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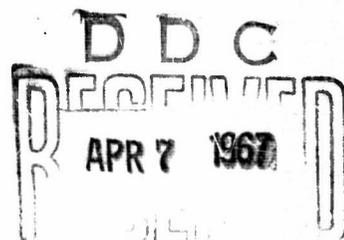
**COMBUSTION MECHANISM
OF
HIGH BURNING RATE SOLID PROPELLANTS**

Contract F04611-67-C-0034

QUARTERLY TECHNICAL REPORT AFRPL-TR-67-99

March 1967

David A. Flanigan
Huntsville Division
Thiokol Chemical Corporation



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Air Force Rocket Propulsion Laboratory
Research and Technical Division
Air Force Systems Command
United States Air Force
Edwards Air Force Base, California 93523

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FOREWORD

(U) This, the first Quarterly Technical Report under Contract No. F04611-67-C-0034, covers the work performed from 15 November 1966 through 28 February 1967. This contract with the Huntsville Division of Thiokol Chemical Corporation was initiated under Air Force Rocket Propulsion Laboratory, Research and Technology Division Project Number 3148. It is being accomplished under the technical direction of R. W. Bargmeyer, 1/Lt., USAF of the Research and Technology Division, Air Force Systems Command, United States Air Force, Edwards Air Force Base, California 93523.

(U) Dr. David A. Flanigan of Thiokol's Research and Development Department is the Principal Investigator and Mr. Carl J. Welchel of the Project Management Directorate is Assistant Project Manager for this program. Full authority for the management control of this program is the responsibility of Mr. G. F. Mangum of the Project Management Directorate. Others who cooperated in the work and in the preparation of this report are Messrs. B. A. Allen, C. S. Combs, C. I. Ashmore and Mrs. E. J. Grice.

(U) This report has been assigned the Thiokol internal number 28-67 (Control No. C-67-28A).

(U) This project is being accomplished as a part of the Air Force program, the overall objective of which is to tailor the burning rate of a propellant predictably and controllably to any desired level in the range from 1 to 10 inches per second. Experiments will be performed to synthesize more efficient burn rate catalysts by maximizing guideline properties determined under Contract AF04(611)-11212 toward development of an ideal catalyst. Following catalyst synthesis, each compound showing potential will be subjected to comprehensive decomposition studies and combustion mechanism evaluation with propellant ingredients.

(U) This report contains no classified information extracted from other classified documents.

STATEMENT OF APPROVAL

(U) Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

W. H. EBELKE, Col., USAF
Chief, Propellants Division
Air Force Rocket Propulsion Laboratory

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CONFIDENTIAL ABSTRACT

Thiokol's program to tailor the burning rate of a propellant predictably and controllably to any desired level in the range from 1 to 10 inches per second is divided into three phases: Phase I - Synthesis of Burning Rate Catalysts, Phase II - Decomposition Studies and Evaluation of Catalysts and Phase III - Decomposition of Advanced Oxidizers, Fuels, and Binders. Experiments will be performed to synthesize more efficient burn rate catalysts by maximizing already determined guideline properties toward development of an ideal catalyst under Phases I and II. Following catalyst synthesis, each compound showing potential will be subjected to comprehensive decomposition studies and combustion mechanism evaluation with propellant ingredients. Effort conducted to date under Phases I and II indicate that esters of ferrocene carboxylic acid may be readily prepared in high yield; a convenient route to copper containing ferrocene derivatives has been discovered and utilized; ferrocene ethers may be prepared easily and in high yield, and acylation of ferrocene with methoxyacetyl chloride cannot be readily achieved. Of the catalysts synthesized to date, the following statements can be made in regard to compatibility with varied propellant ingredients: no compatibility problems are encountered with mixtures of the catalysts and HC polymer; the MAPO polymerization noted is only slightly accelerated in the presence of the catalysts, and no problems are expected in effecting good binder cures in the presence of the catalysts.

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SECTION I

INTRODUCTION

(U) The objective of this program is to tailor the burning rate of a propellant predictably and controllably, to any desired level in the range from 1 to 10 inches per second. Ballistic and mechanical properties of propellants studied will be maintained at the state-of-the-art standards of current Minuteman propellant.

(C) Thiokol's approach to obtain the program objective will be through the continued investigation of iron compound effects on the aluminum-ammonium perchlorate-polybutadiene binder system. It is also designed to systematically evaluate new propellant ingredients as to their effect on burning rate and the related effect on combustion mechanism. New materials which will be evaluated are hydroxyl-ammonium perchlorate, hydrazine dperchlorate and nitronium perchlorate oxidizers; aluminum hydride, beryllium, beryllium hydride fuels; P-BEP, NFPA polymers, and TVOPA plasticizer. The data and conclusions reached under Contract AF04(611)-11212 will be used as a base line guide for the work to be accomplished under this program.

(U) The planned program consists of three major areas: synthesis, evaluation, and advanced ingredient studies. It is designed to progress in a logical manner so that the most promising materials receive the more extensive evaluation and the less desirable materials are discarded at an early date. The three phases of the program are:

(U) Phase I - Synthesis of Burning Rate Catalysts

(U) Burning rate catalysts will be synthesized for use in the AP/Al/PB propellant system. Prior knowledge as a propulsion contractor and the data obtained from Contract AF04(611)-11212 will serve as base line guides. As a new material is synthesized, it will be evaluated in Phase II.

(U) Phase II - Decomposition Studies and Evaluation of Catalysts

(U) Upon completion of synthesis, elemental characterization and physical property determination of each candidate catalyst, an evaluation of the compatibility of the candidate catalysts with other propellant ingredients will be accomplished. Data obtained in this phase will allow recommendations to be made relative to the development of new burning rate catalysts and the development of high burning rate propellants utilizing the improved catalyst.

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(U) Phase III - Decomposition of Advanced Oxidizers, Fuels, and Binders

(U) Phase III effort will be directed toward obtaining a basic fundamental knowledge of the decomposition of advanced fuels, oxidizers, and binders. Laboratory test data will be utilized to postulate a burning mechanism of the advanced ingredient and a comparison made with that of conventional propellant ingredients.

(U) This report covers work performed for the period 15 November 1966 through 28 February 1967 under Contract F04611-57-C-0034. Effort to date has been concerned solely with Phases I and II, which are being conducted concurrently. Phase III will be initiated after the completion of Phases I and II.

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SECTION II

EXPERIMENTAL ACCOMPLISHMENTS

(U) Based on the results of effort expended under Contract AF04(611)-11212, the experiments under this program will be directed toward the synthesis and characterization of more efficient burn rate catalysts.

(U) 1. Phase I - Synthesis of Burning Rate Catalysts

(U) The guidelines for synthesis of more efficient burn rate catalysts have been derived from effort conducted under the above contract and are listed below:

High iron content
Wide liquid range
Readily oxidizable
Compatible with other propellant ingredients
Maximum fuel content (heat release on oxidation)

(U) The synthesis of newer burn rate catalyst will be directed toward maximizing the aforementioned properties into the ideal catalyst. Effort performed in this area of research during this reporting period is presented in subsequent paragraphs.

(C) Dimethylaminomethyl ferrocene was prepared in good yield by the reaction of bis (dimethylamino) methane with ferrocene¹. The ferrocene amine is an orange mobile liquid of b. p. 78°C/0.02 mm and f. p. -18°C.

(C) Esterification of ferrocene carboxylic acid with isopropanol was attempted. Thin layer chromatography indicated that a small amount of product was present after 30 hours of reaction time. The reaction will be repeated using chloro-carbonyl ferrocene.

(C) Attempts to isolate products from the reaction of ferrocene aldehyde and acetone, by the method of Claisen and Schmidt, or the reaction of acetyl ferrocene with 1-ethylethyleneimine were futile.

(C) An attempt was made to prepare ferrocenedimethylcarbinol by treatment of acetyl ferrocene with methyl magnesium bromide in dry ether; 0.5 molar quantities were used, which gave a solid product. Thin layer chromatography showed that approximately 50 percent was product and 50 percent was acetyl

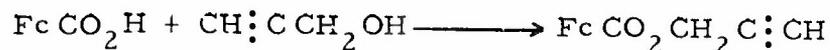
1. Org. Syn., 40, p. 31.

