fuel throughout the temperature range studied although the effect is accentuated at the higher temperatures. The total deposits formed in the presence of the additive were 8493 micrograms of carbon. This represents an increase of 472% over the base fuel (Table 3).

This result is quite surprising in view of the close structural similarity between 2,6-di-t-butylphenol (I) and 2,6-di-t-butyl-4-methylphenol (II). The latter had no noticeable effect on deposit formation (Table 3, Figures 5,6). Additional work is needed to confirm this finding and to elucidate the mechanism of deposit formation under the influence of phenols such as I:



I

2,6-Di-t-butylphenol



II

2,6-Di-t-butyl-4-methylphenol

5.2 Effect of an Anti-icing Additive on Deposit Formation in Deoxygenated JP-5

The anti-icing inhibitor, 2-methoxyethanol, was studied in this program. It was added at a level of 0.124 volume percent near the top of the allowed range (5). The distribution of local deposit formation rates for deoxygenated JP-5 containing this additive are plotted in Figure 9. An Arrhenius plot of the same results is given in Figure 10. This additive appears to be quite deleterious. The total carbonaceous deposits formed when the additive was present in the fuel were 5468 micrograms as compared to 1485 micrograms for the deoxygenated fuel alone (Table 3). This represents an increase of 3983 micrograms or 268% over the base fuel. Most of the increase occurred at temperatures over 750°F (Figures 9 and 10).

5.3 Effect of a Corrosion Inhibitor on Deposit Formation in Deoxygenated JP-5

The commonly used corrosion inhibitor "Hitec-515" was employed at a level of 45 ppm. The conditions in the Advanced Fuel Unit were those described above. The distribution of local deposit formation rates is given in Figure 11 and the Arrhenius plot in Figure 12. This additive was only mildly deleterious to the stability of deoxygenated JP-5. The fuel containing Hitec-515 produced 1747 micrograms of carbon compared to 1485 for the base fuel. However, it did appear to be somewhat more prone to deposit formation in the lower temperature range (Figure 12).

In general, it appears that some additives are deleterious while others do not promote deposit formation. They will have to be evaluated as an individual basis before being incorporated into fuels for high speed aircraft.

