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THE STUDY OF HYDROCARBON FUEL VAPOR DEPOSITS

William F. Taylor

ESSO RESEARCH AND ENGINEERING COMPANY

Technical Report AFAPL-TR-69-77
September 1969

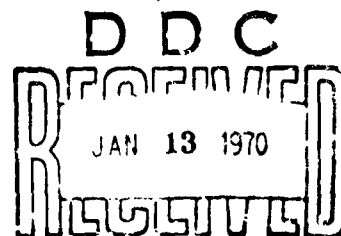
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AFAPL-TR-69-77

THE STUDY OF HYDROCARBON FUEL
VAPOR PHASE DEPOSITS

William F. Taylor

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AIR FORCE AERO PROPULSION LABORATORY
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report was prepared by the Government Research Laboratory, Esso Research and Engineering Company at Linden, New Jersey, under Contract AF33(615)-3575. This program is administered by the Air Force Aero Propulsion Laboratory, Air Force Systems Command with Lt. J. C. Ford serving as coordinator.

This final report covers work conducted from 15 May 1966 to 15 May 1969, and was submitted by the author on 12 June 1969. Dr. William F. Taylor was the principal investigator on the program assisted by Mr. Robert L. Bruncati. The program was administered by Dr. Murray S. Cohen and Dr. Thomas J. Wallace. Helpful discussions with Mr. H. R. Lander, Jr., and Mr. W. G. Dukek are gratefully acknowledged.

This technical report has been reviewed and is approved.

Arthur V. Churchill

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Fuels, Lubrication and Hazards Division
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ABSTRACT

Deposits form in the "empty" wing tank of a supersonic aircraft as a result of a complex free radical autoxidation process. The complete exclusion of oxygen suppresses deposit formation. Deposits are formed much more rapidly when a condensed (liquid) phase is present than when no condensed phase is present. An apparatus was designed which quantitatively measures the rate of deposit formation. Higher total pressure and increasing oxygen pressure increases the level of deposit formation. Trace levels of sulfur and nitrogen compounds markedly increase deposit formation. The nature of metal surfaces to which the fuel is exposed was found to influence the rate of deposit formation. Vanadium containing titanium alloys and copper surfaces were found to be particularly deleterious. The presence of dissolved metals also markedly increased the level of deposit formation. Studies were made with pure compounds and simple binary blends of pure compounds. The broad objective of this work was to elucidate the effect of jet fuel hydrocarbon composition on deposit formation. Currently used antioxidant additives were found to be ineffective in reducing the rate of deposit formation. The use of rust preventive and metal deactivator additives increased the rate of deposit formation. Coating an active metal surface with a polymeric material increased the level of deposit formation.

TABLE OF CONTENTS

	<u>Page</u>
I. INTRODUCTION	1
II. PHASE I STUDIES: ELUCIDATION OF THE UNDERLYING PROCESSES IN DEPOSIT FORMATION	2
A. Survey of Background Technical Information	2
1. Survey of the Literature	2
a. Introduction	2
b. Chemistry and Mechanism of Related Hydrocarbon Reactions	2
1. Liquid Phase Autoxidation	2
2. Oxidative Polymerization	3
3. Vapor Phase Oxidation	5
4. Reactions of Sulfur and Nitrogen Compounds	6
5. Catalytic Effect of Metals	7
6. Jet Fuel Additives	8
c. Deposit Formation During the Storage of Hydrocarbons	8
d. Supersonic Flight Fuel Tank Simulator Results	12
e. Summary	13
2. Field Survey of Airframe Manufacturers	14
B. Study of the Effect of Phase Type on Deposit Formation	15
1. Construction of Phase Study Unit	15
2. Results from the Phase Study	15
C. Development of an Apparatus and Test Procedure to Quantitatively Measure Deposit Formation in the "Empty" Wing Tank Environment	17
1. Design and Construction of the Screening Unit	17
2. Reproducibility of Data Obtained in the Unit	20
3. Weight Increase From Autoxidative Hydrocarbon Deposits Relative to Weight Increase Caused by Oxidative of the Metal	22
4. Temperature Measurements in the Screening Unit	22
D. The Study of the Effect of Variables Such as Temperature, Pressure, Oxygen Partial Pressure and Exposure Time on Deposit Formation	24
1. The Effect of Temperature and Total Pressure on the Rate of Deposit Formation	24
2. The Effect of Oxygen Partial Pressure on the Rate of Deposit Formation	30
3. The Effect of Exposure Time on The Rate of Deposit Formation	33
4. Evaluation of Water Saturated Fuel and Decane	33

TABLE OF CONTENTS (Cont'd)

	<u>Page</u>
E. The Study of the Effect of Trace Impurities on Deposit Formation	37
1. The Effect of Trace Levels of Sulfur Compounds on Deposit Formation	37
2. Studies of the Role of Sulfur Compounds in the Deposit Formation Process	50
3. The Effect of Trace Levels of Nitrogen Compounds	58
4. Interactions Between Trace Contaminants in The Fuel	58
a. Study of the Interactions Between Trace Sulfur and Nitrogen Compounds	58
b. Interactions Between Trace Nitrogen Compounds and Dissolved Metals	62
F. The Study of the Effect of Metal Surfaces and Dissolved Metals on Deposit Formation	66
G. The Study of the Effect of Fuel Composition on Deposit Formation	75
1. Studies with Pure Compounds and Binary Blends of Pure Compounds	75
2. The Study of Interactions Between Aromatics, Naphthenes and Olefins	99
3. Metal Type Effects with Decane	103
H. The Nature of Deposits and the Overall Deposit Formation Process	103
I. Electron Microscope Study of Various Deposit Specimens	106
J. Results of an Exploratory Oxidation Study with n-Decane	107
III. PHASE II STUDIES: INVESTIGATION OF POTENTIAL METHODS TO ALLEVIATE THE PROBLEM	118
A. Evaluation of "Empty" Wing Tank Deposit Formation Tendency of Commercial Jet Fuels	118
1. Quantitative Measurement of the Deposit Formation Rate	118
2. Analytical Characterization of Typical Jet Fuels	118
B. The Effect of Rigorous Exclusion of Oxygen	118
C. The Effect of Current Flows on Deposit Formation	118
D. The Effect of Surface Coatings on Deposit Formation	140
1. Deposit Formation Tendency of Polymer Coated Titanium Alloy Specimens	140
2. Studies of the Effect of Various Surfaces on the Autoxidation of Typical Hydrocarbons	147

TABLE OF CONTENTS (Cont'd)

	<u>Page</u>
a. Design and Construction of a Hydrocarbon Autoxidation Kinetic Unit	147
b. The Effect of Polymeric Surfaces on the Oxidation of Tetralin	149
c. The Effect of Metal Oxides on the Oxidation of Tetralin	168
IV. CONCLUSIONS	175
V. APPENDICES	177
VI. REFERENCES	224

LIST OF ILLUSTRATIONS

<u>Figure</u>	<u>Title</u>	<u>Page</u>
1	Phase Study Unit-Schematic	16
2	Screening Unit-Schematic	19
3	Screening Unit Tests of RAF-176-63 and Thermally Stable Kerosine at 3 psia.	21
4	The Weight Pickup From Hydrocarbon Deposits is Orders of Magnitude Greater Than From the Oxidation of Titanium Metal	23
5	The Effect of Pressure on the Deposit Formation Rate of Baton Rouge Fuel	25
6	Screening Unit Evaluation of Fuels at Atmospheric Pressure	26
7	Evaluation of AAFB-8-67 (AZ-1) at One Atmosphere Total Pressure	28
8	Effect of Pressure on the Deposit Formation Rate of n-Decane	29
9	Effect of Pressure on Deposit Formation of 10% Indene in n-Decane	31
10	Relative Activity as a Function of Oxygen Partial Pressure	32
11	Deposit Formation as a Function of Exposure Time	34
12	Relative Activity for Deposit Formation as a Function of Exposure Time	35
13	Screening Unit Evaluation of Water Saturated Baton Rouge Fuel and Decane	36
14	Cut-Off Temperature as a Function of Sulfur Content	38
15	Cut-Off Temperature as a Function of Final Boiling Point	39

<u>Figure</u>	<u>Title</u>	<u>Page</u>
16	The Effect of the Addition of 1000 ppm S	42
17	The Effect of the Addition of 1000 ppm S	43
18	The Effect of the Addition of 1000 ppm S	44
19	The Effect of the Addition of 1000 ppm S	45
20	The Effect of Sulfur Concentration	47
21	Effect of Concentration on Pyrolysis	52
22	Second Order Plot of Pyrolysis in Hydrocarbon Media	53
23	Second Order Plot of Pyrolysis in Butyl Carbitol	54
24	Second Order Plot of Pyrolysis in Trichlorotoluene	55
25	Pyrolysis of Thianophthene 1,1 Dioxide	56
26	Effect of Doping P&W 523 with 1000 ppm Nitrogen	59
27	The Effect of 2,5 Dimethylpyrrole Concentration in P&W 523	60
28	The Effect of Nitrogen Content on the Rate of Deposit Formation	61
29	Dissolved Metal-Trace Nitrogen Interaction	65
30	Effect of Metal Type on the Deposit Formation Process	67
31	Evaluation of Aluminum Metal	68
32	The Effect of a Copper Metal Surface on the Deposit Formation Process	69
33	The Effect of Vanadium Content of Titanium Alloys on Deposit Formation	70
34	The Effect of the Addition of Metal Acetylacetonates to RAF-176-63 at the 50 ppm Metal Level	71

<u>Figure</u>	<u>Title</u>	<u>Page</u>
35	The Effect on Deposit Formation of Various Levels of Ferric Acetylacetonates	73
36	The Rate of Deposit Formation Exhibits a Square Root Dependence on Metal Concentration	74
37	Deposit Formation With Pure n-Paraffins	76
38	Normal Paraffins - Isomeric Paraffin Blends	77
39	Normal Versus Branched C ₁₂ Paraffins	78
40	Methylnaphthalene in Decane Blends	81
41	Methylnaphthalene in Decane Blends	82
42	The Effect of Concentration	83
43	Butyltoluene and Phenylcyclohexane in Decane	84
44	Tetralin and Decalin in Decane	85
45	Methylnaphthalene and Naphthalene in Decane	86
46	Phenyloctane and Butylcyclohexane in Decane	87
47	Diisopropylbenzene in Decane and Hexadecane	88
48	Effect of Adding Diphenylmethane to Decane	89
49	Fluorene in Decane	90
50	Inhibition Related to Benzylic Hydrogen	91
51	Deposit Formation Rate of Phenyl Olefins in Decane	93
52	Deposit Formation Rate of Cyclic Non-Aromatic Olefins in Decane	94
53	Olefins in Decane	95
54	Results of Interaction Study	101
55	Results of Interaction Study	102

<u>Figure</u>	<u>Title</u>	<u>Page</u>
56	Scanning Electron Micrographs of 362-84-5	108
57	Scanning Electron Micrographs of 362-84-5	109
58	Scanning Electron Micrographs of 390-45-4	110
59	Scanning Electron Micrographs of 390-45-4	111
60	Scanning Electron Micrographs of 362-100-1	112
61	Scanning Electron Micrographs of 390-20-1	113
62	Scanning Electron Micrographs of 390-19-4	114
63	Scanning Electron Micrographs of 390-19-4	115
64	Scanning Electron Micrographs of 362-43-3	116
65	Screening Unit Tests of FA-S-2B, Baton Rouge and P&W 523 Fuels at 3 psi	119
66	Screening Unit Test of AFFB-9-67	120
67	Screening Unit Evaluation of AFFB-12-68 at 3 psia	121
68	Fuel AFFB-4-64 (FA-S-1)	122
69	Screening Unit Evaluation of AFFB-10-67	123
70	Screening Unit Evaluation of Fuel AFFB-11-68 at 3 psia	124
71	Screening Unit Evaluation of RAF-174-63	125
72	Screening Unit Evaluation of AFFB-8-67 at psia	126
73	Evaluation of A022 Additive in RAF-176-63 Fuel	131
74	Evaluation of A029 Additive in Baton Rouge Fuel	132
75	Evaluation of A031 Additive in Baton Rouge Fuel	133
76	Evaluation of Ethyl 733 Additive in Baton Rouge Fuel	134
77	Evaluation of AFA-1 Additive in Baton Rouge Fuel	135

<u>Figure</u>	<u>Title</u>	<u>Page</u>
78	Evaluation of DMD Additive in Baton Rouge Fuel	136
79	Evaluation of Santolene C Additive in Baton Rouge Fuel	137
80	Evaluation of Fluorocarbon Lubricity Additive in Baton Rouge Fuel	138
81	Evaluation of Methyl Cellosolve in Baton Rouge Fuel	139
82	Evaluation of Strips Coated with RS 5660 in Screening Unit at 3 psia	142
83	Evaluation of Strips Coated with 954-01 in Screening Unit at 3 psia	143
84	Evaluation of Strips Coated with TFE 851-204 in Screening Unit at 3 psia	144
85	Evaluation of Strips Coated with Silicone R 671 in Screening Unit at 3 psia	145
86	Evaluation of Strips Coated with 94-003 in Screening Unit at 3 psia	146
87	Hydrocarbon Autoxidation Kinetics Unit	148
88	Oxidation of Tetralin at 90°C	152
89	Oxidation of Tetralin at 65°C	153
90	Initial Rate of the Teflon Catalyzed Oxidation of Tetralin	155
91	The Effect of Temperature on the Induction Period for the Teflon Catalyzed Oxidation of Tetralin	156
92	Teflon Catalyzed Decomposition of Tetralin Hydroperoxide	158
93	Teflon Catalyzed Decompositon of Tetralin Hydroperoxide at 105°C	160
94	Teflon Catalyzed Decomposition of Tetralin Hydroperoxide	161

<u>Figure</u>	<u>Title</u>	<u>Page</u>
95	Products and Reactants During Teflon Catalyzed Oxidation of Tetralin	162
96	Products of the Teflon Catalyzed Decomposition of Tetralin Hydroperoxide	164
97	Ketone Accelerates the Catalyzed Oxidation of Tetralin	169
98	Effect of Temperature on the Metal Catalyzed Oxidation of Tetralin	174

LIST OF TABLES

<u>Numbers</u>	<u>Title</u>	<u>Page</u>
I	Phase Study Unit Experiments with RAF-176-63	18
II	Analysis of Variance of Linear Regressions	40
III	Comparison of Observed Rate of Deposit Formation with Probably Sulfur Compound Initial Decomposition Products	49
IV	Trace Sulfur-Trace Nitrogen-Olefin Interaction Study in n-Decane	63
V	Study of the Interactions Between Trace Levels of Dissolved Metals and Nitrogen Compounds	64
VI	The Effect of Branching in Paraffins on Deposit Formation	79
VII	Summary of Deposit Formation Tendencies of Olefin-n-Decane Binary Blends	96
VIII	The Effect of Olefin Content on Deposit Formation	97
IX	Olefin-Aromatic-Naphthene Interaction Study in Decane	100
X	Infrared Spectral Analyses	117
XI	Physical Inspections of Jet Fuels	127
XII	Distribution of Compound Types in Jet Fuels	128
XIII	Summary of the Effect of Various Additives on Deposit Formation	129
XIV	Coating and Coating Conditions Employed	141
XV	Summary of Polymer Catalyst Activity and Inspections	151
XVI	Relative Rates of Tetralin Hydroperoxide Decomposition as a Function of Concentration and Catalyst Loading	159

<u>Numbers</u>	<u>Title</u>	<u>Page</u>
XVII	Relative Rates of Tetralin Oxidation as a Function of Tetralin Concentration, Oxygen Pressure and Catalyst Loading	167
XVIII	Summary of Hydrocarbon Autoxidation Kinetic Unit Runs with Metal Oxides	171
XIX	Surface Area of Metal Oxide Catalysts	172
XX	Activity of Supported Metal Oxides for the Oxidation of Tetralin	173

I. INTRODUCTION

In a high speed supersonic aircraft aerodynamic heating causes metal skin temperatures to rise considerably above those encountered in subsonic aircraft. It has been estimated for a plane such as the Mach 2.7 Supersonic Transport that exterior surface temperatures could rise to 450°F, and the temperature of an uninsulated fuel tank could rise to 430°F. One particular problem area is the formation of deposits in fuel wing tanks which contain puddles of residual liquid hydrocarbon and hydrocarbon vapor. Such deposits may flake off and contaminate the bulk fuel and cause malfunctions in the fuel system components.

The problem of fuel stability in the storage tanks of a Mach 2 to Mach 3 aircraft environment was first studied in large scale Fuel System Simulator Rig tests. In the five SST tests run in the FAA-CRC programs, deposits occurred in four of them with fuels of widely varying stability (measured in a Fuel Coker). Only with 42 cycles at Mach 2.5 temperatures were tanks found to be completely free of deposits. In all other tests, deposits were found to a varying extent in the vent area and on the heated floor of the "empty" wing tank. In the case of the most unstable fuel, deposits were found also on the heated ceiling of the simulated empty wing tank. In the "fuselage" tank which always contained liquid, no deposits were observed on the walls, but the vent lines showed deposits in all Mach 3 runs. Thus, these Fuel System Simulator tests clearly demonstrated that a fuel stability problem did exist. However, the rig data did not provide a clear understanding of the problem, and actually raised additional questions such as the influence of the liquid and vapor phase on deposit formation. As a result, the Air Force implemented a fundamentally oriented program which would compliment rig test studies, and which had as its objective:

- (a) to elucidate the underlying factors involved in deposit formation in the so-called "empty" wing tank and
- (b) to investigate potential methods for alleviating the deposit formation problem.

A number of significant accomplishments have been achieved under this program. Broadly, this program has resulted in uncovering a great deal of understanding about the deposit formation process in the "empty" wing tank environment. In addition, its results are not only applicable to this specific environment but to the whole problem of the oxidative stability of hydrocarbon fuels at high temperatures. Using a fundamentally oriented research approach, the program identified, and for the first time, quantitatively measured the effect of a large number of variables which control the complex deposit formation process. A number of potential methods for alleviating the "empty" wing tank deposit formation problem were also investigated in depth.

II. PHASE I STUDIES: ELUCIDATION OF THE UNDERLYING PROCESS INVOLVED IN DEPOSIT FORMATION

A. Survey of Background Technical Information

1. Survey of The Literature

a. Introduction

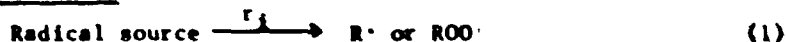
There is a wide spectrum of information available in the literature which we believe is pertinent to the "empty" wing tank deposit problem. This includes recent studies simulating supersonic flight conditions in a fuel tank, studies on the formation of deposits during the storage of hydrocarbon fuels at low temperatures, and an extensive body of literature covering the chemistry and mechanism of reactions believed related to the wing tank deposit problem. A review of this total body of information is presented and discussed in this section of the report.

b. Chemistry and Mechanism of Related Hydrocarbon Reactions

1. Liquid Phase Autoxidation

Liquid phase autoxidation, exclusive of oxidative polymerization which will be treated separately, will be discussed in this section. In general, liquid phase oxidation reactions are faster than the corresponding vapor phase reaction and they are more selective (1). These reactions are catalyzed by metal salts and influenced by other variables such as temperature, oxygen pressure, hydrocarbon concentration and the presence of oxidation inhibitors. In general, hydrocarbon autoxidation consists of two distinct reaction sequences; first, a primary process in which relatively simple free radical reactions result in the formation of a hydroperoxide, and a secondary process in which these hydroperoxides react in different ways to form end products. The following chain reaction mechanism is usually cited (2):

Initiation:



Propagation:



Branching:



Terminations:



} Stable Products

In an oxygen rich system, the hydrocarbon radicals ($\text{R}^\cdot$) are removed rapidly and the propagation step is controlled by Reaction 3 ($r_3 < r_2$). Correspondingly, termination occurs principally by Reaction 7, the disproportionation of two peroxy radicals ($r_7 > r_5$ and r_6), because of the low concentration of hydrocarbon radicals. Therefore, the overall reaction rate at high O_2 partial pressures is:

$$-\frac{dO_2}{dt} = k_2 \left(\frac{r_1}{k_5} \right)^{1/2} [RH] \quad (8)$$

For olefins (2), this high pressure region corresponds to oxygen partial pressures greater than 100 mm Hg. At low oxygen partial pressures, the propagation step is controlled by Reaction 2 ($r_2 < r_3$) because of the low concentration of oxygen. Similarly, the termination step is controlled by Reaction 5 ($r_5 > r_6$ and r_7) because of the high concentration of hydrocarbon radicals relative to peroxy radicals. The overall rate at low O_2 partial pressures is given by:

$$-\frac{dO_2}{dt} = k_1 \left(\frac{r_1}{k_3} \right)^{1/2} [O_2] \quad (9)$$

It is interesting to note that this kinetic analysis predicts that at high O_2 partial pressure the overall rate of oxidation is independent of oxygen partial pressure. However, at low oxygen partial pressures, it is dependent on oxygen partial pressure. For olefins, this low pressure region has been found to exist below 1 mm Hg of oxygen partial pressure (3). Situations with intermediate oxygen partial pressures produce more complex kinetics (4).

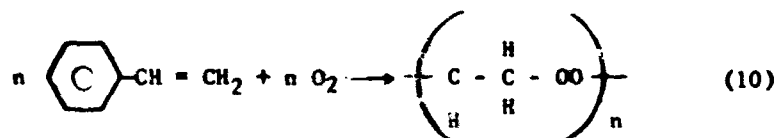
The initiation reaction can be catalyzed by (1) illumination, (2) metals of variable valence, and (3) the decomposition of peroxides into radical fragments. Soluble metal catalysts and insoluble metal oxides have both been shown to influence autoxidation rates. Induction periods are also prevalent in liquid phase autoxidation reactions. The termination process is quite complex because of the large number of reactions that are possible. However, in general, the highest molecular weight product that can be produced is a dimer (RR) or an oxygenated dimer ($ROOR$) of the starting hydrocarbon (RH) so that a simple autoxidation reaction will not produce a high molecular weight polymeric material. Thus, the importance of autoxidation reactions relative to the wing tank deposit problem may be their ability to generate a spectrum of free radical intermediates which can accelerate other reactions such as oxidative polymerization.

2. Oxidative Polymerization

This section is concerned with the low temperature reaction of hydrocarbons with oxygen to produce high molecular weight polymeric products. Two types of oxidative polymerization reactions are possible (5); first, polycondensation reactions between autoxidation products to form polymeric materials with ester linkages, and second, the addition polymerization of olefins. It has been postulated that polycondensation reactions are responsible for sediment formation in hydrocarbon fractions (6). It has been suggested that the hydrocarbon first undergoes autoxidation to form unstable hydroperoxides which then decompose and interact with other hydroperoxides before undergoing polycondensation reactions to form polymeric "sediment" compounds. Condensation polymerization reactions, i.e., monomer molecules are combined with the loss of some simple molecules, are well known (7) and are used commercially to form polymers such as Nylon and Dacron. Condensation polymerization reactions are characterized by the fact that a broad spectrum of molecular weight products is formed, depending on variables such as extent of reaction and the functionality of the reactant molecule (5). Addition polymerization, i.e., monomers are simply added together, occurs by joining together compounds containing olefin linkages. If the reactants have a functionality

of two or better (5), then high molecular weight polymers can result. Addition polymerizations such as ethylene polymerization are characterized by the formation of high molecular weight products even in the early stages of the reaction. Addition polymerization reactions can occur by a free radical reaction catalyzed by peroxide initiators. Thus, any olefins initially present in a hydrocarbon fuel could form a high molecular weight addition polymerization product. Perhaps more important, any compound present in a hydrocarbon fuel which can decompose to form an olefin or react in the presence of oxygen to form an olefin, represents a potential addition polymerization monomer.

The presence of a double bond in a hydrocarbon molecule increases the susceptibility of attack by oxygen to form a hydroperoxide at the carbon atom adjacent to the double bond (methylene groups $\propto$ to double bond). In the case of a polymeric peroxide, the oxygen adds directly to the double bond as in a copolymerization reaction (2). This is illustrated below with styrene.



Although some hydrocarbons containing a double bond active for addition reactions produce a hydroperoxide of the monomer unit or its dimer, the majority of compounds undergo oxidative polymerization to high molecular weight compounds (2).

Formation of material referred to as gum in a hydrocarbon fuel such as gasoline is generally thought to be an oxidative polymerization product (2). The following observations have been made about gum formation:

- Restricting the amount of air available will limit the maximum gum produced.
- Saturated compounds are not major contributors.
- Olefins, particularly conjugated diolefins, are readily oxidized to produce gum.
- Nitrogen and sulfur are incorporated into the gum in appreciable quantities (up to 2 wt%).

The gum is generally a low volatility varnish-like material. Conjugated diolefins react directly with oxygen to form a polymeric product. Simple olefins contribute to gum formation in a secondary manner via the production of autocatalytic hydroperoxide intermediates.

Analysis of a typical gum fraction is tabulated below.

	<u>Wt %*</u>
C	75.2
H ₂	7.6
O	15.5
S	1.5
N	0.15

* Data from Reference 2.

3. Vapor Phase Oxidation

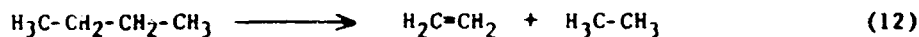
Three general types of vapor phase reactions of hydrocarbons and oxygen (8) can be expected depending on conditions: (1) a kinetically slow, selective oxidation region leading to products such as alcohols and aldehydes, (2) a cool flame region and (3) an explosion region. Variables which influence the boundaries for these regions are hydrocarbon type, temperature, total pressure, oxygen partial pressure, and transport phenomena factors reflected in variables such as volume of the reaction system and surface to volume ratios. For a thermal explosion reaction, at a fixed initial temperature there will be a critical pressure above which an explosion will occur and below which a "normal" reaction will take place. For a branching chain reaction, more complex explosion limits will exist. It has been estimated, for example, that in a jet aircraft wing tank at temperatures above 450 to 500°F, an explosion will occur if the total pressure is above 4 to 5 psia.

Normal vapor phase (kinetically slow) oxidation reactions have been divided into a low and a high temperature region, where presumably different mechanisms are in operation (1). The transition region is generally found in the range of 325 to 450°C and may manifest an anomalous temperature coefficient or negative apparent activation energy (i.e., the rate of oxidation decreases as the temperature is raised). In the low temperature region, selective oxidation to aldehydes, ketones and alcohols occurs, whereas, in the high temperature region other reactions such as cracking and oxidative dehydrogenation begin to occur as manifested by the appearance of olefins as reaction products. For oxidative dehydrogenation an olefin of the same carbon number as the parent hydrocarbon is produced, whereas cracking will produce lower carbon number products. The following will serve to illustrate the typical overall stoichiometry for these reactions, using butane as an illustrative compound (1).

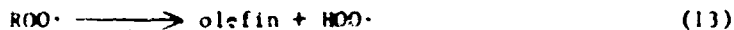
Oxidative dehydrogenation:



Cracking:

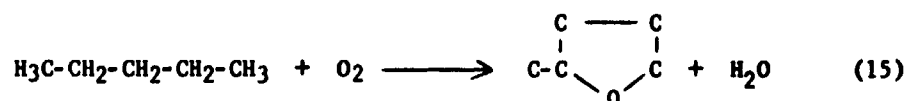


For a given temperature, pressure has a very strong effect on the distribution of reaction products, with low pressure favoring olefin production at the expense of oxygenated products. This effect has been explained by assuming that the reaction leading to oxygenated products involves the formation of an intermediate hydroperoxide molecule, and competition between the following reactions:



The effect of hydrocarbon type and structure varies between the low and high temperature region. In the low temperature region higher molecular weight hydrocarbons react faster than low molecular weight molecules, and normal paraffins react faster than highly branched paraffins. This is because hydrogen atom abstraction is not rate-determining in this regime. In the high temperature region molecular structure has relatively little effect. As the molecular weight of the molecule undergoing oxidation increases, the complexity of reaction products increases. With molecules containing at least a four carbon atom chain, intramolecular

hydrogen abstraction can occur producing cyclic oxygenated compounds. For example, in the oxidation of n-pentane at atmospheric pressure



2-methyltetrahydrofuran is formed.

As far as the "empty" wing tank deposit problem is concerned, both oxidative dehydrogenation and cracking reactions may be important in that they could produce olefins for subsequent polymerization reactions. Concerning these two reactions, the best estimate based on available data (1) is that oxidative dehydrogenation is a relatively more important reaction in the 450-600°F range.

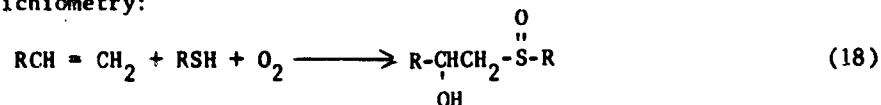
4. Reactions of Sulfur and Nitrogen Compounds

The most prevalent types of sulfur compounds found in petroleum crudes and distillates are thiols, sulfides, disulfides, thiophenes and derivatives of these compounds (9, 10). In jet fuel, there is generally a higher concentration of sulfur compounds than nitrogen compounds. Nitrogen compounds are either basic, e.g., pyridines and aliphatic amines or acidic, e.g., pyrroles and indoles. Acidic type nitrogen compounds such as pyrrole are known to be unstable in the presence of oxygen and are probably the main nitrogen type contributors to the instability of stored petroleum reactions.

It is felt that sulfur compounds contribute to hydrocarbon low temperature instability problems by catalyzing the formation and decomposition of hydroperoxides. Thiols and disulfides appear to be the most deleterious types of sulfur compounds. Thiols are known to form stable radicals and are good radical chain transfer agents. The addition reaction of thiols with olefins to produce sulfides (11) is a well-known free radical reaction.



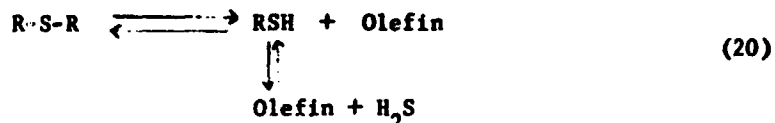
It has also been demonstrated (12) that in the presence of oxygen at room temperatures, thiols will undergo cooxidation with olefins to produce a beta-hydroxysulfide (sulfinyl alcohol). This is also a free radical reaction with the following overall stoichiometry:



At higher temperatures, decomposition reactions of sulfur compounds are probably important. Thiols decompose thermally at temperatures above 300°C, typically producing olefins and H₂S (13). In some cases, sulfides are produced which subsequently decompose to produce olefins and H₂S. A wide spectrum of metals and metal oxides have been reported to catalyze the decomposition of thiols at temperatures between 150 and 300°C (13, 14).



Sulfides have been reported to decompose both thermally and catalytically at temperatures of 230°C and higher forming products such as thiols, olefins, and H₂S (15). Alkyl sulfides have been found to yield the corresponding 1-olefin. Cyclopentyl sulfide yields cyclopentene and H₂S. Addition of H₂S during the decomposition of butyl sulfide in naphtha increases the relative production of butanethiol (15) suggesting the following reaction scheme:



Disulfides are also reported to decompose readily at temperatures above 270°C (16). Typical reaction products include thiols, sulfides, olefins, H₂S and even elemental sulfur. Aliphatic disulfides are reported to be thermally unstable relative to aromatic disulfides. Disulfides are also reported to be readily reduced to thiols (14).

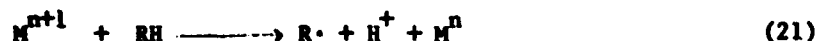
In general, thiols are less stable thermally than other sulfur compounds, followed by sulfides, and then by thiophenes which seem to be quite stable (14). The same relative order of stability has been reported for the reactions of these compounds over a reduced nickel catalyst. Disulfides are also relatively unstable because of a weak S-S bond (14).

Acidic heterocyclic compounds containing nitrogen (pyrroles and indoles) undergo a variety of reactions. They can autoxidize to form hydroperoxides and oxygenated dimers. They can also polymerize in the presence of air at temperatures below 100°C (17, 18, 19). Pyrroles also can undergo condensation reactions with aldehydes and ketones (20) to form high molecular weight polycondensation products.

5. Catalytic Effect of Metals

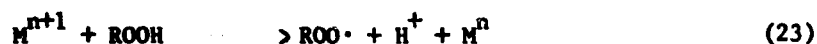
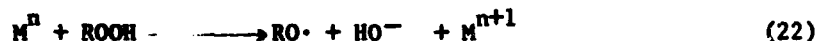
It has been widely shown in the literature that both soluble and insoluble metals can catalyze reactions involved in autoxidation (21, 22, 23). Soluble transition metal compounds such as metal phthalocyanines, stearates, and naphthenates catalyze autoxidation reactions in kerosene. Insoluble metal oxides (24) such as CuO, MnO₂, Cr₂O₃ 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 (21, 22, 23). The theory has been advanced that all hydrocarbon autoxidations are trace metal catalyzed (22). Another complicating factor in the case of soluble metal catalysts is that the catalyst may react with the autoxidation products. In such a case, the catalyst could initially accelerate the reaction, but then precipitate from the liquid phase and have no further effect on the course of the reaction.

It is generally felt that active metals are those with variable oxidation states. For primary catalysis the following reaction is envisioned, where M is the metal



Autoxidation reactions which exhibit primary catalysis generally do not exhibit an induction period.

It is also possible for metals to function as catalysts during a secondary process by decomposing hydroperoxides which are the initial oxidation products. Thus,



Such a secondary catalytic process would exhibit an induction period (in the absence of an added initiator). This induction period can be eliminated by the addition of an initiator such as a hydroperoxide or azoisobutyronitrile.

6. Jet Fuel Additives

Compounds used as antioxidants and metal deactivators are often added to jet fuels to improve storage stability. The function of an antioxidant is to suppress the chain propagating (eq. 2 and 3) and chain branching (eq. 4) steps. The chain propagating step can be inhibited by compounds such as phenols and aromatic amines. The chain branching step is inhibited by the use of sulfides and aliphatic amines. Phenols and amines are mainly employed as inhibitors in motor gasoline. Studies (25) have indicated that inhibitors can contribute to engine deposits by being oxidized or polymerized in the induction system to nonvolatile, hydrocarbon insoluble materials. The effect of such inhibitors on the "empty" wing tank deposit problem is not known. It is interesting to note, that in a Bureau of Mines study (26) on the contribution of a series of Cl^{14} labeled compounds to deposits, a phenolic antioxidant (2,6-di-t-butyl-4-methyl phenol) showed the greatest contribution to deposits. Also, a sharp increase in radiotracer participation in deposit forming reactions occurred at temperatures in the range of 350 to 400°F.

In addition to antioxidants, other compounds are added as metal deactivators, to suppress the catalytic effect of metals on various reactions. The deactivators can precipitate the metal or change its oxidation state, the latter of which may or may not be advantageous. The possible effects of metal deactivators on "empty" wing tank deposit formation is not known.

c. Deposit Formation During the Storage of Hydrocarbons

The problem of hydrocarbon fuel instability during storage, i.e., deposit formation, has been studied extensively in the Petroleum Industry. This section summarizes typical work in this area reported both in the general literature and in internal technical reports of Esso Research and Engineering Company and other affiliates of Standard Oil Company (N.J.). Although most of this work has been done at temperatures below that at which wing tank deposits form (>400°F), the underlying processes are probably quite similar and, thus, are pertinent to the wing tank deposit problem.

A great deal of the Company literature is concerned with the development of tests (bomb oxidation stability) for determining the stability of feeds under simulated storage conditions. Based on the results of these tests, it is possible to obtain a rough estimate of how long a particular feed stock can sit in storage before going off color and depositing sediments. These stability tests have established that heating oil instability is greatest when O₂ is bubbled through the oil but instability still occurs when the feed is N₂ blanketed or if air is allowed to diffuse slowly into the oil (27). Heating oils stored in sunlight produce large amounts of sediment and color in short periods of time. Light also destroys stabilizers and additives. In the presence of U.V. light, which is a catalyst for free radical reactions, decomposition of the oil is more rapid than in plain sunlight (28). Bomb oxidation stability tests have established that heating oil stability is decreased when natural inhibitors such as phenols are removed by caustic washing. Readdition of the phenols reduced the oxidation acidity during the stability test (29).

Some studies have been carried out within the Company to ascertain what factors contribute to instability. Using an Esso fuel oil from Montreal it was found that S reacted with the oil components to form gum. Aromatic thiols and high molecular weight sulfides were found to be harmful and polysulfides were particularly effective in promoting gum formation. Metals accelerate gum formation and their catalytic efficiency is increased when they are solubilized by natural acids (30, 31). Detailed stability studies on six different heat stocks were carried out at the Process Research Division. After 29 weeks of simulated storage, all samples suffered color loss, increased acidity, increased carbon residue, decreased stability tests, and increased coking tendency. Color and color hold were worse for samples dried than for those containing water. An examination of the fuel oil sediments indicated that Fe, Cu, Mg, Pb, Ca and Na were present as their oxides. The black solids were organic in nature since they dissolved in chloroform. Since all feeds were lead sulfide and sulfur sweetened before storage, disulfides were probably part of the sediments. Recent studies have emphasized the deleterious effect of disulfides and have suggested that disulfides interact with diolefins to form sediments (33).

Although simulated storage tests are, in general, useful for predicting the storage life of a sample they are not infallible. For example, 200,000 gallons of an Everett heating oil dropped to 4 T.R.* after nine months storage. The inability of stability tests to predict this was based on the fact that the tests were not designed for this long storage period (34). Kerosenes from Baton Rouge and Baytown have also gone off color on long standing. Addition of 1.5 ppm of duPont metal deactivator led to increased sediment (35). This can hardly be considered sediment, however, since many deactivators function by precipitating the metal.

A large research effort on the stability of naphthas has been carried out at the Process Research Division in the past. Naphthas develop sediment on storage in the field. It has been found that the sediment can be removed by filtration and the feed reinhibited by the addition of commercial inhibitors (36). Studies on the causes of naphtha instability indicated that O₂ solubility decreased in the order paraffin > olefins > aromatics. Deoxygenation decreased gum stability and peroxide formation. The rate of oxidation was found to be temperature dependent. Below 212°F the rate is slower but the final peroxidation was greater. Decreasing the O₂ partial pressure had an even greater effect emphasizing the need for available O₂. All inhibitors were removed from the naphtha by acidic or alkaline solutions and their decomposition was accelerated by iron oxide (37).

* Tag-Robinson number. Decreasing number on 0 to 24 scale indicates increasing fuel degradation.

Specific studies on a Baltimore catalytic naphtha indicated that unless aromatic thiols (mercaptans) were removed by a precaustic wash the feed was oxidized rapidly by air. Caustic washing had to be carried out in absence of air to prevent peroxidation. The gums from a West Texas feed had an unusually high sulfur content (38). These studies were repeated a year later and essentially the same conclusions were reached (39) which again emphasizes that sulfur containing compounds contribute heavily to instability. In more recent studies on the air inhibitor sweetening of naphthas, product degradation was attributed to three main causes: thiols, phenols and peroxides. Aromatic thiols were more deleterious than aliphatic thiols. The greater the concentration of thiols and phenols, the greater the extent of degradation (40).

A considerable effort has been expended on the development of inhibitors for stabilizing gasolines. Most of this work has been on the evaluation of Paradyne A (2,6-di-tert-butyl-p-cresol) (41).

A detailed study on the effect of metals on fuel oil instability was carried out at the Process Research Division (42). Metal salts were employed in 0.39×10^{-3} moles/liter concentration. Using cumene and tetralin, the order of metal ion activity for hydrocarbon oxidation was $\text{Co} > \text{Cu} > \text{Fe} > \text{Ni}$. The rate of O_2 consumption and the rate of hydroperoxide formation followed the same order. Initially, one mole of O_2 produced one mole of hydroperoxide.

An elegant study on the effect of nitrogen compounds on lubricating oil stability has been carried out by Ilnyckyj and Jones (43) at Imperial Oil Limited. Sludges from oxidized lubricating oil contained a 20-fold increase in nitrogen concentration compared to the original oil. Nitrogen compounds were precipitated exclusively when the oxidation time was short or carried out in the presence of an oxygen deficient atmosphere. Pyrrole compounds were the main contributors to the sludge. Commercial hydrofining catalysts did not remove the sludge but they did change the porphyrin pyrroles into monomeric, more reactive pyrroles. The nitrogen compounds were adsorbed on the surface of the catalyst causing rapid deterioration. In time, equilibrium was reached causing a lower level of catalyst activity. The total nitrogen content of the feed did not change but its chemical composition did as evidenced by the increased pyrrole number of the feed. Acidic materials, e.g., phenols, catalyze the formation of polypyrroles.

An early, but informative study on the instability of gasolines was carried out by Brooks (44). Gum formation was attributed to the formation of hydroperoxides which break down to aldehydes, ketones, formaldehyde, carbon dioxide, and water. These substances were found in the fluid gum and could be removed by extraction with sodium bisulfite. The gum contained 18% oxygen when analyzed. Diolefins were found to accelerate gum formation more than mono-olefins. Actually, a loose correlation between the amount of gum formed and the number of olefinic

HC	No. of Double Bonds	Gum (mg./100 cc.)
Pinene	1	40
Limonene	2	1960
Myrcene	3	3960

double bonds was obtained. Peroxide formation was greatest in dry gasoline. This

	Peroxide Oxygen (g./l.)
Dry Gasoline	1.856
Wet Gasoline	0.384

> 6 hrs. aeration

was attributed to hydrolysis of the intermediate hydroperoxides by water. Trace amounts of SO₂ were found to be prime contributors to acidity. This is due to the formation of sulfuric acid from the reaction of SO₂ with hydroperoxides.



In a further study on the formation of hydroperoxides in gasolines, it was found that sunlight accelerated hydroperoxide formation at room temperature (45). More detailed studies on the role of hydrocarbon types in gum formation were carried out by Flood and co-workers (46). Oxidations were carried out at oxygen pressures of 100 lbs./in² at 100°C using olefins that were added to paraffinic gasolines. The largest amounts of gum arose from aliphatic cyclic and acyclic diolefins or mono-olefins attached to a benzene ring. When large concentrations of mono-olefins were present, gum formation was also appreciable.

An excellent study on the mechanism of gum formation in gasolines during simulated storage conditions was carried out by Morrell and co-workers (47). Peroxides could be detected early in the gasoline storage period when no aldehyde, acid, or gum was present. The rate of peroxide formation accelerated with time. Aldehydes begin to appear later in the reaction and their concentration increased more gradually than peroxides. Acid formation began still later in the reaction. Gum deposits appeared when rather large amounts of hydroperoxides were formed but before any large development of aldehyde or acid. A plot of gum content vs. time was similar to a plot of ROOH vs. time. This suggests that aldehydes and acids are products of secondary reactions. Unfortunately, the general structure of these hydroperoxides was never determined. It is possible that the hydroperoxides result not only from the interaction of diolefins with oxygen but also from the co-oxidation of thiols with olefins. In a study on the nature of the gum formed in gasolines, it was found that in addition to C, H and O, N and S were also present in substantial quantities (48). The same order of hydrocarbon reactivity was also observed. In a continuation of their studies, Morrell and co-workers studied the color stabilities of gasolines in a carbon arc lamp (49). Mercaptans added to the gasoline had little effect on color stability but sulfur and/or alkyl disulfides added to the color and haze. Their combined effects were greater than either alone but sulfur was more harmful to cracked gasolines while disulfides were more harmful to the straight run gasolines. Improved stability was obtained by removal of sulfur and disulfides.

The above conclusions have been substantiated to some extent by studies with pure compounds. Morrell (50) found that pure hydrocarbons formed hydroperoxides, aldehydes and acids when exposed to light and oxygen. Color or haze was catalyzed by the presence of sulfur or propyl disulfide. In the presence of N_2 or H_2 the photochemical reaction of sulfur with a paraffin yielded color and hydrogen sulfide. Olefins similarly exposed formed hydrogen sulfide and thiols. n-Propyldisulfide reacted with hydrocarbons to form thiols. Similar studies were carried out by Freund (51). Using pure olefins such as pentene and trimethylethylene Engler and Weissberg (3) found that simple aeration of these compounds at room temperature led to viscous products which contained 45% hydroperoxide content. Although an actual feed stock was used, Hendrickson employed rather fundamental techniques to isolate various components of a California gas oil (52). By means of elution chromatography various sulfur compounds such as thiols, sulfides, disulfides, thiophenes and benzothiophenes were isolated and identified. Nitrogen compounds such as indoles and pyrroles were identified by their strong infrared absorption at 3300 cm^{-1} .

The instability of fuel oils during storage has also received attention. Thompson and co-workers (53) found that pyrroles caused more sedimentation than pyridines when added to fuel oils. 2,5-Dimethylpyrrole was a highly active promoter of sedimentation storage. Some pyrroles are removed by caustic extraction while others are slightly basic and require acid extraction for removal. Removal of aromatic thiols, naphthols, and pyrroles caused sediment formation in catalytically cracked distillate fuel oils. Aromatic thiols were removed by caustic extraction. Aromatic disulfides did not cause instability in thiol free fuels. The presence of pyrroles in thiol free fuels was not harmful but indoles caused sedimentation. The addition of sulfonic acids, which may arise by oxidation of aromatic thiols, had a severe effect on color stability in the presence of oxygen. 2-Naphthalene sulfonic acid was isolated from an oil which had been stored for three months thus lending some support to these conclusions (54). One of the more recent techniques for improving fuel oil stability has been the selective extraction of aliphatic and aromatic thiols by $NH_2CH_2CH_2CH_3$ in ethanolamine. Feeds so treated show a marked improvement in storage stability (55).

An interesting study on gum formation in shale oil naphtha has been carried out by Dinneen and Bickel (56). The distilled naphthas are dark in color and contain a large gum content that consists of 7-9% nitrogen compounds. Oxidation was very critical as far as gum formation was concerned. Using an accelerated bomb oxidation test, the gum content was found to increase with oxidation time. Similar results were obtained on extended storage which substantiated the simulated storage conditions.

A literature survey of research completed in the area of stability of jet fuels was made by the Bureau of Mines (4). It was concluded from this survey that stability is a complex function of hydrocarbon type and that the presence of sulfur and nitrogen compounds and oxygen increased the tendency to deposit formation.

d. Supersonic Flight Fuel Tank Simulator Results

Most of this work is of recent origin and is intimately familiar to those associated with the "empty" wing tank deposit problem. Thus, this section will not recapitulate this work in detail. Rather, we have summarized what we feel are the most pertinent pieces of information accumulated from references 57 to 60 and from our field survey.

Under simulated supersonic flight conditions (~Mach 2.7 and higher), it has been demonstrated that commercial types of jet fuels will form deposits in fuel tanks. This problem is felt to be most severe in a wing tank relative to a fuselage tank since, for a given set of flight conditions, the wing tank's lower surface will reach a higher temperature. These deposits vary from what appears to be (1) a light varnish, (2) a reasonably clear gum or hard surface polymeric residue and (3) a black looking substance which may be raised from the surface. As anticipated, temperature is a major variable in fuel stability. Supersonic Transport test rig results indicate that jet fuels exhibit a no deposit condition at 400°F, but at 500°F they exhibit deposits regardless of the ASTM-CFR Coker Breakpoint Temperature rating. Work in the Esso Heat Transfer Unit indicated that an autoxidation reaction occurs at approximately 500°F, as shown by a rise in fuel peroxide number and consumption of dissolved oxygen. The presence of oxygen also seems to be a major variable since reduced deposit forming tendencies are observed in systems where oxygen is rigorously excluded.

One interesting observation made during the SST Test Rig work with FA-S-1 fuel (58) was that the puddle fuel from the wing tank at the end of the test series contained a marked increase in olefin content (11%) relative to the same fuel contained in the fuselage tank at the end of the test series (2% olefin). In the same work (58) with FA-S-1, two types of deposits were found and they were characterized by infrared spectroscopy. The first was essentially a carbonaceous material and the second was a material which contained a major amount of carbonyl (C=O) compounds. These observations suggest that the varnish like deposits are a polymeric material formed by reactions between olefins, sulfur and nitrogen compounds, oxygen, hydroperoxides and hydroperoxide decomposition products; while the black carbon rich material results from more extensive oxidation of this polymeric material. Studies in the petroleum industry on hydrocarbon residues which deposit on the surface of various catalysts (often called "coke") have indicated that it is possible to selectively oxidize a hydrogen rich portion of this hydrocarbon material. The residue is a carbon rich fraction. The olefins, which presumably are major contributors to the polymerization reactions, may be largely secondary reaction products formed by either the decomposition of sulfur containing compounds (which is known to occur in the temperature range in question) or by an oxidative dehydrogenation reaction (which is known to be favored at subatmospheric pressures).

e. Summary

Deposits can form in hydrocarbon fuels stored at ambient temperatures. Free radical chemistry plays a major role in the deposit formation process. The following variables accelerate the formation of such deposits: the presence of oxygen, high temperatures, high olefin content, presence of sulfur and nitrogen compounds, exposure to sunlight or U.V. light, and presence of metal catalysts.

In a so-called "empty" wing tank, deposits start to form between 400 and 500°F. Higher temperatures accelerate the deposit formation process, as does the presence of oxygen. One analysis of a wing tank "puddle fuel" indicated a markedly increased olefin content.

A number of types of chemical reactions probably play a significant role in the deposit formation process. Autoxidation reactions can produce a variety of molecular weight products up to an oxygenated dimer of the parent hydrocarbon.

Autoxidation reactions are also important in that they generate a spectrum of free radical intermediates which accelerate other reactions. Hydrocarbons, particularly those containing an olefin linkage, react with oxygen to form high molecular weight, polymeric type products in a reaction termed oxidative polymerization. Sulfur and nitrogen compounds, in addition to oxygen, are also readily incorporated into the product from oxidative polymerization. Oxidative polymerization reactions are probably a major contributor to the various polymeric resins found in wind tank deposits. Several types of reactions are possible routes for the production of olefins. Studies of the vapor phase oxidation of hydrocarbons indicate that low pressures (≤ 1 atm) favor the production of olefins, presumably by an oxidative dehydrogenation reaction. Sulfur compounds such as thiols and disulfides are known to decompose into olefins at temperatures of 300°F and higher.

Soluble and insoluble metals are known to catalyze a spectrum of free radical reactions. They may play a primary role by producing hydrocarbon free radicals which initiate autoxidation chains or they may play a role in secondary processes by decomposing hydroperoxides. Metal compounds are also known to accelerate the decomposition of sulfur compounds.

2. Field Survey of Airframe Manufacturers

A field survey of airframe manufacturers was completed. Four companies, i.e., Boeing, Lockheed, North American and Douglas were visited. The primary objective of the field survey was to obtain background orientation in order to make certain that our studies will be pertinent to actual supersonic aircraft fuel tank problems. The field survey was quite useful for this purpose, i.e., providing a general background orientation concerning actual supersonic flight conditions. It was particularly helpful in pinning down the type of environment a jet fuel is likely to encounter in a wing tank during supersonic flight, e.g., temperatures contact times, oxygen partial pressure and possible metal types.

In regard to metal types, it is our understanding that titanium is the most probable metal of construction for a supersonic wing tank with some possibility for the use of stainless steel (62). Thus, in our experimental work, we restricted ourselves to these types of metals. A sample of Ti-8Al-1Mo-1Va alloy, (a Mill Annealed sheet 0.020 inches thick) was obtained from Titanium Metals Corporation of America. We also obtained from Titanium Metals Corporation a sample sheet of Ti-6Al-4Va alloy and Ti-75A "commercially pure titanium" ($\approx 99\% \pm 1\%$ titanium). The Ti-6Al-4Va material is a likely candidate for use in the SST(62). We procured the commercially pure titanium to use as a check against the possibility that the added alloying elements could affect hydrocarbon deposit formation.

B. Study of the Effect of Phase
Type on Deposit Formation

1. Construction of the Phase Study Unit

In order to help settle the important question of the role of phase, i.e., liquid or vapor, in the deposit forming reactions, a Phase Study Unit was constructed. A schematic diagram of this unit is shown in Figure 1. The main section of the unit consists of a heated reactor section (A) which contains a probe reactor finger (B). The temperature of the vapor space surrounding the probe is controlled by a jacket heater (C). The temperature of the probe reactor is controlled independent of the vapor space temperature by means of a heat transfer medium which is circulated within the probe reactor.

The inlet side of the unit is designed to deliver controlled amounts of vaporized hydrocarbons or jet fuel and N_2 and O_2 to the reactor section. Provisions were made for degassing the liquid fuel before vaporization and delivery to the unit, if desired. The discharge side of the reactor is connected to a vacuum pump so that the unit can be operated at subatmospheric pressures. Septum caps are provided at a number of points on the unit so that samples may be withdrawn for analysis via gas chromatography, for example, for oxygen. A sample trap is also available for condensing and recovering the effluent hydrocarbon from the probe assembly.

To test the effect of metal types, we originally planned to roll approximately 2" wide strips of metal into cylindrically shaped sleeves and to attach these sleeves to the inner probe. With stainless steel, it was found that probe sleeves could be prepared rather easily. This was not the case with titanium. Working with a 0.020" thick sheet of Ti-8Al-1Mo-1V alloy, we were unable to form suitable sleeves, even after trying a variety of rolling techniques.

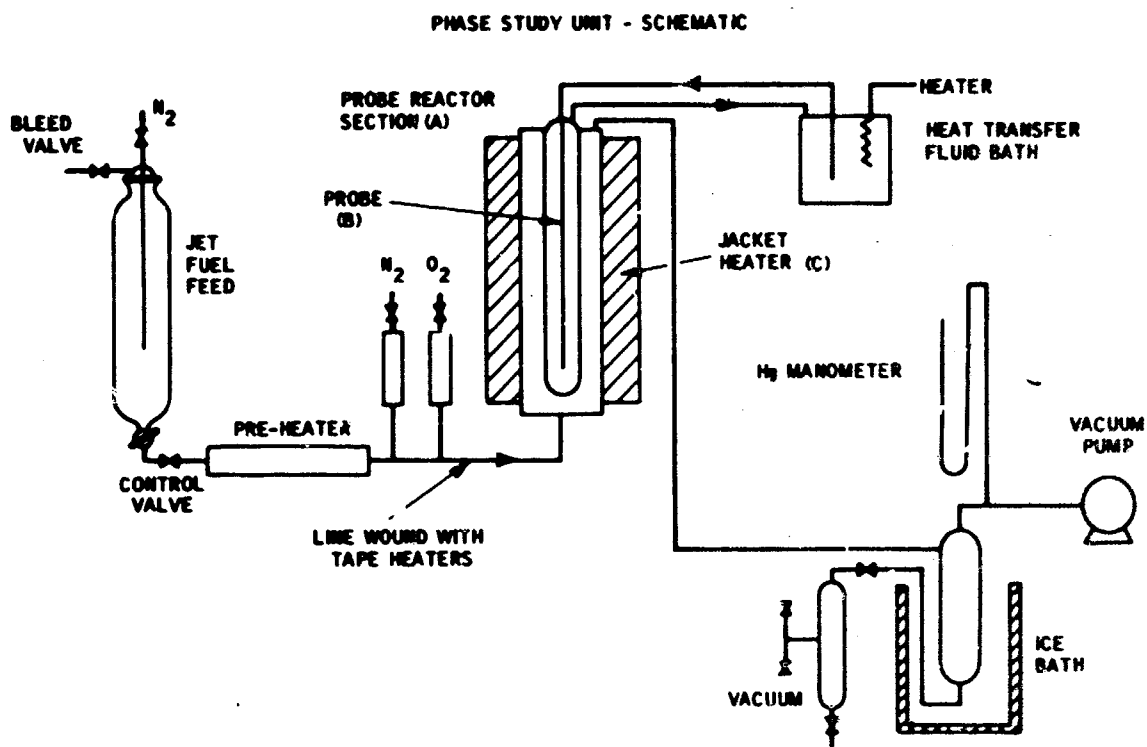
2. Results From the Phase Study Unit

One of the more important questions involved in Hydrocarbon Fuel Vapor Phase Deposit work is the role of the phase (i.e., liquid or vapor) in the deposit forming process. In an effort designed to elucidate the contribution of the liquid and vapor phase, a series of experiments were carried out in the Phase Study Unit. The variables studied were:

- Effect of condensed phase
- Effect of metal surface
- Effect of the presence of air (oxygen)

The experimental approach consisted of a series of runs designed as a 2ⁿ Factorial Experiment with the above three variables. The fuel chosen for the experiments was a Jet A kerosene, RAF-176-63. Other conditions were 3 psia total pressure, full air added to the unit and a contact time equivalent to 3 SST mission cycles (3-4 hours). The preheat sections and reactor heater were controlled at 500°F, which at the 3 psia pressure, completely vaporized the fuel. The temperature of the probe was maintained at 275°F

FIGURE 1



to produce a condensed phase. For runs without a condensed phase, the probe temperature was maintained at 460°F. The metal surface consisted of cylindrical sleeves made from 304 stainless steel which were slipped over the probe.

The results from this series of experiments are shown in Table 1. In the absence of air no deposits were formed even when a condensed phase and a metal surface were present. In the presence of oxygen, deposits formed when a condensed phase was present on both the glass and metal surfaces. If one assumes an apparent activation energy of 10 kcal per mole, this result indicates that the overall rate of deposit formation at 275°F in the condensed phase is at least 12 times faster than the rate in the presence of a vapor phase only. At the conditions chosen, the presence of a stainless steel metal surface vs. a glass surface did not affect the overall deposit formation process as much as the presence of oxygen or a condensed phase. However, the presence of a metal surface affected the fuel degradation process, since color changes were observed when the jet fuel was exposed simultaneously to the presence of a metal surface, oxygen, and a condensed phase.

C. Development of an Apparatus and Test
Procedure to Quantitatively Measure Deposit
in the "Empty" Wing Tank Environment _____

1. Design and Construction of the
Screening Unit _____

To elucidate the variables which control deposit formation quantitatively, a unit was designed to measure the rate of deposit formation. In this apparatus, the reaction kinetic environment experienced by the residual jet fuel is simulated. The salient features of this complex environment are the presence of three phases, that is, metal surface, liquid phase, and vapor phase; a rising temperature sequence; and a reduced pressure characteristics of a wing tank at high altitudes. Typical jet fuels are not very volatile at ambient temperatures. However, the presence of a reduced pressure facilitates the vaporization of various compounds, and since temperatures rise as a supersonic flight progresses, a selective fractionation of the residual liquid fuel occurs. At the extreme conditions, for example, 500 F and 3 psia, the vast majority of compounds present in a fresh, undegraded jet fuel should be in the vapor phase.

The Screening Unit (63,64) used to measure the rate of deposit formation is shown in a schematic drawing in Figure 2. The main section of the unit consists of a glass tubular reactor 3.8 cm. in diameter and 100 cm. in length. The reactor volume is approximately 1130 cc. The unit has five separate reactor heaters, each independently regulated by its own Gardsman temperature control. The reactor is maintained on a slight incline and liquid fuel flows down the reactor in the presence of a constant stream of air. The liquid fuel flow rate is fixed at 125 cc per hour and the gas flow is fixed at 5 liters per minute. The total run

TABLE 1

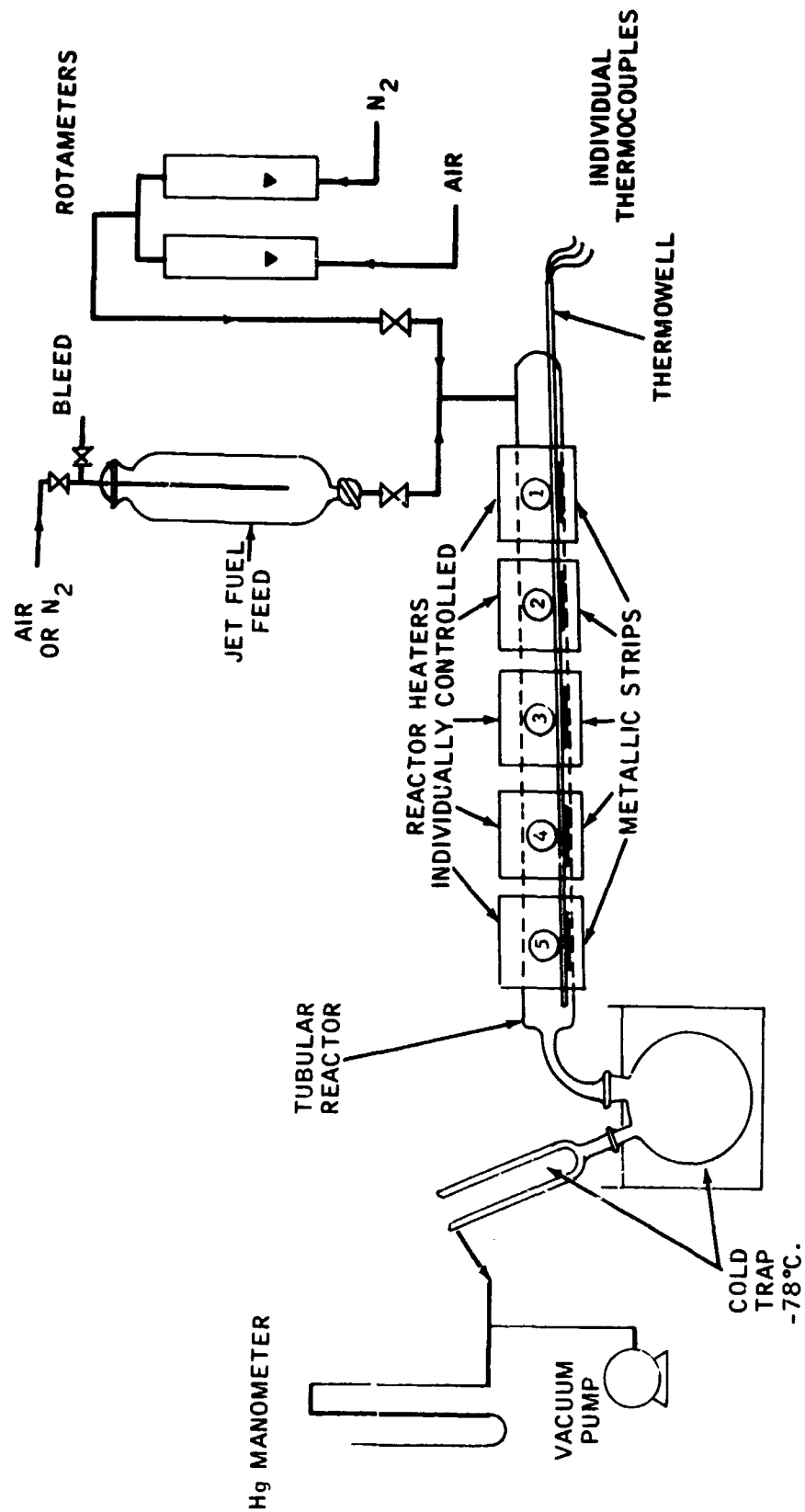
Phase Study Unit Experiments With RAF-176-63

	Condensed Phase (275°F on Probe)		No Condensed Phase (450°F on Probe)	
	Air	No Air	Air	No Air
Metal Present	Experiment #1	Experiment #5	Experiment #3	Experiment #7
	Deposits (light yellow overheads)	No Deposits (white overheads)	No Deposits (dark yellow overheads)	No Deposits (white overheads)
No Metal Present	Experiment #2	Experiment #6	Experiment #4	Experiment #8
	Deposits (white overheads)	No Deposits (white overheads)	No Deposits (white overheads)	No Deposits (white overheads)

- Conditions: RAF-176-63 Jet A kerosene, pre-purged with N₂ (white colored), 3 psia total pressure, 500°F reactor heater temperature, 304 stainless steel metal sleeves (when employed).
- In order to check reproducibility, Experiment #1 was replicated. Both runs produced the same results.

FIGURE 2

SCREENING UNIT - SCHEMATIC



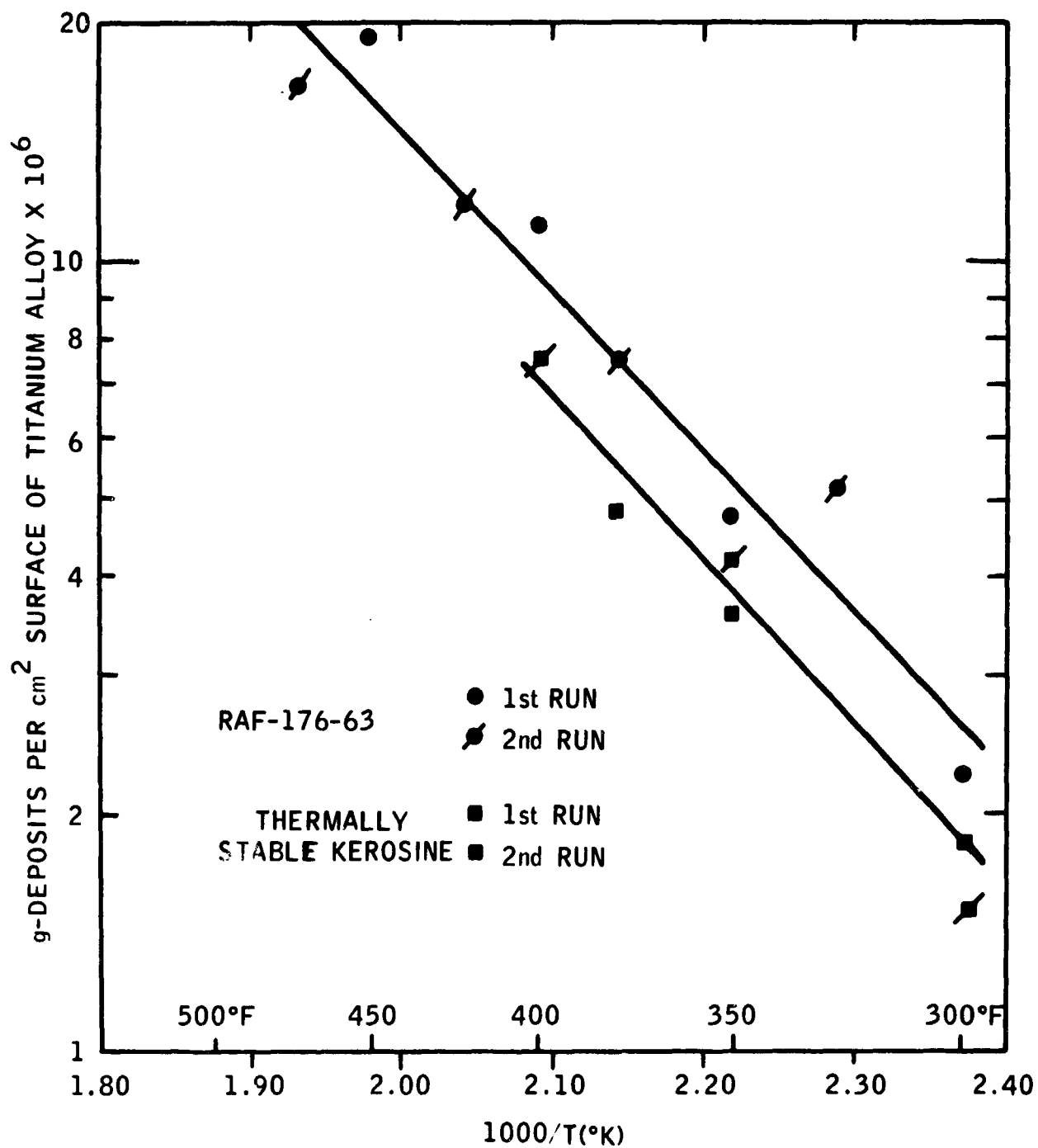
time employed is 4 hours. The reactor heaters are controlled so that the fuel encounters a sequence of rising temperature zones as it flows down the reactor. Carefully weighed metal strips approximately 1.0 cm wide by 10 cm long are positioned in the center section of each heater zone. The average residence time of the flowing hydrocarbon (in the absence of loss by vaporization) is 14 seconds per strip, the time it takes the hydrocarbon stream to flow the length of a single strip. This was measured at ambient temperature and pressure by measuring the time it took an actual jet fuel to travel the length of the reactor. A thermowell extends down the length of the tubular reactor, and an individual thermocouple is positioned in each zone. The reactor heaters are separated by a small distance, so that each reactor sector can be inspected visually; at other times this zone is wrapped with insulation tape to prevent excessive heat loss. The unit is designed so that it can be operated under a controlled, reduced pressure. The liquid fuel is presaturated with air or an air-nitrogen mixture prior to admission to the reactor section. At the conclusion of a run, hydrocarbon fuel is shut off and a full vacuum is applied to the unit (<0.1 torr) while the temperature is maintained at 450°F to remove any physical or chemisorbed jet fuel range hydrocarbon species. Nitrogen is passed down the reactor as the unit is cooled to room temperature. The metal strips are removed carefully and weighed on a precision balance. The deposit formation rate is calculated as grams of deposits per square centimeter of metal surface per 4-hour reactor time.

2. Reproducibility of the Data Obtained in the Unit

In the screening unit, liquid hydrocarbon and air are admitted to a tubular reactor, and flow over a series of metal strips at reduced pressure through a rising temperature sequence. Thus, the kinetic environment encountered by the residual fuel at various stages in the wing tank during a typical supersonic flight mission is simulated along the length of the reactor. The reproducibility of deposit formation rates obtained in the unit was first measured by making replicate runs with two fuels in the presence of Ti-8Al-1Mo-1V metal strips. Other conditions were 3 psia, use of undiluted air, and a $300\text{--}500^{\circ}\text{F}$ temperature distribution. The deposit formation rate was calculated as grams of deposits per square centimeter of total metal surface per 4 hr reaction time. Prior to being weighed, the strips are held at <0.1 torr pressure at 450°F for 30 minutes to remove any physical or chemisorbed jet fuel range hydrocarbon species. After cooling in N_2 , the strips are weighed with a precision balance to six decimal places. An analysis of the data indicated that the deposit formation rate increased with increasing temperature, until a sharp decrease or leveling off point was reached. Subsequent experimental results showed that this decrease or leveling off effect in the deposit formation rate at an elevated temperature was a general phenomenon. The temperature at which this phenomenon occurs has been designated as the "Deposit Formation Cut-Off Temperature." Analyses of the rates obtained below the cut-off temperature indicated that they produced excellent Arrhenius plots. Replicate run data for two different feeds are summarized in an Arrhenius plot in Figure 3. As shown, excellent Arrhenius plots were obtained and the rate data are quite reproducible.

FIGURE 3

SCREENING UNIT TESTS OF RAF-176-63
AND THERMALLY STABLE KEROSENE AT 3 PSIA



This apparatus has been used to rate the deposit formation tendency in the "empty" wing tank environment of a number of fuels. Independent comparisons made with the same fuels indicate that this apparatus is the only small scale test device which ranks the wing tank deposit formation tendencies of fuels the same as an actual Advanced Aircraft Fuel System Simulator (65).