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ferrocene. Distillation would not separate the products; however, the alcohol was converted to methyl vinyl ferrocene with liberation of H₂O.

(C) Esterification of ferrocene carboxylic acid with propargyl alcohol gave propargyl ferrocenoate [m.p. 81 - 84° (dec.)] in high yield.

Reaction:



(C) Esterification of ferrocene carboxylic acid with allyl alcohol afforded allyl ferrocenoate (b.p. 122°/0.15 mm).

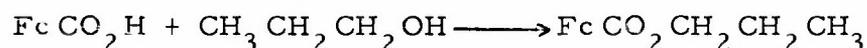
Reaction:



The ester solidified on standing to form crystalline needles which melted just above room temperature.

(C) Esterification of ferrocene carboxylic acid with n-propyl alcohol afforded n-propyl ferrocenoate [b.p. 96°/0.10 mm; f.p. -11° C (12° F)], an orange mobile liquid.

Reaction:



(C) Acetyl ferrocene was reacted with ferrocene aldehyde by the method of Claisen and Schmidt to produce 1,3-diferrocenyl-1-oxo-2-propene²(m.p. 198 - 199°) in 84 percent yield.

Reaction:

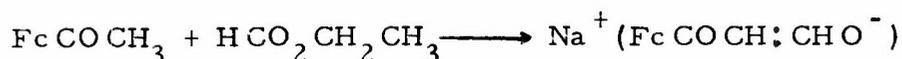


2. H. Egger and K. Schlögl, J. Organometal Chem., 2, 398 (1964).

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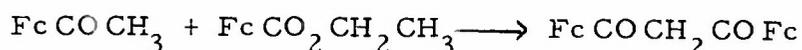
(C) The sodium salt of β -ferrocenyl - β - oxo-propionaldehyde has been prepared for use as a reactive intermediate. The reaction was effected between acetyl ferrocene and ethyl formate by means of strong base.

Reaction:



(C) Acylation of acetyl ferrocene with ethyl ferrocenoate by means of strong base afforded 1, 3 - diferrocenyl - 1, 3 - propanedione in low yield.

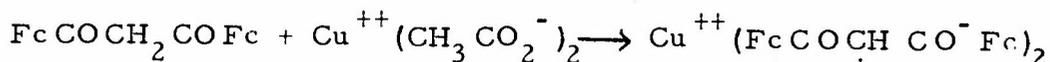
Reaction:



The symmetrical β - diketone decomposes with evolution of gas at 215°.

(C) The copper complex of 1, 3 - diferrocenyl - 1, 3 - propanedione has been prepared by reaction of the β - diketone with cupric acetate in the usual manner³.

Reaction:



The complex decomposes with evolution of gas at 280°.

(C) Esterification of ferrocene carboxylic acid with 2-methoxyethyl 2-methoxyethyl ferrocenoate (m. p., 34 - 35°) in good yield.

Reaction:

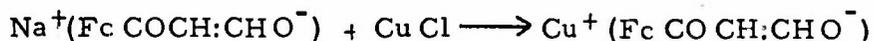


3. Org. Reac., VIII, p. 122.

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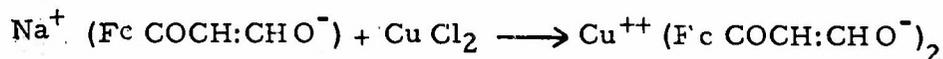
(C) Reaction of the sodium salt of β -ferrocenyl- β -oxopropionaldehyde with Copper (I) chloride afforded the Copper (I) complex of β -ferrocenyl- β -oxopropionaldehyde [m. p., 224 - 225° (dec.)] in very high yield.

Reaction:



(C) The copper (II) complex [m. p., 200° (dec.)] has been prepared in a similar manner.

Reaction:



(C) Methoxymethyl ferrocene⁴ (b. p., 66°/0.025mm; f. p., -22°) was prepared by the reaction of hydroxymethyl ferrocene with methanol in the presence of an acid catalyst.

Reaction:



The crude product was shown by thin-layer chromatography (TLC) to contain ca. 10% hydroxy methyl ferrocene. After distillation the pure ether oxidized when left at room temperature for several days, but the crude product has not shown signs of oxidation.

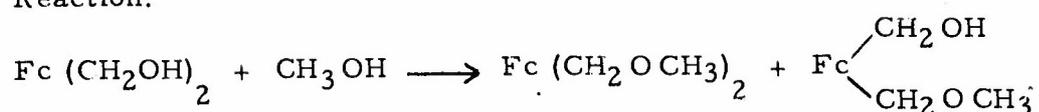
(C) In a like manner, 1, 1'-di(methoxy methyl) ferrocene [b. p., 310° (D. T. A.); (Lit.⁵, b. p., 104°/0.2mm); f. p. < -75°] and 1-hydroxy methyl-1'-methoxy methyl ferrocene [b. p., 280° (D. T. A.); f. p. < -75°] were prepared in a ratio of ca. 4:1 (determined by TLC).

4. Nesmeyanov, A. N., É. G. Perevalova, and Yu. A. Ustynyuk, DAN SSR, 113, 1105 (1960). [É. G. Lomonosov, Yu. A. Ustynyuk, and A. N. Nesmeyanov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 11, 1972 (1963) (Eng. Transl.)]

5. Pauson, P. L., M. A. Sandhu, and W. E. Watts, J. Chem. Soc., 251 (1966).

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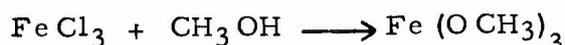
Reaction:



The mixture had f. p. $< -75^\circ$ and the components were separated by means of column chromatography.

(C) Trimethoxy iron⁶ (m. p., $> 300^\circ$) was prepared by the reaction of anhydrous ferric chloride with methanol in the presence of ammonia.

Reaction:



(C) The attempted acylation of ferrocene with methoxyacetyl chloride yielded black tars that were assumed to be decomposition products. This reaction was attempted several times, using varying amounts of materials and under varying conditions.

(C) The attempted esterification of ferrocene carboxylic acid with hydroxymethyl ferrocene resulted in decomposition of the alcohol. The reaction was attempted in chlorobenzene with sulfuric acid as the catalyst.

(U) Attempts to prepare a number of ferrocene ethers have given products of an ambiguous nature. Preparation of the following ethers has been attempted.

1. $\text{Fc} \text{CH}_2 \text{OCH}_2 \text{Fc}$
2. $\text{Fc} \text{CH}_2 \text{OCH}_2 \text{CH}_3$
3. $\text{Fc} \text{CH}(\text{CH}_3) \text{OCH}(\text{CH}_3) \text{Fc}$

Identification of the above compounds has been greatly hindered by the impure nature of starting materials (ferrocene alcohols). This was discovered after a number of reactions had been run and common methods of purification had failed to give satisfactory results. Ferrocene starting materials purchased from Research Organic Chemical Co., 11686 Sheldon, Sun Valley, California, have been found to contain significant amounts of impurities (analysis by thin-layer chromatography). Some materials are of better quality than others, but at the lower end

6. Bradley, D. C., R. K. Multani, and W. Wardlaw, J. Chem. Soc., 126 (1958).

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of the spectrum $\text{Fc CH}(\text{CH}_3)\text{OH}$ has been found to be only about 50 per cent pure.