FIGURE 6

ARRHENIUS PLOT - DEPOSIT FORMATION WITH
2,6-Di-t-BUTYL-4-METHYLPHENOL ANTIOXIDANT

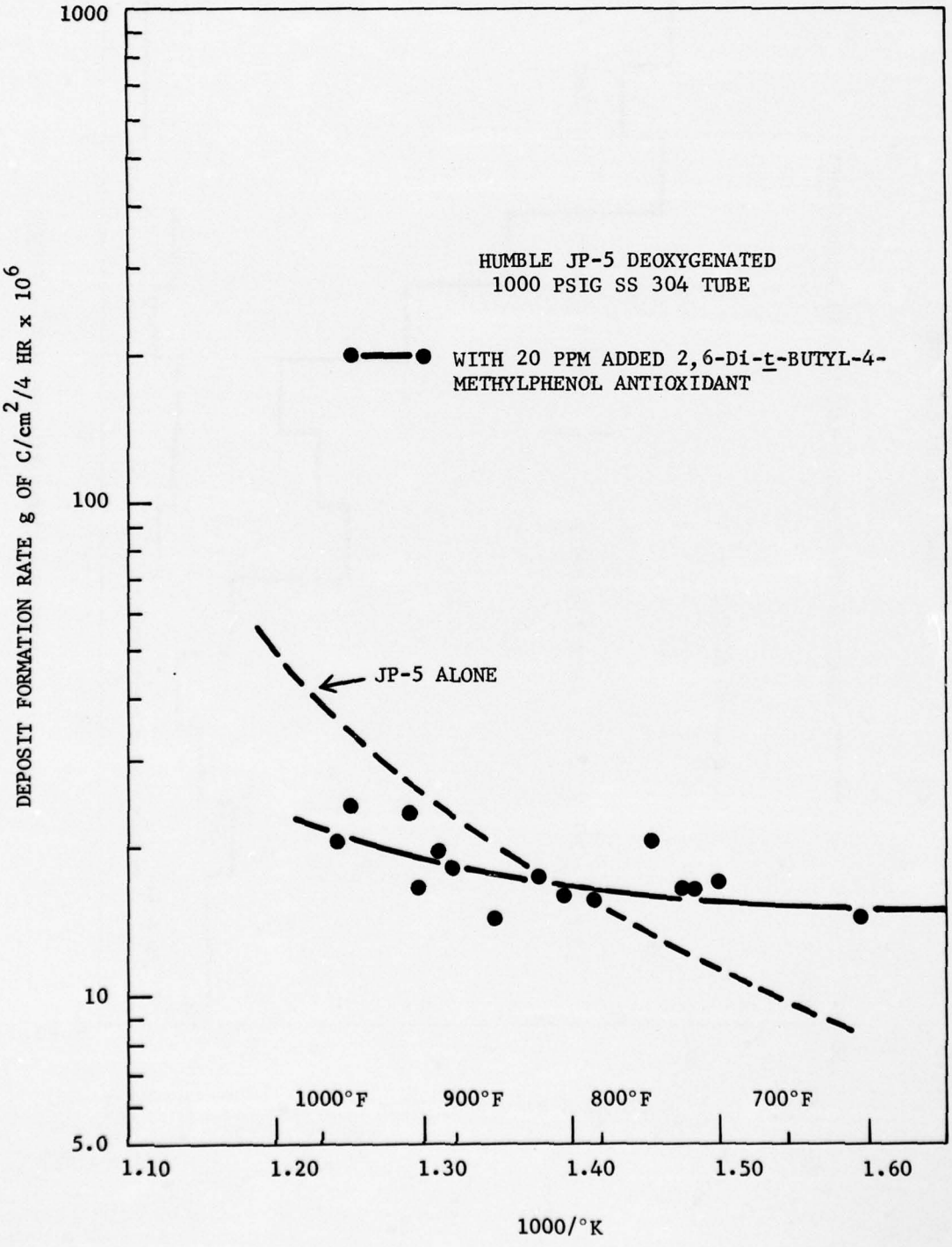


FIGURE 7

DEPOSIT FORMATION WITH 2,6-Di-t-BUTYLPHENOL ANTIOXIDANT

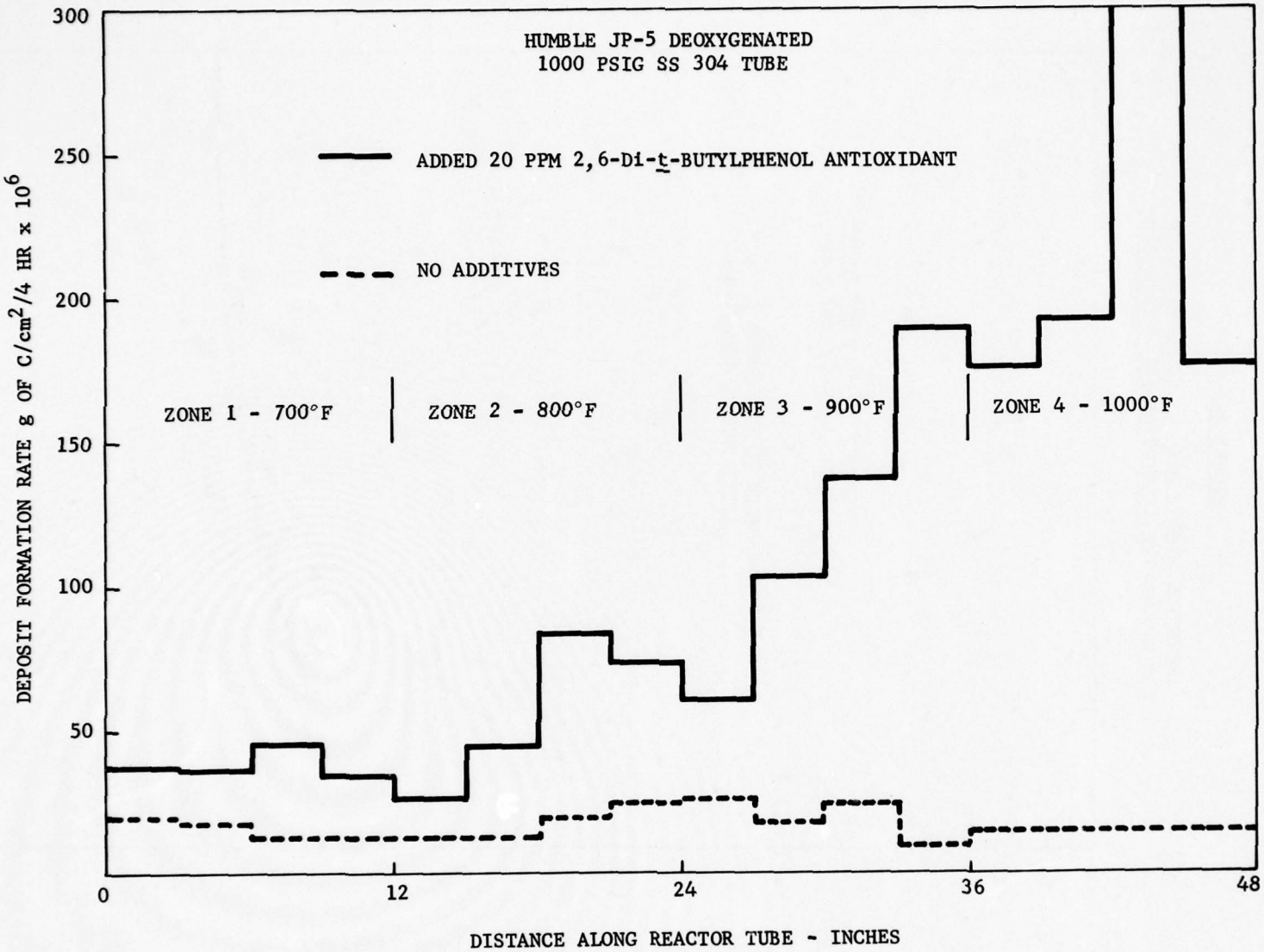


FIGURE 8

ARRHENIUS PLOT - DEPOSIT FORMATION WITH
2,6-Di-t-BUTYLPHENOL ANTIOXIDANT

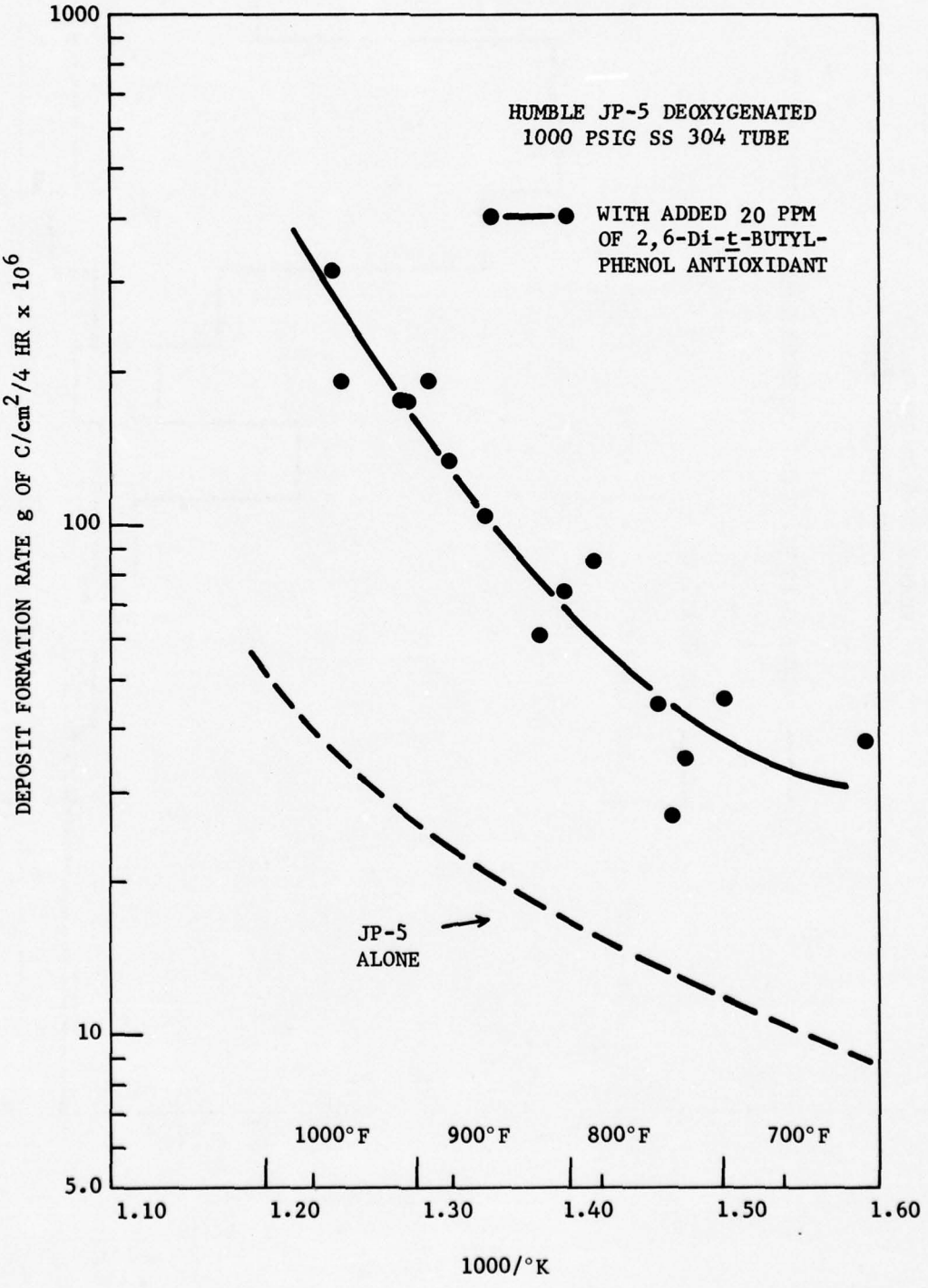


FIGURE 9

DEPOSIT FORMATION WITH 2-METHOXYETHANOL ICING INHIBITOR

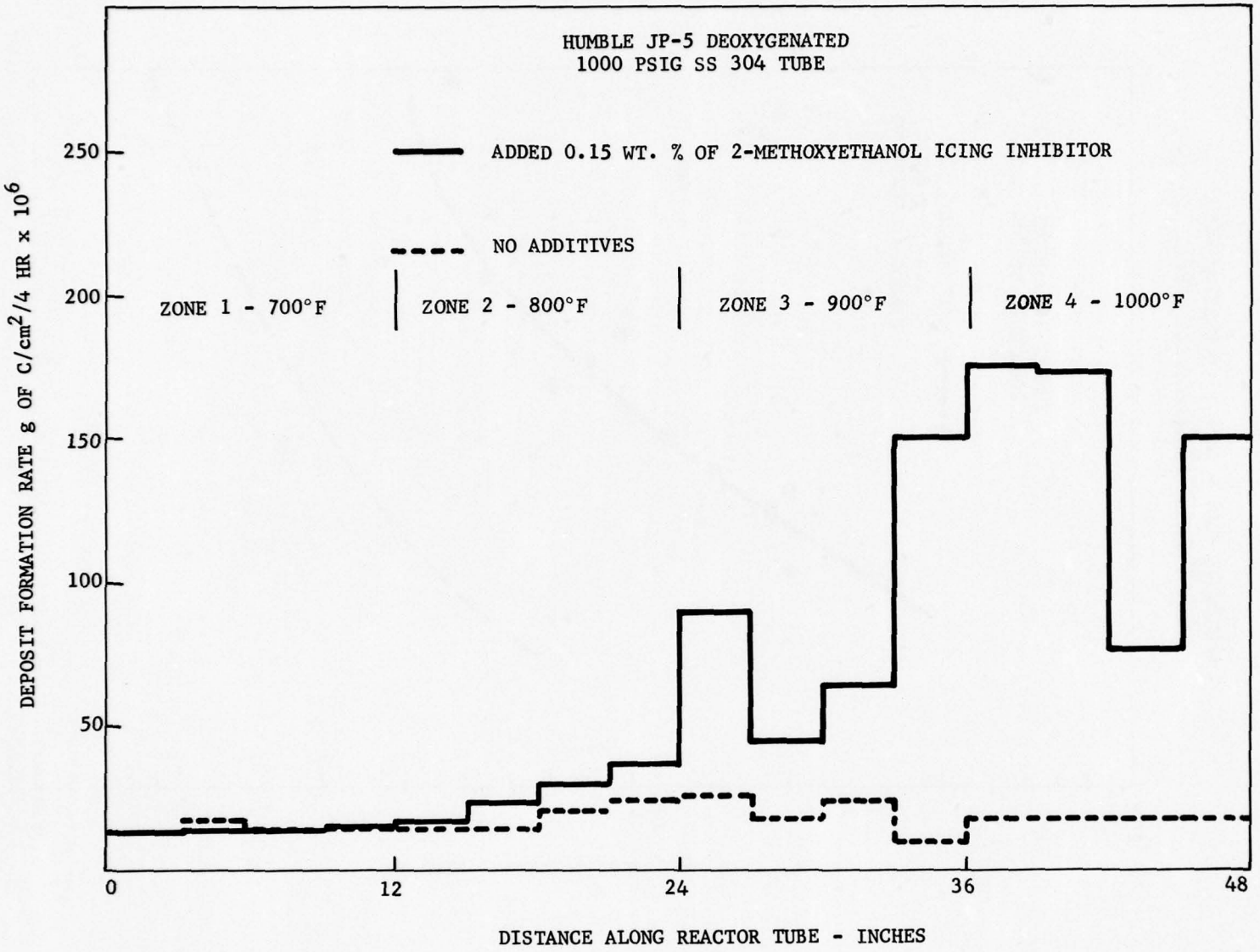


FIGURE 10

ARRHENIUS PLOT - DEPOSIT FORMATION WITH
2-METHOXYETHANOL ICING INHIBITOR

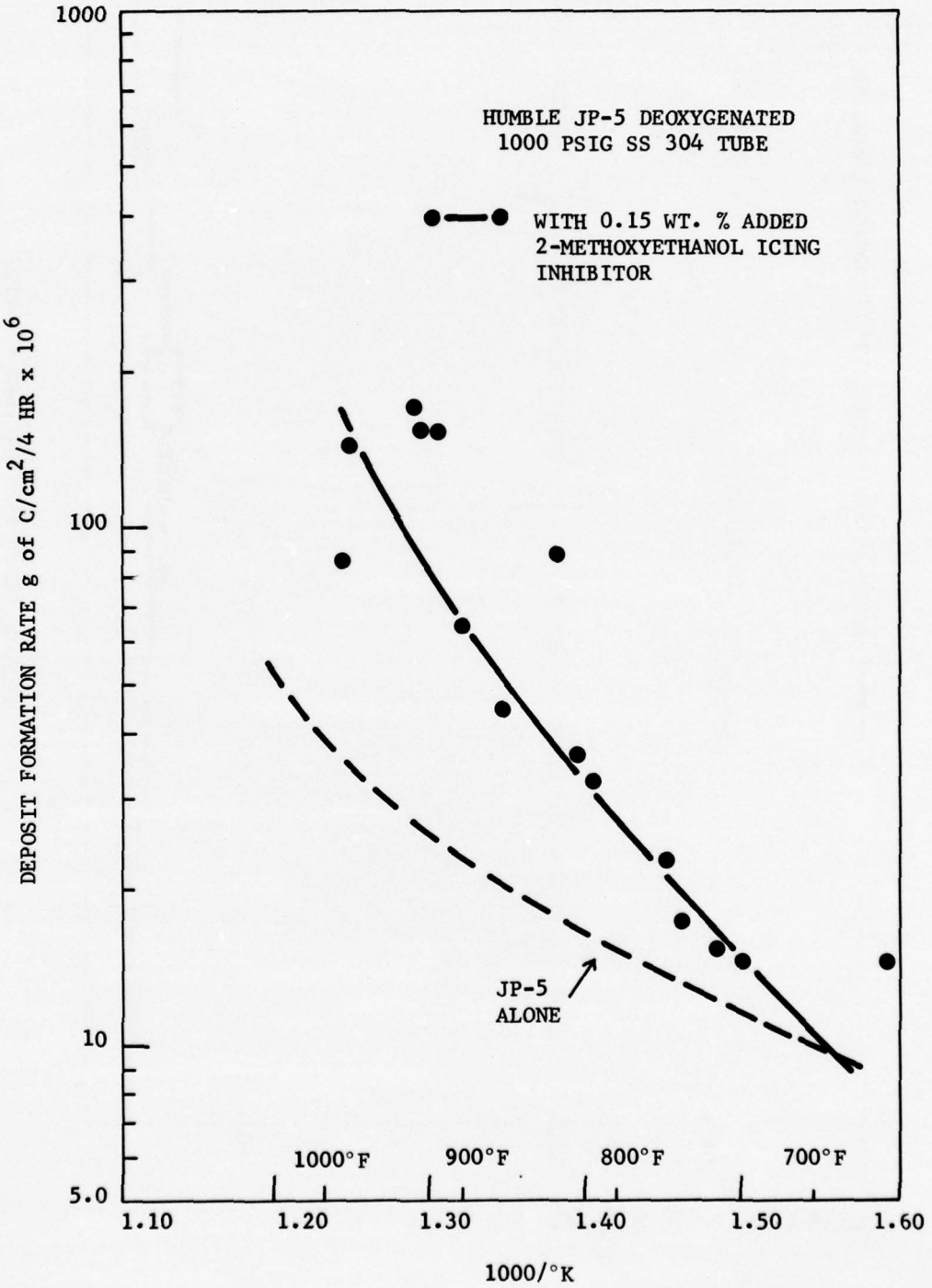


FIGURE 11

DEPOSIT FORMATION WITH "HITEC 515" CORROSION INHIBITOR

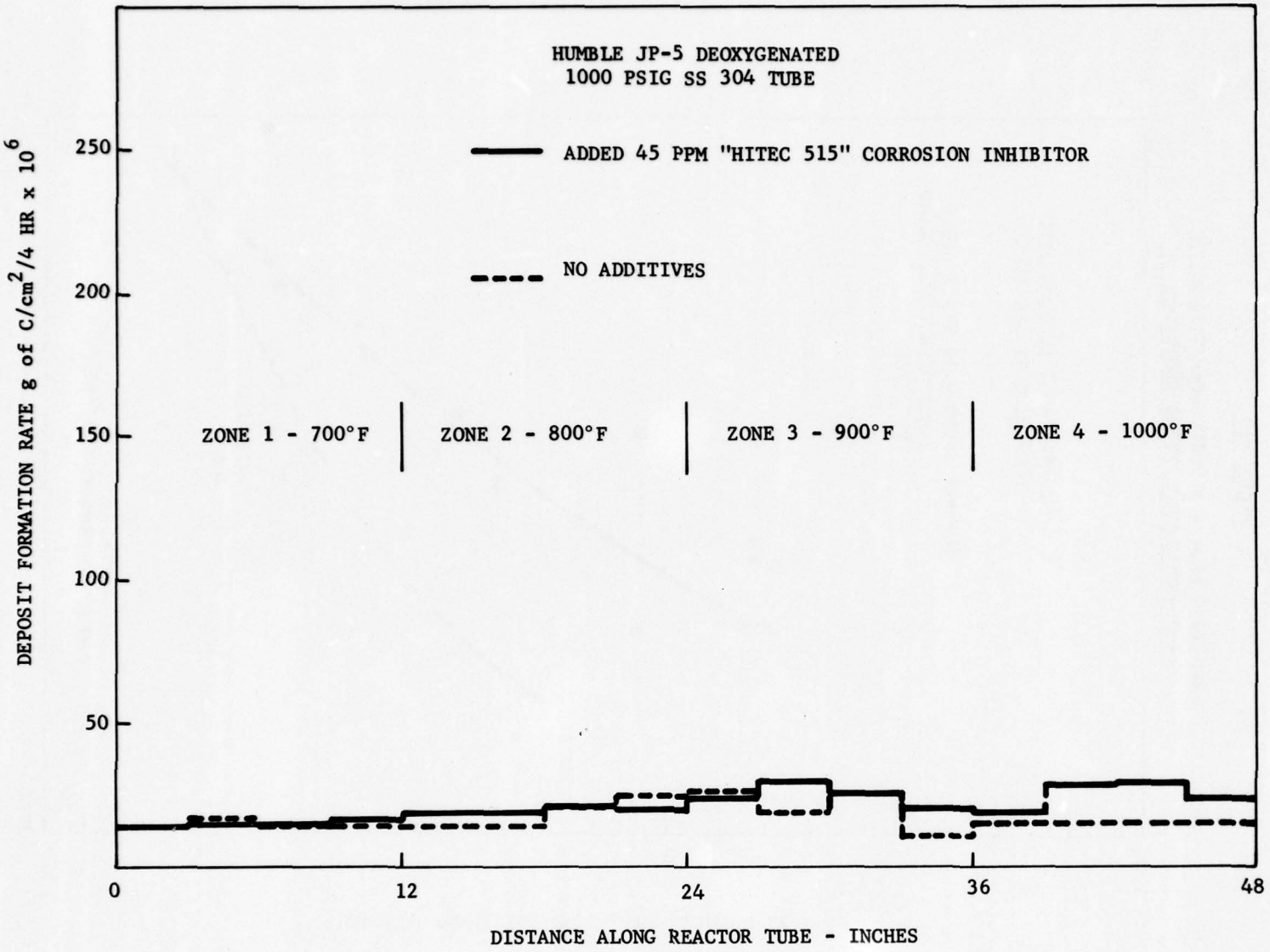
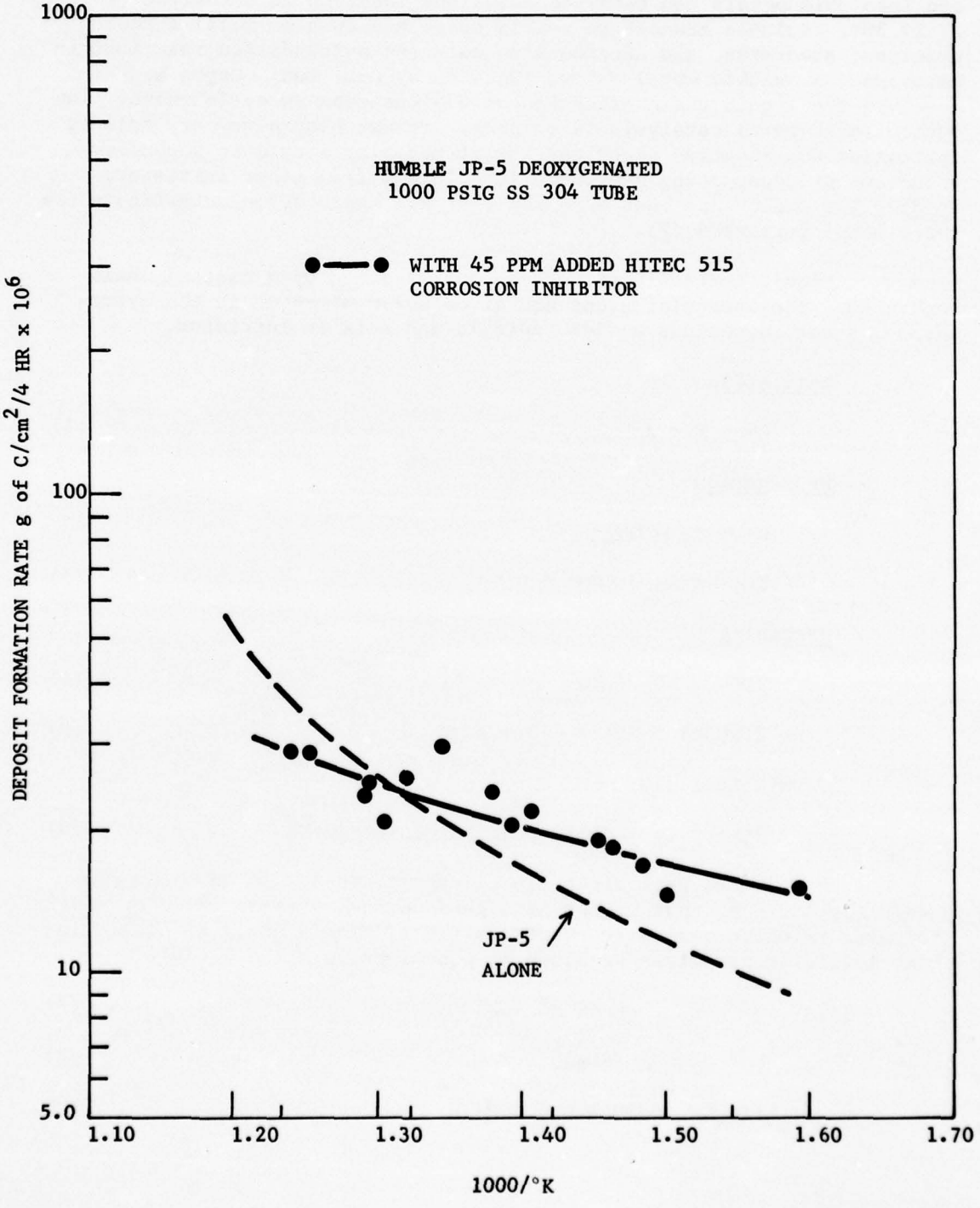


FIGURE 12

ARRHENIUS PLOT - DEPOSIT FORMATION WITH "HITEC 515" CORROSION INHIBITOR



6. EFFECTS OF DISSOLVED METALS ON DEPOSIT FORMATION IN DEOXYGENATED JP-5

It has been widely shown in the literature that both soluble and insoluble metals can catalyze reactions involved in autoxidation (6-8, 27, 29, 30). Soluble transition metals compounds such as metal phthalocyanines, stearates, and naphthenates catalyze autoixdation reactions in kerosene. Insoluble metal oxides (9) such as CuO, MnO_2, Cr_2O_3 and NiO catalyze the liquid phase oxidation of olefins such as cyclohexene. The mechanism of metal catalysis is complex. It may play a primary role by initiating autoxidation reactions, or it may play a role in secondary processes by decomposing hydroperoxides formed from other initiators (6-8). The theory has been advanced that all hydrocarbon autoxidants are trace metal catalyzed (7).

Liquid hydrocarbons undergo autoxidation by a radical chain mechanism. The essential steps are given below where RH is the hydrocarbon, a dot represents a free radical, and X is an initiator.

Initiation

$$RH + X \rightarrow R\cdot \quad (1)$$

Propagation

$$R\cdot + O_2 \rightarrow RO_2\cdot \quad (2)$$

$$RO_2\cdot + RH \rightarrow ROOH + R\cdot \quad (3)$$

Branching

$$ROOH \rightarrow RO\cdot + HO\cdot \quad (4)$$

$$\text{or } 2(ROOH) \rightarrow RO\cdot + H_2O + RO_2\cdot \quad (5)$$

Termination

$$2(R\cdot, RO_2\cdot, RO\cdot) \rightarrow \text{Nonradical products} \quad (6)$$

Metals can participate in all these steps. It has been proposed, for example, that copper is a good chain initiator while iron participates in chain branching reactions (29). Metals can participate in chain initiator reactions as shown in equations 7, 8 and 9 (30):

$$M^{2+} + RH \rightarrow R\cdot + M^{+} + H^{+} \quad (7)$$

$$M^{2+} + O_2 \rightleftarrows (MO_2)^{2+} \quad (8)$$

$$(MO_2)^{2+} + RH \rightarrow M^{2+} + R\cdot\ HO_2\cdot \quad (9)$$

and in propagation or branching as shown in reactions 10 and 11 (30):

$$M^{2+} + ROOH \rightarrow M^{2+} + RO\cdot + OH^{-} \quad (10)$$

$$M^{3+} + ROOH \rightarrow M^{2+} + RO_2\cdot + H^{+} \quad (11)$$

Metals can also participate in chain termination (6,30). If so, they would actually be inhibitor to autoxidation. Apparently, in some cases, inhibition can occur (30). At any rate, all previous work has been carried out with oxygenated systems. Therefore, it was considered important to determine the effect of dissolved metals on the thermal stability of deoxygenated JP-5.

The metals chosen for study were copper vanadium and iron. These are considered most likely to be present in jet fuels as a result of leaching out of fuel lines from high speed aircraft. In addition, the effect of a metal deactivator, benzotriazole, was evaluated as well as n-decanoic acid, a possible catalyst.