3. The Weight Increase from Autoxidative
Deposits Relative to Weight Increase
Caused by Oxidation of the Metal

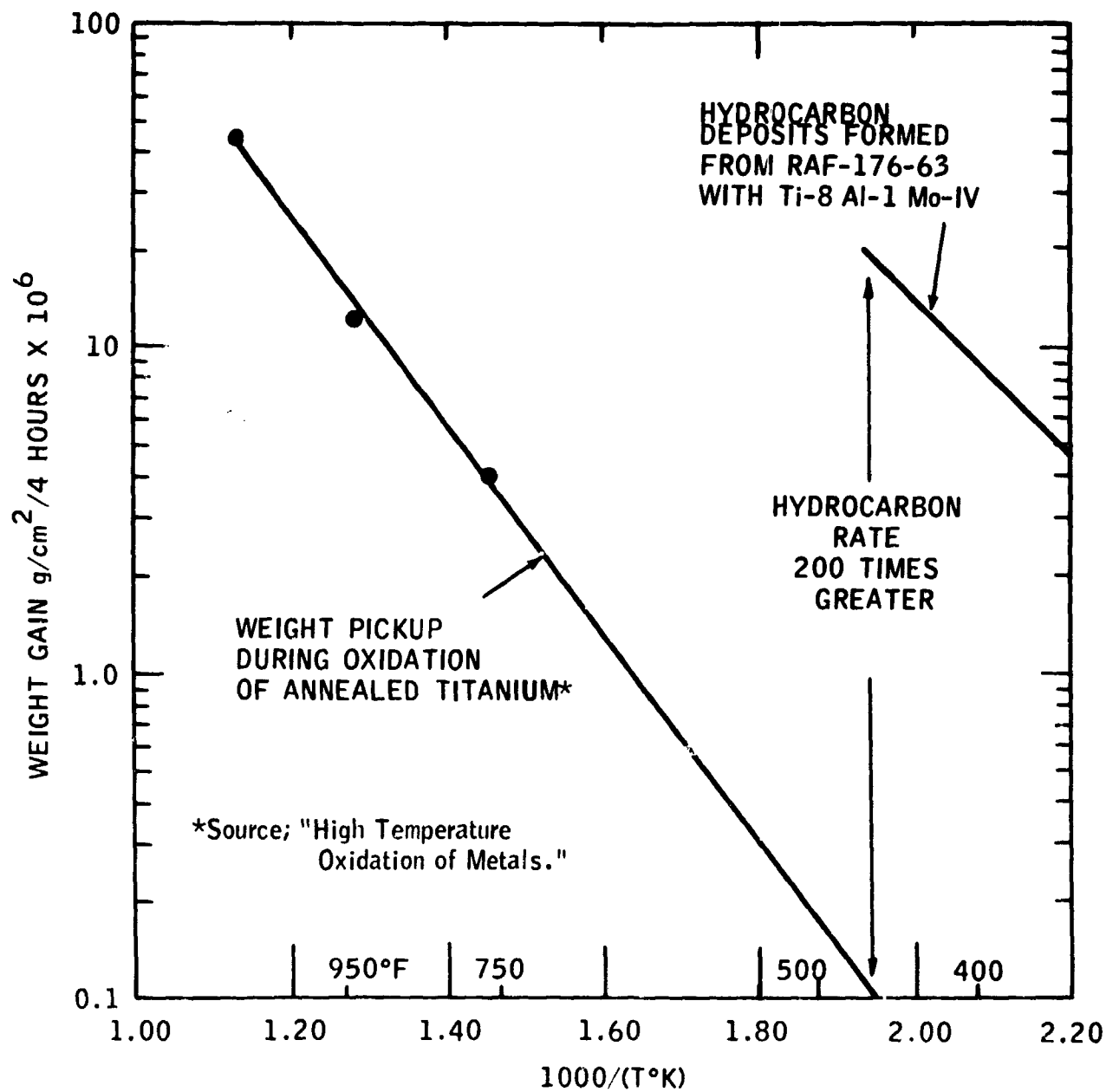
Kofstad's "High Temperature Oxidation of Metals" shows that titanium metal exposed to the presence of oxygen will oxidize and undergo a weight increase. Kofstad (66) presents data on the weight pickup from the oxidation of annealed titanium over the 405°C to 995°C temperature range. In order to assess the relative weight pickup from the oxidation of titanium metal versus that observed from a typical hydrocarbon autoxidation deposit, the data presented by Kofstad was plotted on an Arrhenius plot (Figure 4) and compared with the rate of hydrocarbon deposit formation observed on Ti-8Al-1Mo-1V metal strips using RAF-176-63, Jet A kerosine in a standard 4-hour screening unit run at 3 psia with undiluted air. The Kofstad data exhibited a 15 kcal/mole overall activation energy in the 405°C to 590°C temperature range, and this value was used to extrapolate his data to 246°C (475°F), the highest temperature employed in the hydrocarbon deposit kinetic studies. The weight pickup from the hydrocarbon deposits is 200 times greater at these conditions than the weight pickup from the oxidation of titanium metal. At lower temperatures the difference in the rates would be even greater since the overall activation energy for the hydrocarbon deposit process is only 10 kcal/mole. Since titanium metal surfaces are covered by a metal oxide layer, the oxidation of such metals require diffusion of molecular oxygen through the metal oxide layer. Based on Kofstad's data, this process is quite slow at temperatures below 475°F. More important, Kofstad's data show that the oxidation of the metal strips used in our Screening Unit test has a totally insignificant effect on the hydrocarbon deposit formation rates which we measure.

4. Temperature Measurements in the
Screening Unit

The most direct method of measuring the temperature of the metal strips in the Screening Unit would be to attach a thermocouple to the strip. This was not feasible since attaching a thermocouple directly to the strip would interfere with the highly accurate weight measurements which must be made in order to measure the rate of deposition of hydrocarbon deposits. The temperature of the strip was thus measured by means of two thermocouples, one positioned on the outside wall of the tubular reactor, and one positioned inside a glass thermowell inside the reactor which rests on top of the metal strips. In order to see if these thermocouple measurements correspond to the metal strip temperature, a thermocouple was soldered to the metal strip which was positioned in the middle reaction section, and a screening unit run was made under standard conditions (i.e., 3 psia, 125 cc/hour Jet Fuel, 5 l/min air flow). The unit was lined out and a series

FIGURE 4

THE WEIGHT PICKUP FROM HYDROCARBON DEPOSITS
IS ORDERS OF MAGNITUDE GREATER THAN
FROM THE OXIDATION OF TITANIUM METAL



of temperature measurements made comparing the metal strip temperature with the temperature at the wall and in the thermowell. Typical values are shown below.

<u>Metal Strip</u>	<u>Outside of Reactor Wall</u>	<u>Inside of Thermowell</u>
310	312	305
360	360	355

It can be seen that the temperatures measured in the screening unit at present are quite close to those which would be measured if a thermocouple were attached directly to the metal strips.

D. The Study of the Effect of Variables
Such as Temperature, Pressure, Oxygen
Partial Pressure and Exposure Time on
Time Formation

1. The Effect of Temperature and Total
Pressure on the Rate of Deposit Formation

Studies with a number of jet fuels indicate that the effect of temperature and pressure is interrelated. In general, higher total pressure increases the level of deposit formation and also results in a higher apparent activation energy for deposit formation.

The effect of total pressure on the deposit formation tendency of Baton Rouge jet fuel was investigated. In addition, the apparent activation energy for deposit formation was measured as a function of a total pressure. This work was done in the Screening Unit using Baton Rouge fuel employing Ti-8Al-1Mo-1V strips with standard flow rates of hydrocarbon and air. Results of this study are shown in Arrhenius plot in Figure 5. As can be seen, increasing the total pressure not only increased the level of deposit formation at a given temperature, but also increased the apparent activation energy for the deposit formation process.

<u>Total Pressure psia</u>	<u>Apparent Activation Energy, kcal/mole</u>
3	10
6	17
12	23
14.7	28

Thus, at a higher total pressure, the rate of deposit formation will increase more rapidly with increasing temperature than the rate does at lower pressure.

The effect also of 1 atm pressure on the deposit formation rate of RAF-176-63 and P&W 523, was measured. This work was done in the Screening Unit using Ti-8Al-1Mo-1V strips and standard flow rates. Detailed data from these runs are shown in an Arrhenius plot in Figure 6.

FIGURE 5

THE EFFECT OF PRESSURE ON THE DEPOSIT
FORMATION RATE OF BATON ROUGE FUEL

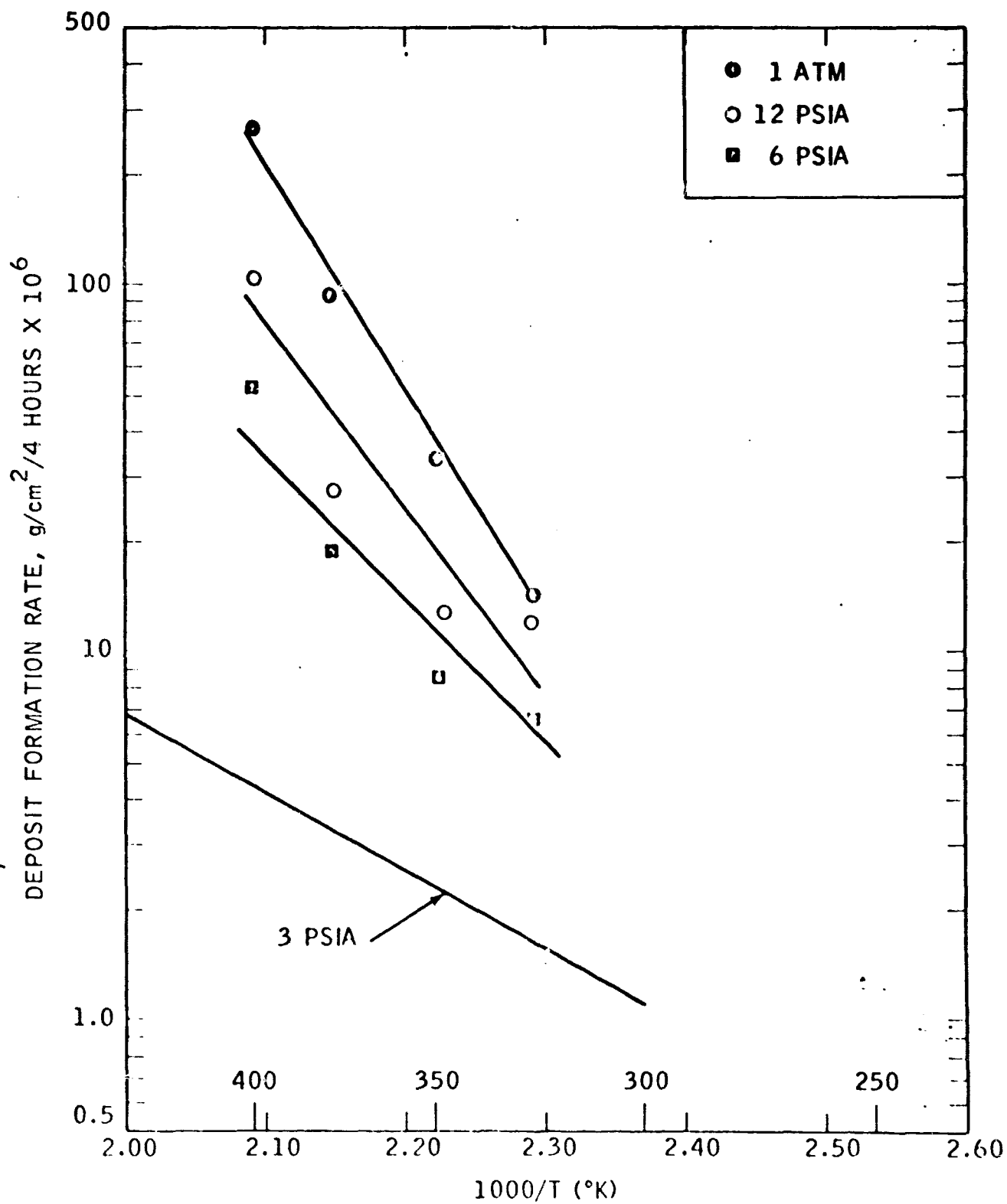
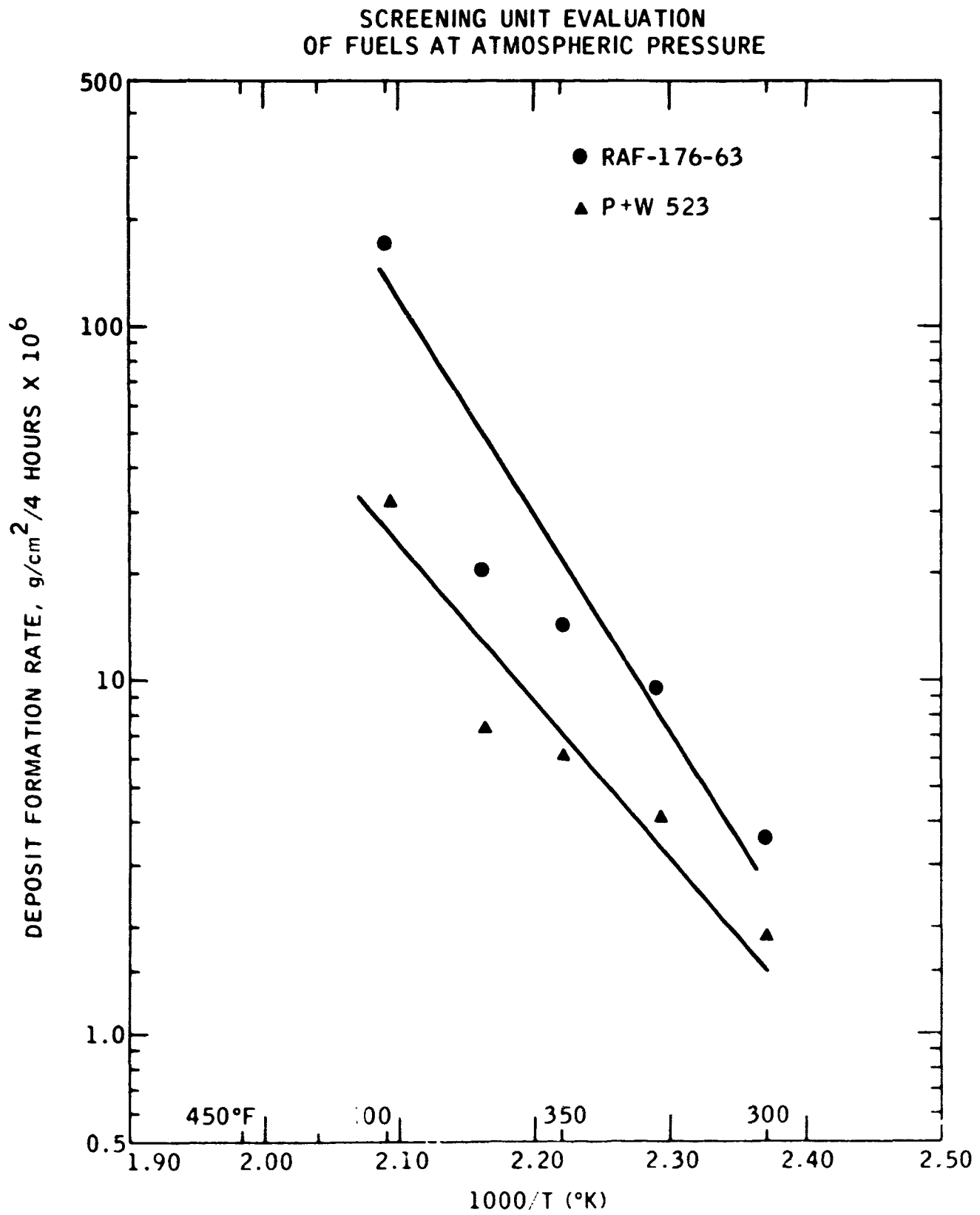


FIGURE 6



A comparison with previous data obtained at 3 psia indicates that increasing total pressure not only increased the level of deposits at temperatures in excess of 300°F but also increased the temperature dependence of the deposit formation process. A comparison with the Baton Rouge fuel results indicate that increasing total pressure with the Baton Rouge fuel increased the level of deposit formation to a greater extent than was observed with RAF-176-63, even though both fuels exhibit the same apparent activation energy at 1 atm total pressure. As a result, the Baton Rouge fuel becomes more deleterious toward deposit formation than RAF-176-63 at 1 atmosphere total pressure.

Fuel	Ratio of Deposit Formation Rate at 1 atm Versus 3 psia @ 350°F	Apparent Activation Energy kcal/mole
Baton Rouge	15	28
RAF-176-63	4.2	28
P&W 523	3.9	20

Directionally the results obtained with the RAF-176-63 and P&W 523 fuels are the same as that obtained with the Baton Rouge fuel. Since these jet fuels cover a spectrum of compositions and range from a deleterious to a highly stable fuel, it is concluded that, in general, raising total pressure will raise the level of deposit formation and the apparent activation energy for the deposit formation process.

We had evaluated fuel AFFB-8-67 (AZ-1) in a standard Screening Unit test (3 psia, Ti-8Al-1Mo-1V strips). In order to pinpoint the performance of this fuel at conditions closer to those encountered in a Fuel System Simulator, we have evaluated it in the Screening Unit at 1 atm total pressure using stainless steel strips. For this run, nitrogen was added to the inlet air so that the oxygen partial pressure was held at 32 mm Hg. Thus, the oxygen partial pressure in this run corresponds to that encountered in a standard screening test at 3 psia using undiluted air. Results of this test are shown in the Arrhenius plot in Figure 7. Included is a predicted deposit formation rate case for the use of stainless steel at 3 psia. Raising the total pressure at a fixed oxygen pressure increased the rate of deposit formation with AFFB-8-67. A similar effect was previously observed with RAF-176-63. One reason that total pressure has such an effect on deposit formation is the fact that at reduced pressure (i.e., 3 psia), reactive species are probably volatilized in many instances before they can participate in the deposit formation process, which takes place mainly in the liquid phase.

The effect of pressure on the deposit formation tendency of pure compounds was also investigated. The effect of total pressure on the deposit formation rate of n-decane was investigated on the Screening Unit using pure titanium strips (Ti 75A) and full air flow. The results of this study are shown in the Arrhenius plot in Figure 8. It can be seen that with n-decane, increasing the total pressure from 3 psia to 1 atm

FIGURE 7

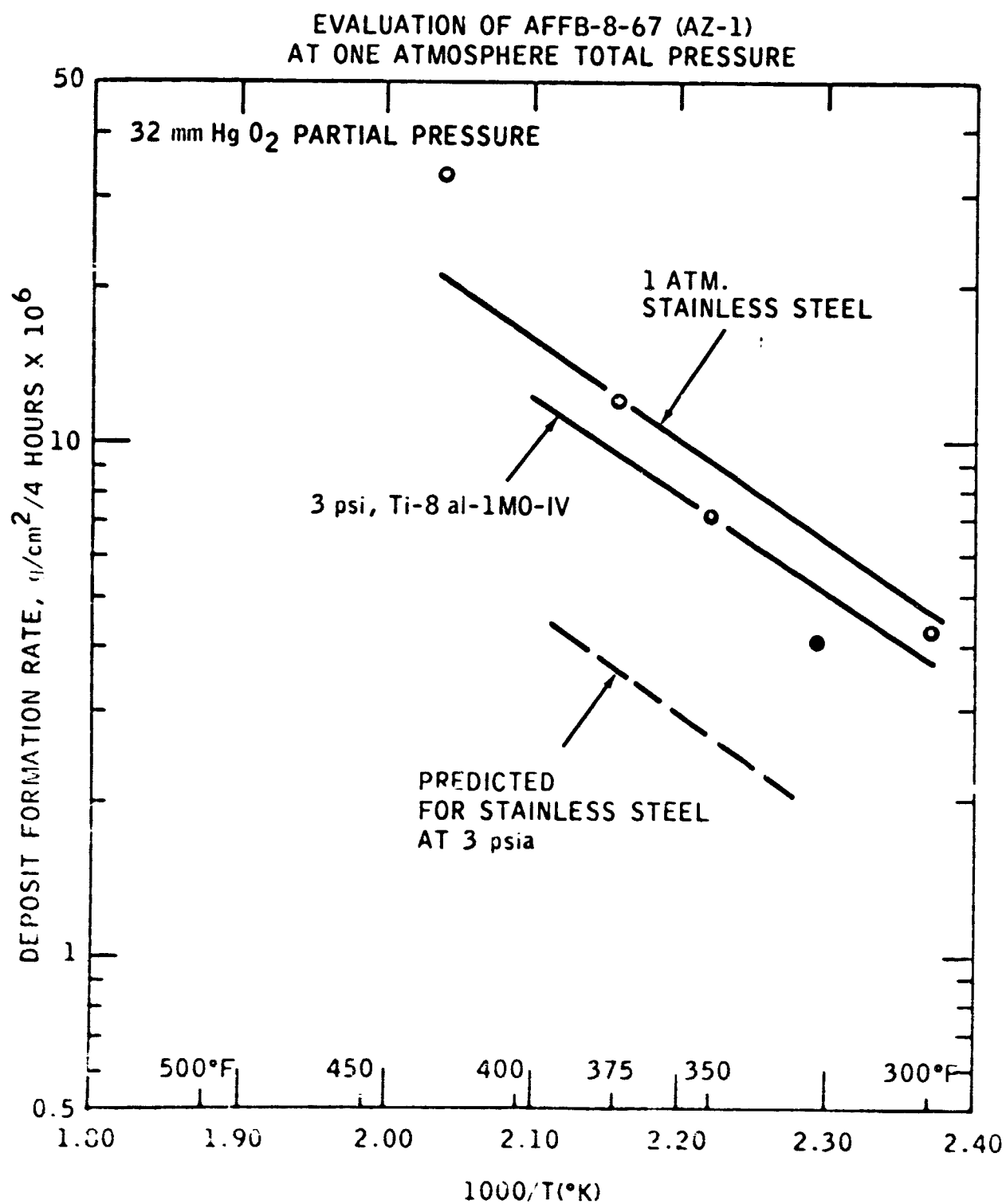
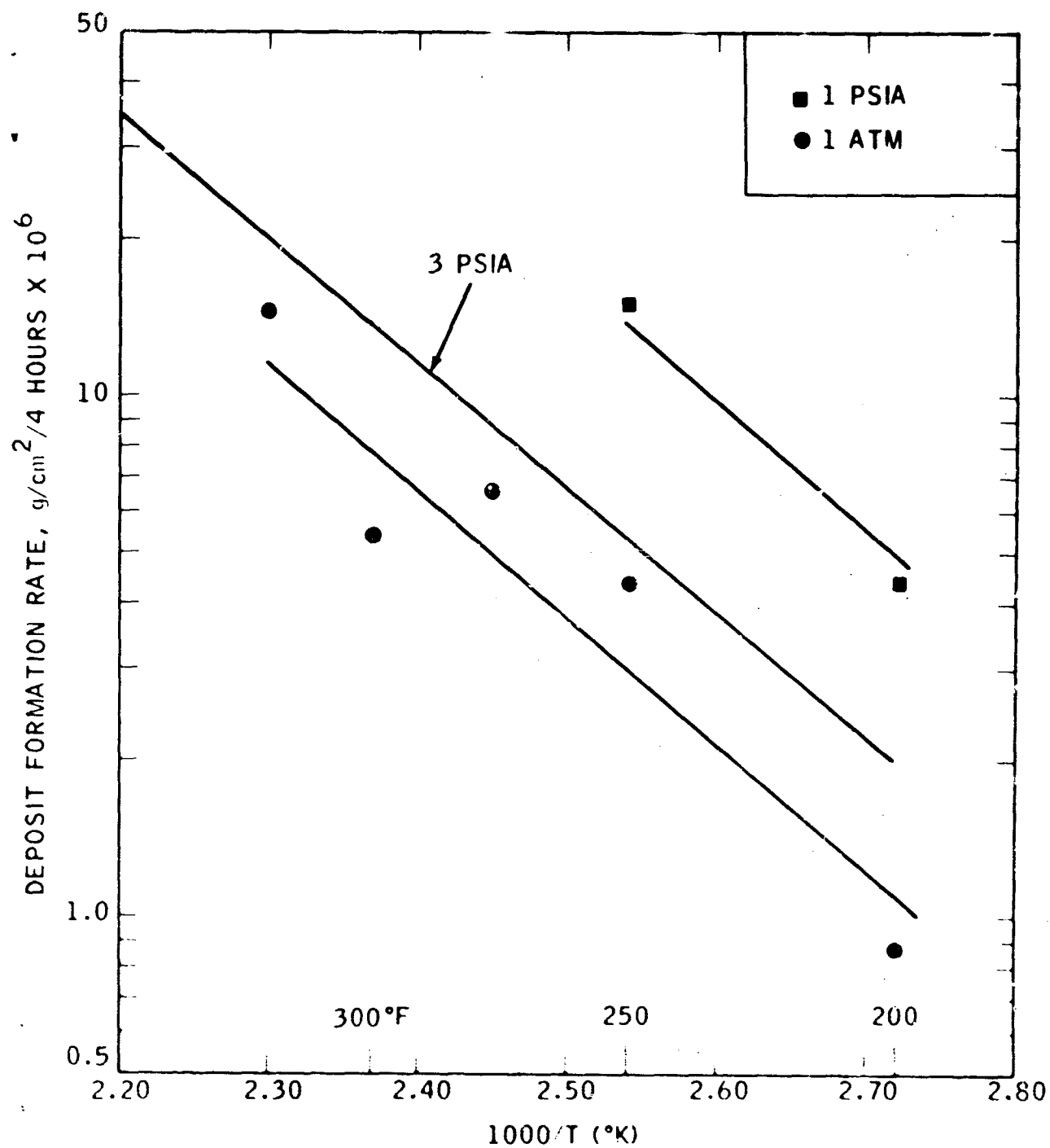


FIGURE 8

EFFECT OF PRESSURE ON THE DEPOSIT
FORMATION RATE OF n-DECANE



reduced the rate of deposit formation. This effect is, of course, opposite to that observed with jet fuels and suggests that the effect of total pressure on deposit formation reflects an effect on the non-paraffin portion of the fuel.

To check this hypothesis and to further elucidate the effect of pressure on the deposit formation process, the effect of pressure on the deposit formation rate of an olefin in paraffin blend has been determined. This was done by measuring the deposit formation rate of a 10 wt % indene in n-decane blend in the Screening Unit at atmospheric pressure. Results are shown in an Arrhenius plot in Figure 9. Also shown are the data obtained with the same blend previously at 3 psia at otherwise identical conditions. It can be seen that at the higher pressure the olefin containing blend exhibited apparent activation energy for deposit formation (i.e., 16 versus 9 kcal/mole). These results, thus, confirm the previous conclusion that the non-paraffin portion of the fuel is responsible for the observed pressure dependence with actual jet fuels. All detailed data are shown in Appendix 1.

2. The Effect of Oxygen Partial Pressure on The Rate of Deposit Formation

A short study was made in the Screening Unit to determine the effect of oxygen partial pressure on the deposit formation rate. Jet A kerosine RAF-176-63 was chosen for this initial study. The Screening Unit was operated at one atmosphere total pressure using Ti-8Al-1Mo-IV metal strip and the standard hydrocarbon flow rate of 125 cc/hour and a four-hour reaction period. The total gas flow was fixed, and the oxygen partial pressure was varied by delivering various amounts of N₂ and air to the unit. The jet fuel was pre-saturated with the N₂/air mixture prior to admission to the reaction tube. Increasing the oxygen partial pressure in the range of 16 to 160 mm Hg increased the rate of deposit formation.

Oxygen Partial Pressure (at atm. total pressure) mm Hg	Rate of Deposit Formation at 450°F, Grams per cm ² Surface	Relative Activity for Deposit Formation at 450°F
16	21 x 10 ⁻⁶	0.81
80	26 x 10 ⁻⁶	1.00
160	35 x 10 ⁻⁶	1.34

A plot of log of the relative activity versus log of the partial pressure (See Figure 10) indicates that the deposit formation rate is approximately 0.2 order in oxygen partial pressure. This low positive order in oxygen is typical of many hydrocarbon oxidation reactions carried out at moderate oxygen partial pressures (67,68). From Figure 10, it is possible to predict a deposit formation rate at 31 mm Hg O₂ partial pressure, which corresponds to the O₂ partial pressure in the Screening Unit runs at 3 psia with full air. A comparison of this rate with the rate obtained in the Screening Unit at 3 psia with RAF-176-63 indicates that the deposit formation process is faster at 1 atmosphere total pressure.

FIGURE 9

EFFECT OF PRESSURE ON DEPOSIT
FORMATION OF 10% INDENE IN *n*-DECANE

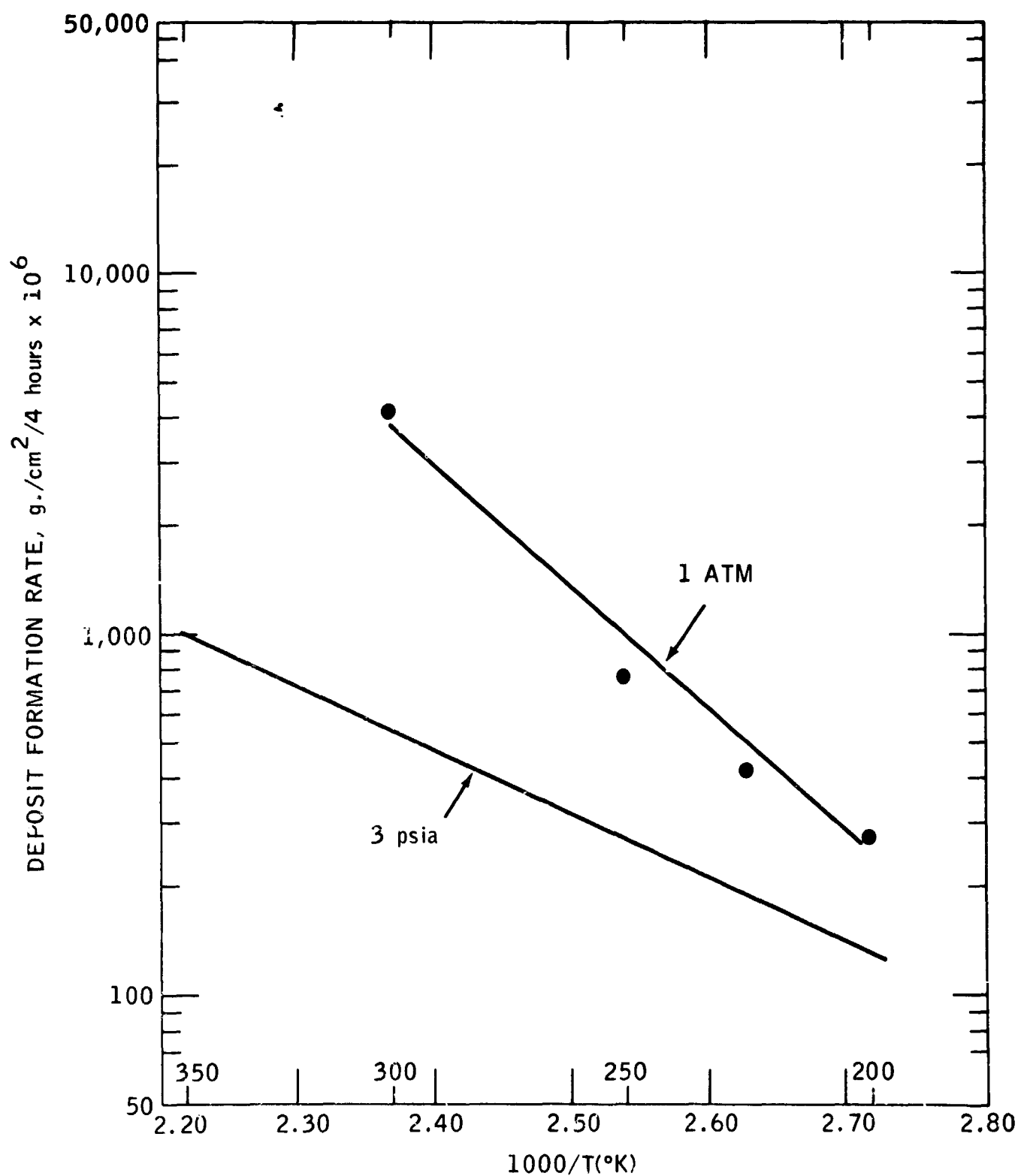
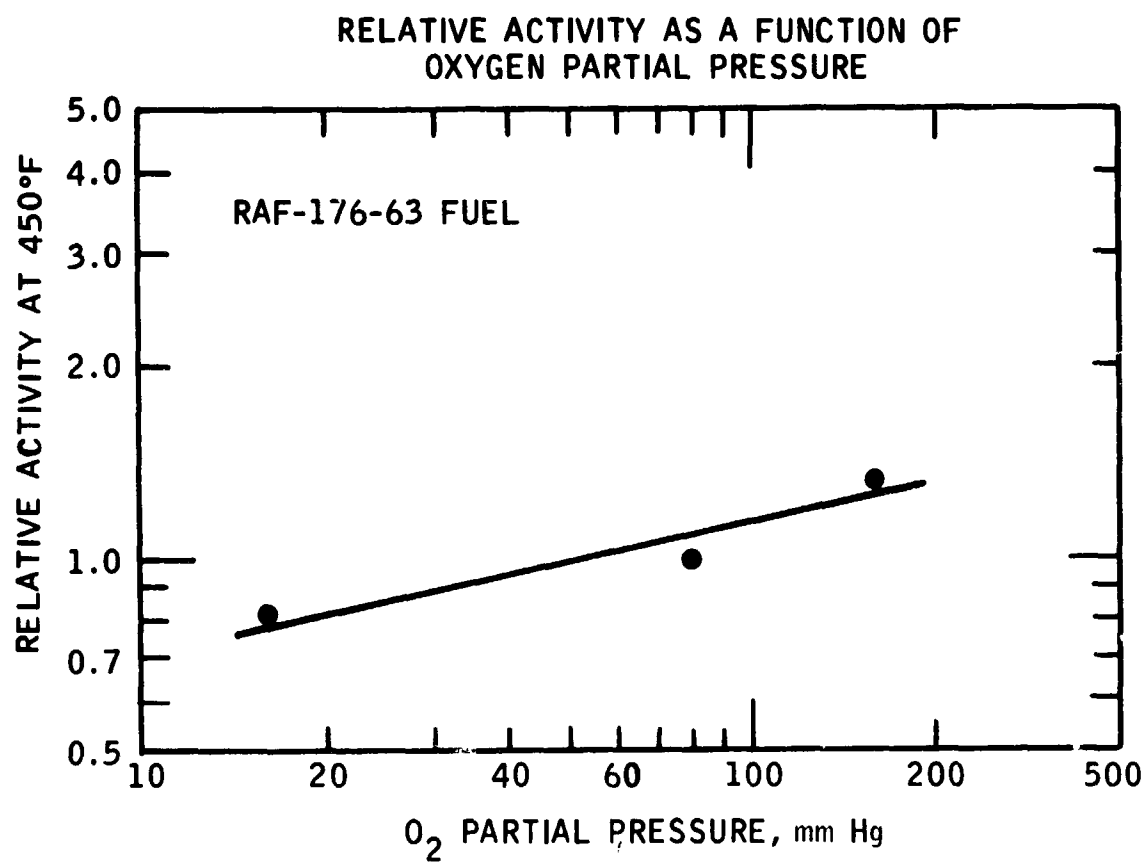


FIGURE 10



<u>Total Pressure (with 31 mm Hg O₂ partial pressure), psia</u>	<u>Rate of Deposit Formation at 450°F, Grams per cm² Surface</u>	<u>Relative Activity for Deposit Activity at 450°F</u>
6	16×10^{-6}	1.00
14.7	23×10^{-6}	1.43

Thus, a higher total pressure, at a fixed oxygen partial pressure, increases the rate of deposit formation. A dependence on total pressure, at a fixed oxygen partial pressure, is also characteristic of many hydrocarbon autoxidation reactions. Detailed data are shown in Appendix 2.

3. The Effect of Exposure Time on the Rate of Deposit Formation

A study was completed of the effect of exposure time on the rate of deposit formation. Our standard test in the Screening Unit involves a fixed four-hour reaction time and thus provides the average rate of deposit formation over the first four hours of exposure of a fresh metal surface. We decided to study the effect of exposure time on the rate of deposit formation so that (a) we could determine how rapidly deposits build up during extended exposure in multi-mission flights, and (b) make sure that our standard four-hour reaction time Screening Unit test is providing meaningful information. The study was carried out by making Screening Unit runs for a total of 1, 3, and 8 hours exposure to degrading fuel and comparing these results with those obtained from our standard four-hour test. Jet A kerosine RAF-176-63 was chosen as the fuel. Other conditions were 3 psia, Ti-8Al-1Mo-1V strips and the use of undiluted air. The deposit formation rates were calculated as grams of deposits per cm² of total metal surface per hour of total exposure to fuel. This deposit formation rate represents the average rate of deposit formation over the total length of time that the fuel has been exposed to the metal surface. An Arrhenius plot of this data is shown in Figure 11. The data show that the deposit formation rate is highest when the metal surface is first exposed to fuel and then falls off with continued exposure time. In Figure 12, the relative activity for deposit formation at 350°F is plotted as a function of total exposure time. This relative activity was obtained by dividing the rate of deposit formation at the various exposure times by the rate obtained in the normal four-hour exposure time Screening Unit run. As shown, the greatest drop in the level of the rate of deposit formation occurs in the first two hours of exposure. The rate subsequently falls off rather slowly. Thus, we feel that the rates obtained from our standard four-hour exposure time test are quite representative of the lined out deposit rates which would be obtained using more prolonged exposure times.

4. The Evaluation of Water Saturated Jet Fuel and Decane

Although the water content of jet fuels is normally quite low (reflecting the low solubility of water in hydrocarbon media), water is known to exert an influence on many reaction systems. As a result, a short study of the effect of water saturation on both n-decane and Baton Rouge fuel was carried out. The fuels were prepared by addition of excess water to the sample and then the water containing sample was bubbled with air at

FIGURE 11

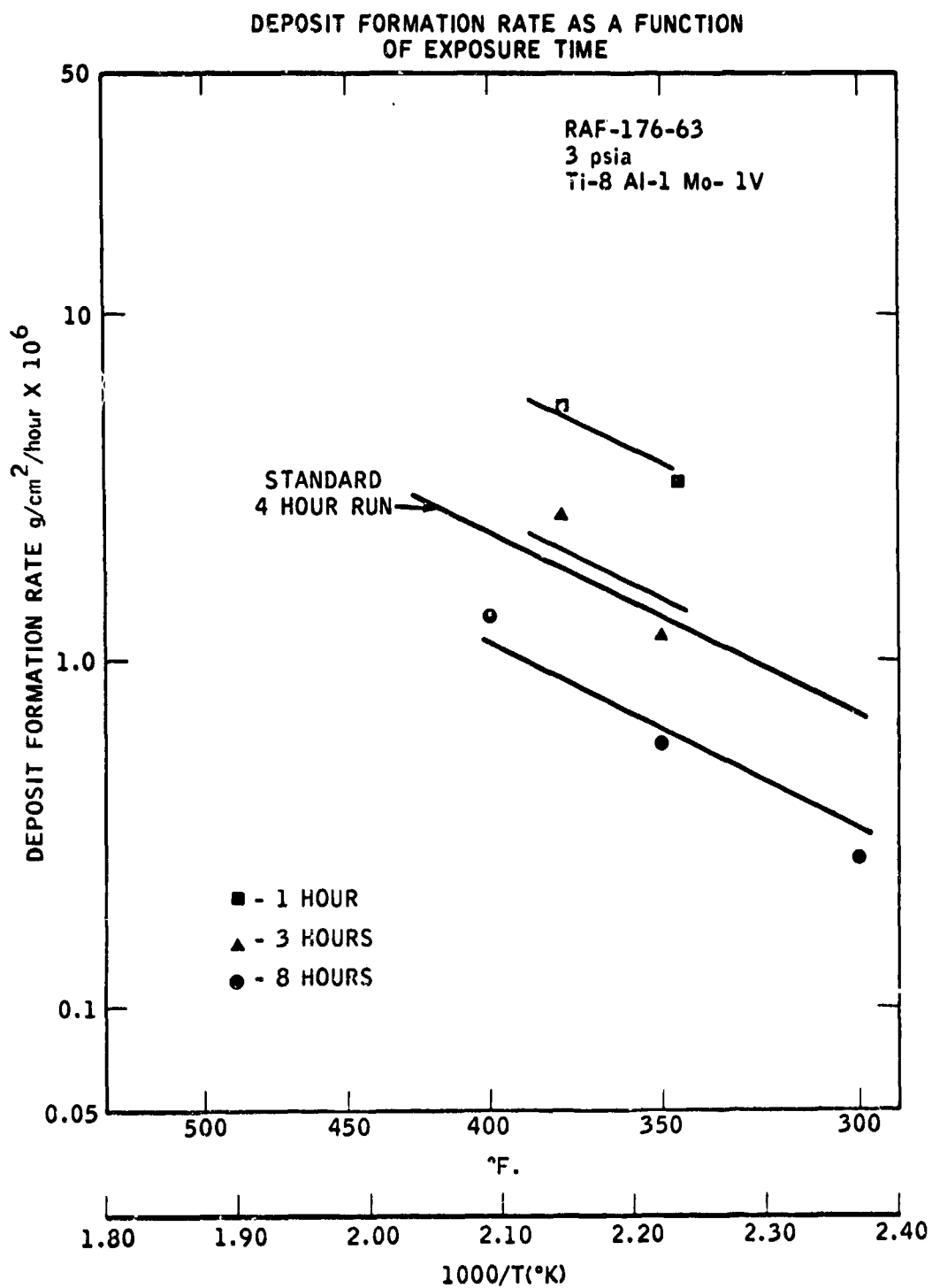


FIGURE 12

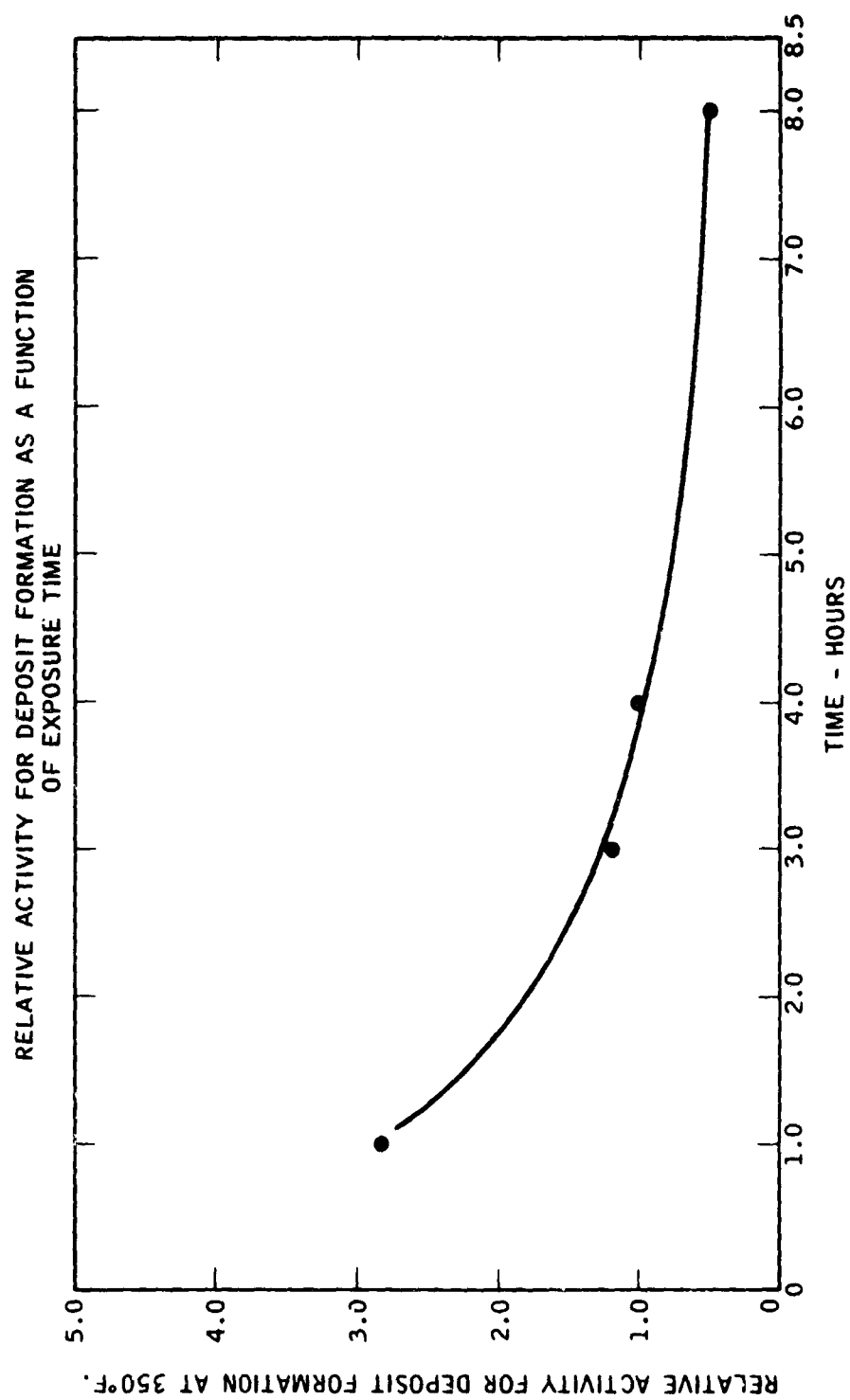
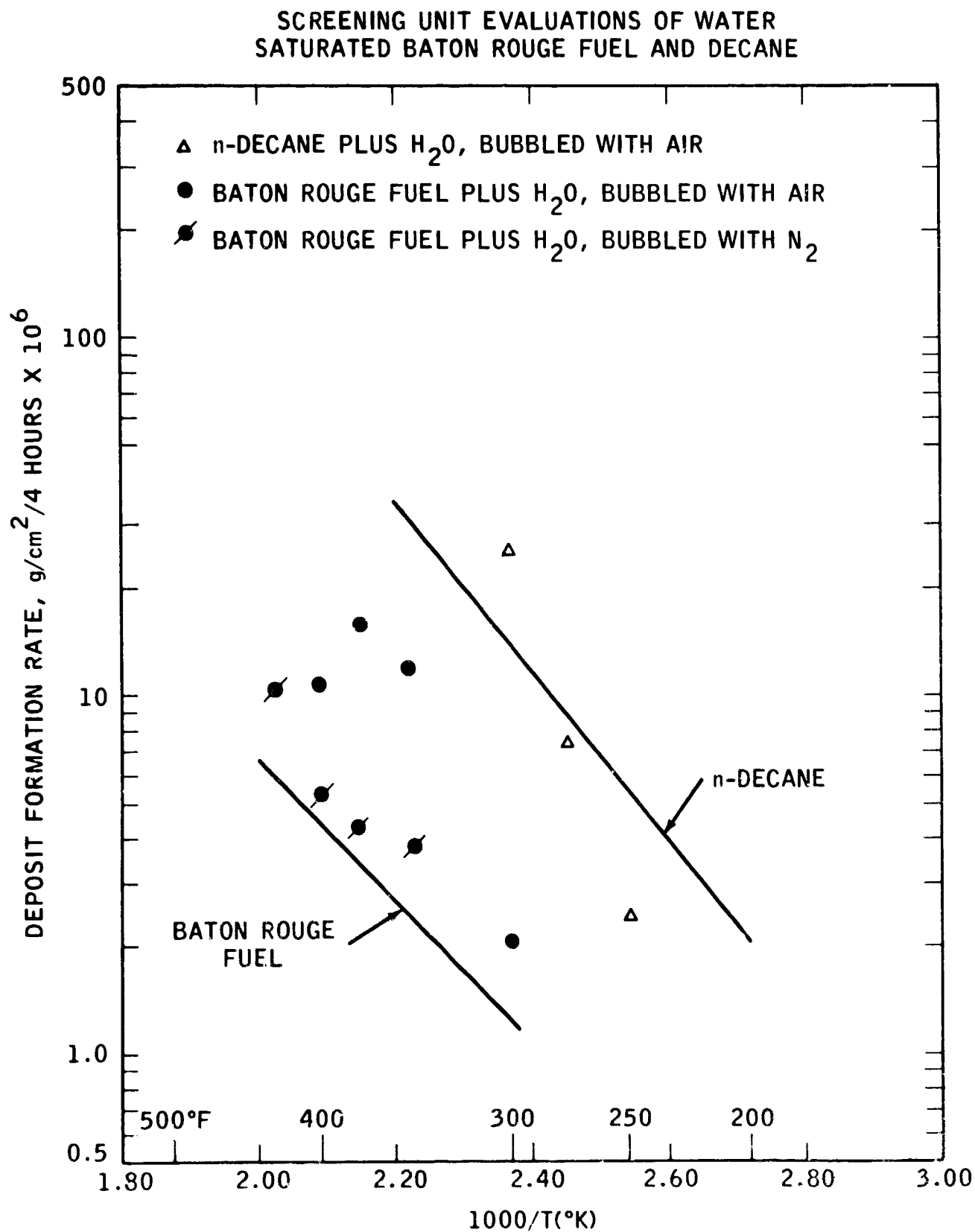


FIGURE 13



room temperature to insure that the material was saturated with water at those conditions. To check the effect of air sparging, a sample of Baton Rouge fuel was also saturated with water by sparging with N₂. The water saturated fuels were then tested in the Screening Unit at 3 psia using Ti-8Al-1Mo-1V strips. Results are shown in Figure 13. As can be seen, presaturating n-decane with water by sparging with air had no significant effect on the rate of deposit formation. In contrast, presaturating the Baton Rouge fuel with water, by bubbling the fuel containing excess water with air, increased the rate of deposit formation significantly in the 350 to 400°F range. Substituting nitrogen for air during the preparation of the water saturated Baton Rouge fuel essentially reduced the deposit formation tendency of the water treated fuel to that of the standard Baton Rouge fuel. That water can influence deposits formation at 350°F is surprising since liquid water itself will boil at 3 psia at 142°F. These results suggest that an oxygen-water-fuel interaction occurred in the Baton Rouge fuel, which lead to the increased rate of deposit formation at 350 to 400°F in a Screening Unit test. In this respect, it is interesting to note that Emanuel(69) has reported that peroxy radicals will form complexes with water. It is also well known that water will form solid hydrates with some hydrocarbons (70,71,72). In any event it is clear that water is capable, in some circumstances, of exerting an influence on the deposit formation process at "empty" wing tank deposits. Related data are shown in Appendix 4.

E. The Study of the Effect of Trace Impurities on Deposit Formation

1. The Effect of Trace Levels of Sulfur Compounds on Deposit Formation

We felt that the sulfur content of a given fuel could be important because it has been established in the literature that (a) elemental sulfur catalyzes the formation of free radicals, (b) organic sulfur compounds decompose into radical fragments under the present experimental conditions, and (c) many sulfur derivatives, e.g., sulfides, are readily autoxidized by a free radical chain process under the present experimental conditions. Thus, sulfur and its derivatives could initiate the complex series of reactions that lead to deposit formation. Initial work in the Screening Unit established that the deposit formation "cut-off temperature" could be correlated with the fuel sulfur level at a statistically significant confidence level. (14 and 15, Table II) On the other hand, the rate of deposit formation at lower temperatures, i.e., 350°F, could not be related to the total sulfur level of the fuel in a simple manner. This again emphasizes the complex nature of the overall deposit formation process. These results indicated the need for a more extensive study of the effect of trace quantities of sulfur compounds on the deposit formation process (73).

We decided that the most direct method of investigating the effect of trace levels of sulfur compounds on the overall deposit formation process would be to add known quantities of pure sulfur compounds to an actual jet fuel. We chose P&W 523 as the jet fuel to be doped with sulfur compounds because (a) it has been demonstrated that this fuel is highly

FIGURE 14

CUT-OFF TEMPERATURE AS A FUNCTION OF SULFUR CONTENT

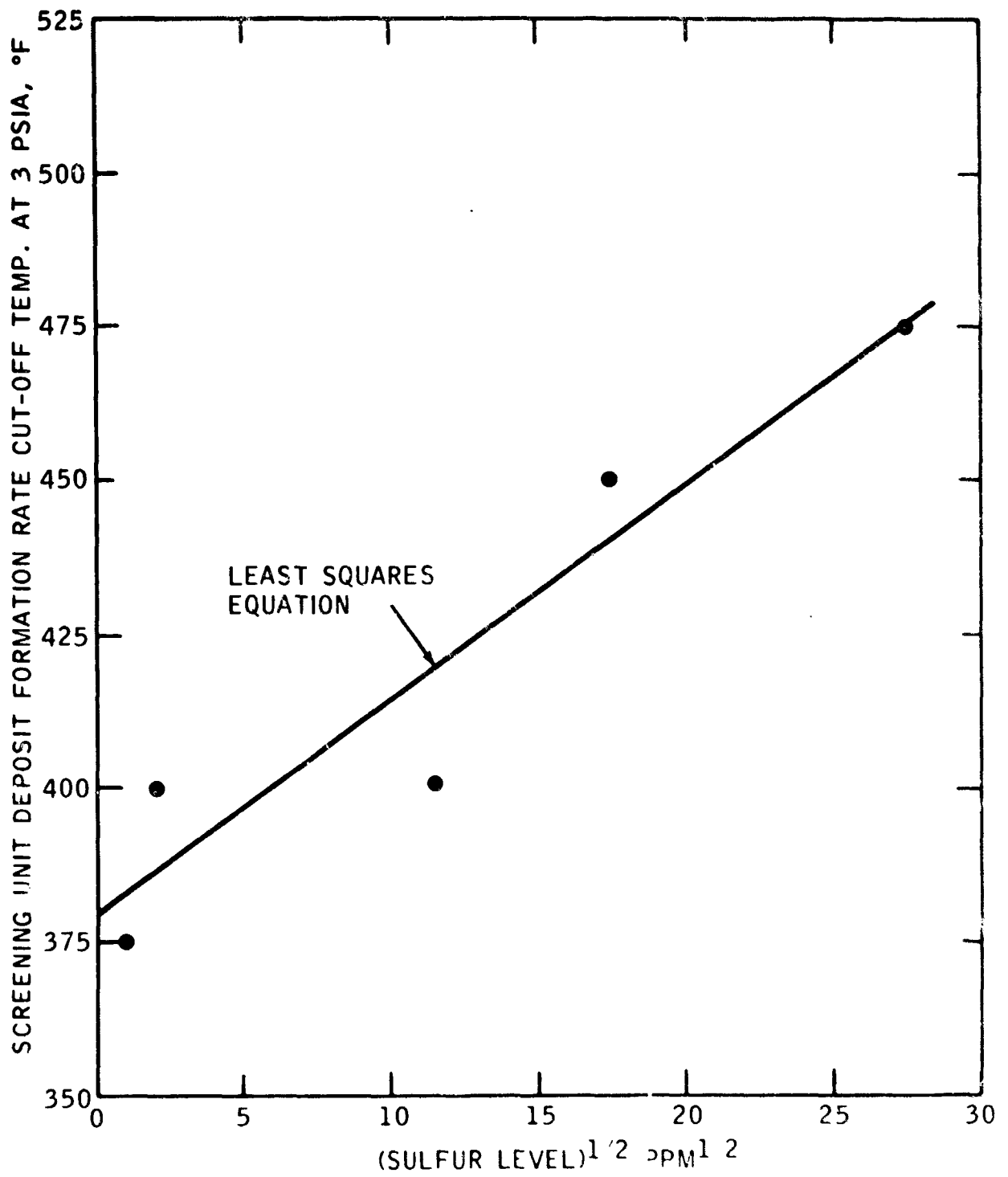


FIGURE 15

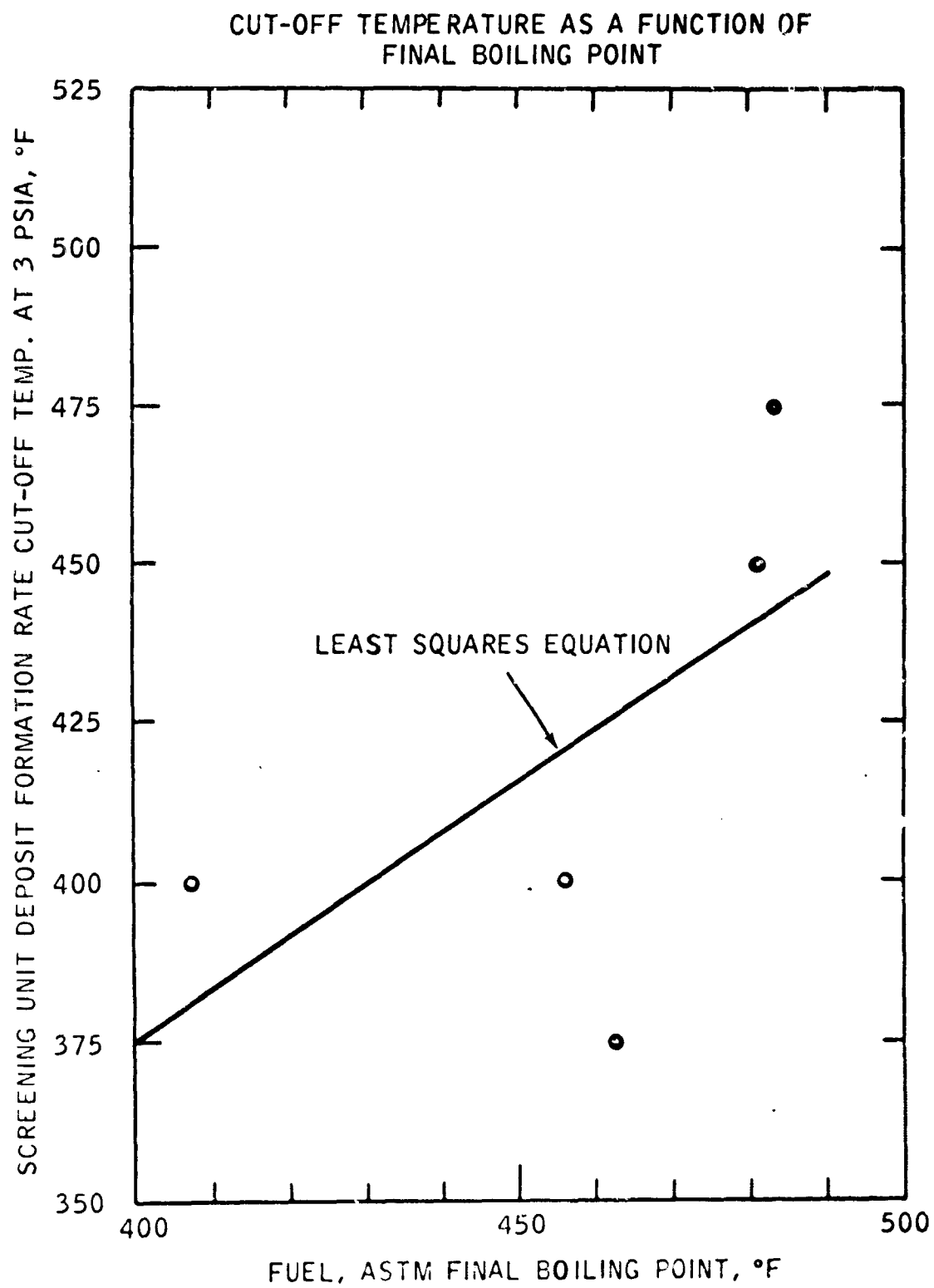


TABLE II

Analyses of Variance of Linear Regressions^(a)

A. Regression of Cut-off Temperature on Square Root of Sulfur Level

<u>Source of Variation</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>
Due to regression	6,050	1	6,050
About regression	700	3	233
Total	<u>6,750</u>	<u>4</u>	

F = 26.0 (from regression)

F (1,3) 95% = 10.1 (required for significant test)

Conclusion: Regression is significant at greater than 95% confidence levels.

B. Regression of Cut-off Temperature on Final Boiling Point

<u>Source of Variation</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>
Due to regression	2,270	1	2,270
About regression	4,480	3	1,495
Total	<u>6,750</u>	<u>4</u>	

F = 1.52 (from regression)

F (1,3) 95% = 10.1 (required for significant test)

Conclusion: Regression is not significant.

(a) Source: O. L. Davies, "Statistical Methods in Research and Production," 3rd Edition, Hafner Publishing Co., N.Y., 1957.

stable toward deposit formation, and (b) this fuel is essentially sulfur free (analyzed < 0.2 ppm S) so that any effects would be attributed directly to the added sulfur compounds.

The sulfur doped P&W 523 fuel was tested in our Screening Unit at 3 psia. This was done so that its deposit formation rate could be compared with our previous evaluation of the undoped fuel. Other conditions were also maintained the same; i.e., full air, four-hour reaction time, Ti-8Al-1Mo-1V metal strips, and the standard hydrocarbon and air flow rates.

U.S. commercial and military specifications for aviation turbine fuels generally limit the total sulfur level to 3000 to 4000 ppm and the thiol (RSH) sulfur level to 10 to 50 ppm maximum. Thus, thiol sulfur is restricted to approximately 10% or less of the total sulfur content of a finished jet fuel.

The 1000 ppm S level was chosen as a representative level for the sulfur content of an actual jet fuel. The distribution of sulfur compound types in the nonthiol fraction will vary with the crude type, processing steps, and environment employed during refinement of the fuel; however, sulfides are normally the predominant type of sulfur compound - for example, Hartough (74) has shown wide variations in the distribution of thiols and disulfides among various crude types. Rall et al, (75) have pointed out that disulfides may not be present in virgin crude but are produced subsequently by thiols by a facile oxidation. Sweetening processes produce disulfides from thiols by oxidation with molecular oxygen of air. The addition of such sweetened stocks to a jet fuel obviously increases the disulfide content of the fuel. Wallace (78,79) has also shown that in the absence of air, thiols can be oxidized to disulfides by metal oxides and soluble metal salts at low temperatures. Thus, representative thiols, sulfides, and disulfides were included in this study.

To evaluate differences between compound types, a variety of pure sulfur compounds were used in the study, including sulfides, disulfides, thiols, and condensed thiophenes. Structural effects within a given class of compounds were investigated with a series of phenyl and benzyl sulfides. In general, sufficient quantities of these compounds were added to the hydrocarbon to raise the sulfur level of the hydrocarbon fuel to 1000 ppm of S by weight. Thus, the sulfides, thiols, and condensed thiophene were evaluated at the same mole concentration, whereas the disulfides were present at only half the mole concentration of the other compounds.

The deposit formation rates obtained with the various 1000 ppm S-contaminated hydrocarbon materials are shown in the Arrhenius plots in Figures 16 to 19 and Appendix 5. The rate obtained with the uncontaminated hydrocarbon is also shown. The addition of diphenyl sulfide and dibenzothiophene did not significantly increase the rate of deposit formation over the range of temperatures tested. The rate of deposit formation was increased by all the other sulfur compounds added to the hydrocarbon material at a sufficiently high temperature, in some cases, by as much as a factor of 20. Thus, thiols, sulfides, disulfides, and some condensed thiophenes are capable of markedly increasing the rate of deposit formation at trace levels at a sufficiently high temperature.

FIGURE 16

THE EFFECT OF THE ADDITION OF 1000 PPM S

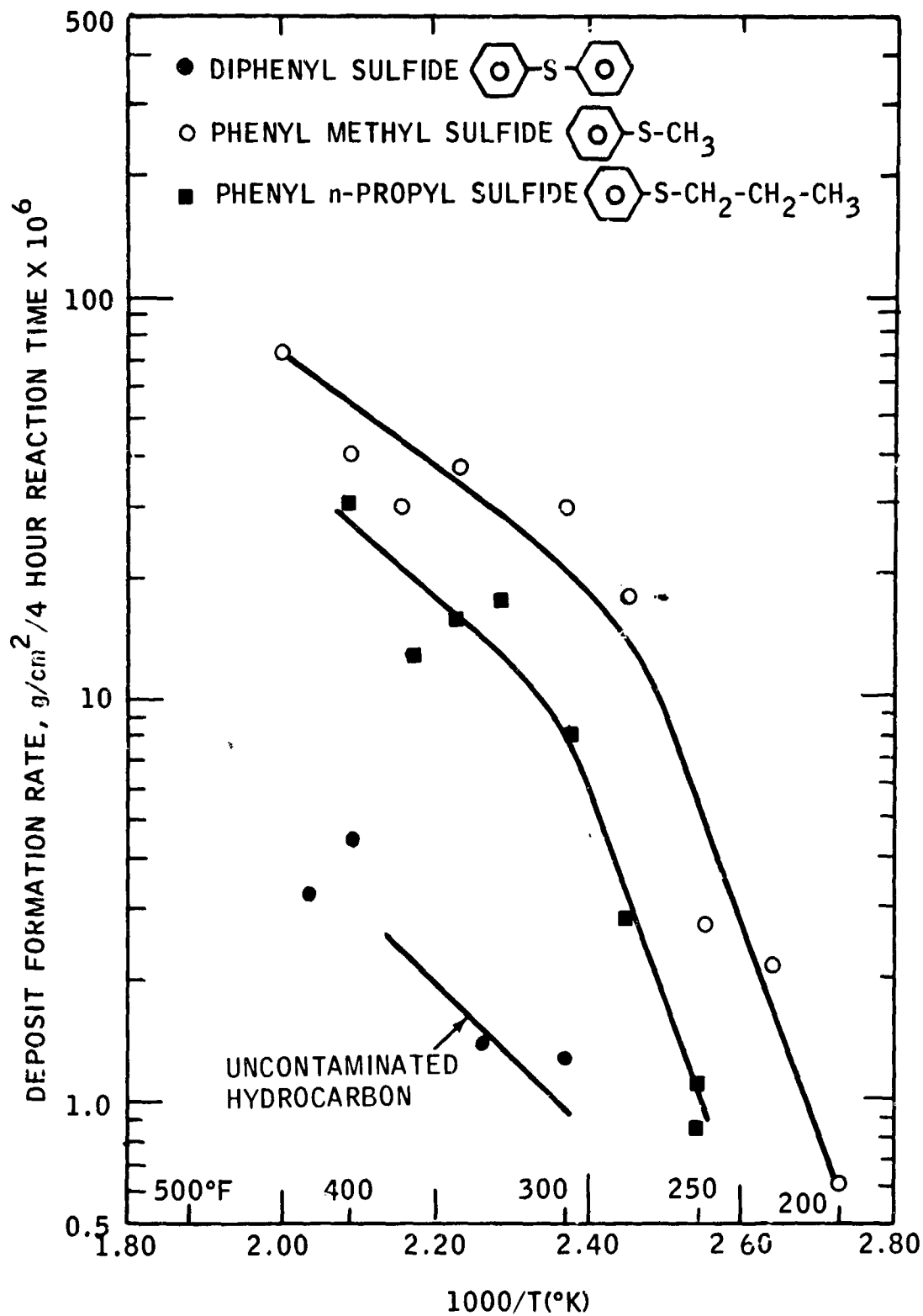


FIGURE 17

THE EFFECT OF THE ADDITION OF 1000 PPM S

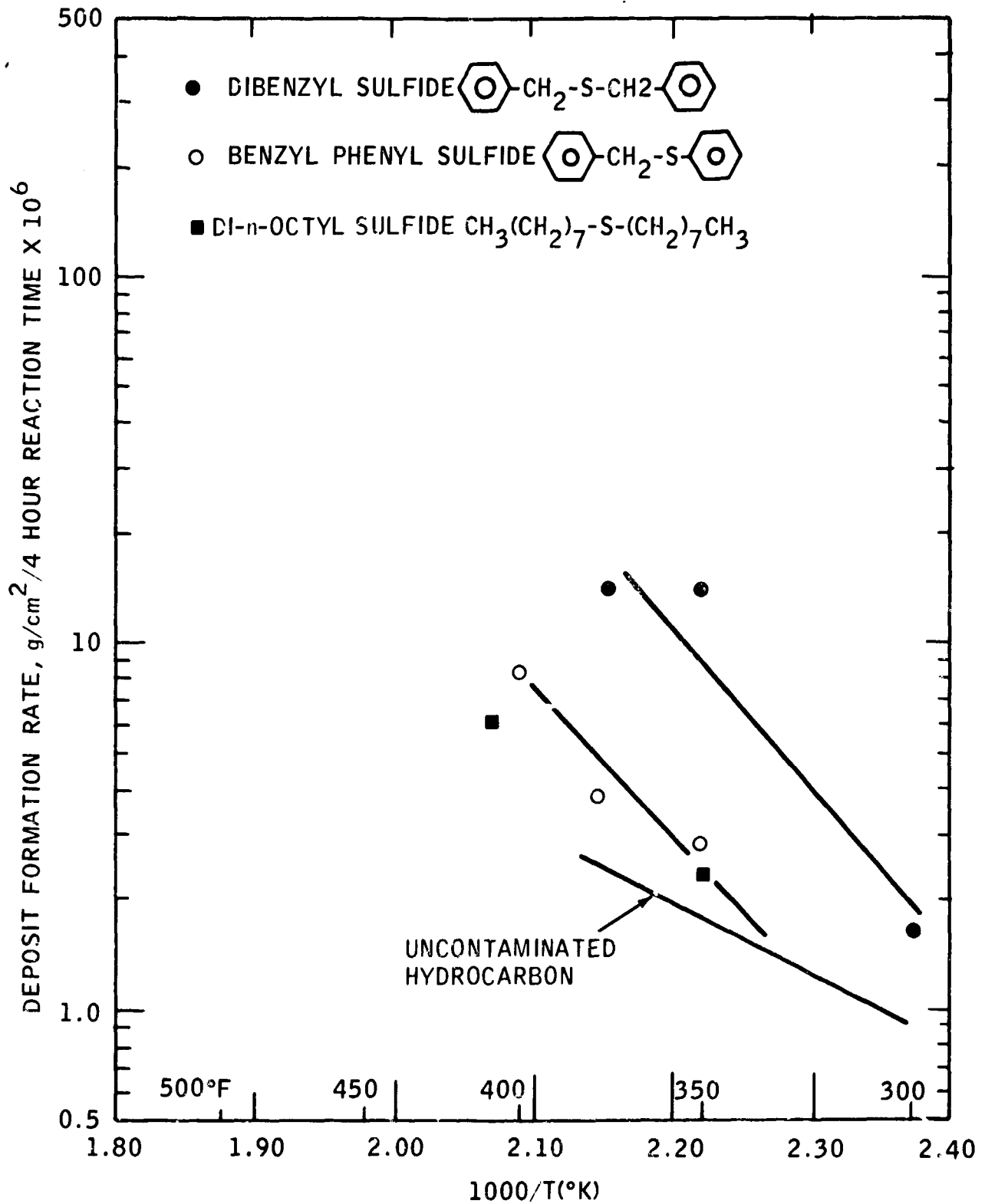


FIGURE 18

THE EFFECT OF THE ADDITION OF 1000 PPM S

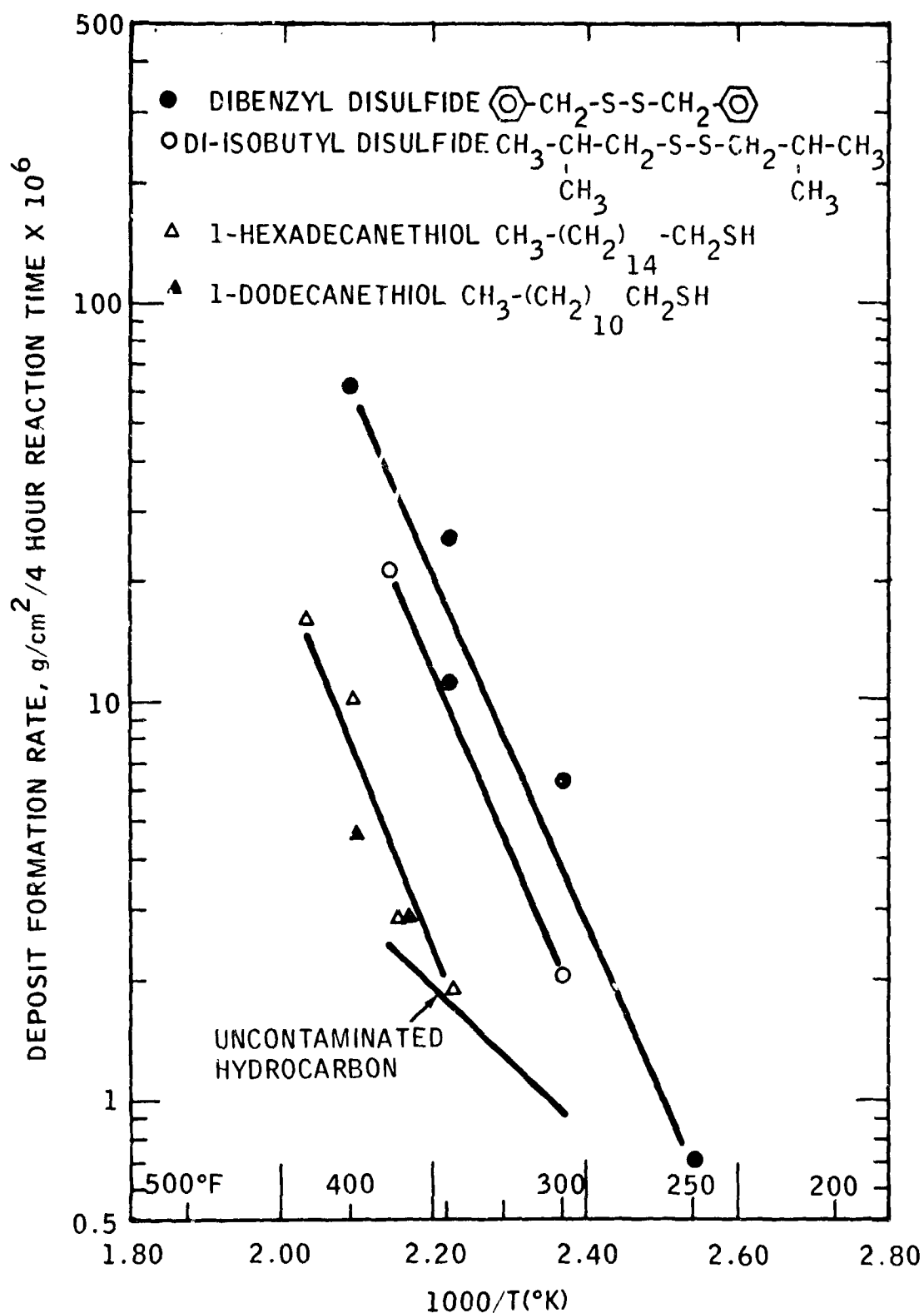
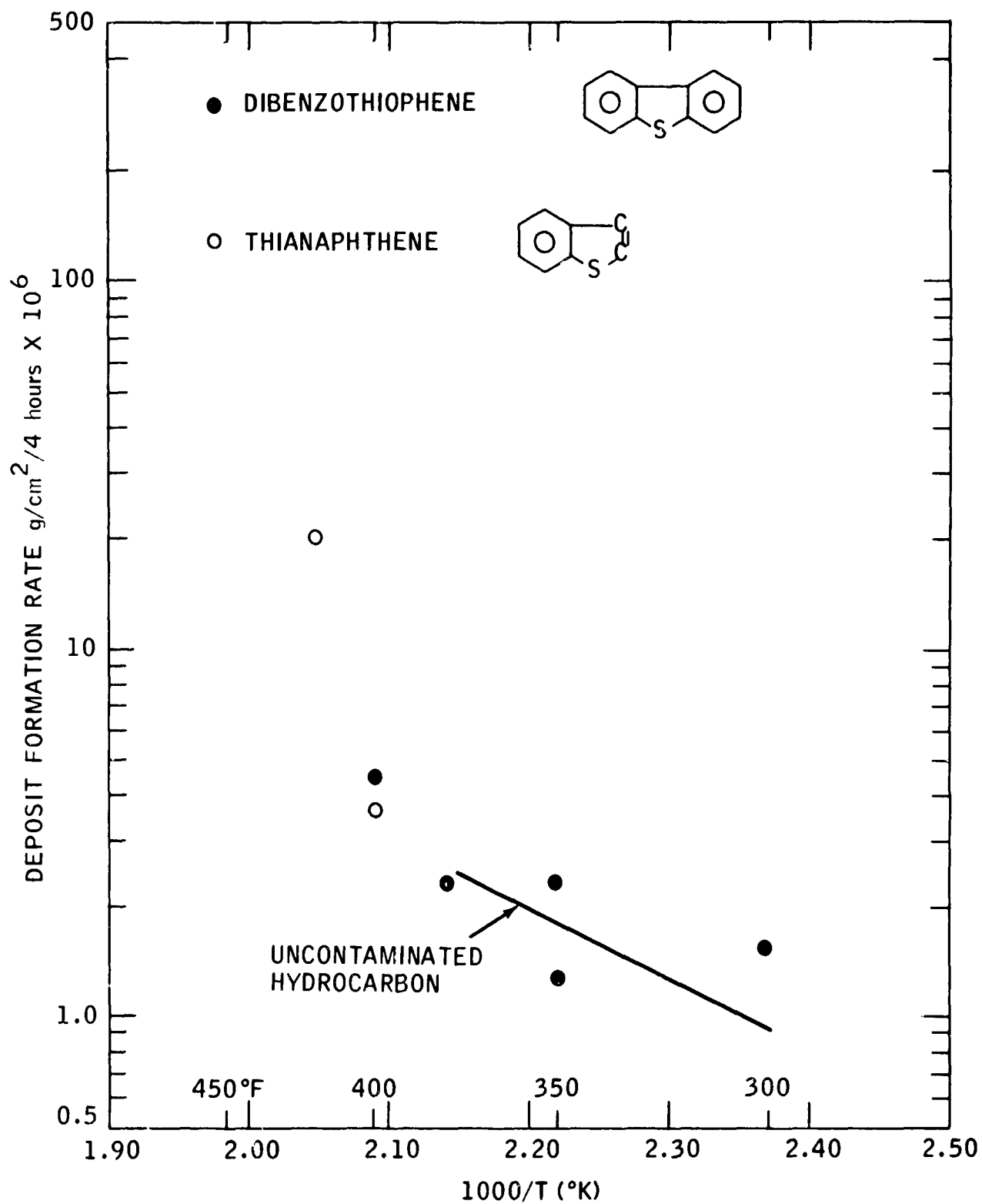


FIGURE 19

THE EFFECT OF THE ADDITION OF 1000 PPM S



The phenyl methyl sulfide- and phenyl propyl sulfide-contaminated hydrocarbons produced a complex - i.e., nonlinear - Arrhenius plot. At low temperatures, the materials exhibited an apparent activation energy of approximately 20 kcal. per mole, which decreased to 10 kcal per mole as the temperature increased. The hydrocarbon exhibited an apparent activation energy of 10 kcal per mole. The other sulfide and disulfide compounds also exhibited an apparent activation energy of approximately 20 kcal per mole.

