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AFRPL-TR-71-3

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**QUARTERLY PROGRESS REPORT
THERMALLY STABLE
BURNING RATE ACCELERATORS (U)**

Contract F04611-70-C-0066

January 1971

**Prepared for
Air Force Systems Command
Air Force Propulsion Laboratory
Edwards Air Force Base, California 93523**

Prepared by

Thiokol
CHEMICAL CORPORATION
HUNTSVILLE DIVISION
HUNTSVILLE, ALABAMA



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Control No. C-71-04A

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1 September through 30 November 1970

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TABLE OF CONTENTS

Foreword	<u>Page</u> iii
Abstract	iv
Introduction	1
Program Objectives	2
Discussion	4
Task I - Thermally Stable AP	4
Task II - Thermally Stable Catalysts	12
Distribution	17

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UNCLASSIFIED FOREWORD

This report is prepared in accordance with the requirements of Contract F04611-70-C-0066.

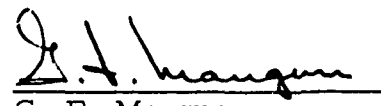
Program Structure Number	623148
Project Number	3148
Program Element Number	6.23.02F
Program Monitors	Capt. Larry Ennis and 1/Lt. D. J. Yardley USAF/RPMPC
Prime Contractor	Thiokol Chemical Corporation Huntsville Division Huntsville, Alabama

This report, the second quarterly progress report to be issued under this program, covers effort performed for the period 1 September through 30 November 1970. This report has been assigned the Thiokol internal number 4-71 (Control No. C-71-04A).

The principal investigators on the program are Dr. W. D. Stephens, Dr. D. A. Flanigan, and Mr. J. O. Hightower. Dr. M. Miller is serving as Program Manager. In addition to those contributions by the principal investigators, major contributions to the program were made by Dr. T. C. Willis, Messrs. J. W. Blanks, C. M. Christian, Mrs. Patricia B. Walters, and Dr. R. E. Rogers. The over-all Project Director is Mr. G. F. Mangum.

STATEMENT OF APPROVAL

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


G. F. Mangum
Project Director

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ABSTRACT

THERMALLY STABLE UFAP

Significant progress has been made in improving the thermal stability of ammonium perchlorate. For example, purified ammonium perchlorate which has been freeze-dried in order to effect particle size reduction, has been shown to be stable (1% weight loss by TGA) for 400 hours at 375°F. Samples of shock precipitated ammonium perchlorate which had good thermal stability were shown to be rendered less stable by exposure to moist air. Studies to define the effect of humidity on thermal stability showed, in general, that the lower the humidity to which the AP was exposed the greater the thermal stability. It has been shown that sublimation of the AP does not effect an improvement in the thermal stability. Likewise, grinding with a mortar and pestle does not significantly affect thermal stability. Results with ultrasonic grinding have been inconclusive and further work is being performed to assess the effects of this particle size reduction technique upon thermal stability. Oxidizer which has been ground by the fluid energy mill has been shown to be inherently stable when exposed at high temperatures. Mixtures of thermal stable ammonium perchlorate and purified HC polymer have been shown to be thermally stable at 350°F for times up to 94 hours.

THERMALLY STABLE CATALYST

Decylferrocene, tridecylferrocene, decenylferrocene, decanoylferrocene, and benzoylferrocene have been prepared as part of the synthetic effort in the area of thermally stable catalysts and have yielded five of the necessary models for structure-stability correlations. Critical impurities have been removed by the procedures which evolved from work during the previous quarter. Thermal stability measurements have been initiated on model compounds alone, as well as in propellant.

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INTRODUCTION

(C) The purpose of this program is to research the methods and materials that will produce thermally stable AP and burning rate catalyst. They will be used with other thermally stable propellant ingredients to produce a solid propellant that is capable of withstanding a temperature environment of -75° to 350°F .