The test matrix employed is shown in Table 4. The levels of each metal chosen for study are those which have been observed in jet fuels (31). The solutions studied were obtained by dissolving the appropriate quantity of finely divided metal powder in Humble JP-5 fuel. The fuel was then deoxygenated to <1 ppm O_2 by spargin with helium. The conditions employed in the Advance Fuel Unit for all runs were 1000 psig, SS-304 tube and temperature zones at 700, 800, 900 and 1000°F. The feed rate was 10 cc/min and the duration of the run was four (4) hours.

Since the fuel had been stored for some time since the previous runs, a new standard run was made with deoxygenated fuel containing no additives. The results of this run are shown in Table 5 and Figures 13 and 14. These results were used as a standard comparison of the effects of all dissolved metals.

6.1 Effects of Dissolved Copper

Since metals most likely cause increased deposit formation by catalyzing autoxidation, it might be anticipated that their effects will be much less noticeable in deoxygenated systems. This is apparently the case as the data in Table 5 and Figures 15 and 16 show. In deoxygenated systems, the presence of 100 ppb dissolved copper produced only 30% more carbonaceous deposits in deoxygenated systems. This increase was distributed fairly evenly throughout the temperature range (Figure 16). In air saturated fuel, the same level of copper produced an increase in deposit of about 80% over the base fuel.

At the 200 ppb level, dissolved copper produced more than double the carbonaceous deposits than those observed in the standard fuel (Table 5, Figures 18 and 19). In this case the increased deposit formation was somewhat greater at higher temperatures (Figure 19). The general shapes of all curves are similar; however, (Figures 18 and 20). This suggests a similar mechanism of carbon formation in all three cases.

TABLE 4

MATRIX FOR STUDY OF EFFECTS OF DISSOLVED
METALS ON DEPOSIT FORMATION IN DEOXYGENATED JP-5

Metals	Fuel		Addn. of (ppm)	
	Air Sat.	Deoxygenated	Benzotriazole (10)	n-Decanoic Acid (100)
Copper				
100 ppb	X	X	X*	X*
200 ppb		X		
Iron				
10 ppb		X		
100 ppb		X		
Vanadium				
10 ppb		X		

Conditions to be used in the Advanced Fuel Unit: 1000 psig, zones at 700, 800, 900, and 1000°F, SS 304 tube, 4 hour run, 10 cc/min. feet rate. Fuel deoxygenated to less than 1 ppm O_2.

* using deoxygenated fuel.

TABLE 5

EFFECTS OF DISSOLVED METALS ON
HIGH TEMPERATURE STABILITY OF HUMBLE JP-5

Additive	Level	Total Carbonaceous Deposits[a]	
		Micrograms Carbon	As ppm Based on Fuel
None		2263	1.17
Copper	100 ppb	2963	1.53
	200 ppb	4763	2.46
	100 ppb[b]	4006	2.07
Iron	10 ppb	4240	2.19
	100 ppb	5853	3.02
Vanadium	100 ppb	1118	0.58
Copper (100 ppb) plus n-decanoic acid (100 ppm O)		2501	1.29
Copper (100 ppb) plus benzotriazole (10 ppm) [c]		5490	2.84

(a) Cumulative deposits formed in a 4 hour run in the Advanced Fuel Unit. Conditions: <1000 psig, SS 304 tube, 700-1000°F. All fuels deoxygenated to 1 ppm O_2 unless otherwise noted.
(b) Air saturated, O_2 > 50 ppm.
(c) Calculated as benzotriazole.

FIGURE 13

DEPOSIT FORMATION IN DEOXYGENATED JP-5 ALONE (STANDARD RUN)

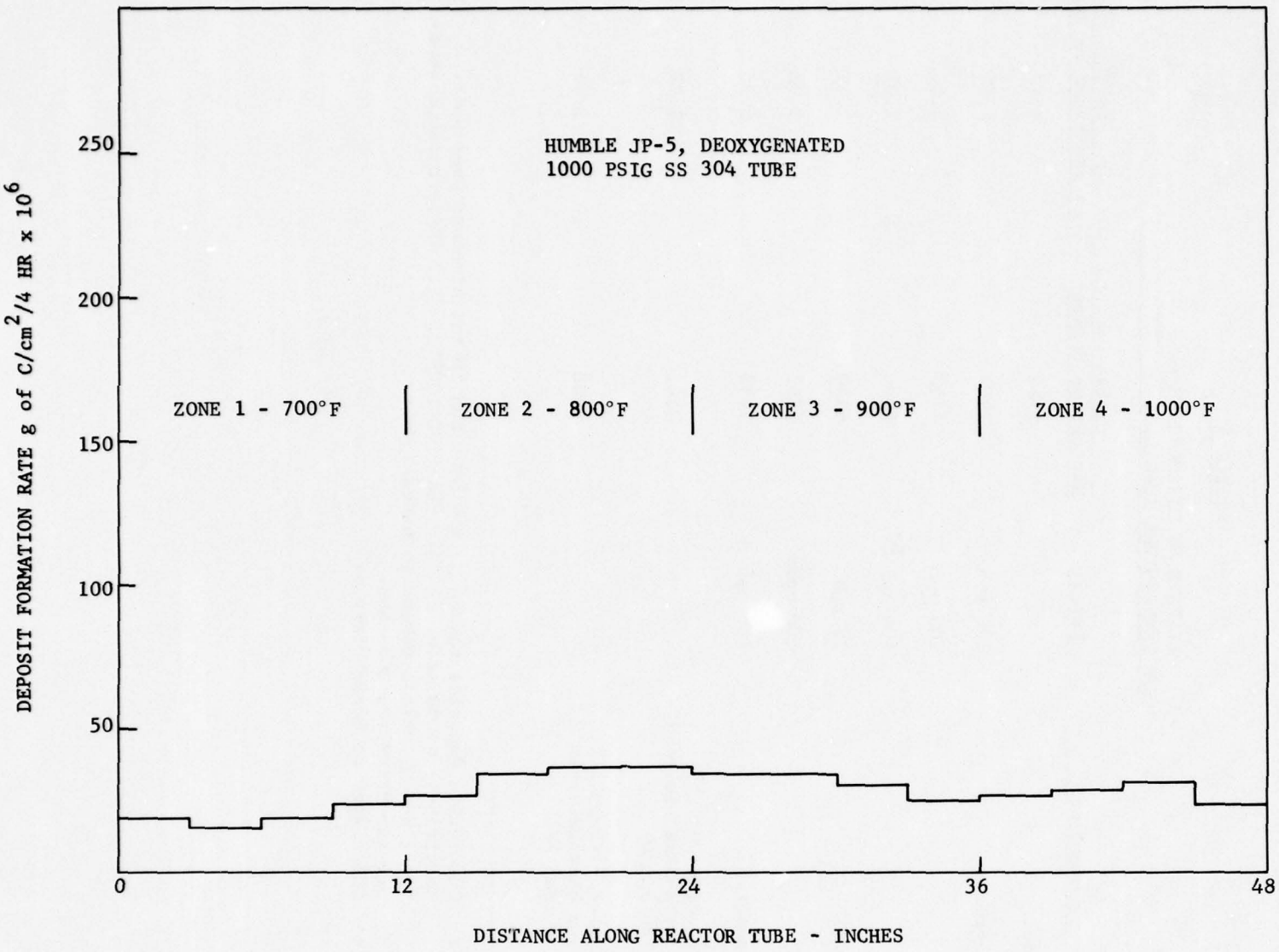


FIGURE 14

ARRHENIUS PLOT - DEPOSIT FORMATION WITH DEOXYGENATED JP-5 ALONE
(STANDARD RUN)