The effect of sulfur concentration was investigated with phenyl methyl sulfide (5000 ppm of S), dibenzyl disulfide (10 ppm of S) and diisobutyl disulfide (10 and 100 ppm of S)-doped hydrocarbon fuels. Higher sulfur levels resulted in higher levels of deposit formation. The deposit formation rate, however, did not increase linearly with increasing sulfur content. A comparison of the relative deposit formation rate vs. the square foot of the relative sulfur level is shown in Figure 20. Increasing the sulfur level by a factor of 50 approximately tripled the rate of deposit formation.

At high temperatures ($>900^{\circ}\text{F}$), sulfur compounds pyrolyze via a homogeneous free-radical process. With the aid of a radical scavenger technique, phenyl methyl sulfide was shown to decompose to phenyl thiyl and methyl radicals (80), benzyl methyl sulfide decomposed to benzyl and methyl thiyl radicals (81), and various thiols decomposed via rupture of the C-S bond to alkyl and hydrosulfide radicals (82). At lower temperatures, the mode of thiol decomposition varies with structure. For example, 2-methyl-2-propanethiol decomposes by a radical process, and 1-pentanethiol fragments to produce 1-pentene and hydrogen sulfide (83). In the former case, homolysis of the C-S bond produces a tertiary alkyl radical which is more stable than a primary alkyl radical. This is apparently the reason for the different modes of decomposition.

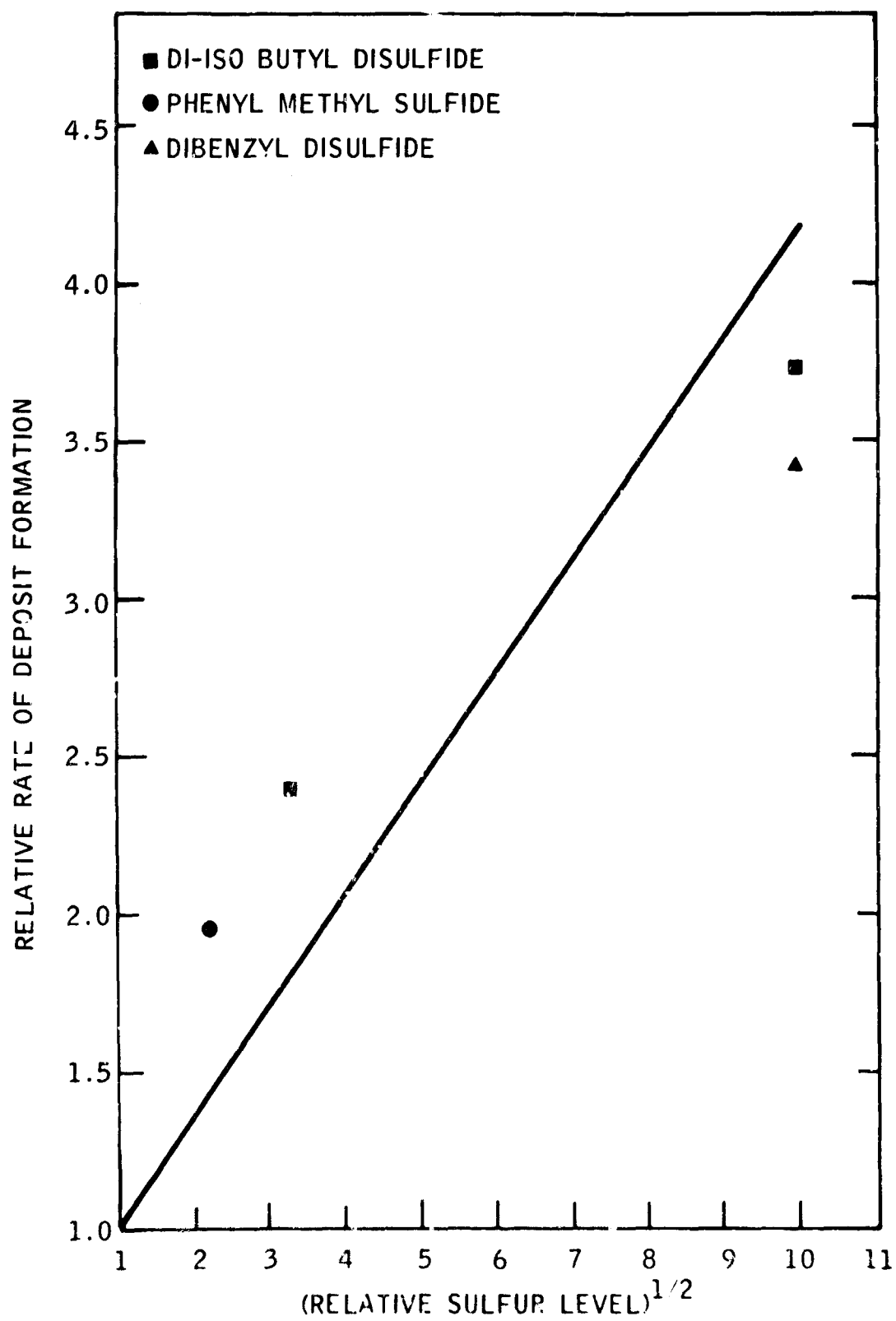
The heterogeneous decomposition of thiols occurs at 390° to 930°F and usually yields olefins, sulfides, and hydrogen sulfide (84). Sulfides and disulfides both (85,86) undergo a complex heterogeneous decomposition in the 390° to 930°F range. Rudenko and Gromova (87) passed a series of sulfur compounds over iron and reported the minimum temperature at which decomposition became significant as evidenced by evolution of hydrogen sulfide. Thiols, disulfides, and dialkyl sulfides readily decomposed at 300° to 750°F . Diaryl sulfides decomposed at 840°F , but thiophene was stable at 932°F .

Sulfur reacts with various hydrocarbons to produce initially alkyl and hydrosulfide radicals. These radical fragments react further to produce hydrogen sulfide and an olefin (88). Thiols are known to add to olefins via a free-radical chain process (89). Fabuss et al (90) have shown that trace quantities of sulfur compounds can either increase or decrease the rate of thermal pyrolysis of various hydrocarbons.

In the presence of oxygen at room temperature, thiols and olefins are co-oxidized to produce β -hydroxysulfoxides (91). Sulfides and thiols react with oxygen at low temperatures via free-radical processes (92,93). Walling (94) has indicated that sulfides undergo oxidation more rapidly than the corresponding hydrocarbon.

FIGURE 20

THE EFFECT OF SULFUR CONCENTRATION



In the present system, deposits are formed via free radical autoxidation reactions, and the role of sulfur compounds in this process must be complex. Only the hydrocarbon fuel doped with diphenyl sulfide and dibenzothiophene failed to show a significant increase in the rate of deposit formation. Bateman and Cunneen (95) have shown that diphenyl sulfide is markedly stable to oxidation relative to other sulfides, and Rudenko and Gromova (87) have shown that thiophene is less susceptible to heterogeneous decomposition than diphenyl sulfide. The present results show that these compounds do not accelerate the deposit formation process because they do not decompose under the conditions studied. Their stability is due to the strength of the aryl C-S bonds. The other sulfur compounds undergo decomposition via free radical processes and thus accelerate the complex autoxidation process which leads to the formation of deposits. This picture is consistent with the observation that sulfur is present in the deposits (64). Sulfoxides and sulfones are known to be less stable than their corresponding sulfides (96,97,98). Thus, selective oxidation of the bivalent sulfur atom by intermediate hydroperoxides could precede the thermal or surface catalyzed decomposition of these compounds.

It is interesting to examine the effect on the rate of deposit formation of the various phenyl and benzyl sulfides in terms of the type of radical fragments which these compounds could initially produce when they undergo decomposition. In Table III these compounds are assumed to decompose in the deposit formation environment in the same manner as they undergo pyrolysis - i.e., by rupture of the alkyl C-S bond. This assumption is reasonable, since this bond is weaker than the aryl C-C and C-S bonds. The lowest rate of deposit formation occurred with the benzyl phenyl sulfide-contaminated hydrocarbon, which presumably produced only benzyl and phenyl thiyl radicals. Benzyl radicals are known to be very stable; the phenyl thiyl radical is in the same category, so that the benzyl or phenyl thiyl radical produced should be much less active than the phenyl methyl thiyl, propyl, and methyl radicals. Dolgoplosk, et al. (99) have reported that the ratio of activities of methyl radicals relative to propyl radicals for hydrogen abstraction varies from 2.1 to 2.7, whereas the ratio of deposit formation rates for these two fuels is 2.2. One could also argue that the sulfur compound producing the most energetic products is the least stable, so that the observed decrease in the rate of deposit formation among these contaminated hydrocarbon fuels reflects the increased stability of the individual sulfur compounds. In any event, the stability of an individual sulfur compound, which of course reflects the structure of the compound, clearly governs to a great extent its influence on the rate of deposit formation. The fact that trace levels of sulfur compounds greatly influence the deposit formation process results from the lower stability of these compounds relative to jet fuel range hydrocarbons at higher temperatures.

With the compounds tested, an increase in the sulfur level did not linearly increase the rate of deposit formation. If a sulfur compound decomposed to produce a single active free radical, and deposits were produced via a radical-radical recombination reaction, a square root dependence of formation rate on sulfur level could be expected. Considering the complexity of the reaction system, it is concluded that the observed dependency of deposit formation rate on sulfur level is in reasonable agreement with such an oversimplified picture.

TABLE III

Comparison of Observed Rate of Deposit Formation With
Probable Sulfur Compound Initial Decomposition Products

Sulfur Compound Added to Hydrocarbon Fuel at 1000 ppm S <u>Level</u>	Carbon and Sulfur Structure of Probable Initial Free Radical Decomposition <u>Products</u>	Rate of Deposit Formation at 325°F, <u>g/cm²/4 hr x 10⁶</u>
 -S-CH ₃	 -S· + C ₁ ·	28.0
 -S-C ₃ H ₇	 -S· + C ₃ ·	12.5
 -CH ₂ -S-CH ₂ - 	 -C· +  -C-S·	4.3
 -S-CH ₂ - 	 -C· +  -S·	1.3

2. Studies on the Role of Sulfur Compounds in the Deposit Formation Process

We have demonstrated that trace quantities of various sulfur compounds can markedly influence the deposit formation process. Thiols, sulfides, disulfides and condensed thiophene compounds are all capable of increasing the rate of deposit formation. The effect of individual sulfur compounds on the rate of deposit formation was markedly different. This undoubtedly explains why the deposit formation rate of various jet fuels cannot be quantitatively related to the total sulfur level. Obviously, fuels which have a low sulfur content will be stable and those with high sulfur levels will be much less stable. The differences observed with the various sulfur compounds reflect such factors as the stability of the compound at "empty" wing tank conditions and the relative activity of the radical fragments produced when the compound decomposes. Because of both the importance of sulfur compounds and their complex role in the deposit formation process, we extended our studies in this area.

One question related to the influence of sulfur compounds on the deposit formation process is: Why are these compounds deleterious at empty "wing" tank conditions. It is known that typical sulfur compounds are stable at temperatures below 1000°F in the absence of oxygen or a catalyst. One possibility is that sulfur compounds are oxidized to sulfoxides (e.g. R-SO-R') and/or sulfones (e.g. R-SO₂-R') prior to their decomposition, which partially initiates the complex free radical process leading to the formation of deposits. In order to investigate this possibility, we have studied the stability of a typical sulfur compound and its corresponding sulfone at empty wing tank temperatures. Thianaphthene (benzothiophene) was chosen for this study because it represents one of the classes of sulfur compounds found in jet fuels at all sulfur levels. It is known, for example, that condensed thiophene compounds are relatively difficult to remove from hydrocarbon fuels even in a strenuous catalytic hydrotreating processing step.

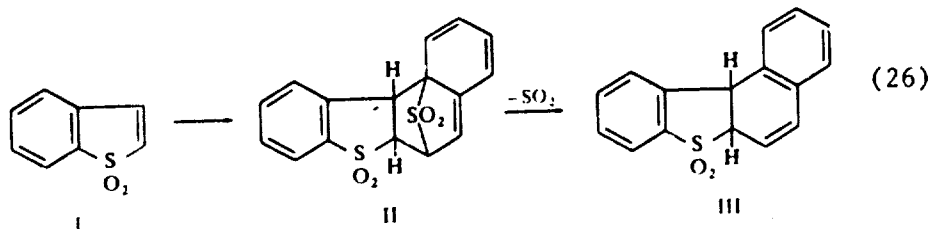
The stability of these compounds was studied in liquid phase hydrocarbon media in a reactor immersed in a well controlled temperature bath. Progress of the reaction was determined by gas chromatographic analysis of samples of the reaction mixture. The reaction mixture was vigorously deoxygenated prior to the pyrolysis study in a vacuum apparatus in which the mixture was subjected to a series of sequential freezing and degassing steps at low pressure (<0.1 torr)

Thianaphthene was heated in a mixture of hexadecane (CH₃-(CH₂)₁₄-CH₃) and tetradecane (CH₃-(CH₂)₁₂-CH₃) at various temperatures up to 500°F. Analysis indicated that there was no decomposition of the thianaphthene even at 500°F.



Thus, thianaphthene itself is stable to pyrolysis over the entire "empty" wing tank temperature range.

The pyrolysis of thianaphthene 1,1 dioxide (TNDO) was next investigated (100). Various concentrations of this sulfone were dissolved in a hydrocarbon media (42 wt % tetradecane, 58 wt % naphthalene) and the blend was vigorously deoxygenated as before. Gas chromatographic analysis of the reaction blend showed that the compound undergoes pyrolysis at 350°F. Runs at different initial mole concentrations of TNDO in the hydrocarbon media indicated that the reaction was second order. A second order plot of this data is shown in Figure 21. As a result, second order rate constants were calculated from the pyrolysis data. Pyrolysis runs were made at various temperatures in several solvents, i.e., hydrocarbons, butyl carbitol and Δ, Δ, Δ trichlorotoluene. Second order plots of these rate data are shown in Figures 22, 23 and 24. An Arrhenius plot of the second order rate constants determined from these plots is shown in Figure 25. The apparent activation energy of pyrolysis in hydrocarbon media is 16.5 kcal/mole and in butyl carbitol it is 23.5 kcal/mole. At 350°F and below a single reaction product results. At temperatures above 375°F, the results indicate that this product undergoes further decomposition to a more complex reaction product.



The pyrolysis of the neat primary dimeric reaction product at higher temperatures was investigated briefly in a mass spectrometer (101).

The decomposition of compound was carried out in a CEC 21-103 (modified) Mass Spectrometer. The sample reservoir was maintained at 315° and the ion source temperature was 290°F. The ionisation potentials were 11 and 70 volts and ionisation currents 20 and 50 microamps. The ion acceleration voltage was 2300 volts at m/e of 85. The pressure of the instrument was 10^{-6} to 10^{-7} Torr. The results of the decomposition study are summarized below.

Summary of Mass Spectrometric Results

M/e	Elimination	Relative Intensity	
		11 Volt Ionization Potential	70 Volt Ionization Potential
204	-SO ₂	100	100
234	-H ₂ O ₂	19	19
236	-O ₂	6	8
250	-H ₂ O	2	4
266	-H ₂	4	3
268	Parent (I)	16	18

FIGURE 21

EFFECT OF CONCENTRATION ON PYROLYSIS

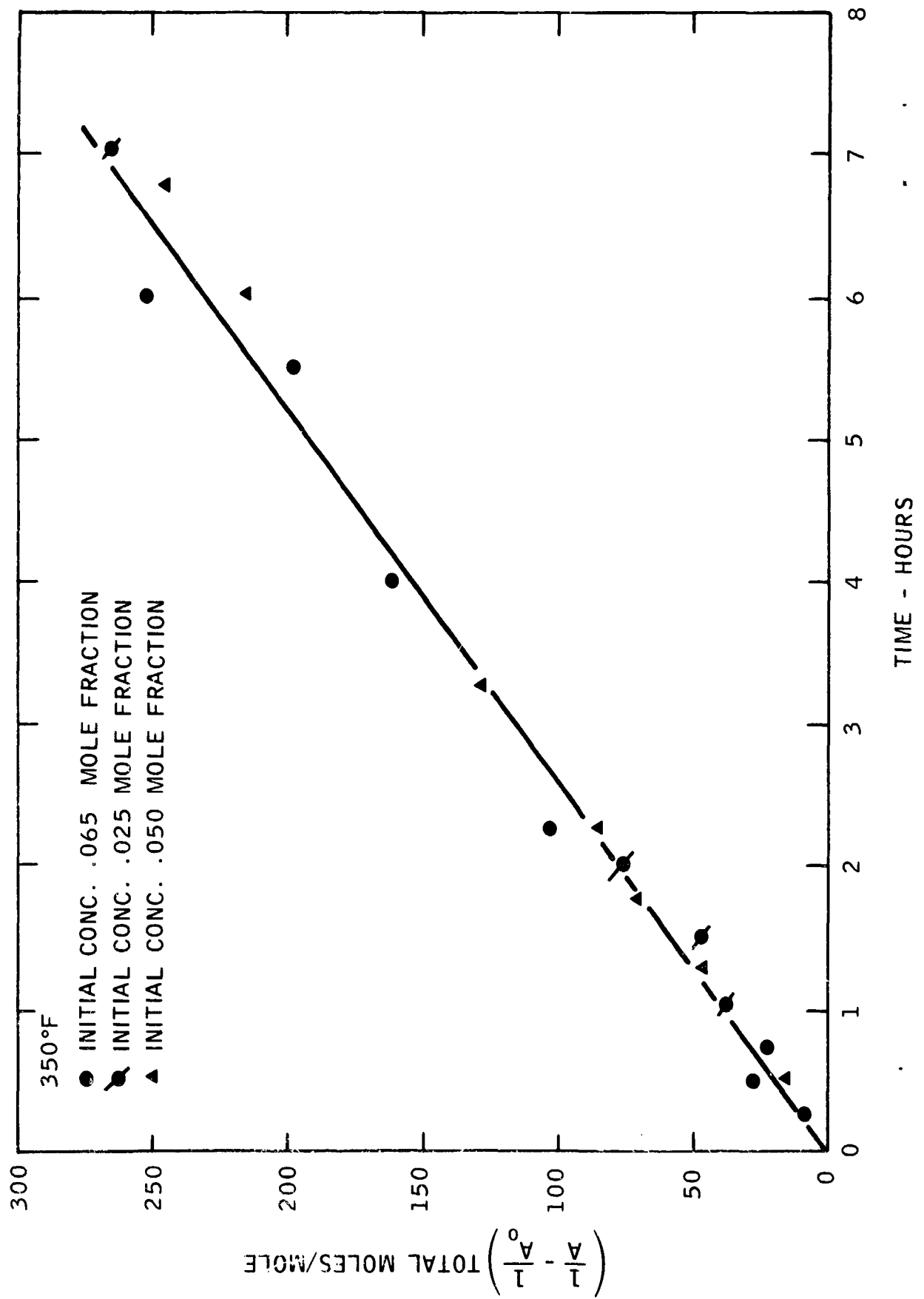


FIGURE 22

SECOND ORDER PLOT OF PYROLYSIS IN HYDROCARBON MEDIA

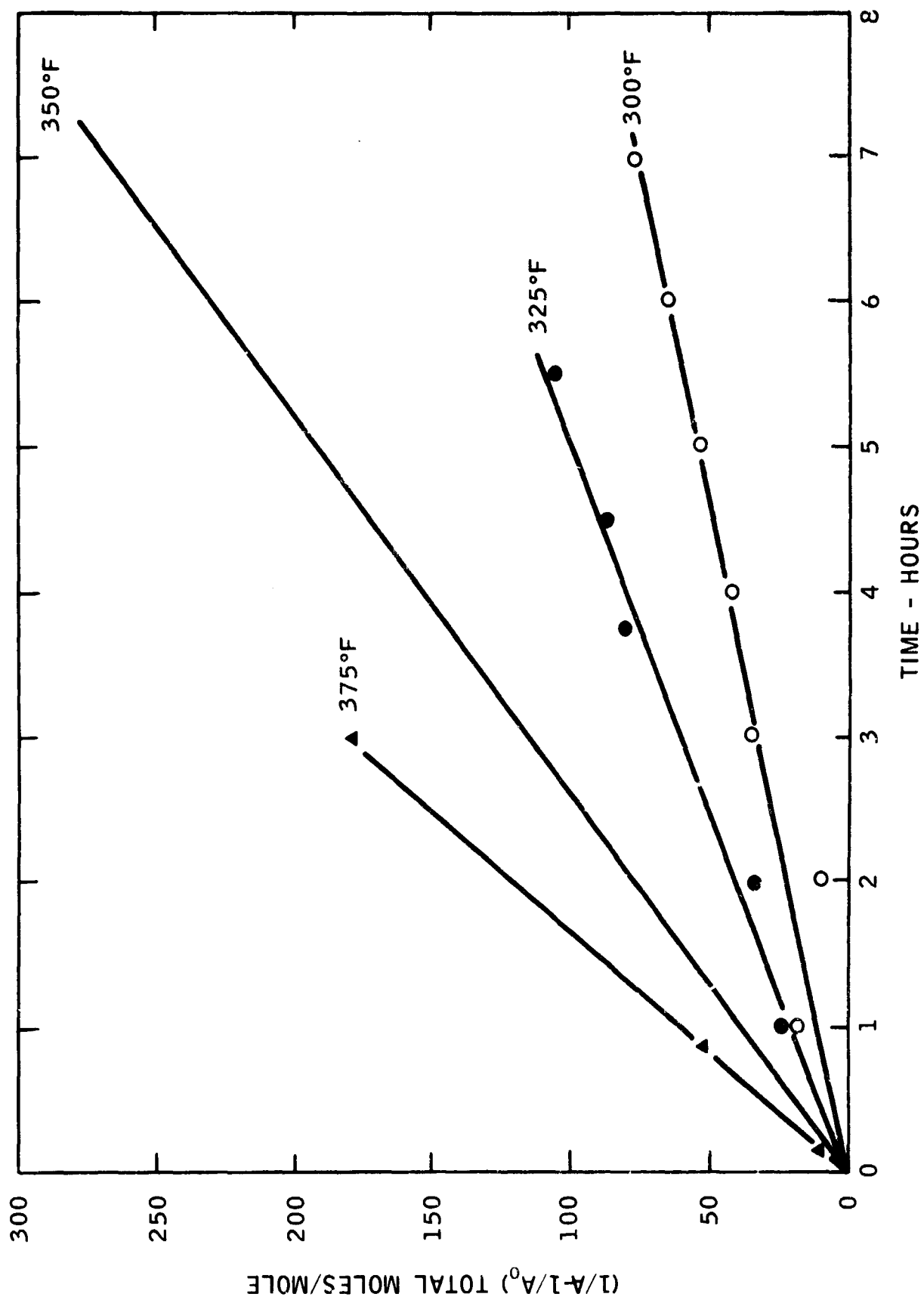


FIGURE 23

SECOND ORDER PLOT OF PYROLYSIS IN BUTYL CARBITOL

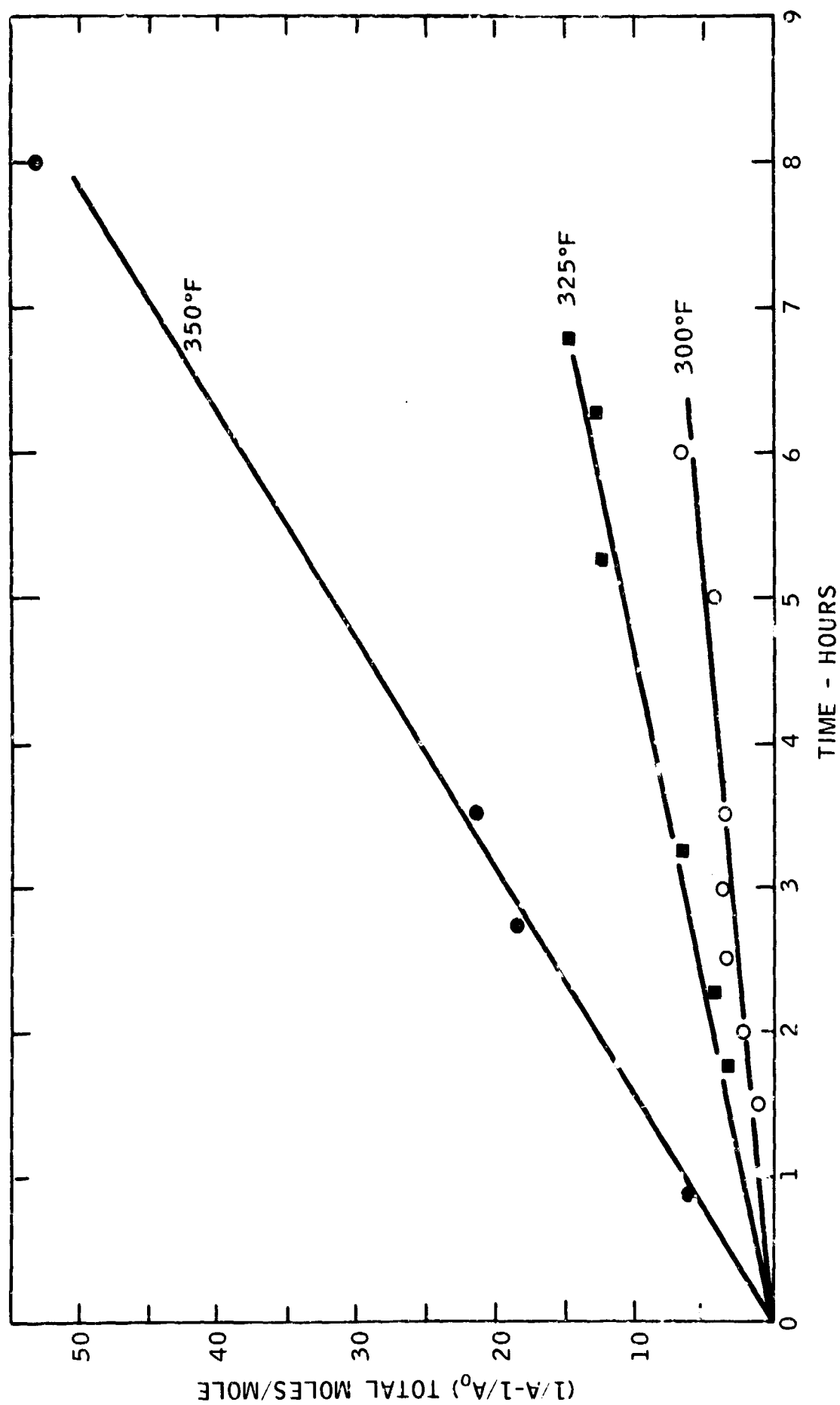


FIGURE 24

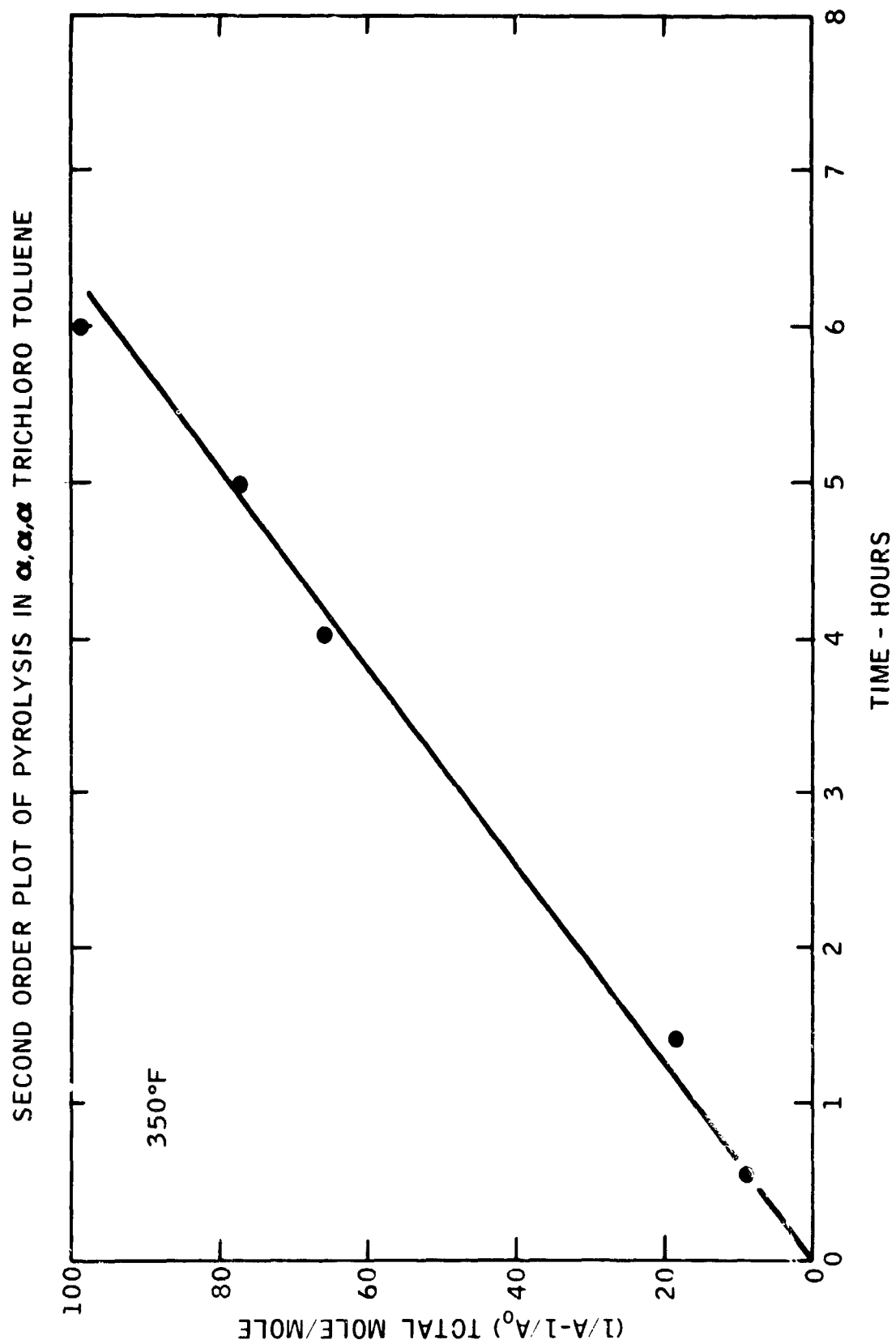
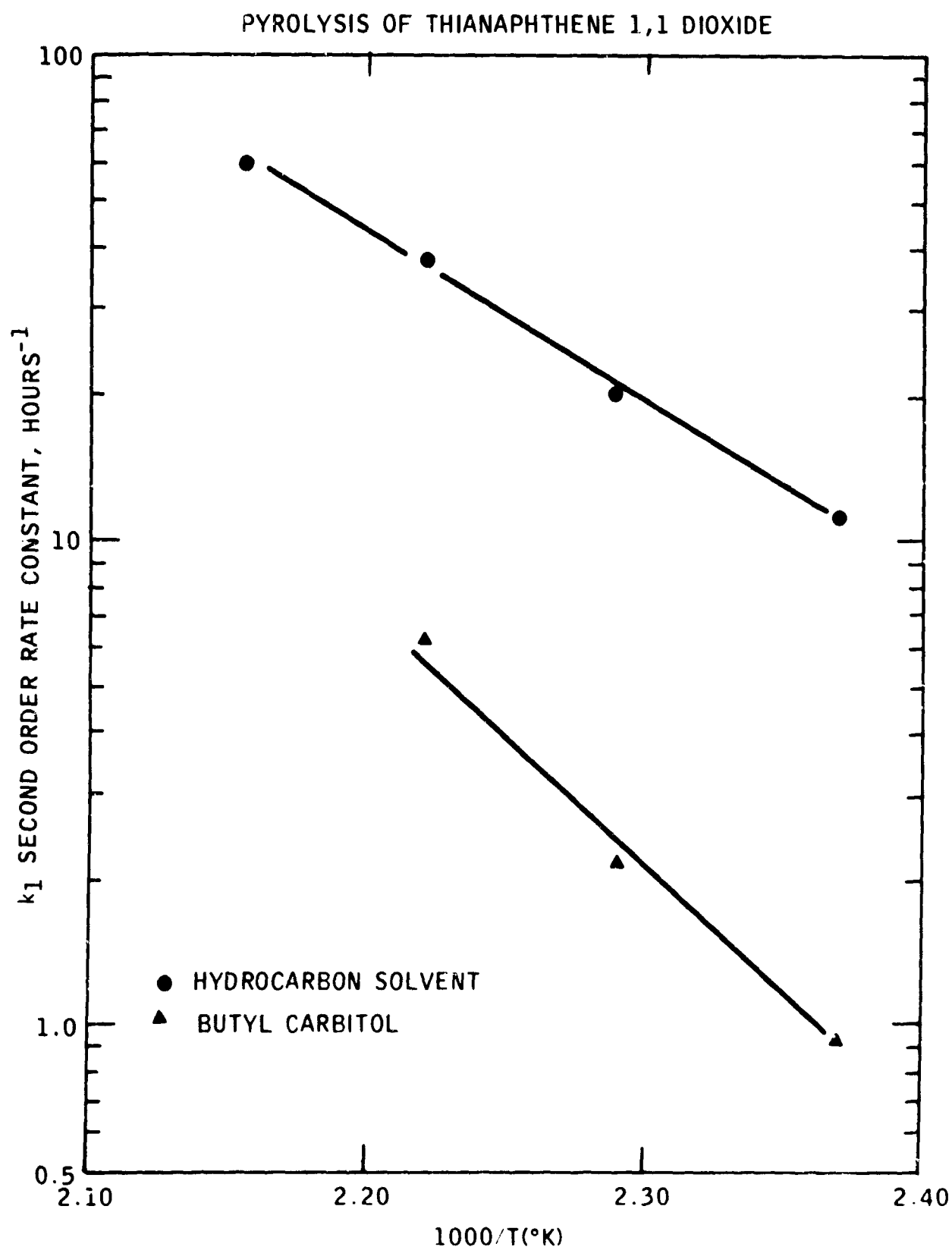
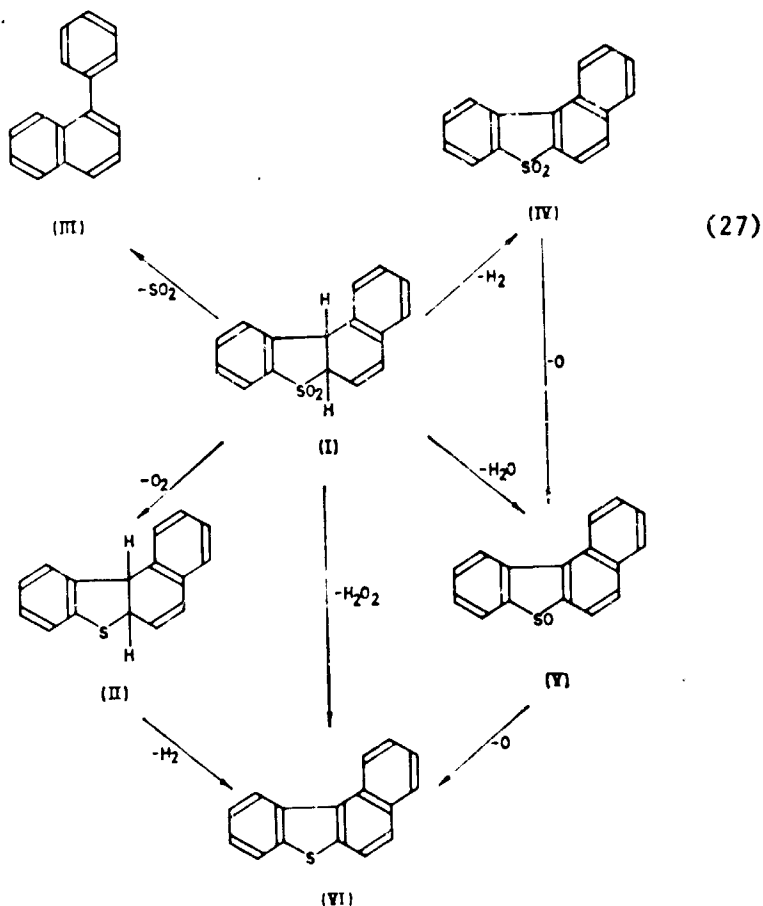


FIGURE 25



As shown, the 70 volt and 11 volt spectra are very similar. Thus, there is parallel behavior at high and low energy modes of operation. The most striking features of this process are the absence of CO and SO eliminations which indicates that the corresponding furan derivative is not formed, the low yield of the corresponding thiophene (loss of O₂), and the high yield of λ -phenylnaphthalene (SO₂ elimination). The paths of decomposition most consistent with these results are summarized below.



The major route to compound (VI) is presumably via (II) or perhaps by loss of H₂O₂. It seems unlikely that the majority of (VI) arises from (IV) since this compound would undergo SO elimination. It seems likely that the transformation of (I) into (III) occurs readily because the hydrocarbon is a strain-free molecule. At any rate, the results suggest that the mode of decomposition of thiophene dioxides will vary with structure of the molecule.

It can be seen that the pyrolysis of a sulfone such as thianthrene 1,1 dioxide is quite complex. The data also indicate that sulfur compounds in all probability undergo an oxidation prior to their decompositions. Thus, oxygen contributes to the instability of sulfur compounds as well as hydrocarbons. These results again emphasize the very strong role that the presence of oxygen plays in the deposit formation process.

3. The Effect of Trace Levels of Nitrogen Compounds

Although nitrogen compounds are present in typical jet fuels at relatively low levels, for example, in comparison with sulfur compounds, it was felt that it is nevertheless important to know what effect such compounds have on the rate of deposit formation (102). Three pure nitrogen compounds, that is 2,5 dimethylpyrrole, indole, and 2 ethylpyridine, were added to P&W 523 at the 1000 ppm nitrogen level. This is the same fuel as was previously employed in our study of the effect of trace levels of sulfur compounds. This fuel was selected for both these studies because it is a highly refined, quite stable fuel essentially free of trace impurities, such as sulfur and nitrogen compounds. Thus, any increase in the rate of deposit formation can be directly attributed to the addition of the nitrogen compound. Test conditions in the Screening Unit were 3 psia, use of Ti-8Al-1Mo-1V strips, and a 4 hr run with a standard hydrocarbon and air flow rates. Results from these tests are shown in the Arrhenius plot in Figure 26. It can be seen that the addition of these nitrogen compounds markedly increased the rate of deposit formation.

The effect of the concentration of nitrogen compounds was also evaluated. This was done both to allow us to assess the effect of nitrogen compounds at lower, more representative levels, and also to allow us to gain more insight into the role of nitrogen compounds in the complex, free radical, autoxidative process leading to the formation of deposits. This study, shown in Figure 27, was carried out by evaluating P&W 523 doped with 2,5 dimethylpyrrole at the 100 and 10 ppm N level. Increasing the nitrogen content of the fuel increases the rate of deposit formation at a fixed temperature. Figure 28 is a plot of the relative activity for deposit formation at 300°F versus the square root of relative nitrogen concentration. As can be seen, an excellent correlation results. This square root dependence of deposit formation on nitrogen concentration is the same as found previously with trace levels of sulfur compounds, and presumably indicates that nitrogen compounds also contribute to the initiation step in the complex free radical, chain reaction autoxidation process leading to the formation of deposits. Data are shown in Appendix 6.

4. Interactions Between Trace Contaminants in the Fuel

a. A Study of Interactions Between Trace Sulfur and Nitrogen Compounds

A study was made of possible interactions between trace sulfur and nitrogen compounds. As before our study consisted of evaluating the effect of compound type on deposit formation in binary and ternary pure compound blends contained in a paraffin rich mixture. The experimental study was planned as a 2^3 full factorial, statistically designed experiment involving three variables, (a) presence or absence of trace levels of a sulfur compound, (b) presence or absence of trace levels of a nitrogen compound, and (c) presence or absence of an olefin in a paraffin rich blend. Phenyl methyl sulfide was chosen as the sulfur compound, 2,5 dimethyl pyrrole as the nitrogen compound and 1-decene as the olefin. The 1000 ppm S level,

FIGURE 26

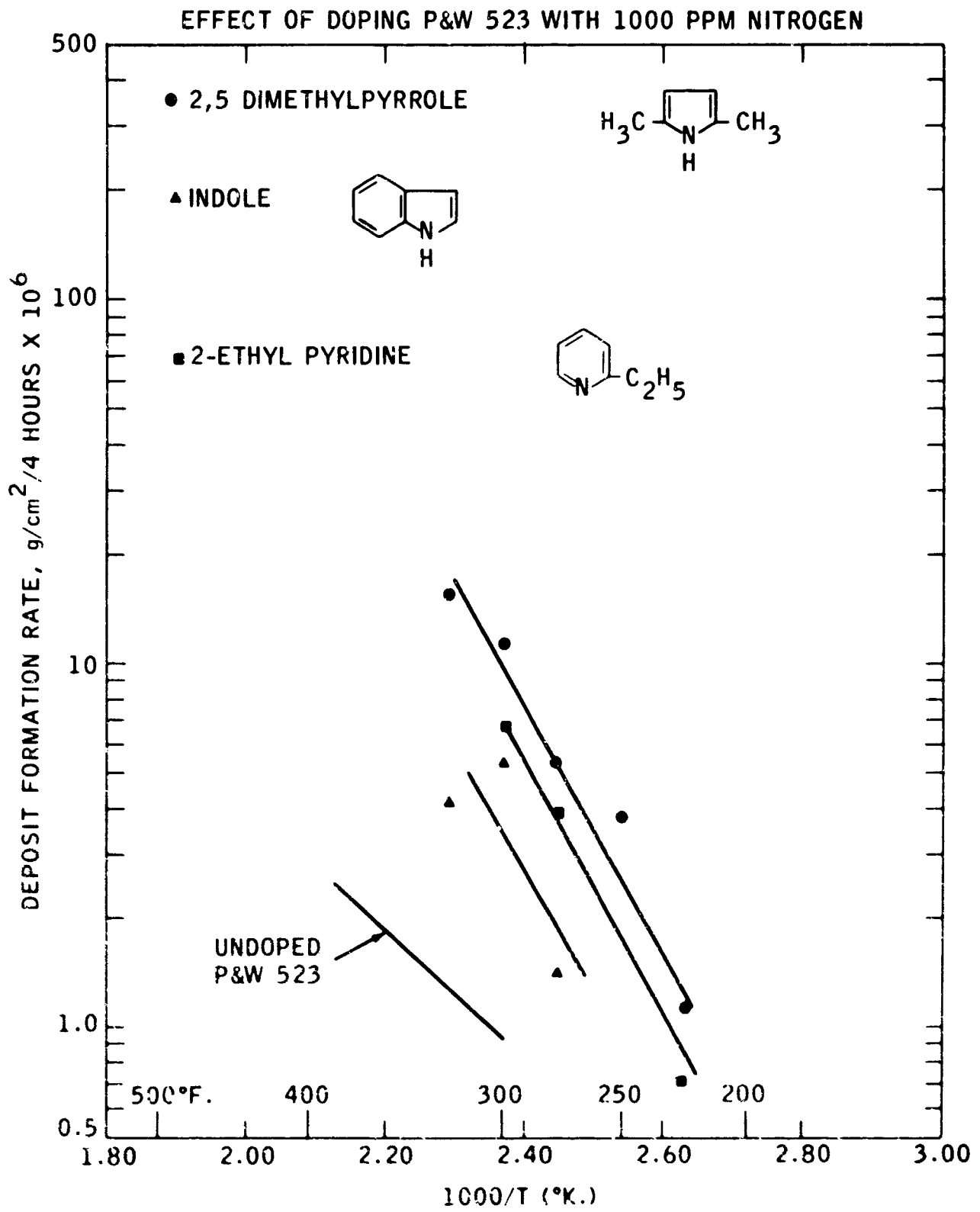


FIGURE 27

THE EFFECT OF 2,5 DIMETHYLPYRROLE
CONCENTRATION IN P&W 523

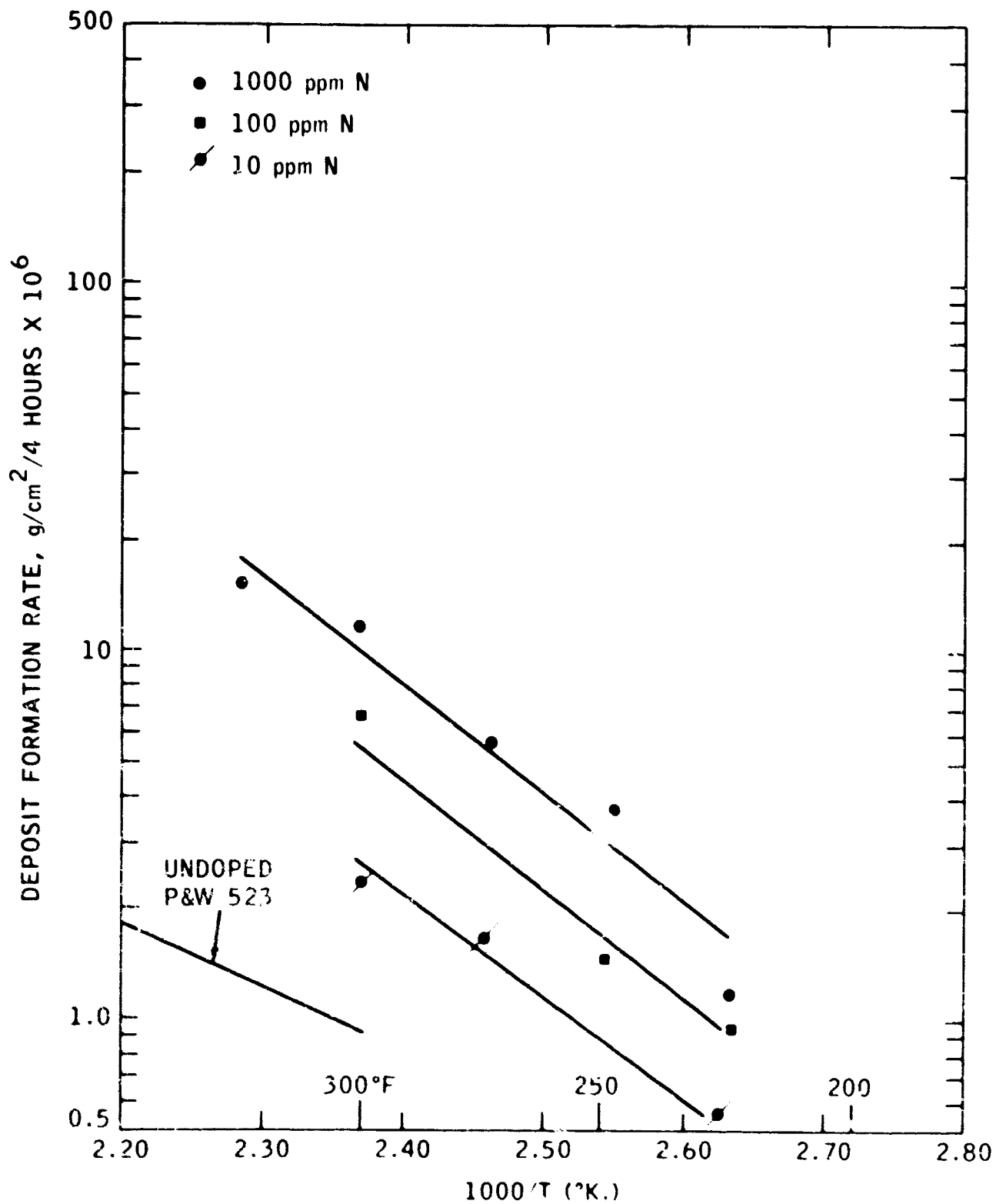
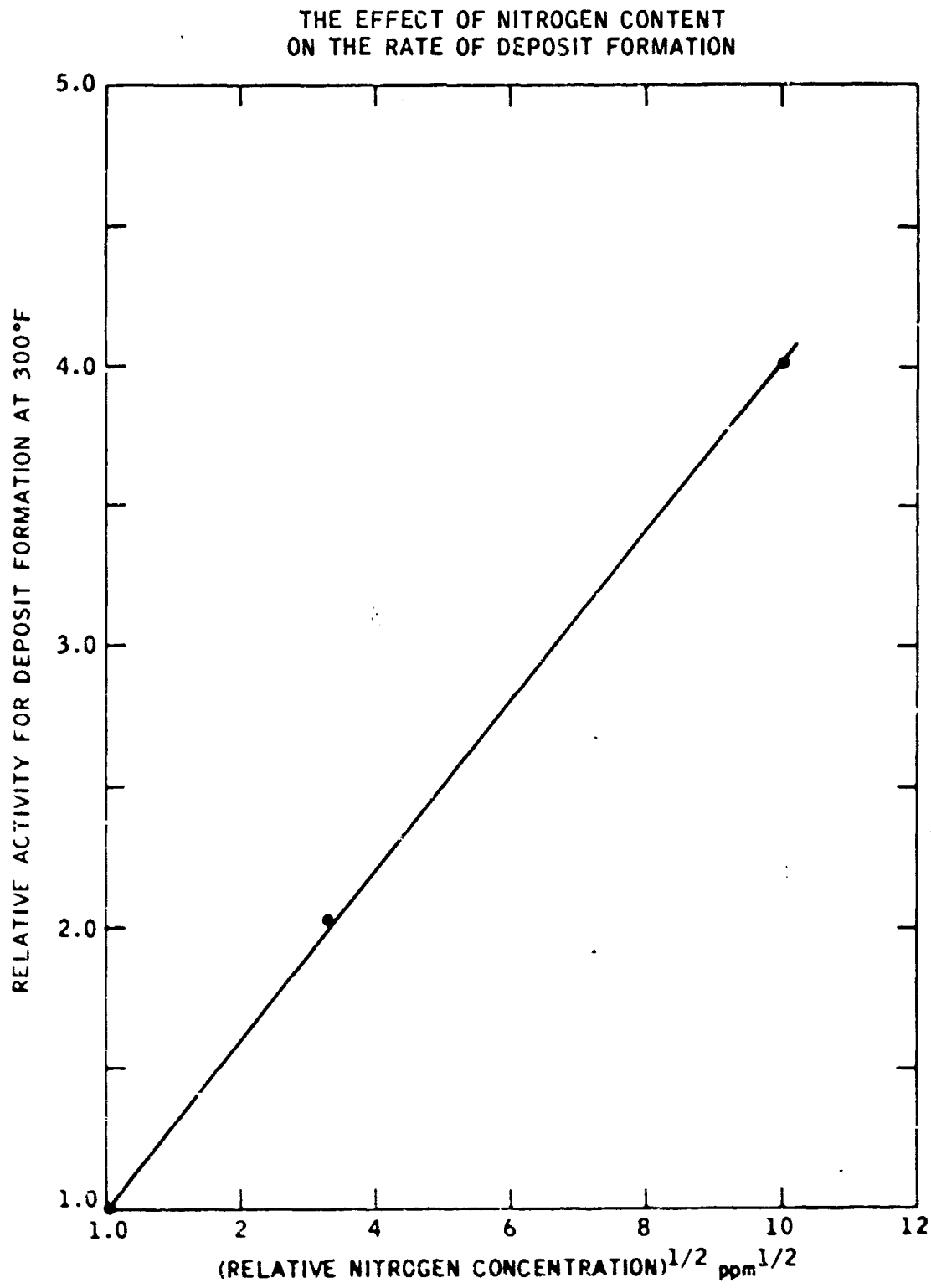


FIGURE 28



10 ppm N level and 2 wt% olefin level were chosen as being representative of typical sulfur, nitrogen and olefin levels present in actual jet fuels. Screening Unit conditions were 3 psia, use of pure titanium metal strips, standard hydrocarbon and air flows and a 4 hour run time. The layout of the runs is shown in Table IV. Also shown for each experimental run is the relative cumulative deposits formed in each standard Screening Unit test. This value is the sum of all the deposits formed at the five temperatures employed, relative to the sum of deposits found for pure n-decane. Thus, by definition pure n-decane has a relative cumulative deposit formation value of 100. The relative cumulative deposits formed provides a convenient, single value which can be used to characterize the effect of a variable on the overall level of deposits formed. An examination of the data shown in Appendix 32 indicates a number of interesting effects. First, in a paraffin system only (no olefin present, runs 1 to 4) there seems to be little effect on deposit formation caused by the presence of either trace levels of sulfur or nitrogen. This is in contrast to our experience with the effect of trace levels of sulfur or nitrogen in actual feed, where increases in deposit formation occurred. These results suggest that fuel components other than paraffins interact selectively with trace levels of sulfur and nitrogen to increase deposit formation. As found previously, the presence of an olefin increases the deposit formation level. With an olefin present, the addition of a sulfur or nitrogen compound (runs 6 and 7 versus run 5) increased the deposit formation level somewhat. The greatest increase in deposit formation, however, occurred when both sulfur and nitrogen were simultaneously present in the olefin system (run 8). Thus, sulfur and nitrogen compounds interact in the presence of an olefin to produce a highly deleterious deposit formation system. It is known from the literature (103) that certain nitrogen compounds catalyze the oxidation of sulfur compounds such as thiols by hydroperoxides. Thus it is reasonable to expect, in general, that a sulfur-nitrogen compound interaction will exist, i.e., the magnitude of the influence of trace levels of sulfur compounds on deposit formation will depend on the presence or absence of trace levels of nitrogen compounds. Data are shown in Appendix 7.

b. Interactions Between Trace Nitrogen Compounds and Dissolved Metals

A study was made of the interactions between trace levels of nitrogen and dissolved metals. The layout of the experiments is shown in Table V. A highly refined fuel essentially free of trace contaminants, i.e., P&W 523, was employed as the base fuel. In runs with added nitrogen 2,5 dimethyl pyrrole was added to the base fuel to the 10 ppm N level. In runs with added metal, ferric acetylacetonate was added to the base fuel to the 10 ppm iron level. Deposit formation rate measurements were made in our Screening Unit at 3 psia using Ti-8Al-1Mo-1V titanium alloy strips. Results are shown in Figure 29.

It can be seen that the addition of both iron or nitrogen alone increased the deposit formation level. The most deleterious situation, however, occurred when both iron and nitrogen were present in the fuel. At 300°F, the simultaneous presence of trace levels of nitrogen and iron increased the rate of deposit formation by a factor of approximately 30. These results again emphasize the strong effect that trace contaminants have on the overall deposit formation process.

TABLE IV

TRACE SULFUR - TRACE NITROGEN - OLEFIN INTERACTION
STUDY IN n-DECANE

Relative Cumulative Deposits Formed (1)
In Standard Screening Unit Test

	No Sulfur Present		Sulfur Present	
	No Nitrogen Present	Nitrogen Present	No Nitrogen Present	Nitrogen Present
No Olefin Present	Base $\equiv$ 100 (1)	103 (2)	98 (3)	90 (4)
Olefin Present	133 (5)	141 (6)	143 (7)	172 (8)

(Run number in parenthesis)

Olefin present: 2 wt% 1-decene in n-decane.

Trace Sulfur present: 1000 ppm wt S using phenyl methyl sulfide in n-decane.

Trace Nitrogen present: 10 ppm wt N using 2,5 dimethyl pyrrole in n-decane.

Standard test conditions: 3 psia, Ti 75A pure titanium strips, standard flow rates of air and hydrocarbon, 200, 250, 275, 300 and 325°F.

- (1) Sum of all deposits formed at the five temperatures employed relative to the sum of deposits found with n-decane at the same conditions

TABLE V

Study of the Interactions Between Trace Levels
of Dissolved Metals and Nitrogen Compounds

	No nitrogen	Nitrogen added (a)
No metal	Run 1 (Base Fuel)	Run 2
Metal added (b)	Run 3	Run 4

• Base fuel: P&W 523

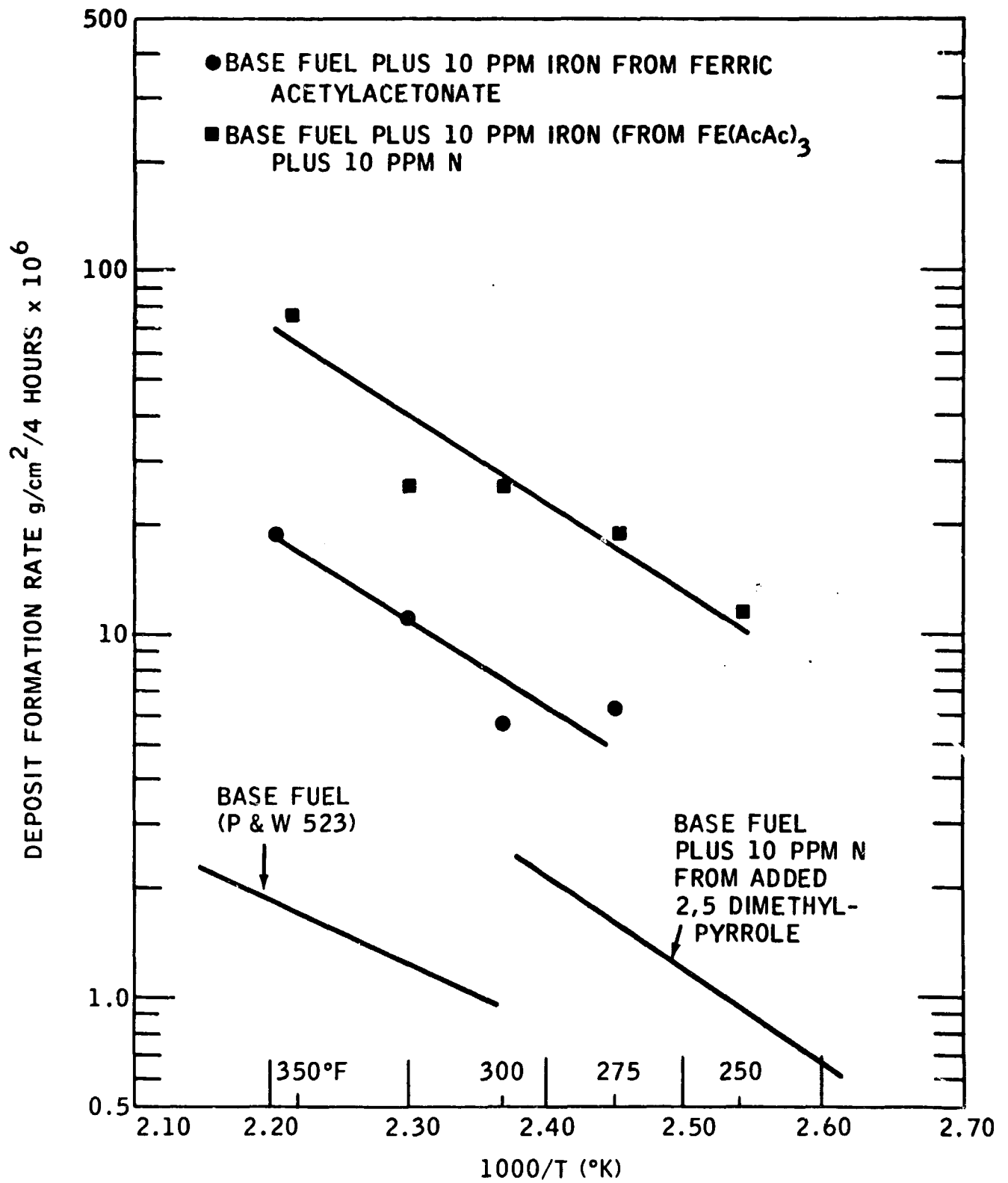
• Conditions: 3 psia, Ti-8Al-1Mo-1V

(a) 10 ppm wt N added to base fuel using
2,5 dimethyl pyrrole

(b) 10 ppm wt Fe added to base fuel using
ferric acetylacetonate

FIGURE 29

DISSOLVED METAL - TRACE NITROGEN INTERACTION



F. The Study of the Effect of Metal Surfaces and Dissolved Metals on Deposit Formation

The effect of both heterogeneous metals (i.e., metal surfaces) and homogeneous metals (i.e., dissolved metals) was studied (104). The effect of heterogeneous metals, that is, metal surfaces, was investigated using a variety of pertinent metals. Included in this study were aluminum, stainless steel 304, pure titanium, two titanium alloys (Ti-6Al-4A and Ti-8Al-1Mo-1V), and copper. Such titanium alloys have been reported as likely candidates for use in the SST (105). Pure titanium was included in order to assess the effect of the added elements present in the alloy. Although copper is not normally a metal of construction for fuel tanks, it has occasionally been inadvertently introduced into jet fuel systems, for example, by use of copper containing bearings in pumps.

Results of this study are shown in Arrhenius plots in Figures 30, 31 and 32. The apparent activation energy derived from the slopes of these curves is approximately 10 kcal/mole. The other metals all also exhibited the same temperature dependence. A comparison of the relative activity of the various metals toward deposit formation is shown below.

Metal Surface	Deposit Formation	
	Rate at 400°F (gr/cm ² /4 hr) x 10 ⁶	Relative Activity at 400°F
Copper	21.0	5.7
Ti-6Al-4V	15.0	4.0
Ti-8Al-1V-1Mo	9.6	2.6
Pure Titanium	3.7	1.0
Stainless Steel 304	3.7	1.0
Aluminum	3.7	1.0

It can be seen that copper is the most deleterious metal surface, followed by the titanium alloys. Pure titanium, stainless steel, and aluminum were all equivalent in their deposit formation tendencies. An inspection of the composition of the titanium alloys suggested that the increase in deposit formation was related to the vanadium content. In Figure 33 the relative activity toward deposit formation at 400°F is plotted versus the square root of the vanadium content of the titanium alloys tested. As can be seen, an excellent correlation results. Data are shown in Appendix 8.