(C) With the present capability of aircraft to fly at supersonic speeds, a new requirement now exists for missiles which can be carried externally. The major development problem arises from the effects of aerodynamic heating, causing missile skin temperatures of several hundred degrees Fahrenheit. In addition, the external carry means that a missile in the airstream is exposed to temperatures of about -65°F (the temperature in the isothermal layer). Missiles and missile components therefore are subject to temperatures from -65°F to well over 300°F .

(C) Propellants that will survive this treatment, and also possess the desirable ballistic properties, are not available. Two general approaches to assure the rocket motor's operation at all times are to insulate the motor or develop a propellant to withstand the environment. Internal or external insulations increase the motor cross sectional area and weight. Also, internal insulation decreases propellant volume. Since the missile is normally exposed to these conditions for a relatively short time, the insulation approach is inefficient. The penalties paid for insulation are too great; thermally stable propellant is a better solution.

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PROGRAM OBJECTIVES AND ORGANIZATION

OBJECTIVES:

(C) Very small particle oxidizer (less than one micron) and burning rate catalysts have been used to achieve high burning rates; however, commercially available ammonium perchlorate is prone to thermal decomposition which, in turn, degrades propellant. Some liquid burning rate catalysts also have undesirable characteristics such as crystallization, migration, or volatilization and are subject to thermal and oxidative decomposition. The objectives of this program are: (1) to develop methods of production of stable ultrafine ammonium perchlorate (UFAP), (2) to demonstrate improved methods of burning rate catalysis, and (3) utilization of these rate augmentation techniques in propellants which must survive temperature cycling up to 350°F.

PROGRAM ORGANIZATION:

(U) This program is divided into three tasks as follows:

Task I, Thermally Stable UFAP, is subdivided into three subtasks. The first defines AP thermal stability and identifies the qualities that AP must have to be stable. In the second, new methods of preparing UFAP are examined and in the third subtask, the method of preparing UFAP is chosen and enough UFAP prepared for the demonstration part of the program.

Task II, Thermally Stable Catalysts, is divided into four subtasks. These include impurity investigations, structure investigations, improved catalysts, and synthesis of material for Task III.

Task III, Demonstration, is that part of the program in which the thermally stable UFAP and an improved catalyst are combined into a propellant for demonstration.

Figure 1 gives a schematic diagram of the program outline.