(U) The physical constants of the above catalysts are shown below:

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Compound	M. p., °C	B. p., °C	F. p. ^(a) , °C	Theo. % Fe	Theo. % Cu
Dimethylaminomethyl ferrocene	---	78/0.02 mm	-18	23	---
Propargyl ferrocenoate	81-84 (dec.)	---	---	21	---
Allyl ferrocenoate	36-36.5	122/0.15 mm	---	21	---
n-Propyl ferrocenoate	---	96/0.10 mm	-11	21	---
1,3-Diferrocenyl-1-oxo-2-propene	198-199	---	---	26	---
Sodium salt of β -ferrocenyl- β -oxo propionaldehyde	240-242 (dec.)	---	---	20	---
1,3-Diferrocenyl-1,3-propanedione	215 (dec.)	---	---	25	---
Copper complex of 1,3-diferrocenyl-1,3-propanedione	280 (dec.)	---	---	24	7
2-methoxyethyl ferrocenoate	34-35	---	---	19	---
Copper (I) complex of β -ferrocenyl- β -oxopropionaldehyde	224-225 (dec.)	---	---	18	20
Copper (II) complex of β -ferrocenyl- β -oxopropionaldehyde	200 (dec.)	---	---	20	11
Methoxy methyl ferrocene	---	66/0.025	-22	24	---
1,1'-Di(methoxy methyl) ferrocene	---	310	<-75	20	---
1-Hydroxy methyl-1'-methoxy methyl ferrocene	---	280	<-75	22	---
Trimethoxy iron	>300	---	---	38	---

a. The freezing points were determined by gradual cooling of the compound in a dry ice-acetone bath. As the material crystallizes, the temperature of the solid rises slightly (heat of crystallization) and levels off. The maximum temperature reached in the temperature rise is called the freezing point.

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(U) The structural assignments of the compounds given above have been confirmed by infrared spectrometry. Elemental analyses are in progress.

(U) Continuing effort in this area will include a more comprehensive identification of the above mentioned compounds, the continued preparation of ferrocene ethers, and the preparation of ferrocene derivatives belonging to classes not yet investigated. Organometallic compounds other than ferrocene derivatives may also be prepared.

(U) 2. Phase II - Decomposition Studies and Catalyst Evaluation

(U) Upon completion of synthesis, elemental characterization and physical property determination of each candidate catalyst, an evaluation of the compatibility of the candidate catalysts with other propellant ingredients will be accomplished. Following this study, actual effectiveness of the candidate catalysts will be measured by determining the propellant processing characteristics as well as the burning rate.

(U) a. Differential Thermal Analysis

(C) A comparison of the effect of each newly synthesized catalyst candidate upon the decomposition temperature of ammonium perchlorate has been made by differential thermal analysis (DTA). Figure 1 depicts a comparison of the effect of a typical alkyl ferrocene, n-butyl ferrocene⁷, with that of a series of ferrocene esters. The esters are more efficient plasticizers than the alkyl ferrocenes and have a larger liquid range. However, the iron content of the esters is slightly lower than that of the corresponding alkyl derivatives and this slight difference results in a similar percentage loss in burn rate at a given weight percent loading. The significant differences in the DTA's are the shift to higher oxidizer decomposition temperatures with decreasing iron content and very slight differences in pre-endotherm oxidation reaction intensity.

(C) Figure 2 depicts a series of three solid ferrocene derivatives, one of which contains both iron and copper. No significant differences are noted between the effect of these derivatives on the decomposition of ammonium perchlorate and that of pure ferrocene. The interesting liquid compound, dimethylaminomethyl ferrocene, exhibits, in the presence of ammonium perchlorate, a preliminary exotherm at 180°C. Such an exotherm is felt to be strong enough to generate enough heat for ignition in a burning process. This exotherm can be attributed to the reaction of the amine with ammonium perchlorate at that temperature.

7. Thiokol Trademark, Reg. U. S. Patent Office.

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(C) The differential thermal analyses of another series of ferrocene esters and ethers and copper containing ferrocene derivatives are shown in Figures 3 and 4. No significant lowering of the decomposition temperature of ammonium perchlorate is exhibited over that obtained with n-butyl ferrocene. Methoxy methyl ferrocene (Figure 3) evidences a considerable exotherm prior to the endotherm, which is considered to be oxidation of the catalyst. The pure material has been observed to oxidize slightly at room temperature in air.

(U) b. Compatibility Studies

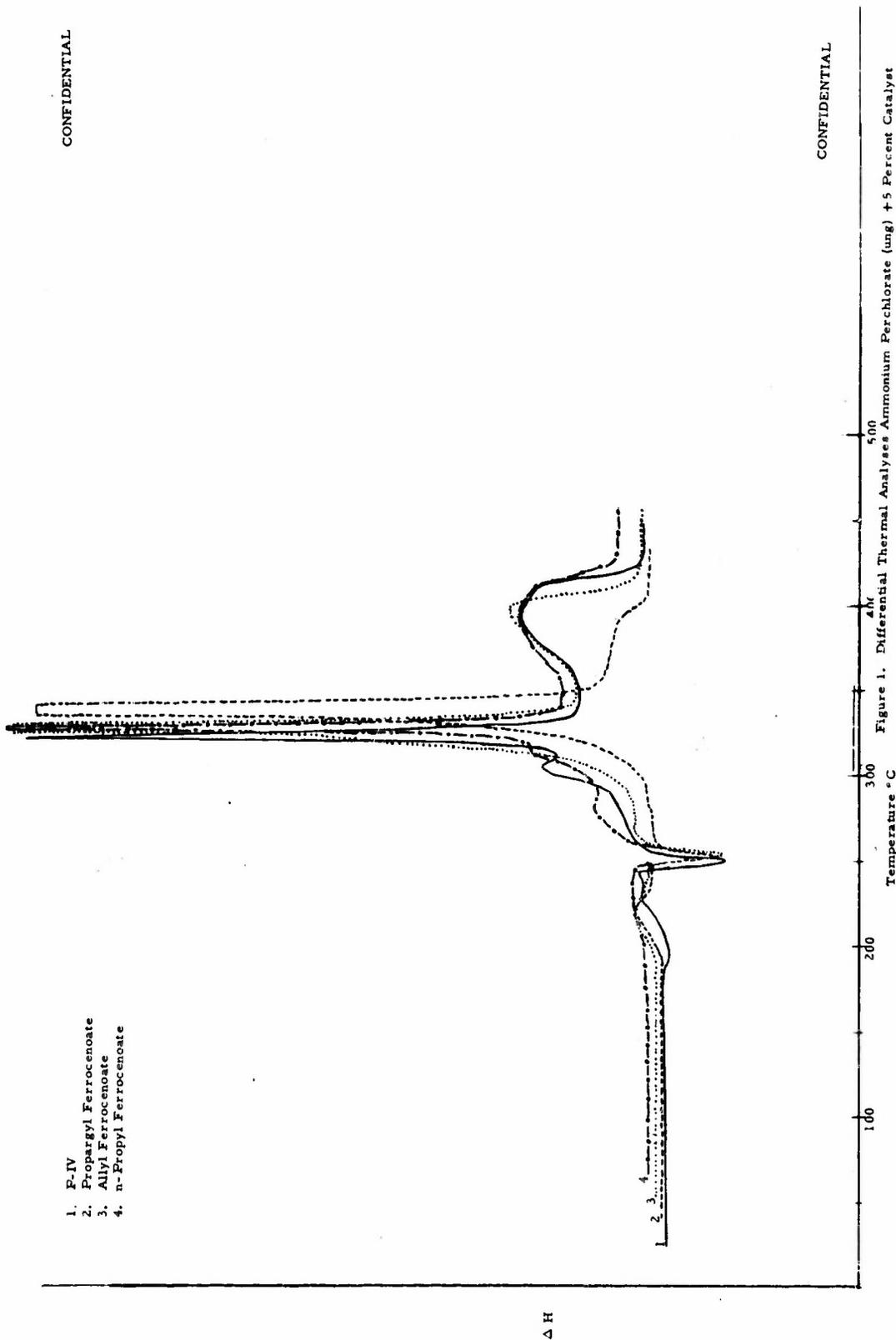
(C) Fifteen of the more promising catalysts were subjected to compatibility testing in air at room temperature and at 160°F. Those samples evaluated at room temperature (75°F) exhibited no marked change, with the exception of dimethylamino methyl ferrocene $[\text{FcCH}_2\text{N}(\text{CH}_3)_2]$, which oxidized slightly. The methoxy methyl ferrocene used in this test was the crude material which shows no tendency to oxidize at room temperature. This study is continuing and changes will be reported as they occur.

(C) Results of testing at higher temperature (160°F) are summarized in Table I. Thin layer chromatography supports visual observations that the dimethylamino methyl ferrocene oxidized. Also, allyl ferrocenoate either oxidized or polymerized as is indicated by the disappearance of the trace at 0.4 R_f and change in ratio. 1,1'-di(methoxymethyl) ferrocene and 1 hydroxy methyl-1'-methoxy methyl ferrocene evidenced considerable oxidation and the mixture of these compounds showed only slight oxidation.