The effect of homogeneous metals on the rate of deposit formation was studied by adding various metal complexes to the fuel. Metal acetylacetonates M(AcAc)_x were chosen for this study. These complexes have been employed previously in a number of reaction kinetic studies (105-110). Ferric, nickel, copper, and cobalt acetylacetonates were added to samples of the fuel so that each sample contained 50 ppm of a given metal. This level, which is higher than normally expected in jet fuels, was chosen so as to magnify any differences between the various chelates. The rate of deposit formation obtained with these "doped" fuels is shown in the Arrhenius plot in Figure 34 it can be seen that the rate of deposit formation increased by a factor of 40-120 at 300°F with the addition of these metal complexes to the fuel, with the copper

FIGURE 30

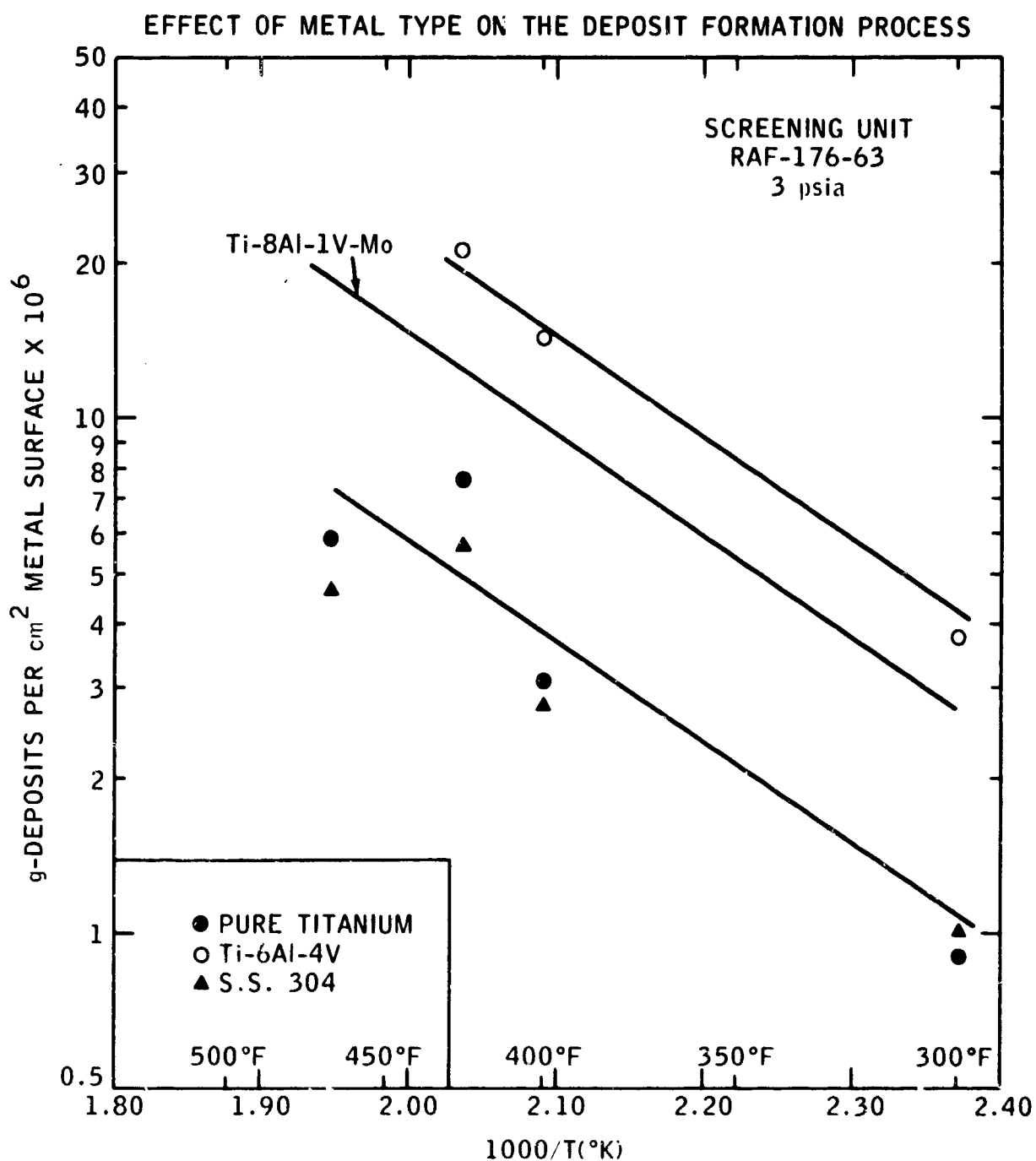


FIGURE 31

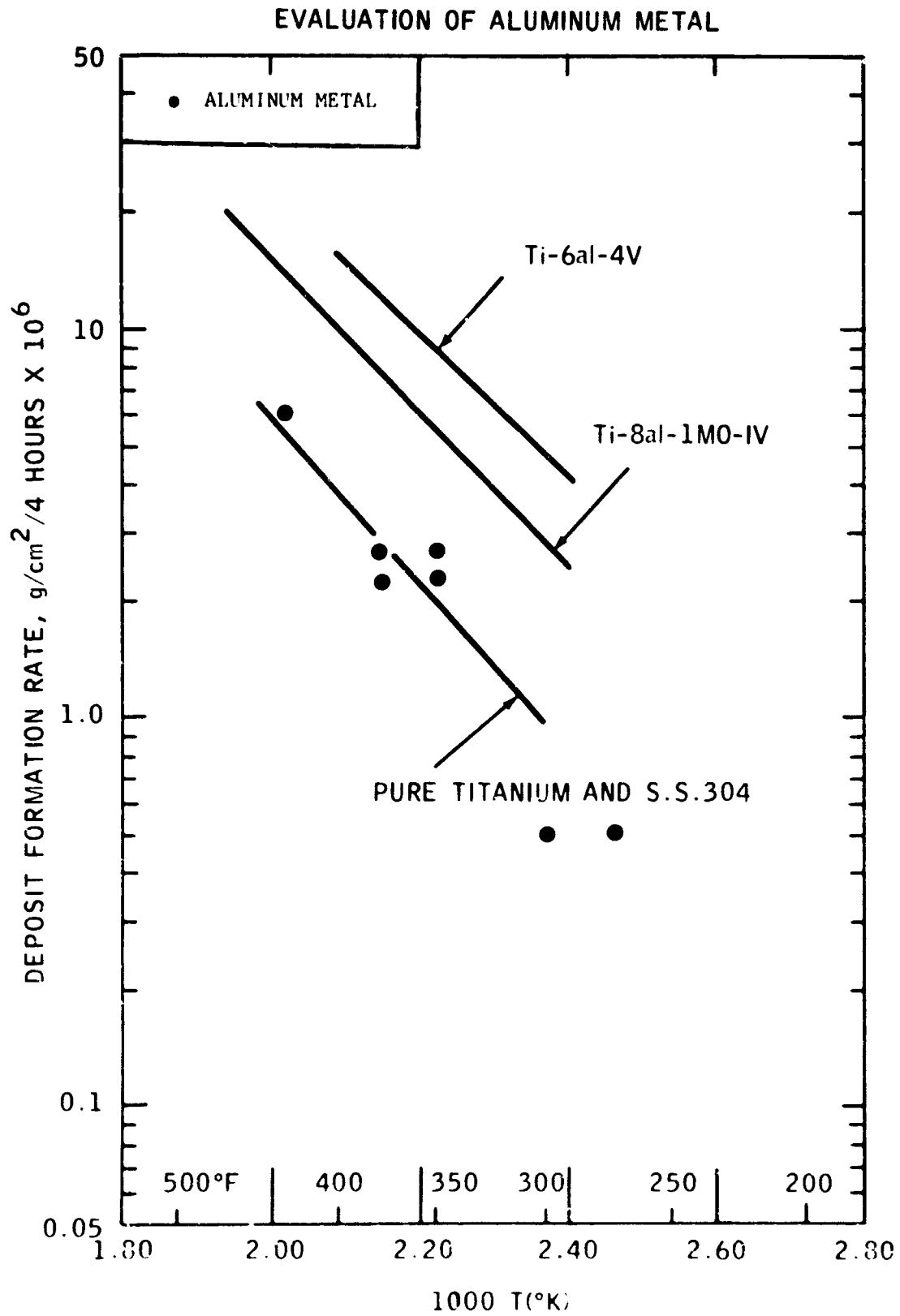


FIGURE 32

THE EFFECT OF A COPPER METAL SURFACE
ON THE DEPOSIT FORMATION PROCESS

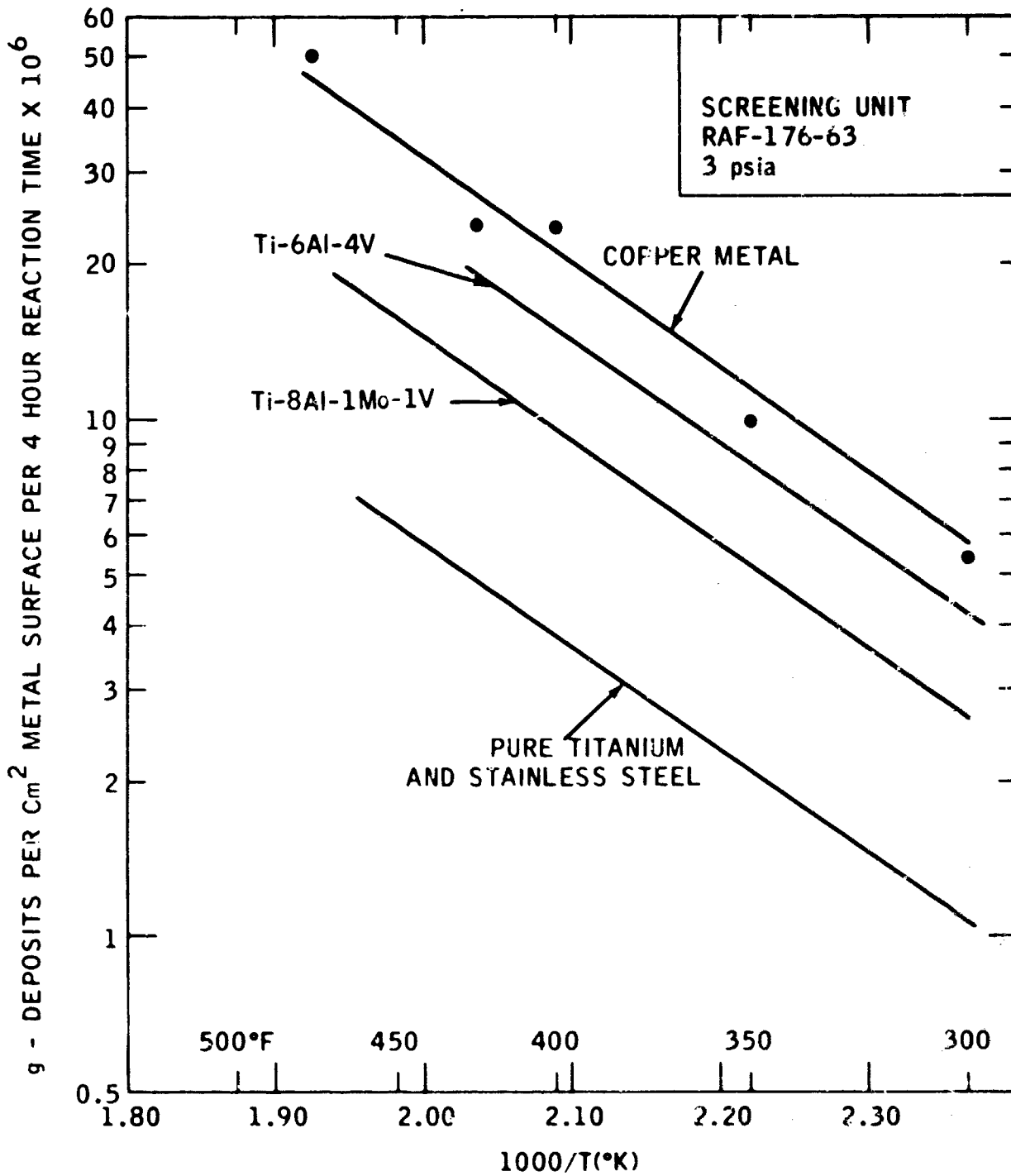


FIGURE 33

THE EFFECT OF VANADIUM CONTENT OF
TITANIUM ALLOYS ON DEPOSIT FORMATION

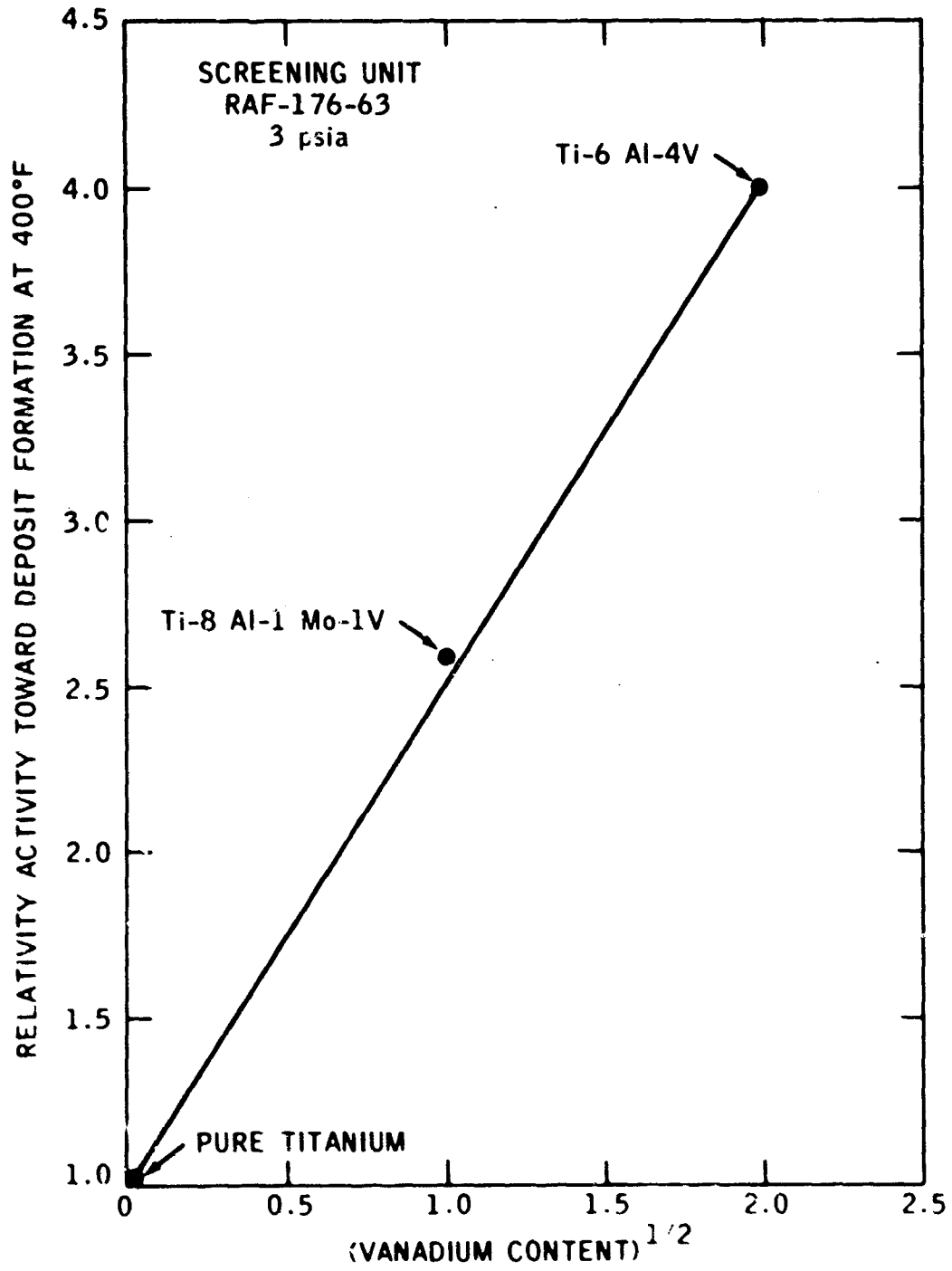
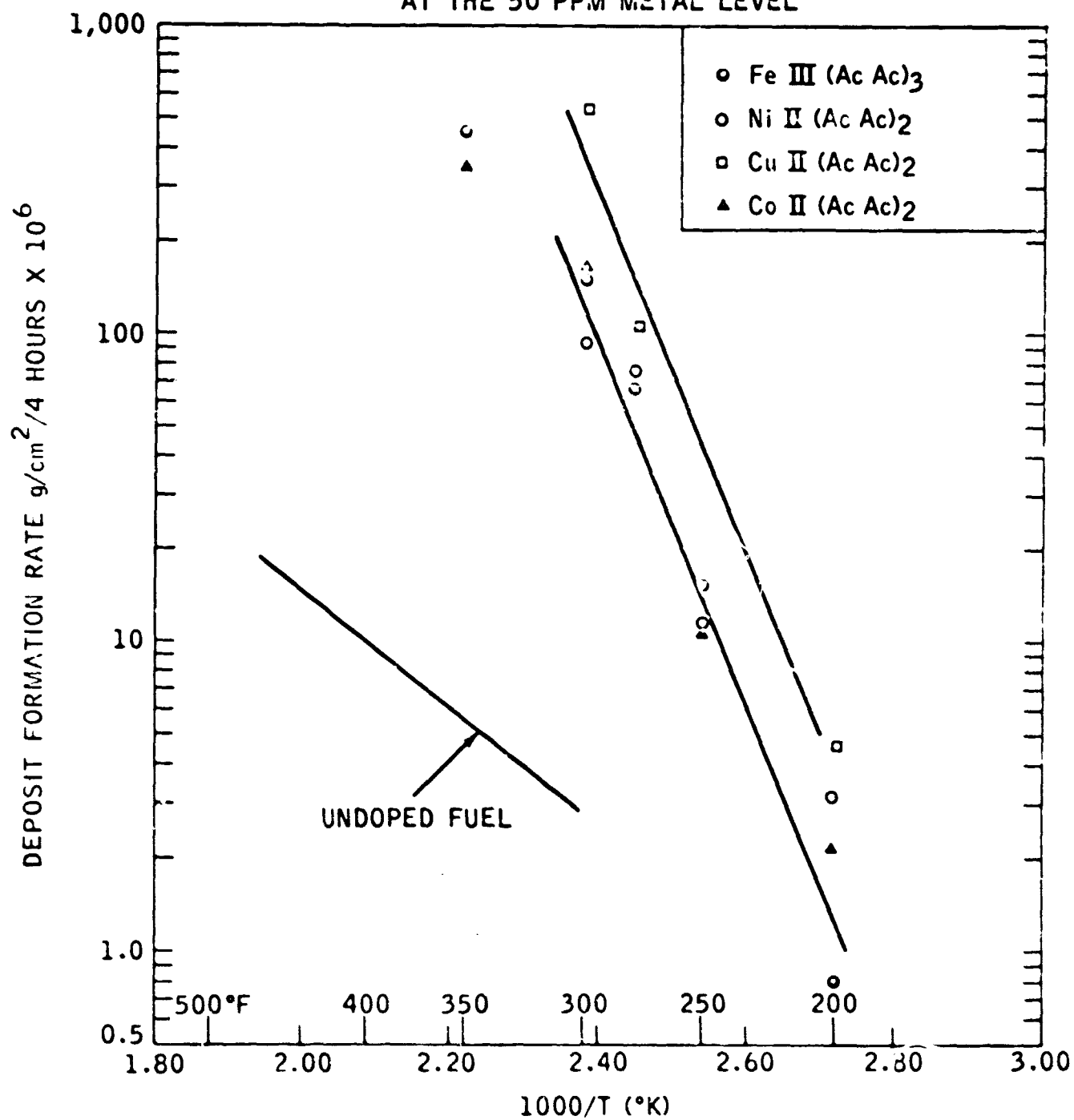


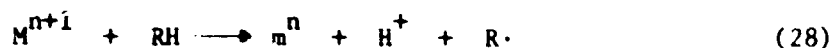
FIGURE 34

THE EFFECT OF THE ADDITION
OF METAL ACETYLACETONATES TO RAF-176-63
AT THE 50 PPM METAL LEVEL



complex producing the highest rate of deposit formation. The effect of complex concentration on the deposit formation process was investigated using ferric acetylacetonate. Fuel samples containing 2, 5, 20, and 100 ppm metal using $\text{Fe III}(\text{AcAc})_3$ were evaluated (Figure 35). In Figure 36 the relative rate of deposit formation at 325°F (using the 2 ppm metal "doped" fuel as the base case) is plotted versus the square root of the relative iron concentration. As can be seen, an excellent correlation results.

Metal effects on hydrocarbon autoxidation reactions have been widely studied, although the detailed mechanism of such metal catalysis is not completely understood (111,112). Although the majority of this work has been done with homogeneous metals, several studies have shown that heterogeneous metal and metal oxide surfaces are capable of increasing the rate of reaction of hydrocarbons with oxygen in the liquid phase (113-115). The work of Burger et al (113) indicated that the presence of solid suspended metal oxides both eliminated the autoxidation induction period, and resulted in a reaction that was half order in solids concentration; presumably indicating that the solid surfaces initiated the reaction by catalyzing the formation of free radicals, which then enter the liquid phase and participate in the autoxidation chain reaction. Although the autoxidative process which results in the formation of deposits from jet fuel hydrocarbons must indeed be complex, the observed effect of the vanadium content of the titanium alloys on deposit formation supports the concept that the surfaces catalyze the free radical initiation process. The surfaces of these metals are undoubtedly covered with an oxide layer, and following the suggestion of Uri (112) could produce a radical in the following manner:



Uri also predicts that those elements will be active which can undergo easy reduction by one electron transfer, which agrees with our observation that the most active metal surfaces were copper and vanadium containing alloys. It is also pertinent to note that vanadium and copper oxides are well known as active heterogeneous oxidation catalysts, and are extensively employed for this purpose in industrial catalysis.

Homogeneous metals are known to participate in hydrocarbon autoxidations either by catalyzing the free radical initiation step or by catalyzing the decomposition of the hydroperoxides which form in the autoxidation sequence (111). Metal acetylacetonates have been shown to initiate vinyl polymerization reactions at low temperatures (107-109). In the present study the addition of metal acetylacetonates to the fuel increased the apparent activation energy for the deposit formation process from approximately 10 to 25 kcal/mole. In this respect, Bamford (108) observed an apparent activation energy of 26 kcal/mole in his polymerization studies with $\text{Mn III}(\text{AcAc})_3$, and Arnett also observed a half order dependence on chelate concentration. This latter observation is in agreement with the effect observed in the present study of $\text{Fe III}(\text{AcAc})_3$ concentration on the relative rate of deposit formation. Both Bamford (108) and Arnett (110) postulate a unimolecular decomposition of the chelate as follows:

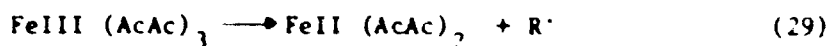


FIGURE 35

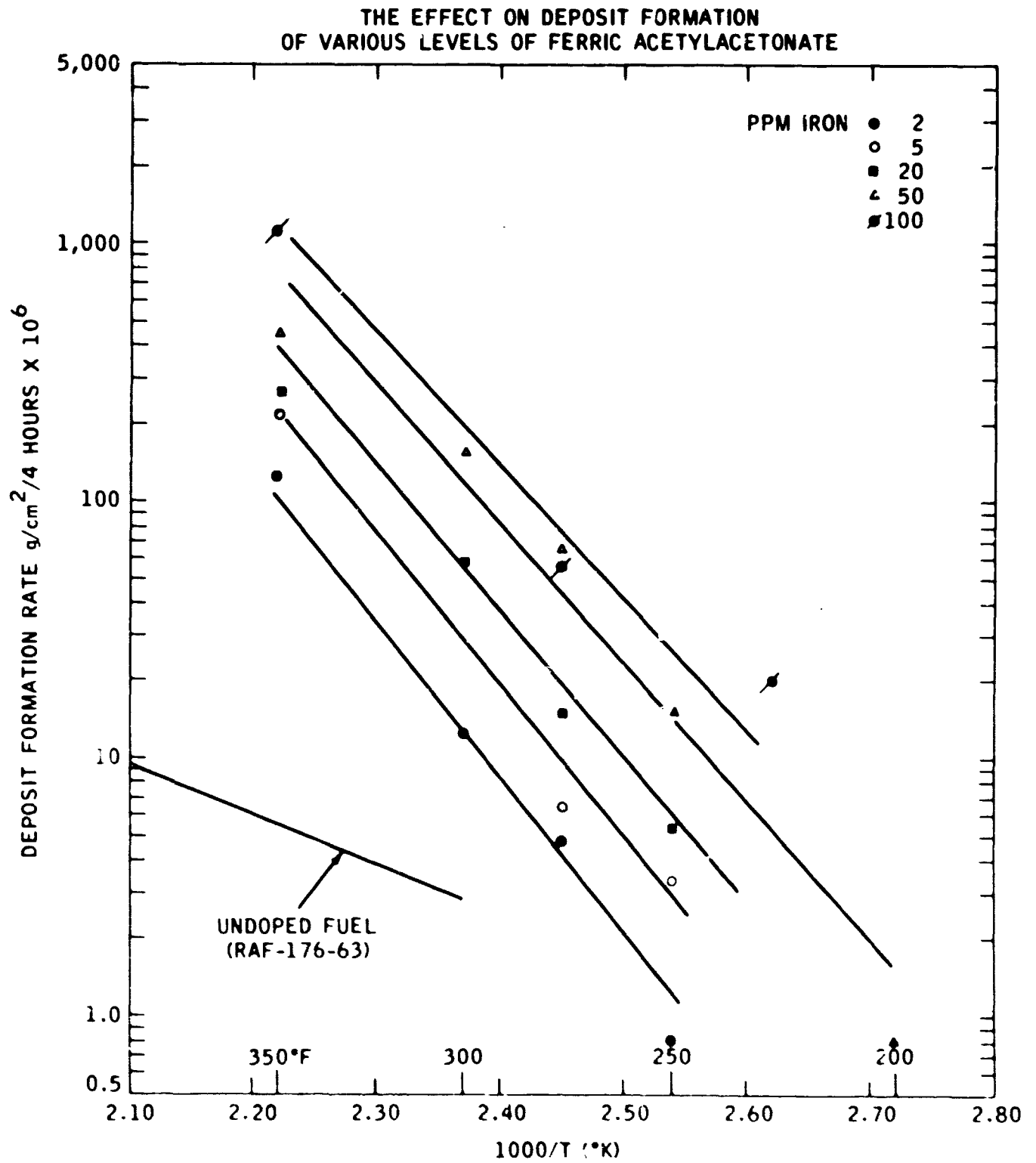
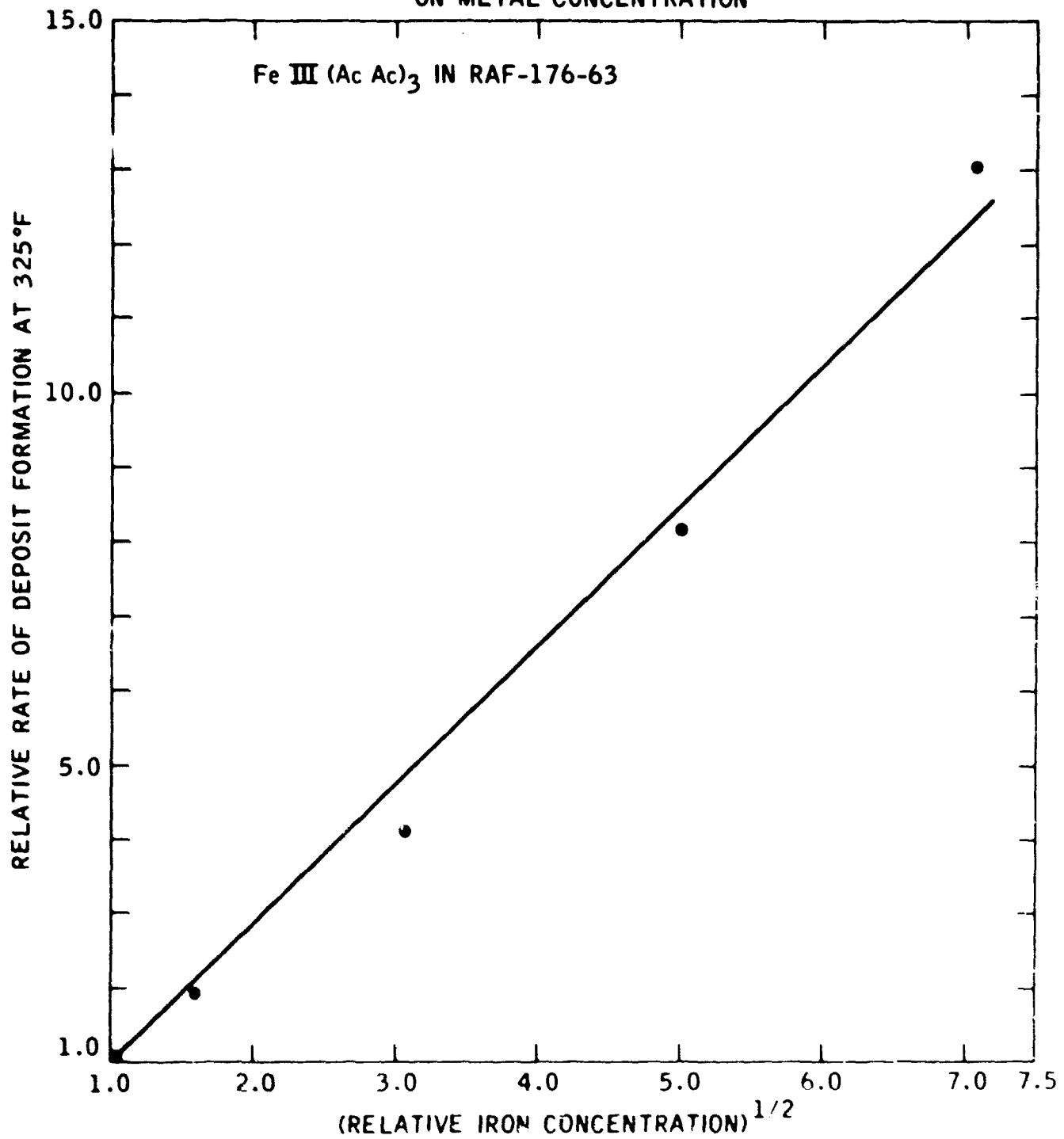


FIGURE 36

THE RATE OF DEPOSIT FORMATION
EXHIBITS A SQUARE ROOT DEPENDENCE
ON METAL CONCENTRATION



Arnett (110) has also found that the same metal acetylacetonates which are readily attacked by oxygen were also polymerization promoters, and concludes that acetylacetonate chelates which undergo ready autoxidation and pyrolysis should function as a source of radicals for radical promoted reactions. It should be noted, however, that the autoxidative reaction system leading to the formation of deposits from jet fuel hydrocarbons at 300-500°F is a far more complex kinetic system than encountered, for example, in low temperature polymerization of styrene. In any event, it is clear that the presence of homogeneous metals, such as metal acetylacetonates, are capable of exerting a major influence on the kinetics of the hydrocarbon autoxidation process which leads to the formation of deposits.

G. The Study of the Effect of Fuel
Composition on Deposit Formation

An extensive study of the effect of various pure hydrocarbon compounds on the deposit formation process was made. The broad objective of this study is to determine the effect of jet fuel hydrocarbon composition on the rate of deposit formation. Ultimately, such an understanding of the effect of fuel composition on autoxidative fuel degradation would (a) allow the deposit formation tendency of various fuels to be predicted from fuel inspections, and (b) provide a sound basis for preparing a fuel with a given, desired autoxidative stability by adjusting its hydrocarbon composition. Detailed data are shown in Appendix 10.

1. Studies with Pure Compounds and
Binary Blends of Pure Compounds

The deposit formation rate of a series of pure paraffins typical of those found in jet fuels was first determined. The data obtained with a series of n-paraffins is shown in the Arrhenius plot in Figure 37. It can be seen that the rate of deposit formation at a given temperature decreases with increasing carbon number. The apparent activation energy observed with these n-paraffins is 10 kcal/mole which is the same temperature dependency as that observed with typical jet fuels. The effect of branching in paraffins was also investigated using both neat paraffins and binary blends. These results are listed in Figures 38, 39 and Table VI. The deposit formation rate obtained with a highly branched C₁₂ was higher than that obtained with pure n-dodecane. Similarly a binary blend containing 10 wt % iso-octane in decane produced a higher rate of deposit formation than a corresponding binary blend containing 10% n-octane in n-decane. Thus, branching increases the deposit formation rate of paraffins.

Although typical jet fuels are a paraffin rich material, they also contain other compounds such as naphthenes and aromatics. Thus, the effect on deposit formation of the addition of various aromatics and naphthenes to a paraffin was investigated. The effect of concentration was first investigated in a paraffin-aromatic mixture. The deposit formation rate was measured of binary blends of 1-methylnaphthalene and n-decane which contained 2, 10, 23, 50, 77, and 90 wt % 1-methylnaphthalene. Pure 1-methyl naphthalene was also evaluated. The apparent activation energy for 1-methyl naphthalene was 21 kcal/mole, and at temperatures in excess of 275°F it was more deleterious toward deposit formation than pure n-decane.

FIGURE 37

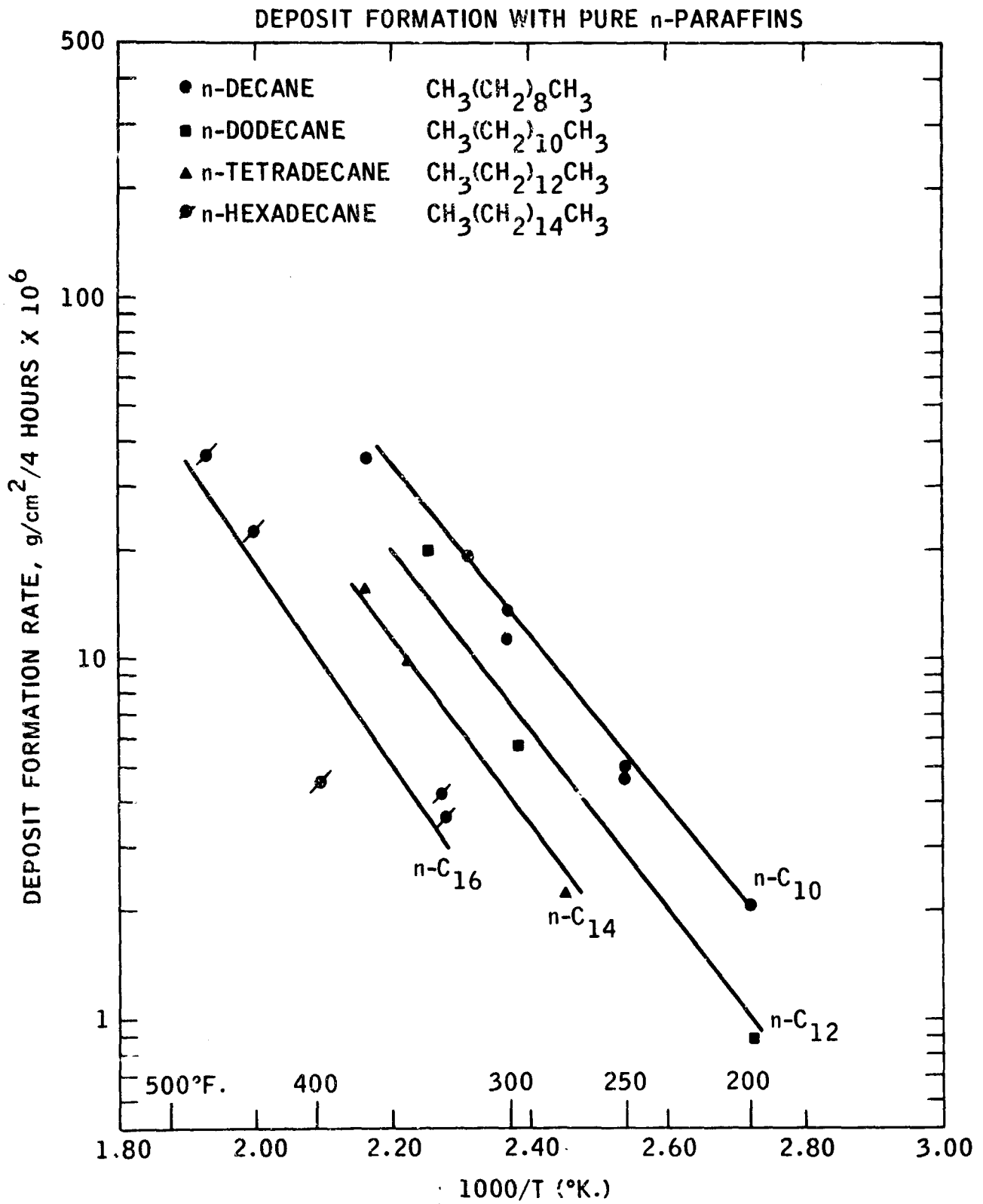


FIGURE 38

NORMAL PARAFFIN - ISOMERIC PARAFFIN BLENDS

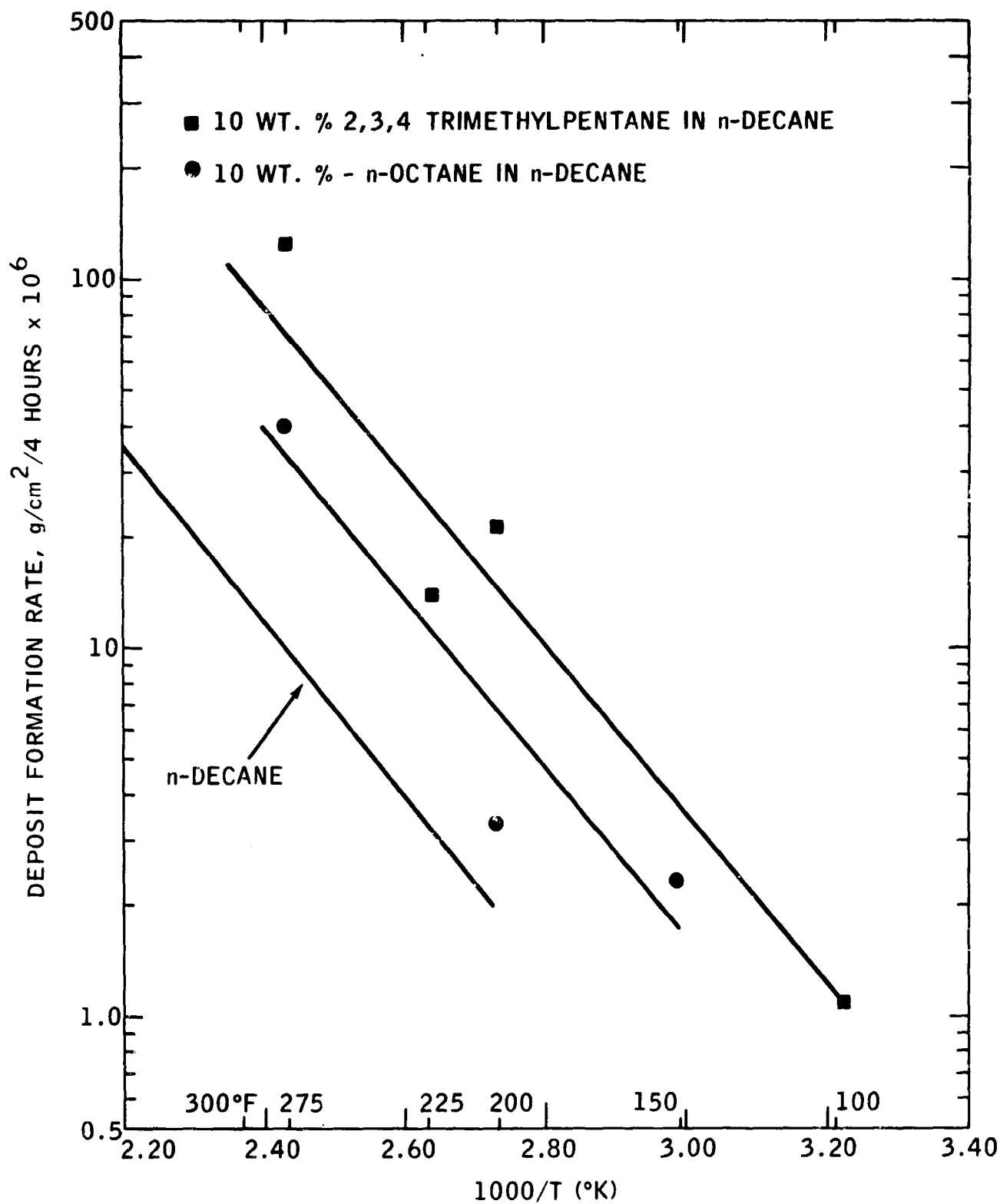


FIGURE 39

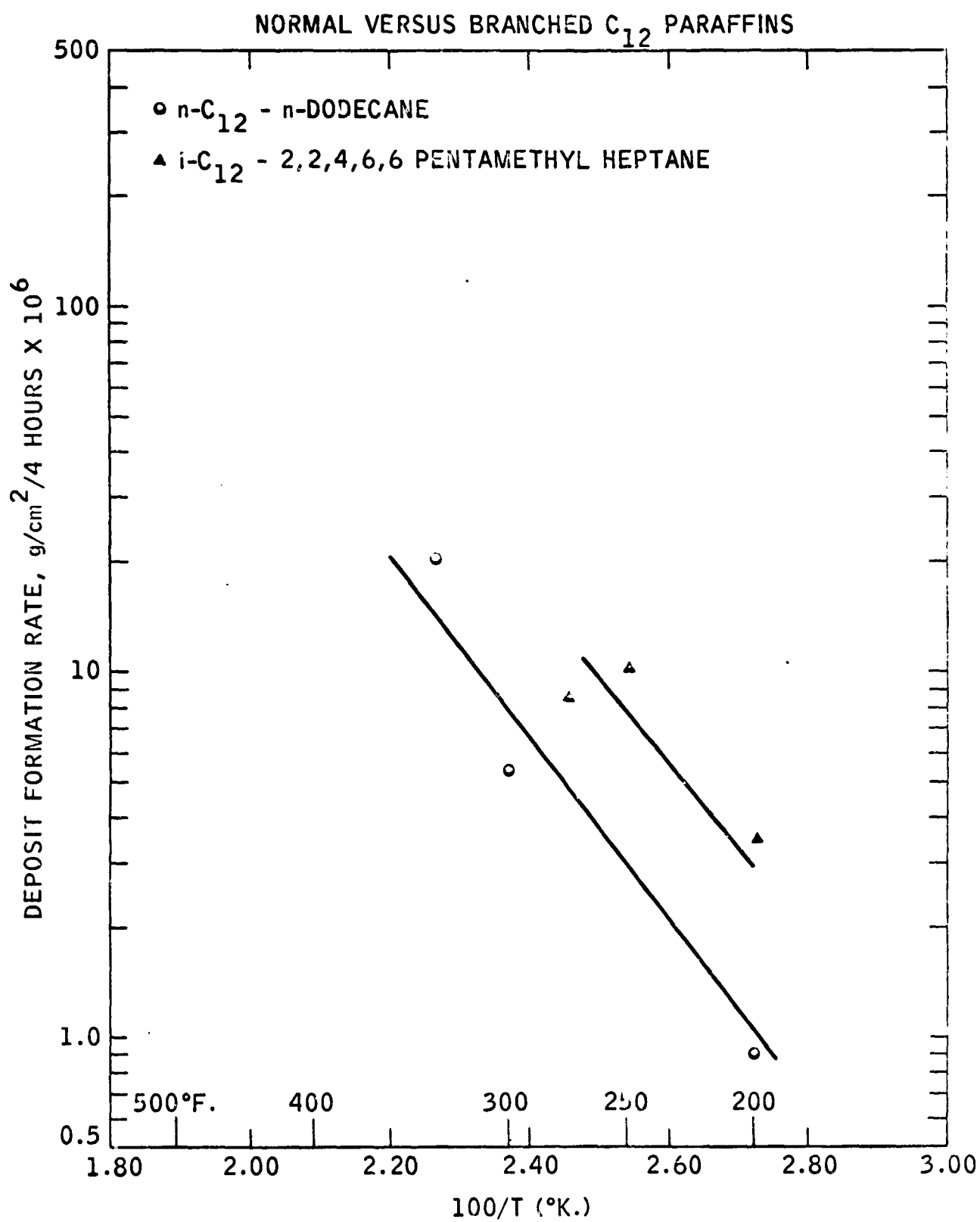


TABLE VI

THE EFFECT OF BRANCHING IN
PARAFFINS ON DEPOSIT FORMATION

<u>Type</u>	<u>Paraffin(s)</u>	<u>Relative Rate of Deposit Formation</u>
n-C ₁₂	n-Dodecane	1.00 (base) ^(a)
i-C ₁₂	2,2,4,6,6-Pentamethyl- heptane	2.29 ^(a)
n-C ₈ + n-C ₁₀	10 wt % n-Octane in n-Decane	1.00 (base) ^(b)
i-C ₈ + n-C ₁₀	10 wt % 2,3,4-Trimethyl- pentane in n-Decane	2.20 ^(b)

(a) Measured at 250°F

(b) Measured at 200°F

The apparent activation energy of the binary blends increased from 12 to 20 kcal/mole as the 1-methyl naphthalene concentration increased. The results of this study are shown in Figures 40 and 41 and the deposit formation rate at various temperatures is plotted as a function of 1-methyl naphthalene concentration in Figure 42. It can be seen that the effect of 1-methyl naphthalene concentration is complex. At low temperatures, i.e., 200 to 250°F, the presence of 1-methyl naphthalene inhibits the deposit formation process at all concentrations. At higher temperatures, i.e., 275 to 325°F, the addition of 1-methyl naphthalene initially inhibits the deposit formation process until its concentration reaches at least 60%, at which point, depending on the temperature, the rate of deposit formation obtained with the blend exceeded that of pure n-decane.

<u>Temperature °F</u>	<u>Maximum 1-methyl naphthalene Concentration for Inhibition, Wt. %</u>
200	None
250	None
275	87
300	75
325	68

(a) Concentration of 1-methyl naphthalene in n-decane at which point the blend deposit formation rate first exceeds that of pure n-decane.

This composition-temperature effect on inhibition, of course, reflects the increase in apparent activation energy of the blends as the 1-methyl naphthalene concentration increases.

The effect of various aromatic and naphthenic compounds at low concentrations in a paraffin rich binary blend was next investigated. The 10 wt. % level was chosen for these studies and various binary blends were prepared using n-decane as the paraffin, and their deposit formation rate measured in the Screening Unit at 3 psia. In general, the presence of an aromatic or naphthene inhibited the rate of deposit formation at 200 to 350°F. At higher temperatures, in many cases, this inhibition effect became less pronounced. Data are shown in the Arrhenius plots in Figures 43 to 49. It can be seen from this data that the magnitude of the inhibition effect varies with compound type. In some cases the inhibition effect was temperature dependent with the greatest inhibition occurring at lower temperatures. An examination of these results suggested that those compounds with hydrogen atoms attached to a benzylic carbon atom produced the greatest inhibition effect at lower temperature. In Figure 50, the activity of the binary blend relative to the activity of pure n-decane at 250°F is plotted against the number of benzylic hydrogen atoms present in the added compound. As can be seen a reasonable correlation result, with the exception of those aromatics in which the hydrogen atoms are attached to a carbon atom between two separate π electron systems, i.e., fluorene and diphenyl methane which inhibit the deposit formation process more strongly.