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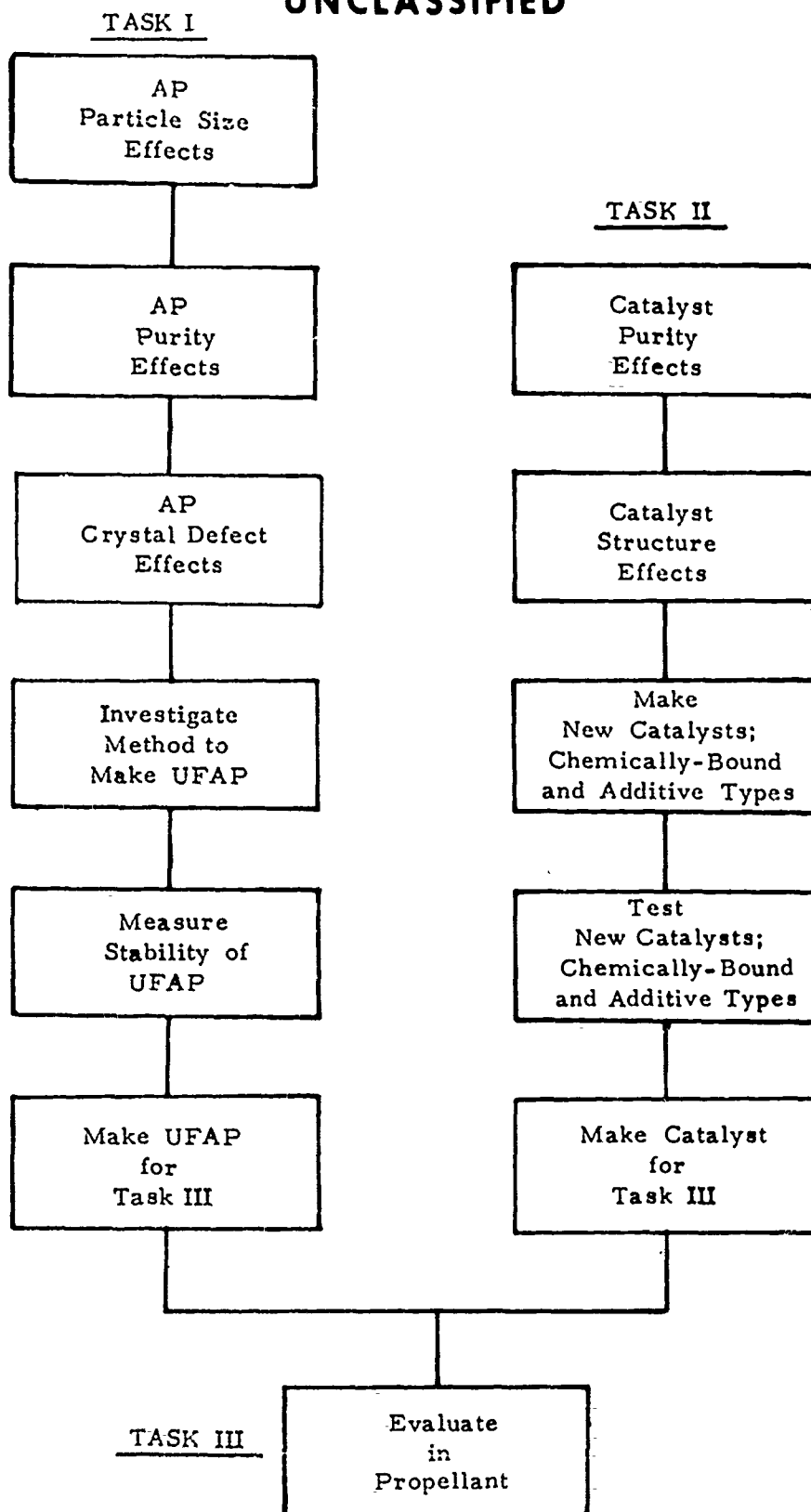


FIGURE 1. PROGRAM OUTLINE

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DISCUSSION

TASK I - THERMALLY STABLE AP

It was shown previously, Quarterly Progress Report, AFRPL-TR-70-122 that the thermal stability of AP could be improved by recrystallizing the AP from isopropanol. However, the first attempt at scaling up the selected technique for producing thermally stable ammonium perchlorate resulted in an oxidizer sample which exhibited very poor thermal stability. Much effort was expended in this report period to determine what parameters were involved in the scale-up process which adversely affected the thermal stability of the product. Recrystallization rate from isopropanol was varied significantly not only by varying the agitation rate of the isopropanol before the water solution of oxidizer was added but also by varying the temperature of the isopropanol. Ultra-pure water was likewise utilized, and stringent purification of isopropanol was employed to eliminate a possible source of induced instability in the oxidizer. The ratio of solvent to non-solvent was also varied. None of these variations provided oxidizer which exhibited greater than 12.5 hours of thermal stability at 375°F. In examining various techniques of drying the oxidizer sample after it was recrystallized it was found that exposure to moist air during the drying process gave a detrimental effect on the thermal stability. For example, in filtering the recrystallized oxidizer from the isopropanol/water mixture, if moist air were allowed to pass over the oxidizer crystal in the filter flask following alcohol removal, the thermal stability of that oxidizer sample was quite poor. Therefore, a scale-up was attempted in which a rubber dam was utilized in the Buchner funnel to prevent exposure of the crystal to air during the drying process. The resultant thermal stability of that sample was 38.6 hours. Four 100-gram batches of oxidizer have since been prepared with thermal stability values ranging between 30.4 hours and 33.5 hours utilizing the technique of shock recrystallization from isopropanol followed by drying without exposure to moist air. Whether exposure to moist air after the oxidizer crystal has been dried would result in reduced thermal stability is a subject of a series of experiments now underway. These recently prepared oxidizer samples have been submitted for analysis and the comparative data relating the purity of the as-received oxidizer to that prepared through shock recrystallization from isopropanol is shown in Table I. Note the marked reduction in chlorate, sulfate, chloride, and phosphate ion concentration. The particle size of the oxidizer prepared by this technique is approximately 40 microns and the particles are nearly spherical in shape.