(C) It should be pointed out that the high weight loss levels observed with the candidate liquid catalysts can be attributed to a high exposed surface area to weight ratio used for this testing.

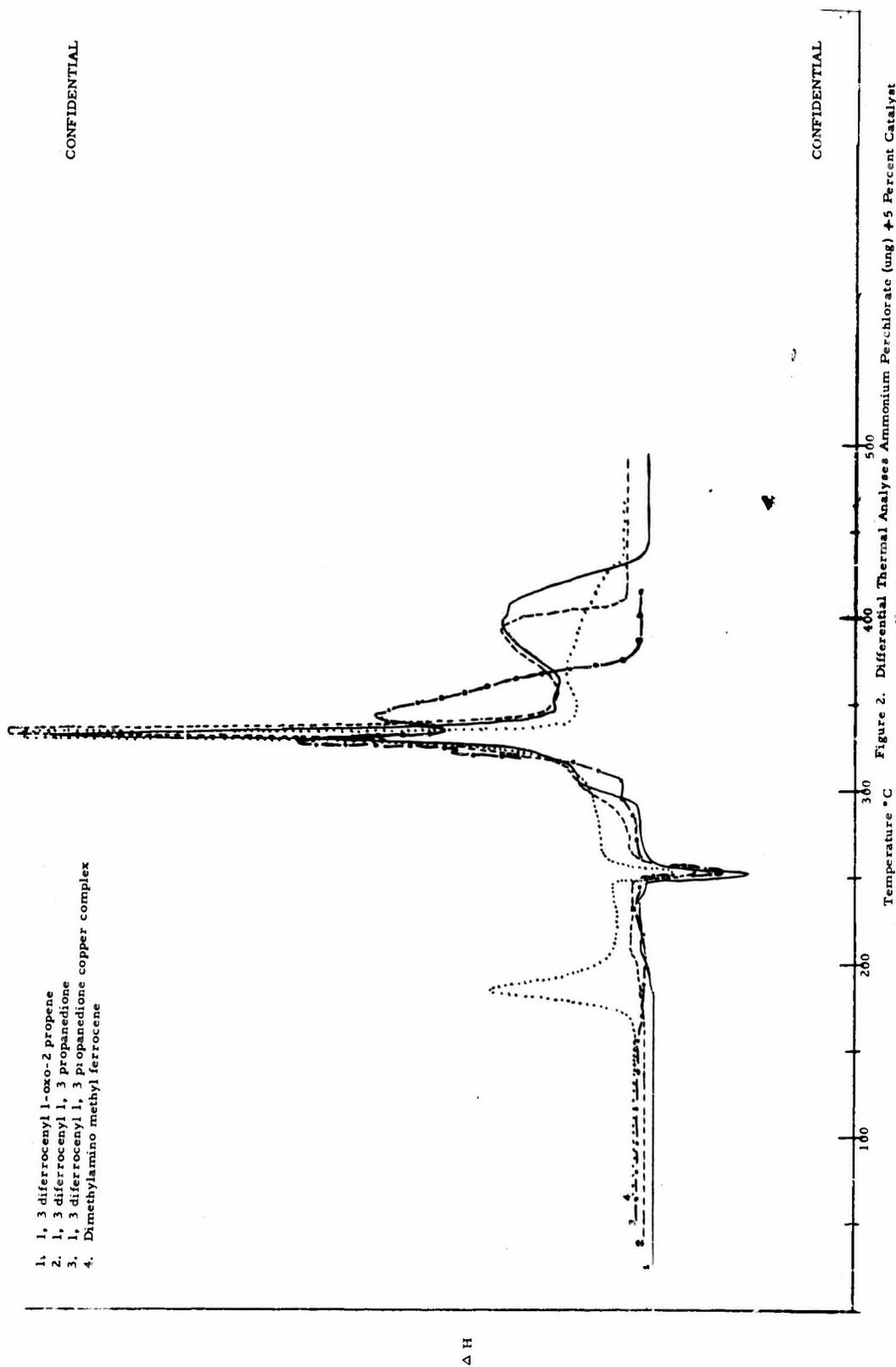
(C) Catalyst compatibility with propellant materials are partially summarized in Table II. In these experiments, polymerization of MAPO is simply homopolymerization and not due to the influence of the catalyst. Results of compatibility studies at ambient temperature show that there is no significant change in either HC polymer, aluminum powder or MAPO after testing for 144 hours. After 64 hours at 160°F, the catalyst/aluminum powder mixture evidenced no change, except in the case of liquid catalysts which volatilized. No evidence of gassing of mixtures of catalyst and propellant materials was encountered during this evaluation. Compatibility of catalyst and ammonium perchlorate is still in progress. Data will be reported as they become available. Each newly synthesized catalyst will continue to be evaluated in the same manner.

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Figure 2. Differential Thermal Analyses Ammonium Perchlorate (ung) +5 Percent Catalyst

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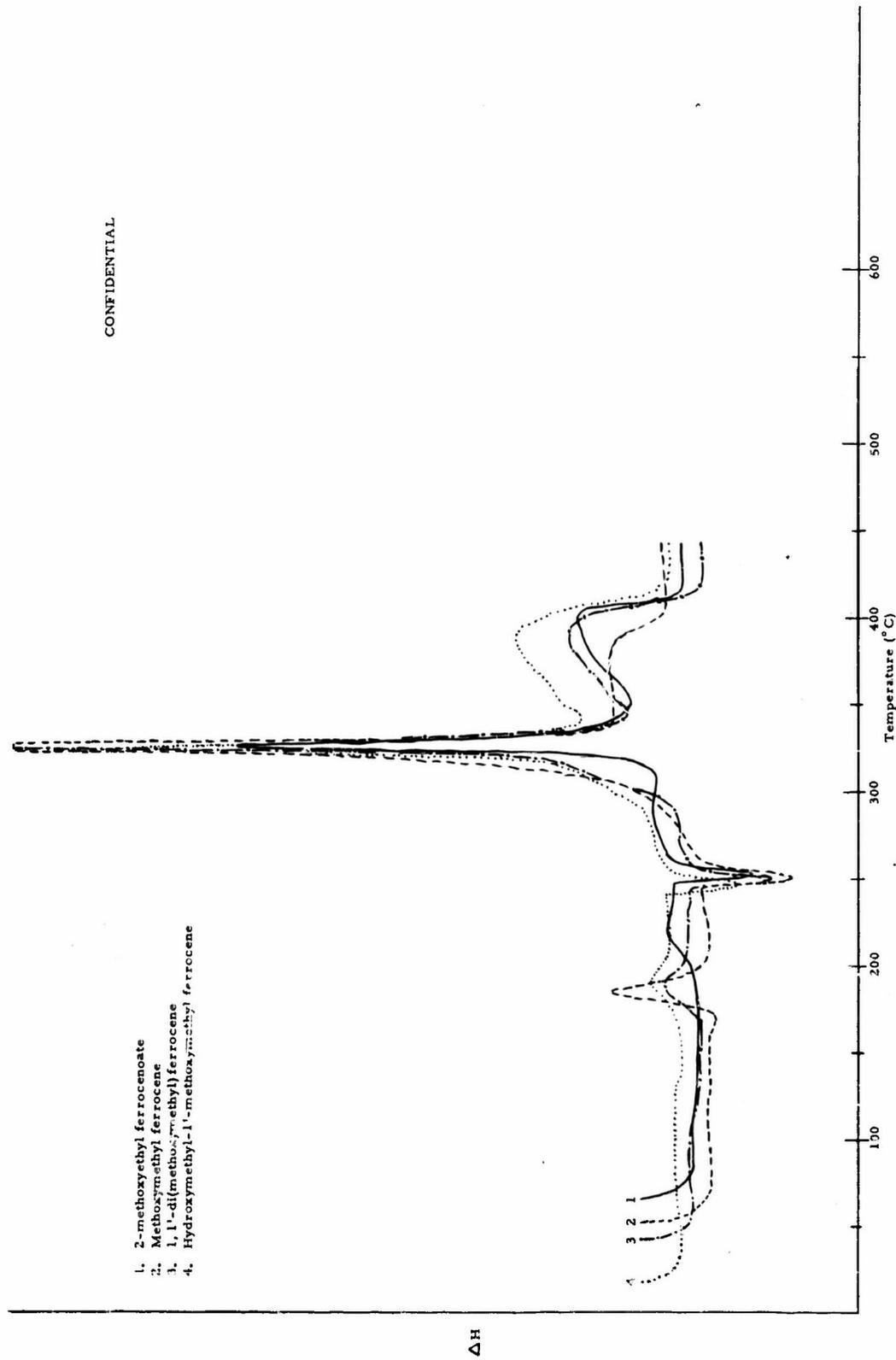


Figure 3. Differential Thermal Analysis of Synthesized Compounds.