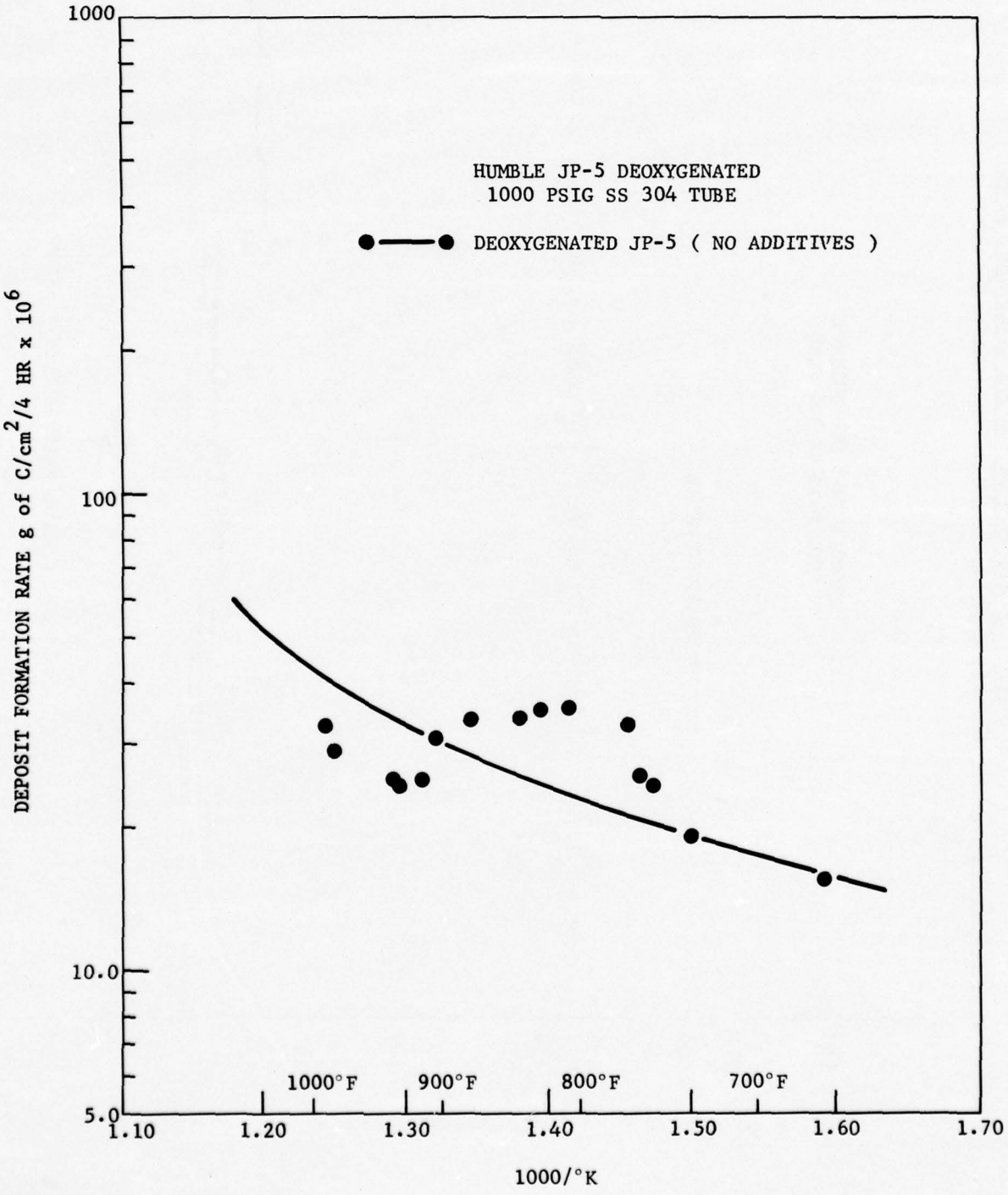


FIGURE 15

DEPOSIT FORMATION WITH 100 PPB DISSOLVED COPPER

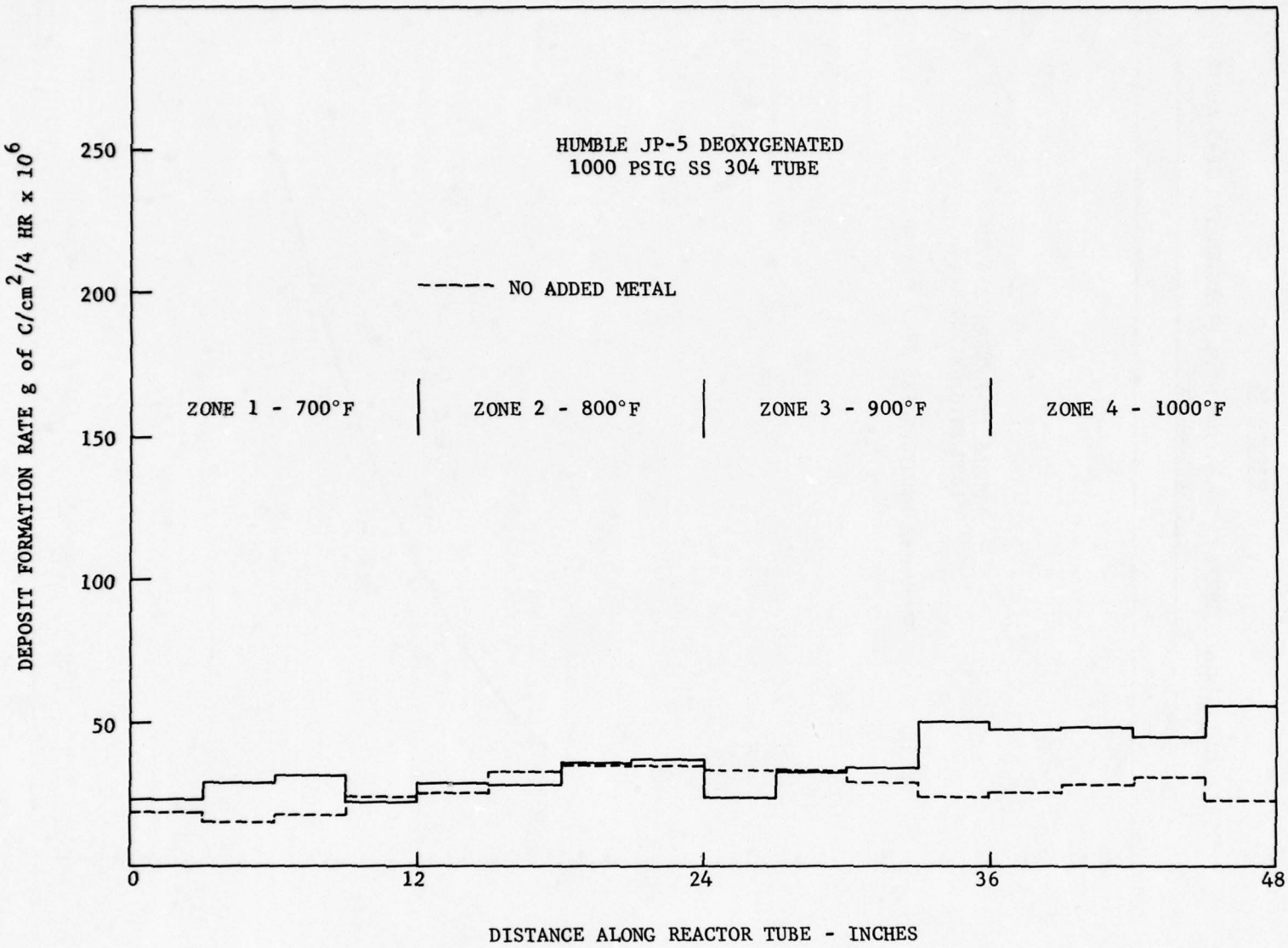


FIGURE 16

ARRHENIUS PLOT - DEPOSIT FORMATION WITH 100 PPB DISSOLVED COPPER

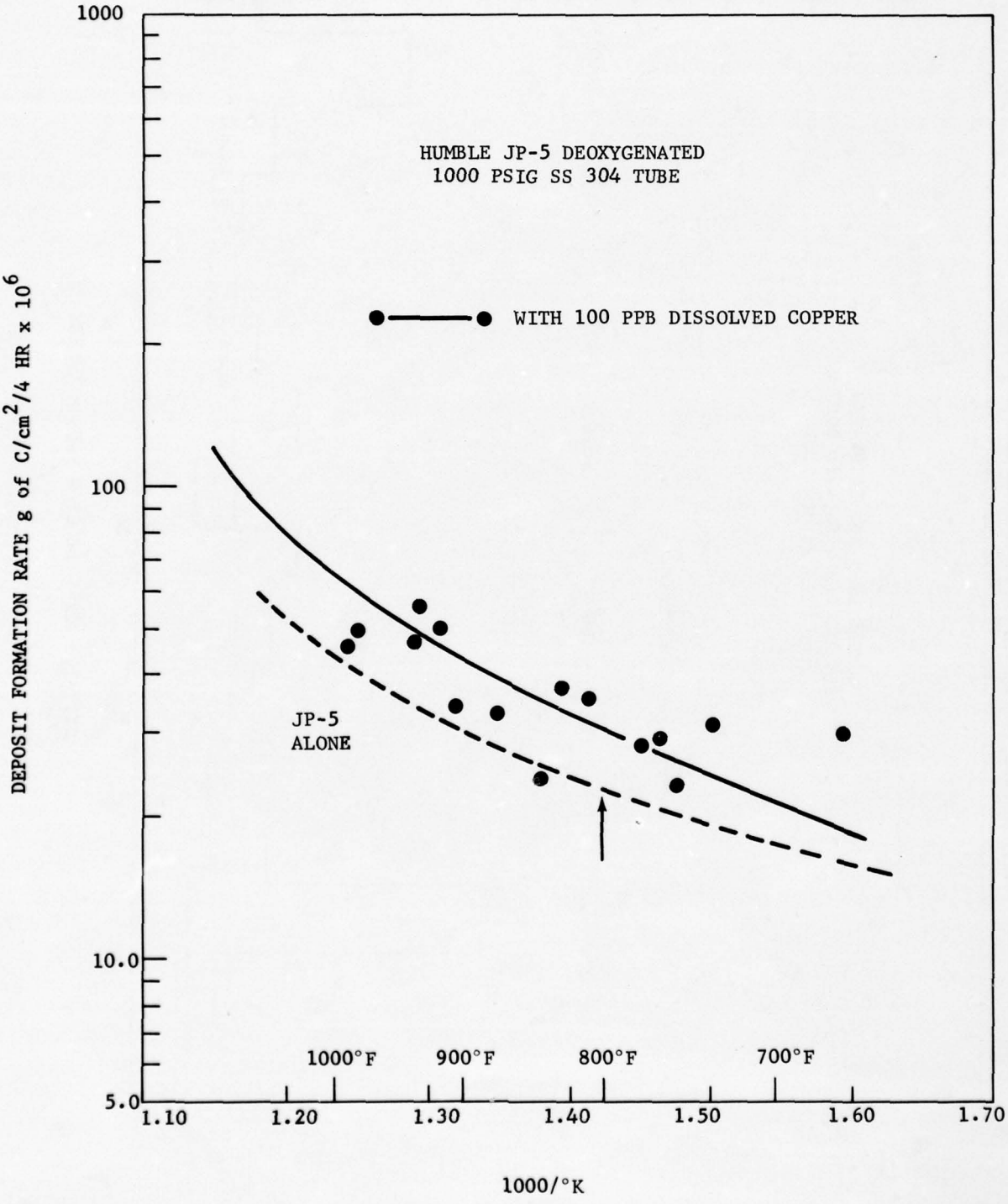


FIGURE 17

DEPOSIT FORMATION WITH 100 PPB COPPER IN AIR SATURATED FUEL

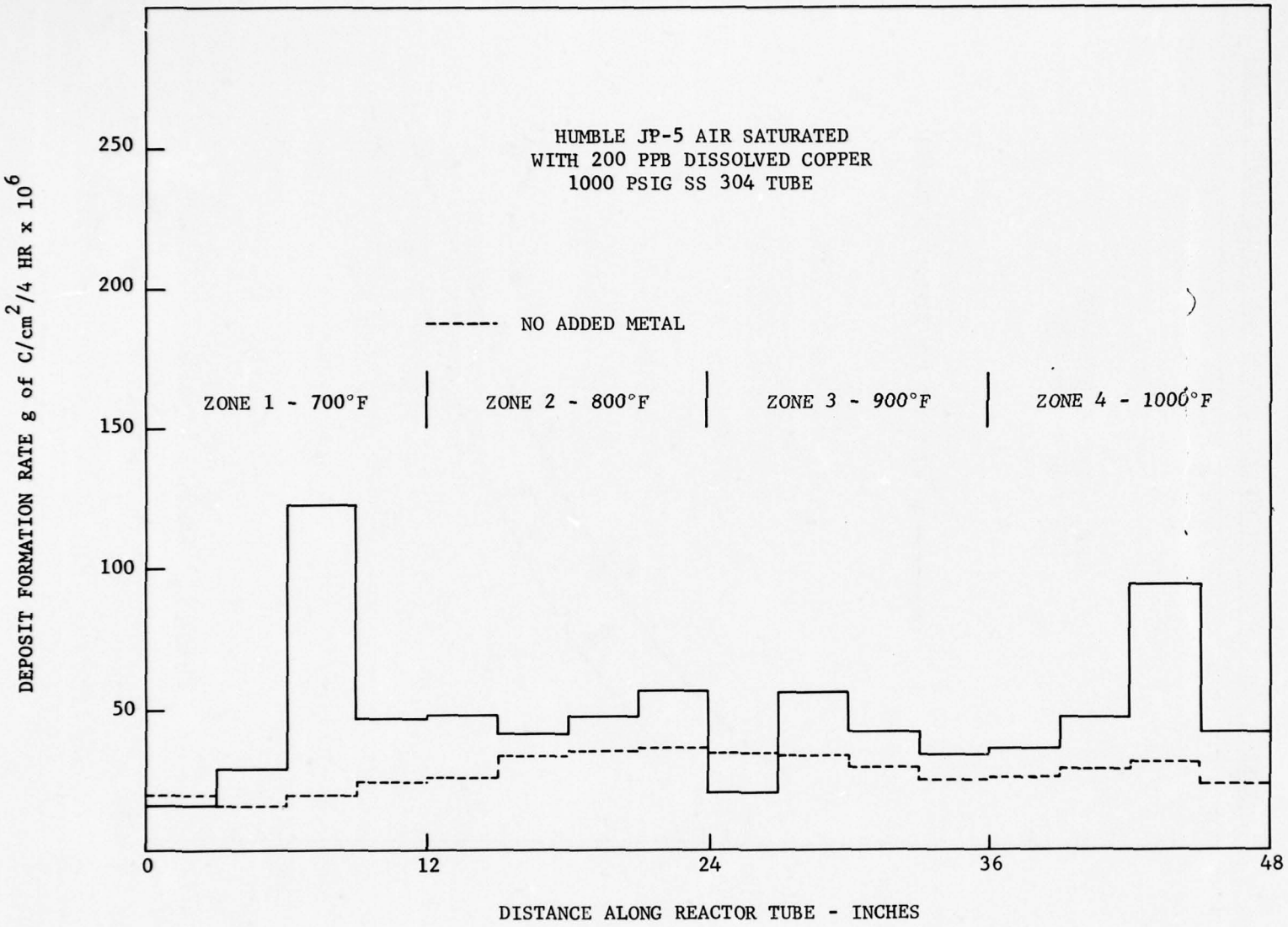


FIGURE 18

ARRHENIUS PLOT - DEPOSIT FORMATION WITH 100 PPB COPPER IN AIR SATURATED FUEL

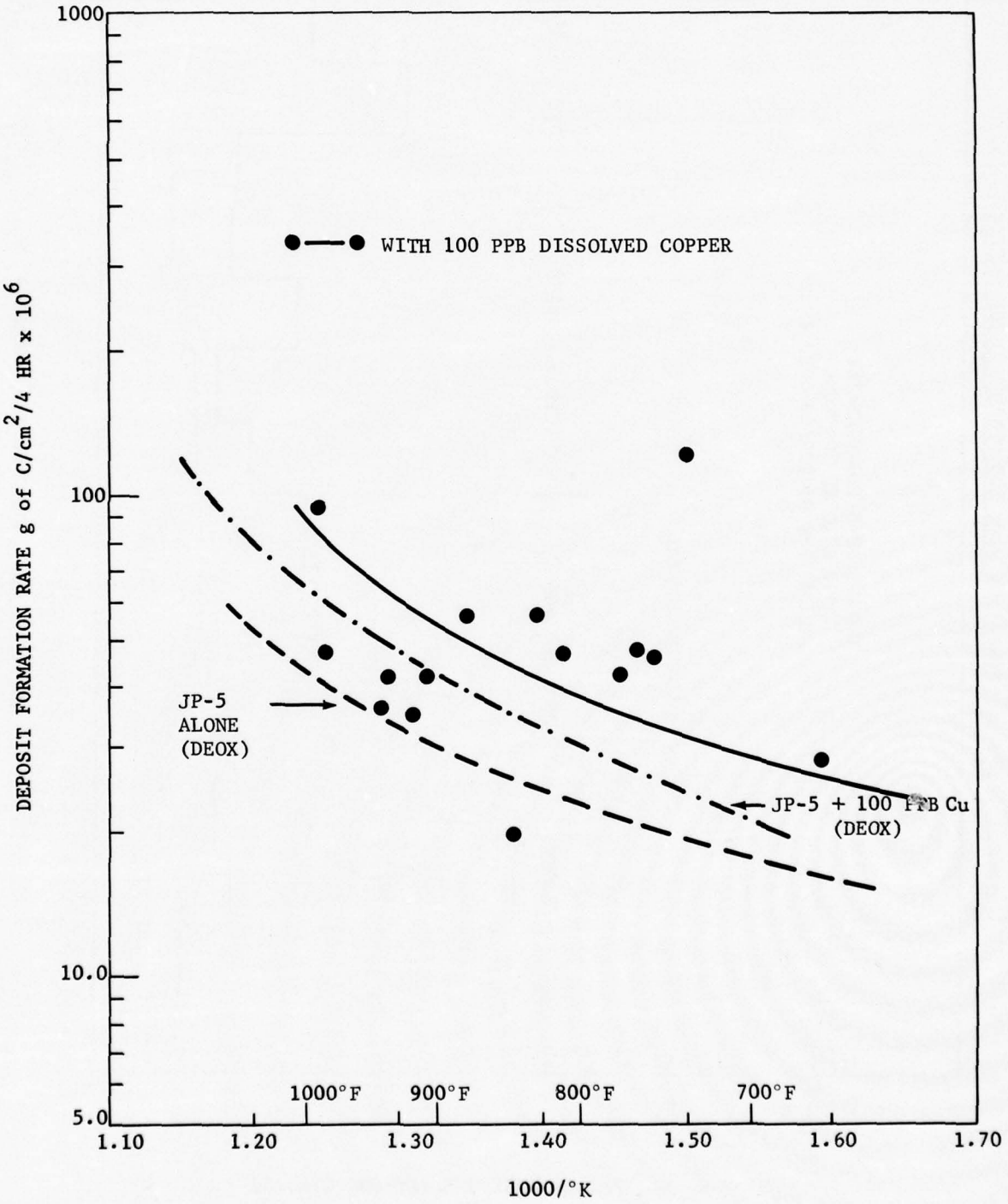


FIGURE 19

DEPOSIT FORMATION WITH 200 PPB DISSOLVED COPPER

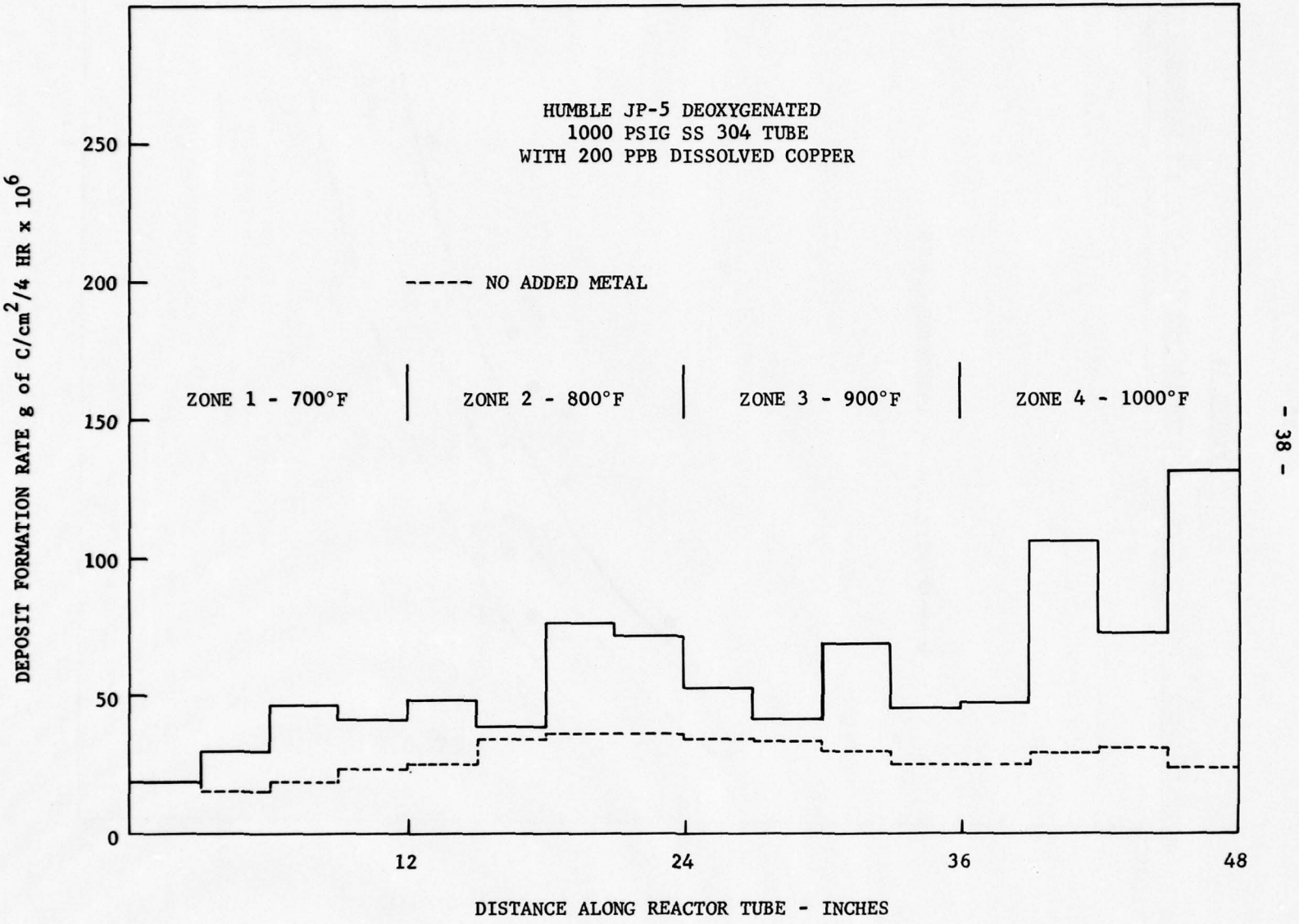
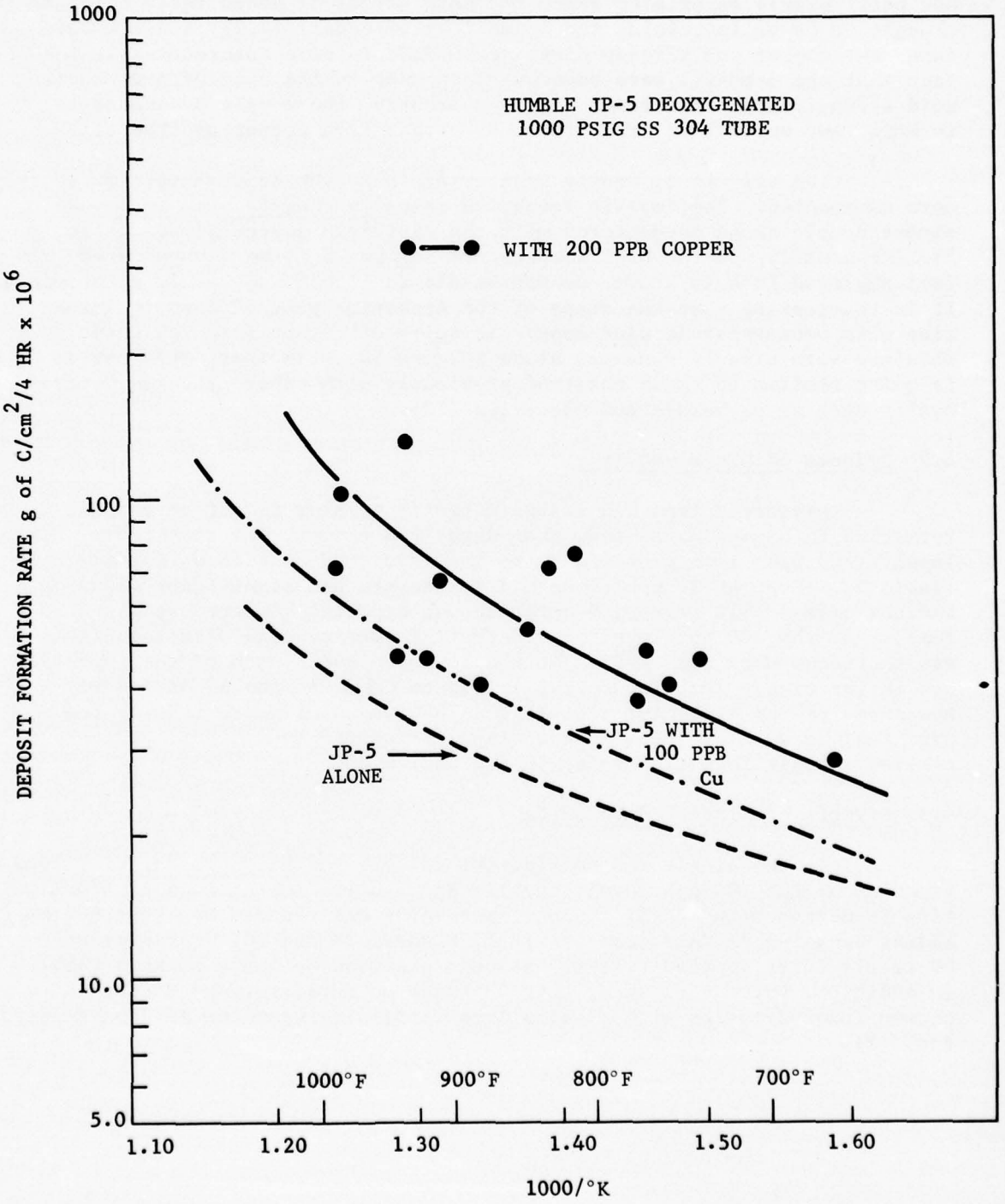


FIGURE 20

ARRHENIUS PLOT - DEPOSIT FORMATION WITH 200 PPB DISSOLVED COPPER



The addition of n-decanoic acid to the fuel containing 100 ppb dissolved copper produced about the same amount of carbonaceous deposits as the fuel containing only the copper (Table 5, Figure 21,22). This is not particularly surprising since the main effect of added fatty acids is thought to be on increasing the solubility of metals (9,27) and, in this case, the copper was already dissolved. What is more interesting is the fact that the deposits were somewhat less than in the case of n-decanoic acid alone (compare reference 13). Apparently, the copper decanoate is no more, and maybe less, reactive than either free copper or free acid.

The effects of adding benzotriazole to the copper-doped fuel were unexpected. The deposit formation rates in deoxygenated fuel were almost double those encountered with the dissolved copper alone (Table 5). Apparently, in the high temperature regimes and the deoxygenated fuel employed in this study, benzotriazole is itself moderately deleterious. It is interesting that the shape of the Arrhenius plot of deposit formation with benzotriazole plus copper is quite different from the curve obtained with dissolved copper alone (Figure 24). In fact, this curve is quite similar to those obtained previously with other nitrogen heterocycles such as carbazole and quinoline (12).

6.2 Effects of Dissolved Iron

Dissolved iron had a significantly greater effect on deposit formation in deoxygenated fuel than dissolved copper. At comparable levels (100 ppb) iron promoted twice the deposit formation as copper (Table 5). Even at 10 ppb, iron had a moderate but significant deleterious effect (87% increased carbonaceous deposits compared to standard fuel). At the 100 ppb level, the deposit formation with dissolved iron was increased more than 150%. At the 100 ppb level, much of the increase was in the higher temperature range (Figure 28). At the 10 ppb level, the shape of the Arrhenius plot (Figure 26) was similar to that of the base fuel as well as those of the dissolved copper runs. This suggests similar deposit formation modes in the two cases.

6.3 Effects of Dissolved Vanadium

In the single run carried out in this series of tests, dissolved vanadium at the 100 ppb level actually appeared to inhibit deposit formation in deoxygenated JP-5. Deposit formation was reduced by about 50% by adding vanadium in this case (Table 5, Figures 29 and 30). Stabilization by metals in oxygenated systems has been observed by other workers (30). In addition, prior work under this contract on metal surface effects showed lower deposits with metal alloys containing vanadium in deoxygenated fuel (2).

FIGURE 21

DEPOSIT FORMATION WITH 100 PPB DISSOLVED
COPPER PLUS N-DECANOIC ACID (100 PPM O)

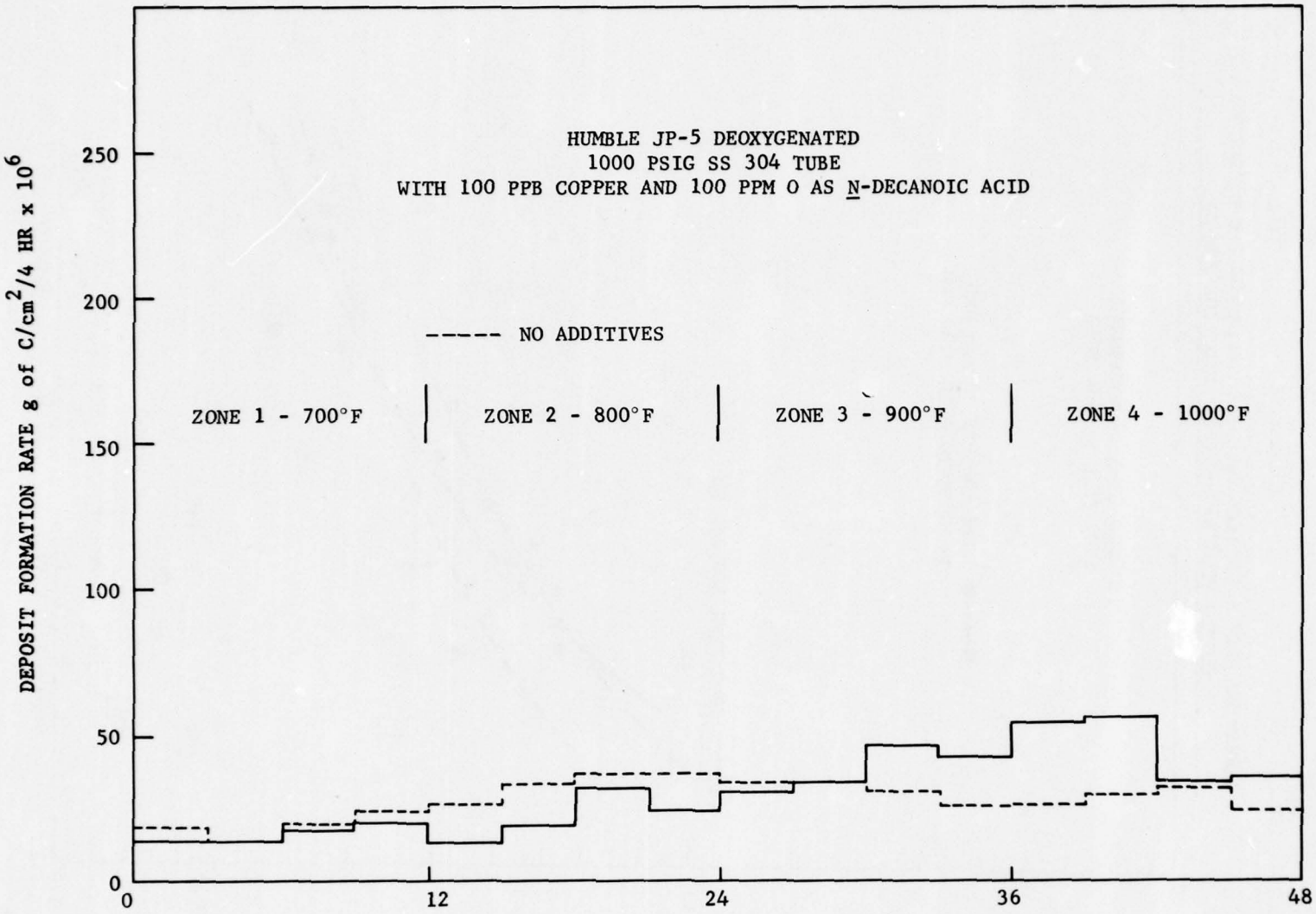


FIGURE 22

ARRHENIUS PLOT - DEPOSIT FORMATION WITH 100 PPB DISSOLVED COPPER PLUS N-DECANOIC ACID (100 PPM O)