In order to assess the effect of crystal defects upon thermal stability three techniques for reducing the particle size of the ultra pure ammonium perchlorate are to be utilized. Those techniques to be examined are sublimation,

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TABLE I
AMMONIUM PERCHLORATE ASSAY

	% Chloride	% Bromate	% Chlorate	% Sulfate	% H ₂ O Insol.	% Phosphate	% Sulfated Ash	% H ₂ O
Lot 3426 w/ TCP As Received (7.64 hrs thermal stability)	0.0284	0.00096	0.0036	Positive Spot test	0.191	0.089	0.200	0.046
Lot 3426 Shock Recryst. from isopropanol (38.7 hrs thermal stability)	Not Detect- able	<< 10 ppm	<0.00011	Negative Spot test 10 ppm	0.0017	0.00015	0.031	0.035

51

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simple grinding in a mortar and pestle, and fracture by ultrasonic radiation. These three techniques were selected because they will result in either the formulation of or elimination of certain types of defects.

Several samples of the ultra-pure ammonium perchlorate have been sublimed in order to determine the most efficient temperature-pressure relationship for maximum yield and minimum particle size. The primary temperature utilized was 350°C and the pressure was 0.1 mm of mercury. The product obtained from that sublimation exhibited a particle size of approximately nine microns and the thermal stability as measured at 375°F was 30.2 hours. No significant reduction in thermal stability resulted from subliming ultra-pure ammonium perchlorate. Sublimation theoretically should remove occlusions of mother liquor from the oxidizer crystal but should not eliminate defects such as edge and screw dislocations. The particle shape as seen under the microscope is quite irregular. The particle size was larger than expected but this can be attributed to the fact that significant layering of the oxidizer did occur in the sublimation process because a large sample was needed for thermal stability measurement. Variations in the distance of the cold finger in the sublimator from the heat source are now being made, and studies at lower pressure and lower temperature are in progress.

Grinding the ammonium perchlorate prepared through shock recrystallization from isopropanol in a mortar and pestle only reduced the particle size to approximately 15-20 microns. However, the thermal stability as measured at 375°F, was 32.9 hours. As was the case with sublimation, only slight degradation in overall thermal stability was noted. Grinding in a mortar and pestle should not remove absorbed mother liquor and would probably introduce more defects in the oxidizer crystal than were present as a result of the recrystallization.

The third technique, particle size reduction through ultrasonic radiation, has been evaluated. This technique should result in fracture at structurally weak points in the crystal lattice and would be predicted to remove the great majority of defects that might be present. Since this technique utilizes a non-solvent for the oxidizer, one would expect that occluded mother liquor would likewise be removed. A sample with a particle size of 4 microns was obtained by exposure to ultrasonic energy in a slurry of Freon. However, during the drying process the material was inadvertently exposed to moist air. The resultant thermal stability was only 12.3 hours compared with 38.7 hours for the starting material. The experiment is being repeated in such a way that no exposure to moist air is possible.

Prior experimentation indicated that exposure of freshly recrystallized oxidizer to moisture resulted in decreased thermal stability at 375°F. In order to determine whether such was, indeed, the case, samples of ammonium perchlorate prepared by shock recrystallization (precipitation) from isopropyl alcohol were exposed to various relative humidities for a period of three weeks. The material utilized in these experiments exhibited thermal stability of 43.7 hours at 375°F. The humidities to which samples of this oxidizer

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were exposed were 100, 75, 47, and 15%. Thermal stability measurements were then made on each of these samples by performing an isothermal TGA at 375°F. The resulting data are shown on Figure 1. Exposure to 100% relative humidity resulted in a marked decrease in the thermal stability whereas an improvement was demonstrated when the AP was conditioned at low humidities. It is important to point out that exposure to the 15% relative humidity for the three-week time period resulted in an apparent improvement in the thermal stability. It does appear that exposure of the oxidizer to relative humidities less than 40% will result in improved thermal stability. Further experimentation with shorter exposure times is desirable in order to determine whether the source of the thermal instability is provided after very short exposures to the higher humidities.