FIGURE 40

METHYLNAPHTHALENE IN DECANE BLENDS

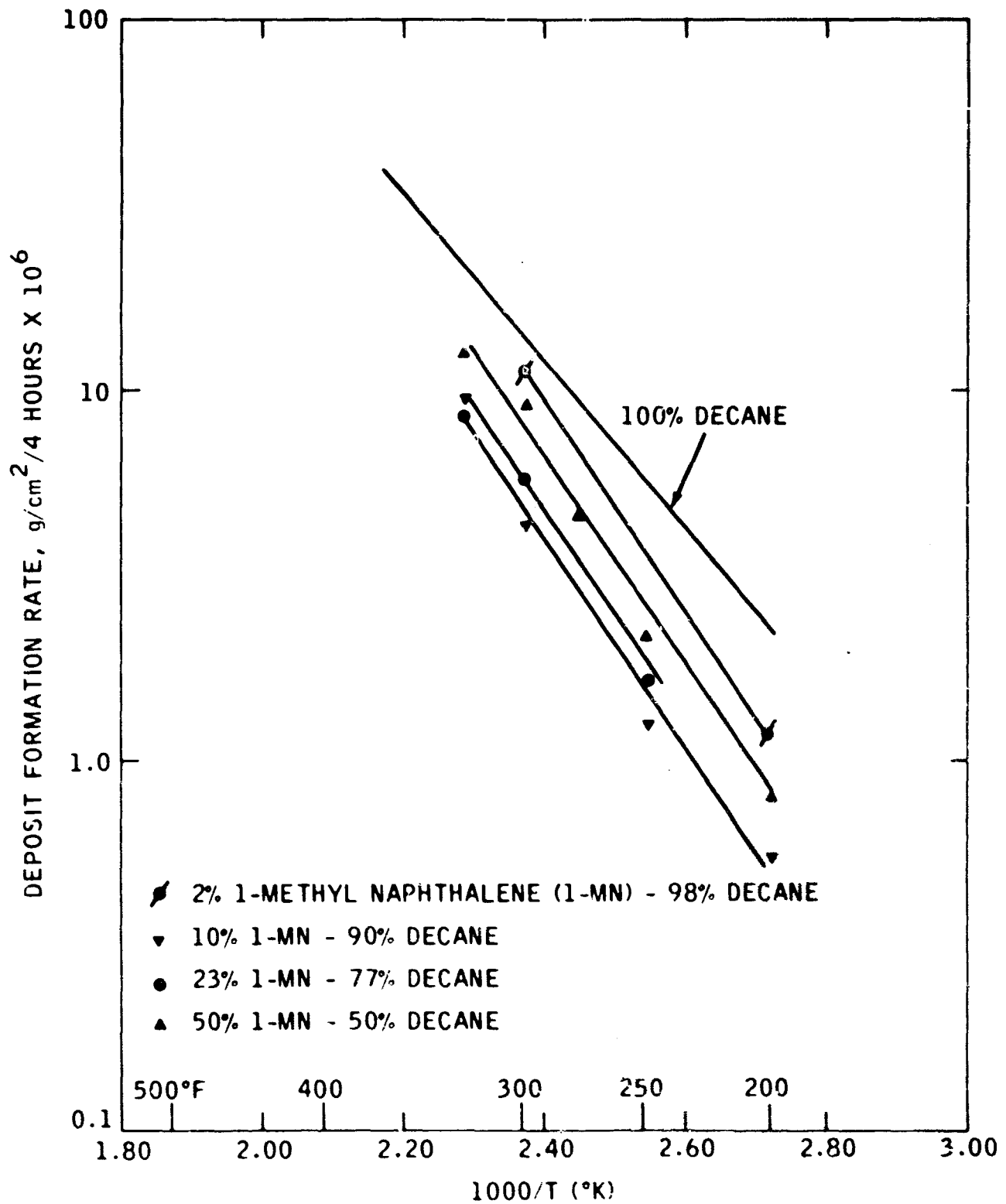


FIGURE 41

METHYLNAPHTHALENE IN DECANE BLENDS

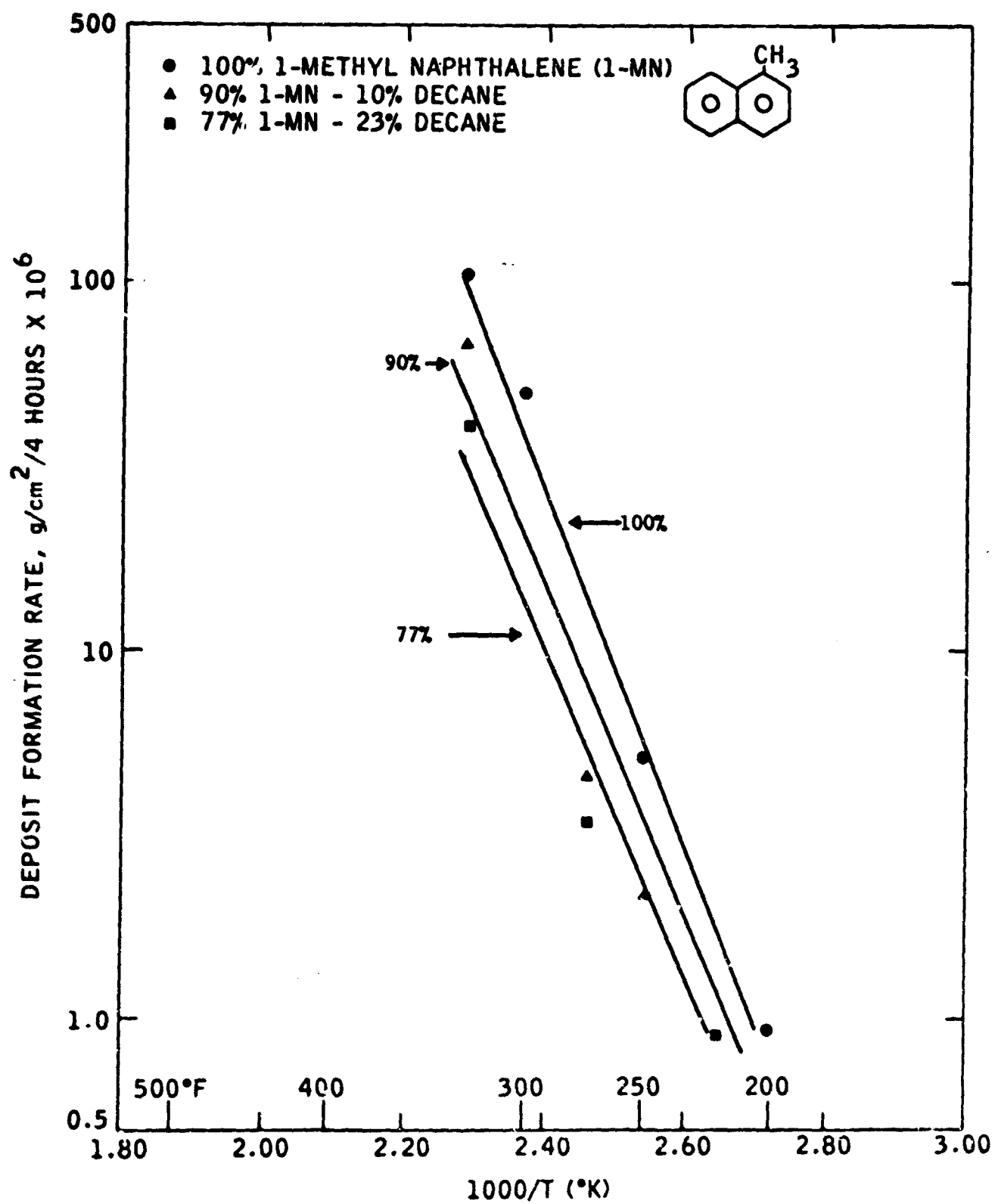


FIGURE 42

THE EFFECT OF CONCENTRATION

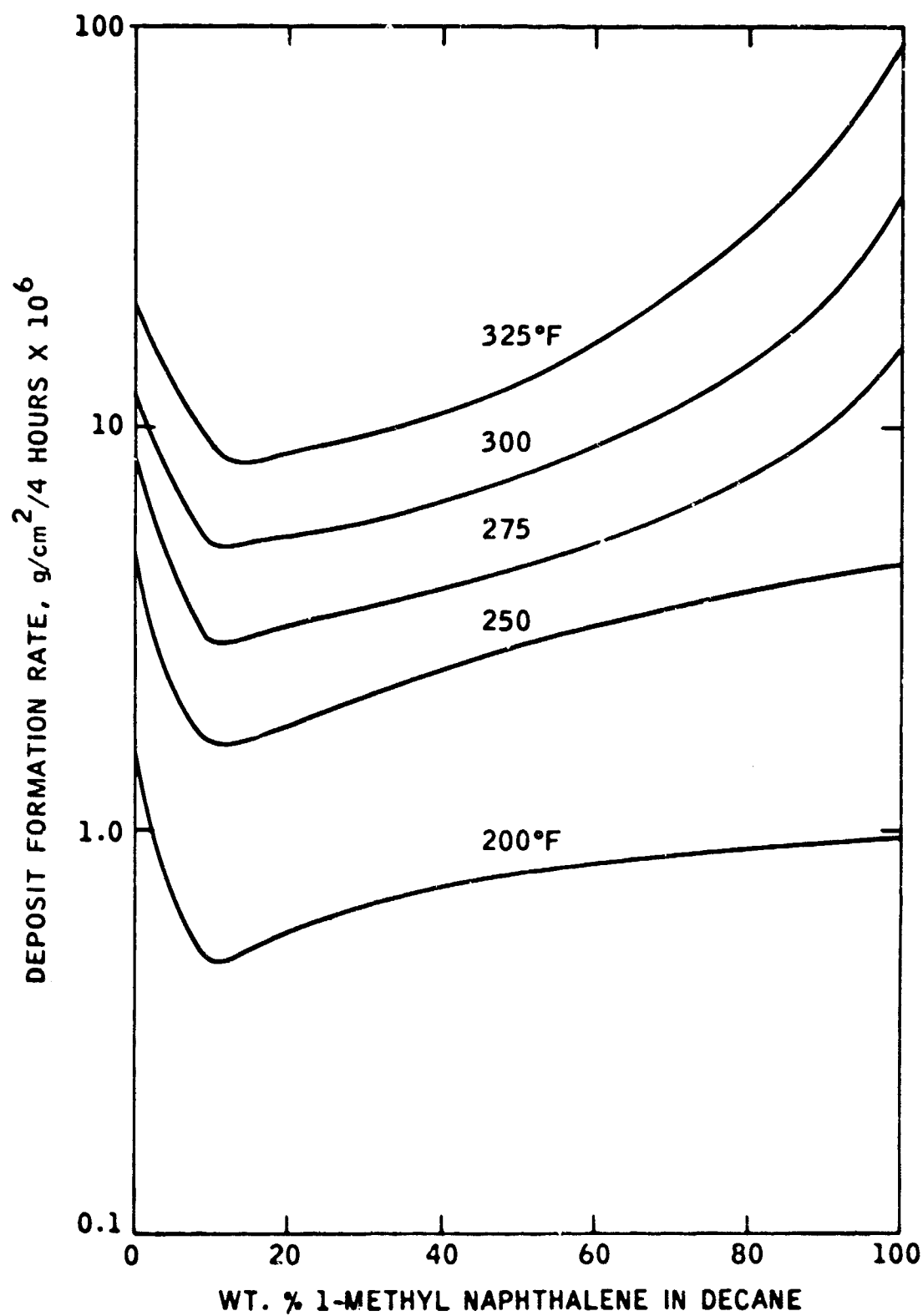


FIGURE 43

BUTYLTOLUENE AND PHENYLCYCLOHEXANE IN DECANE

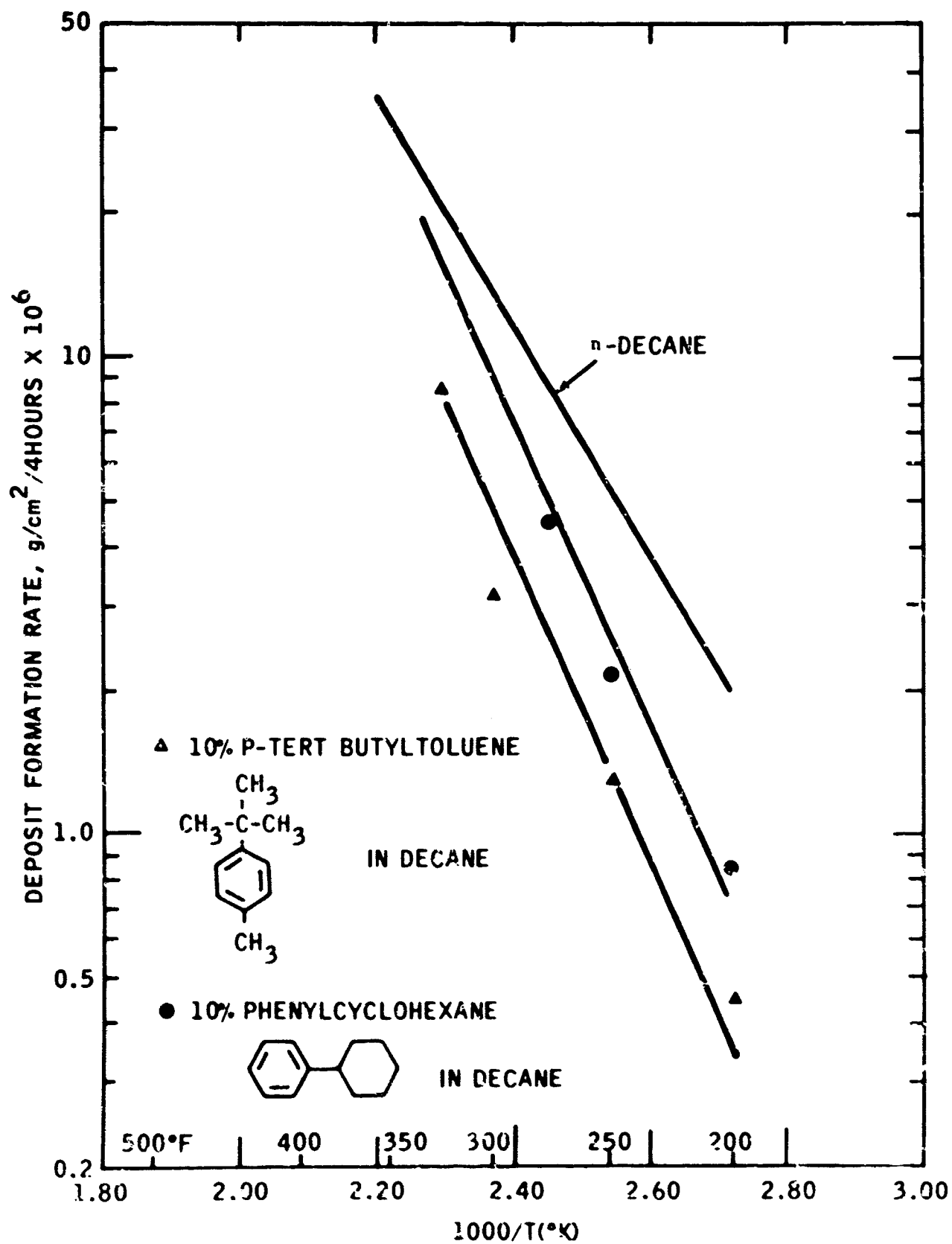


FIGURE 44

TETRALIN AND DECALIN IN DECANE

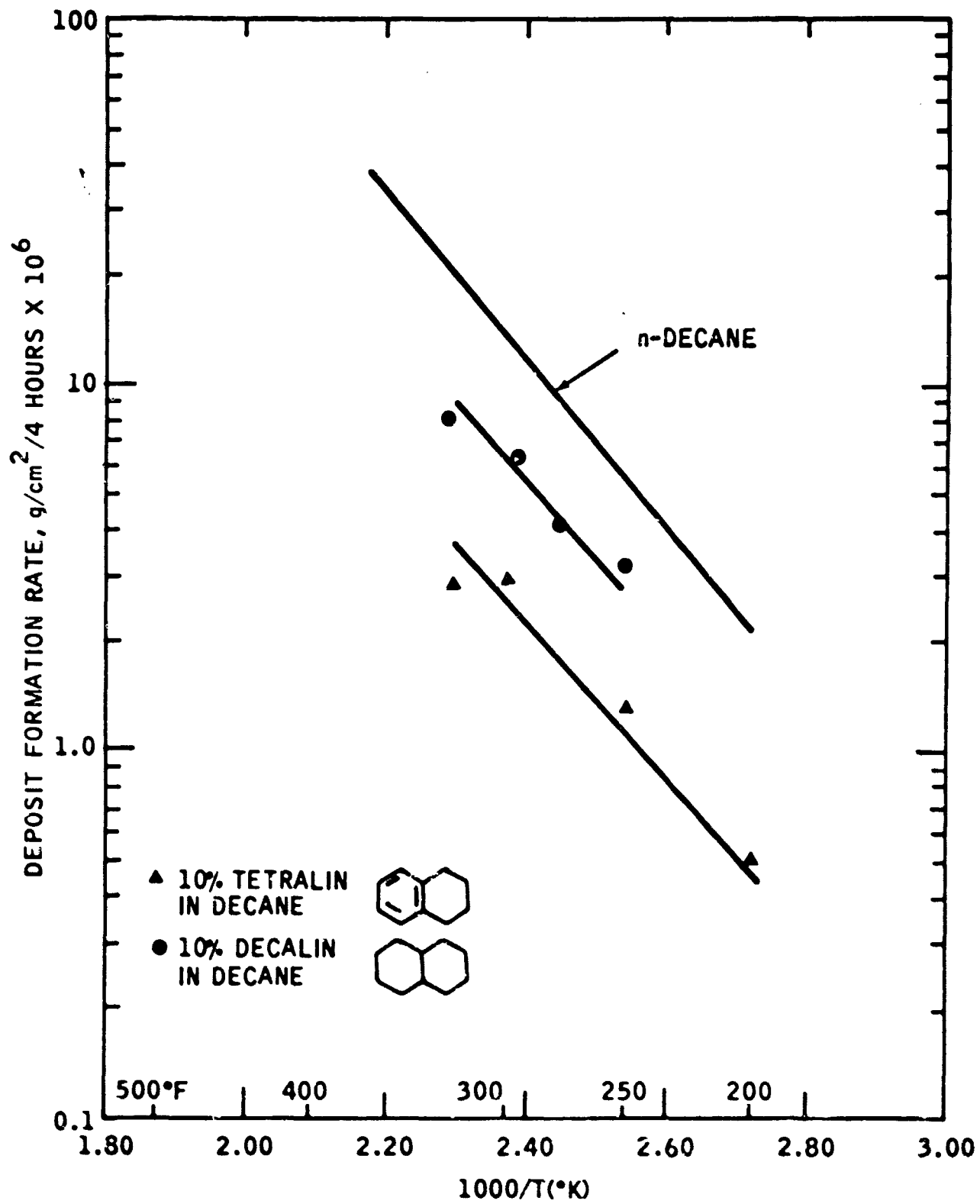


FIGURE 45

METHYLNAPHTHALENE AND NAPHTHALINE IN DECANE

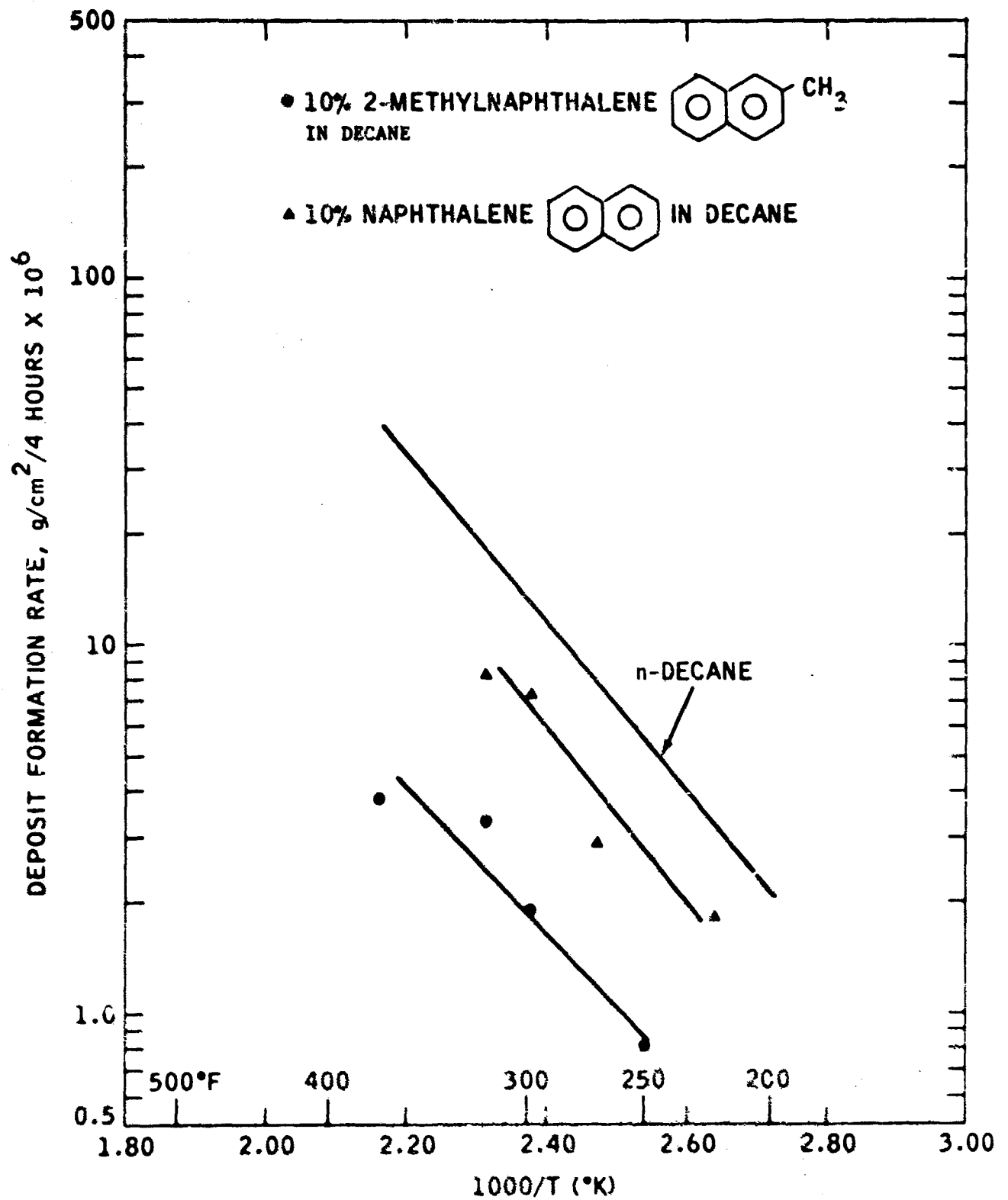


FIGURE 46

PHENYLOCTANE AND BUTYLCYCLOHEXANE IN DECANE

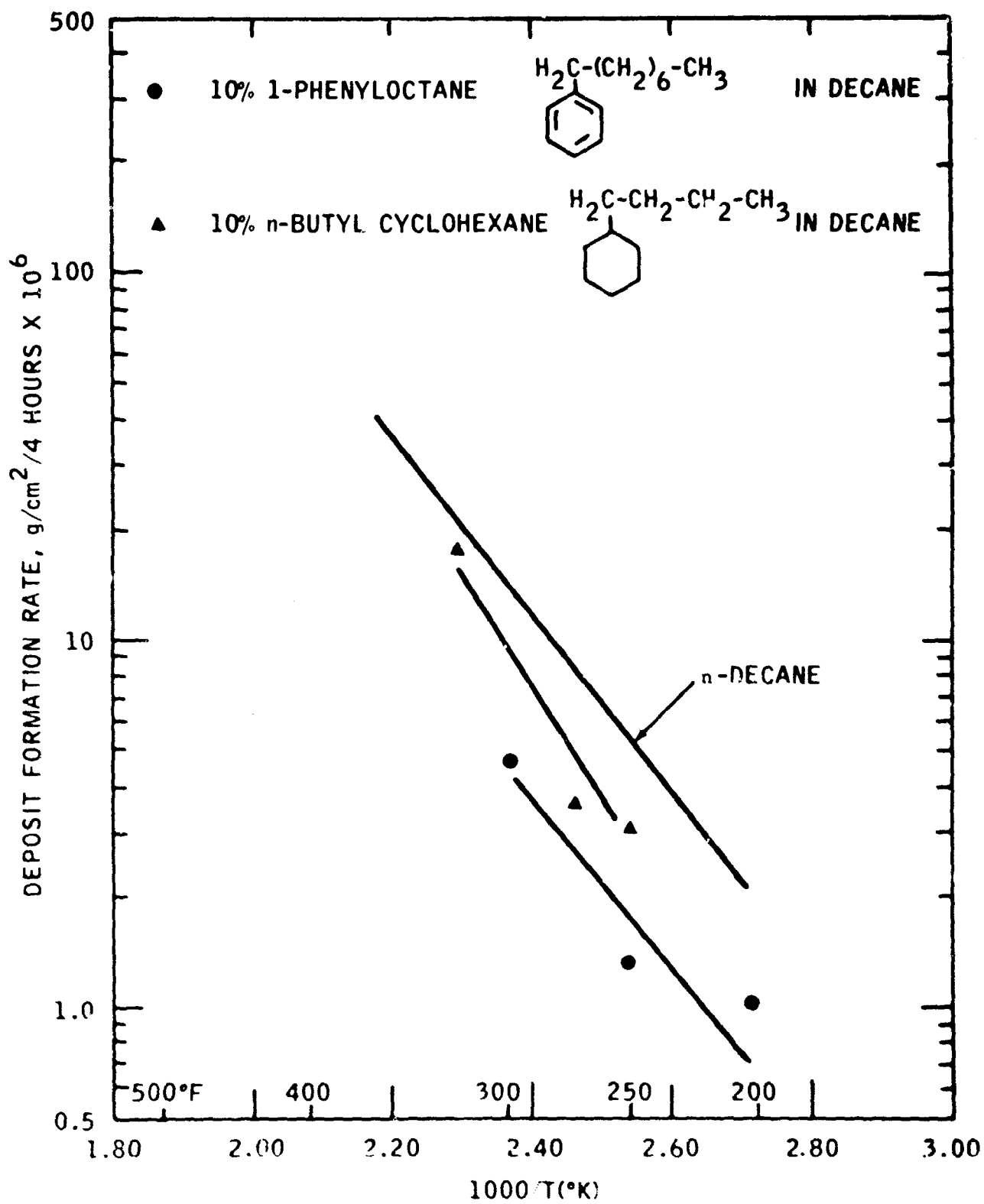


FIGURE 47

DIISOPROPYLBENZENE IN DECANE AND HEXADECANE

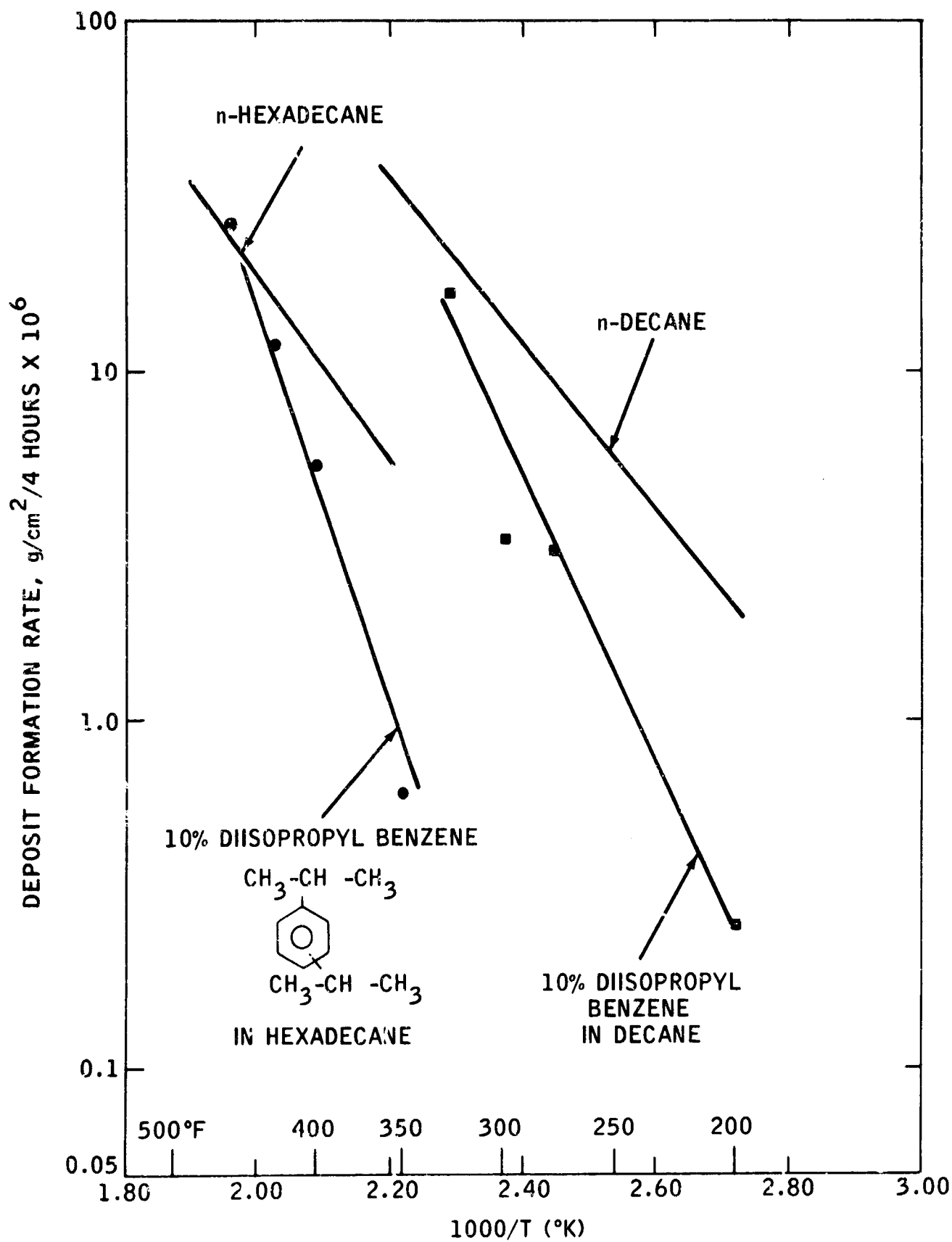


FIGURE 48

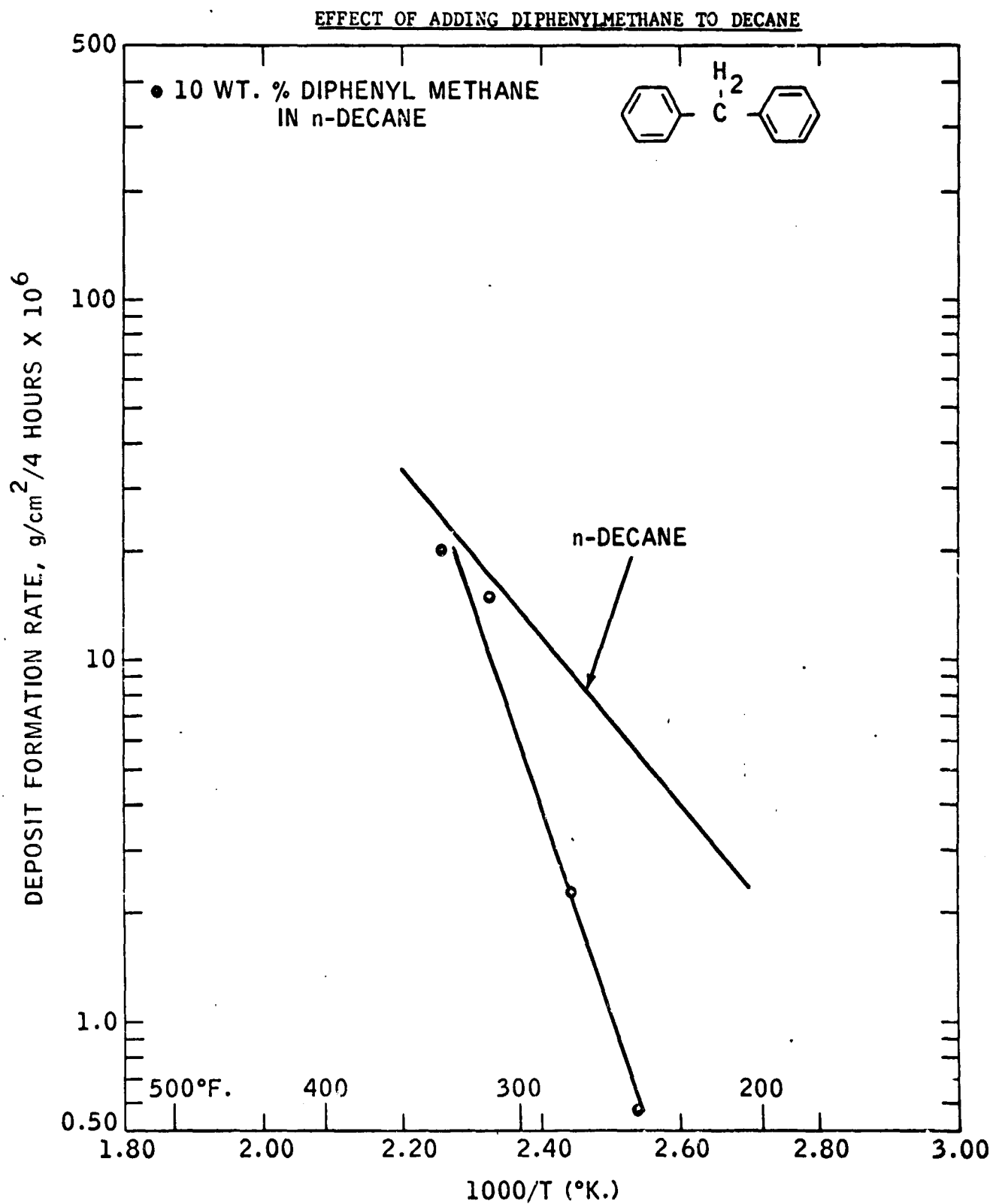


FIGURE 49

FLUORENE IN DECANE

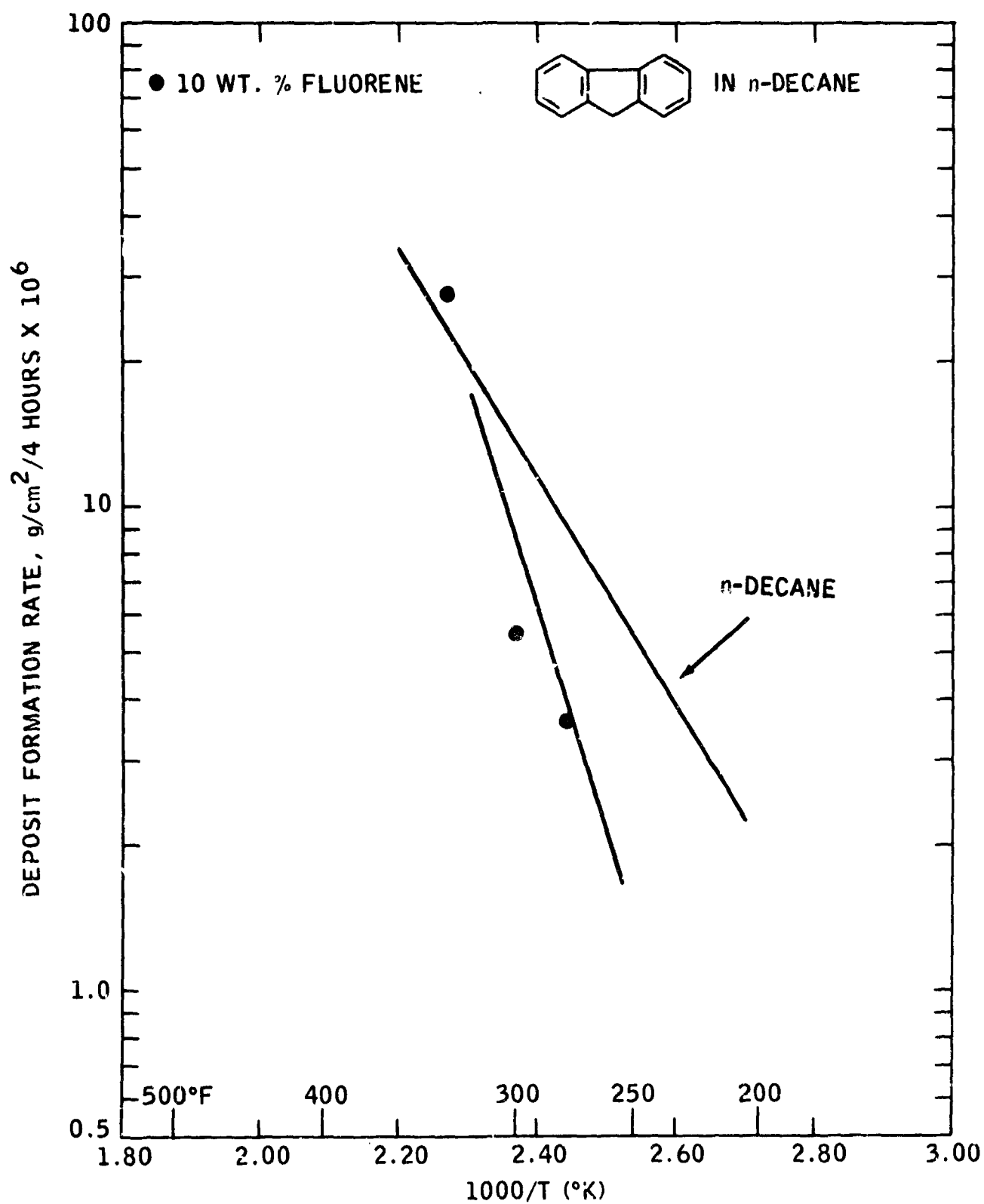
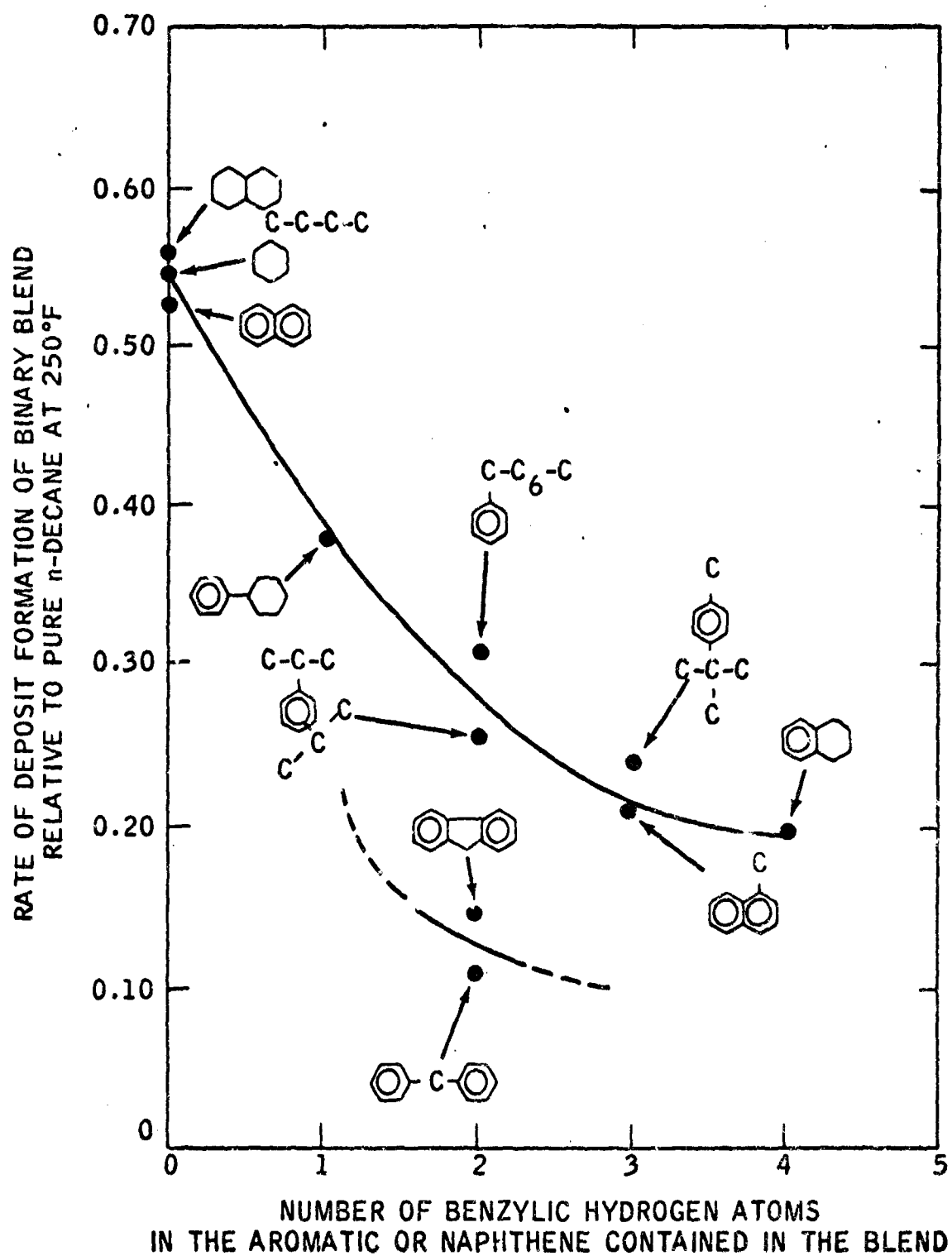


FIGURE 50

INHIBITION RELATED TO BENZYLIC HYDROGEN



The effect of various olefins in a paraffin rich blend at low concentrations was next investigated. As before, this was done by adding 10 wt % of the olefin to n-decane, and then testing the binary blends in the Screening Unit at 3 psia. In general, the addition of an olefin to n-decane increased the level of deposit formation. Data are shown in the Arrhenius plot in Figures 51 to 53. Results are summarized in Table VII. It can be seen that the magnitude of the increase in deposit formation varied markedly depending on the olefin employed.

The effect of olefin concentration on deposit formation was investigated with indene-decane blends at indene concentrations below 10 wt %, which are more typical of olefin levels in actual jet fuels. These results are summarized in Table VIII. It can be seen that the relative rate of deposit formation increased essentially linearly with higher olefin content.

In the present study, the addition of an olefin to a paraffin rich mixture increased the rate of autoxidation deposit formation. The magnitude of this effect, however, varied widely with the olefin type. It has been generally recognized that olefins are deleterious components which often increase sediment and deposit formation during hydrocarbon fuel storage. Mayo (116) has recently reviewed much of the literature on the oxidation of unsaturated hydrocarbons. Olefins can either react with oxygen to initially form hydroperoxides via a hydrogen abstraction mechanism or they can undergo an addition mechanism to form polyperoxides. Deposit precursors are hydrocarbon insoluble compounds which have incorporated significant quantities of oxygen into their structure (64). Thus, autoxidative deposit precursors in the present study with olefins could either be oxygen containing species formed by termination reactions involving peroxy radicals during the course of the hydrogen abstraction mechanism, or they could be polyperoxides formed via the addition mechanism. Mayo's results indicate that both the addition and abstraction mechanism can occur simultaneously.

The observed linear dependence of the relative rate of deposit formation on olefin content would seem to be, in general, consistent with both of these mechanisms, as in both cases the rate limiting step is envisioned as a reaction between an olefin and a peroxy radical.

It is interesting to compare the results of these oxidation studies with the observed effect of various olefins on deposit formation. For example, at 70°F indene oxidizes approximately 22 times faster than does vinylcyclohexane (116). For the same olefins in the present study deposit formation was found to increase by a factor of 12 (Appendix 62). Similarly, cyclohexene was found to oxidize faster than vinylcyclohexane by a factor of approximately 5 (116). This difference in reactivity is presumably reflected in the present study in the much higher deposit formation tendency of vinylcyclohexene relative to vinylcyclohexane. In the present work it was also found that 7-methyl-3-methylene 1,6-octadiene was much more deleterious toward deposit formation than 1-decene. This effect presumably reflects the general tendency noted by Mayo of olefins with conjugated unsaturation to be more reactive toward oxidation. In general, it appears that the relative effect of various olefins on deposit formation in paraffin-olefin blends closely parallels their observed reactivity toward oxidation.

FIGURE 51

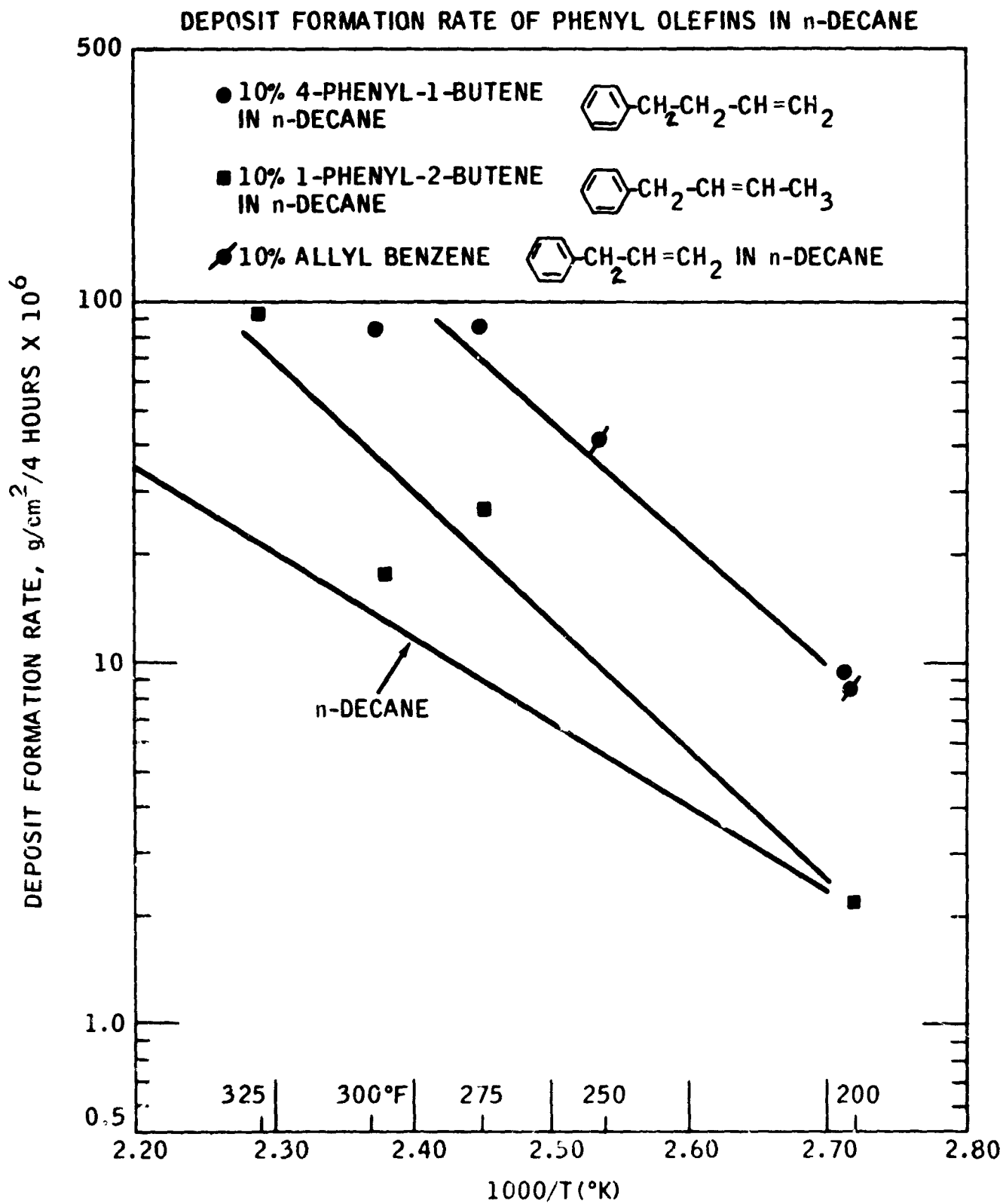


FIGURE 52

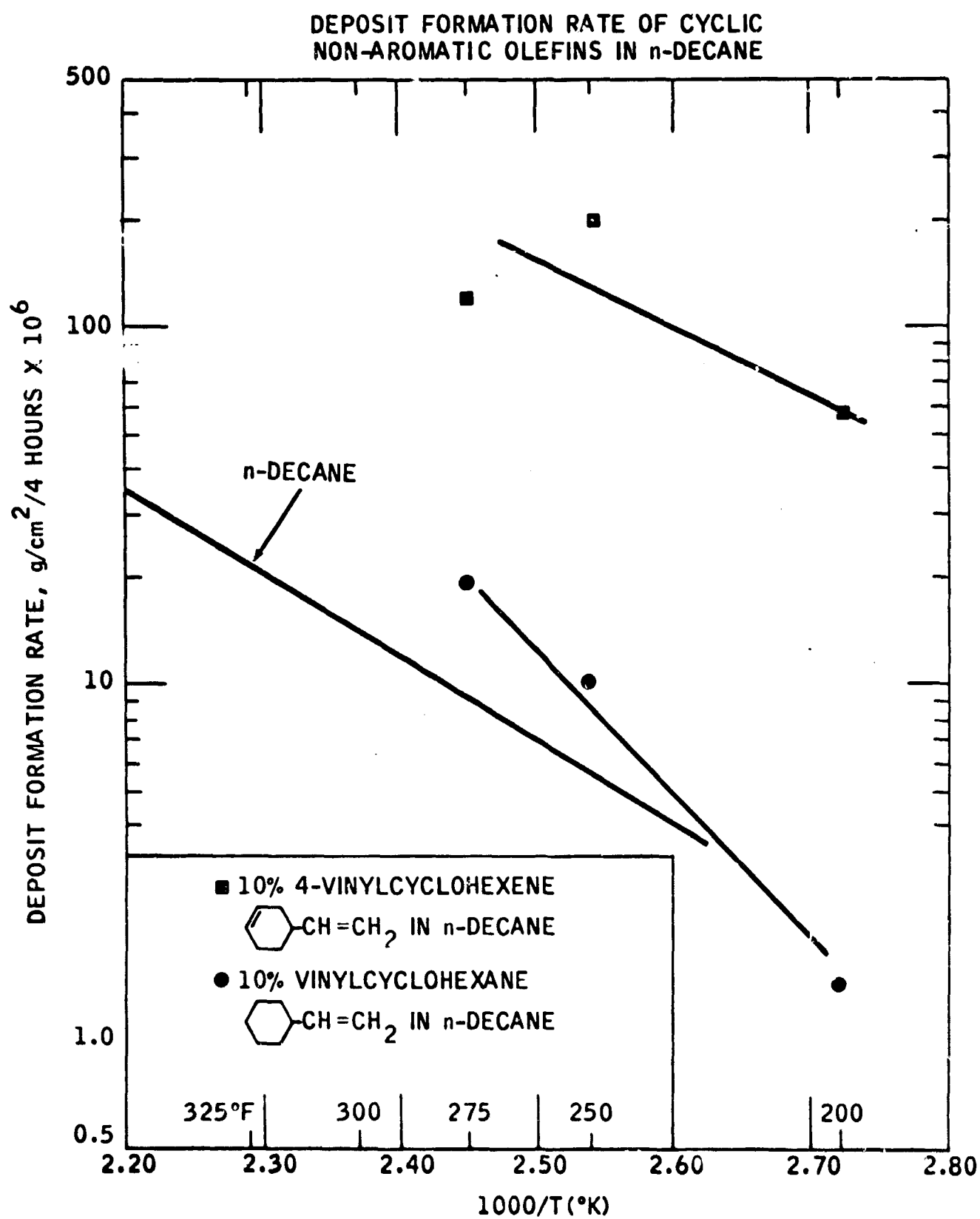


FIGURE 53

OLEFINS IN DECANE

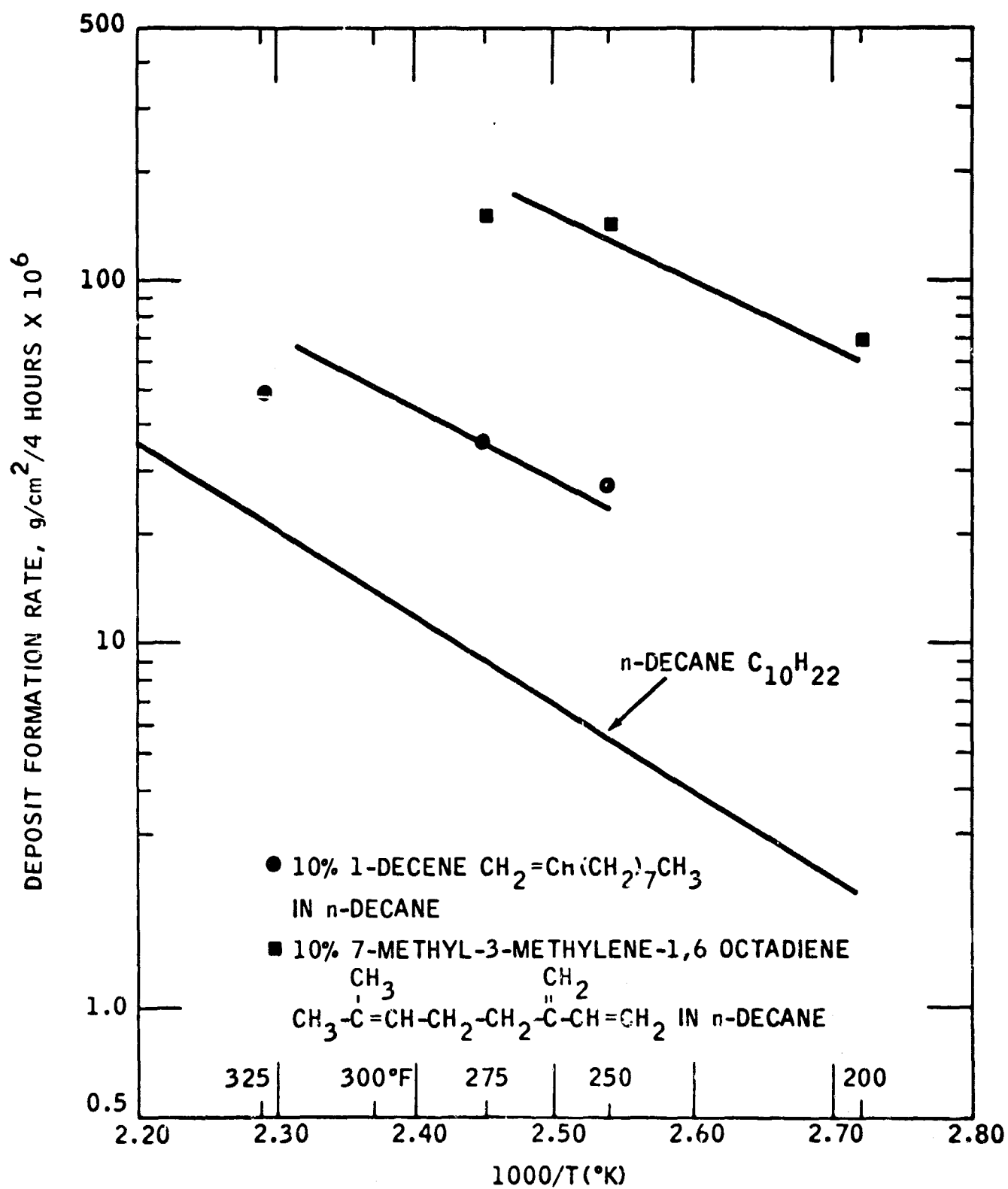
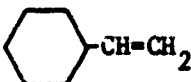
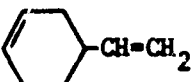
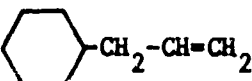
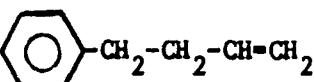
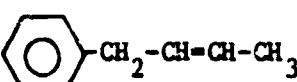
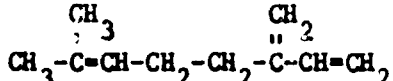
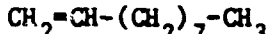


TABLE VII

SUMMARY OF DEPOSIT FORMATION TENDENCIES
OF OLEFIN-n-DECANE BINARY BLENDS

<u>Olefin Added</u> <u>To Binary Blend (a)</u>	<u>Structure of Olefin</u>	<u>Rate of Deposit Formation</u> <u>of Blend at 275°F,</u> <u>g/cm²/4 hours x 10⁶</u>
Vinylcyclohexane		29.4
4-Vinylcyclohexene		198.
Allylbenzene		91.2
4-Phenyl-1-butene		86.9
1-Phenyl-2-butene		26.5
7-Methyl-3-methylene 1,6 octadiene		190.
1-Decene		35.6
Indene		354.

(a) 10 wt % olefin in n-decane in all blends

TABLE VIII

THE EFFECT OF OLEFIN CONTENT
ON DEPOSIT FORMATION

<u>Wt % Indene in n-Decane</u>	<u>Deposit Formation Rate @ 200°F g/cm²/4 hrs x 10⁶(a)</u>	<u>Relative Rate of Reaction at 200°F</u>
1.0	9.6	1.0 (base)
5.0	47.6	4.9
10.0	122.	12.7

Although 1-methyl naphthalene is more deleterious toward deposit formation than n-decane, the addition of small amounts of 1-methyl naphthalene to n-decane lowered the rate of deposit formation. Russell (117) studied the cooxidation of tetralin and cumene and found that small quantities of tetralin added to cumene would markedly lower the rate of oxidation, even though neat tetralin oxidized ten times as fast as cumene at the same temperature and initiation rate. Similar effects have been observed in other cooxidation studies (118). Thus, it can be seen that the observed effect of 1-methyl naphthalene concentration in decane closely parallels the effects observed on oxidation rate when cooxidizing compounds with differing reactivities.

The addition of various aromatics and naphthenes to decane was found, in general, to inhibit deposit formation at lower temperatures. In addition, it was found that the magnitude of this inhibition could be reasonably correlated with the presence of hydrogen atoms attached to a benzylic carbon atom. This inhibition effect, in general, would seem to reflect the observed inhibition effects in cooxidation studies. That the effect is more pronounced at lower temperatures undoubtedly reflects the general tendency for selectively effects to manifest themselves most strongly at milder conditions. The importance of hydrogen abstraction reactions has been recognized by many workers. As discussed by Ingold (119), a peroxy radical is a relative unreactive radical which is quite selective in its hydrogen abstraction from hydrocarbons, and should have a preference for the most weakly bound hydrogen atom.



The hydrogen abstraction reaction (30) is the limiting reaction during chain propagation, since the reaction of a hydrocarbon radical with molecular oxygen (31) occurs quite rapidly in the presence of higher concentrations of oxygen.



A consideration of the energetics of Eq. 30 indicates that the hydrogen abstraction reaction will occur fastest when the bond which is formed (ROO-H) is stronger than the bond which is broken (R'-H). Such is the case with a benzylic C-H bond (hydrogen on a carbon atom $\propto$ to a π electron system), reflecting the fact that the radical formed is resonance stabilized. Thus, the correlation of the effect of the number of benzylic hydrogen atoms contained in the added compound on the reduction in deposit formation tendency of the various blends with n-decane (Figure 50) would seem to reflect the effect of bond strength during hydrogen abstraction (Eq. 30) in the cooxidation system. Ingold (119) also points out that hydrogen atoms attached to a carbon atom between two separate π electron systems should form more stable radicals than hydrogen atoms attached to a carbon adjacent to a single π system. This presumably explains the greater inhibiting effect observed with diphenylmethane and fluorene blends with decane.

For the same carbon number, it was found that branched paraffins form deposits more rapidly than n-paraffins. However, among pure n-paraffins it was found that the deposit formation tendency decreased with increasing

carbon number. As pointed out by Twigg (120), the oxidation of paraffins is more complex relative to other compounds because of the lack of an activating group and the general greater strength of carbon-hydrogen bonds. An analysis based on hydrogen abstraction considerations only, i.e., the relative bond strengths of primary, secondary and tertiary C-H bonds in these paraffins, would predict that branched paraffins should oxidize more rapidly than n-paraffins, and that increasing the carbon number would increase the rate of oxidation because of the greater number of secondary C-H bonds. Thus, the observed differences in autoxidative deposit formation among the paraffins cannot be explained by any such simple analysis. It is possible that the formation of deposits from pure paraffins is dominated by physical processes rather than kinetic processes. In addition, the role of reactions such as oxidative dehydrogenation during deposit formation at the reduced pressures employed in the present study is not known.

The oxidation stability of a number of single pure compounds have been determined in the fuel coker (121). Such data is undoubtedly useful in predicting the stability of a neat compound which might be employed as a fuel in a high Mach number aircraft. However, in light of the presently observed complex effect of fuel composition on autoxidative deposit formation, it is doubtful whether such single compound data will be particularly helpful in predicting stability effects in actual jet fuel mixtures.

2. The Study of Interactions Between Aromatics, Naphthenes and Olefins

A study was carried out involving pure compounds designed to determine if any unusual fuel component interactions occur during the deposit formation process. Earlier pure compound studies involving binary mixtures of aromatics and naphthenes in a paraffin such as n-decane indicated that both aromatics and naphthenes inhibited the deposit formation process. The magnitude of this inhibition effect varied from compound to compound, with the largest inhibition effect occurring with those aromatic compounds which contain hydrogen atoms attached to a benzylic carbon atom. The experimental study was planned as a 2³ full factorial statistically designed experiment involving three variables, (a) presence or absence of an aromatic, (b) presence or absence of a naphthene, and (c) presence or absence of an olefin in a paraffin rich blend. The 10 wt% level involving 1-methylnaphthalene as the aromatic and decalin as the naphthene and the 2 wt% level involving 1-decene in n-decane were chosen as being representative of typical compounds present in a jet fuel. The layout of the experiments is shown in Table IX. Screening unit conditions were 3 psia, use of pure titanium metal strips and standard hydrocarbon and air flow rates. Results of runs 1 through 4 (no olefin present) are shown in the Arrhenius plot in Figure 54. The results of runs 5 to 8 involving the presence of an olefin are shown in the Arrhenius plot in Appendix 66. The presence of decalin or 1-methylnaphthalene inhibited the deposit formation process at low temperatures in both studies (i.e., with and without the presence of olefin). The presence of aromatic inhibited the deposit formation process more than the presence of naphthene at low temperatures; this difference being most pronounced in the presence of olefin, where the addition of 10% decalin to

TABLE IX

Olefin-Aromatic-Naphthene Interaction Study in n-Decane

	No Aromatic Present		Aromatic Present	
	No Naphthene Present	Naphthene Present	No Naphthene Present	Naphthene Present
No Olefin Present	1	2	3	4
Olefin Present	5	6	7	8

(Run Number indicated in box)

- Olefin present: 2 wt% 1-decene in n-decane
- Aromatic present: 10 wt% 1-methylnaphthalene in n-decane
- Naphthene present: 10 wt% decalin in n-decane

Conditions: 3 psia, Ti 75A pure titanium strips
standard flow rates of air and
hydrocarbon

FIGURE 54

RESULTS OF INTERACTION STUDY

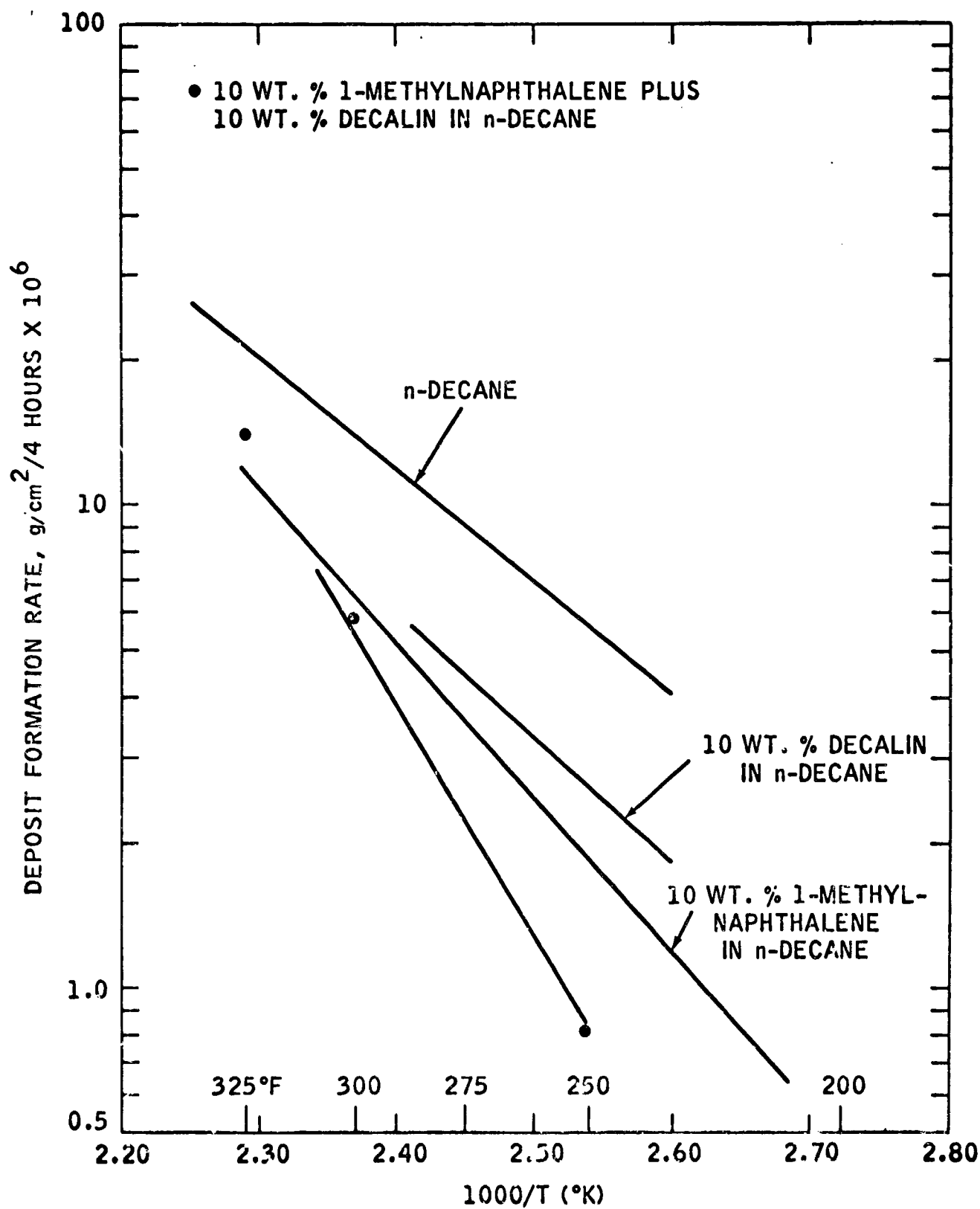
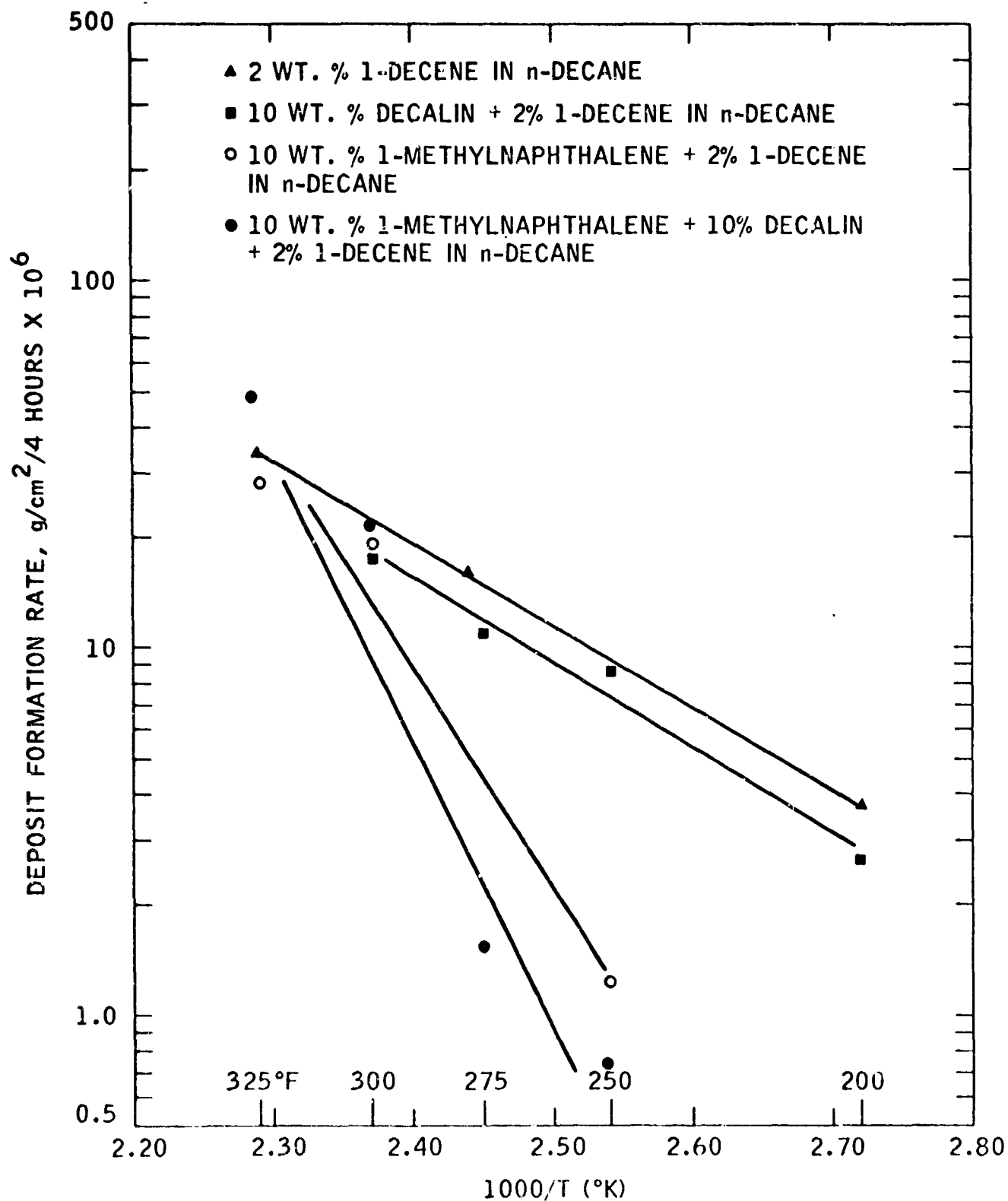


FIGURE 55

RESULTS OF INTERACTION STUDY



2 decane-1-decene blend only slightly inhibited the deposit formation process. This data suggests that the inhibition effect of naphthenes at low temperatures may be rather small when olefins are present. The simultaneous presence of the aromatic and naphthene was slightly better than presence of aromatic alone in both studies (i.e., with and without olefin). This is consistent with the results obtained from the individual effect of the presence of an aromatic or naphthene. Thus, the most significant interaction uncovered in this study is the effect of the presence of olefin in reducing the ability of a naphthene to inhibit the deposit formation process at low temperatures.

3. Metal Type Effects with Decane

Our pure compound study has employed pure titanium metal in all our Screening Unit runs. In order to see if the effect of metal type previously determined with actual jet fuels would also apply to a pure paraffin we measured the rate of deposit formation of hexadecane over Ti-8Al-1Mo-1V alloy. These results are compared below to those obtained with a Jet A kerosine.

<u>Metal Type</u>	<u>Deposit Formation Rate @ 350°F</u>		<u>Relative Activity With Jet A Kerosine (RAF-176-63)</u>
	<u>With Hexadecane (a)</u>	<u>Relative Activity With Hexadecane</u>	
	<u>g/cm²/4 hrs x 10⁶</u>		
Pure Titanium	4.5	1.00 (base)	1.00 (base)
Ti-8Al-1Mo-1V	13.4	3.0	2.6

(a) Other Conditions: 3 psia, 4 hour run, standard flow rates.

It can be seen that the effect of metal type observed with a Jet A kerosine is approximately the same as that observed with pure n-hexadecane.

H. The Nature of Deposits and the Overall Deposit Formation Process

The deposit formed on surfaces from hydrocarbon jet fuel at high temperatures in the presence of oxygen are light to dark brown in color, insoluble in jet fuel range hydrocarbon media, and nonvolatile at temperatures up to 450°F and pressures as low as 0.1 torr. Infrared analyses of typical specimens indicate the presence of oxygenated functional groups (>C=O, -OH). Analyses indicated that the deposit contained higher sulfur content than was present in the parent fuel (0.49 wt. % versus 0.076 wt. %), and it contained 21% oxygen.

A number of studies on the low temperature stability of hydrocarbon fuels have shown that free radical autoxidation reactions play a major role in the degradation of the fuel leading to gum and deposit formation (122). The gums formed at low temperatures, for example, 100°F, during the storage of a hydrocarbon such as jet fuel or gasoline contain carbon, hydrogen, oxygen, and a larger fraction of the sulfur and nitrogen than originally present in the parent hydrocarbon. Because of the complex nature of the autoxidation processes involved in the degradation of hydrocarbon fuels, the exact structure of such gums is not known.

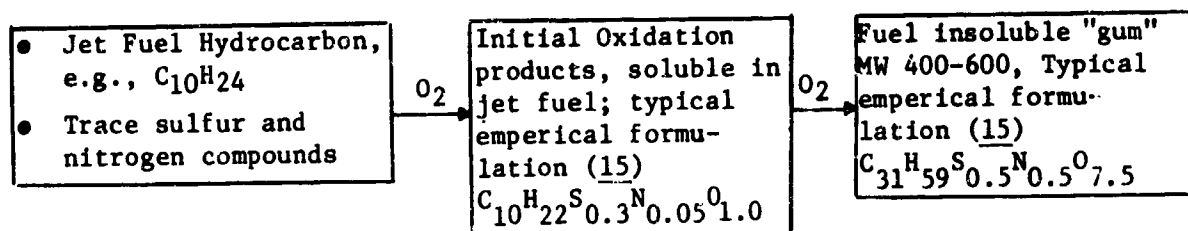
The oxidation of higher molecular weight pure hydrocarbons can lead to a great variety of reaction products. A number of investigators have reported the production of a nonvolatile "residue" among the products of the oxidation of various pure hydrocarbons. The oxidation of 1-hexene, (123) decalin (124) and dimethylcyclohexane (125) produced hydrocarbon insoluble, brownish, highly viscous liquids whose composition was not identified in detail. However, in several excellent studies of single hydrocarbon compounds, the nature of such residues was elucidated. In the oxidation of cyclic and acyclic alkenes at 50-100°C (126,127), nonvolatile residues were found among the products. The residues consisted of dimeric and trimeric peroxides and higher molecular weight polymers with peroxide linkages. The low temperature oxidation of styrene and methyl styrene (128,129) was shown to produce polymeric peroxides with molecular weights up to approximately 2000. As pointed out by Mayo (130), the production of deposits in a hydrocarbon fuel undoubtedly involves the reaction steps postulated for autoxidation, polymerization, and free radical coupling reactions. Jet fuels are generally low in olefin content, although saturated hydrocarbons can undergo an oxidative dehydrogenation to form olefins at low pressures such as those found in the "wing tank" environment (131). Thus, the formation of oxypolymers from olefins is possible. Peroxide dimers formed from the higher molecular weight hydrocarbons present in jet fuels should be highly viscous, nonvolatile, and insoluble in hydrocarbon media. Thus, both oxidative polymerization and termination reactions could contribute to deposit formation. However, because of the wide spectrum of compounds present in jet fuels, and the wide range of temperatures potentially present in an "empty" SST wing tank, both the autoxidation reaction system leading to the formation of deposits and the structure of the deposits themselves in this environment must indeed be complex.

It is interesting to consider the overall autoxidative fuel degradation process which ultimately results in the formation of deposits. This overall system includes both physical and chemical processes. Although the physical and chemical process are in all probability inter-related it is convenient to consider them separately.

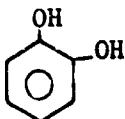
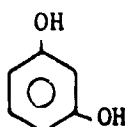
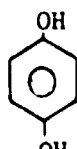
The chemical processes which ultimately lead to the formation of deposits are free radical, chain reaction autoxidation reactions which occur much more rapidly in the liquid phase than in the vapor phase (64,116). Such reactions can be catalyzed by both metal oxide surfaces (104,113-115) and by homogeneous (dissolved) metals (104,112). Trace levels of sulfur and nitrogen compounds play a major role in such processes (73,102) presumably because of the lower stability of sulfur and nitrogen compounds relative to hydrocarbons (94). The formation of fuel insoluble

materials, which are the "building blocks" for deposit formation, involves a continuous incorporation of oxygen, forming initial oxidation products which are soluble, followed by the formation of fuel insoluble "gums" which contain higher oxygen levels (132). This process is shown in a simplified schematic below:

Gross Chemical Process in Deposit Formation

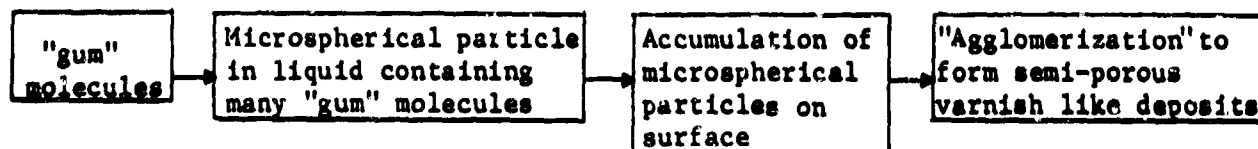


The solubility of the intermediate oxidation products depends greatly on the number and distribution of oxygen containing groups; however, in general, the solubility drops off markedly with increasing oxygen content. This can be illustrated by considering the solubility of various oxygenated benzene molecules in benzene (133).

Compound	Structure	Solubility in Benzene 20°C
Phenol C_6H_6O		10 wt. %
1,2 benzenediol $C_6H_6O_2$		0.60 mole %
1,3 benzenediol $C_6H_6O_2$		0.15 mole %
1,4 benzenediol $C_6H_6O_2$		0.02 mole %

The physical processes leading to the formation of deposits probably involve the following steps (132,134,135)

Gross Physical Process in Deposit Formation



Evidence also exists that at high temperatures in the presence of oxygen, the varnish-like deposits can be converted to black, brittle material which often tends to blister and flake off surfaces. It is known that hydrogen can be selectively removed via reaction with oxygen from carbonaceous material which accumulates on typical petroleum processing catalysts (e.g., Pt/Al₂O₃ Hydroforming Catalysts) to yield a carbon rich residue. It is possible that a similar phenomenon occurs in this further reaction of varnish-like deposits with oxygen.

The complexity of the autoxidative deposit formation system emphasizes the need for as direct a measurement as possible of the problem area in question. For example, if heat exchanger failing is the problem area, a test device which simulates the complex physicochemical system in the heat exchanger should be used which employs a direct measurement of the variable in question; e.g., loss of heat exchanger efficiency. Similarly, if "empty" wing tank deposit formation is the problem in question, deposits should be measured directly in a test device which simulates this environment as closely as possible. Because of the complexity of the system, any indirect test which attempts to predict, for example, an effect on heat exchanger failing will produce at best only qualitative results which can not be related in any fundamental, direct manner to the problem of actual concern.

I. Electron Microscope Study of Various Deposit Specimens

A number of metal strips on which various amounts of deposits had formed in our Screening Unit were examined under the Scanning Electron Microscope by R. M. Schirmer of Phillips Petroleum Company, Bartlesville, Oklahoma. The specimen selected and other information regarding the environment in which the deposits were formed in the Screening Unit are shown below.

<u>Specimen Number</u>	<u>Gross Physical Appearance</u>	<u>Hydrocarbon Fuel</u>	<u>Metal Type</u>	<u>Temperature</u>
362-84-5	light tan to yellow color deposits	n-Hexadecane	Ti-75A	475°F
390-45-4	dark brown to black, heavy deposits	AFFB-4-65	Ti-8Al-1Mo-1V	275°F
362-100-1	clear deposits	P&W 523 containing 1000 ppm S from phenyl methyl sulfide	Ti-8Al-1Mo-1V	300°F
390-20-1	clear deposits	99% n-decane-indene 1%	Ti-75A	200°F
390-19-4	heavy irregular yellow deposits on lacquer substrate	95% n-decane-5% indene	Ti-75A	300°F
362-43-1	tan to light yellow deposits	RAF-176-63	Ti-8Al-1Mo-1V	400°F

Scanning Electron Micrographs of the various specimens are shown in Figures 56 to 64, along with the original magnification employed. As shown in the table above, the gross physical appearance of the deposits varied quite a bit. Examination of these specimens under the electron microscope also indicates considerable variation in appearance. These results again emphasize the complex nature of the autoxidative reaction process which results in the formation of deposits.

J. Results of an Exploratory
Oxidation Study with n-Decane

Pure n-decane was passed through the Phase Study Unit in the presence of air to see if it would react at "empty" wing tank conditions. A paraffin was chosen for this exploratory run because we feel that paraffins represent the main type of hydrocarbon present in highly stable jet fuels (i.e., P&W 523 is a highly paraffinic fuel). In this run, the decane overhead from the Phase Study Unit was simply condensed, collected, and analyzed by both gas chromatography and infrared spectroscopy. No metal was present in the reactor, and the probe was held at a sufficiently high temperature to preclude the presence of a condensed phase in the hot reaction zone. At 3 psia total pressure (152 mm Hg), no detectable reaction occurred at 350 and 400°F. At 450°F, a reaction product other than decane was observed. At a fixed temperature of 475°F, runs were made with decane at 75, 152, and 300 mm Hg total pressure. Analyses of the condensed overhead product indicated increased decane conversion and a wider spectrum of reaction products as the total pressure was increased. Infrared spectra indicate the presence of carbonyl (C=O) and hydroxyl (OH) groups in the product. The product obtained under our most severe conditions (475°F and 300 mm Hg total pressure) consisted of both an aqueous and a nonaqueous phase. Vacuum distillation of the reaction product coupled with gas chromatographic and infrared analyses of the individual fractions indicated a very large number of compounds were present. Oxygenated compounds were present in both phases. The aqueous phase included a hydrocarbon insoluble high molecular weight material (boiling point in excess of 160°C at 0.1 mm Hg pressure). It is significant that this "polymer" material is insoluble in hydrocarbon media. This suggests that any such material formed in an "empty" wing tank will not be washed out by a fresh charge of jet fuel. This material was a brownish, highly viscous liquid. An infrared spectral analysis was made of this hydrocarbon insoluble polymer. Absorption bands and absorbing groups assigned to these bands are shown in Table X. Assignments were made according to References (136 and 137). Among the groups present were OH, C=O, and C=C. The spectrum of the polymer is quite similar to those obtained when typical drying oils are oxidatively polymerized to solid films (137). Also shown in Table X are spectra of a Deposit formed in a Screening Unit run with RAF-176-63. The spectra of this material are quite similar to that obtained from the hydrocarbon insoluble "polymer" formed with n-decane. The data indicate that this type of oxidative reaction product is probably a direct precursor of "empty" wing tank type deposits.

FIGURE 56

Scanning Electron Micrographs of 362-84-5



X 2,300



X 2,220

FIGURE 57

Scanning Electron Micrographs of 362-84-5



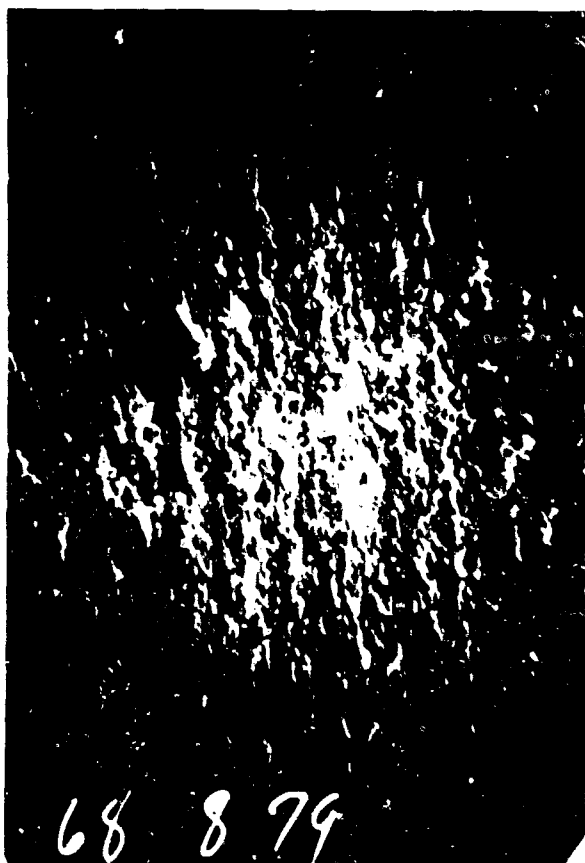
X 22,500 Q 45



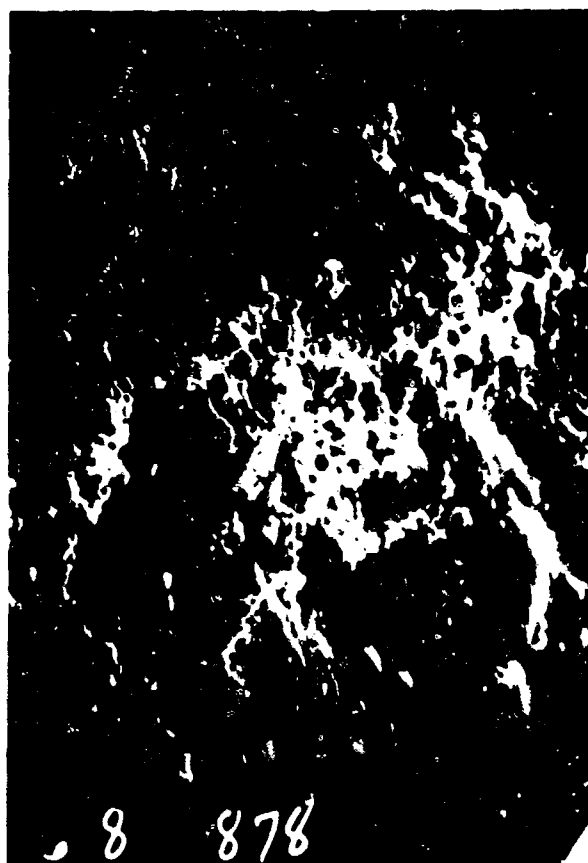
X 2,250

FIGURE 58

Scanning Electron Micrographs of 390-45-4



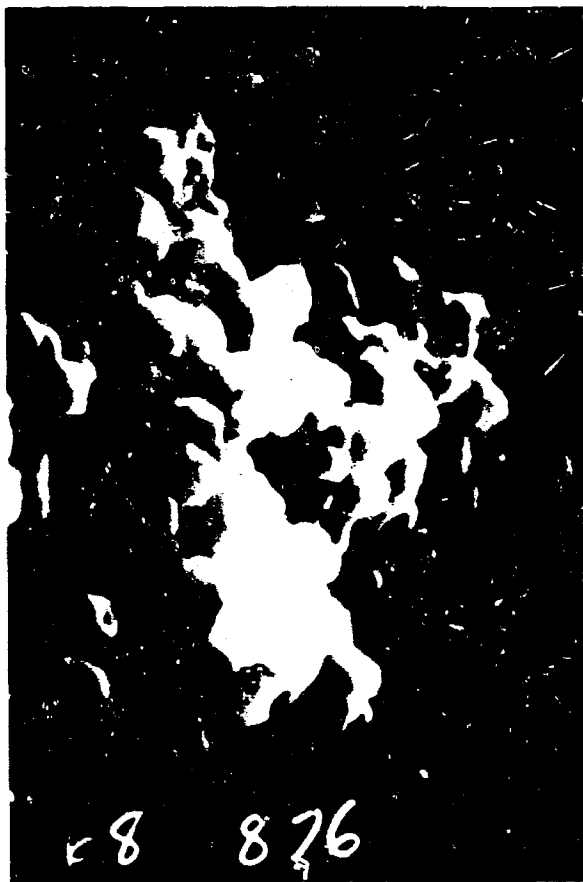
X 210



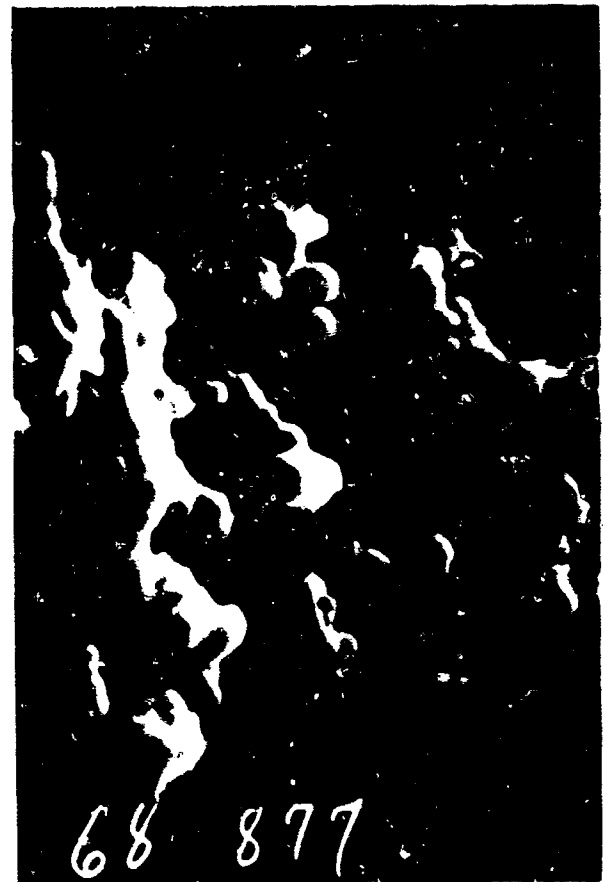
X 2,100

FIGURE 59

Scanning Electron Micrographs of 390-45-4



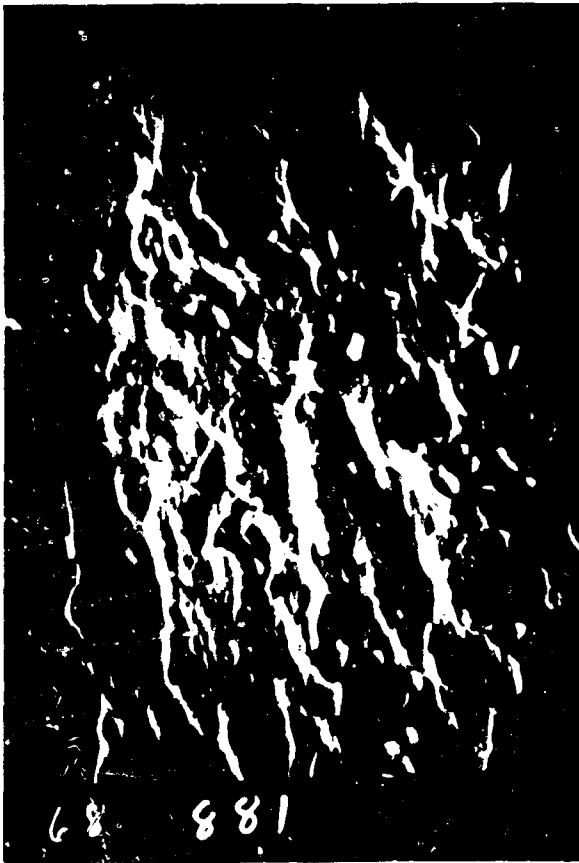
X 21,700 @ 45



X 21,000

FIGURE 60

Scanning Electron Micrographs of 362-100-1



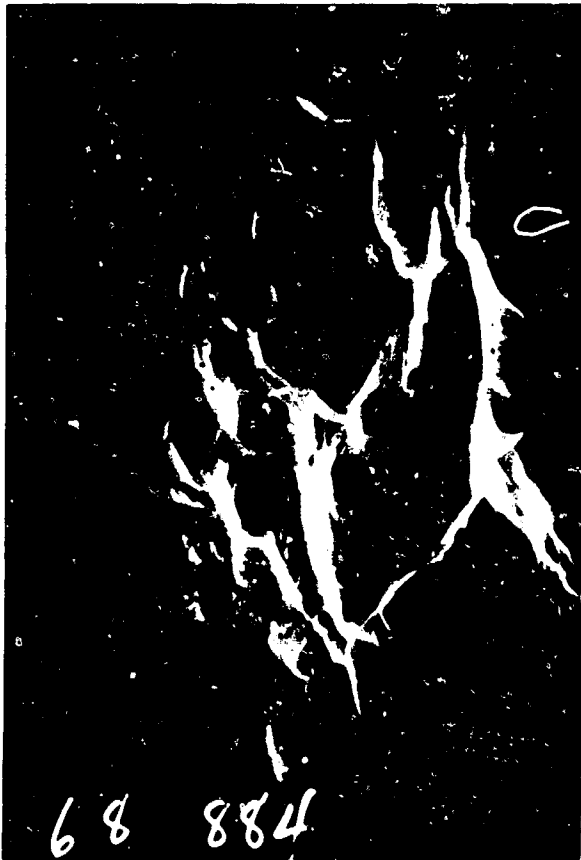
X 2,120



X 21,200 @ 45

FIGURE 61

Scanning Electron Micrographs of 390-20-1



X 2,260



X 22,600 @ 45

FIGURE 62

Scanning Electron Micrographs of 390-19-4



X 228



X 220

FIGURE 63

Scanning Electron Micrographs of 390-19-4



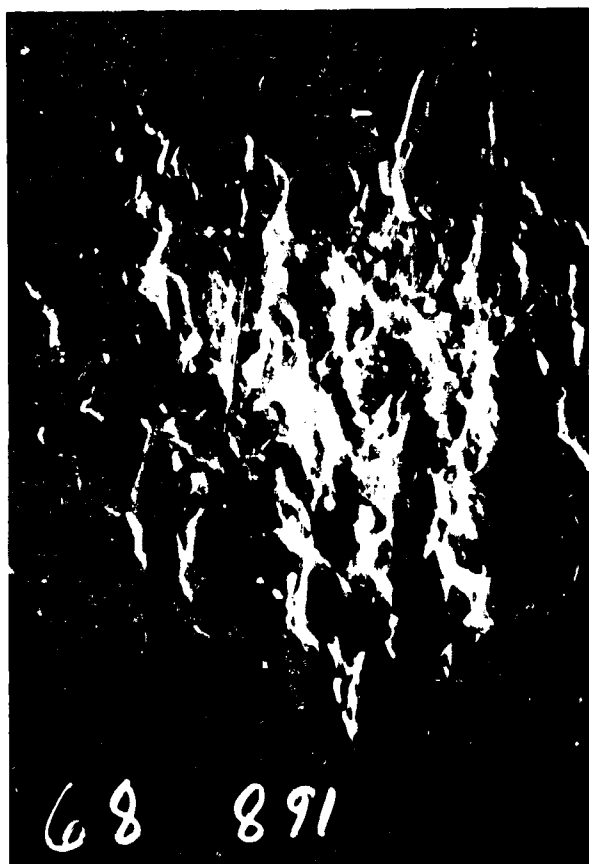
X 2,280



X 22,300 @ 45

FIGURE 64

Scanning Electron Micrographs of 362-43-3



X 2,020



X 20,200 @ 45

TABLE X

Infra-red Spectral Analyses

Hydrocarbon Insoluble "Polymer" from Decane Oxidation		Deposit Formed in the Screening Unit from RAF-176-63	
Position of Absorption Band and Intensity ^(a)	Absorbing Group ^(b)	Position of Absorption Band and Intensity ^(a)	Absorbing Group ^(b)
3500 cm^{-1} (M)	OH	3500 cm^{-1} (M)	OH
2950 cm^{-1} (S) 2910 2870	CH	2950 cm^{-1} (S) 2910 2870	CH
1720 cm^{-1} (S)	C=O	1720 cm^{-1} (S) 1745 (M)	C=O
1600 cm^{-1} (W)	C=C	1630 cm^{-1} (M) to 1600 cm^{-1} (M)	C=C
1450 cm^{-1} (W)	CH	1450 cm^{-1} (S)	CH
1360 cm^{-1} (M)	CH OH, C-O	1360 cm^{-1} (M)	CH OH, C-O
1150 cm^{-1} (M)	C-C		

(a) (S) = strong, (M) = medium, (W) = weak.

(b) Assignment per references (1) and (2).

III. PHASE II STUDIES: INVESTIGATION OF POTENTIAL METHODS TO ALLEVIATE THE PROBLEM

A. Evaluation of the "Empty" Wing Tank Deposit Formulation Tendency of Commercial Jet Fuels

1. Quantitative Measurement of the Deposit Formation Rate of Various Fuels

The deposit formation rates of a number of jet fuels were measured. In general, a standard Screening Unit test involving 3 psia pressure, use of Ti-8Al-1Mo-1V strips and a four hour run period with undiluted air was employed. Results of these tests are shown in Figures 65 to 72. As can be seen considerable variation in the deposit formation tendency of jet fuels exists. Data are shown in Appendix 11.

2. Analytical Characterization of Typical Jet Fuels

Analytical characterization of the five jet fuels included in our program has been completed. The results are tabulated in Tables XI and XII. The analyses show that the composition of the different fuels varies considerably, both in compound type and quantity of trace impurities, e.g., sulfur compounds. Typical pure compound boiling points show that the paraffins present in a typical jet fuel should fall in a C_8 to C_{16} carbon number range. The majority of naphthenes and aromatics present are single ring compounds. Based on pure compound boiling points, these mono ring compounds should have a C_9 carbon number or higher.

B. The Effect of Rigorous Exclusion of Oxygen

As part of the studies conducted in the Phase Study Unit, the effect of vigorous exclusion of oxygen on the overall deposit formation process was investigated. An examination of these results indicate that the rigorous exclusion of oxygen suppressed deposit formation at temperatures up to 460°F even in the presence of a liquid phase and a metal surface. These results undoubtedly reflect the suppression of autoxidative reactions which the complete removal of oxygen effects.