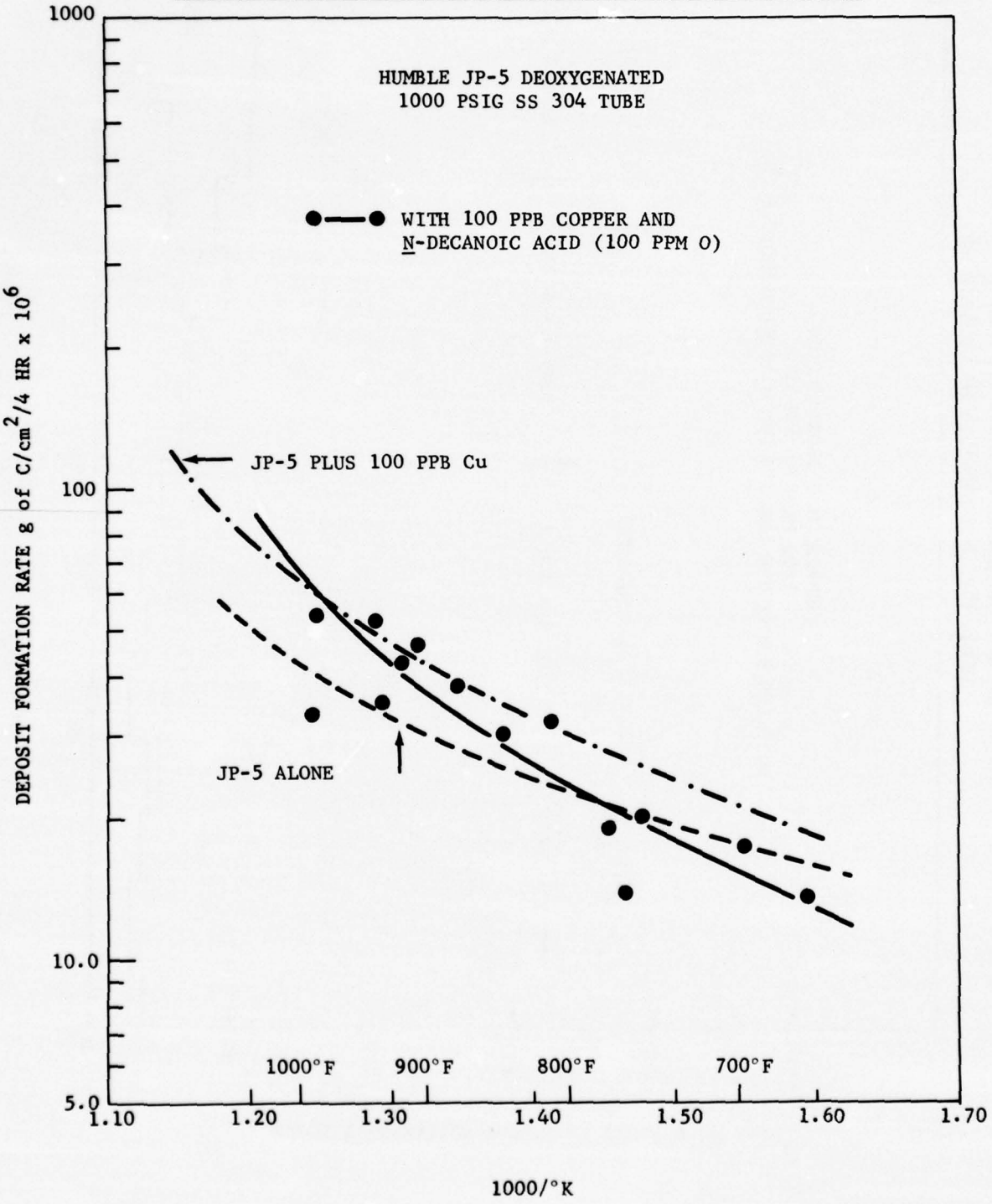


FIGURE 23

DEPOSIT FORMATION WITH BOTH 100 PPB DISSOLVED COPPER AND 10 PPM BENZOTRIAZOLE

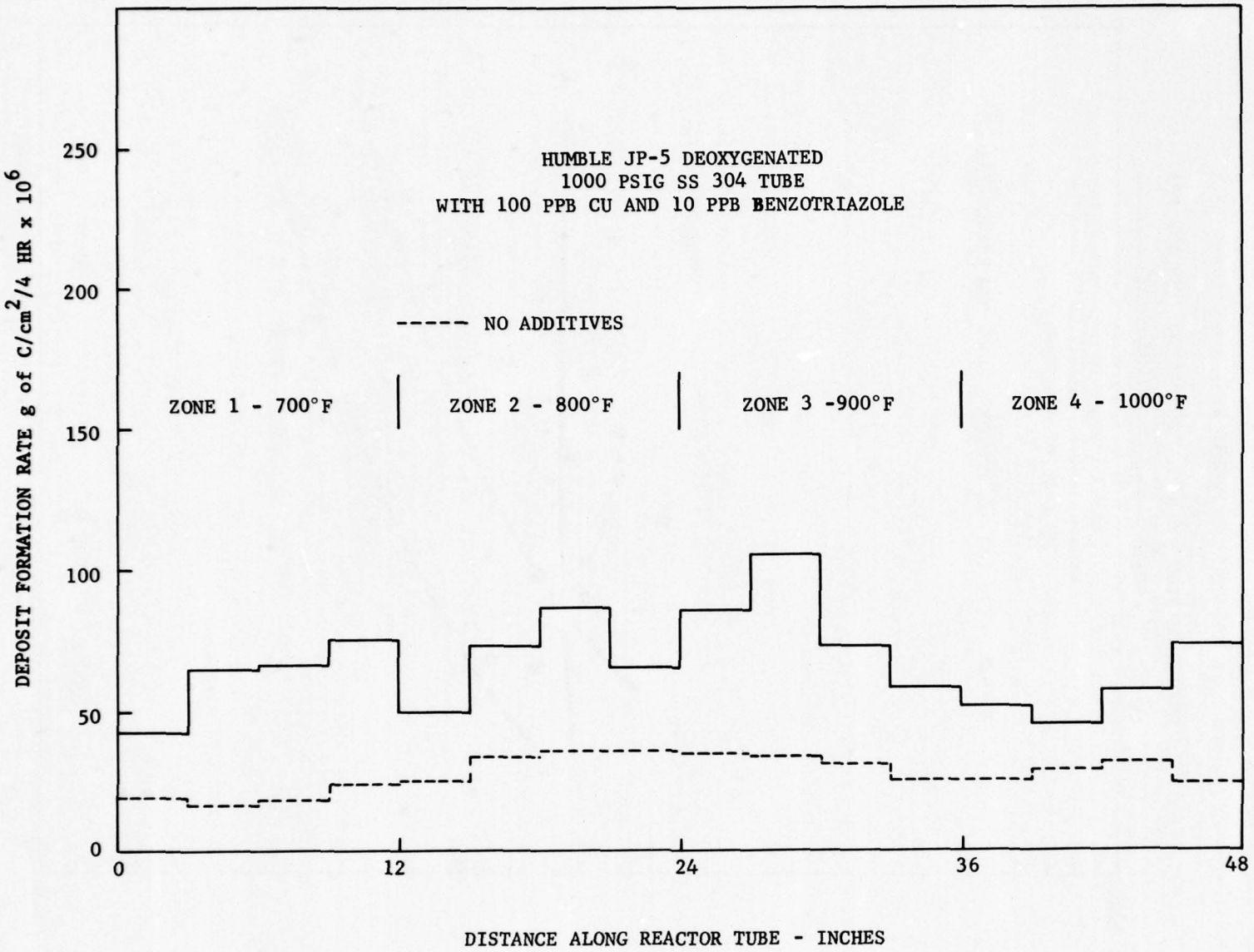


FIGURE 24

ARRHENIUS PLOT - DEPOSIT FORMATION WITH 100 PPB COPPER PLUS 10 PPM BENZOTRIAZOLE

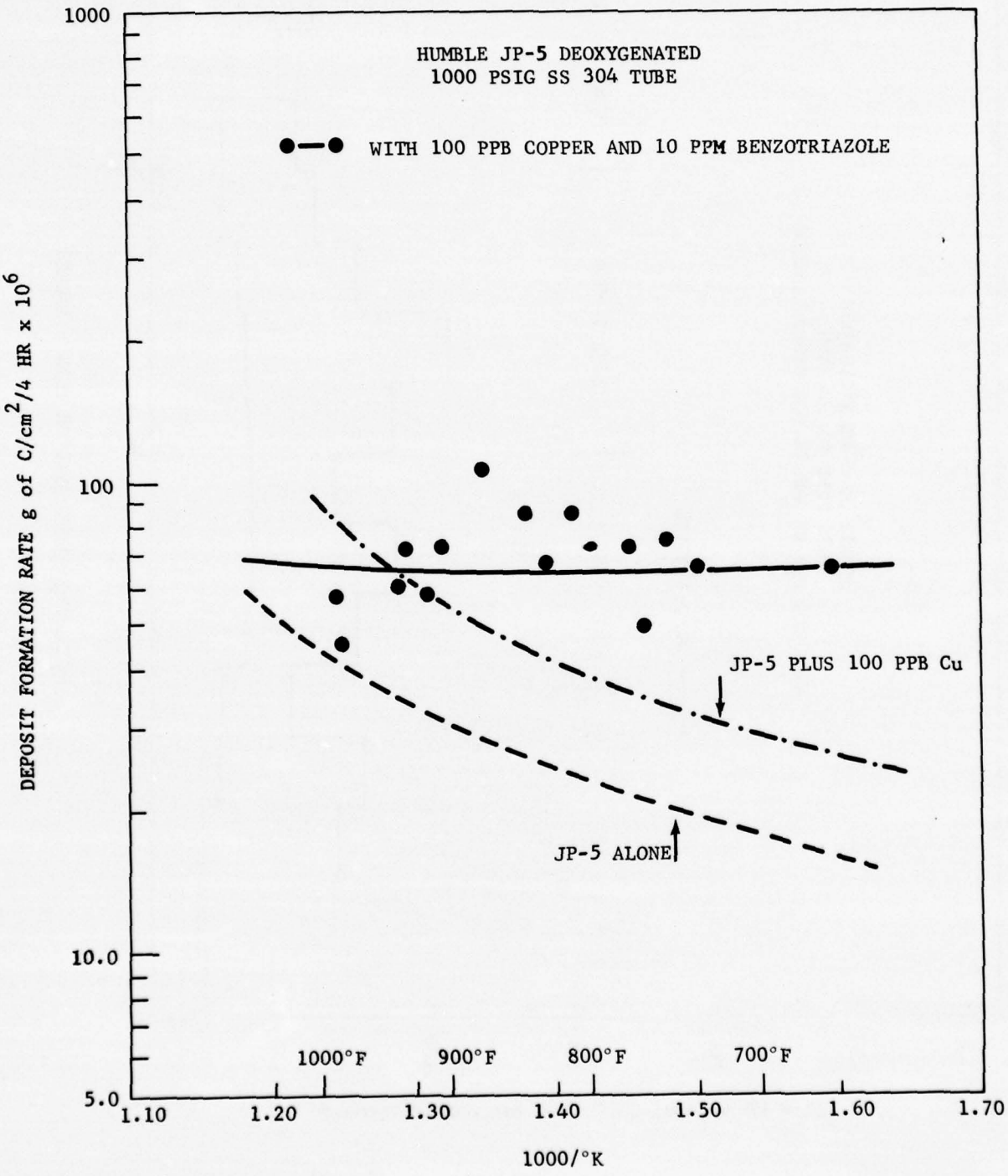


FIGURE 25

DEPOSIT FORMATION WITH 10 PPB DISSOLVED IRON

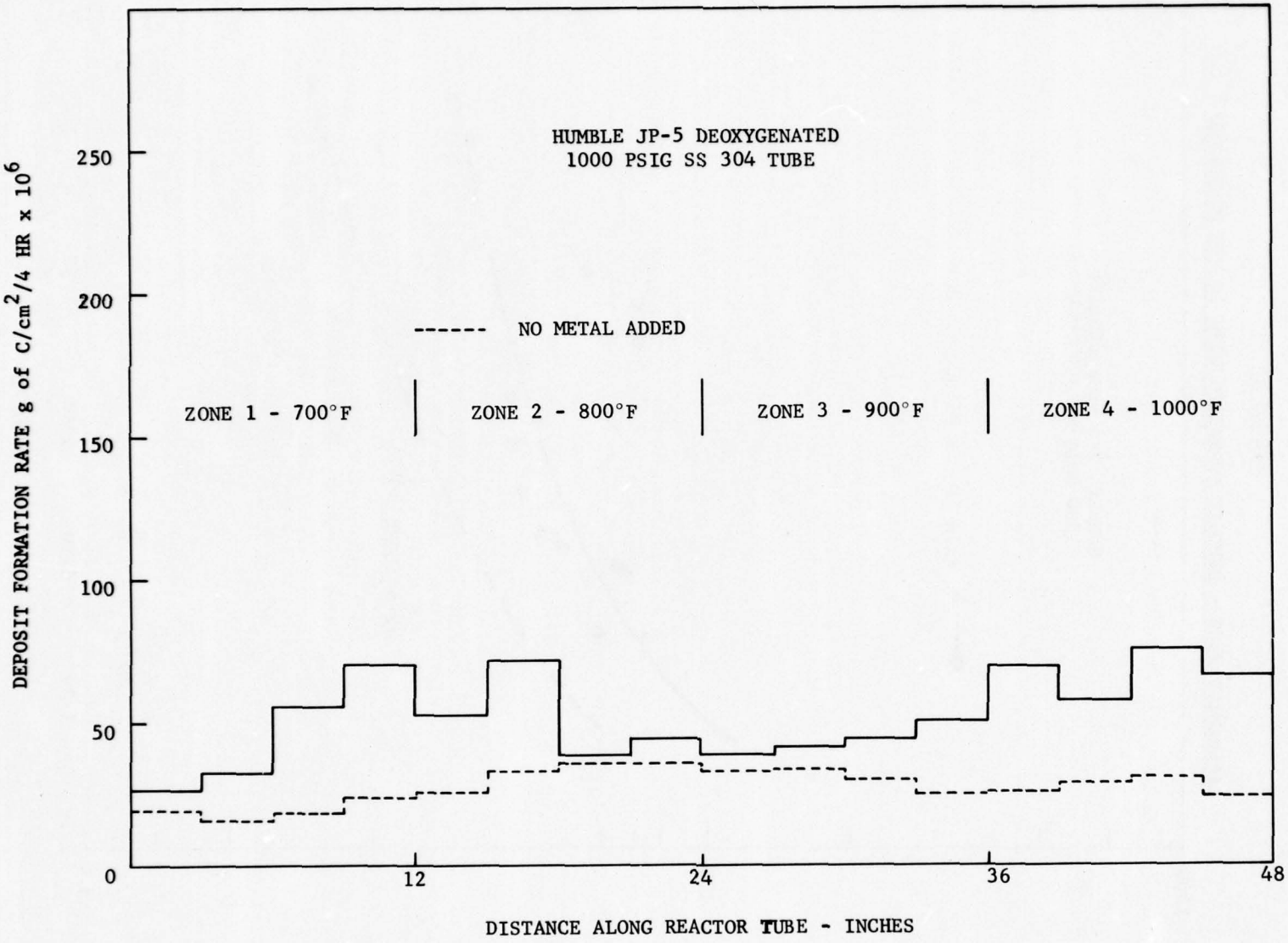


FIGURE 26

ARRHENIUS PLOT - DEPOSIT FORMATION WITH 10 PPB DISSOLVED IRON

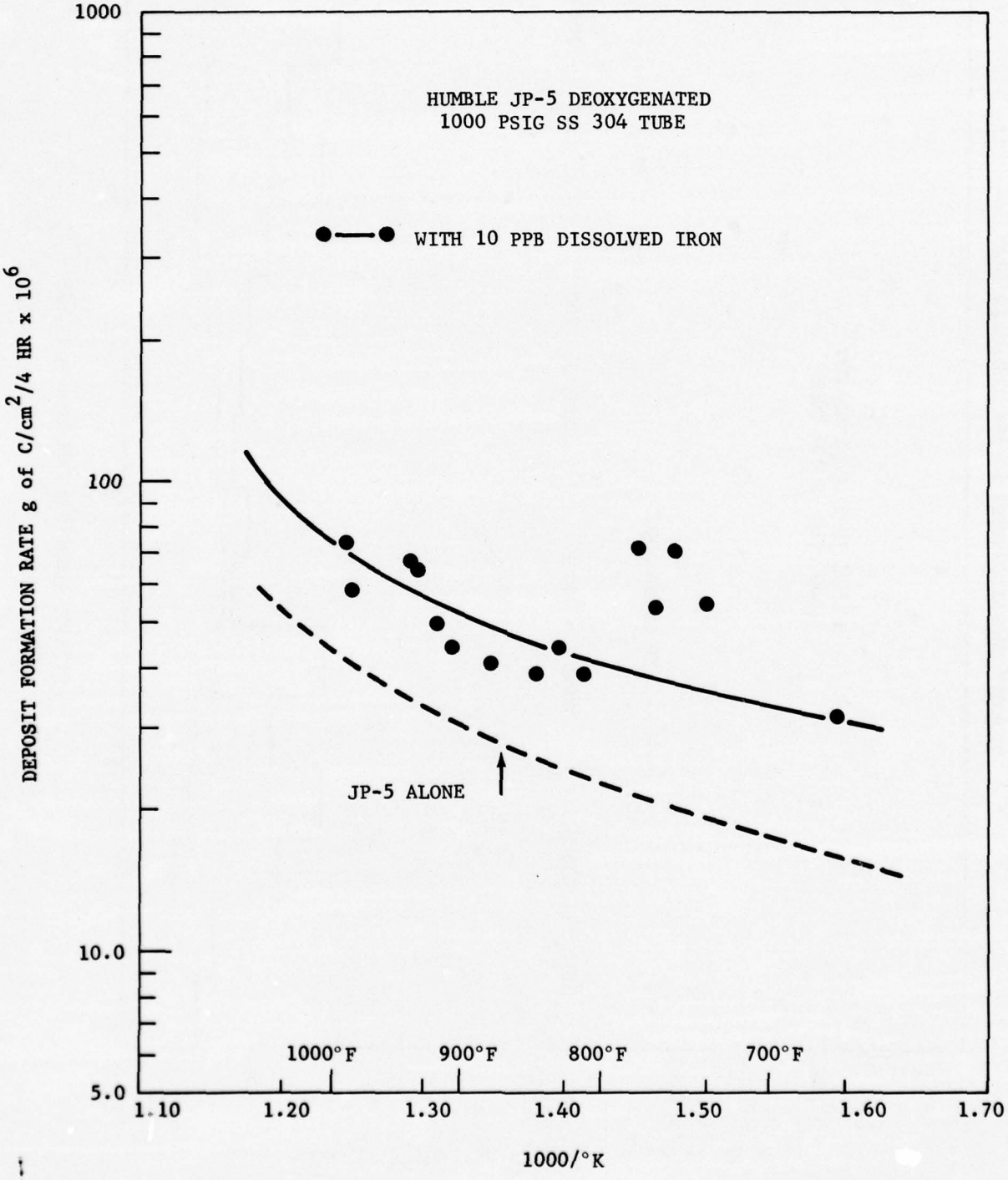


FIGURE 27

DEPOSIT FORMATION WITH 100 PPB DISSOLVED IRON

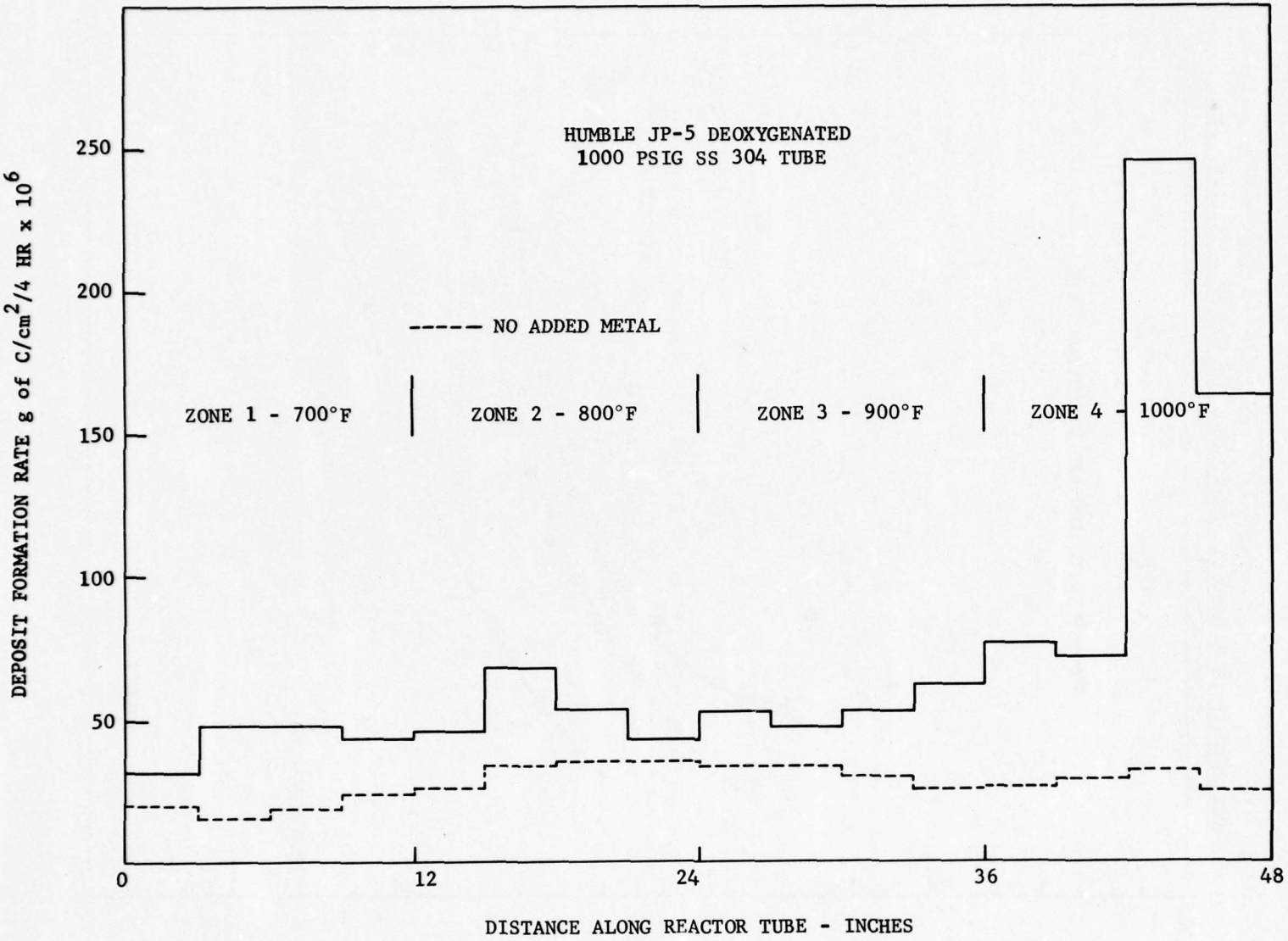


FIGURE 28

ARRHENIUS PLOT - DEPOSIT FORMATION WITH 100 PPB DISSOLVED IRON

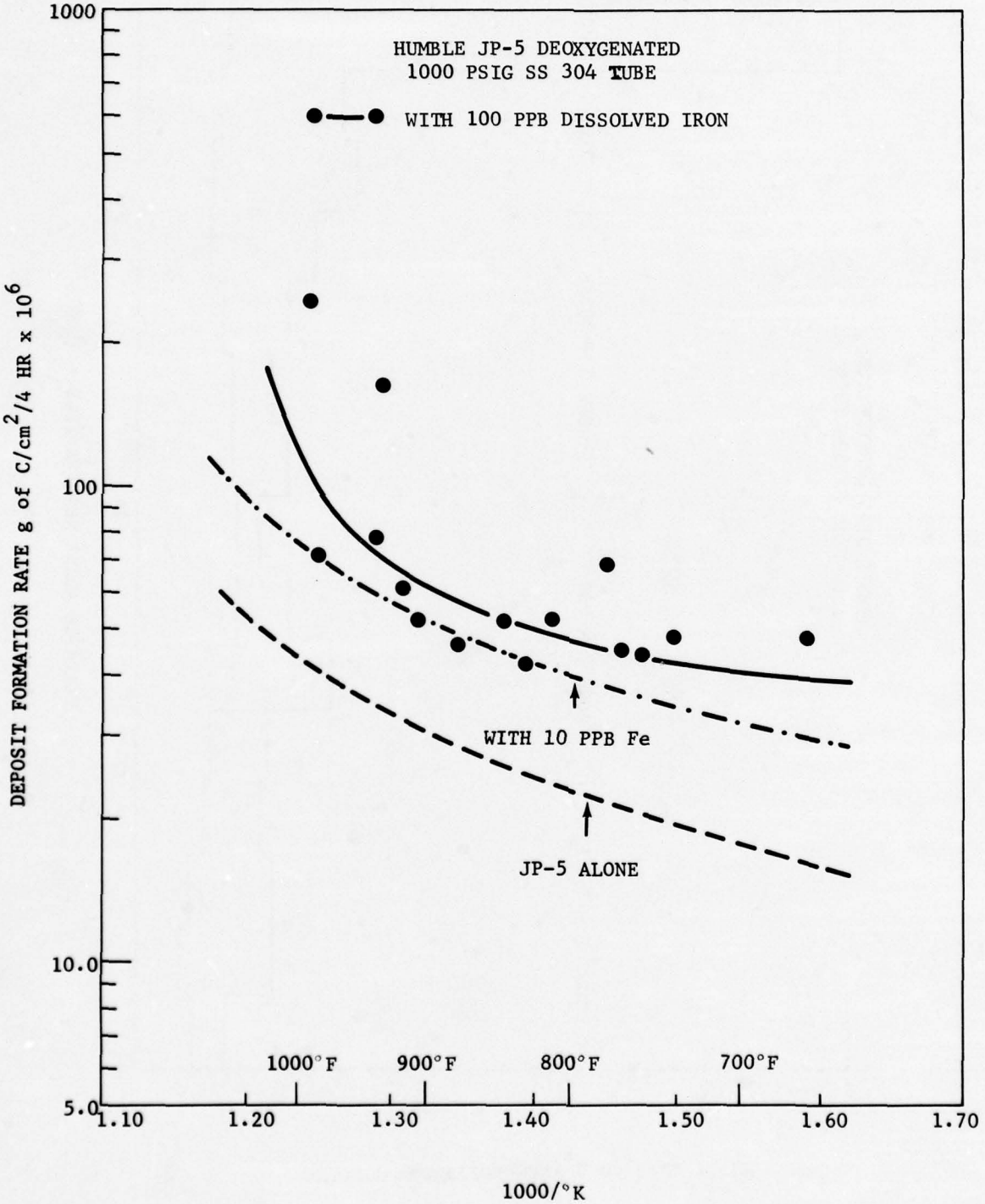


FIGURE 29

DEPOSIT FORMATION WITH 100 PPB DISSOLVED VANADIUM

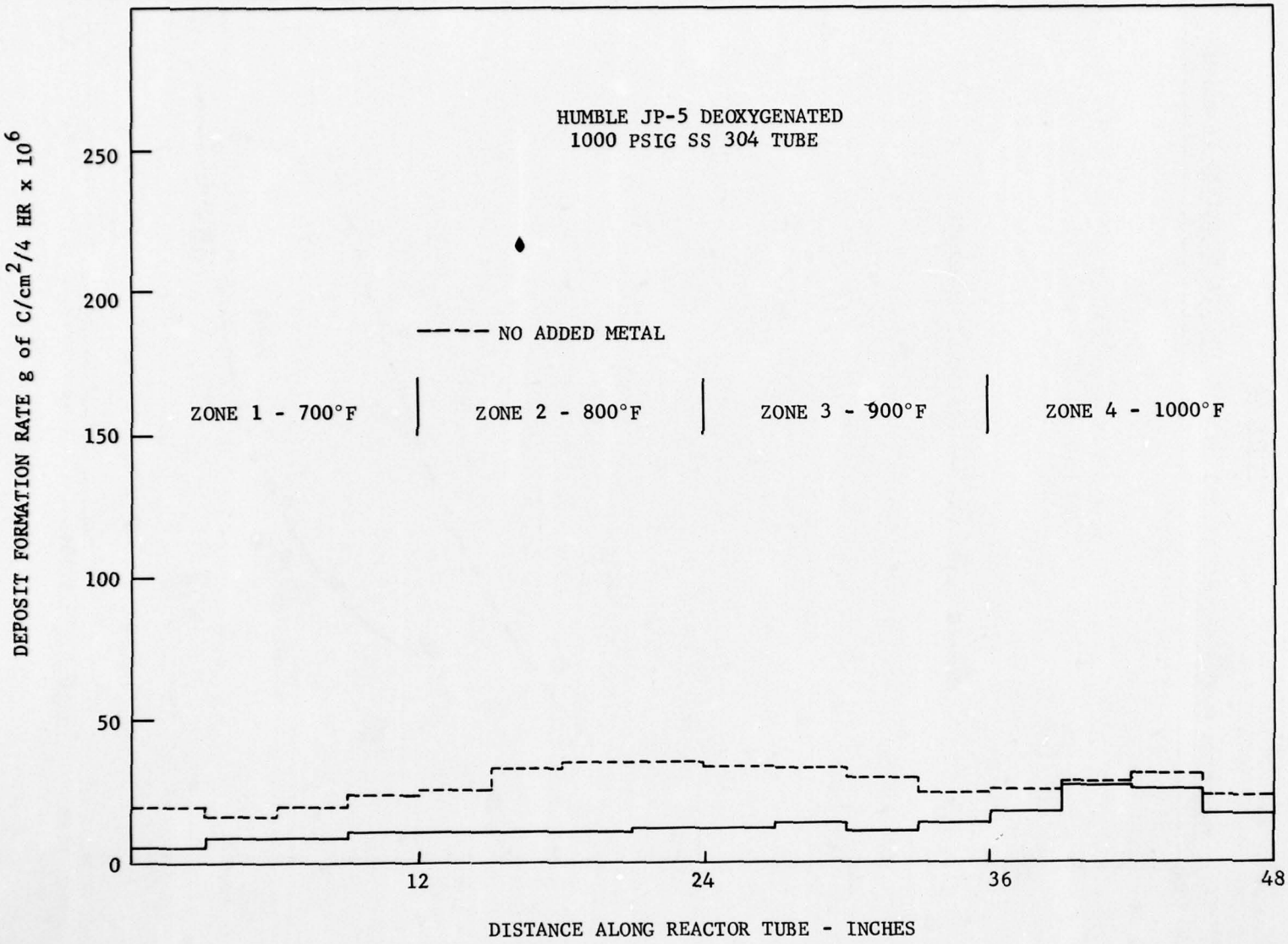
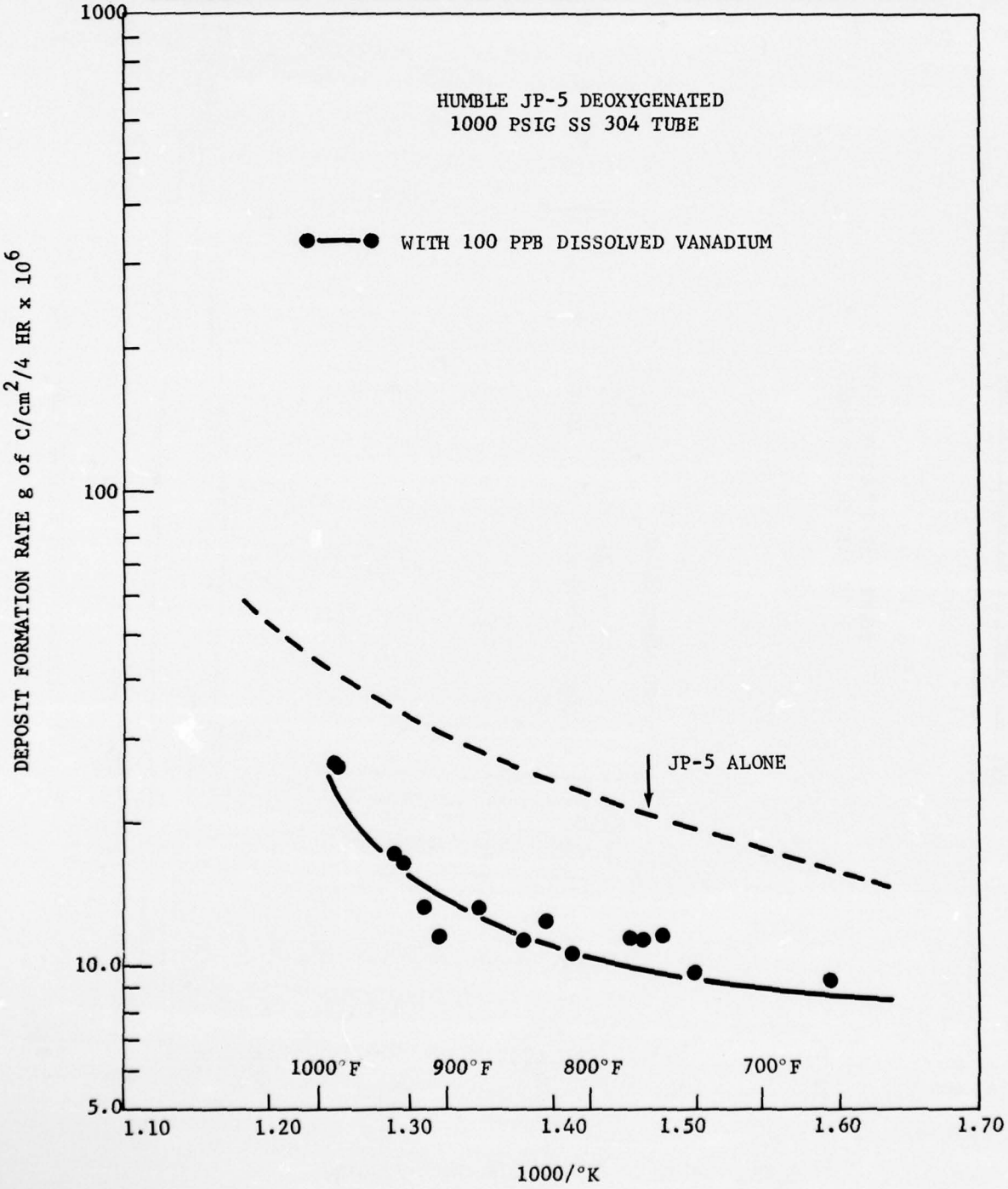


FIGURE 30

ARRHENIUS PLOT - DEPOSIT FORMATION WITH 100 PPB DISSOLVED VANADIUM



7. RECOMMENDATIONS FOR ESTABLISHING SPECIFICATIONS FOR HIGH STABILITY FUEL

As a result of the extensive studies of the effects of various impurities on the thermal stability of deoxygenated fet fuels, it appears that some of the existing specifications for JP-5 may have to be modified. In addition, some new specifications may have to be established and inspection tests developed to monitor different materials.

The present military specification for JP-4 and JP-5 are shown in Table 6. Of particular interest to this program are the acid number and sulfur, mercapton and olefin requirements. These may have to be modified for a thermally stable fuel. In addition, others may have to be added as described in the following subsections. It should be noted that present results serve only to indicate trends and are not in themselves sufficient to establish maximum levels or set specifications. Additional work will be required in certain areas before final specifications can be set.

7.1 Control of Molecular Oxygen Levels in High Stability JP-5

Prior work under this program has established that the single most important factor in promoting thermal stability of ordinary JP-5 is deoxygenation (10). Deoxygenation of a fresh JP-5 fuel to less than one ppm O_2 increased its fuel stability "breakpoint" temperature from 550-1100°F (10). In addition, total deposits were reduced from over 11,000 μg C (per 4 l of fuel) to less than 1500 μg C when tested in the Advanced Fuel Unit. The beneficial effect of deoxygenation increases as the O_2 content is reduced (Table 7). However, there is no simple correlation between oxygen content vs total deposits formed. It appears, therefore, that if JP-5 is to be used for high speed aircraft, a maximum oxygen level will have to be specified. Obviously, for maximum fuel stability, this should be as low as possible. Deoxygenation procedures should be considered both on board the aircraft and for during fuel storage (see Section 9 of this report). Reduction of the O_2 content to one ppm appears to be sufficient (Table 7, (10)) but such a level may be difficult to achieve and to maintain. The actual specification will have to be set by means of trade-offs on such considerations as fuel stability, cost, storage considerations, and contemplated end usage (type of aircraft, etc.).

7.2 Limiting Certain Hydrocarbon Types

Previous work has shown that paraffinic, naphthenic hydrocarbons and most unsaturated hydrocarbons are not deleterious to fuel stability. However, certain types of unsaturated hydrocarbons are deleterious and their levels may have to be controlled. Those identified so far fall into three classes:

Table 6*

Chemical and Physical Requirements and Test Methods

Requirements	Fuel		Test Method
	Grade JP-4	Grade JP-5	ASTM Standards
Color, Saybolt	(1)	(1)	D 156
Total acid number, mg KOH/g, mas.	0.015	0.015	D 3242
Aromatics, vol. percent, max.	25.0	25.0	D 1319
Olefins, vol. percent, max.	5.0	5.0	D 1319
Mercaptan sulfur, weight percent, max. (2)	0.001	0.001	D 1323
Sulfur, total weight percent, max.	0.40	0.40	D 1266, D 1552, D 2622
Distillation temperature, °C			D 86 (3) or D 2887
(D 2887 limits in parentheses)			
Initial boiling point	(1)	(1)	
10 percent recovered, max. temp.	(1)	205 (185)	
20 percent recovered, max. temp.	145 (130)	(1)	
50 percent recovered, max. temp.	190 (185)	(1)	
90 percent recovered, max. temp.	245 (250)	(1)	
End point, max. temp.	270 (320)	290 (320)	
Residue, vol. percent, max. (for D 86)	1.5	1.5	
Loss, vol. percent, max. (for D86)	1.5	1.5	
Explosiveness percent, max.	---	50	(4)
Flash point, °C (°F), min.	---	60 (140)	D 93
Density, kg/m^3, min. (°API, min.) at 15°C	751 (57.0)	788 (48.0)	D 1298
Density, kg/m^3, max. (°API, min.) at 15°C	802 (45.0)	845 (36.0)	D 1298
Vapor pressure, 37.8°C (100°F), kPa (psi), min.	14 (2.0)	---	D 323 or D 2551
Vapor pressure, 37.8°C (100°F), kPa (psi), max.	21 (3.0)	---	D 323 or D 2551
Freezing point, °C (°F), max.	-58 (-72)	-46 (-51)	D 2386
Viscosity, at -20°C, max., mm^2/s (centistokes)	--	8.5 (8.5)	D 445
Heating value, Aniline-gravity product, min., or Net heat of combustion, MJ/kg (Btu/lb) min.	42.8 (18,400)	42.6 (18,300)	D 240, D 2382 or D 3338 (5)
Hydrogen content, wt. percent, min.	13.6	13.5	D 1018 or 3343 (6)
or Smoke point, mm, min.	20.0	19.0	D 1322

Table 6 (Cont.)

Requirements	Fuel		Test Method
	Grade JP-4	Grade JP-5	ASTM Standards
Copper strip corrosion, 2 hr. at 100°C (212°F) max.	1b.	1b.	D 130
Thermal stability:			
Change in pressure drop; mm of Hg, max.	25	25	D 3241 (7)
Preheater deposit code, less than	3	3	
Existent gum, mg/100 ml, max.	7.0	7.0	D 381
Particulate matter, mg/liter, max.	1.0	1.0	D 2276 (8)
Filtration time, minutes, max.	15	---	(8)
Water reaction			
Interface rating, max.	1b.	---	D 1094
Separation rating, max.	1	---	
Water separation index, modified, min.	70	85	D 2550
Fuel system icing inhibitor, vol. percent min.	0.10	0.10	(9)