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1. Copper (II) Complex of β -ferrocenyl- β -oxo-propionaldehyde
2. Copper (I) Complex of β -ferrocenyl- β -oxo-propionaldehyde
3. Trimethoxy iron.

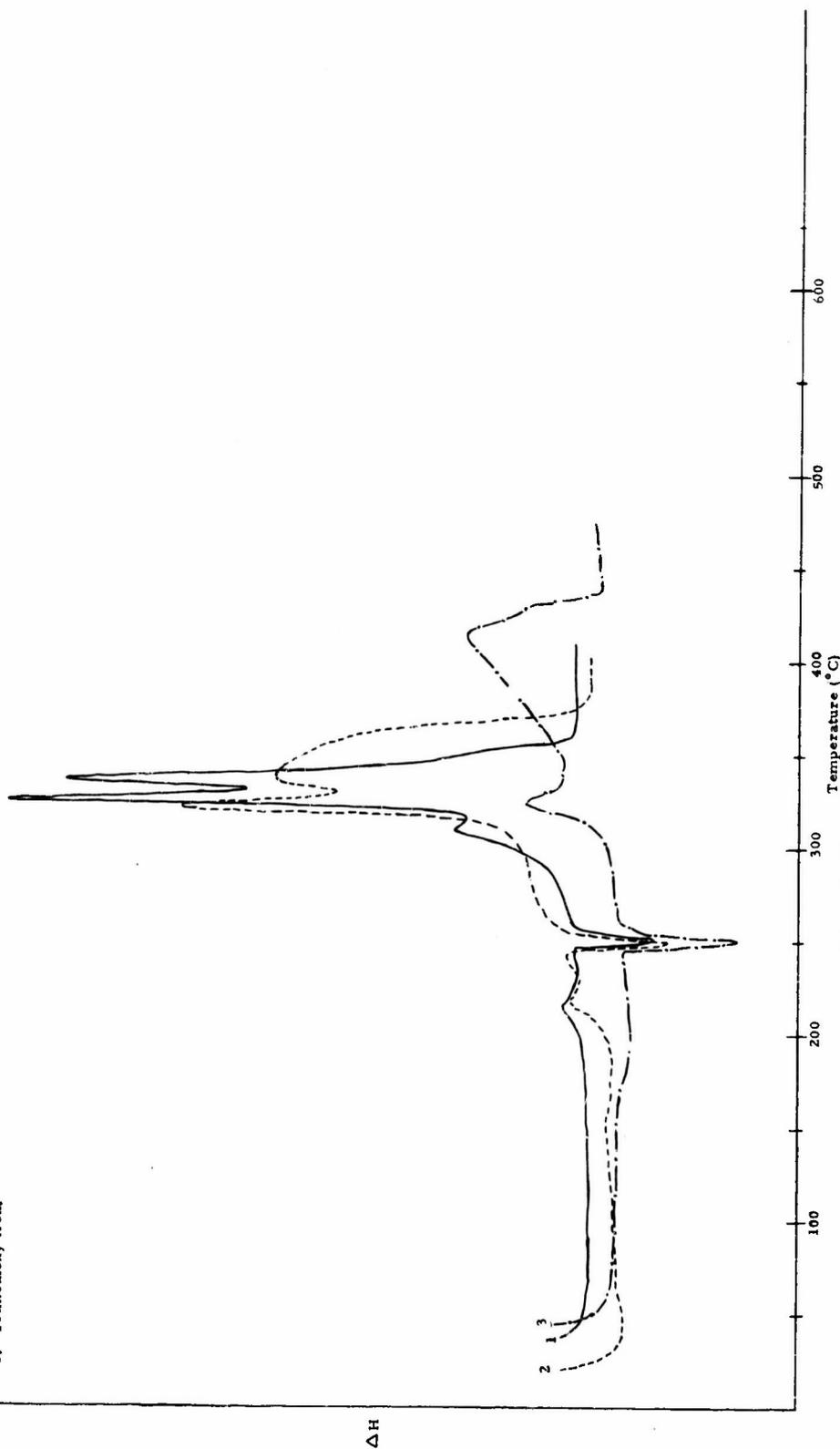


Figure 4. Differential Thermal Analysis of Synthesized Compounds.

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TABLE I
CATALYST COMPATIBILITY - STABILITY IN AIR (160°F)

Catalyst	Original Sample (Wt. - g)	Loss in 1 Week (g)	Loss in 1 Week (%)	Thin Layer Chromatography Results		Visual Observations
				Original Values	Values at 1 Week - 160°F	
1. Trimethoxy Iron $\text{Fe}(\text{OCH}_3)_3$	0.0069	0.0023	33.33	$R_f = 0$	$R_f = 0$	Darkened - Brownish Orange Color.
2. Methoxymethyl Ferrocene $\text{FcCH}_2\text{OCH}_3$	0.340	0.0053	15.59	$R_f = 0.6$ & $R_f = 0.4$ Ratio 9/1	$R_f = 0.6$ & 0.4 Ratio 9/1	Apparently oxidized (Acetone insolubles).
3. $\text{FcCH}(\text{OH})\text{CH}_2\text{CH}=\text{CH}_2$	0.0094	0.0014	14.89	$R_f = 0.6$ & $R_f = 0.4$ Ratio 9/1	$R_f = 0.6$ & 0.4 (Streaked to Origin) $R_f = 0$ Ratio 5/3/2 [Spot at lower R_f (0.4) is red and spot at higher R_f (0.6) is yellow.]	Polymerized - Dark Brown, Sticky Solid.
4. Copper (I) Complex of β -ferrocenyl- β -oxo-propionaldehyde $\text{Cu}^+ \left[\text{Fc} \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ \text{CH} = \text{CHO}^- \end{array} \right]$	0.0064	No-Loss in 3 Wks.		Badly Streaked $R_f = 0 - 0.5$	Badly Streaked $R_f = 0 - 0.8$	Apparently Oxidized - Color Changed From Red to Almost Brown.
5. Copper (II) Complex of β -ferrocenyl- β -oxo-propionaldehyde $\text{Cu}^{++} \left[\text{Fc} \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ \text{CH} = \text{CHO}^- \end{array} \right]_2$	0.0028	0.0006	21.43	Badly Streaked $R_f = 0 - 0.5$	$R_f = 0 - 0.5$	Apparently no change.
6. 2-methoxyethyl ferrocenatone $\text{Fc} \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ \text{OCH}_2\text{CH}_2\text{OCH}_3 \end{array}$	0.0050	0.0008	16.00	$R_f = 0.6$	$R_f = 0.6$	Liquified.
7. Copper Complex of 1,3-diferrocenyl-1,3-propanedione $\text{Cu}^{++} \begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{Fc} \text{---} \text{C} \text{---} \text{C} \text{---} \text{Fc} \\ \quad \\ \text{CH}_2 \quad \text{C} \quad \text{CH}_2 \end{array} \text{Fc}$	0.0019	0.0004	21.05	Trace at $R_f = 0.3$ $R_f = 0$	$R_f = 0.3$ & $R_f = 0$	Apparently no change.
8. 1,3-diferrocenyl-1,3-propanedione $\text{Fc} \begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{C} \text{---} \text{C} \text{---} \text{C} \\ \quad \\ \text{CH}_2 \quad \text{C} \quad \text{CH}_2 \end{array} \text{Fc}$	0.0028	0.0005	17.86	$R_f = 0.3$ Streaked	$R_f = 0.3$	Darkened Slightly.