C. The Effect of Current Additives on Deposit Formation

The effect of various additives on the deposit formation process was evaluated using two different additive free jet fuels as the reference fuel. These fuels were chosen because of their different stability toward deposit formation. In addition to antioxidants, other additives currently employed in jet fuels were evaluated. Additive treating levels were chosen to correspond to current practice. The additives employed and the levels used are shown in Table XIII. All additive treated fuels were evaluated in at least two separate, replicate runs. A run with the base fuel

FIGURE 65

SCREENING UNIT TESTS OF FA-S-2B, BATON
ROUGE AND P&W 523 FUELS AT 3 PSI

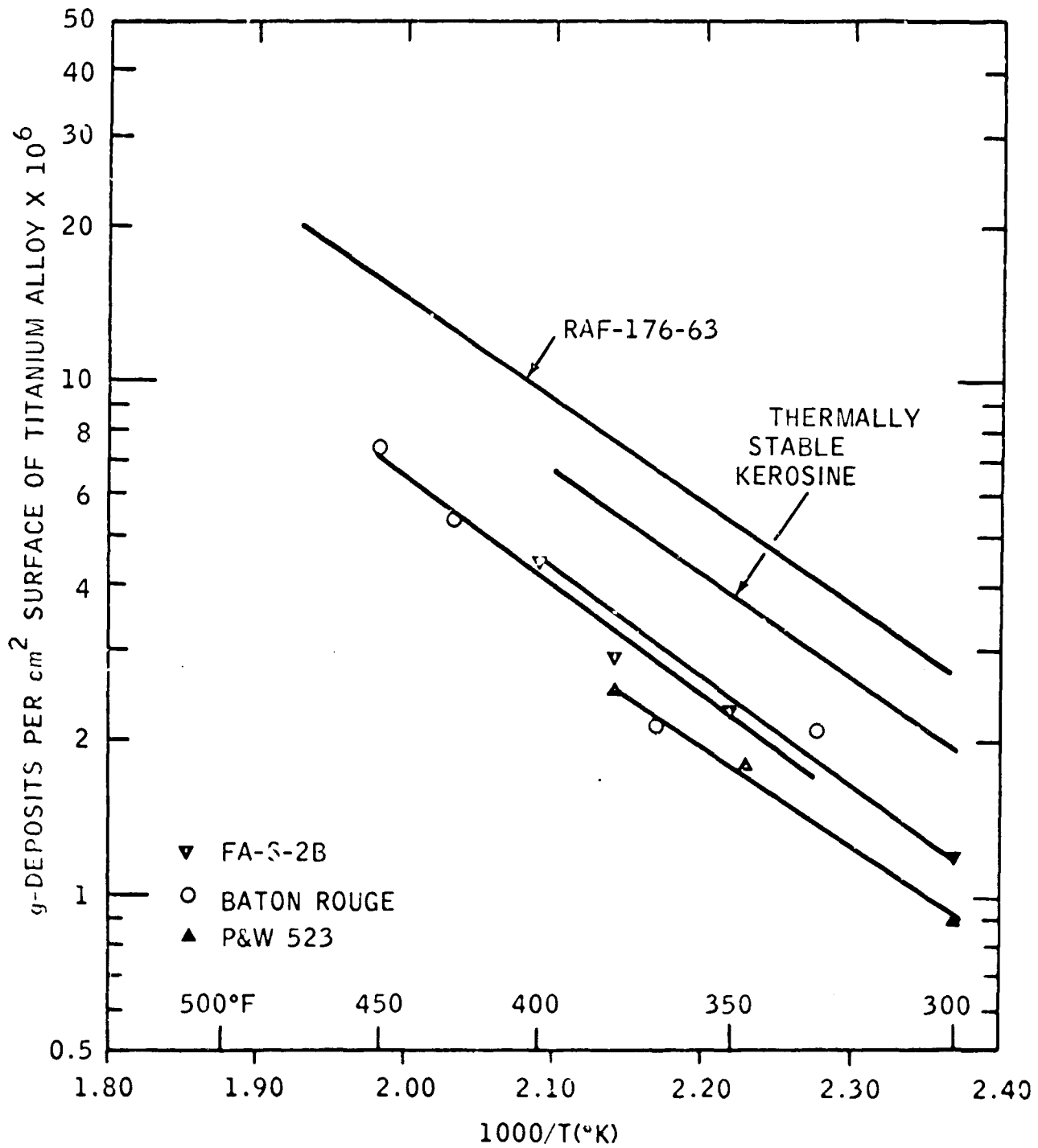


FIGURE 66

SCREENING UNIT TEST OF AFFB-9-67

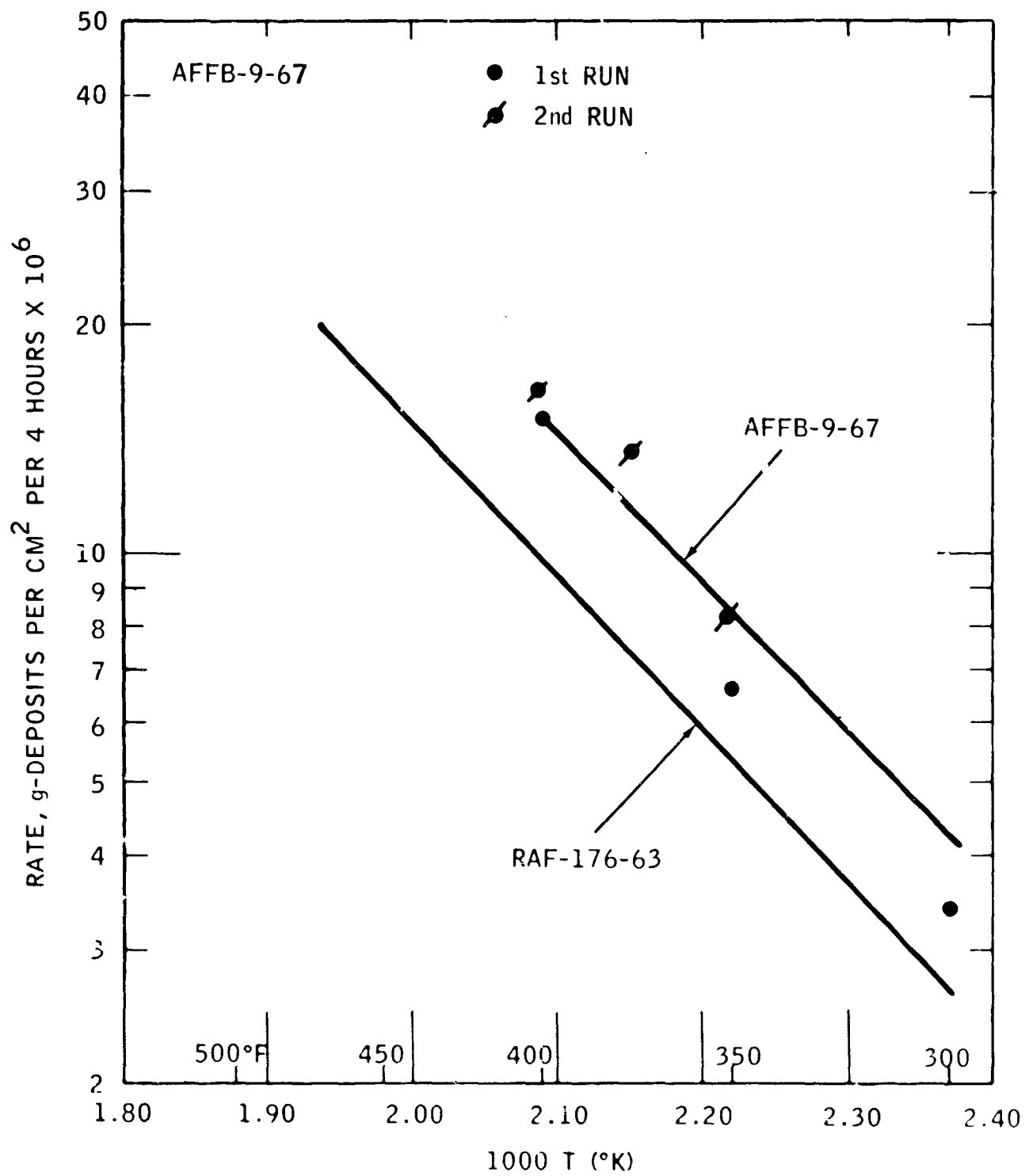


FIGURE 67

SCREENING UNIT EVALUATION
OF AFFE-12-68 AT 3 PSIA

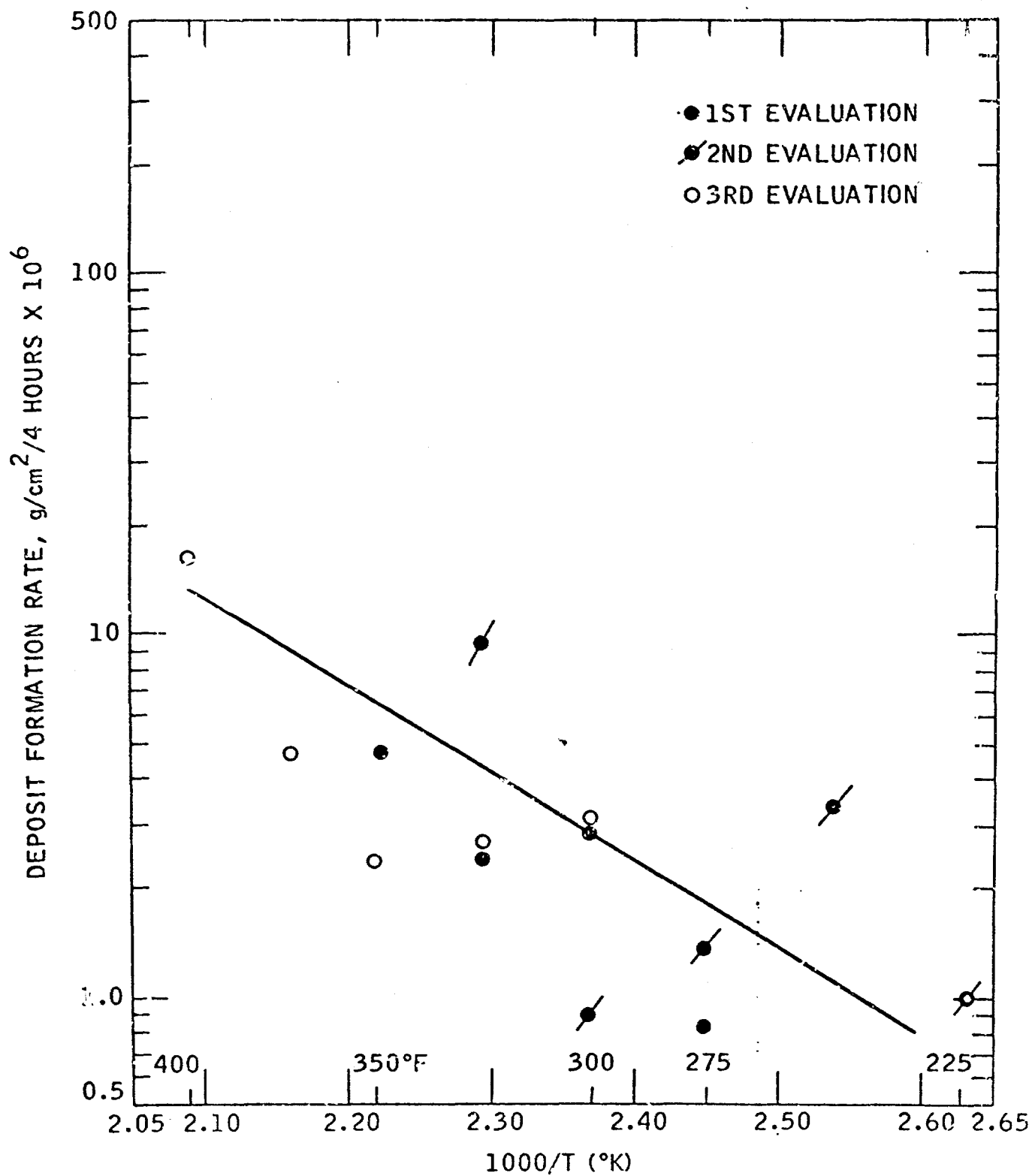


FIGURE 68

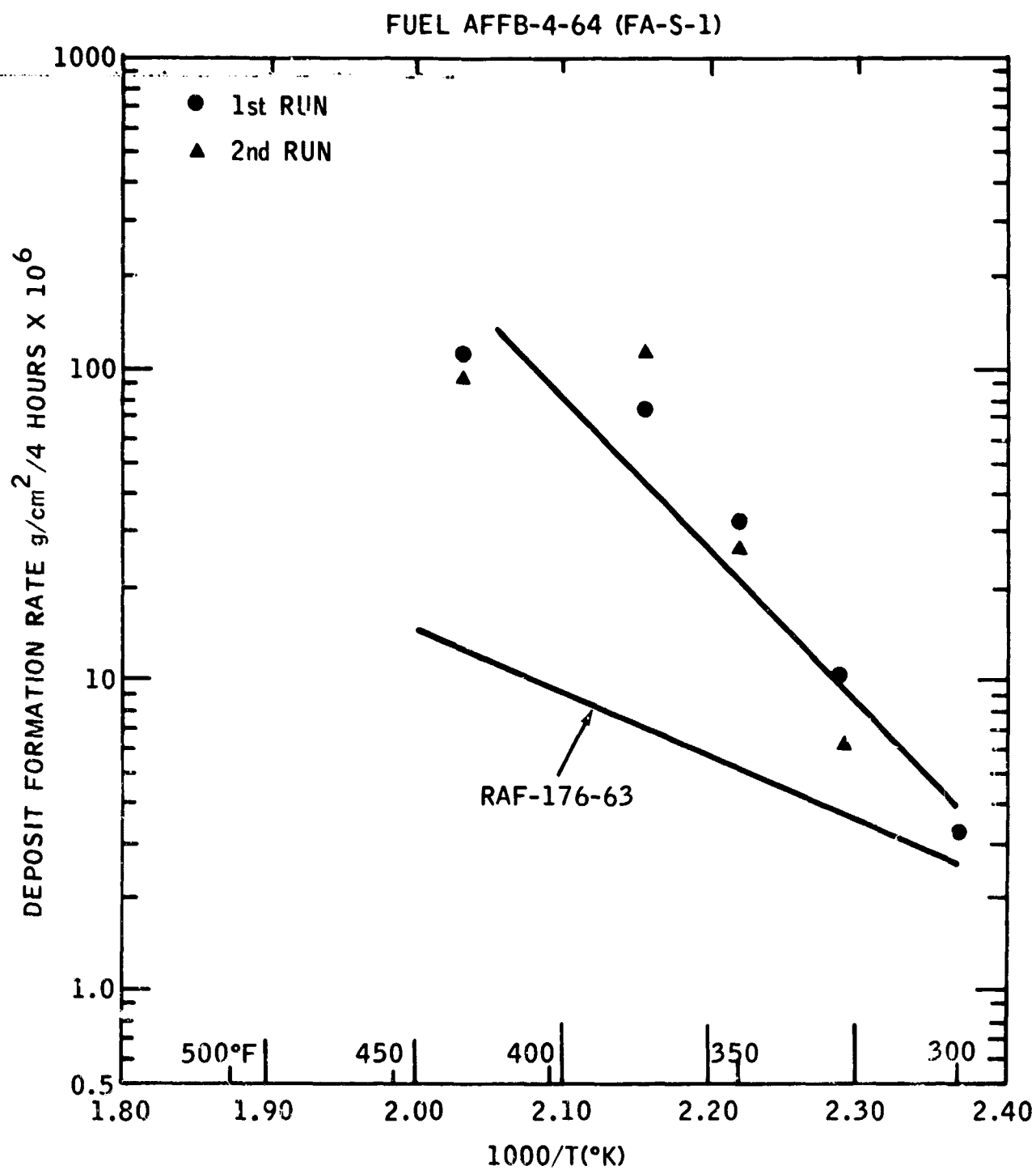


FIGURE 69

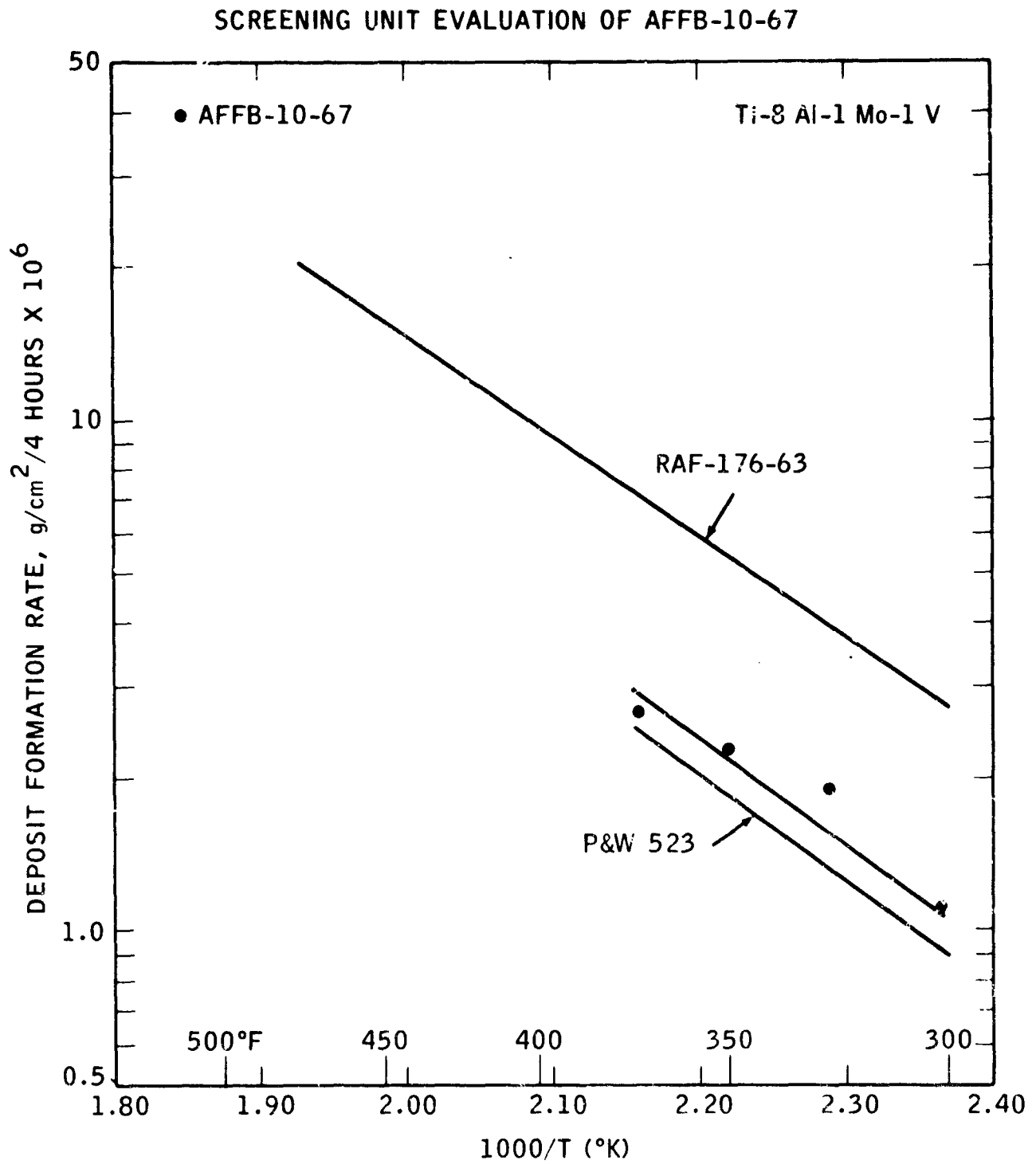


FIGURE 70

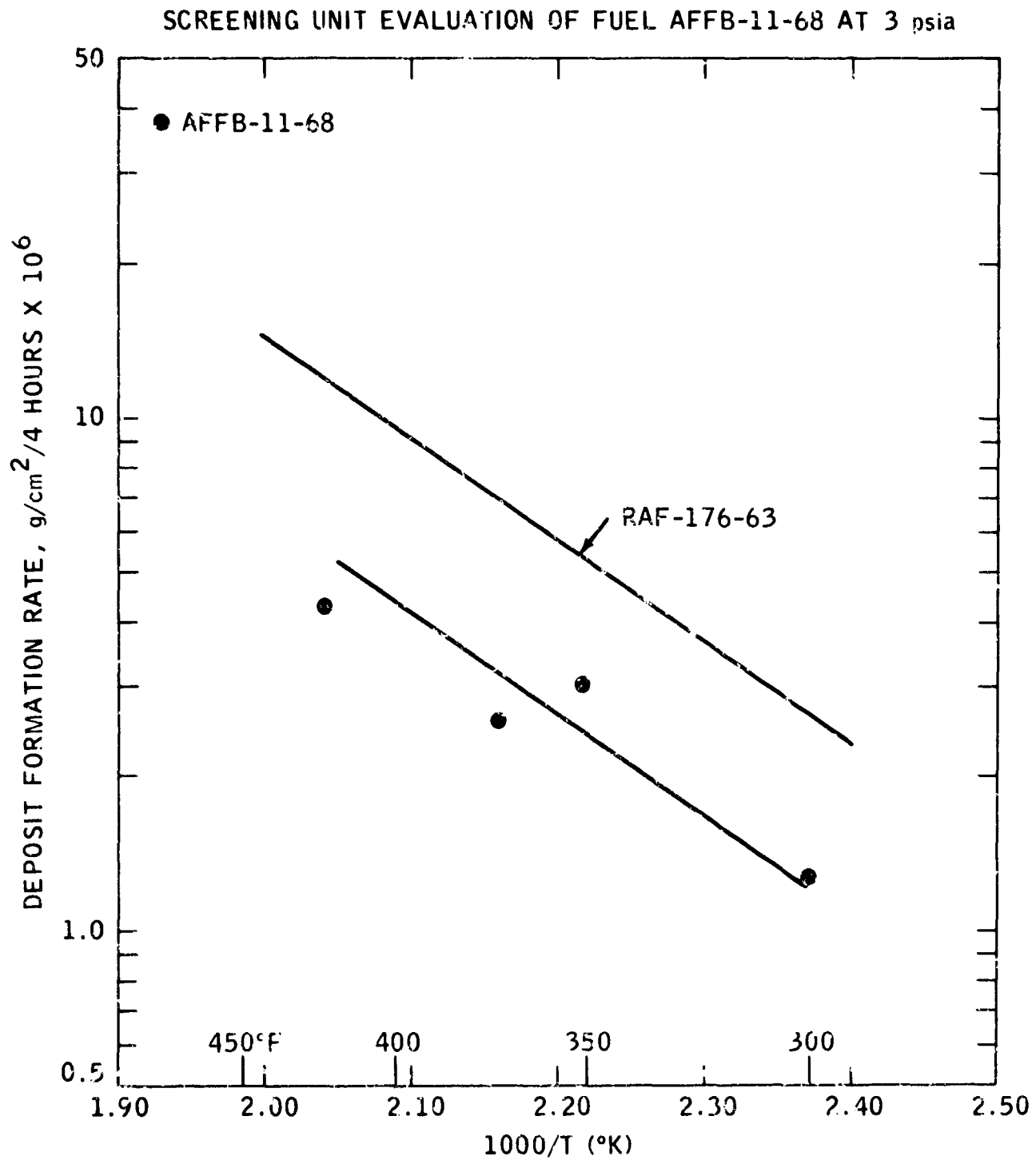


FIGURE 71

SCREENING UNIT EVALUATION OF RAF-174-63

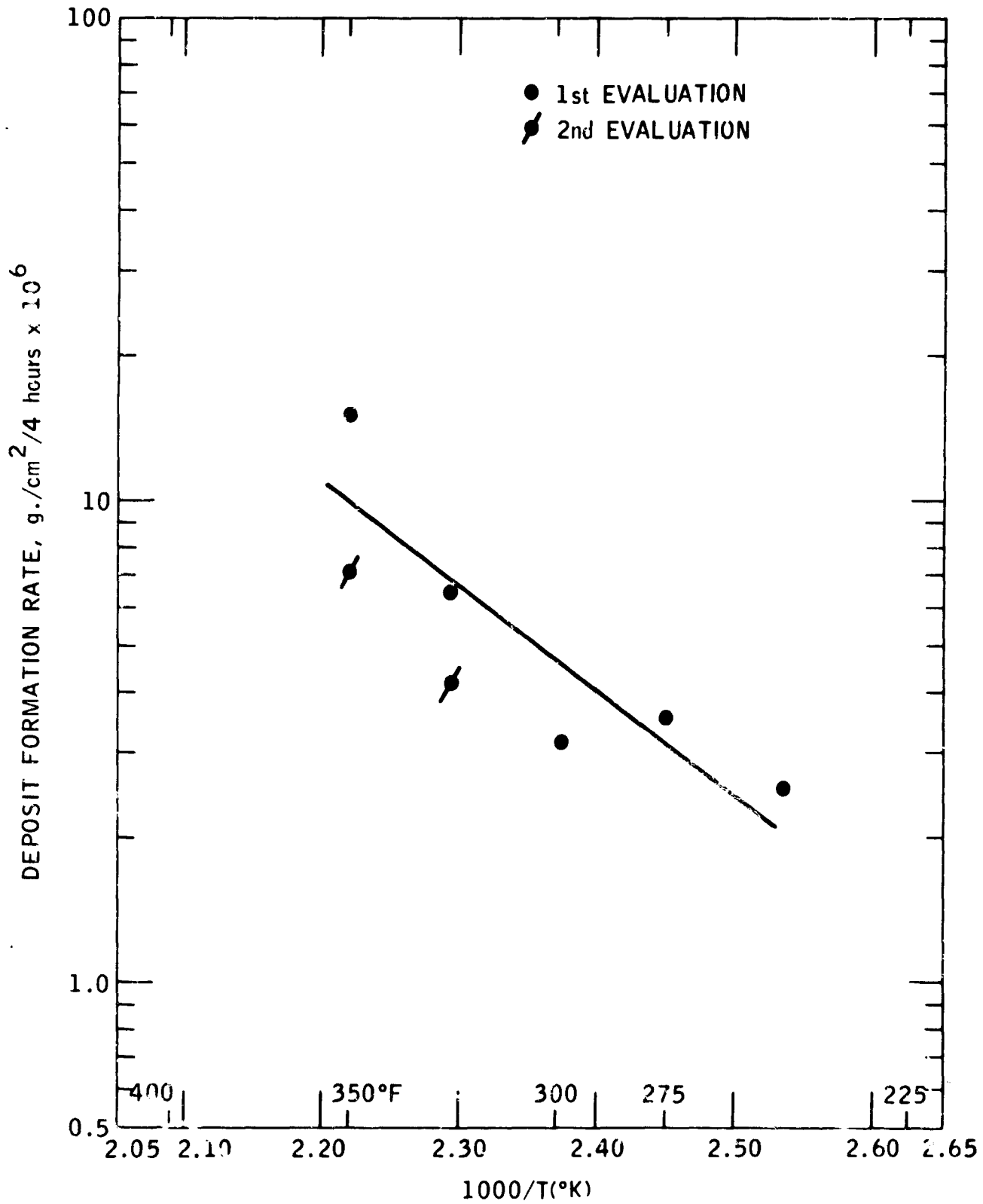


FIGURE 72

SCREENING UNIT EVALUATION
OF AFFB-8-67 AT 3 psia

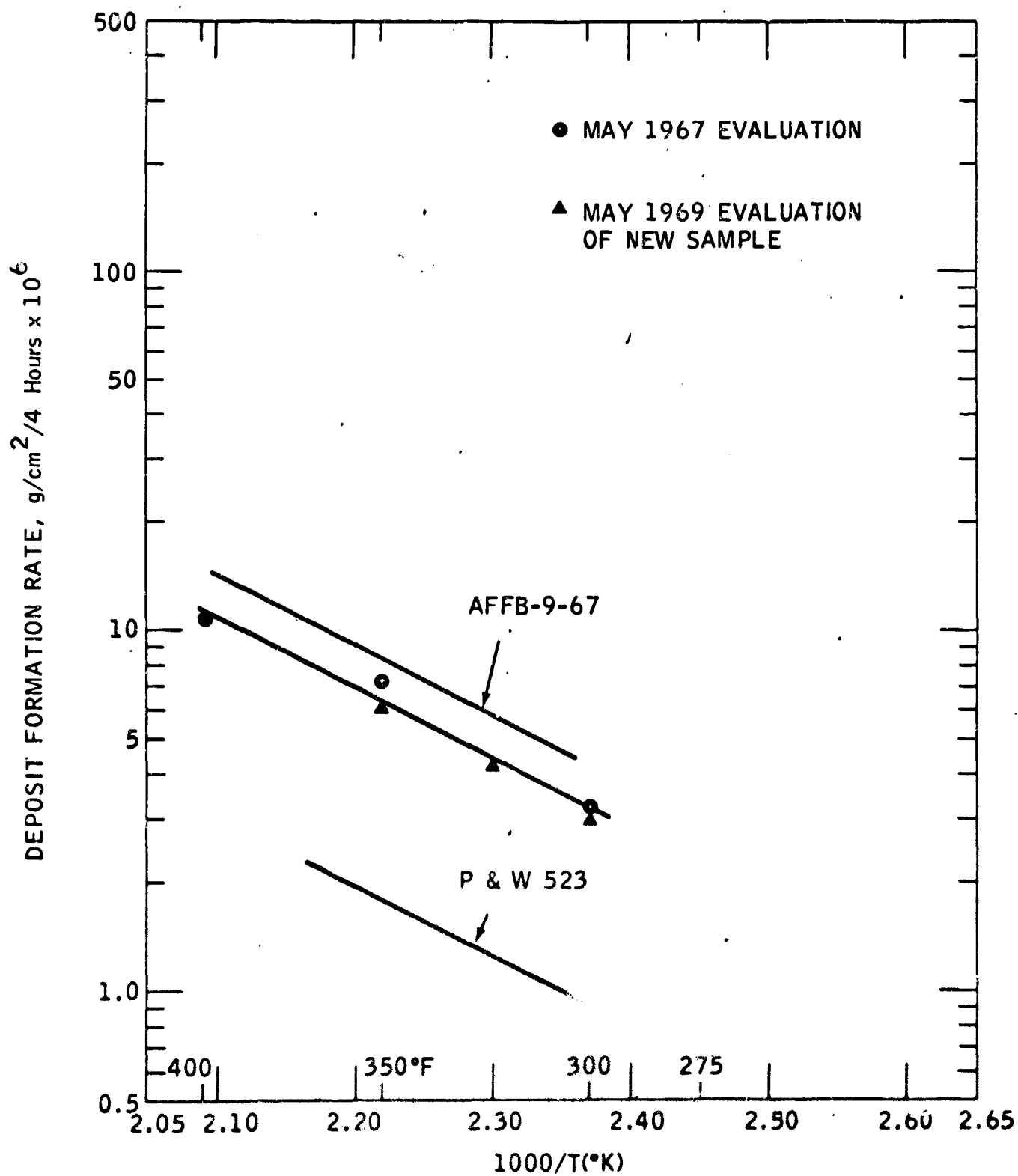


TABLE XI

Physical Inspections of Jet Fuels

	RAF-176-63	FA-S-2B (AFFB-3-64)	Baton Rouge SST Test Fuel	Thermally Stable Kerosene (Humble Formula 86)	Supersonic Jet Fuel P&W 523 (Humble Formula 90)
Distillation, ASTM, °F					
IBP	334 ^(a)	330 ^(a)	336	368	403
5%	348	-	355	372	412
10%	356	344	364	373	414
20%	366	348	379	374	417
30%	374	-	389	376	419
40%	384	-	398	377	422
50%	394	362	407	378	426
60%	406	-	417	380	429
70%	419	-	428	382	434
80%	435	-	442	384	440
90%	454	-	458	384	449
95%	466	-	471	397	457
F.B.P.	484	456	481	409	463
Recovery %	99.0	99.2	98.0	98.0	98.0
Loss %	-	0.8	-	-	-
Residual %	1.0	0.8	2.0	2.0	2.0
Total Sulfur, Wt. %	.07; .076 ^(a)	.0070; .02 ^(a)	.03	.0008	<.00002
Mercaptan Sulfur, Wt. %	.0005; .0005 ^(a)	.0002 ^(a)	.00032	<.0003	<.0003
Total Nitrogen, ppm	<5 ^(a)	<1.0	1.9	1.1	<1.0
Basic Nitrogen, ppm	2.1 ^(a)	<1	-	<1	<1
C, Wt. %	-	84.98	85.93	85.76	84.73
H, Wt. %	-	14.73	13.75	14.50	15.11
Peroxide No. Millequiv. of O ₂ per liter	Nil	0.41	Nil	Nil	Nil
Trace Metals, ash at 1000°F, Wt. %	<.001 ^(b)	<.001 ^(b)	<.001 ^(b)	<.001 ^(b)	<.001 ^(b)
Additives added to the fuel	No	No	No	Yes	Yes

(a) Reported in North American Aviation report NA-65-753, November, 1965.

(b) Insufficient ash for trace metals analyses by emission spec.

TABLE XI

Distribution of Compound Types in Jet Fuels

	RAF-17b-63	FA-S-2B (AFFB-3-64)	Baton Rouge SST Test Fuel	Thermally Stable Kerosene (Humble Formula 86)	Supersonic, Jet Fuel P&W 523 (Humble Formula 90)
Paraffin, Naphthene, Aromatic Distribution, Wt.%(a)					
Paraffins	41.6	55.6	41.7	64.6	87.7, 87.6 ^(b)
Naphthenes (cycloparaffins)					
Non Condensed	26.0	36.4	23.9	18.5	6.9
2 Ring Condensed	13.4	.4	12.5	5.7	0.8
3 Ring Condensed	1.7	0.1	4.5	0.4	2.8
Total	41.7	42.9	40.9	24.6	10.5, 10.8 ^(b)
Aromatics:					
Alkyl Benzenes	10.2	1.3	10.8	9.4	0.9
Indans	3.3	0.2	2.4	1.4	0.9
Naphthalenes	3.2	0.0	4.2	0.0	0.0
Total	16.7	1.5	17.4	10.8	1.8, 1.6 ^(b)
Grand Total	100.0	100.0	100.0	100.0	100.0
Olefin, Non-Olefin Distribution, Vol.%(c)					
Olefins (non-aromatic)	1.5	2.3	1.0	1.5	0.7
Other	98.5	97.7	99.0	98.5	99.3
Total	100.0	100.0	100.0	100.0	100.0

(a) Analysis by mass spectrometer.

(b) Independent analysis obtained by Products Research Division, Esso Research and Engineering Company.

(c) Analysis by FIA.

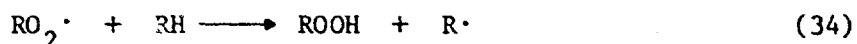
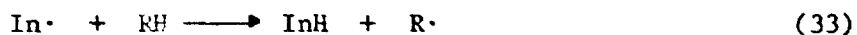
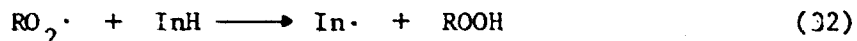
TABLE XIII
SUMMARY OF THE EFFECT OF
VARIOUS ADDITIVES ON DEPOSIT FORMATION

Additive	Type	Chemical Identification (a)	Additive Level and Fuel Employed	Relative Activity of Treated Fuel for Deposit Formation at 375°F (b)
A	Antioxidant	N,N'-disubstituted-butyl Paraphenylenediamine	30 ppm wt. in Fuel A	1.0
B	Antioxidant	2,6-Ditertiarybutyl 4-methyl phenol	30 ppm wt. in Fuel B	1.0
C	Antioxidant	2,4-dimethyl 6 tertiary butyl phenol (72%) plus mixed alkylated phenols (28%)	30 ppm wt. in Fuel B	1.0
D	Antioxidant	2,6-ditertiarybutyl phenol (75%) 2,4,6-tritertiary butyl phenol (13%), ortho tertiarybutyl phenol	30 ppm wt. in Fuel B	1.0
E	Rust Preventive	Alkylaminoalkyl phosphate (80%), kerosene (20%)	66 ppm wt. in Fuel B	7.8
F	Rust Preventive	Santolene C(c)	66 ppm wt in Fuel B	8.6
G	Metal Deactivator	N,N'-disubstituted, 1,2 propane-diamine (80%) solvent (20%)	8 ppm wt. in Fuel B	4.7
H	Anti-icing	Ethylene glycol monoethyl ether acetate	0.07 vol. % in Fuel B 0.15 vol. % in Fuel B	1.0 1.0

- (a) Based on manufacturers disclosure for the additives identified in the experimental reagent section.
- (b) Rate of deposit formation of treated fuel relative to the rate of deposit formation of untreated base fuel at 375°F
- (c) Composition not disclosed but indicated by manufacturers to contain 0.31 wt. % (minimum) phosphorus.

containing no additives was also made at the same time so as to both concretely establish the deposit formation rate with the reference fuel and to verify the accuracy and reproducibility of the test procedure during the additive evaluation program. Deposit formation rates were determined in the Screening Unit at 3 psia using Ti-8Al-1Mo-1V titanium alloy strips. Tests with the antioxidant containing fuels indicated that the addition of these antioxidants at the levels employed did not significantly reduce the rate of deposit formation at 300 to 425°F. Data are shown in detail in the Arrhenius plots in Figures 73 to 76. Results are summarized in Table XIII. Similarly, the use of methylcellosolve and a fluoro-carbon lubricity additive resulted in no measurable effect on the rate of deposit formation in the 300 to 425°F temperature range (Figures 80 to 91). By contrast, fuels treated with rust inhibitor and metal deactivator additives all showed a marked increase in the deposit formation level, particularly at temperatures above 350°F. Data are shown in detail in the Arrhenius plots in Figures 77, 78 and 79. Results are summarized in Table XIII. Data are in Appendix 12.

The addition of typical antioxidants to jet fuels did not suppress the autoxidative process which leads to the formation of deposits at 300 to 425°F. The inhibition of autoxidative reactions by small quantities of an additive has been studied extensively, and a number of excellent summaries are available (22,138). In general, an effective inhibitor, InH, (a) must react rapidly with the chain carrying peroxy radicals, Eq. 32, and (b) form a relatively stable radical product, i.e., the rate of reaction of the radical In·, Eq. 33, must be much lower than the rate of reaction of peroxy radicals, Eq. 34.



Thus, an effective inhibitor basically scavenges active radicals from the reaction system, and as a result of this suppresses the overall rate of oxidation.

As pointed out by Emanuel et al (138) oxidation inhibitors tend to be much less effective in a degenerately branched reaction, reflecting, for example, the relatively high concentration of radicals in such a system. In the present work, deposits form as the result of autoxidative degradation of the hydrocarbon fuel at 300°F and higher, and in the presence of catalytically active metal surfaces. Extensive decomposition of hydroperoxides must take place in this temperature range and environment so that reduced inhibitor effectiveness would be expected. In addition, the antioxidants tested were basically developed to improve the low temperature stability of hydrocarbons (e.g., storage at ambient conditions), where the relative rate of typical autoxidation reactions are probably quite different than those encountered at higher temperatures. Thus, the present failure of these inhibitors to suppress autoxidative deposit formations would seem to simply reflect to a great extent the high temperature stress being placed on the fuel.

FIGURE 73

EVALUATION OF A022 ADDITIVE
IN RAF-176-63 FUEL

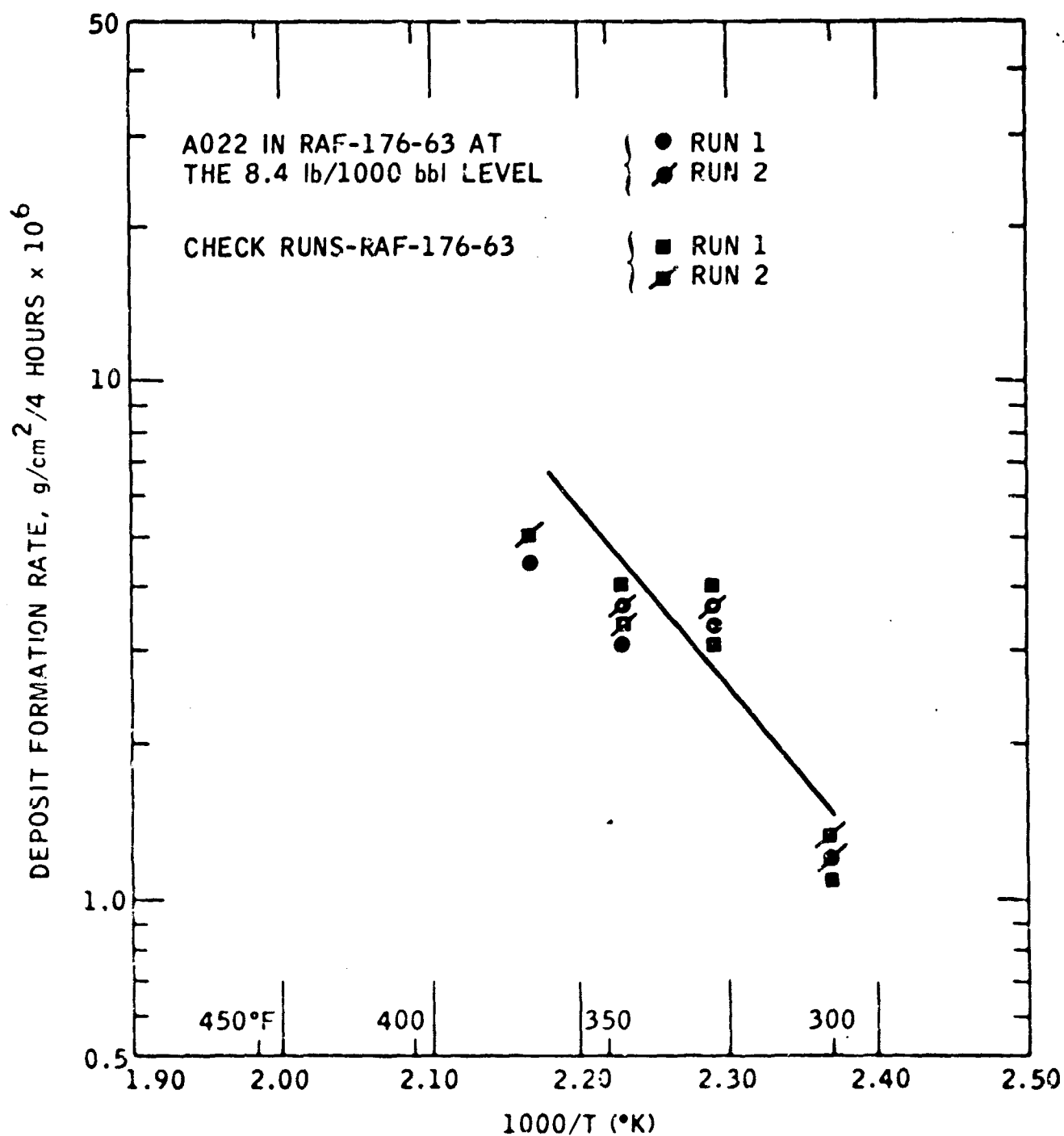


FIGURE 74

EVALUATION OF A029 ADDITIVE
IN BATON ROUGE FUEL

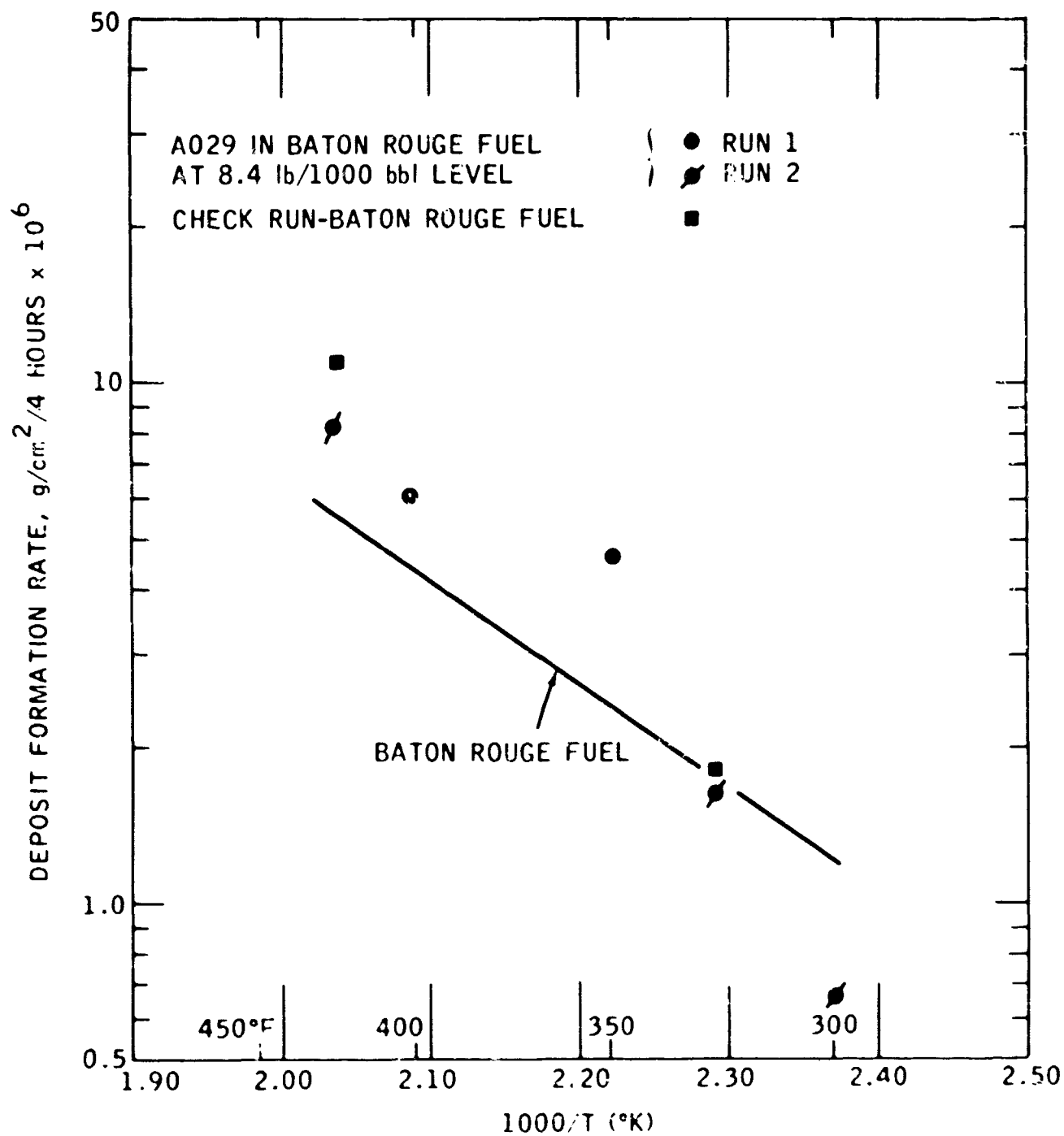


FIGURE 75

EVALUATION OF A031 ADDITIVE
IN BATON ROUGE FUEL

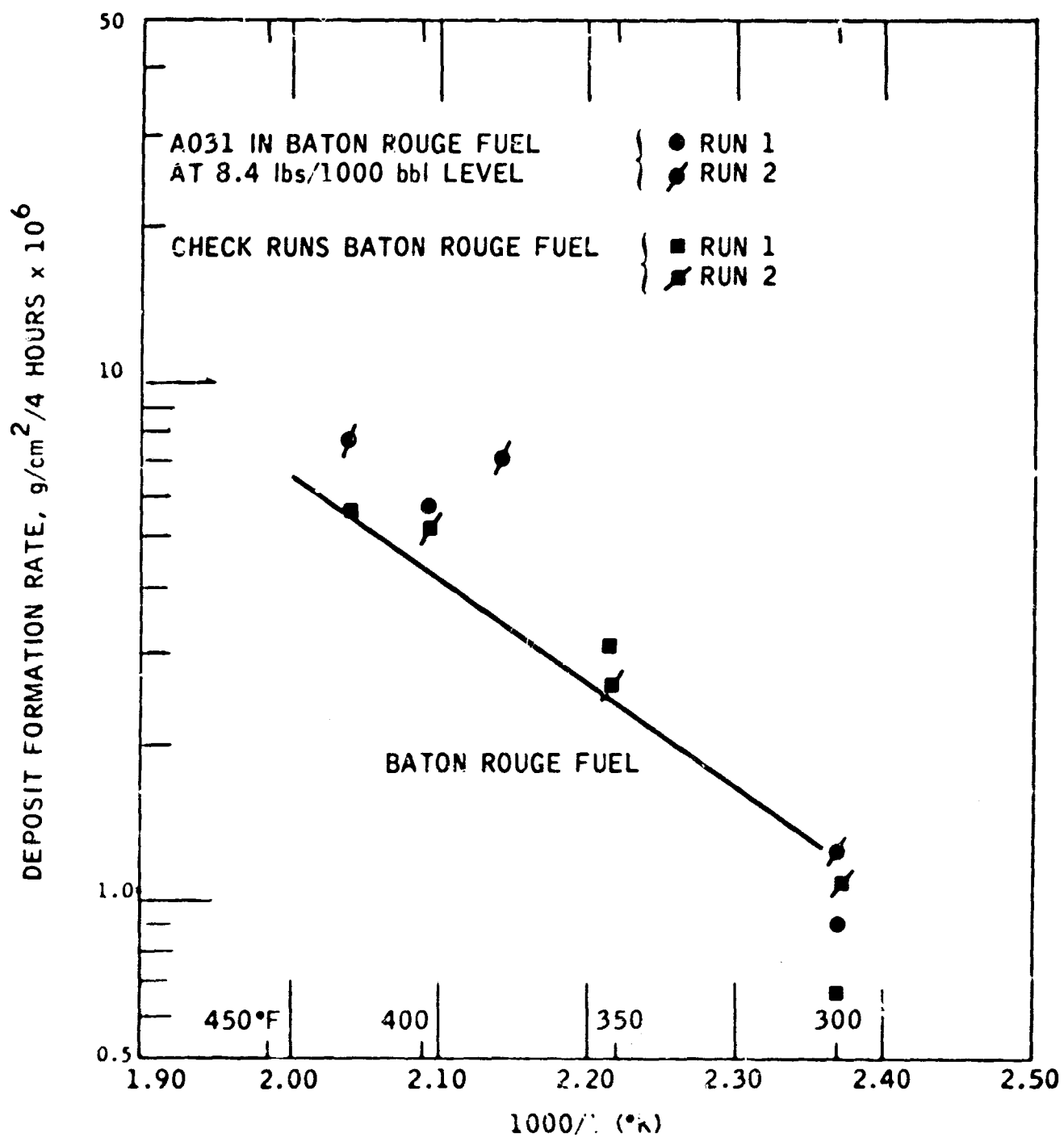


FIGURE 76

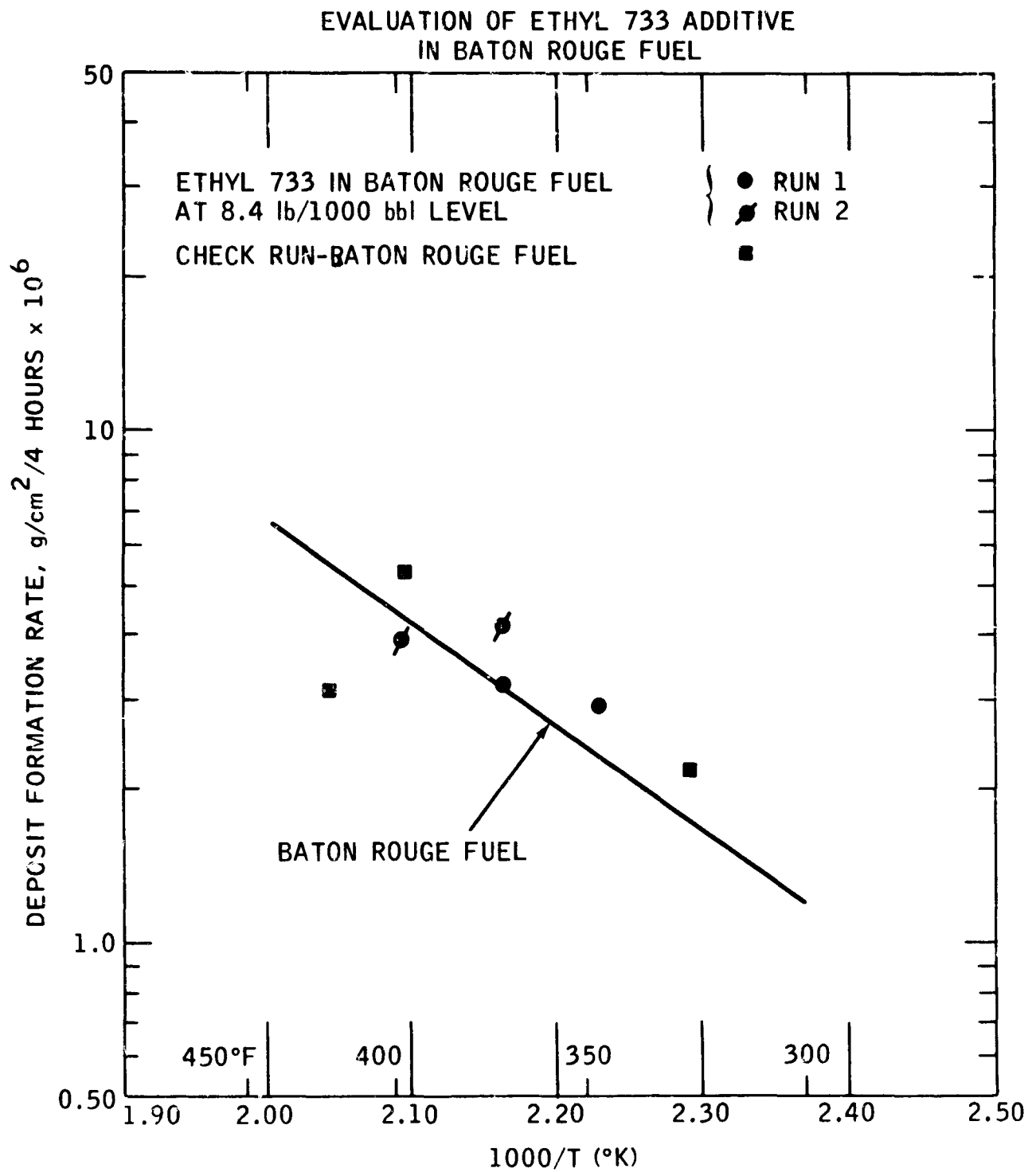


FIGURE 77

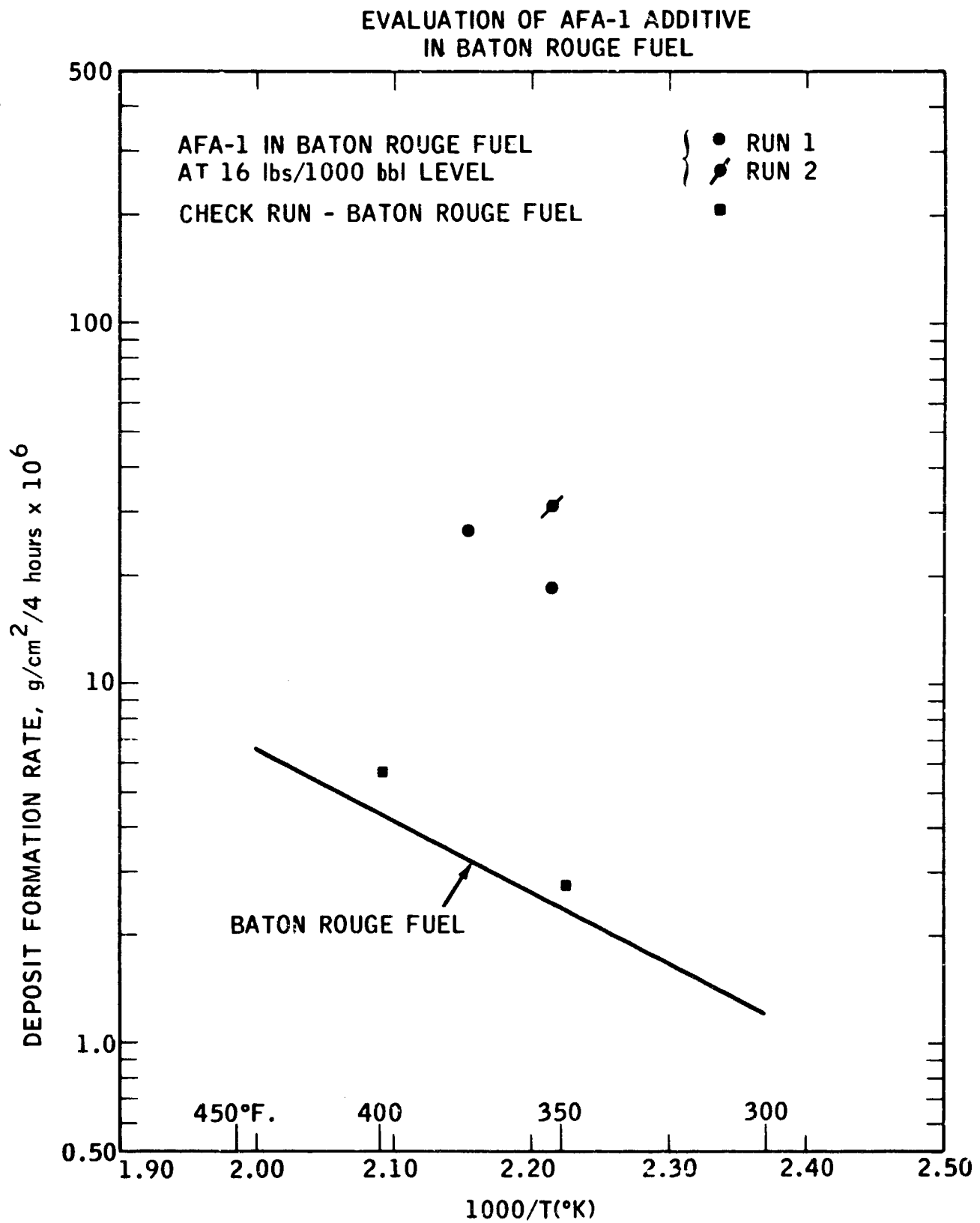


FIGURE 78

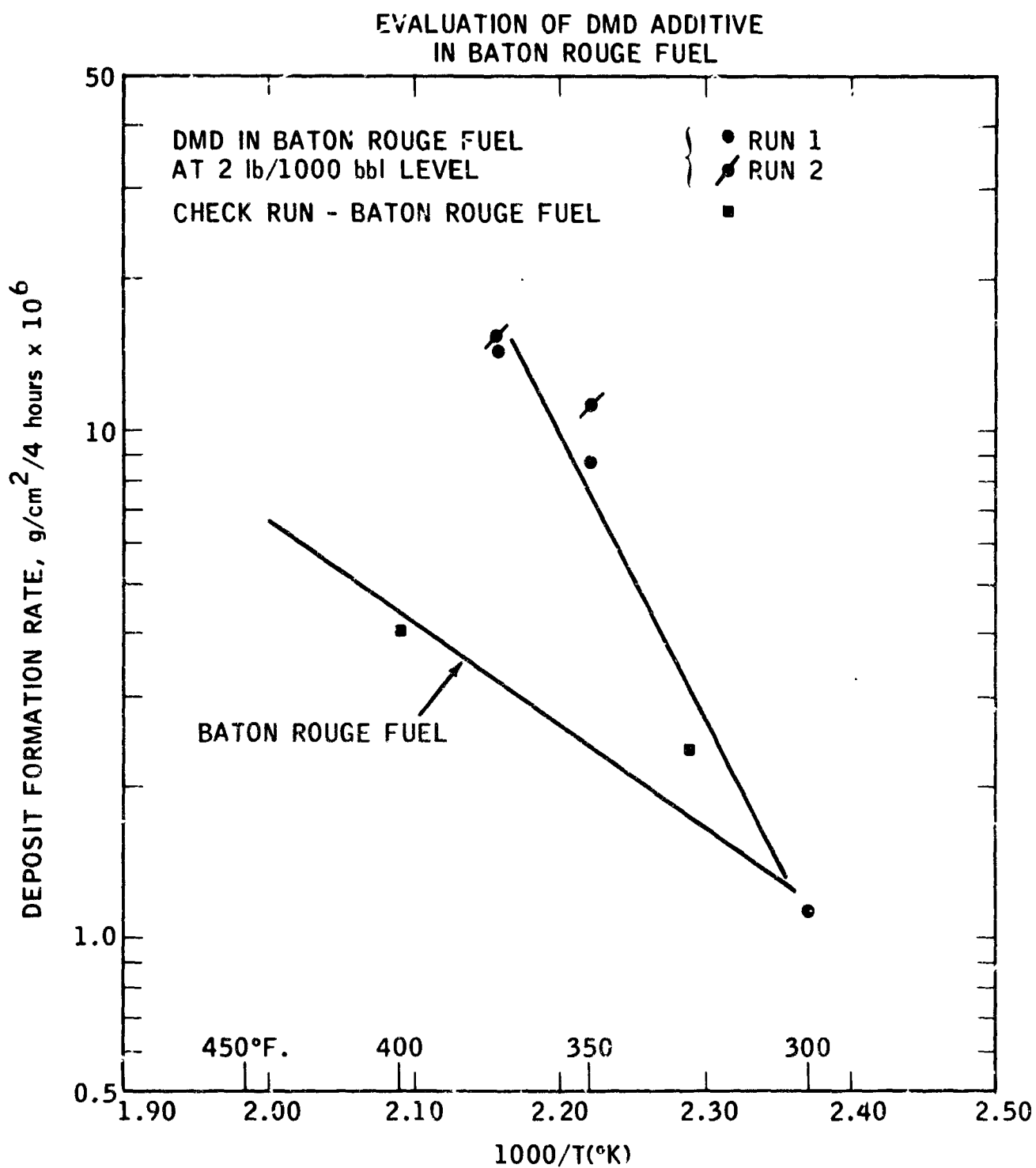


FIGURE 79

EVALUATION OF SANTOLENE C
ADDITIVE IN BATON ROUGE FUEL

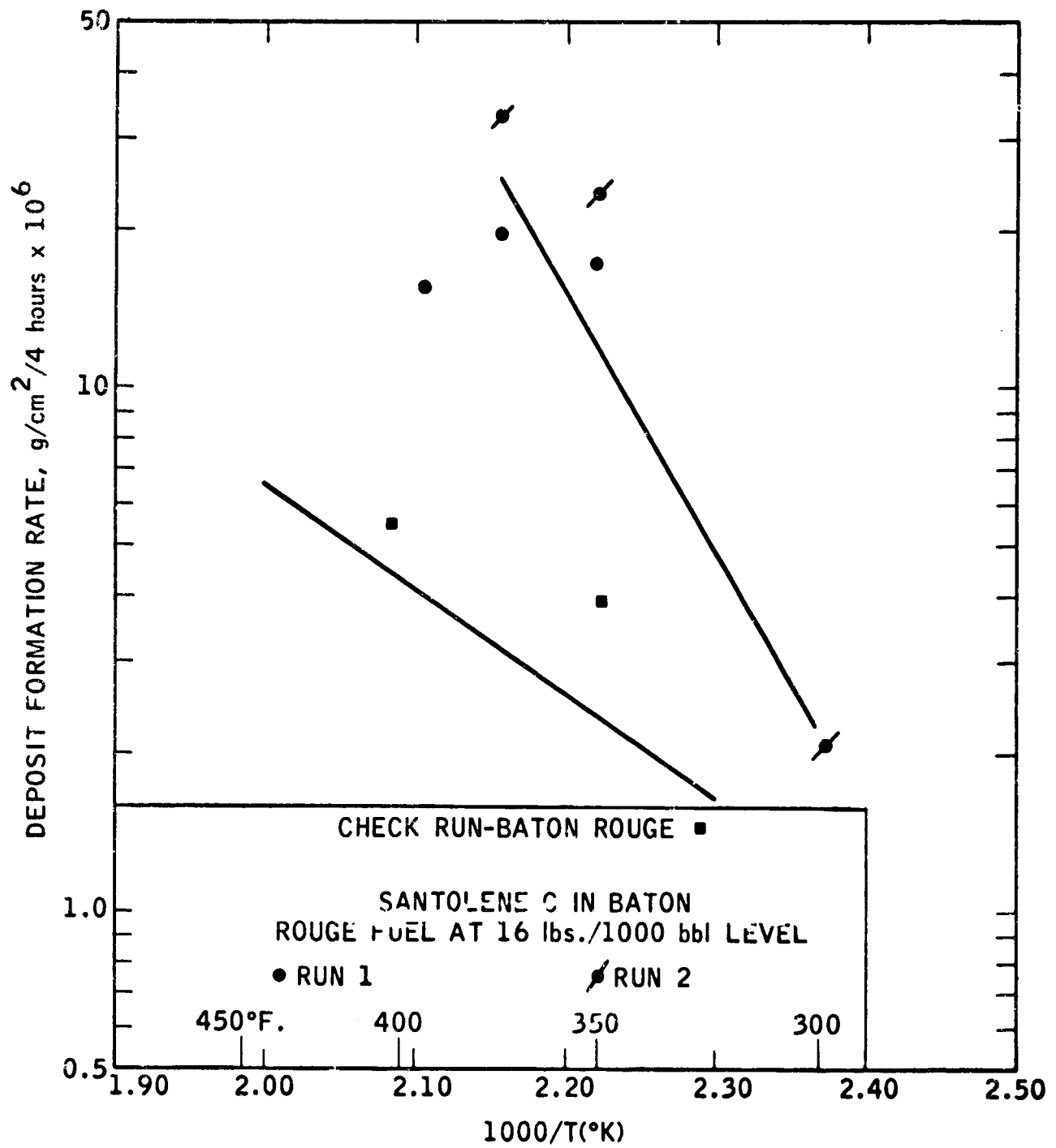


FIGURE 80

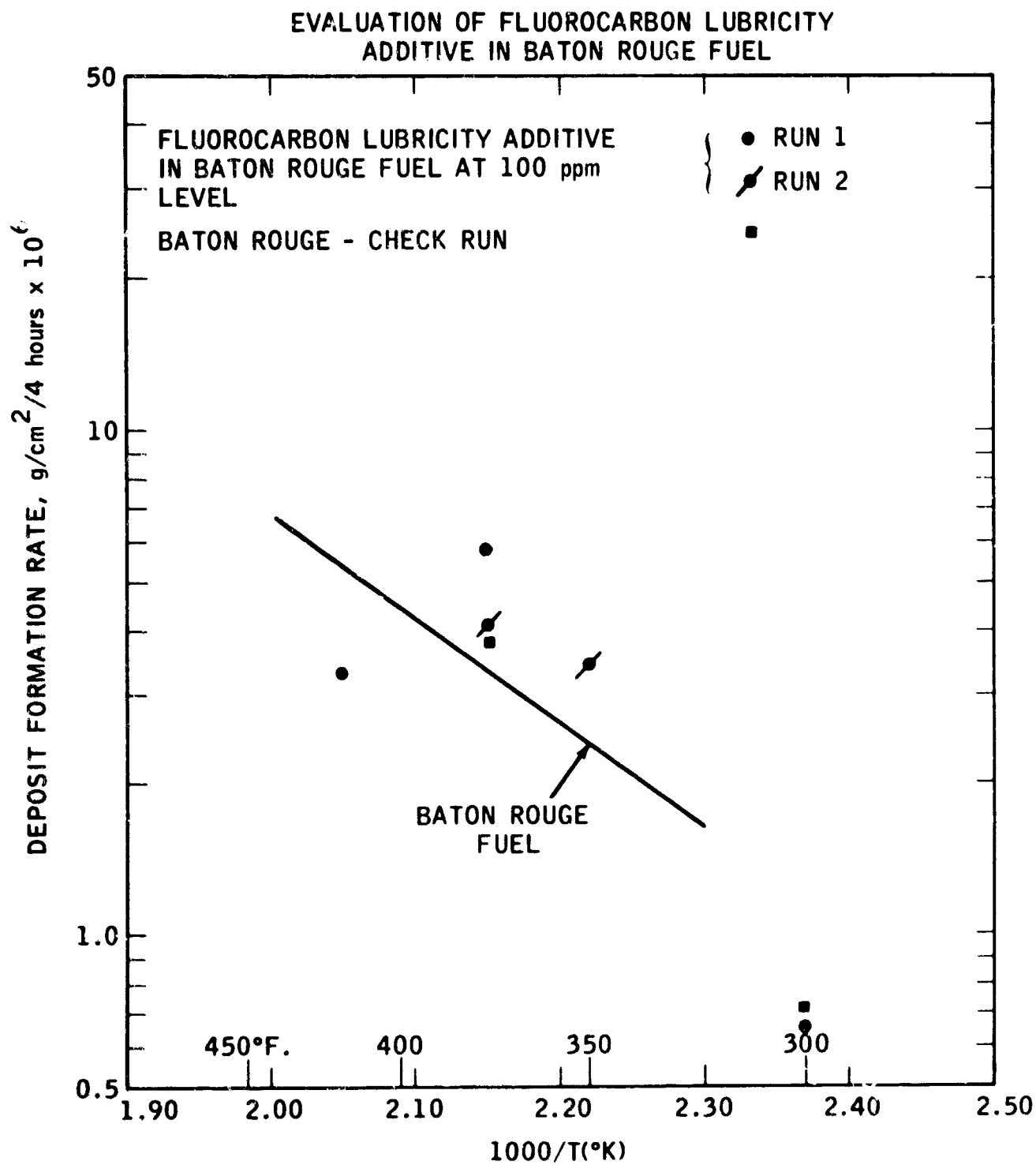
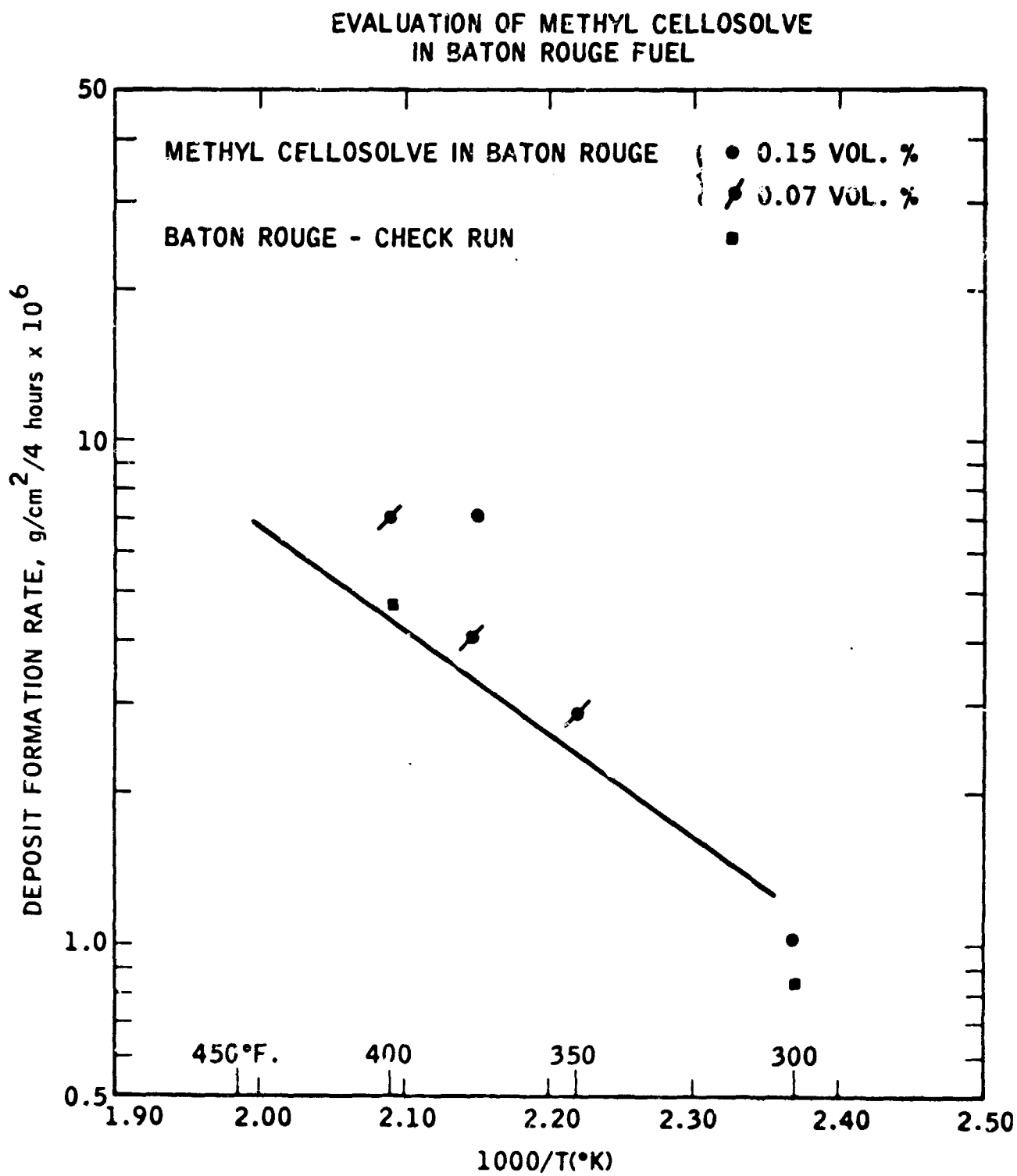


FIGURE 81



The addition of rust inhibitor and metal deactivators to the fuel resulted in a marked increase on deposit formation at higher temperatures. Two of these additives contain phosphorus; and Nixon (139) indicates that even in low temperature stability tests use of metal deactivators can render hydrocarbon fuels more deleterious. Thus, the tendency of these additives to increase deposit formation at much higher temperatures is not surprising. The increase in both the levels of deposit formation and the apparent activation energy with these additive containing fuels clearly indicates that these additives are influencing the deposit formation reaction system, perhaps undergoing decomposition to radical fragments and/or fuel insoluble products. The addition of an anti-icing additive did not affect the deposit formation process; a result which might not be expected because of the high oxygen content of this material. In any event, these results clearly indicate that additives which are effective in hydrocarbon fuels at lower temperatures may either be of no value or deleterious when added to fuels exposed to temperatures in the 300 to 425°F range.