Careful examination of the hydrolytic behavior of AP indicates that the criticality of moisture as related to thermal instability of AP should not be unexpected. The oxidizer will hydrolyze readily as illustrated by the fact that the pH of a water solution of AP is normally about 5.5. The normal specification for pH on "as received" AP is between 5.0 and 6.2. As the purity of the oxidizer is improved it does appear that pH of a water solution decreases. Such is illustrated by the fact that the starting material utilized for these aforementioned experiments exhibits a pH of 4.6 in water solution.

The exact implications of the hydrolysis of AP upon the resultant thermal stability is still open to conjecture, but since products similar to those obtained from the thermal decomposition of the oxidizer are obtained in the hydrolysis step, one could draw a comparison between the two, since the presence of decomposition products seemingly accelerates the rate of decomposition of the AP.

The thermal stability measurements during the course of this program had been obtained at 375°F instead of 350°F in order to realize maximum effectiveness of the thermal gravimetric balance for extended periods of time. However, it was decided to examine the thermal stability of the material which had been shock recrystallized from isopropanol at the lower temperature of 350°F. A sample of the oxidizer which had exhibited a thermal stability of 42.8 hours at 375°F was subjected to an isothermal TGA at 350°F and the time to 1% decomposition was measured as 165 hours. In order to get a preliminary indication of the degradation of thermal stability obtained when this oxidizer was mixed with CTPB polymer, a sample of HC-434 polymer was purified by solution in benzene followed by precipitation in isopropyl alcohol. This technique provided a narrow molecular weight distribution as well as removal of the anti-oxidant and low boiling moieties. A mixture of the shock recrystallized AP (70%) with 30% of the HC-434 polymer was subjected to an isothermal TGA at 350°F. The time to 1%