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TABLE I (Cont'd)

Catalyst	Original Sample (Wt.-%)	Loss in 1 Week (g)	Loss in 1 Week (%)	Thin Layer Chromatography Results		Visual Observations
				Original Values	Values at 1 Week - 160°F	
9. Dimethylaminomethyl ferrocene $\text{FcCH}_2\text{N}(\text{CH}_3)_2$	0.0158	0.0045	28.48	Streaked $R_f = 0.2$ Trace Spots at $R_f = 0.6$ Trace Spots at $R_f = 0.35$ Trace Spots at $R_f = 0.3$	$R_f = 0.2$ $R_f = 0.6$ $R_f = 0.35$ $R_f = 0.3$	Solid Particles Settled Out.
10. Allyl Ferrocenoate $\text{Fc} \begin{array}{c} \diagup \\ \text{O} \\ \diagdown \end{array} \text{CH}_2\text{CH} = \text{CH}_2$	0.0159	0.0025	15.72	$R_f = 0.7$ Trace at $R_f = 0.4$ Trace at $R_f = 0$	$R_f = 0.7, R_f = 0$ Ratio 4/1	Possible Polymerization
11. n-propyl ferrocenoate $\text{Fc} \begin{array}{c} \diagup \\ \text{O} \\ \diagdown \end{array} \text{CH}_2\text{CH}_2\text{CH}_3$	0.0093	0.0016	17.20	$R_f = 0.7$	$R_f = 0.7$	No Apparent Change.
12. 1,3-diferrocenyl-1-oxo-2-propene $\text{Fc} \begin{array}{c} \diagup \\ \text{O} \\ \diagdown \end{array} \text{CH} = \text{CHFc}$	0.0018	0.0007	38.89	$R_f = 0.6$	$R_f = 0.6$	No Apparent Change.
13. Propargyl ferrocenoate $\text{Fc} \begin{array}{c} \diagup \\ \text{O} \\ \diagdown \end{array} \text{COCH}_2\text{C} = \text{CH}$	0.0034	0.0010	29.41	$R_f = 0.7$ Trace at $R_f = 0$	$R_f = 0.7$ $R_f = 0$	Apparently oxidized - soluble in acetone before test. Has acetone insolubles after 1 week at 150°F.
14. Mixture of $\text{Fc}(\text{CH}_2\text{OCH}_3)_2$ and $\text{Fc} \begin{array}{c} \diagup \\ \text{O} \\ \diagdown \end{array} \text{CH}_2\text{OCH}_3$	0.0206	0.0032	15.53	$R_f = 0.6$ & $R_f = 0.4$ Ratio 4/1	$R_f = 0.6$ & $R_f = 0.4$ Ratio 4/1	May have oxidized slightly - solids present.
15. 1,1'-di(methoxymethyl)ferrocene PURE $\text{Fc}(\text{CH}_2\text{OCH}_3)_2$	0.0263	0.0031	11.79	$R_f = 0.6$ & Trace at $R_f = 0$	$R_f = 0.6$ & Trace at $R_f = 0$	Apparently oxidized.

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TABLE II
CATALYST COMPATIBILITY WITH PROPELLANT MATERIALS

Catalyst	HC POLYMER			MAPC			Observations
	Solubility/Miscibility Ambient Temp.	24 Hrs. at 160° F.	44 Hrs. at 160° F.	144 Hrs. at 160° F.	Solubility/Miscibility Ambient Temp.	16 Hrs. at 160° F.	
1. Trimethoxy Iron $Fe(OCH_3)_3$	Only slightly soluble	No noticeable change	No noticeable change	Slight Polymerization	Insoluble	Drying	Polymerized
2. Methoxymethyl Ferrocene $FeCH_2OCH_3$	Miscible	No noticeable change	No noticeable change	Slight Polymerization	Readily Miscible	Drying	Polymerized
3. $FeCHCH_2CH=CH_2$	Miscible	Slight Increase in Viscosity	Polymerized	No Change From Previous	Readily Miscible	Drying	Polymerized
4. Copper (I) Complex of 8-ferrocenyl-5-oxo-propanaldehyde $Cu^+ [Fe \begin{matrix} O \\ \\ C \\ \\ CH = CHO \end{matrix}]$	Slightly Soluble - Disperses	Polymerizing	90% Polymerized	Fully Polymerized	Insoluble	Drying	Polymerized
5. Copper (II) Complex of 8-ferrocenyl-8-oxo-propanaldehyde $Cu^{++} [Fe \begin{matrix} O \\ \\ C \\ \\ CH = CHO \end{matrix}]_2$	Slightly Soluble - Disperses	Slight Increase in Viscosity	70 - 80% Polymerized	No Change	Insoluble	Drying	Polymerized
6. 2-Methoxyethyl Ferrocenate $Fe \begin{matrix} O \\ \\ C \\ \\ OCH_2CH_2OCH_3 \end{matrix}$	Soluble	Slight Increase	40% Polymerized	50% Polymerized	Readily Soluble	Still Liquid	Polymerized
7. Copper Complex of 1,3-diferrocenyl-1,3-propanedione $Cu^{++} [Fe \begin{matrix} O \\ \\ C \\ \\ C \\ \\ C \\ \\ O \end{matrix} Fe]_2$	Insoluble, Disperses	No Noticeable Change	Polymerizing	No Change from Previous	Insoluble	Dried Out	Polymerized
8. 1,3-diferrocenyl-1,3-propanedione $Fe \begin{matrix} O \\ \\ C \\ \\ C \\ \\ C \\ \\ O \end{matrix} Fe$	Insoluble, Disperses	Very Slight Increase in Viscosity	Polymerizing	Polymerized at edges 70-80% Polymerization in Bulk	Soluble	Polymerized	Polymerized
9. Dimethylaminomethyl ferrocene $FeCH_2N(CH_3)_2$	Miscible	Slight Change in Viscosity	No Change from Previous	No Change from Previous	Readily Miscible	Polymerized	Polymerized

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TABLE II (Cont'd)