D. The Effect of Surface Coatings
on the Deposit Formation Process

1. Deposit Formation Tendency of
Polymer Coated Titanium
Alloy Specimens

The effect of surface coatings on the deposit formation process was also evaluated in the Screening Unit at 3 psia over the temperature range of 250 to 400°F. The rate of deposit formation was measured with both coated and uncoated metal strips. Coating types evaluated are shown in Table XIV. The coated strips were evaluated on a two step procedure. First the strips were exposed in the Screening unit to the reduced pressure and temperature in the absence of fuel that each specimen would subsequently experience in the presence of degrading fuel. Measurements indicated that the polymer coated strips lost weight under these conditions. Then the rate of deposit formation resulting from the autoxidative degradation of the fuel was determined by the weight increases observed after exposure to fuel in the Screening Unit. Visual observations also confirmed the formation of deposits. However, because of the possibility of some addition weight loss from the polymer coating, the measured increase in weight caused by deposit formation is essentially a minimum value; and thus represents a conservative estimate of the effect of polymeric surface coatings on the deposit formation processes. The data indicated that coating the titanium alloy surface with a polymeric coating did not eliminate the formation of deposits. On the contrary, use of these coatings actually increased the level of deposit formation at temperatures in excess of 350°F. Data are shown in the Arrhenius plots in Figures 82 to 86.

Heterogeneous metal oxide surfaces have been shown to be capable of increasing the rate of the liquid phase autoxidation of hydrocarbons (113,114,115). The work of Burger et al (113) indicated that such surfaces catalyze the formation of free radicals which then enter the liquid phase and accelerate the autoxidative reaction sequence. In the

TABLE XIV

Coating and Coating Conditions Employed

<u>Coating Identification</u>	<u>Film Application (a)</u>	<u>Minutes of Cure Time</u>	<u>At Cure Temperature °F</u>
None (Nitric-HF acid etched)	None	None	None
Polyimide Varnish Monsanto RS5660	Drip-drain	20	150
		20	300
		20	500
Silicone R671 Dow Corning	Spray coat	60	70
		15	400
		45	500
Dow Corning 94-003 Fluorosilicone, Dispersion Coating	Drip-drain	24 hours	70
		20	400
DuPont Teflon S 954-01	Spray coat	10	70
		13	473
DuPont Teflon TFE 851-204	Spray coat	10	70
		15	725

(a) All specimens were supplied by the Boeing Company and Nitric-HF acid etched prior to coating application. One coat applied to all sets.

FIGURE 82

EVALUATION OF STRIPS COATED WITH
RS 5660 IN SCREENING UNIT AT 3 psia

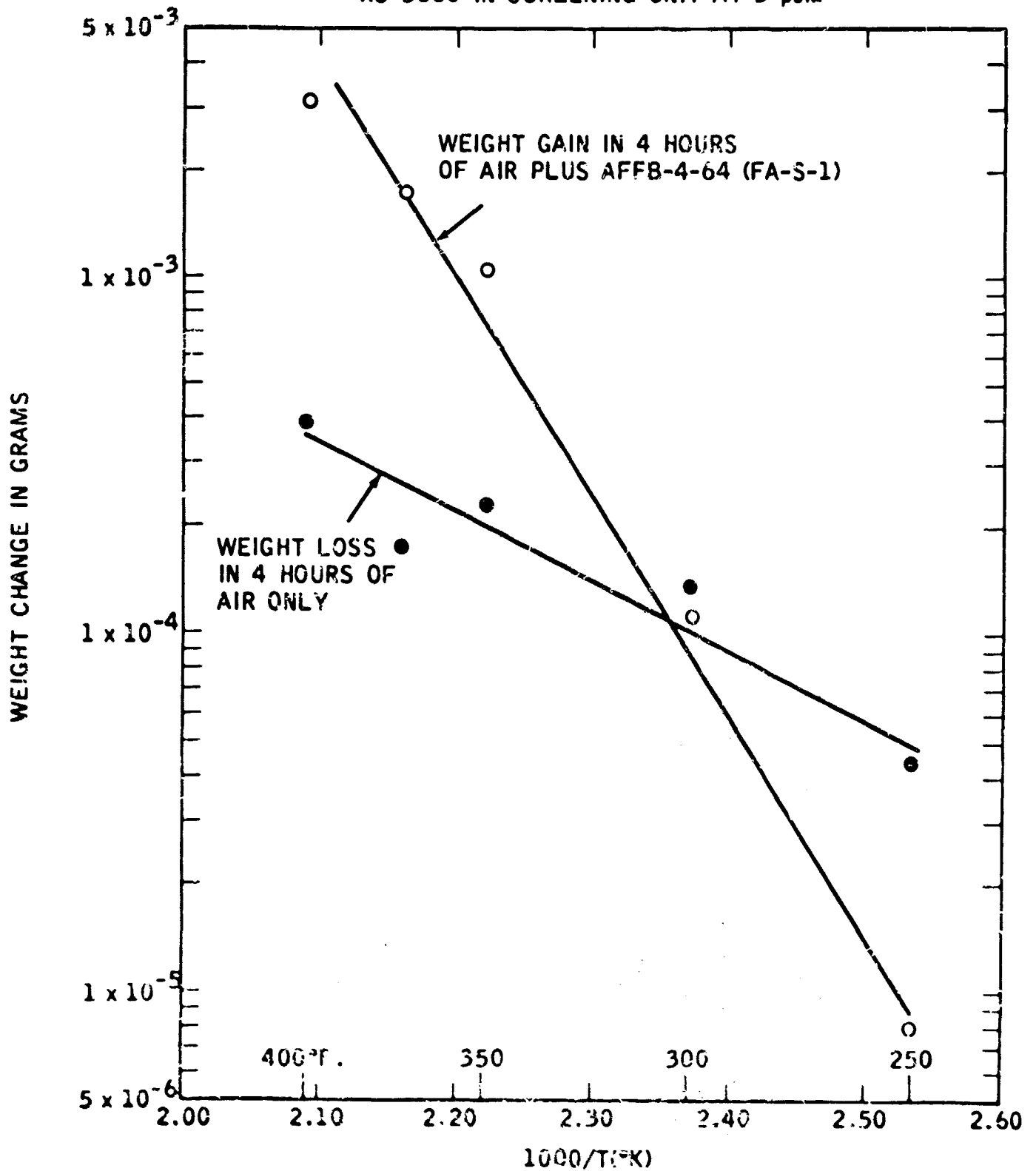


FIGURE 83

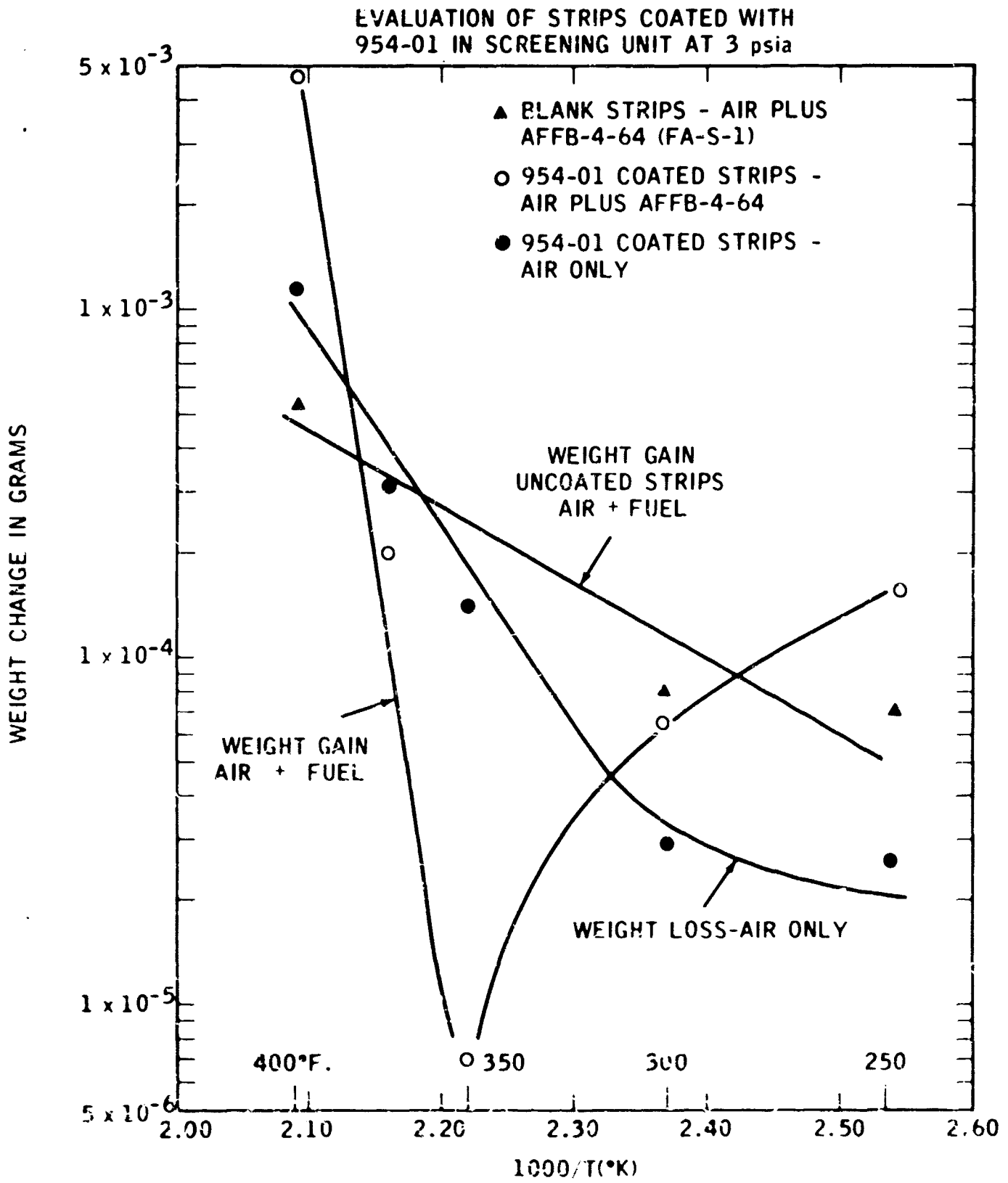


FIGURE 84

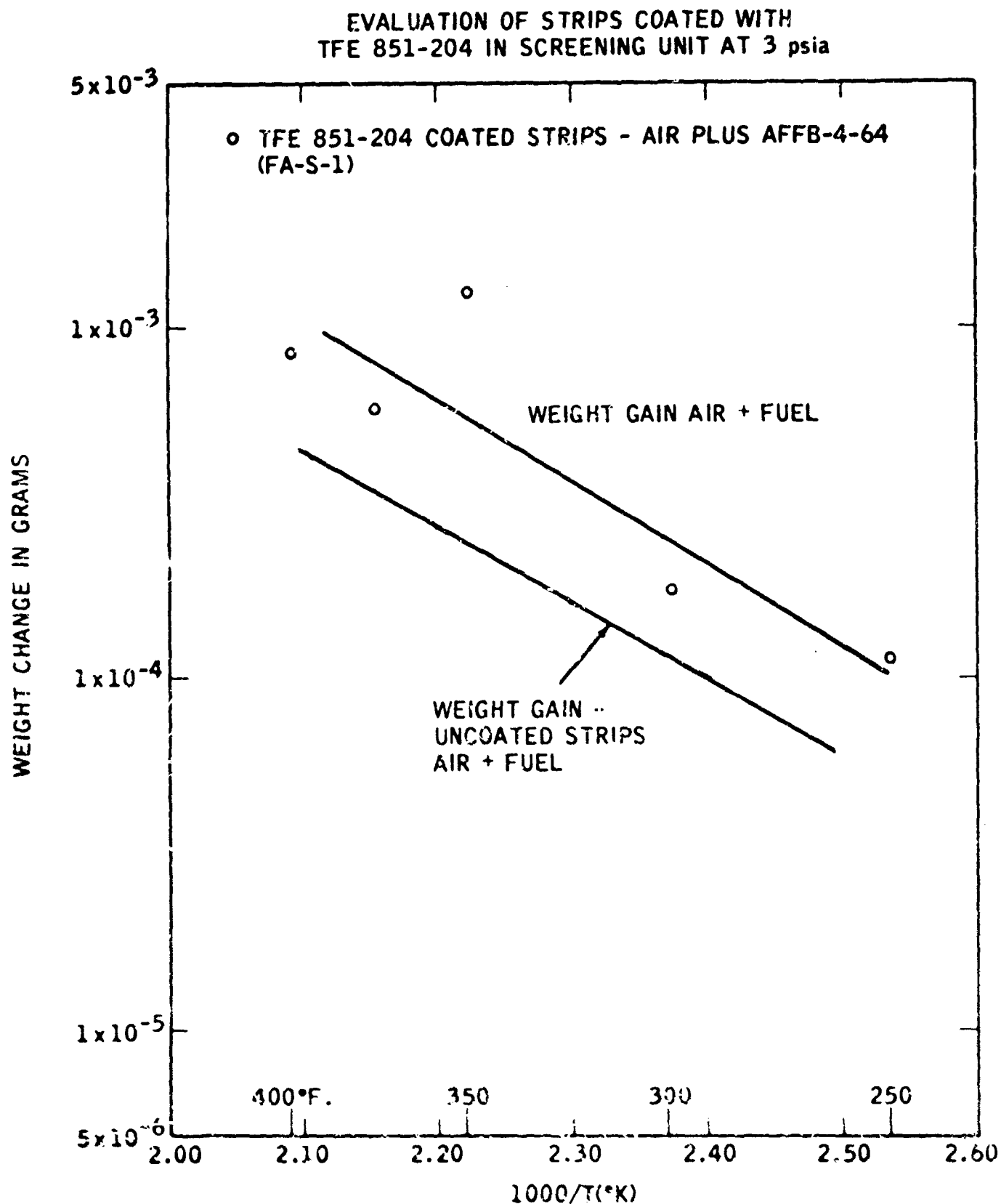


FIGURE 85

EVALUATION OF STRIPS COATED WITH
SILICONE R671 IN SCREENING UNIT AT 3 psia

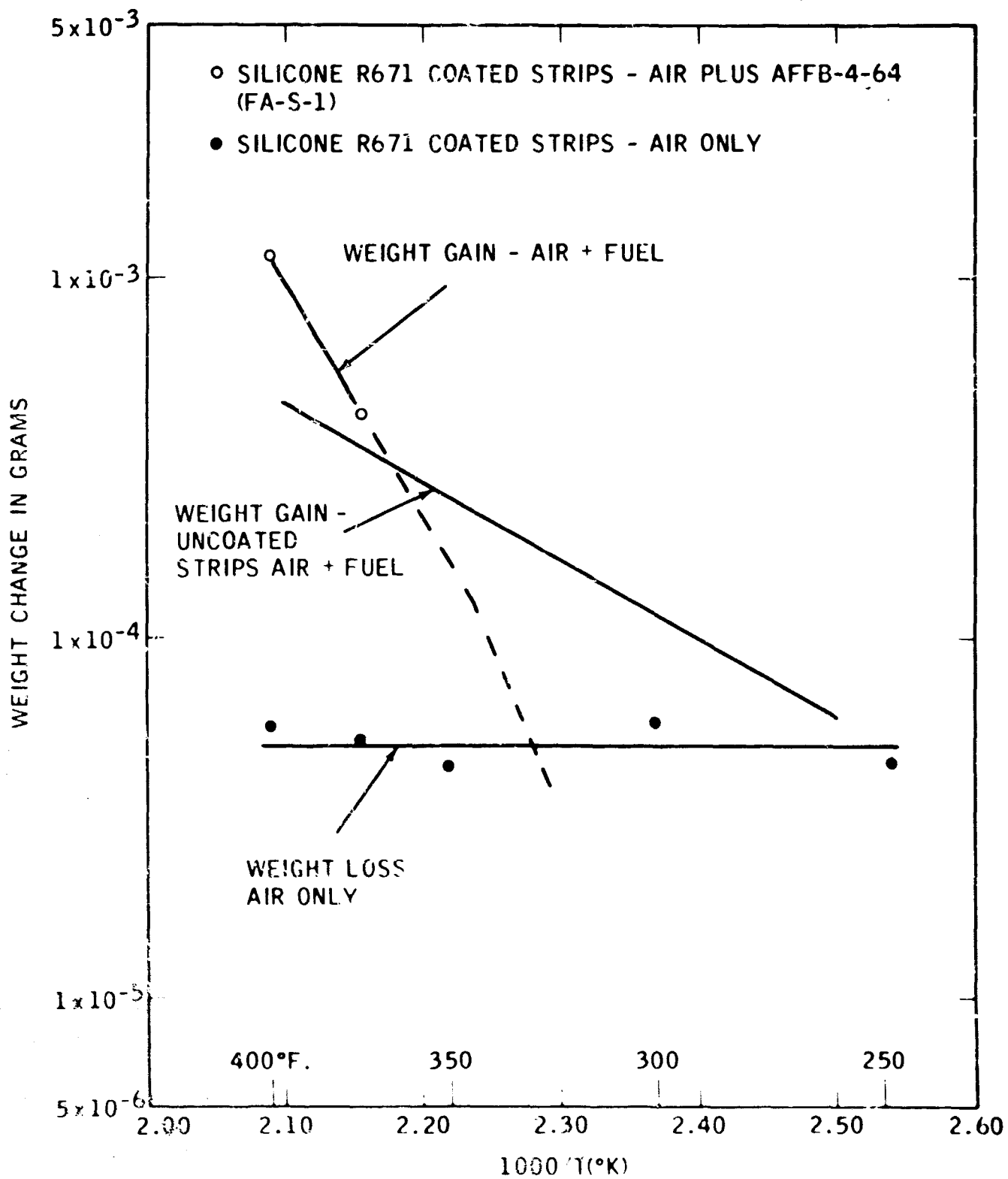
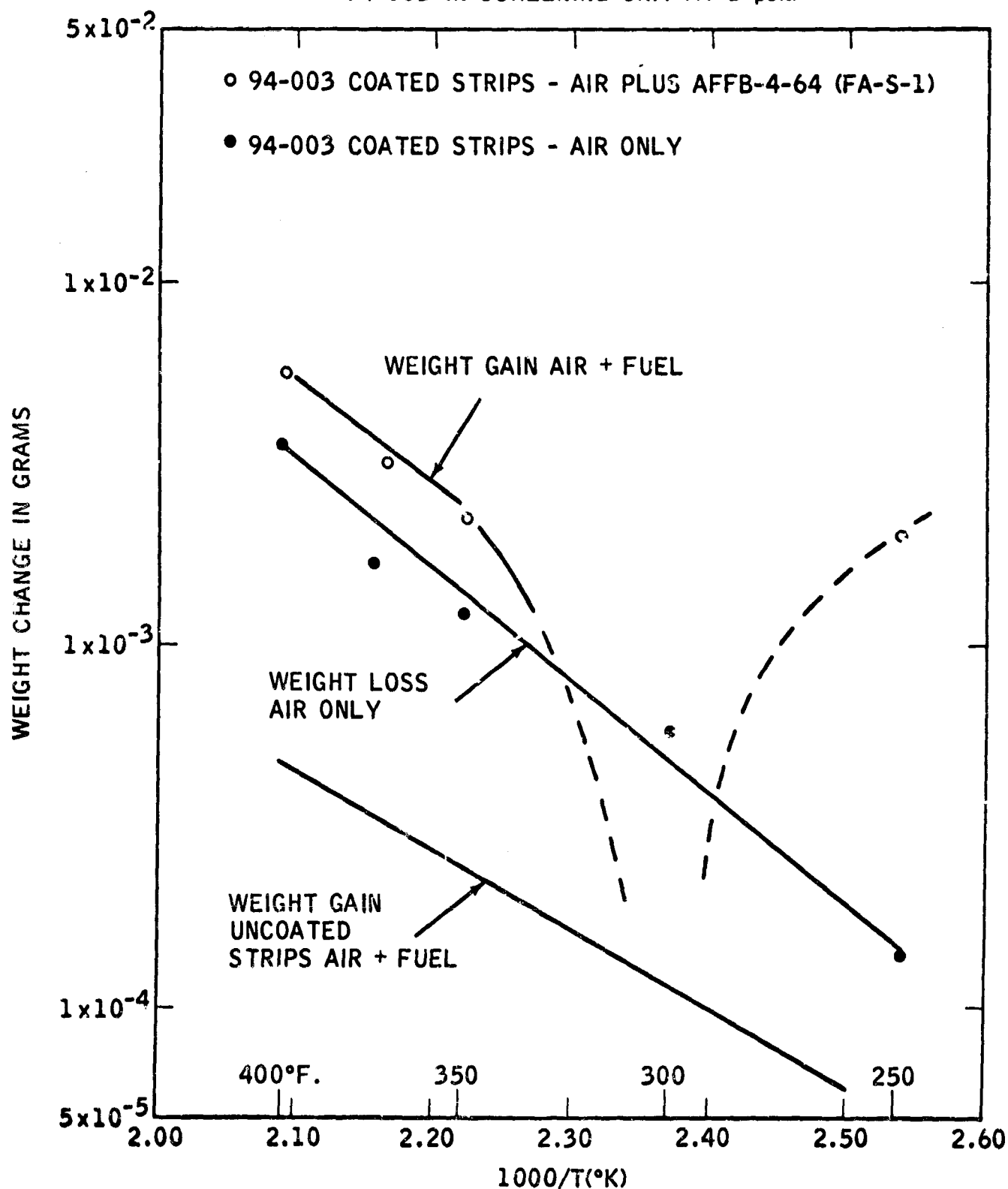


FIGURE 86

EVALUATION OF STRIPS COATED WITH
94-003 IN SCREENING UNIT AT 3 psia



more complex autoxidative process which results in the formation of deposits from jet fuel, it was shown (104) that metal oxide surfaces can catalyze this process, possibly in a manner similar to that suggested by Burger et al (113).

It has recently been reported by Emanuel (140) that coating the wall of a reactor with Teflon accelerated the rate of the liquid phase autoxidation of propene compared to the results obtained in a steel or glass reactor. It was suggested that this acceleration of the oxidation rate occurred because the Teflon surface catalyzed the decomposition of the intermediate hydroperoxide to free radical fragments faster than did the other surfaces or than would occur via pyrolysis in the liquid phase. The present results clearly show that the presence of the polymeric coating accelerates the deposit formation process, particularly at higher temperatures. Although the autoxidative degradation of jet fuel hydrocarbons which ultimately leads to the formation of deposits must indeed be complex, these data suggest that polymer surfaces are catalytically more active than metal oxide surfaces for either primary or secondary radical producing reactions in the autoxidation sequence. From a practical viewpoint, these results indicate that coating metal wing tank surfaces with polymeric materials will not necessarily eliminate the high temperature autoxidative fuel degradation but may actually lead to the increased formation of deposits. Detailed data are shown in Appendix 13.

2. Studies of the Effect of Various Surfaces on the Autoxidation of Typical Hydrocarbons

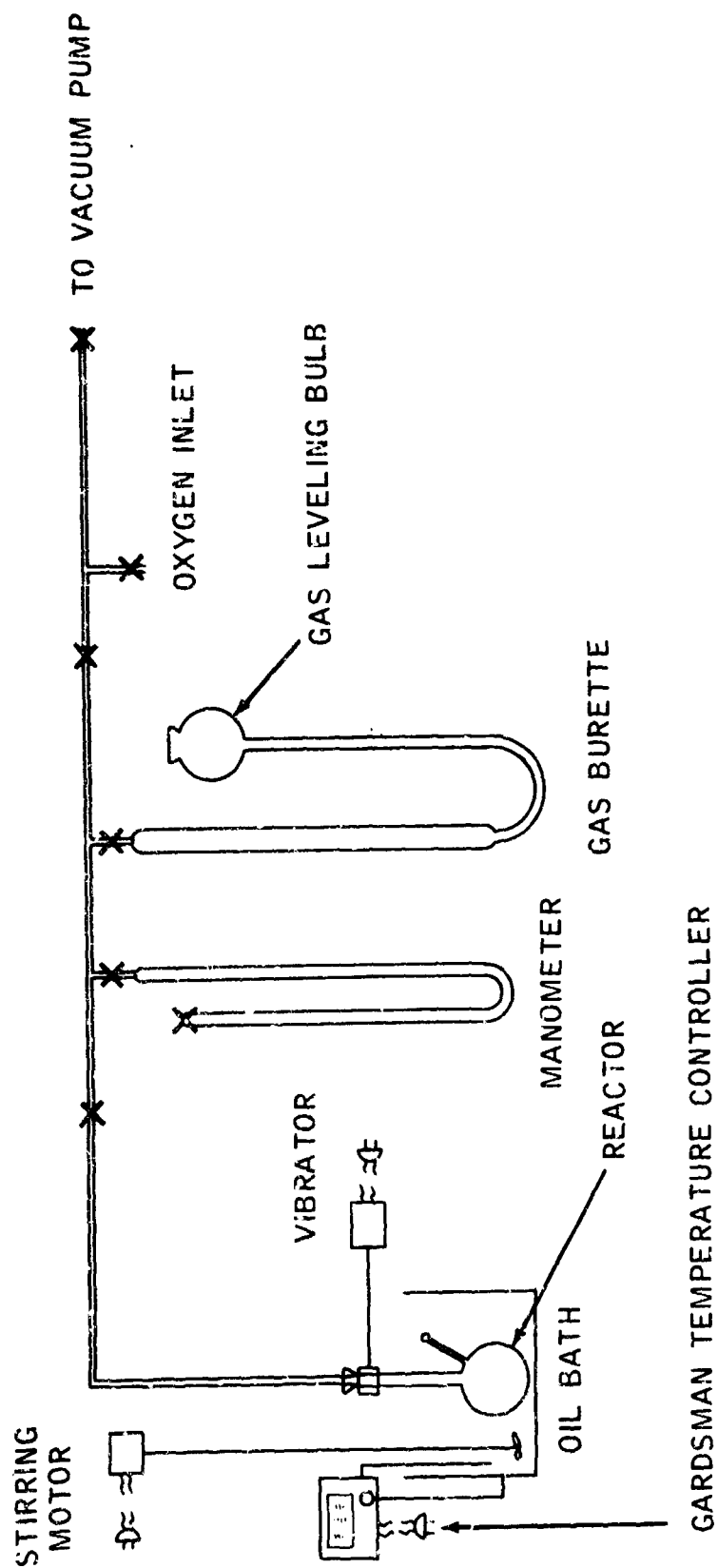
a. Design and Construction of a Hydrocarbon Autoxidation Kinetics Unit

Previous work in the Screening Unit has shown that coating a titanium alloy surface with a polymeric surface coating, rather than suppressing deposit formation, increased the rate of deposit formation at higher temperatures. We designed and constructed a hydrocarbon Autoxidation Kinetics Unit in order to more thoroughly and fundamentally study the effect of polymers on the autoxidative reactions involved in the deposit formation process. In our Screening Unit studies deposits are measured gravimetrically, and the data obtained in the absence of fuel with polymer coated strips indicated that the polymers lost weight at "empty" wing tank temperatures and pressures in the Screening Unit. In an actual Screening Unit run in the presence of fuel, weight gains (from the formation of deposits) and losses (from the polymer coating) take place simultaneously, so that the net weight increase recorded is at best an estimate of the lower limits of deposit formation. As a result, our kinetic unit has been designed to employ non-gravimetric measurement techniques. A schematic of the unit is shown in Figure 87. The hydrocarbon reactant, contained in a suitable solvent, is added to the reactor. Solid polymer in the form of a 60/80 mesh powder is added to the reaction mixture and the reactor immersed in a temperature controlled bath. The reactor is attached to a vibrator which supplies sufficient agitation to the solid-liquid slurry so as to minimize mass transfer limitations on the reaction system. Oxygen is admitted at a constant pressure to the reactor from a burette measuring system. The rate of oxidation of the model hydrocarbon can be measured both from the rate of oxygen uptake and by gas chromatographic analyses of the samples

HYDROCARBON AUTOXIDATION KINETICS UNIT

- 148 -

FIGURE 87



of the reaction mixture taken through a septum cap on a side arm attached to the reactor. Thus the rate of consumption of hydrocarbon and oxygen and the rate of appearance of products can all be measured directly. Other analyses made of aliquot samples include infrared, chemical titration for hydroperoxide content and mass spectrometer analyses.

b. The Effect of Polymeric Surfaces on
the Oxidation of Tetralin

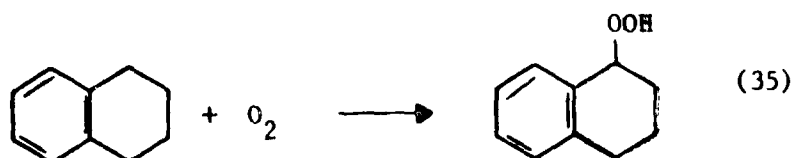
It is well known that homogeneous metals catalyze the liquid phase autoxidation of compounds such as hydrocarbons. Other studies have shown that heterogeneous metal oxides are capable of increasing the rate of reaction of hydrocarbons with oxygen in the liquid phase. Because of this known activity, attempts have been made to render metal surfaces quiescent for autoxidative hydrocarbon reactions leading to deposit formation by coating these surfaces with polymeric materials. Studies, however, indicate that rather than suppressing autoxidative hydrocarbon deposit formation, polymer coatings increased their rate of formation, suggesting that polymeric surfaces function as a catalyst for autoxidative reactions. Similarly, Emanuel has reported that coating the wall of a reaction with poly(tetrafluoroethylene) accelerated the rate of liquid phase autoxidation of propene compared with results obtained in a steel or glass reactor (140). To further elucidate these effects we have carried out a study of the catalytic influence of various polymeric surfaces on the liquid phase autoxidation of a typical hydrocarbon. Tetralin was chosen as a model compound for this study. Because of the importance of specific reaction rate, i.e., rate per unit area of catalyst, in studies of this nature (141,142,143), the specific activity of polypropylene and poly(tetrafluoroethylene) are also compared.

The Hydrocarbon Autoxidative Kinetic Unit was used. The rate of oxidation was measured at atmospheric pressure. The reactor was immersed in a temperature bath controlled to 0.5°C. Mass transfer limitations were minimized by vibrating the reactor at a speed of 800 cycles per minute. Experiments demonstrated that the rate of oxidation was independent of vibration speed at this level. In each run 2 cc of tetralin, 2 cc of chlorobenzene and 0.30 g of catalyst were charged to the reactor, hooked into the reaction system and the reactants degassed by freezing with liquid N₂, evacuation, thawing, refreezing and re-evacuation. The reactor was then filled with O₂ and immersed in the temperature controlled bath. Aliquot samples for analysis during the run were removed via a syringe through a septum cap attached to a side-arm on the reactor. Tetralin conversion was measured using an F&M Model 500 temperature programmed gas chromatograph with a 2 ft. column containing 10% QF-1 (fluorinated silicone oil) on 45/60 mesh Chromosorb W. The column was programmed from 50 to 175°C at 7.9°C/min. The tetralin hydroperoxide content was determined chemically by the method of Wagner, et al (144). Oxygen uptake, tetralin conversion and tetralin hydroperoxide content data all confirmed that the initial oxidation product is tetralin hydroperoxide.

Tetralin (Matheson, Coleman and Bell, practical grade) was purified by washing with concentrated sulfuric acid until the washings were colorless, followed by washing with distilled water to remove residual acidity and drying with anhydrous MgSO_4 (145). The resulting tetralin was then repeatedly distilled in a spinning band column until a fraction was obtained which showed no impurities by glpc analyses. Glpc pure chlorobenzene (Matheson, Coleman and Bell) was employed.

The polymer catalysts were all prepared as 60/80 mesh powders by cooling with liquid N_2 , grinding in a Waring blender, sieving and washing with a solvent. Methylene chloride was used with poly(tetrafluoroethylene) and acetone with polyethylene and polypropylene. All inspections were obtained on the prepared powder. The poly(tetrafluoroethylene) was obtained from E. I. duPont de Nemours & Company, Wilmington, Delaware. Powdered catalysts were prepared from both molded samples and from Teflon 7 granular resin which was pressed at 24,000 psi prior to starting the normal preparative procedure. Tests indicated that the resultant 60/80 mesh poly(tetrafluoroethylene) powders were essentially equivalent in activity. The polypropylene was obtained from the Enjay Chemical Company, Linden, N.J., in an extruded form. The polyethylene was obtained from Ace Scientific Co., Linden, N.J., in an extruded form.

Polymer surfaces tested for their catalytic activity, included poly(tetrafluoroethylene), polyethylene and polypropylene. All were tested as 60/80 mesh powders. Detailed inspections of these powders are shown in Table XV. It can be seen that metal impurity levels are quite low. Rate measurements were made over the range of 65 to 115°C at atmospheric pressure using chlorobenzene as a solvent. Quantitative analyses confirmed that the initial oxidation product is tetralin hydroperoxide.



Data for the oxidation of tetralin at 90°C in the presence of both polypropylene and poly(tetrafluoroethylene) are shown in Figure 89. Data obtained at 65°C in the presence of polyethylene and poly(tetrafluoroethylene) and for the uncatalyzed oxidation of tetralin are shown in Figure 88. As can be seen from the presence of the various polymeric surfaces markedly changed the rate of oxidation of tetralin, as manifested both by a dramatic reduction in the induction period and by the actual rate of oxygen consumption. For the poly(tetrafluoroethylene) catalyzed reaction the maximum rate measured occurred initially after the induction period, whereas when polypropylene was employed the rate continued to increase with time before it finally began to level off.

TABLE XV

SUMMARY OF POLYMER CATALYST
ACTIVITY AND INSPECTIONS

	<u>Poly(tetrafluoro ethylene)</u>	<u>Polyethylene</u>	<u>Polypropylene</u>
Initial activity, g-moles O ₂ per hour per gram of poly- mer per ml of tetralin			
90°C	14.9 x 10 ⁻⁴ (a)	--	44.7 x 10 ⁻⁴ (b)
65°C	3.38 x 10 ⁻⁴ (a)	7.59 x 10 ⁻⁴ (a)	--
B.E.T. Surface area, m ² /g	0.69	--	0.21
Specific activity, g-moles O ₂ per hour per ml of tetralin per m ² of polymer			
90°C	2.16 x 10 ⁻³ (a)	--	21.3 x 10 ⁻³ (b)
65°C	4.90 x 10 ⁻⁴ (a)	--	--
Ash Content, wt. %	0.010 @ 800°C	0.080 @ 550°C	0.082 @ 550°C
Metal Components of Ash by emission spectra:			
Major	--	Si	Ca
Minor	--	Mg Fe	Al
Trace	Si, Mg, Fe, Cu, Ag, Na, Zn, Ti, Ni, Ca, Al	Na, Cu, Al, Ca, Cr	Ti, Fe, Si, Mg

(a) Rate of oxidation immediately following induction period.
Other conditions: 2 cc tetralin in 2 cc of chlorobenzene with
0.30 g catalyst.

(b) Maximum rate which occurred during first minutes after
induction period.

FIGURE 88

Oxidation of Tetralin at 90°C

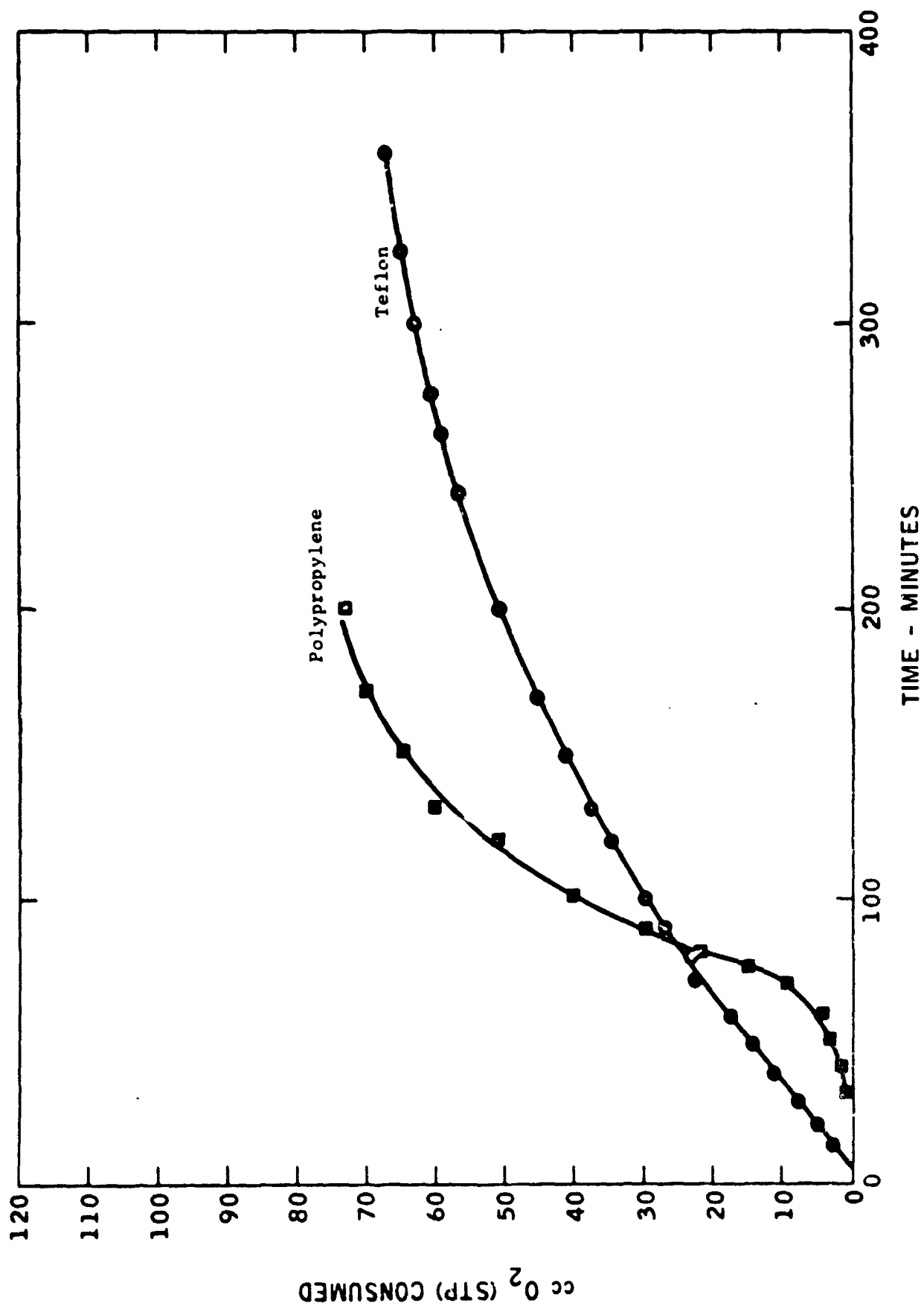
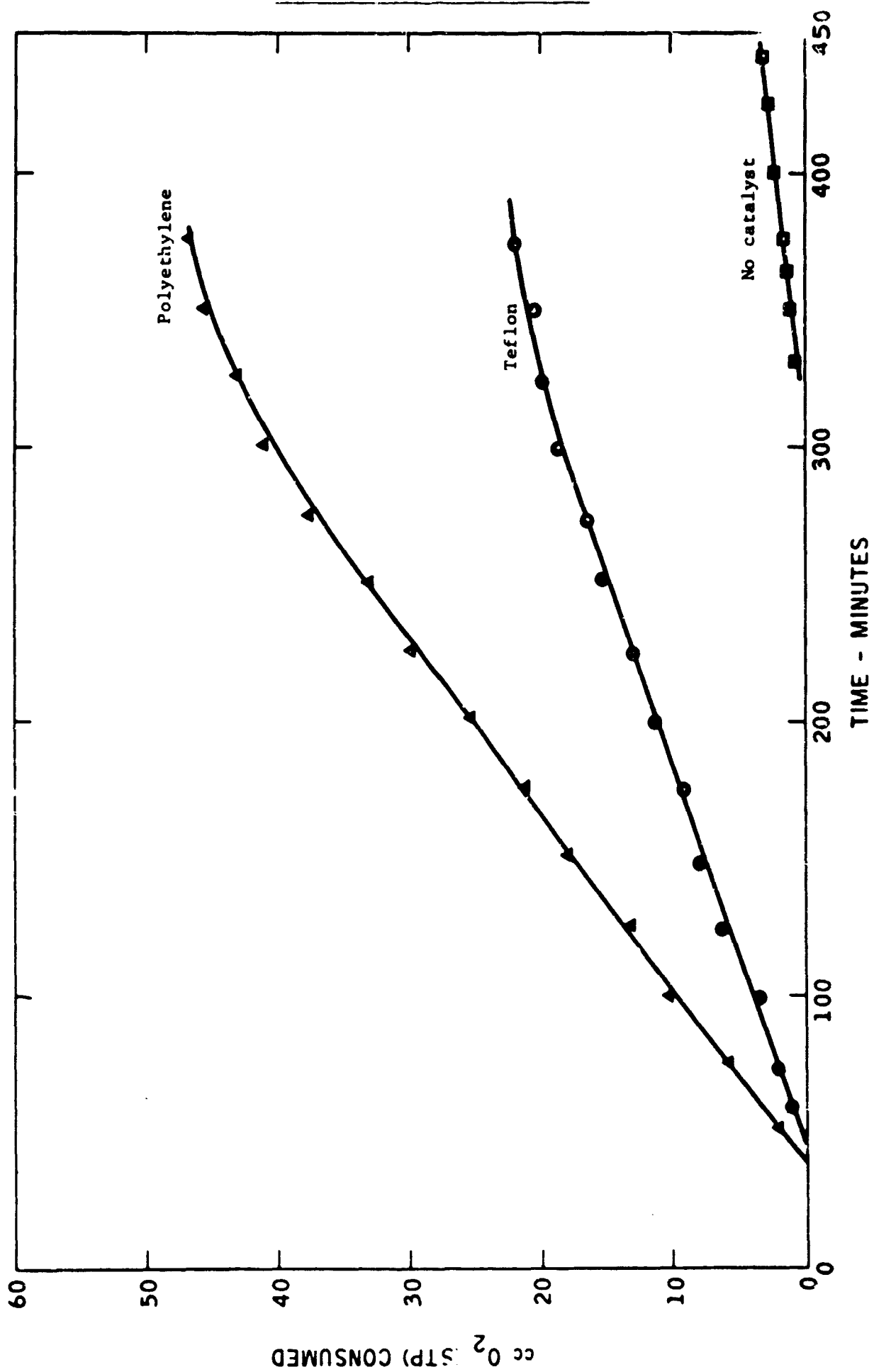


FIGURE 89

Oxidation of Tetralin at 65°C



Data on the effect of temperature on the initial rate of oxidation of tetralin in the presence of poly(tetrafluoroethylene) over the range of 65 to 115°C are shown in Figure 90. The apparent activation energy derived from this Arrhenius plot is 17.0 kcal/mole. The induction period for the poly(tetrafluoroethylene) catalyzed oxidation of tetralin was found to decrease as the reaction temperature increased. In Figure 91 an Arrhenius plot is shown of the reciprocal of the induction period observed with the poly(tetrafluoroethylene) catalyzed oxidation of tetralin. Each induction period shown is the average of at least three separate experimental determinations. The apparent activation energy derived from this plot is 16.7 kcal/mole. In Table XV the specific activity, i.e., the rate per unit area, is tabulated for the various polymers employed. These values were obtained by dividing the initial rate of oxidation per gram of catalyst by the total surface area of the polymer powder per gram of polymer. It can be seen that the specific activity of polypropylene is higher than that of poly(tetrafluoroethylene) at 90°C by a factor of approximately 10.

The autoxidation of tetralin has been studied extensively including uncatalyzed studies (146,147,148), homogeneously catalyzed studies (149-153) and heterogeneously catalyzed metal oxide catalyzed oxidation of tetralin, apparent activation energies ranging from 9 to 10 kcal/mole were reported (145), compared with 17.0 kcal/mole found for poly(tetrafluoroethylene) in the present study. The activation energy for the thermal initiation reaction was measured during the oxidation of tetralin in the presence of an inhibitor and was reported to be 23.0 kcal/mole (148). Apparent activation energies from this range down to 13 kcal/mole have been reported for the homogeneously catalyzed oxidation (152,153). Mukherjee (145) presents extensive data at 65°C for the heterogeneous catalyzed oxidation of both pure tetralin and tetralin in chlorobenzene. A very striking and complex effect of the amount of catalyst on the rate of oxidation is also reported, i.e., a critical catalyst concentration above which the rate is inhibited which is dependent on the concentration of tetralin in chlorobenzene (145). A comparison at 65°C and otherwise identical conditions (3.7 M/l tetralin in chlorobenzene, 6.7 ml tetralin per gram of catalyst) indicates that the most active catalyst in this work (Figure 2 in Ref. 145), i.e., Mn_2O_3 , is approximately 10 times more active than poly(tetrafluoroethylene) and 5 times more active than polyethylene. The other metal oxide catalysts were less active than Mn_2O_3 at 65°C by a factor of from 3 to 6 (Figure 1 in Ref. 145, comparison of catalysts at a tetralin to catalyst ratio of 6.7 ml/g). Thus polymer catalysts are comparable to these less active metal oxide catalysts, e.g., PbS , NiO , at 65°C.

Because of the higher apparent activation energy of poly(tetrafluoroethylene) as compared to the metal oxides studied (i.e., 17 versus 9 kcal/mole), a comparison at temperatures higher than 65°C would be more favorable to this polymer. In view of this, it is difficult to see how the activity of these polymeric materials could result from the trace levels of metallic impurities present. In addition, it should be pointed out that no surface areas are reported for the metal oxide catalysts, so that specific activities cannot be compared.

FIGURE 90

Initial Rate of the Teflon
Catalyzed Oxidation of Tetralin

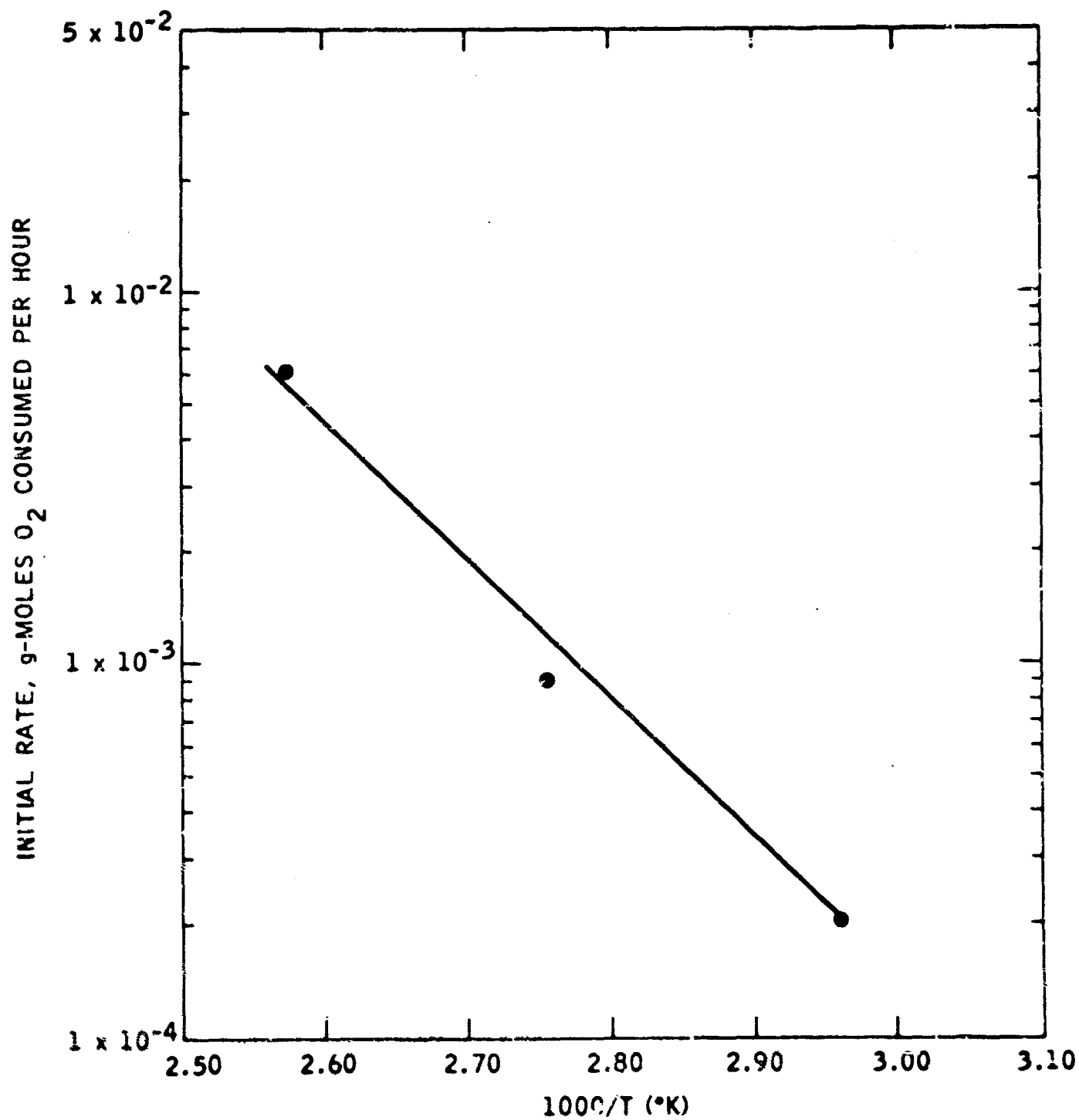
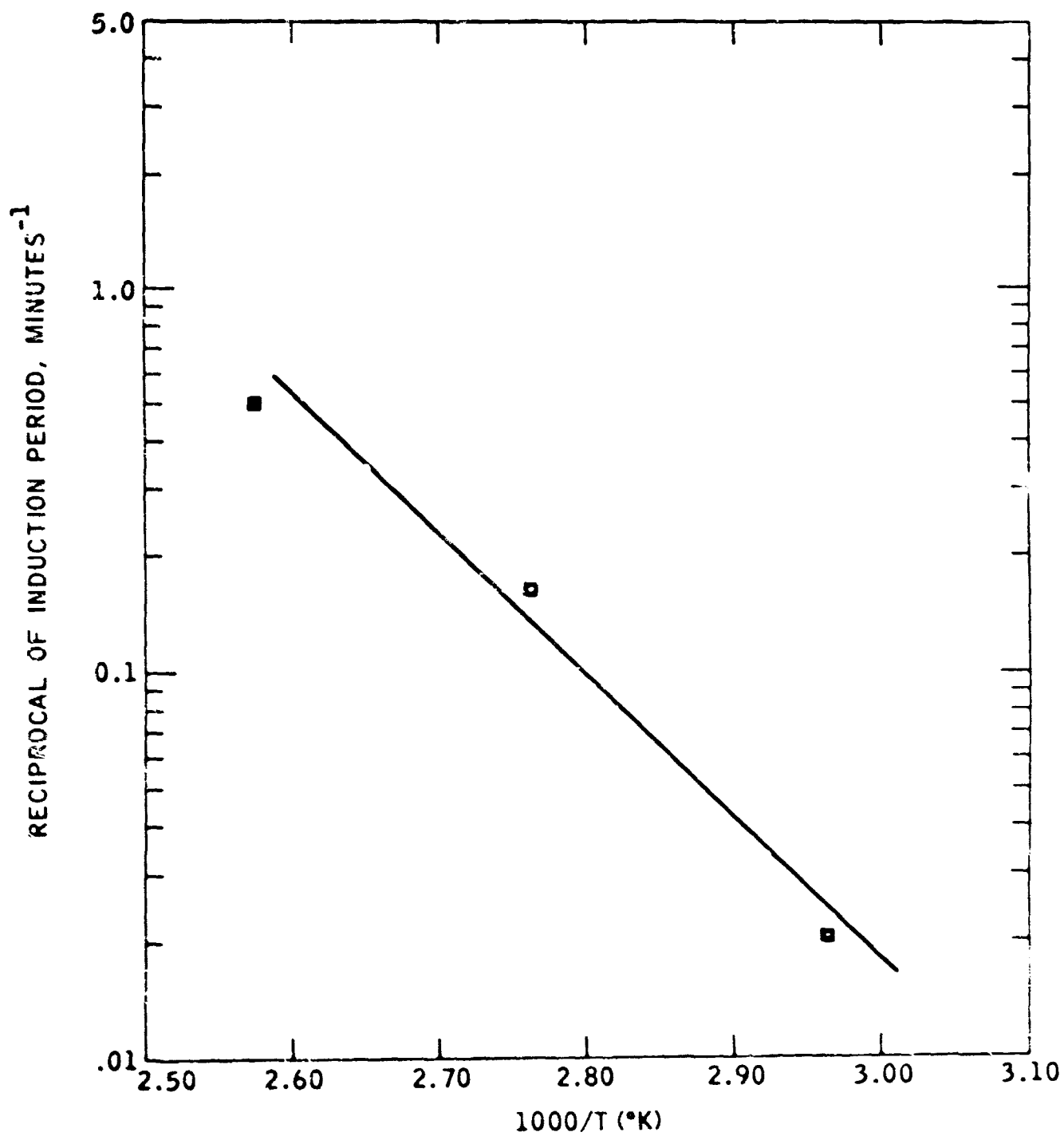


FIGURE 91

THE EFFECT OF TEMPERATURE ON THE INDUCTION PERIOD
FOR THE TEFLON CATALYZED OXIDATION OF TETRALIN



A number of studies have indicated that hydrocarbons will adsorb on low surface energy solids such as poly(tetrafluoroethylene) and polypropylene. Included in these adsorption studies are ethane on polypropylene (155), ethane, n-butane and n-octane on poly(tetrafluoroethylene) (156) and n-hexane and benzene on poly(tetrafluoroethylene) (157). A consideration of isosteric heats of adsorption as a function of surface coverage led Graham (155,156) to conclude that both polypropylene and poly(tetrafluoroethylene) surfaces are highly heterogeneous. Such a conclusion is certainly consistent with the ability of such surfaces to catalyze the autoxidation of tetralin. Graham (155) has also pointed out that poly(tetrafluoroethylene) is a lower surface energy solid than polypropylene. The observed higher specific activity of polypropylene relative to poly(tetrafluoroethylene) could reflect this difference in surface energy between these solids.

To gain further insight into the polymer catalyzed autoxidation of hydrocarbons, we studied the Teflon catalyzed decomposition of tetralin hydroperoxide. This study was carried out in our Hydrocarbon Autoxidation Kinetics Unit with 0.40 g of Tetralin hydroperoxide dissolved in 4 cc of chlorobenzene solvent using 0.30 g of Teflon 60/80 mesh powder under a N₂ blanket. Teflon was found to catalyze the decomposition of tetralin hydroperoxide.

Catalyst	% Tetralin Hydroperoxide Decomposed after 1 hour at 115°C
None	10 ^(a)
Teflon	39

(a) From reference 147. Data
for chlorobenzene solvent at 116°C.

Detailed data are shown in Figure 92. The effect of tetralin hydroperoxide concentration and catalyst loading was also studied. Results are summarized in Table XVI. Initial rate data indicated that the teflon catalyzed decomposition of tetralin hydroperoxide is first order in hydroperoxide concentration was confirmed by an integral first order plot (Figure 93). An Arrhenius plot of the first order rate constants for the catalyzed decomposition of tetralin hydroperoxide is shown in Figure 94.

Aliquot liquid and gas samples were taken during both the catalyzed oxidation of tetralin studies and the catalyzed tetralin hydroperoxide study so as to quantitatively determine the major reaction products. Analytical techniques included quantitative chemical titration for tetralin hydroperoxide content, gas chromatographic, infrared and mass spectrometric analyses liquid samples and gas chromatographic analyses of gas samples. In Figure 95 are shown the change in reactants and liquid products involved in the poly(tetrafluoroethylene) catalyzed oxidation of tetralin at 115°C as a function of reaction time. A comparison of tetralin conversion, oxygen uptake and tetralin hydroperoxide content confirms that the initial reaction

FIGURE 92

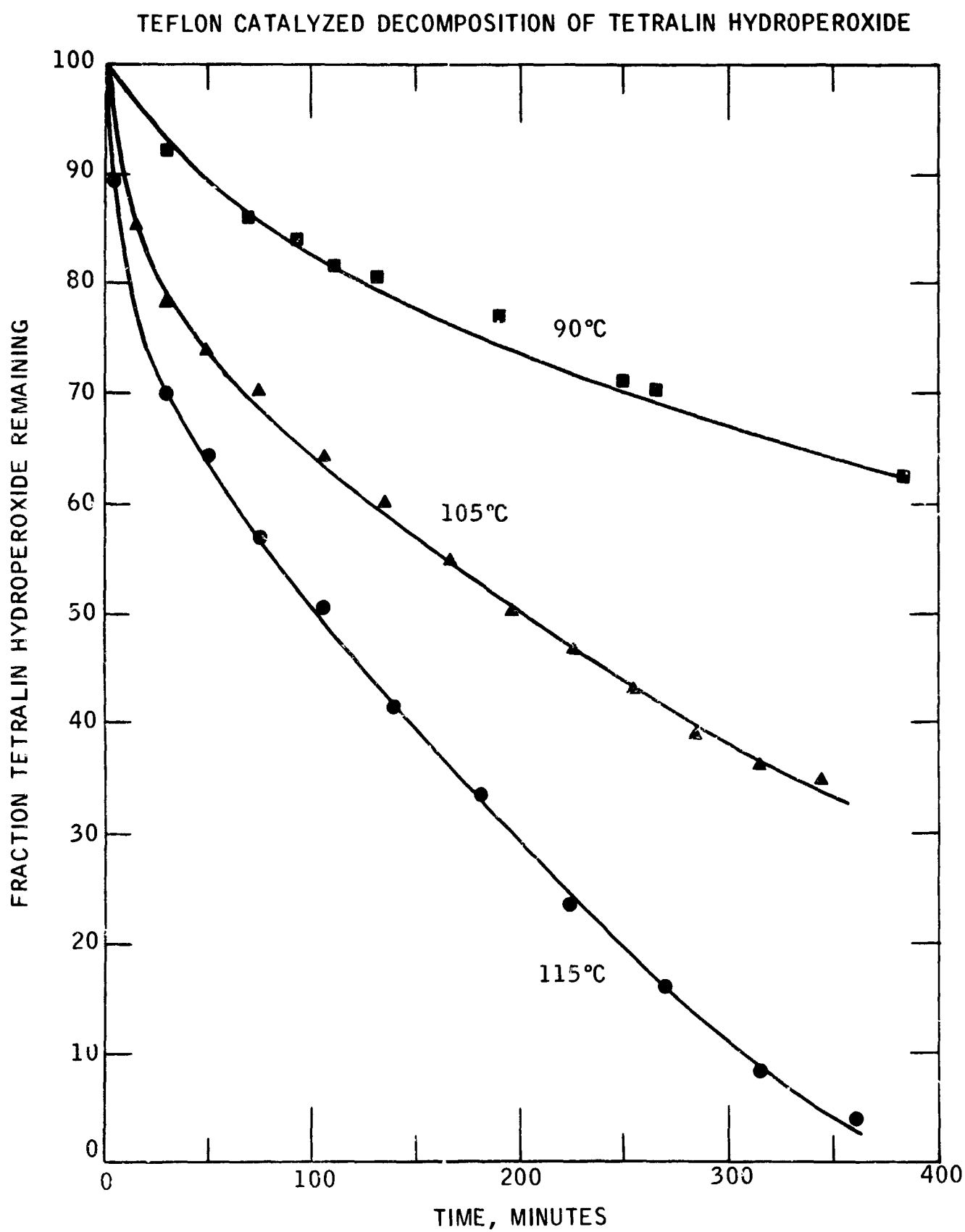


TABLE XVI

Relative Rates of Tetralin Hydroperoxide Decomposition as
a Function of Tetralin Hydroperoxide
Concentration and Catalyst Loading^(a)

<u>Tetralin Hydroperoxide Concentration, wt %</u>	<u>Catalyst Loading Grams</u>	<u>Relative Rate of Decomposition r/r_o</u>
4.37	0.30	0.58 (b)
8.30	0.30	1.00 (base) (b)
15.3	0.30	1.92
8.30	0.15	0.47 (c)
8.30	0.30	1.00 (base) (c)
8.30	0.60	2.21 (c)

(a) Conditions: 105°C, tetralin hydroperoxide added to 4 cc chlorobenzene solvent, 1 atm N₂

(b) Relative rates calculated from observed first order rate constants corrected for thermal (non-catalytic) contribution at same conditions.

(c) Relative rates calculated from initial rate of tetralin hydroperoxide conversion in grams per hour.

FIGURE 93

Teflon Catalyzed Decomposition of
Tetralin Hydroperoxide at 105°C

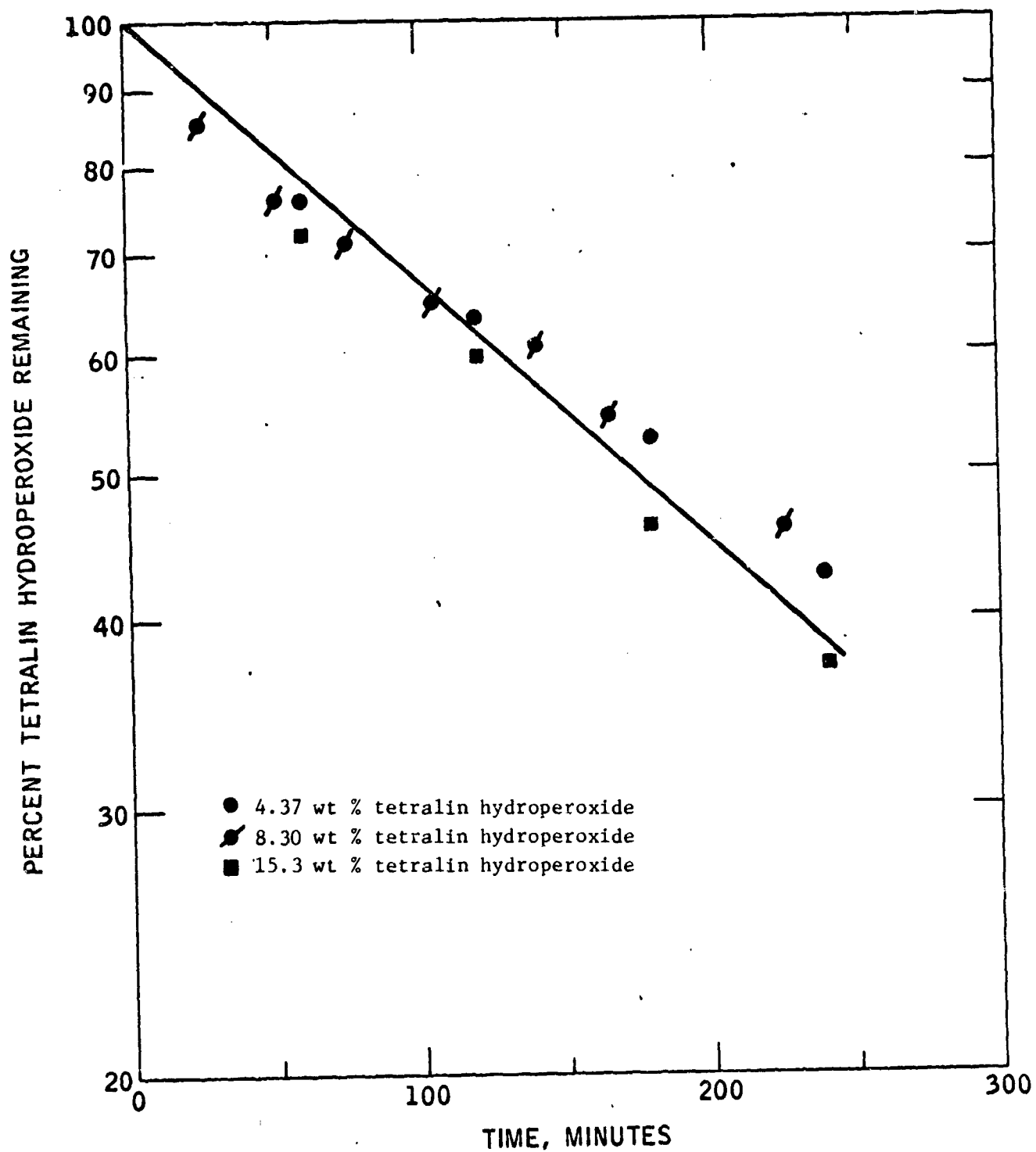


FIGURE 94

Teflon Catalyzed Decomposition of
Tetralin Hydroperoxide

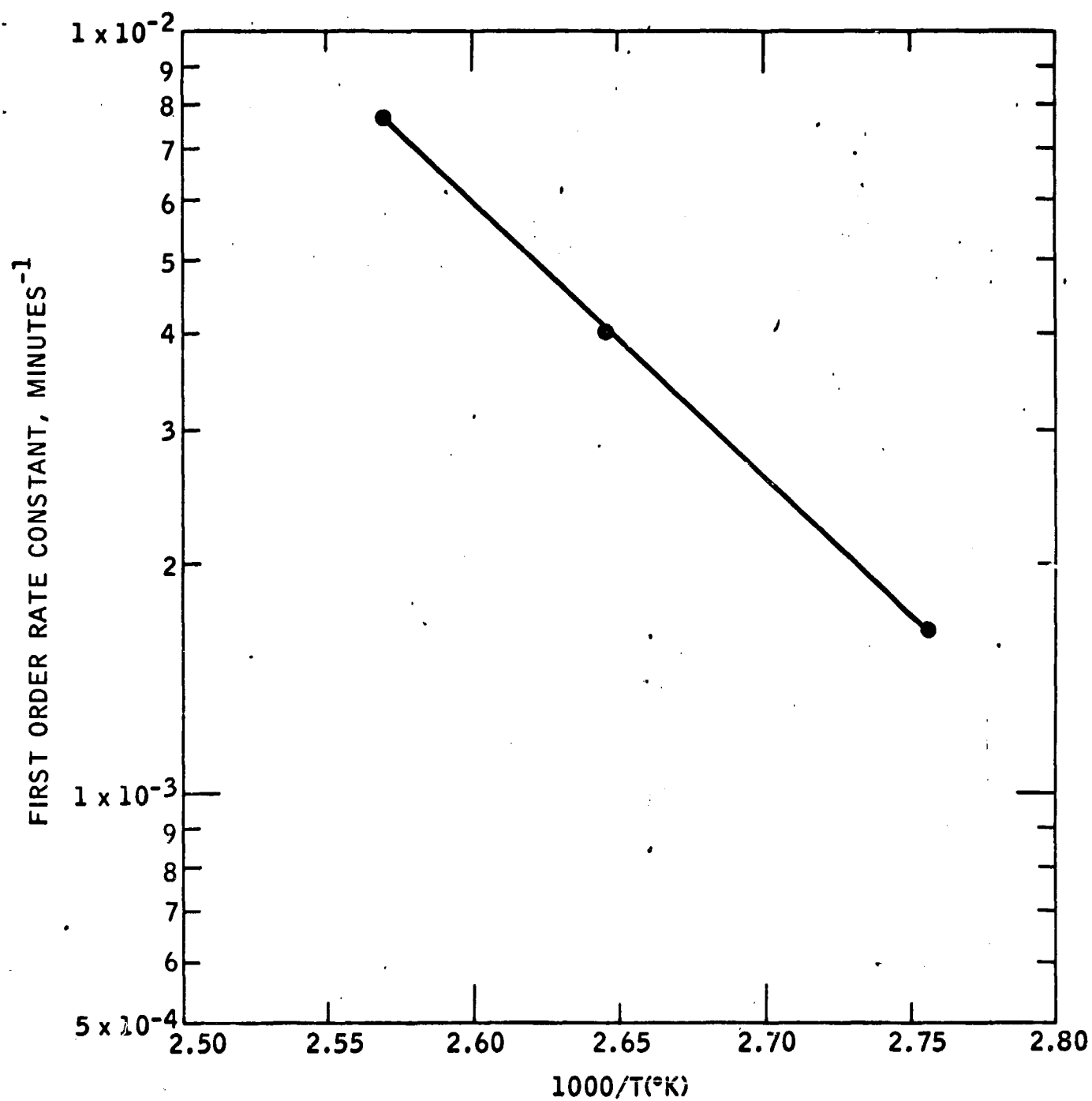
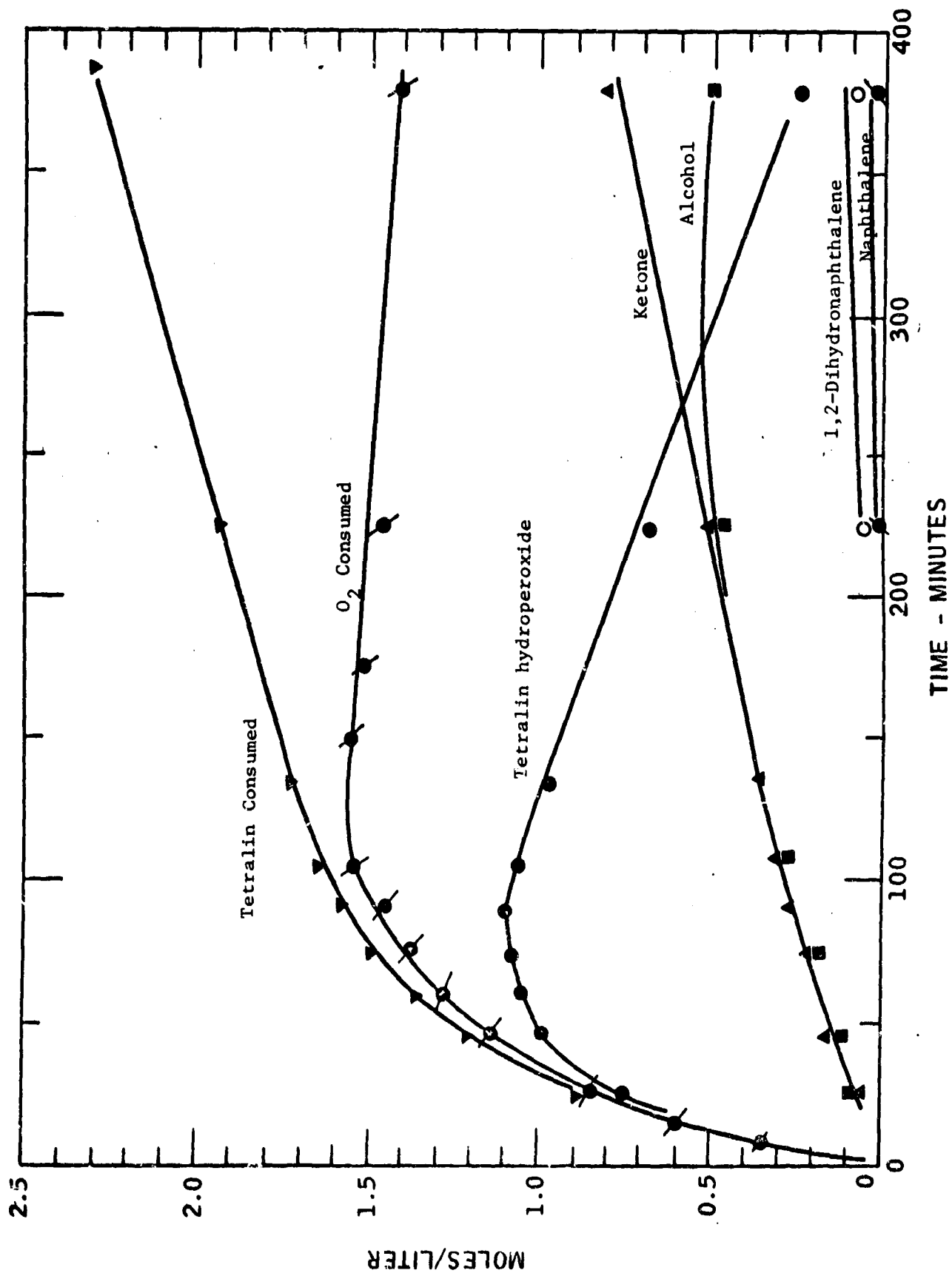


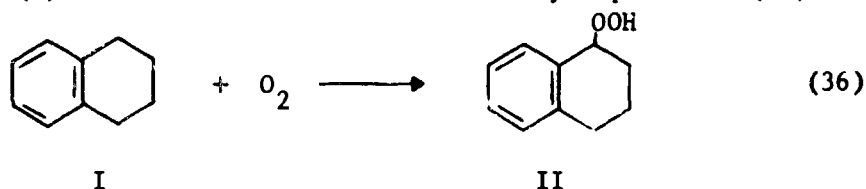
FIGURE 95

PRODUCTS AND REACTANTS DURING TEFLON
CATALYZED OXIDATION OF TETRALIN

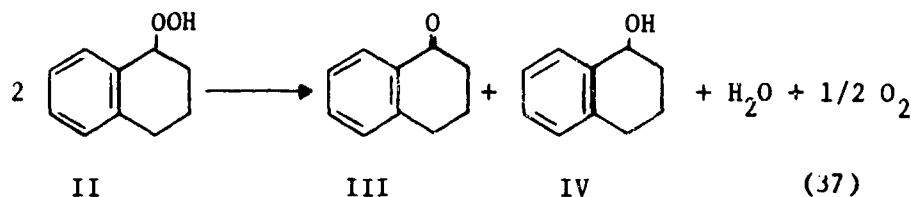


product is tetralin hydroperoxide. As the reaction progresses, however, the tetralin hydroperoxide is converted to other products. In addition to the liquid products, H_2O and H_2 were also detected in samples of the gas phase. At this point, it should be noted that the oxygen uptake data obtained from volumetric changes no longer can be used as a measure of the forward progress of the reaction, i.e., tetralin conversion, as light gases are being produced which make the measured volumetric change difficult to interpret. Thus, autoxidation studies dependent solely on oxygen uptake data for a measurement of the rate of progress of the reaction may be subject to some error if extensive secondary reactions have taken place. Similar analyses were made of the products of catalyzed decompositions of tetralin hydroperoxide. Results of the analyses of the liquid samples are shown in Figure 96. Analyses of samples of the gas phase indicated the presence of H_2O , O_2 and H_2 .