Fuel system icing inhibitor, vol. percent max.	0.15	0.15	(9)

(1) To be reported - not limited.
(2) The mercaptan sulfur determination may be waived at the option of the inspector if the fuel is "doctor sweet" when tested in accordance with the doctor test of ASTM D 484.
(3) A condenser temperature of 32° to 40 F (0° to 4°C) shall be used for the distillation of grade JP-5. For JP-4, use group 3 test conditions. Distillation shall not be corrected for 760 mm pressure.
(4) Test shall be performed in accordance with method 1151 Federal Standard 791.
(5) ASTM D 3338, for calculating the heat of combustion, is only allowed for use with JP-4 fuel. When the fuel distillation test is also performed using ASTM D 2887, the average distillation temperature, for use in ASTM D 3338, shall be calculated as follows:

$$V = \frac{10\% + 50\% + 95\%}{3}$$

Table 6 (Cont.)

(6) ASTM D 3343, for calculating the hydrogen content of the fuel, is only allowed for use with JP-4 fuel. When the fuel distillation test is also performed using ASTM D 2887, the average distillation temperature for use in D 3343 shall be calculated as follows:

$$V = \frac{10\% + 50\% + 95\%}{3}$$

(7) See 4.7.1.1 for ASTM D 3241 test conditions and test limits.
(8) A minimum sample size of one gallon shall be filtered. Filtration time will be determined in accordance with the procedure of Appendix A. The procedure in Appendix A may also be used for the determination of particulate matter as an alternate to ASTM D 2276.
(9) Test shall be performed with method 5327 of Federal Standard 791.

* Taken from MIL-T-5624K, 1 April, 1976.

TABLE 7

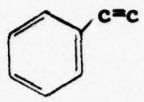
The Effect of Oxygen Concentration on Total Deposit Formation with Fresh and Aged JP-5 Fuels (10)

Fuel	Oxygen Content ppm O_2	Total Carbonaceous Deposits[a] Micrograms of Carbon	Total Carbonaceous Deposits[a] As ppm Based on Total Fuel
Fresh Humble JP-5	0.4	1,485[b]	0.77
	0.8	1,586	0.82
	1.6	3,843	1.98
	64.0 (air saturated)	11,085	5.71
Aged JP-5 (AFFB-9-67)	0.3	4,739	2.43
	14.6	4,431	2.28
	58.0 (air saturated)	9.105	4.68

(a) Cumulative deposits formed in a 4 hour run in the Esso Advanced Fuel Unit. Other conditions: 1,000 psig; S.S. 304 tube; Zone 1-700°F; Zone 2-800°F; Zone 3-900°F; Zone 4-1,000°F.

(b) Adjusted linearly to account for missing local deposit formation rate value.

- Highly reactive multiply bonded carbon compounds such as acetylenes.
- Di-olefins with terminal double bonds, $H_2C = CH\ (CH_2)_xCH = CH_2$
- Aromatics with unsaturated side chains conjugated to the ring:



Many of these compounds have proved to be especially deleterious at low temperatures (11). Fortunately, mild hydrofining (see Section 8.1) will generally reduce these types of reactive unsaturated materials before hydrogenating the aromatic ring.

Additional work will be required to set the absolute limits for these types of compounds. In addition, new tests will have to be developed to determine them or to verify their removal during fuel processing.

7.3 Control of Trace Impurity Levels

The effects of various compound classes, normally found in jet fuels, on the thermal stability of deoxygenated JP-5 are summarized in Table 8. The effects of testing each compound class alone are shown as well as "deleterious interactions". "Deleterious interactions" are those in which two or more otherwise harmless impurities produce excessive deposits when acting in conjunction. Detailed descriptions of the effects of various impurities have been given in previous reports (1,2, 10). Effects of interactions are detailed in reference (11). It appears that the amounts of certain types of compounds will have to be regulated in a thermally stable fuel of the JP-5 type or their effects negated in some manner. In addition, some compounds, innocuous when present alone, must be considered on the basis of their interactions with other trace impurities. Some general recommendations, by compound type, follow. In some cases, new analytical procedures will have to be developed. These are pointed out where appropriate

7.3.1 Control of Sulfur Compounds

Sulfur containing impurities are among the most deleterious identified so far (10). Moreover, the different classes of sulfur compounds varied greatly in their effects on stability. Thus, condensed ring aromatic sulfur compounds (thiophenes) are not deleterious, mercaptans (thiols) are moderately deleterious while sulfides, disulfides and polysulfides are highly deleterious (10).

Thiols are currently restricted in JP-5 to 10 ppm S maximum. This level is probably restrictive enough to also be applied to other deleterious sulfur compounds such as sulfides, disulfides and polysulfides. In any event, sweetening processes, used to eliminate thiols, and which may introduce di- and polysulfides should not be employed in the preparation of fuel or fuel blending stocks. Higher levels of these deleterious sulfur compounds may be acceptable but would require further work to pinpoint the maximum tolerable levels for each class of compounds.

TABLE 8

Summary of Compound Type on
Thermal Stability of Deoxygenated JP-5(1)

Tested Alone		
Deleterious	Non-Deleterious (4)	Deleterious Interactions
HYDROCARBONS (2-20%)		
Some di-olefins	Paraffins	
Acetylenes	Naphthenes	
	Aromatics	
	Condensed Aromatics	
	Mono Olefins	Pyrroles
SULFUR COMPOUNDS (4,000 ppm S)		
Sulfides	Thiophenes	Pyrroles
Thiols		
Di-Polysulfides		
NITROGEN COMPOUNDS (100 ppm N)		
	Pyrroles	Thiophenes, acids, olefins
	Amines	
	Amides	
	Pyridines	
OXYGEN COMPOUNDS (100 ppm O)		
Peroxides	Phenols	Pyrroles(2)
Acids(3)	Furans	
	Naphthenic acids and esters	
	Ketones	
	Alcohols	
	Aliphatic esters	

(1) Details may be found in references 1, 2, 10, 11.
(2) Shows moderate interaction with phenols, but a strong interaction with acids.
(3) Tested at levels down to 10 ppm.
(4) Includes some mildly deleterious species.