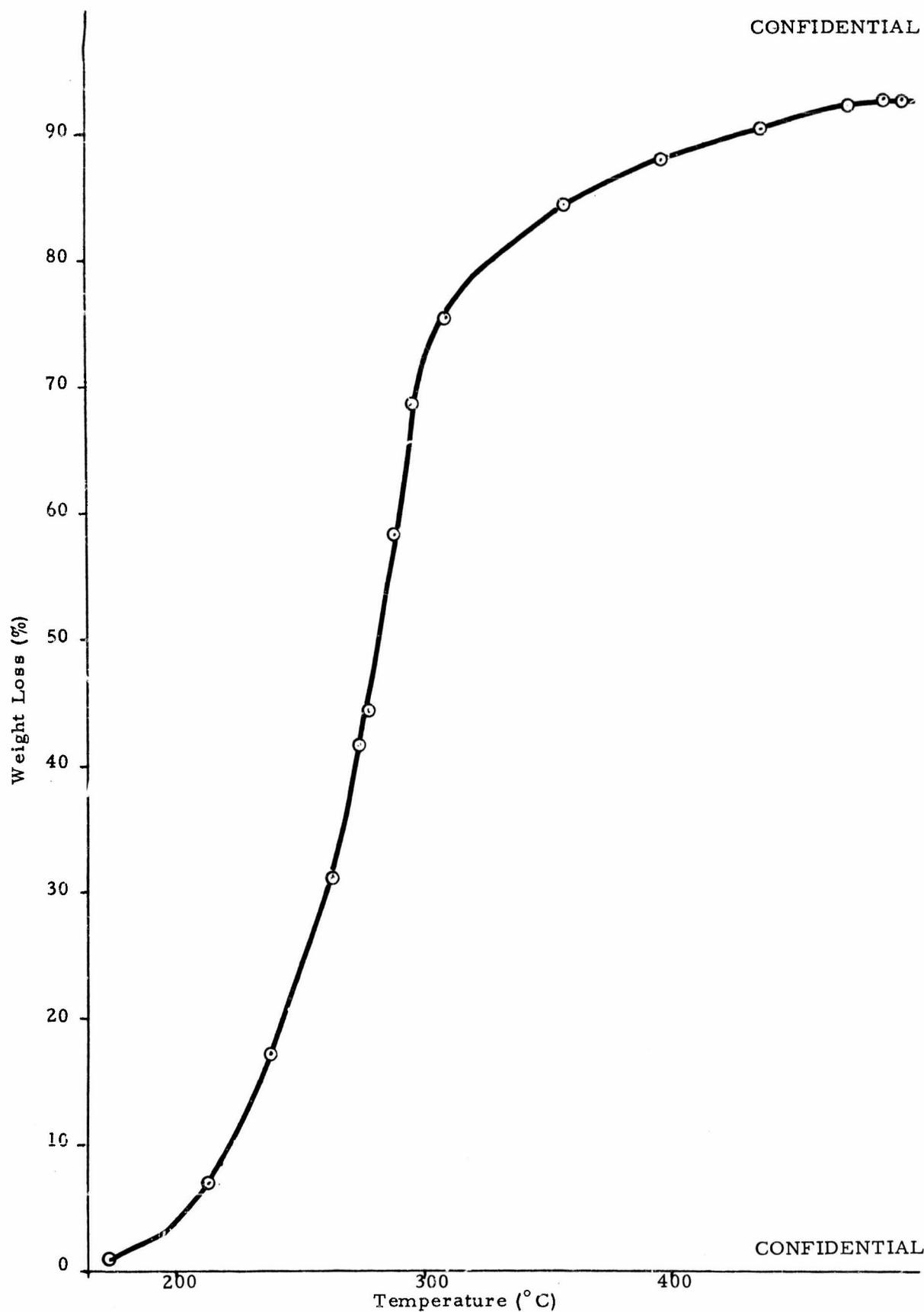
Catalyst	HC POLYMER				MAPO		Observations
	Solubility/Miscibility Ambient Temp.	24 Hrs. at 160° F	44 Hrs. at 160° F	144 Hrs. at 160° F	Solubility/Miscibility Ambient Temp.	16 Hrs. at 160° F	
10. Allyl Ferrocenolate $\text{Fc} \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ \parallel \\ \text{O} \end{array} \text{CH}_2 \text{CH} = \text{CH}_2$ (NOTE: Needle-like crystals which melt at 36-36.5° C.)	Slightly Soluble/ Miscible	No noticeable change	Slight Change in Viscosity	Polymerized at edge, 70-80% polymerization in bulk	Readily Soluble/ Miscible	Started Polymerizing	Polymerized MAPO shows polymerization at 16 hours in thin layers near bulk of material. HC polymer/catalyst fully polymerized after 216 hours at 160° F.
11. n-propyl ferrocenolate $\text{Fc} \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ \parallel \\ \text{O} \end{array} \text{CH}_2 \text{CH}_2 \text{CH}_3$	Readily Miscible	No noticeable change	Polymerizing (10 - 20%)	Polymerized	Readily miscible	Drying	Polymerized
12. 1,3-diferrocenyl-1-oxo-2- propene $\text{Fc} \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ \parallel \\ \text{O} \end{array} \text{CH} = \text{CHFc}$	Slightly Soluble, Disperses	No noticeable change	Polymerizing (10 - 20%)	Polymerized	Insoluble, disperses quickly	Paste	Drying
13. Propargyl ferrocenolate $\text{Fc} \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ \parallel \\ \text{O} \end{array} \text{CH}_2 \text{C} = \text{CH}$	Insoluble, Disperses poorly	No noticeable change	Polymerizing (10 - 20%)	80% Polymerized	Soluble	Drying	Polymerized HC polymer/catalyst fully polymeri- zed after 216 hours at 160° F.
14. Mixture of $\text{Fc}(\text{CH}_2 \text{OCH}_3)_2$ and $\text{Fc} \begin{array}{c} \text{CH}_2 \text{OCH}_3 \\ \diagdown \\ \text{C} \\ \diagup \\ \text{CH}_2 \text{OH} \end{array}$	Readily Miscible	No noticeable change	Slight Change in Viscosity	No Change from Previous	Very Miscible	Drying	Polymerized Catalysts reduce the viscosity of HC polymer drastically; viscosity of HC polymer/catalyst increased after 216 hours at 160° F -- 50% polymerized.
15. 1,1'-di(methoxymethyl) ferrocene PURE $\text{Fc}(\text{CH}_2 \text{OCH}_3)_2$	Readily Miscible	No noticeable change	Slight Change in Viscosity	No Change from Previous	Very Miscible	Drying	Polymerized Catalyst reduces the viscosity of HC polymer drastically; HC poly- mer/catalyst 85 - 90% polymerized at edge, bulk remains at approxi- mately 5%.
16. 1-hydroxymethyl-1'- methoxymethyl ferrocene PURE $\text{Fc} \begin{array}{c} \text{CH}_2 \text{OCH}_3 \\ \diagdown \\ \text{C} \\ \diagup \\ \text{CH}_2 \text{OH} \end{array}$	Readily Miscible	No noticeable change	Slight Change in Viscosity	No Change from Previous	Very Miscible	Drying	Polymerized Catalyst reduces the viscosity of HC polymer drastically; viscosity of HC polymer/catalyst increased after 216 hours at 160° F -- 50% polymerized.

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(U) Results of thermal gravimetric analysis (TGA) for methoxymethyl ferrocene and trimethoxy iron are shown on Figures 5 and 6, respectively. The results for n-butyl ferrocene, shown on Figure 7, are given for comparison. These weight loss studies are continuing.

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Figure 5. Percent Weight Loss versus Temperature by TGA Method
Methoxymethyl Ferrocene ($\text{Fc CH}_2 \text{O CH}_3$).

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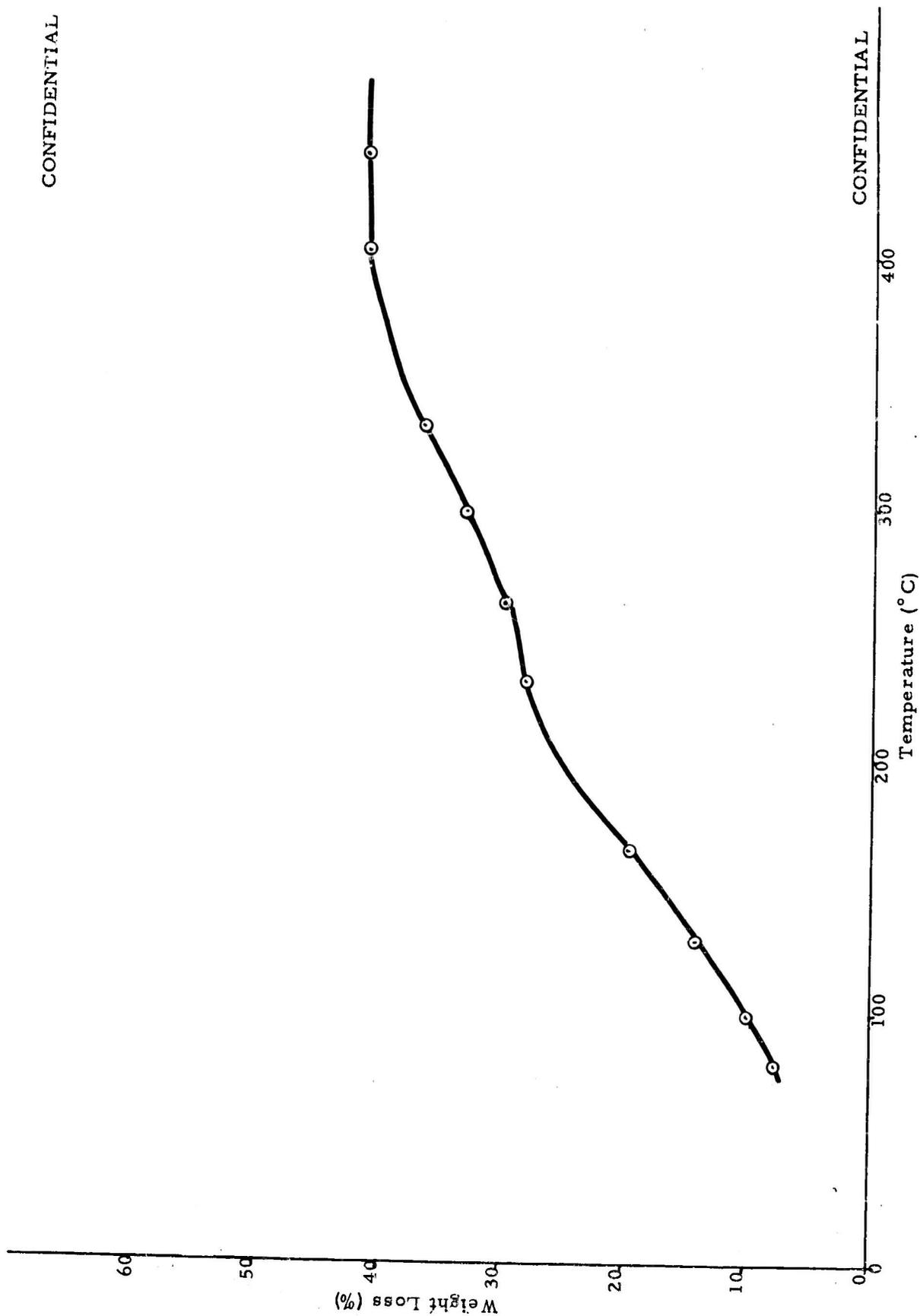