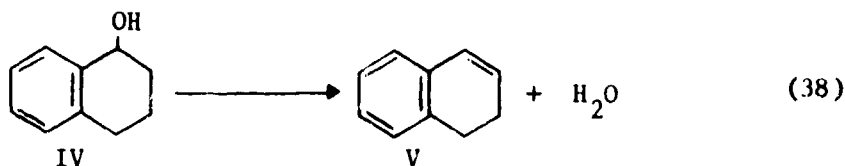
A consideration of all the product analyses indicates that the poly(tetrafluoroethylene) catalyzed oxidation of tetralin consists of a series of sequential reactions. In this analyses, light gases detected were assigned to the reaction steps as dictated by the stoichiometry required by the changes in liquid constituents. As has been well established, tetralin (I) is first oxidized to tetralin hydroperoxide (II).



Following this, the tetralin hydroperoxide decomposes to produce approximately equal molar quantities of the ketone, 1-tetralone (III), and the alcohol, 1,2,3,4-tetrahydro-1-naphthol (IV).



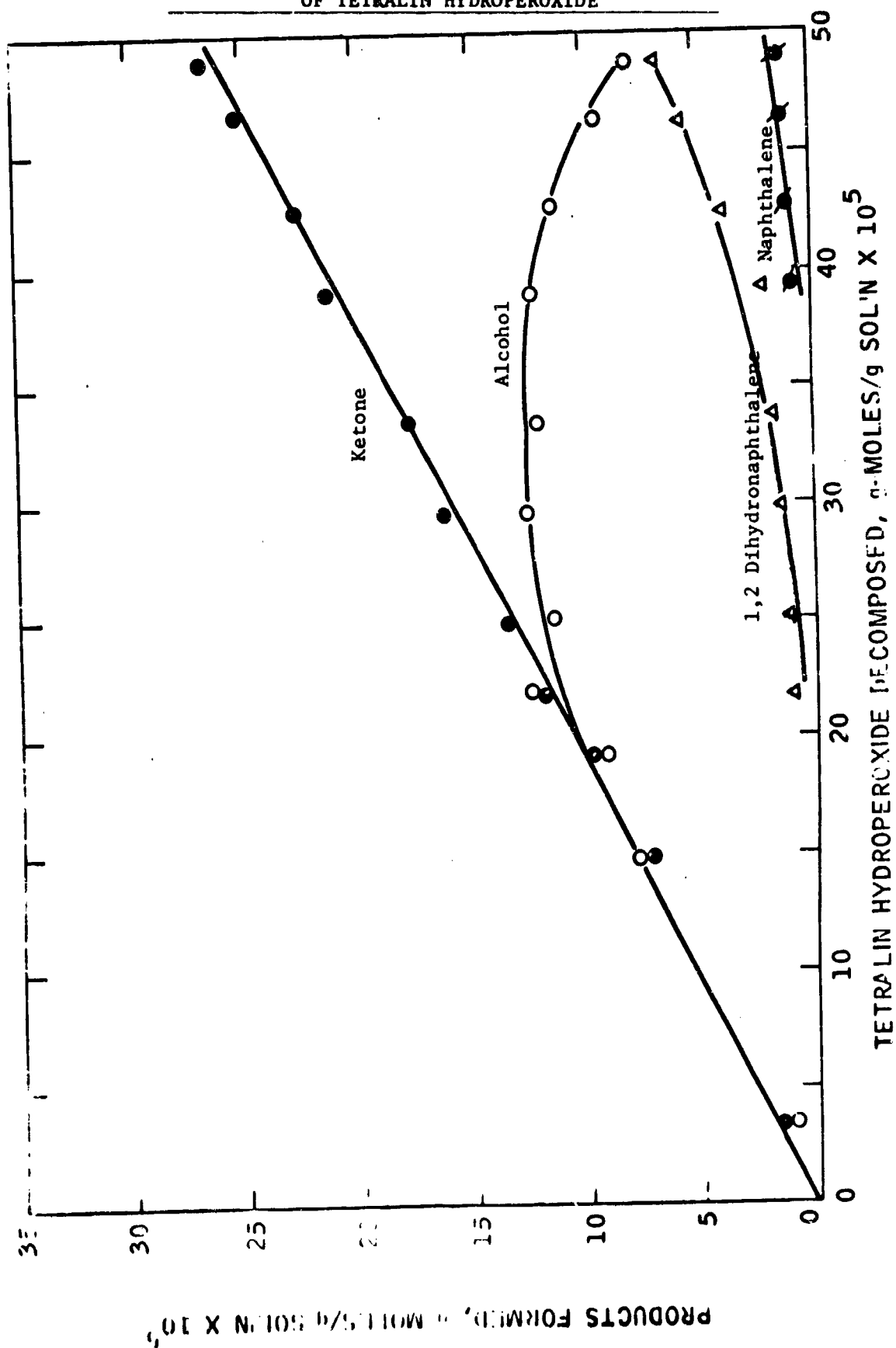
The ketone (III) is essentially stable in the reaction system. However, the alcohol (IV) undergoes further reaction to the olefin 1,2-dihydronaphthalene (V).

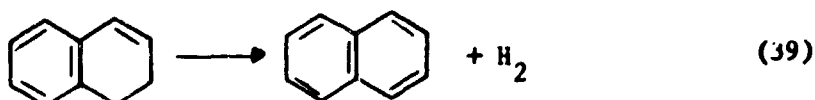


This olefin (V) then undergoes further reaction to produce naphthalene (VI).

FIGURE 96

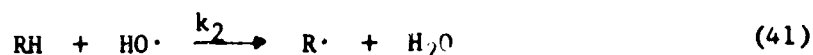
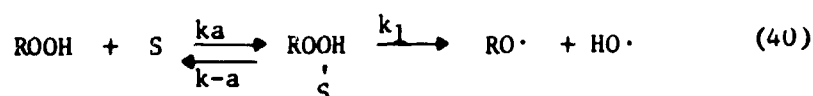
PRODUCTS OF THE TEFLON CATALYZED DECOMPOSITION
OF TETRALIN HYDROPEROXIDE





Reactions 36 through 39 represent the main routes for the poly(tetrafluoroethylene) catalyzed oxidation of tetralin for the conditions and reaction times studied. There is a possibility that other products formed at the end of the run at 115°C as material balances showed a tendency to fall below their normal 100% level. Although oxidative dehydrogenation of saturated hydrocarbons to form olefins is generally considered in the literature to be an important reaction only at much higher temperatures, e.g., 500 to 600°F (158), the present study clearly shows that this need not be the case. Moreover, the data suggest that oxidative dehydrogenation at low temperatures is probably a major reaction path in the complex autoxidative deposit formation process, and certainly merits further attention.

As pointed out by Walling (159) it is difficult to elucidate all the reactions in a complex system such as occurs in the oxidation of tetralin. Nevertheless, it is useful to consider possible mechanisms which can account for the salient features of the reaction system. The present results suggest that a major role of the catalyst surface is to increase radical production via decomposition of the intermediate hydroperoxide. Thus, during the initial portion of the oxidation in the presence of an inert solvent, the initiation step will involve adsorption on the catalyst surface, S, followed by decomposition, as follows:



Propagation steps are assumed to follow the conventional reactions, while termination is assumed to involve a rapid reaction between alkoxy radicals to produce the alcohol and ketone, and conventional termination of peroxy radicals.



It is reasonable to assume that the fraction of the catalyst surface covered with hydroperoxide, θ , reaches an equilibrium. Applying such a treatment to the reaction scheme yields

$$\frac{d\theta}{dt} = k_a k_4 [RO_2 \cdot] [RH] (1-\theta) - k_{-a} \theta - k_1 \theta = 0 \quad (46)$$

From which it follows:

$$k_4 K [RO_2 \cdot] [RH] = \frac{\theta}{1-\theta} \quad (47)$$

$$\text{Where } K = \frac{k_a}{k_{-a} + k_3}$$

An application of the conventional steady state treatment to the $R\cdot$, $RO_2\cdot$ and $HO\cdot$ radical productions results in the following relationships:

$$[RO_2 \cdot] = \left(\frac{k_1 \theta}{k_6} \right)^{1/2} \quad (48)$$

Substituting (H) into (G) and assuming that the fraction of the surface covered by hydroperoxide is low (i.e., $[\theta/(1-\theta)]^2 \approx \theta^2$) yields the following approximate solution.

$$\theta = \frac{k_1 k_4^2 K^2 [RH]^2}{k_6} \quad (49)$$

Following an analogous treatment by a number of authors (5,6), this solution is then coupled into a conventional oxidation rate expression to yield for the initial oxidation rate where ω is the weight of catalyst (the

$$\frac{dO_2}{dt} = \frac{k_4^2 k_1 K}{k_6} [RH]^2 \omega^{1/2} \quad (50)$$

total surface in the reaction vessel is directly proportional to the weight of catalyst). As can be seen this expression predicts the observed zero order dependence on oxygen pressure, second order dependence on hydrocarbon concentration and half order dependence on catalyst weight. (Table XVII)

TABLE XVII

RELATIVE RATES OF TETRALIN OXIDATION
AS A FUNCTION OF TETRALIN CONCENTRATION,
OXYGEN PRESSURE AND CATALYST LOADING

<u>Tetralin Concentration moles/liter</u>	<u>Oxygen, to rr</u>	<u>Catalyst Loading, grams</u>	<u>Relative Initial Rate of Oxidation $r/r_o^{(a)}$</u>
3.68	660	0.30	1.1
3.68	710	0.30	1.0
3.68	760	0.30	1.00 (base) ^(b)
3.68	810	0.30	1.0
3.68	760	0.15	0.68
3.68	760	0.30	1.00 (base) ^(c)
3.68	760	0.60	1.34
2.45	760	0.30	0.44
3.68	760	0.30	1.00 (base) ^(c)
4.91	760	0.30	1.86

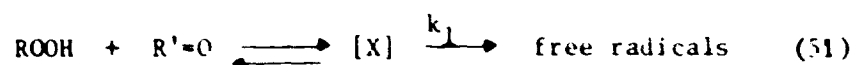
(a) Initial rate of oxidation at given conditions
relative to initial rate at standard conditions as shown.

(b) Study conducted at 65°C

(c) Study conducted at 90°C

A study was also made of the effect of the various products from the decomposition of tetralin hydroperoxide on the catalyzed rate of oxidation of tetralin. Included in this study were the effect of the ketone (III), the alcohol (IV), 1,2-dihydronaphthalene (V) and naphthalene (VI). In general, these studies were carried out by sequentially injecting the compound in question into the reaction mixture after the run was in progress and observing its effect on the subsequent portion of the run. One advantage of this method is that it assures that the catalyzed oxidation is proceeding in a normal manner before the effect of the added component is assessed. Studies were made at both 65 and 115°C. Results of the effect of the addition of the alcohol (IV) and the ketone (III) at 65°C are shown in Figure 97. At these conditions data obtained from oxygen uptake and tetralin conversion are equivalent. It can be seen that the presence of the alcohol (IV) had no significant effect on the course of the reaction, whereas the addition of the ketone (III) accelerated the rate of oxidation. The results obtained at 115°C confirm the earlier data. The presence of the alcohol (IV), dihydronaphthalene (V) and naphthalene (VI) had no significant effect on the rate of oxidation. However, the presence of the ketone (III), again increased the catalyzed rate of oxidation of tetralin.

In the present study, the ketone (III) was found to accelerate the rate of oxidation whereas the alcohol (IV) and other products (IV, VI) exerted no significant effect on the reaction. Robertson and Waters (147) also observed no significant effect of alcohols on the oxidation of tetralin. However, it has been found that ketones such as cyclohexanone can accelerate the decomposition of hydroperoxides (160). Following the treatment of Emanuel, this acceleration presumably reflects the formation of a complex of the hydroperoxide and ketone.



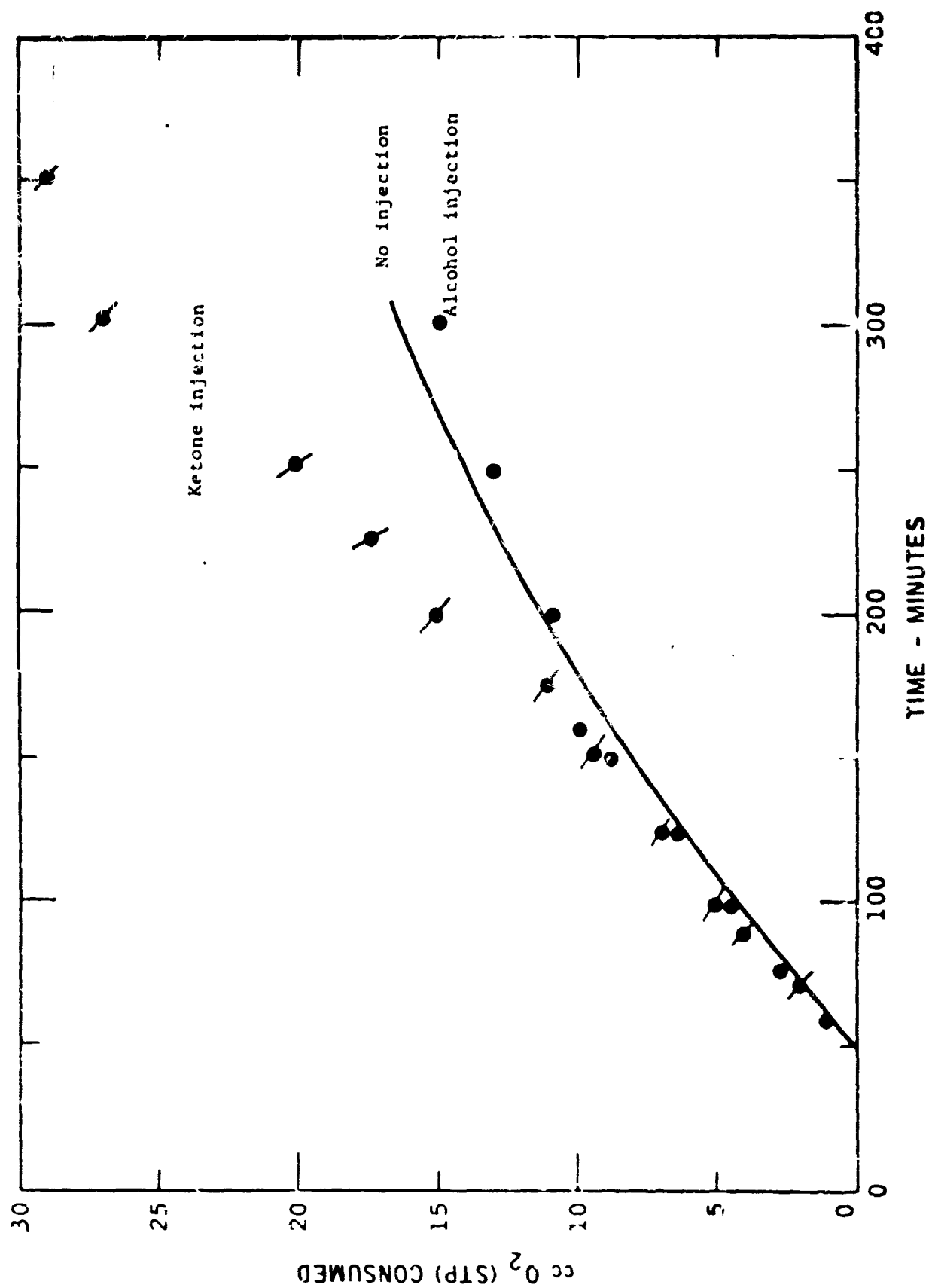
Initiation involves both direct hydroperoxide decomposition (reaction 40) and reaction 51. The complex [X] is assumed to decompose more rapidly than the hydroperoxide itself, so that at the latter stages of the reaction where the ketone concentration rises, reaction 51 would dominate the initiation process.

c. The Effect of Metal Oxides on the Oxidation of Tetralin

We extended our studies in the hydrocarbon autoxidation kinetics to metal oxide surfaces. Using this unit we previously demonstrated that polymeric surfaces are capable of catalyzing the autoxidation of typical jet fuel range hydrocarbons. These studies indicated that Teflon, polyethylene and polypropylene surfaces catalyze the autoxidation of tetralin, a typical jet fuel range hydrocarbon. In addition, these studies demonstrated that Teflon surfaces catalyze the decomposition of tetralin hydroperoxide. The present studies with metal oxides were designed (a) to provide a comparison of metal oxides versus polymeric surfaces for tetralin autoxidation, and (b) to extend our previous work on the effect of metal surfaces on jet fuel autoxidative deposit formation in the "empty" wing environment to a kinetically simpler system. As before, tetralin contained in chlorobenzene solvent was

FIGURE 97

KETONE ACCELERATES THE CATALYZED OXIDATION OF TETRALIN



added to the reactor. Solid catalyst in the form of a 60/80 mesh powder was then added to the reaction mixture and the reactor immersed in a temperature controlled bath. The reactor was attached to a vibrator designed to provide sufficient agitation to the solid-liquid slurry so as to minimize mass transfer limitation in the reaction system. The vibrator was operated at 800 rpm and separate experiments indicated that the rate of oxidation was independent of vibration speed at this fast rate. Oxygen was admitted at a constant pressure to the reactor from a burette measuring system. The rate of oxidation was measured by oxygen uptake. The primary reaction product is tetralin hydroperoxide, which was quantitatively determined by chemical titration. Gas chromatographic and infrared analysis of aliquot samples were made as before.

A variety of metal oxides were tested for their catalytic activity. Results of these studies are summarized in Table XVIII. Data are also shown for the uncatalyzed oxidation of tetralin at the same conditions. It can be seen that copper oxide (cupric and cuprous), cobalt oxide and nickel oxide are catalytically active for the autoxidation of tetralin. In the case of cobalt and nickel oxides, the highest oxidation rates were observed initially after the induction period, followed by a gradual decline in the rate of oxidation. In contrast, both the cuprous and cupric oxide catalyzed autoxidation of tetralin exhibited an increasing rate of oxidation past the induction period which passed through a maximum before exhibiting a gradual decline. This latter effect suggests that cuprous and cupric oxide are particularly effective in catalyzing the decomposition of the tetralin hydroperoxide initially produced. In any event, the high activity exhibited by the cuprous and cupric oxides confirms our previous experience with the effect of metal surface type on the rate of autoxidative deposit formation where copper surfaces were found to be highly deleterious.

The surface areas of the majority of the catalysts tested were also determined. This was done so that specific reaction rates (i.e., the rate of oxidation per unit area of catalyst) could be calculated and compared to see if the differences in reactivity could be explained in terms of simple differences in surface area. This data is shown in Table XIX. As can be seen, the more active cupric oxide had the lowest surface area, so that increased surface area per se does not guarantee increased catalyst activity. To further test this effect, we measured the activity of a high surface area (i.e., 300 m²/g) silica for the autoxidation of tetralin. This data is also shown in Table XVIII. In spite of the high surface area of the SiO₂, it was found to be completely inactive for the oxidation of tetralin at 90°C.

To further investigate this observation, we measured the activity and apparent activation energy of CuO, CoO, and NiO supported on a very high area silica. Results indicate that the apparent activation energies exhibited by these high surface area supported metal oxides are quite low, confirming the inverse dependence of apparent activation energy on surface area. Such a phenomena may explain to a great extent why copper containing wear debris from pump parts are so very deleterious. It would be expected that such copper particles would be quite low in surface area (i.e., the total surface should only be proportional to the bulk surface area of the debris particles which would be covered by an oxide coating in the presence of oxygen), and thus could exhibit a particularly high apparent activation energy for autoxidative deposit formation. Results are tabulated in Figure 98 and Table XX.

TABLE XVIII

SUMMARY OF HYDROCARBON AUTOXIDATION
KINETICS UNIT RUNS WITH METAL OXIDES

<u>Catalyst</u>	<u>Conditions (a)</u>	<u>Kinetic Parameters</u>	
		<u>Induction Period</u>	<u>Oxidation Rate cc O₂ (STP)/hr</u>
None	65°C	5 1/2 hrs	1.1
CuO	90°C	< 5 min	15 (initial) 120 (maximum)
Cu ₂ O	65°C	1 1/2 hrs	8 (initial) 30 (maximum)
CoO	90°C	< 3 min	52
NiO	90°C	< 5 min	40
SiO ₂	90°C	--	inactive

(a) Other conditions: 2 cc tetralin in 2 cc chlorobenzene,
1 atm O₂, 0.30 g. catalyst where
employed

TABLE XIX

SURFACE AREAS OF METAL OXIDE CATALYSTS

	<u>B.E.T. Surface Area, m²/g</u>
NiO	9.55
CoO	3.47
CuO	0.15
SiO ₂	300

TABLE XX

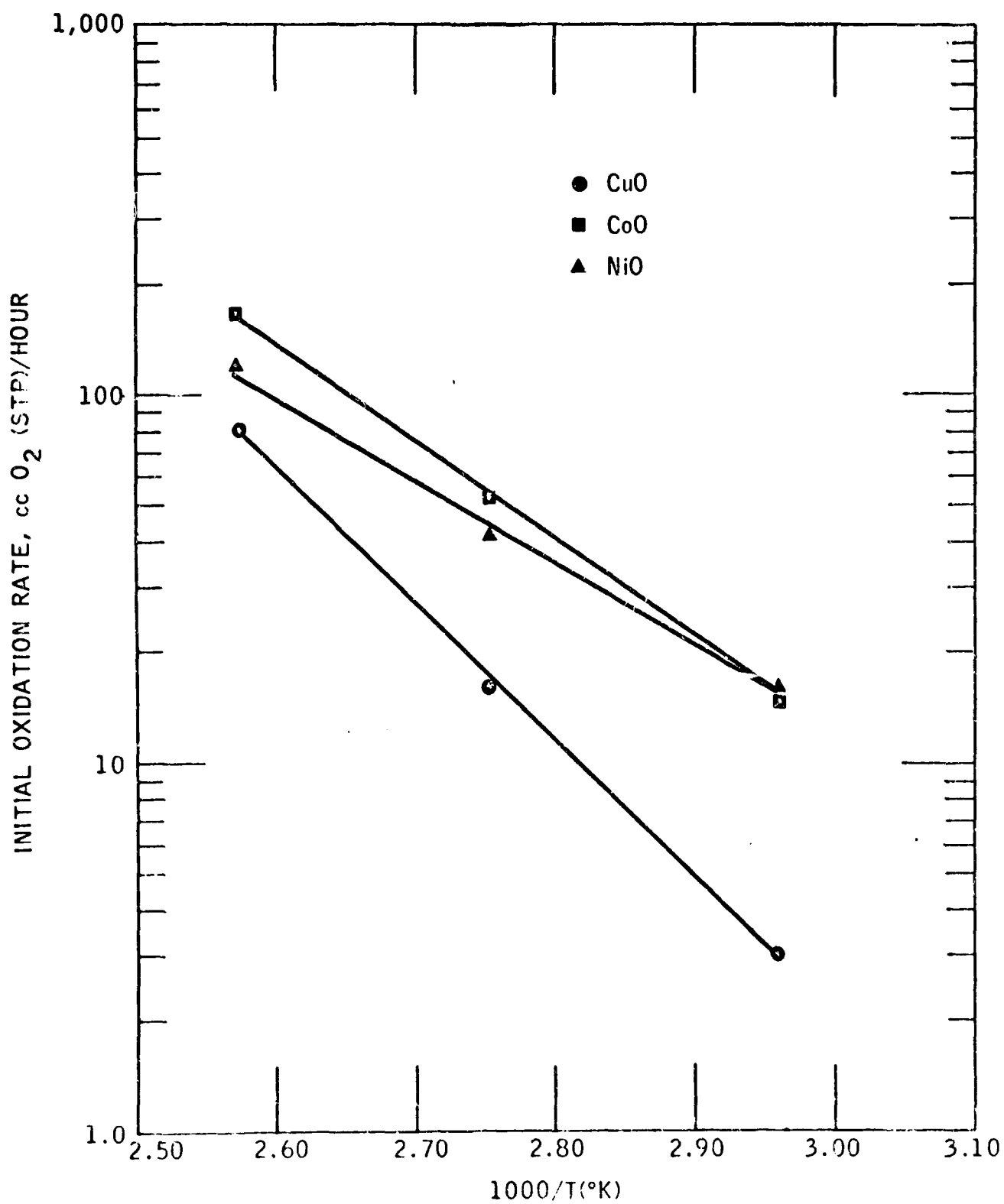
Activity of Supported Metal Oxides
for the Oxidation of Tetralin

<u>Catalyst</u>	<u>Temperature, °C</u>	<u>Initial Oxidation Rate, ClO₂ (STP) Per Hour</u>
CuO/SiO ₂	115	12
	90	9
CoO/SiO ₂	115	66
	90	55
NiO/SiO ₂	115	44
	90	33

Conditions: 2 cc of tetralin in 2 cc of chlorobenzene, 1 atm O₂
and 0.30 g catalyst

FIGURE 98

EFFECT OF TEMPERATURE
ON THE METAL OXIDE CATALYZED,
OXIDATION OF TETRALIN



IV. CONCLUSIONS

A program has been completed which was designed to (1) elucidate the underlying processes involved in deposit formation in the "empty" wing tank environment of a supersonic aircraft and (2) investigate potential methods to alleviate the problem. The deposits formed are nonvolatile and essentially insoluble in jet fuel hydrocarbons and are produced as a result of a complex free radical autoxidation process. The complete exclusion of oxygen suppresses deposit formation. Deposits are formed much more rapidly when a condensed (liquid) phase is present than when no condensed phase is present, i.e., only a vapor phase is present. An apparatus was designed which simulates the complex kinetic environment present in the "empty" wing tank. This unit quantitatively measures the rate of deposit formation in an accurate and reproducible manner and enables various jet fuels to be properly ranked in terms of their "empty" wing tank deposit formation tendency.

Higher total pressure increases both the level of deposit formation and the apparent activation energy for deposit formation. At 3 psia most fuels exhibit a 10 kcal/mole apparent activation energy which increases to the 20 to 30 kcal/mole range at atmospheric pressure. Increasing oxygen partial pressure at a fixed total pressure also increases the rate of deposit formation, but to a much lower extent than increasing total pressure.

Trace levels of various pure sulfur compounds markedly influence the rate of deposit formation. Structural effects are important, as individual sulfur compounds differ greatly in their effect on the rate of deposit formation. The addition of various pure sulfur compounds including thiols, sulfides, disulfides, and condensed thiophenes to an essentially sulfur-free hydrocarbon material at the 1000 ppm S level increased the rate of deposit formation to a factor of 20. The addition of diphenyl sulfide and dibenzothiophene at the same level did not increase the rate of deposit formation. The sulfur compounds which increase the rate of deposit formation decompose at the conditions studied into radical fragments which initiate the complex free-radical autoxidation reaction that lead to the formation of deposits. The presence of trace levels of nitrogen compounds also increases the rate of deposit formation. Trace contaminants such as sulfur and nitrogen compounds are also capable of interacting in the fuel to produce particularly deleterious deposit formation situations.

The nature of metal surfaces to which the fuel is exposed was found to influence the rate of deposit formation. Vanadium containing titanium alloys and copper surfaces were found to be particularly deleterious. The presence of dissolved metals also markedly increased the level of deposit formation. The results indicate that metals increase deposit formation by catalyzing the formation of free radicals which then initiate the complex autoxidation process which lead to deposits.

Studies were made with pure compounds and simple binary blends of pure compounds. The broad objective of this work was to elucidate the effect of jet fuel hydrocarbon composition on deposit formation. The deposit formation tendency of a pure n-paraffin decreases with increasing carbon number. For a given carbon number branched paraffins are more

deleterious than n-paraffins. The presence of an aromatic or naphthene in a binary blend with a paraffin inhibits deposit formation, particularly at lower concentrations and temperatures. The magnitude of this inhibition effect can be correlated with the number of benzylic hydrogen atoms present in the aromatic or naphthene contained in the blend. Olefins, in general, were found to be deleterious, although the effect of individual olefin compounds was found to vary widely.

Currently used antioxidant additives such as alkyl substituted phenols and a phenylenediamine were found to be ineffective in reducing the rate of deposit formation. The use of rust preventive and metal deactivator additives increased the rate of deposit formation, particularly at temperatures above 350°F. Thus, currently employed additives do not alleviate the "empty" wing tank problem of a high speed aircraft, and in certain cases may contribute to the problem.

The effect on deposit formation of coating an active metal surface with a polymeric material was investigated. It had been expected that such coatings would render these surfaces inactive for autoxidative reactions and thus reduce the level of deposit formation. Screening unit tests of polymer coated titanium alloys indicated, however, that the use of this polymeric coatings actually increased the level of deposit formation, particularly at higher temperatures. Independent experiments confirmed that polymers are catalysts for the autoxidation of jet fuel range hydrocarbons. Results indicate that polymeric surfaces catalyze the decomposition of the intermediate hydroperoxide which accelerates the autoxidative process which ultimately leads to the formation of deposits.

V. APPENDICES

APPENDIX 1

Screening Unit Evaluation of Baton Rouge
Fuel at Various Pressures

Conditions: Ti-8Al-1Mo-1V titanium strips, 4 hour run with
undiluted air at 5 l/hr flow rate, 125 cc/hr of hydro-
carbon fuel pretreated with air prior to admission to
reactor.

<u>Feed</u>	<u>Temperature, °F</u>	<u>Deposit Formation Rate g/cm²/4 hours x 10⁶</u>
Baton Rouge Fuel at 6 psia	325	6.90
	350	8.72
	375	19.3
	400	51.1
Baton Rouge fuel at 12 psia	325	11.5
	350	12.9
	375	27.6
	400	103
Baton Rouge fuel at 1 atm	325	14.7
	350	33.8
	375	93.9
	400	268

APPENDIX 1 continued

SCREENING UNIT EVALUATION OF VARIOUS
FUELS AT ATMOSPHERIC PRESSURE

Conditions: 1 atm, Ti-8Al-1Mo-1V strips, 4 hour run with undiluted air at 5 l/hr flow rate, 125 cc/hr of hydrocarbon fuel pretreated with air prior to admission to reactor.

<u>Feed</u>	<u>Temperature, °F</u>	<u>Deposit Formation Rate g/cm²/4 hours x 10⁶</u>
RAF-176-63	300	3.55
	325	9.80
	350	15.4
	375	21.2
	400	173.
F&W 523	300	1.96
	325	4.23
	350	6.20
	375	7.25
	400	34.7

APPENDIX 1 continued

Screening Unit Evaluation on n-Decane at Various Pressures

Conditions: Pure (Ti 75A) titanium strips, 4 hour run with undiluted air at 5 l/hr flow rate, 125 cc/hr of hydrocarbon fuel pretreated with air prior to admission to reactor.

<u>Feed</u>	<u>Temperature, °F</u>	<u>Deposit Formation Rate g/cm²/4 hours x 10⁶</u>
n-decane at 1 psia	200	4.45
	250	15.1
n-decane at 1 atm	200	0.88
	250	4.39
	275	6.78
	300	5.27
	325	14.8

APPENDIX 2

Effect of Oxygen Partial Pressure on Deposit Formation in the Screening Unit

Conditions: 1 atm total pressure, KAT-175-63 fuel, 125 cc/hour fuel feed rate,
Ti-6Al-1Fe-IV strips, fuel presaturated with same composition gas as is
passed through reactor during run, 4 hour run.

<u>Flowing Gas Composition</u>		<u>Temperature °F</u>	<u>Deposit formation rate, μ per cm²</u>
<u>O₂ partial pressure mm Hg</u>	<u>N₂ partial pressure mm Hg</u>		
16	764	350	5.92 x 10 ⁻⁶
		400	14.9 x 10 ⁻⁶
		450	20.7 x 10 ⁻⁶
80	680	450	26 x 10 ⁻⁶
		500	34.0 x 10 ⁻⁶
152	608	300	6.69 x 10 ⁻⁶
		350	14.7 x 10 ⁻⁶
		500	51.3 x 10 ⁻⁶

APPENDIX 3

SCREENING UNIT STUDIES OF THE DEPOSIT
FORMATION RATE AS A FUNCTION OF EXPOSURE TIME

Other Conditions: 3 psia, RAF-176-63 jet A kerosine at 125 cc/hour,
Ti-8Al-1Mo-1V strips, undiluted air at 5 l/minute,
fuel presaturated with air prior to admission to reactor.

<u>Run Length</u>	<u>Temperature, °F</u>	<u>Deposit Formation Rate Per Hour, g/cm²/hour x 10⁶</u>
1 Hour	350	3.25
	375	5.51
3 Hours	350	1.20
	375	2.69
8 Hours	300	0.27
	350	0.59
	400	1.35

APPENDIX 4

Screening Unit Evaluation of Water Saturated
n-Decane and Baton Rouge Fuel

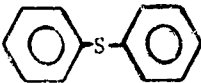
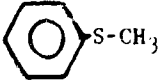
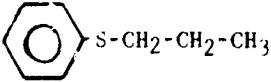
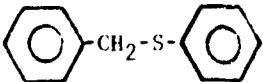
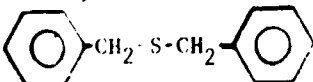
Conditions: 3 psia, 4 hour run with undiluted air at 5 l/hr flow rate,
125 cc/hr of hydrocarbon, Ti-8Al-1Mo-1V strip.

<u>Feed</u>	<u>Temperature °F</u>	<u>Deposit Formation Rate g/cm²/4 hours x 10⁶</u>
n-decane plus H ₂ O bubbled with air	250	2.39
	275	7.78
	300	25.9
Baton Rouge fuel plus H ₂ O bubbled with air	300	2.05
	350	12.0
	375	16.5
	400	10.8
Baton Rouge fuel plus H ₂ O bubbled with N ₂	350	3.94
	375	4.33
	400	5.32
	425	10.6

APPENDIX 5

SCREENING UNIT TESTS OF P6W 523 DOPED
WITH VARIOUS SULFIDES TO THE 1000 PPM S LEVEL

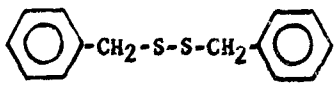
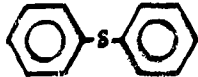
Other Conditions: 3 psia, 125 cc/hour of jet fuel, Ti-8Al-1Mo-1V strips,
4 hour run with undiluted air at 5 l/minute, fuel
presaturated with air prior to admission to reactor.

<u>Dopant</u>	<u>Temperature, °F</u>	<u>Deposit Formation Rate, g/cm²/4 hours x 10⁶</u>
Diphenyl Sulfide	300	1.28
	350	1.60
	400	4.50
	425	3.21
Phenyl Methyl Sulfide	300	30.6
	350	37.3
	375	30.5
	400	40.6
	450	72.9
	200	0.62
	225	2.36
	250	2.81
	275	17.6
Phenyl n-Propyl Sulfide	250	0.85
	300	7.92
	350	15.2
	400	30.1
	250	1.09
	275	2.82
	325	17.0
	375	12.7
Di n-Octyl Sulfide	350	2.33
$\text{CH}_3(\text{CH}_2)_7\text{S}-(\text{CH}_2)_7\text{CH}_3$	425	6.04
Benzyl Phenyl Sulfide	350	2.90
	375	3.71
	400	8.20
Dibenzyl Sulfide	300	1.60
	350	14.0
	375	13.8

APPENDIX 5 continued

SCREENING UNIT TESTS OF P&W 523
DOPED WITH OTHER SULFUR COMPOUNDS TO THE 1000 PPM S LEVEL

Other Conditions: 3 psia, 125 cc/hour of jet fuel flow, Ti-8Al-1Mo-1V strips,
4-hour run with undiluted air at 5 l/minute flow rate,
fuel presaturated with air prior to admission to reactor.

<u>Deposit</u>	<u>Temperature, °F</u>	<u>Deposit Formation Rate, g/cm²/4-hour run x 10⁶</u>
Dibenzyl Disulfide 	300	6.42
	350	11.0
	400	7.05
	425	6.33
Diphenylsulfide 	350	3.21
	375	2.83
	400	6.22
	425	3.68

APPENDIX 5 continued

SCREENING UNIT TESTS OF P&W 523
DOPED WITH CONDENSED THIOPHENES

<u>Dopant</u>	<u>Temperature, °F</u>	<u>Deposit Formation Rate, g/cm²/4 hours x 10⁶</u>
Dibenzothophene	350	2.31
	375	2.29
	300	1.53
	350	1.22
	400	4.40
Thianaphene	400	3.55
	425	20.1
		

APPENDIX 5 continued

SCREENING UNIT TESTS OF P&W 523
DOPED WITH PRIMARY ALKYL THIOLS TO THE 1000 PPM S LEVEL

Other Conditions: 3 psia, 125 cc/hour of jet fuel flow, Ti-8Al-1Mo-1V strips,
4-hour run with undiluted air at 5 l/minute flow rate,
fuel presaturated with air prior to admission to reactor.

<u>Deposit</u>	<u>Temperature, °F</u>	<u>Deposit Formation Rate, g/cm²/4-hour run x 10⁶</u>
1-Heptanethiol CH ₃ (CH ₂) ₆ SH	300	< 1
	400	3.5
	425	0.4
1-Dodecanethiol CH ₃ (CH ₂) ₁₁ SH	300	< 1
	350	2.06
	375	2.81
	400	4.62
	425	2.67
1-Hexadecanethiol CH ₃ (CH ₂) ₁₅ SH	300	0.79
	350	1.92
	375	2.87
	400	10.6
	425	16.4

APPENDIX 5 continued

SCREENING UNIT TESTS OF ISOBUTYL DISULFIDE DOPED P&W 523

Other Conditions: 3 psia, 125 cc/hour of jet fuel flow, Ti-8Al-1Mo-1V strips,
4-hour run with undiluted air at 5 l/minute flow rate,
fuel presaturated with air prior to admission to reactor.

<u>Sulfur Level of Isobutyl Disulfide Doped P&W 523, ppm S (Wt)</u>	<u>Temperature, °F</u>	<u>Deposit Formation Rate, g/cm²/4-hour run x 10⁶</u>
10	300	3.22
	350	4.13
	375	6.30
	400	2.02
	425	3.56
100	300	2.72
	350	3.24
	375	14.8
	400	1.33
	425	0.77
1000	300	2.04
	350	2.05
	375	23.7
	400	17.5
	425	2.34

APPENDIX 6

Screening Unit tests of P&W 523
Doped With Pure Nitrogen Compounds

Conditions: 3 psia, Ti-8Al-1Mo-1V titanium strips, 4 hour run with undiluted air at 5 l/hr flow rate, 125 cc/hr of hydrocarbon fuel pretreated with air prior to admission to the reactor.

<u>Feed</u>	<u>Temperature °F</u>	<u>Deposit Formation Rate g/cm²/4 hrs x 10⁶</u>
P&W 523 doped with 1000 ppm N using 2-ethylpyridine	225	0.67
	275	3.81
	300	6.22
P&W 523 doped with 1000 ppm N using indole	275	1.38
	300	5.30
	325	4.43
P&W 523 doped with 1000 ppm N using 2,5 dimethylpyrrole	225	1.10
	250	3.75
	275	5.52
	300	11.8
	325	15.1
P&W 523 doped with 100 ppm N using 2,5 dimethylpyrrole	200	0.95
	250	1.44
	300	6.87
P&W 523 doped with 10 ppm N using 2,5 dimethylpyrrole	200	0.56
	275	1.71
	300	2.33

APPENDIX 7

Screening Unit Evaluation of Sulfur-Nitrogen-Olefin
Interaction Study Blends

Conditions: 3 psia, pure (Ti 75A) titanium strips, 4 hour run with undiluted air at 5 l/hr flow rate, 125 cc/hr of hydrocarbon fuel pretreated with air prior to admission to reactor.

<u>Feed</u>	<u>Temperature, °F</u>	<u>Deposit Formation Rate g/cm²/4 hours x 10⁶</u>
2,5 Dimethylpyrrole (10 ppm N) in n-decane	200	5.01
	250	7.85
	275	6.42
	300	9.10
	325	13.9
Methylphenyl sulfide (1000 ppm S) in n-decane	200	0.5
	250	0.6
	275	11.6
	300	12.0
	325	15.3
Methylphenyl sulfide (100 ppm S) + 2,5 dimethylpyrrole (10 ppm N) in n-decane	200	3.61
	250	3.94
	275	6.95
	300	7.05
	325	15.4
2,5 Dimethylpyrrole (10 ppm N) + 2% 1-decene in n-decane	200	2.16
	250	5.12
	275	9.60
	300	5.72
	325	35.4
Methylphenylsulfide (1000 ppm S) + 2% 1-decene in n-decane	200	1.38
	250	5.12
	275	13.7
	300	17.9
	325	23.9
Methylphenylsulfide (1000 ppm S) + 2,5 Dimethylpyrrole (10 ppm N) + 2% 1-decene in n-decane	200	1.61
	250	5.11
	275	17.2
	300	25.7
	325	21.6

APPENDIX 8

SCREENING UNIT TESTS OF VARIOUS METALS

Other Conditions: 3 psia, 125 cc/hour of jet fuel RAF-176-63, 4-hour run with undiluted air at 5 l/minute flow rate, fuel presaturated with air prior to admission to reactor.

<u>Metal Strip Type</u> ⁽¹⁾	<u>Temperature, °F</u>	<u>Deposit Formation Rate, g/cm²/4-hour run x 10⁶</u>
Pure Titanium (Ti 75A)	300	0.90
	400	3.11
	425	7.70
	475	5.90
Ti-6Al-4V	300	3.72
	400	14.2
	425	21.1
Stainless Steel 304	300	1.0
	400	2.74
	425	5.76
	475	4.65

(1) All Titanium samples procured from Titanium Metals Corp. of America, Toronto, Ohio.

APPENDIX 8 continued

SCREENING UNIT EVALUATION OF ALUMINUM METAL

Other Conditions: 3 psia, 125 cc/hr of RAF-176-63, 4 hour run with undiluted air at 5 l/min flow rate, fuel pre-saturated with air prior to admission to reactor. Aluminum was 6061 alloy.

<u>Temperature</u> <u>°F</u>	<u>Deposit Formation Rate</u> <u>g/cm²/4 hours X 10⁶</u>
275	0.50
300	0.52
350	2.31
375	2.24
350	2.65
375	2.60
425	6.23

APPENDIX 9

SCREENING UNIT TESTS OF METAL ACETYLACETONATE
DOPED RAF-176-63

Other Conditions: 3 psia, 125 cc/hour fuel flow rate, Ti-8Al-1Mo-1V strips, 4 hour run with undiluted air at 5 l/min flow rate, fuel pre-saturated with air prior to admission to reactor.

<u>Dopant and Concentration</u>	<u>Temperature, °F</u>	<u>Deposit Formation Rate g/cm²/4 hours X 10⁶</u>
CoII (AcAc) ₂ (500 ppm CoII)	200	2.34
	250	11.9
	300	161.
	350	345.
VOII (AcAc) ₂ (50 ppm VOII)	200	22.7
	250	30.2
	275	89.8
	350	156.
VIII (AcAc) ₃ (50 ppm VIII)	200	88.6
	250	104.
	275	96.3
	300	153.
	350	405.
FeIII (AcAc) ₃ (2 ppm FeIII)	250	0.80
	275	4.83
	300	12.6
	350	128.
FeIII (AcAc) ₃ (5 ppm FeIII)	250	3.34
	275	6.32
	350	215.
FeIII (AcAc) ₃ (20 ppm FeIII)	250	5.20
	275	15.3
	300	58.8
	350	252.
FeIII (AcAc) ₃ (100 ppm FeIII)	225	19.7
	275	55.1
	350	1,148.

APPENDIX 9 continued

SCREENING UNIT TESTS OF RAF-176-63 DOPED WITH
METAL ACETYLACETONATES TO THE 50 PPM METAL LEVEL

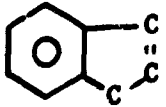
Other Conditions: 3 psia, 125 cc/hour of jet fuel, Ti-8Al-1Mo-1V strips,
4 hour run with undiluted air at 5 l/minute, fuel
presaturated with air prior to admission to reactor.

<u>Dopant</u>	<u>Temperature, °F</u>	<u>Deposit Formation Rate g/cm²/4 hours x 10⁶</u>
Ferric Acetylacetonate Fe III (C ₅ H ₇ O ₂) ₃	200	0.68
	250	15.1
	275	68.7
	300	154.
	350	452.
Nickel Acetylacetonate Ni II (C ₅ H ₇ O ₂) ₂	200	3.05
	250	10.5
	275	77.4
	300	93.1
Copper Acetylacetonate Cu II (C ₅ H ₇ O ₂) ₂	200	4.77
	275	105.
	300	524.

APPENDIX 10

SCREENING UNIT TESTS OF PURE HYDROCARBONS

Conditions: 3 psia, 125 cc/hr of hydrocarbon, pure titanium strip (Ti75A),
4 hour run with undiluted air at 5 l/min flow rate, fuel
presaturated with air prior to admission to reactor.

<u>Feed</u>	<u>Temperature, °F</u>	<u>Deposit Formation Rate g/cm²/4 hours X 10⁶</u>
n-decane	200	2.10
CH ₃ (CH ₂) ₈ CH ₃	250	4.61
	300	13.1
	325	19.2
	250	4.83
	300	11.2
	375	37.0
n-tetradecane	275	2.25
CH ₃ (CH ₂) ₁₂ CH ₃	350	9.82
	375	15.2
n-hexadecane	325	3.83
CH ₃ (CH ₂) ₁₄ CH ₃	400	4.50
	425	23.2
	325	4.37
	475	37.9
10 wt% 1-hexadecene	300	16.5
CH ₂ =CH(CH ₂) ₁₃ CH ₃	350	33.2
in hexadecane	400	109.
	450	210.
10 wt% indene	200	122
	250	318
	275	354
	300	648
in decane	350	1,028

APPENDIX 10 continued

Screening Unit Tests of Pure Hydrocarbon Compounds

Conditions: 3 psia, pure titanium strips (Ti 75A) 4 hour run with undiluted air at 5 l/min flow rate, 125 cc/hr of hydrocarbon feed pre-treated with air prior to admission to the reactor.

<u>Feed</u>	<u>Temperature °F</u>	<u>Deposit Formation Rate g/cm²/4 hrs x 10⁶</u>
n-dodecane	200	0.70
CH ₃ (CH ₂) ₁₀ CH ₃	300	5.21
	325	21.8
10 wt% diphenylmethane + 90 wt% n-decane	250	0.54
	275	2.26
	300	15.7
	325	20.5
2,2,4,6,6 Pentamethyl heptane	200	3.60
	250	10.2
	275	8.63
$ \begin{array}{ccccccc} & \text{CH}_3 & & \text{CH}_3 & & \text{CH}_3 & \\ & & & & & & \\ \text{CH}_3 & - \text{C} & - \text{CH}_2 & - \text{CH} & - \text{CH}_2 & - \text{C} & - \text{CH}_3 \\ & & & & & & \\ & \text{CH}_3 & & & & \text{CH}_3 & \end{array} $		

APPENDIX 10 continued

Screening Unit Tests of Pure Hydrocarbons:
Methyl Naphthalene in Decane Concentration Study

Conditions: 3 psia, pure titanium strips (Ti75A), 4 hour run with undiluted air at 5 l/min flow rate, 125 cc/hr of hydrocarbon, fuel pretreated with air prior to admission to reactor.

<u>Feed</u>	<u>Temperature °F</u>	<u>Deposit Formation Rate g/cm²/4 hrs. x 10⁶</u>
2 wt% 1-methyl naphthalene- 98 wt% n-decane	200	1.18
	300	11.0
10 wt% 1-methyl naphthalene- 90 wt% n-decane	200	0.54
	250	1.29
	300	4.35
	325	9.68
23 wt% 1-methyl naphthalene- 77 wt% n-decane	250	1.61
	300	5.95
	325	8.49
50 wt% 1-methyl naphthalene- 50 wt% n-decane	200	0.81
	250	2.15
	275	4.57
	300	9.15
	325	12.9
77 wt% 1-methyl naphthalene- 23 wt% n-decane	225	0.94
	275	3.54
	325	41.1
90 wt% 1-methyl naphthalene- 10 wt% decane	250	2.16
	275	4.67
	325	67.9
100% 1-methyl naphthalene	200	0.94
	250	5.10
	300	51.4
	325	105.

APPENDIX 10 continued

**Screening Unit Tests of Pure Hydrocarbons:
Binary Blends of an Aromatic or Naphthene in a Paraffin**

Conditions: 3 psia, pure titanium strips (Ti 75A), 4 hour run with undiluted air at 5 l/min flow rate, 125 cc/hr of hydrocarbon, fuel pretreated with air prior to admission to reactor.

<u>Feed</u>	<u>Temperature °F</u>	<u>Deposit Formation Rate g/cm²/4 hrs. x 10⁶</u>
10 wt% diisopropyl benzene (50 meta, 40 para and 10 ortho) - 90 wt% n- hexadecane	350	0.62
	400	5.43
	425	12.0
	475	24.9
10 wt% diisopropyl benzene (50 meta, 40 para and 10 ortho) - 90 wt% n-decane	200	0.26
	275	3.01
	300	3.21
	325	16.9
10 wt% 1-phenyl octane- 90% n-decane	200	1.03
	250	1.35
	300	4.86
10 wt% n-butyl cyclohexane- 90 wt% n-decane	250	3.02
	275	3.50
	325	18.6
10 wt% para-tert butyl toluene- 90 wt% n-decane	200	0.45
	250	1.34
	300	3.25
	325	8.81
10 wt% Phenylcyclohexane-90 wt% n-decane	200	0.86
	250	2.08
	275	4.50
	325	21.7
10 wt% 2-methyl naphthalene- 90 wt% n-decane	250	0.80
	300	1.94
	325	3.35
	375	3.85
10 wt% naphthalene-90 wt% n-decane	225	1.80
	275	2.85
	300	7.10
	325	8.65
10 wt% tetralin-90 wt% n-decane	200	0.50
	250	1.35
	300	2.95
	325	2.90
10 wt% decalin - 90 wt% n-decane	250	3.35
	275	4.05
	300	6.84
	325	7.06

APPENDIX 10 continued

SCREENING UNIT EVALUATION
OF PURE COMPOUND BLENDS

Conditions: 3 psia, pure (Ti 75A) titanium strips, 4 hour run with undiluted air at 5 l/hr flow rate, 125 cc/hr of hydrocarbon fuel pretreated with air prior to admission to reactor.

<u>Feed</u>	<u>Temperature, °F</u>	<u>Deposit Formation Rate</u> <u>g/cm²/4 hours x 10⁶</u>
10 wt. % fluorene in n-decane	275	3.20
	300	4.85
	325	25.7
10 wt. % n-octane in n-decane	150	2.28
	200	4.18
	275	40.3
10 wt. % 2,3,4-trimethyl- pentane in n-decane	100	1.11
	200	22.3
	225	14.6
	275	127

APPENDIX 10 continued

Screening Unit Evaluation of Olefins in n-Decane

Conditions: 3 psia, pure (Ti 75A) titanium strips, 4 hour run with undiluted air at 5 l/hr flow rate, 125 cc/hr of hydrocarbon fuel pretreated with air prior to admission to reactor.

<u>Feed</u>	<u>Temperature, °F</u>	<u>Deposit Formation Rate g/cm²/4 hours x 10⁶</u>
10 wt% 4-vinylcyclohexene in n-decane	200	56.6
	250	197
	275	118
10 wt% vinylcyclohexane in n-decane	200	1.40
	250	10.3
	275	29.4
10 wt% allylbenzene in n-decane	200	7.35
	250	41.6
10 wt% 4-phenyl-1-butene in n-decane	200	8.64
	275	86.9
	300	82.9
10 wt% 1-phenyl-2-butene in n-decane	200	2.15
	275	26.5
	300	17.3
	325	91.8
10 wt% 7-methyl-3 methylene- 1,6 octadiene in n-decane	200	66.8
	250	143
	275	148

APPENDIX 10 continued

SCREENING UNIT EVALUATION OF INDENE-DECANE
BLEND AT ATMOSPHERIC PRESSURE

Conditions: Pure titanium (Ti75A) strips, 4 hour
run with undiluted air, fuel pretreated
with air prior to admission to reactor

<u>Feed</u>	<u>Temperature, °F</u>	<u>Deposit Formation Rate g/cm²/4 hours x 10⁶</u>
10 wt % indene	200	271.
	225	422.
	250	782.
in n-decane	300	4,050.

APPENDIX 10 continued

Screening Unit Tests of Olefins in Decane

Conditions: 3 psia, pure titanium strips (Ti 75A), 4 hour run with undiluted air at 5 l/min flow rate, 125 cc/hr of hydrocarbon, fuel pretreated with air prior to admission to reactor.

<u>Feed</u>	<u>Temperature °F</u>	<u>Deposit Formation Rate g/cm²/4 hrs. x 10⁶</u>
10 wt% 1-decene - 90 wt% n-decane	250	28.5
	275	36.8
	325	48.9
1 wt% indene - 99 wt% n-decane	200	9.60
	300	30.8
5 wt% indene 95 wt% n-decane	200	47.6
	300	266.

APPENDIX 10 continued

Screening Unit Evaluation of Olefin-Naphthene-
Aromatic Interaction Study Blends

Conditions: 3 psia, pure (Ti 75A) titanium strips, 4 hour run with undiluted air at 5 l/hr flow rate, 125 cc/hr of hydrocarbon fuel pretreated with air prior to admission to reactor.

<u>Feed</u>	<u>Temperature, °F</u>	<u>Deposit Formation Rate g/cm²/4 hours x 10⁶</u>
10 wt% 1-methylnaphthalene + 10% decalin in n-decane	250	0.81
	300	5.92
	325	14.1
2 wt% 1-decene in n-decane	200	3.95
	275	14.6
	325	34.7
10 wt% decalin + 2% 1-decene in n-decane	200	2.67
	250	8.71
	275	10.6
	300	17.5
10 wt% 1-methylnaphthalene + 10% decalin + 2% 1-decene in n-decane	250	0.61
	275	1.51
	300	21.5
	325	48.5
10 wt% 1-methylnaphthalene + 2% 1-decene in n-decane	250	1.20
	300	19.9
	325	29.7

APPENDIX 11

SCREENING UNIT EVALUATION OF AFFB-12-68

Conditions: 3 psia, Ti-8Al-1Mo-1V titanium strips,
4 hour run with undiluted air at 5 l/hr
flow rate, 125 cc/hr of hydrocarbon fuel
pretreated with air prior to admission
to reactor

<u>Evaluation</u>	<u>Temperature, °F</u>	<u>Deposit Formation Rate</u> <u>g/cm²/4 hours x 10⁶</u>
First	275	0.85
	300	2.80
	325	2.30
	350	4.61
Second	225	1.00
	250	3.40
	275	1.35
	300	0.90
	325	9.52
Third	300	3.31
	325	2.65
	350	2.40
	375	4.60
	400	16.6

APPENDIX 11 continued

SCREENING UNIT TEST OF AFFB-8-67 AND AFFB-9-67

Other Conditions: 125 cc/hr of fuel, 4 hour run, total gas flow of 5 l/min

<u>Fuel and Conditions</u>	<u>Temperature °F</u>	<u>Deposit Formation Rate g/cm²/4 hours X 10⁶</u>
AFFB-9-67 3 psia, Ti-8Al-1Mo-1V undiluted air	300	3.38
	350	6.52
	400	15.2
	350	8.31
	375	13.6
	400	16.8
AFFB-8-67 (AZ-1) 1 atm total pressure stainless steel 32 mm Hg O ₂ partial pressure	300	4.35
	325	4.10
	350	7.01
	375	11.9
	425	34.3

APPENDIX 11 continued

Screening Unit Evaluation of Fuel AFFB-10-67

Conditions: 3 psia, Ti-8Al-1Mo-1V titanium strips, 4 hour run with undiluted air at 5 l/hr flow rate, 125 cc/hr of hydrocarbon fuel pretreated with air prior to admission to the reactor.

<u>Temperature °F</u>	<u>Deposit Formation Rate g/cm²/4 hrs x 10⁶</u>
300	1.12
325	1.94
350	2.23
375	2.72

APPENDIX 11 continued

Screening Unit Evaluation of Fuel
AFFB-4-64 (FA-S-1)

Conditions: 3 psia, Ti-8Al-1Mo-1V, 4 hour run with undiluted air at 5 l/min flow rate, 125 cc/hr of hydrocarbon, fuel pre-treated with air prior to admission to reactor.

<u>Run</u>	<u>Temperature °F</u>	<u>Deposit Formation Rate g/cm²/4 hrs x 10⁶</u>
1	300	3.40
	325	10.8
	350	34.6
	375	72.3
	425	110.5
2	325	6.56
	350	28.0
	375	111.4
	425	96.0

APPENDIX 11 continued

SCREENING UNIT EVALUATION OF RAY-174-63

Conditions: 3 psia, Ti-8Al-1Mo-1V titanium strips,
4 hour run with undiluted air at 5 l/hr
flow rate, 125 cc/hr of hydrocarbon fuel
pretreated with air prior to admission
to reactor

<u>Evaluation</u>	<u>Temperature, °F</u>	<u>Deposit Formation Rate</u> <u>g/cm²/4 hours x 10⁶</u>
First	250	2.55
	275	3.50
	300	3.20
	325	6.51
	350	15.3
Second	325	4.12
	350	7.03
	375	2.85
	400	1.30

APPENDIX 11 continued

Screening Unit Evaluation of Fuel AFFB-11-68

Conditions: 3 psia, Ti-8Al-1Mo-1V titanium strips, 4 hour run with undiluted air at 5 l/hr flow rate, 125 cc/hr of hydrocarbon fuel pretreated with air prior to admission to the reactor.

<u>Temperature °F</u>	<u>Deposit Formation Rate g/cm²/4 hours x 10⁶</u>
300	1.22
350	3.06
375	2.55
425	4.27

APPENDIX 12

Screening Unit Evaluation of Additive A022 in RAF-176-63

Conditions: 3 psia, Ti-8Al-1Mo-1V titanium strips, 4 hour run with undiluted air at 5 l/hr flow rate, 125 cc/hr of hydrocarbon fuel pretreated with air prior to admission to the reactor.

<u>Feed</u>	<u>Temperature °F</u>	<u>Deposit Formation Rate g/cm²/4 hrs x 10⁶</u>
RAF-176-63	300	1.16
	325	3.78
	350	3.88
RAF-176-63 plus 8.4 lb/1000 bbl of A022	325	3.39
	350	3.05
	375	4.44
RAF-176-63 plus 8.4 lbs/1000 bbl of A022	300	1.22
	325	3.66
	350	3.61
RAF-176-63	300	1.36
	325	3.39
	350	3.56
	375	5.02

APPENDIX 12 continued

Screening Unit Evaluation of Additive A031
In Baton Rouge Fuel

Conditions: 3 psia, Ti-8Al-1Mo-1V titanium strips, 4 hour run with undiluted air at 5 l/hr flow rate, 125 cc/hr of hydrocarbon fuel pretreated with air prior to admission to the reactor.

<u>Feed</u>	<u>Temperature °F</u>	<u>Deposit Formation Rate</u> <u>g/cm²/4 hrs x 10⁶</u>
Baton Rouge	300	0.56
	350	3.05
	425	5.50
Baton Rouge plus 8.4 lbs/1000 bbls A031	300	0.89
	400	5.82
Baton Rouge plus 8.4 lbs/1000 bbls A031	300	1.28
	375	7.11
	425	7.73
Baton Rouge	300	1.11
	350	2.61
	400	5.28

APPENDIX 12 continued

Screening Unit Evaluation of Additive A029
in Baton Rouge Fuel

Conditions: 3 psia, Ti-8Al-1Mo-1V titanium strips, 4 hour run with undiluted air at 5 l/hr flow rate, 125 cc/hr of hydrocarbon fuel pretreated with air prior to admission to the reactor.

<u>Feed</u>	<u>Temperature °F</u>	<u>Deposit Formation Rate g/cm²/4 hrs x 10⁶</u>
Baton Rouge	325	1.62
	425	11.0
Baton Rouge plus 8.4 lbs/1000 bbl A029	350	4.88
	400	6.10
Baton Rouge plus 8.4 lbs/1000 bbl A029	300	0.55
	325	1.66
	425	8.20

APPENDIX 12 continued

Screening Unit Evaluation of Additive Ethyl 733
In Baton Rouge Feed

Conditions: 3 psia, Ti-8Al-1Mo-1V titanium strips, 4 hour run with undiluted air at 5 l/hr flow rate, 125 cc/hr of hydrocarbon fuel pretreated with air prior to admission to the reactor

<u>Feed</u>	<u>Temperature °F</u>	<u>Deposit Formation Rate</u> <u>g/cm²/4 hrs x 10⁶</u>
Baton Rouge	325	2.25
	400	5.38
	425	3.06
Baton Rouge plus 8.4 lbs/ 1000 bbl of Ethyl 733	350	2.93
	375	3.17
Baton Rouge plus 8.4 lbs/ 1000 bbl of Ethyl 733	375	4.27
	400	3.89

APPENDIX 12 continued

Screening Unit Evaluation of Fluorocarbon Lubricity
Additive in Baton Rouge Fuel

Conditions: 3 psia, Ti-8Al-1Mo-1V titanium strips, 4 hour run with undiluted air at 5 l/hr flow rate, 125 cc/hr of hydrocarbon fuel pretreated with air prior to admission to the reactor.

<u>Feed</u>	<u>Temperature, °F</u>	<u>Deposit Formation Rate g/cm²/4 hrs x 10⁶</u>
Baton Rouge	300	0.67
	375	3.89
Baton Rouge plus 100 ppm wt. Fluorocarbon Lubricity Additive	350	3.47
	375	3.78
Baton Rouge plus 100 ppm wt. Fluorocarbon Lubricity Additive	300	0.55
	375	5.95
	425	3.16

APPENDIX 12 continued

Screening Unit Evaluation of Methyl Cellosolve Additive
in Baton Rouge Fuel

Conditions: 3 psia, Ti-8Al-1Mo-1V titanium strips, 4 hour run with undiluted air at 5 l/hr flow rate, 125 cc/hr of hydrocarbon fuel pretreated with air prior to admission to the reactor.

<u>Feed</u>	<u>Temperature °F</u>	<u>Deposit Formation Rate g/cm²/4 hrs x 10⁶</u>
Baton Rouge	300	0.84
	400	4.68
Baton Rouge plus 0.07 Vol % Methyl Cellosolve	350	2.93
	375	4.12
	400	7.22
Baton Rouge plus 0.15 Vol % Methyl Cellosolve	300	1.06
	375	7.18

APPENDIX 12 continued

Screening Unit Evaluation of Additive Santolene C
in Baton Rouge Fuel

Conditions: 3 psia, Ti-8Al-1Mo-1V titanium strips, 4 hour run with undiluted air at 5 l/hr flow rate, 125 cc/hr of hydrocarbon fuel pretreated with air prior to admission to the reactor.

<u>Feed</u>	<u>Temperature °F</u>	<u>Deposit Formation Rate g/cm²/4 hrs x 10⁶</u>
Baton Rouge	350	4.10
	400	5.50
Baton Rouge plus 16 lbs/1000 bbl Santolene C	350	17.8
	375	19.6
	400	15.2
Baton Rouge plus 16 lbs/1000 bbl Santolene C	350	23.9
	375	36.4

APPENDIX 12 continued

Screening Unit Evaluation of Additive AFA-1
in Baton Rouge Fuel

Conditions: 3 psia, Ti-8Al-1Mo-1V titanium strips, 4 hour run with undiluted air at 5 l/hr flow rate, 125 cc/hr of hydrocarbon fuel pretreated with air prior to admission to the reactor.

<u>Feed</u>	<u>Temperature °F</u>	<u>Deposit Formation Rate g/cm²/4 hrs x 10⁶</u>
Baton Rouge	350	2.89
	400	5.87
Baton Rouge plus 16 lbs/1000 bbl AFA-1	350	18.8
	375	26.1
Baton Rouge plus 16 lbs/1000 bbl AFA-1	350	31.5

APPENDIX 12 continued

Screening Unit Evaluation of Additive DMD
in Baton Rouge Fuel

Conditions: 3 psia, Ti-8Al-1Mo-1V titanium strips, 4 hour run with undiluted air at 5 l/hr flow rate, 125 cc/hr of hydrocarbon fuel pretreated with air prior to admission to the reactor.

<u>Feed</u>	<u>Temperature °F</u>	<u>Deposit Formation Rate g/cm²/4 hrs x 10⁶</u>
Baton Rouge	325	2.39
	400	3.97
Baton Rouge plus 2.0 lbs/ 1000 bbl of DMD	300	1.12
	350	8.96
	375	14.4
Baton Rouge plus 2.0 lbs/ 1000 bbl of DMD	350	11.1
	375	15.0

APPENDIX 13

Screening Unit Evaluation of RS 5660 Coated
Coated Ti-6Al-4V Strips

General Conditions: 3 psia, 4 hour run with undiluted air at 5 l/hr flow rate, 125 cc/hr of hydrocarbon fuel (when used) pre-treated with air prior to admission to reactor.

<u>Conditions</u>	<u>Temperature °F</u>	<u>Weight Change Grams x 10⁶</u>
Air Only	250	41 (loss)
	300	72 (loss)
	350	45 (loss)
	375	67 (loss)
	400	89 (loss)
Air plus AFFB-4-64	250	8 (gain)
	300	110 (gain)
	350	1037 (gain)
	375	1713 (gain)
	400	3203 (gain)

APPENDIX 13 continued

Screening Unit Evaluation of 954-01 Coated
Ti-6Al-4V Strips

General Conditions: 3 psia, 4 hour run with undiluted air at 5 l/hr flow rate, 125 cc/hr of hydrocarbon fuel (when used) pre-treated with air prior to admission to reactor.

<u>Conditions</u>	<u>Temperature</u>	<u>Weight Change Grams x 10⁶</u>
Air Only	250	26 (loss)
	300	29 (loss)
	350	140 (loss)
	375	310 (loss)
	400	1168 (loss)
Air plus AFFB-4-64	250	166 (gain)
	300	65 (gain)
	350	7 (gain)
	375	198 (gain)
	400	4098 (gain)

APPENDIX 13 continued

Screening Unit Evaluation of TFE 851-204 Coated
Ti-6Al-4V Strips

General Conditions: 3 psia, 4 hour run with undiluted air at 5 l/hr flow rate, 125 cc/hr of hydrocarbon fuel (when used) pre-treated with air prior to admission to reactor.

<u>Conditions</u>	<u>Temperature °F</u>	<u>Weight Change Grams x 10⁶</u>
Air plus AFB-4-64	250	112 (gain)
	300	179 (gain)
	350	1251 (gain)
	375	588 (gain)
	400	827 (gain)

APPENDIX 13 continued

Screening Unit Evaluation of 94-003 Coated
Ti-6Al-4V Strips

General Conditions: 3 psia, 4 hour run with undiluted air at 5 l/hr flow rate, 125 cc/hr of hydrocarbon fuel (when used) pretreated with air prior to admission to reactor.

<u>Conditions</u>	<u>Temperature °F</u>	<u>Weight Change Grams x 10⁶</u>
Air Only	250	144 (loss)
	300	585 (loss)
	350	1227 (loss)
	375	1698 (loss)
	400	3672 (loss)
Air plus AFTB-4-64	250	2235 (gain)
	300	888 (loss)
	350	2252 (gain)
	375	3303 (gain)
	400	5752 (gain)

APPENDIX 13 continued

Screening Unit Evaluation of Silicone R671
Coated Ti-6Al-4V Strips

General Conditions: 3 psia, 4 hour run with undiluted air at 5 l/hr flow rate, 125 cc/hr of hydrocarbon fuel (when used) pre-treated with air prior to admission to reactor.

<u>Conditions</u>	<u>Temperature °F</u>	<u>Weight Change Grams x 10⁶</u>
Air Only	250	46 (loss)
	300	58 (loss)
	350	44 (loss)
	375	51 (loss)
	400	57 (loss)
Air plus APTB-4-64	250	163 (loss)
	300	135 (loss)
	350	88 (loss)
	375	421 (gain)
	400	1175 (gain)

APPENDIX 13 continued

Screening Unit Evaluation of Coated Boeing Strips

Temperature °F	Weight Change in Grams x 10 ⁶			
	350-204 TFE Plus 855-109 TFE Coated Strips		856-301 FEP Plus 856-200 FEP Coated Strips	
	Air Only ⁽¹⁾	Air ⁽¹⁾ Plus Fuel	Air Only ⁽¹⁾	Air Plus ⁽¹⁾ Fuel
250	127 (loss)	9 (gain)	255 (loss)	70 (loss)
300	92 (loss)	93 (gain)	229 (loss)	96 (loss)
350	150 (loss)	366 (gain)	252 (loss)	145 (loss)
375	153 (loss)	366 (gain)	240 (loss)	193 (loss)
400	157 (loss)	3,232 (gain)	297 (loss)	475 (gain)

(1) Screening Unit run at 3 psia, 4 hours with standard flow rate of air and fuel (when used). Fuel employed was AFFB-4-64 (FA-S-1).

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13. ABSTRACT		
Deposits form in the "empty" wing tank of a supersonic aircraft as a result of a complex free radical autoxidation process. The complete exclusion of oxygen suppresses deposit formation. Deposits are formed much more rapidly when a condensed (liquid) phase is present than when no condensed phase is present. An apparatus was designed which quantitatively measures the rate of deposit formation. Higher total pressure and increasing oxygen pressure increases the level of deposit formation. Trace levels of sulfur and nitrogen compounds markedly increase deposit formation. The nature of metal surfaces to which the fuel is exposed was found to influence the rate of deposit formation. Vanadium containing titanium alloys and copper surfaces were found to be particularly deleterious. The presence of dissolved metals also markedly increased the level of deposit formation. Studies were made with pure compounds and simple binary blends of pure compounds. The broad objective of this work was to elucidate the effect of jet fuel hydrocarbon composition on deposit formation. Currently used antioxidant additives were found to be ineffective in reducing the rate of deposit formation. The use of rust preventive and metal deactivator additives increased the rate of deposit formation. Coating an active metal surface with a polymeric material increased the level of deposit formation.		

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