7.3.2 Control Nitrogen of Compounds

There is currently no specification limiting the nitrogen level in JP-5 fuels. Present petroleum derived jet fuels normally contain far less than 100 ppm N (12). As a result, all nitrogen containing impurities studied in this program were added at the maximum anticipated (100 ppm N) level. None were found to be deleterious to deoxygenated JP-5 when tested alone. As a result, it appears that no nitrogen specification will be required to control high temperature deposit formation for ordinary deoxygenated JP-5 which is derived from petroleum.

However, the levels of nitrogen in fuels derived from coal or shale ("synfuels") may be much higher than this. As pointed out in Section 3 of this report, certain nitrogen containing compounds, especially pyrroles, are deleterious to the storage stability of jet fuels. Fuels likely to contain large quantities of such compounds may have to be treated to remove the deleterious species. In addition, deleterious interactions were encountered between pyrroles and thiophenes, acid and olefins. As a result, both a total nitrogen and pyrrolic nitrogen specification may have to be established.

Clearly, more work is required to determine which types of nitrogen compounds are deleterious to storage stability and at what levels they are likely to reach in new synfuels. In addition, analytical techniques may have to be developed to measure such compounds in the presence of other, non-deleterious materials.

7.3.3 Control of Oxygen Containing Impurities

Oxygenated compounds vary considerably in their effects on deposit formation in deoxygenated JP-5 (Table 6-3). Most phenols, furans, alcohols, and esters were non-deleterious at the 100 ppm O level and would not have to be controlled in high stability JP-5. Other types of oxygen containing impurities are definitely harmful and specifications may have to be written limiting their concentrations.

Ketones and some aromatic esters were found to be only mildly deleterious to fuel stability at the 100 ppm O level. It is likely that no new specifications will be needed for such species.

Acidic substances, such as aliphatic acids and some phenols were found to be deleterious to fuel stability (13). For example, n-decanoic acid was deleterious at levels down to 10 ppm (13). This is below the level currently specified (by acid number, Table 6-1), for JP-5 fuel. As a result, the acid number specification may have to be lowered for High Stability JP-5. Phenols were variable in their effects; most were non-deleterious (13, Section 4 of this report), but at least one, di-t-butylphenol, was highly deleterious (see Section 4, above). Although confirmatory work is required, it appears that levels of phenolic species may have to be specified as well. In addition, a strong deleterious interaction was found between a carboxylic acid and a pyrrole even at room temperature. This may have considerable significance on specifications set for synfuels as discussed in Section 4 above.

Peroxides of all types are among the most deleterious species found in jet fuels (13). At the 100 ppm O level, some peroxides increased deposit formation by as much as 800% (13). As a result, peroxide levels will have to be controlled to less than 1 ppm. In addition, improved analytical tests may be needed to verify that these low levels have been achieved.

7.4 Limitations to Current Jet Fuel Additives

The results of tests described in Section 5 of this report indicate that some jet fuel additives in current use may not be acceptable (as well as unnecessary) for High Stability JP-5. For example, the antioxidant DuPont #22 (N,N-di-s-butyl-p-phenylenediame) appears non-deleterious to JP-5 stability while di-t-butyl phenol, another common additive was highly deleterious. Although antioxidants will not be necessary in rigorously deoxygenated fuels, it may be desirable to include such additives in fuel stocks which are to be stored for extended periods. If so, the antioxidant should be carefully chosen and its level of addition rigorously controlled.

The corrosion inhibitor Hitec 515 appears to be non-deleterious to fuel stability. On the other hand, the anti-icing additive, 2-methoxyethanol may be highly deleterious. It is likely that other anti-icing materials will be needed.

It should be emphasized that only a very few of the many possible additives have been evaluated. This was done mainly to point up the possible problems that can arise with various added materials. We would recommend that each contemplated additive be tested on an individual basis before inclusion in high stability fuel specifications. In addition, all additives will have to be tested for mutual compatability under high temperature conditions.

7.5 Effects of Metal Surfaces and Dissolved Metals

The influences of metal surfaces (2) and dissolved metals (Section 6 above) were evaluated briefly as part of this study. An importing finding was the fact that deoxygenated JP-5 behaves quite differently from air saturated fuels with respect to both metal effects. The use of pure titanium for fuel lines is not recommended for high speed aircraft using deoxygenated fuel. The preferred materials are stainless steel 304 and a Ti-3 Al-2.5 V alloy (2). This is in contrast to results obtained in a saturated fuel where pure titanium was among the best tubing material evaluated (2).

As discussed in Section 6 of this report dissolved metals are somewhat less deleterious to fuel stability in deoxygenated than in air saturated JP-5. The most deleterious metal studied was iron. This was moderately deleterious at the 100 ppb level. As a result, iron levels should be reduced to less than 10 ppb and, preferably, to 10 ppb.

It should also be noted that, in deoxygenated fuels, the metal deactivator, benzotriazole, is not needed and may actually be deleterious to high temperature stability.

7.6 Impact of New Synfuels on Fuel Specifications

Stability will be more of a problem with synthetic fuels such as derived from shale oil than fuel derived from petroleum, particularly because of the much higher levels of nitrogen in shale crude oil. Present nitrogen removal technology requires very severe conditions to bring nitrogen levels in jet fuels derived from shale oil down to the very low levels presently found in petroleum derived fuels; and higher nitrogen levels will directionally degrade fuel stability. Even if better nitrogen removal technology is developed, e.g. improved catalytic hydrodenitrogenation processes, the higher cost and the resultant loss of the energy efficiency of the overall processing system may preclude such drastic nitrogen removal and force a tradeoff to be made between reduced upgrading severity and increase nitrogen levels versus reduced product fuel storage and thermal stability properties.

At this time it is not possible to say just what form such a trade off will take. Clearly, much additional research will be required in this area before specifications can be established.

8. GENERAL MANUFACTURING PROCESSES

The general objectives in the preparation of High Stability JP-5 fuel were discussed in Section 1. In this section, the refinery processes which could be employed to prepare High Stability JP-5 or the blending stocks which are used to prepare the fuel are discussed in light of these objectives. This discussion of necessity is of a general nature since (1) considerable variation exists between refinery designs, and (2) even where the identical process is employed, different refineries may operate the process at different conditions, e.g. temperature, pressure, space velocity and catalyst loading and/or type.

The chemistry involved in the various treating processes was discussed in detail in a previous report (11) and will only be summarized here.

8.1 Catalytic Treatment with Hydrogen

Catalytic treatment with hydrogen can accomplish all the reactions desired for the production of High Stability JP-5.

- Removal of thiols, sulfides, disulfides, and polysulfides
- Removal of hydroperoxides, peroxides and carboxylic acids
- Hydrogenation of alkylenes, di-olefins and conjugated aromatic mono-olefins.

There are a wide number of catalytic processes involving treatment with hydrogen which differ in the type of catalyst(s) used, the process conditions (e.g., temperature, pressure, and space velocity) employed. All these factors influence the type of reactions carried out (23-26). In addition to the desirable reactions listed above, catalytic treatment processes employing hydrogen can also effect a number of reactions which (1) may not be necessary for the production of High Stability JP-5, or (2) may remove fuel components which have desirable properties. Some of these reactions are as follows:

- Removal of condensed sulfur compounds such as benzothiophenes and dibenzothiophenes, which could inhibit deposit formation if left in the fuel.

- Removal of organic oxygen compounds such as alcohols, ketones and furans which could inhibit deposit formation if left in the fuel.

- Hydrogenation of aromatics and/or monoolefins (non-aromatic conjugated) which may result in needless hydrogen consumption during processing and correspondingly higher costs.

Thus, although processes involving catalytic treatment with hydrogen can accomplish all the reactions necessary for the production of High Stability JP-5, the exact process end conditions to be employed must be selected with care.

8.2 Treatment with Caustic (11,14,15,17)

Alkaline reagents are used to remove acidic constituents in petroleum and to neutralize the sulfuric acid after acid treatment. The most common reagent is sodium hydroxide although others are occasionally used. The most important compounds removed include the following:

- Naphthenic acids and fatty acids
- Lower aliphatic mercaptans
- Phenols and arylmercaptans
- Hydrogen sulfide and carbon dioxide
- Residual acid (H_2SO_4) from acid treating

The salts of the lower naphthenic and fatty acids are quite water soluble and are readily removed. However, acids in the C_{10}-C_{14} range, which occur in jet fuel have greatly reduced water solubility (14,18). Appreciable amounts of such soaps will remain in the oil phase. This enhances emulsion formation, a serious problem in some refinery operations and in distribution and handling (14). If lime is used in place of NaOH the problem is aggravated because of the decreased solubility of the calcium salts formed relative to the corresponding sodium derivatives.

In addition to disulfide and soap formation, caustic treatment can promote other deleterious reactions such as aldehyde polymerization and isomerization of certain hydrocarbons (11). Severe caustic washing is best avoided in producing High Stability fuel.

8.3 Use of Adsorbents

The use of adsorbents to treat jet fuel, particularly as a final treating step, is often employed (19-22). Adsorbents are employed to remove undesirable species from the fuel. The nature of the compounds removed and level of their removal will depend on factors such as (1) the nature of the adsorbent material, (2) the nature of activation step used to pretreat the adsorbents, and (3) the provess variables employed such as temperature, pressure, contact time, and adsorbent particle size. Inexpensive adsorbents such as bauxites, clays, fullers earth and charcoals are generally employed, although the use of more expensive adsorbents such as molecular sieves and high surface area aluminas is possible. Compound types potentially removed include polar molecules (e.g., sulfur, nitrogen and oxygen containing compounds), unsaturated hydrocarbons and metal containing compounds.

It would appear that the use of adsorbents can have a beneficial effect on High Stability fuel by removing deleterious materials without adding harmful species.

8.4 Sweetening Processes

The major steps in one type of sweetening process is so called "doctor sweetening" are summarized below. In sweetening processes, thiols are removed via oxidation to a disulfide using molecular oxygen, sulfur, or lead compounds as the oxidation agent (10). The disulfides generally remain in heavier fuels such as JP-5. In addition, the use of elemental

sulfur can result in the formation of polysulfides. Since polysulfides are highly deleterious to the stability of deoxygenated fuel, doctor sweetening cannot be employed in the manufacture of high stability fuel.

Major Reaction Steps in Doctor Sweetening

I. Doctor Solution Preparation

$$PbO + NaOH \rightarrow Na_2PbO_2 \text{ (Sodium Plumbite)}$$

II. Doctor Solution Added to the Fuel

$$2\ RSH + Na_2PbO_2 \rightarrow (RS)_2Pb + 2\ NaOH \text{ (Lead Mercaptide)}$$

III. Elemental Sulfur Added to the Blend

A. Desired Reaction to Disulfides

$$(RS)_2Pb + S \rightarrow RSSR + PbS$$

B. Side Reactions to Polysulfides

$$2\ RSH + S_n \rightarrow RS_{n+1}R + H_2S$$
(Excess Thiol)

$$(RS)_2Pb + S_n \rightarrow RS_{n+1}R + PbS$$
(Excess Sulfur)

A more modern sweetening process, which has largely replaced "doctor" sweetening in refinery operations is the so-called Merox process (32). In this procedure, mercaptans are oxidized to disulfides over a suitable catalyst (32):

$$4\ RSH + O_2 \rightarrow 2\ RSSR + 2\ H_2O$$

Although this process avoids the addition of elemental sulfur and the formation of polysulfides, disulfides are produced. Since disulfides are deleterious to fuel stability under high temperature conditions (10), Merox sweetening should not be used in the manufacture of High Stability JP-5.

It appears that "sweetening" of JP-5 is best achieved by use of hydrofining techniques (Section 8.1) if the introduction of deleterious species is to be avoided.

8.5 Acid Treating (11, 14-16)

When hydrocarbon oils are treated with sulfuric acid, not only do many chemical reactions take place but in addition the acid acts as a refining solvent. It is the most versatile refining agent known and, by the proper selection of treating conditions, it is possible to effect reaction with any of the many constitutents of crude oil, although admittedly the very severe conditions required to obtain appreciable reaction with paraffins and other very chemically stable compounds are not used

commercially in the oil industry. Furthermore, sulfuric acid is cheap and readily available. It is, therefore, not surprising that sulfuric acid was one of the first materials to be used for refining petroleum products, there being references to its use even as far back as 1852. Other acids have been used in petroleum refining but none have found nearly the extensive application that sulfuric has enjoyed. Recently, however, the use of sulfuric acid in petroleum processes has been steadily declining in favor of hydrogen treating. This is because of two major drawbacks from the standpoint of the oil refiner: the appreciable loss of valuable oil components in the acid sludge and the problems associated with disposal of such sludge (14). Still, it is unlikely that acid treating will be completely abandoned, at least in the near future.

The major purpose in acid treating is twofold, the reduction of sulfur content and the removal of highly reactive gum forming hydrocarbons. In addition, many other undesirable materials are removed including oxygenated compounds and basic nitrogen compounds. Unfortunately, certain desirable components are also lost. The selective action of sulfuric acid in attacking deleterious species without affecting desirable components can be controlled to a considerable degree by varying the conditions of treatment. Acid concentration, temperature and contacting time are important processing variables.

In general, acid washing removes many olefinic species and other reactive unsaturated hydrocarbons. Most other hydrocarbons are inert although aromatics can be removed by vigorous treatment (15,16). Many undesirable sulfur compounds, nitrogen compounds, and nearly all oxygenated species are soluble in H_2SO_4 and are removed. However, many other species, deleterious to high stability fuel, may be introduced. Examples are disulfides, traces of which may remain in the fuel after acid treatment. It appears that acid washing can do more harm than good and is best avoided as a manufacturing process for high stability JP-5.

9. RECOMMENDED STORAGE AND HANDLING PROCEDURES

A thermally stable jet fuel can undergo a number of reactions on storage which are deleterious to its quality. Nixon (27) has shown that some fuels decreased in thermal stability by as much as 20 to 70% on prolonged storage. Among the most important reactions occuring during storage is autooxidation (27):

$$R\text{-}H + \text{initiator} \rightarrow R\cdot + \text{product} \qquad (1)$$

$$R\cdot + O_2 \rightarrow R\text{-}O\text{-}O\cdot \qquad (2)$$

$$R\text{-}O\text{-}O\cdot + R\text{-}H \rightarrow R\cdot + R\text{-}O\text{-}O\text{-}H \qquad (3)$$

$$R\cdot + \text{inhibitor} \rightarrow \text{products} \qquad (4)$$

$$R\text{-}O\text{-}O\cdot + \text{inhibitor} \rightarrow \text{products} \qquad (5)$$

Autoxidation results in the build up of hydroperoxides ROOH and peroxides ROOR, species which are highly deleterious to fuel stability (13,27). Since the autoxidation process requires O_2 (eq. (2) above), High Stability JP-5 should be stored under conditions which exclude molecular oxygen to the greatest extent possible. As this may not always be feasible, an antioxidant additive may be desirable. If so, as pointed out in Sections 5 and 8 of this report, the additive must be chosen carefully. Some antioxidants are quite deleterious to high temperature fuel stability. In addition to the results given in this study (Sections 5 and 8) Nixon (27) discovered that some additives actually decreased the storage stability of jet fuels. On the other hand, others were quite beneficial (27). Periodic spot checks for the presence of peroxides are highly desirable.

Autoxidation is catalyzed by light (27,28) which serves as an initiator (reaction (1) above). In addition, sludge formation is accelerated by light (see Section 4). As a result, fuels should be stored with exclusion of light.

Autoxidation and sludge formation, like most organic reactions, are accelerated by temperature. Consequently, High Stability fuel should be stored under cool temperatures, if possible.

Special attention should be paid to fuels with high nitrogen and oxygen contents such as those derived from shale and some coals. These fuels may develop large amounts of sludge at room temperature storage (Section 4 above). Special storage and handling techniques may be necessary for such "synfuels". These fuels have not yet been adequately characterized, nor have their storage properties been studied sufficiently for recommendations as to storage and handling conditions. Clearly, much additional work is required in the area of storage stability of synfuels.

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11. APPENDIX - ADVANCED FUEL UNIT RUN DATA

General Procedure: Prior to the run, the test tubing length is cleaned inside and out with both acetone and chloroform and blown dry with nitrogen. The fuel is filtered and charged to the sparge tank where it is bubbled with air or oxygen free helium, usually for an hour. The fuel is then transferred from the sparge tank, through the cell holding the polarographic oxygen analyzer sensor to the double-piston fuel delivery cylinder. The oxygen content of the fuel is monitored throughout the complete transfer period. Unit pressure is then set, flow of the fuel established, zone heaters turned on and the surface temperatures brought up to the control points. Run length normally consists of four hours with the temperatures at the set points. The heaters are then turned off, and the unit cooled off with fuel flow maintained. Following the run, the reactor tube is removed, drained of fuel, evacuated, washed on the outside with acetone and cleaned with fine sandpaper, and then cut into 3-inch sections.

Tests with tube specimens which had not been used in runs indicated that the fresh tube contained some carbonaceous material even after the standard washing procedure with acetone and chloroform. Fresh tube specimens were also placed in the unit Zone heaters and heated to various temperatures without the presence of any fuel. This "blank" reading was found to be temperature dependent, indicating that some of the residual carbonaceous material was oxidized off the tube. Since the external surface area of the thick walled tube is much larger than the internal area, it was assumed that the majority of this loss also occurs during an actual run. Thus, a series of blank corrections were set so as to evaluate deposit formation rates on a conservative basis, i.e., to insure that the reported net formation of carbonaceous deposits is never lower than the probable actual net formation. The following blank corrections were employed (in micrograms of carbon): 300°F zone, 40; 400°F zone, 35; 500°F zone, 30; 600°F zone, 25; 700°F zone, 20; 800°F zone, 15; 900°F zone, 10; 1,000°F zone, 5; higher temperatures, none.

Run: #147 (NB 589-106)

Run Conditions:

Fuel: Humble JP-5 plus 20 ppm of Dupont #22 Antioxidant (N,N-Di-sec-butyl-p-phenylenediamine). Helium sparged O_2 < 1 ppm.

Pressure: 1,000 psig

Temperatures: Zone 1 - 700°F
Zone 2 - 800°F
Zone 3 - 900°F
Zone 4 - 1000°F

Fuel Flow Rate: 10 cc/min.

Total Run Length: 4 hours

Tube: 1/4" OD type 304 stainless steel, .083" wall

Bulk Fuel Inlet Temperature: 95°F

Bulk Fuel Exit Temperature: 750°F

Analysis of Tube Specimens After Run

Position	Length, Inches	Total Micrograms of Carbon	Local Deposit Formation Rate: g of Carbon per cm^2 per 4 hours x 10^6
Zone 1-1 (inlet)	3	66	12.9
1-2	3	64	12.5
1-3	3	65	12.7
1-4 (exit)	3	62	12.1
Zone 2-1 (inlet)	3	65	12.7
2-2	3	74	14.5
2-3	3	68	13.3
2-4 (exit)	3	62	12.1
Zone 3-1 (inlet)	3	74	14.5
3-2	3	65	12.7
3-3	3	80	15.6
3-4 (exit)	3	97	19.0
Zone 4-1 (inlet)	3	129	25.2
4-2	3	102	20.0
4-3	3	97	19.0
4-4 (exit)	3	101	19.8
Total Reactor Tube		1271	

Run: #148 (NB 589-108)

Run Conditions:

Fuel: Humble JP-5 plus 45 ppm "Hitec-515" corrosion inhibitor.
Helium sparged, O_2 < 1 ppm.

Pressure: 1,000 psig

Temperatures: Zone 1 - 700°F
Zone 2 - 800°F
Zone 3 - 900°F
Zone 4 - 1000°F

Fuel Flow Rate: 10 cc/min.