Figure 6. Percent Weight Loss versus Temperature by TGA Method - Trimethoxy Iron $Fe(OCH_3)_3$.

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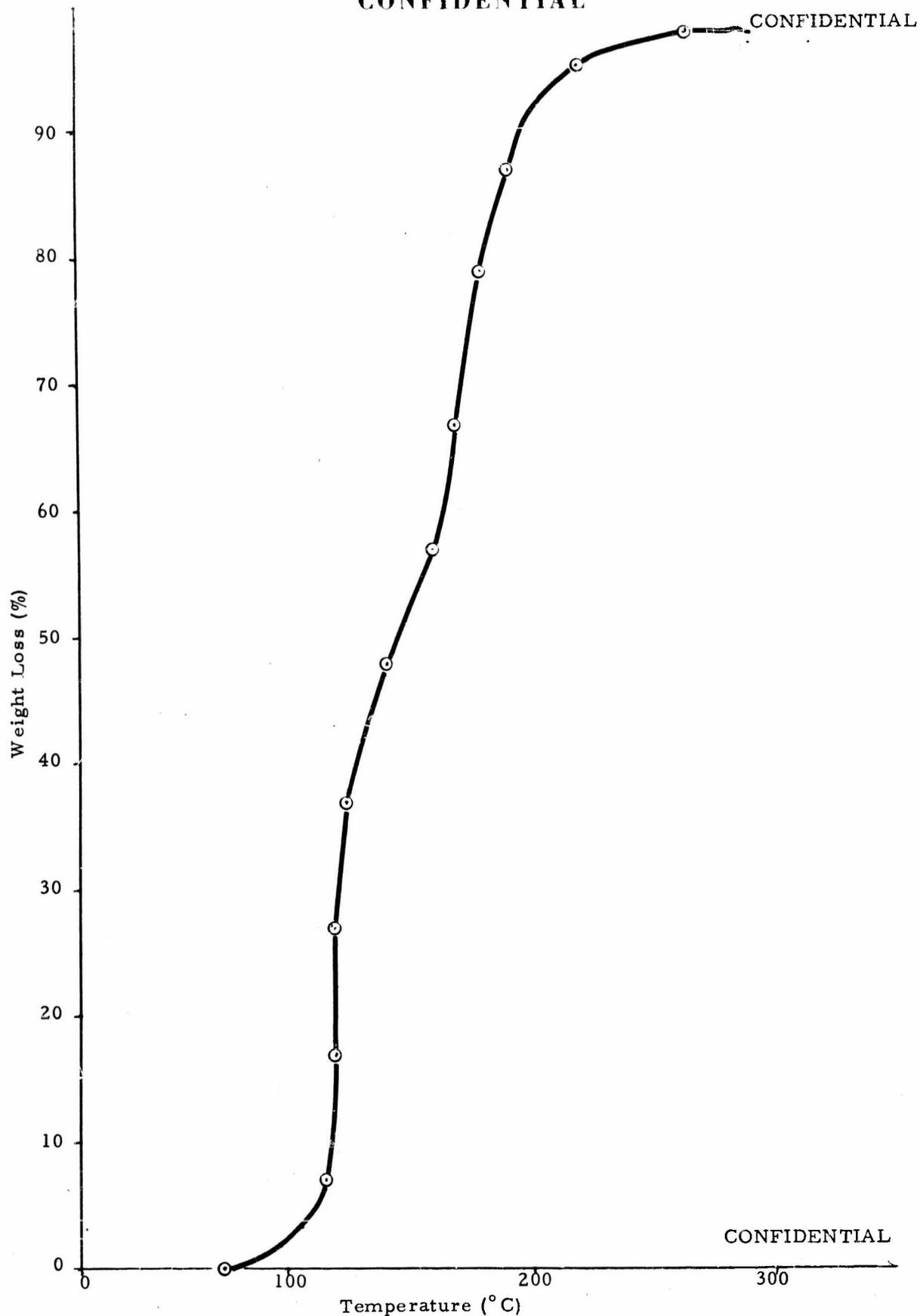


Figure 7. Percent Weight Loss versus Temperature by TGA Method - Butyl Ferrocene (P-IV; Thiokol Trademark, Reg. U. S. Patent Office)

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SECTION III

CONCLUSIONS

(U) 1. Phase I - Synthesis of Burning Rate Catalysts

(U) The following conclusions may be drawn from the data obtained:

- (C) 1. Esters of ferrocene carboxylic acid may be readily prepared in high yield.
- (C) 2. A convenient route to copper containing ferrocene derivatives has been discovered and utilized.
- (C) 3. Ferrocene ethers may be prepared easily and in high yield.
- (C) 4. Acylation of ferrocene with methoxyacetyl chloride cannot be readily achieved.

(U) 2. Phase II - Decomposition Studies and Catalyst Evaluation

(U) Of the catalysts synthesized to date, the following statements can be made in regard to compatibility with varied propellant ingredients:

- (C) 1. No compatibility problems are encountered with mixtures of the catalysts and HC polymer.
- (C) 2. The MAPO polymerization noted is only slightly accelerated in the presence of the catalysts.
- (C) 3. No problems are expected in effecting good binder cures in the presence of the catalysts.

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Security Classification

DOCUMENT CONTROL DATA - R&D		
<i>(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)</i>		
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		2b. GROUP IV
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11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Air Force Rocket Propulsion Laboratory Research and Technology Division Edwards Air Force Base, California 93523
13. ABSTRACT (C) Thiokol's program to tailor the burning rate of a propellant predictably and controllably to any desired level in the range from 1 to 10 inches per second is divided into three phases: Phase I - Synthesis of Burning Rate Catalysts, Phase II - Decomposition Studies and Evaluation of Catalysts and Phase III - Decomposition of Advanced Oxidizers, Fuels, and Binders. Experiments will be performed to synthesize more efficient burn rate catalysts by maximizing already determined guideline properties toward development of an ideal catalyst under Phases I and II. Following catalyst synthesis, each compound showing potential will be subjected to comprehensive decomposition studies and combustion mechanism evaluation with propellant ingredients. Effort conducted to date under Phases I and II indicate that esters of ferrocene carboxylic acid may be readily prepared in high yield; a convenient route to copper containing ferrocene derivatives has been discovered and utilized; ferrocene ethers may be prepared easily and in high yield, and acylation of ferrocene with methoxyacetyl chloride cannot be readily achieved. Of the catalysts synthesized to date, the following statements can be made in regard to compatibility with varied propellant ingredients: no compatibility problems are encountered with mixtures of the catalysts and HC polymer; the MAPO polymerization noted is only slightly accelerated in the presence of the catalysts, and no problems are expected in effecting good binder cures in the presence of the catalysts.		

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14. KEY WORDS	LINK A		LINK B		LINK C	
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Combustion Mechanism Burn Rate Catalyst synthesis Decomposition studies						

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