Total Run Length: 4 hours

Tube: 1/4" OD type 304 stainless steel, .083" wall

Bulk Fuel Inlet Temperature: 100°F

Bulk Fuel Exit Temperature: 760°F

Analysis of Tube Specimens After Run

Position	Length, Inches	Total Micrograms of Carbon	Local Deposit Formation Rate: g of Carbon per cm^2 per 4 hours x 10^6
Zone 1-1 (inlet)	3	71	13.9
1-2	3	76	14.9
1-3	3	73	14.3
1-4 (exit)	3	83	16.2
Zone 2-1 (inlet)	3	95	18.0
2-2	3	95	18.6
2-3	3	108	21.1
2-4 (exit)	3	102	20.0
Zone 3-1 (inlet)	3	122	23.9
3-2	3	151	29.5
3-3	3	130	25.4
3-4 (exit)	3	105	20.5
Zone 4-1 (inlet)	3	119	23.3
4-2	3	147	28.8
4-3	3	150	29.4
4-4 (exit)	3	123	24.1
Total Reactor Tube		1747	

Run: #149 (NB 589-110)

Run Conditions:

Fuel: Humble JP-5 plus 20 ppm 2,6-Di-t-butylphenol. Helium sparged, O_2 < 1 ppm.

Pressure: 1,000 psig

Temperatures: Zone 1 - 700°F
Zone 2 - 800°F
Zone 3 - 900°F
Zone 4 - 1000°F

Fuel Flow Rate: 10 cc/min.

Total Run Length: 4 hours

Tube: 1/4" OD type 304 stainless steel, .083" wall

Bulk Fuel Inlet Temperature: 95°F

Bulk Fuel Exit Temperature: 705°F

Analysis of Tube Specimens After Run

Position	Length, Inches	Total Micrograms of Carbon	Local Deposit Formation Rate: g of Carbon per cm^2 per 4 hours x 10^6
Zone 1-1 (inlet)	3	194	38
1-2	3	192	37.6
1-3	3	232	45.4
1-4 (exit)	3	175	34.2
Zone 2-1 (inlet)	3	137	26.8
2-2	3	229	44.8
2-3	3	430	84.1
2-4 (exit)	3	375	73.4
Zone 3-1 (inlet)	3	315	61.6
3-2	3	526	102.9
3-3	3	701	137.2
3-4 (exit)	3	979	191.0
Zone 4-1 (inlet)	3	900	176.1
4-2	3	983	192.4
4-3	3	1671	327.0
4-4 (exit)	3	904	176.9
Total Reactor Tube		8943	

Run: #150 (NB 589-114)

Run Conditions:

Fuel: Humble JP-5 plus 0.15 wt. % of 2-Methoxyethanol (icing inhibitor). Helium sparged, O_2 < 1 ppm.

Pressure: 1,000 psig

Temperatures: Zone 1 - 700°F
Zone 2 - 800°F
Zone 3 - 900°F
Zone 4 - 1000°F

Fuel Flow Rate: 10 cc/min.

Total Run Length: 4 hours

Tube: 1/4" OD type 304 stainless steel, .083" wall

Bulk Fuel Inlet Temperature: 95°F

Bulk Fuel Exit Temperature: 750°F

Analysis of Tube Specimens After Run

Position	Length, Inches	Total Micrograms of Carbon	Local Deposit Formation Rate: g of Carbon per cm^2 per 4 hours x 10^6
Zone 1-1 (inlet)	3	71	13.9
1-2	3	74	14.5
1-3	3	75	14.7
1-4 (exit)	3	77	15.1
Zone 2-1 (inlet)	3	90	17.6
2-2	3	115	22.5
2-3	3	165	32.3
2-4 (exit)	3	185	36.2
Zone 3-1 (inlet)	3	458	89.6
3-2	3	229	44.8
3-3	3	330	64.6
3-4 (exit)	3	773	151.3
Zone 4-1 (inlet)	3	901	176.3
4-2	3	753	147.4
4-3	3	393	76.9
4-4 (exit)	3	779	152.4
Total Reactor Tube		5468	

Run: #151

Run Conditions:

Fuel: Humble JP-5 plus 20 ppm of 2,6-Di-t-butyl-4-methylphenol (Antioxidant). Helium sparged, O_2 < 1 ppm.

Pressure: 1,000 psig

Temperatures: Zone 1 - 700°F
Zone 2 - 800°F
Zone 3 - 900°F
Zone 4 - 1000°F

Fuel Flow Rate: 10 cc/min.

Total Run Length: 4 hours

Tube: 1/4" OD type 304 stainless steel, .083" wall

Bulk Fuel Inlet Temperature: 90°F

Bulk Fuel Exit Temperature: 745°F

Analysis of Tube Specimens After Run

Position	Length, Inches	Total Micrograms of Carbon	Local Deposit Formation Rate: g of Carbon per cm^2 per 4 hours x 10^6
Zone 1-1 (inlet)	3	80	15.6
1-2	3	73	14.3
1-3	3	88	17.2
1-4 (exit)	3	83	16.2
Zone 2-1 (inlet)	3	83	16.2
2-2	3	104	20.4
2-3	3	80	15.6
2-4 (exit)	3	82	16.0
Zone 3-1 (inlet)	3	90	17.6
3-2	3	74	14.5
3-3	3	94	18.4
3-4 (exit)	3	101	19.8
Zone 4-1 (inlet)	3	120	23.5
4-2	3	124	24.3
4-3	3	105	20.5
4-4 (exit)	3	84	16.4
Total Reactor Tube		1465	

Run: #152 (NB-589-124)

Run Conditions:

Fuel: Humble JP-5, no additives (standard run), Helium sparged $O_2 < 1$ ppm

Pressure: 1,000 psig

Temperatures: Zone 1 - 700°F
Zone 2 - 800°F
Zone 3 - 900°F
Zone 4 - 1000°F

Fuel Flow Rate: 10 cc/min.

Total Run Length: 4 hours

Tube: 1/4" OD type 304 stainless steel, .083" wall

Bulk Fuel Inlet Temperature: 105°F

Bulk Fuel Exit Temperature: 740°F

Analysis of Tube Specimens After Run

Position	Length, Inches	Total Micrograms of Carbon	Local Deposit Formation Rate: g of carbon per cm^2 per 4 hours x 10^6
Zone 1-1 (inlet)	3	99	19.4
1-2	3	80	15.6
1-3	3	98	19.2
1-4 (exit)	3	127	24.8
Zone 2-1 (inlet	3	131	25.6
2-2	3	170	33.3
2-3	3	182	35.6
2-4 (exit)	3	181	35.4
Zone 3-1 (inlet)	3	174	34.0
3-2	3	170	33.3
3-3	3	154	30.1
3-4 (exit)	3	128	25.0
Zone 4-1 (inlet)	3	129	25.2
4-2	3	149	29.2
4-3	3	164	32.1
4-4 (exit)	3	127	24.8
Total Reactor Tube		2263	

Run: #153 (NB-589-128)

Run Conditions:

Fuel: Humble JP-5 plus 100 ppb dissolved Cu.
Helium sparged O_2 <1 ppm.

Pressure: 1,000 psig

Temperatures: Zone 1 - 700°F
Zone 2 - 800°F
Zone 3 - 900°F
Zone 4 - 1000°F

Fuel Flow Rate: 10 cc/min.

Total Run Length: 4 hours

Tube: 1/4" OD type 304 stainless steel, .083" wall

Bulk Fuel Inlet Temperature: 100°F

Bulk Fuel Exit Temperature: 705°F

Analysis of Tube Specimens After Run

Position	Length, Inches	Total Micrograms of Carbon	Local Deposit Formation Rate: g of carbon per cm^2 per 4 hours x 10^6
Zone 1-1 (inlet)	3	121	23.7
1-2	3	153	29.9
1-3	3	159	31.1
1-4 (exit)	3	118	23.1
Zone 2-1 (inlet	3	149	29.2
2-2	3	145	28.2
2-3	3	183	35.8
2-4 (exit)	3	190	37.2
Zone 3-1 (inlet)	3	123	24.1
3-2	3	166	32.5
3-3	3	175	34.2
3-4 (exit)	3	257	50.3
Zone 4-1 (inlet)	3	245	47.9
4-2	3	253	49.5
4-3	3	236	46.2
4-4 (exit)	3	290	56.8
Total Reactor Tube		2963	

Run: #153 (NB-589-128)

Run Conditions:

Fuel: Humble JP-5 plus 100 ppb dissolved Cu.
Helium sparged O_2 <1 ppm.

Pressure: 1,000 psig

Temperatures: Zone 1 - 700°F
Zone 2 - 800°F
Zone 3 - 900°F
Zone 4 - 1000°F

Fuel Flow Rate: 10 cc/min.

Total Run Length: 4 hours

Tube: 1/4" OD type 304 stainless steel, .083" wall

Bulk Fuel Inlet Temperature: 100°F

Bulk Fuel Exit Temperature: 705°F

Analysis of Tube Specimens After Run

Position	Length, Inches	Total Micrograms of Carbon	Local Deposit Formation Rate: g of carbon per cm^2 per 4 hours x 10^6
Zone 1-1 (inlet)	3	121	23.7
1-2	3	153	29.9
1-3	3	159	31.1
1-4 (exit)	3	118	23.1
Zone 2-1 (inlet	3	149	29.2
2-2	3	145	28.2
2-3	3	183	35.8
2-4 (exit)	3	190	37.2
Zone 3-1 (inlet)	3	123	24.1
3-2	3	166	32.5
3-3	3	175	34.2
3-4 (exit)	3	257	50.3
Zone 4-1 (inlet)	3	245	47.9
4-2	3	253	49.5
4-3	3	236	46.2
4-4 (exit)	3	290	56.8
Total Reactor Tube		2963	

Run: #154 (NB-589-130)

Run Conditions:

Fuel: Humble JP-5 plus 200 ppb dissolved copper. Helium sparged O_2 <1 ppm.

Pressure: 1,000 psig

Temperatures: Zone 1 - 700°F
Zone 2 - 800°F
Zone 3 - 900°F
Zone 4 - 1000°F

Fuel Flow Rate: 10 cc/min.

Total Run Length: 4 hours

Tube: 1/4" OD type 304 stainless steel, .083" wall

Bulk Fuel Inlet Temperature: 100°F

Bulk Fuel Exit Temperature: 720°F

Analysis of Tube Specimens After Run

Position	Length, Inches	Total Micrograms of Carbon	Local Deposit Formation Rate: g of carbon per cm^2 per 4 hours x 10^6
Zone 1-1 (inlet)	3	93	18.2
1-2	3	147	28.8
1-3	3	236	46.2
1-4 (exit)	3	208	40.7
Zone 2-1 (inlet	3	250	48.9
2-2	3	194	38.0
2-3	3	386	75.5
2-4 (exit)	3	368	72.0
Zone 3-1 (inlet)	3	269	52.6
3-2	3	212	41.5
3-3	3	348	68.1
3-4 (exit)	3	235	46.0
Zone 4-1 (inlet)	3	242	47.4
4-2	3	538	105.3
4-3	3	370	72.4
4-4 (exit)	3	667	130.5
Total Reactor Tube		4763	

Run: #155 (NB-589-132)

Run Conditions:

Fuel: Humble JP-5 plus 100 ppb dissolved copper plus 100 ppm O as n-decanoic acid. Helium sparged O_2 <1 ppm.

Pressure: 1,000 psig

Temperatures: Zone 1 - 700°F
Zone 2 - 800°F
Zone 3 - 900°F
Zone 4 - 1000°F

Fuel Flow Rate: 10 cc/min.

Total Run Length: 4 hours

Tube: 1/4" OD type 304 stainless steel, .083" wall

Bulk Fuel Inlet Temperature: 100°F

Bulk Fuel Exit Temperature: 720°F

Analysis of Tube Specimens After Run

Position	Length, Inches	Total Micrograms of Carbon	Local Deposit Formation Rate: g of carbon per cm^2 per 4 hours x 10^6
Zone 1-1 (inlet)	3	71	13.9
1-2	3	70	13.7
1-3	3	89	17.4
1-4 (exit)	3	103	20.2
Zone 2-1 (inlet	3	70	13.7
2-2	3	97	19.0
2-3	3	166	32.5
2-4 (exit)	3	120	23.5
Zone 3-1 (inlet)	3	157	30.7
3-2	3	196	38.4
3-3	3	240	47.0
3-4 (exit)	3	216	42.3
Zone 4-1 (inlet)	3	274	53.6
4-2	3	282	55.2
4-3	3	170	33.3
4-4 (exit)	3	180	35.2
Total Reactor Tube		2501	

Run: #156 (NB-589-134)

Run Conditions:

Fuel: Humble JP-5 plus 100 ppb dissolved copper plus 10 ppm benzotriazole. Helium sparged O_2 <1 ppm.

Pressure: 1,000 psig

Temperatures: Zone 1 - 700°F
Zone 2 - 800°F
Zone 3 - 900°F
Zone 4 - 1000°F

Fuel Flow Rate: 10 cc/min.

Total Run Length: 4 hours

Tube: 1/4" OD type 304 stainless steel, .083" wall

Bulk Fuel Inlet Temperature: 95°F

Bulk Fuel Exit Temperature: 725°F

Analysis of Tube Specimens After Run

Position	Length, Inches	Total Micrograms of Carbon	Local Deposit Formation Rate: g of carbon per cm^2 per 4 hours x 10^6
Zone 1-1 (inlet)	3	217	42.5
1-2	3	330	64.6
1-3	3	337	65.9
1-4 (exit)	3	384	75.1
Zone 2-1 (inlet	3	252	49.3
2-2	3	373	73.0
2-3	3	437	85.5
2-4 (exit)	3	344	67.3
Zone 3-1 (inlet)	3	439	85.9
3-2	3	540	105.7
3-3	3	376	73.6
3-4 (exit)	3	299	58.5
Zone 4-1 (inlet)	3	259	50.7
4-2	3	234	45.8
4-3	3	294	57.5
4-4 (exit)	3	375	73.4
Total Reactor Tube		5490	

Run: #157 (NB-589-136)

Run Conditions:

Fuel: Humble JP-5 plus 100 ppb dissolved copper. Air sparged O_2 >50 ppm.

Pressure: 1,000 psig

Temperatures: Zone 1 - 700°F
Zone 2 - 800°F
Zone 3 - 900°F
Zone 4 - 1000°F

Fuel Flow Rate: 10 cc/min.

Total Run Length: 4 hours

Tube: 1/4" OD type 304 stainless steel, .083" wall

Bulk Fuel Inlet Temperature: 100°F

Bulk Fuel Exit Temperature: 745°F

Analysis of Tube Specimens After Run

Position	Length, Inches	Total Micrograms of Carbon	Local Deposit Formation Rate: g of carbon per cm^2 per 4 hours x 10^6
Zone 1-1 (inlet)	3	80	15.6
1-2	3	146	28.6
1-3	3	630	123.3
1-4 (exit)	3	237	46.4
Zone 2-1 (inlet	3	246	48.1
2-2	3	216	42.3
2-3	3	241	47.2
2-4 (exit)	3	289	56.6
Zone 3-1 (inlet)	3	103	20.2
3-2	3	290	56.8
3-3	3	216	42.3
3-4 (exit)	3	181	35.4
Zone 4-1 (inlet)	3	187	36.6
4-2	3	244	47.7
4-3	3	485	94.9
4-4 (exit)	3	215	42.1
Total Reactor Tube		4006	

Run: #158 (NB-589-138)

Run Conditions:

Fuel: Humble JP-5 plus 100 ppb of dissolved iron. Helium sparged $O_2 < 1$ ppm.

Pressure: 1,000 psig

Temperatures: Zone 1 - 700°F
Zone 2 - 800°F
Zone 3 - 900°F
Zone 4 - 1000°F

Fuel Flow Rate: 10 cc/min.

Total Run Length: 4 hours

Tube: 1/4" OD type 304 stainless steel, .083" wall

Bulk Fuel Inlet Temperature: 85°F

Bulk Fuel Exit Temperature: 700°F

Analysis of Tube Specimens After Run

Position	Length, Inches	Total Micrograms of Carbon	Local Deposit Formation Rate: g of carbon per cm^2 per 4 hours x 10^6
Zone 1-1 (inlet)	3	159	31.1
1-2	3	248	48.5
1-3	3	247	48.3
1-4 (exit)	3	228	44.6
Zone 2-1 (inlet	3	231	45.2
2-2	3	348	68.1
2-3	3	271	53.0
2-4 (exit)	3	217	42.5
Zone 3-1 (inlet)	3	269	52.6
3-2	3	237	46.4
3-3	3	268	52.4
3-4 (exit)	3	317	62.0
Zone 4-1 (inlet)	3	326	75.9
4-2	3	369	72.2
4-3	3	1255	245.6
4-4 (exit)	3	840	164.4
Total Reactor Tube		5830	

Run: #159 (NB-589-140)

Run Conditions:

Fuel: Humble JP-5 plus 10 ppb of dissolved iron. Helium sparged $O_2 < 1$ ppm.

Pressure: 1,000 psig

Temperatures: Zone 1 - 700°F
Zone 2 - 800°F
Zone 3 - 900°F
Zone 4 - 1000°F

Fuel Flow Rate: 10 cc/min.

Total Run Length: 4 hours

Tube: 1/4" OD type 304 stainless steel, .083" wall

Bulk Fuel Inlet Temperature: 95°F

Bulk Fuel Exit Temperature: 735°F

Analysis of Tube Specimens After Run

Position	Length, Inches	Total Micrograms of Carbon	Local Deposit Formation Rate: g of carbon per cm^2 per 4 hours x 10^6
Zone 1-1 (inlet)	3	132	25.8
1-2	3	166	32.5
1-3	3	285	55.8
1-4 (exit)	3	304	70.4
Zone 2-1 (inlet	3	277	54.2
2-2	3	368	72.0
2-3	3	200	39.1
2-4 (exit)	3	228	44.6
Zone 3-1 (inlet)	3	202	39.5
3-2	3	210	41.1
3-3	3	229	44.8
3-4 (exit)	3	257	50.3
Zone 4-1 (inlet)	3	356	69.7
4-2	3	304	59.5
4-3	3	385	75.3
4-4 (exit)	3	337	65.9
Total Reactor Tube		4240	

Run: #160 (NB-589-142)

Run Conditions:

Fuel: Humble JP-5 plus 100 ppb of dissolved vanadium. Helium sparged $O_2 < 1$ ppm.

Pressure: 1,000 psig

Temperatures: Zone 1 - 700°F
Zone 2 - 800°F
Zone 3 - 900°F
Zone 4 - 1000°F

Fuel Flow Rate: 10 cc/min.

Total Run Length: 4 hours

Tube: 1/4" OD type 304 stainless steel, .083" wall

Bulk Fuel Inlet Temperature: 95°F

Bulk Fuel Exit Temperature: 725°F

Analysis of Tube Specimens After Run

Position	Length, Inches	Total Micrograms of Carbon	Local Deposit Formation Rate: g of carbon per cm^2 per 4 hours x 10^6
Zone 1-1 (inlet)	3	25	4.9
1-2	3	48	9.4
1-3	3	50	9.8
1-4 (exit)	3	60	11.7
Zone 2-1 (inlet	3	58	11.4
2-2	3	59	11.5
2-3	3	55	10.8
2-4 (exit)	3	63	12.3
Zone 3-1 (inlet)	3	58	11.4
3-2	3	68	13.3
3-3	3	60	11.7
3-4 (exit)	3	69	13.5
Zone 4-1 (inlet)	3	89	17.4
4-2	3	135	26.4
4-3	3	136	26.6
4-4 (exit)	3	85	16.6
Total Reactor Tube		1118	

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

An extended program has been completed which meets the original objective of developing a High Stability JP-5 fuel. This fuel exhibits the markedly improved thermal stability characteristics required for high speed aircraft and yet retains the general physical characteristics of present day JP-5. This development makes possible the design of an improved performance Mach 4-5 speed range aircraft without resorting to cryogenic or specialty fuels and simplifies logistic problems because of its ability to be used in lower speed aircraft.

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Phase III of this contract was devoted to a study of the effects of selected jet fuel additives and of certain dissolved metals on the thermal stability of deoxygenated JP-5. In addition, a room temperature interaction between a pyrrole and a carboxylic acid, previously found to be deleterious to storage stability, was studied in more detail. The results of fuel stability research over the length of the contract are summarized in this report and the implications of these results for establishing new fuel specifications are discussed. The potential effects of various refinery processes on fuel stability are reviewed. Recommendations concerning storage and handling techniques are also summarized.