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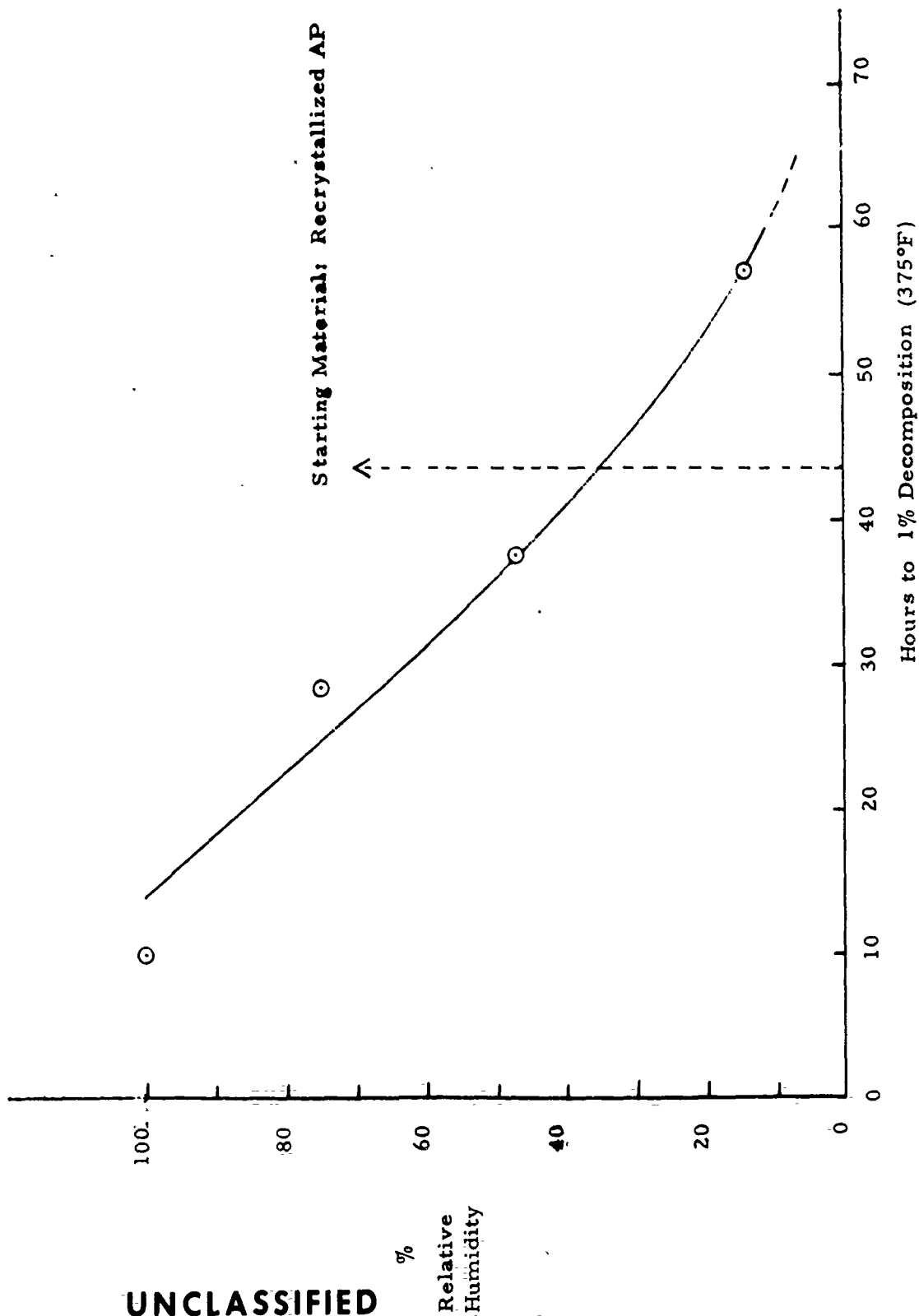


Figure 1. Effect of Humidity on Thermal Stability of AP (after three weeks conditioning)

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decomposition was measured at 94 hours. It should be pointed out that no curing agent was added to this mixture. Further experimentation with oxidizer and polymer mixtures will continue and will involve addition of a curing agent as well as thermally stable burning rate catalysts as they become available.

Studies for reducing the particle size of the pure AP by techniques such as freeze drying, spray drying, ultrasonic energy, and modified fluid energy mill have been initiated. As these samples are obtained, the particle size as well as the resultant thermal stability will be measured.

The highest level of ammonium perchlorate thermal stability that had been achieved to this point was provided through shock precipitation of the ammonium perchlorate out of isopropyl alcohol followed by exposure to 15% relative humidity for a two week time period. A time to a 1% decomposition at 375°F of 58 hours was achieved. It is important to maintain a moisture-free atmosphere during the removal of excess isopropyl alcohol from the oxidizer. If moist air is allowed to come in contact with the oxidizer during this time period, hydrolysis will occur and the thermal stability will be markedly degraded.

During this report period, experimentation at reducing the particle size of the specially purified ammonium perchlorate was initiated.

As a preliminary experiment in examining the technique of reducing the particle size of the pure oxidizer on the fluid energy mill, a sample of fluid energy mill oxidizer which had been ground in 1968 and stored below 0°C since that time period was removed from the freezer and the thermal stability of that oxidizer measured. The particle size of the oxidizer had not changed since it was placed in storage (2.3 microns). The thermal stability at 375°F was measured to be 104 hours, nearly double any thermal stability that had been achieved through purification. The fluid energy milled material was prepared from a standard production lot of ammonium perchlorate and no special attempts were made to prepurify the material before it was ground. A first look at this degree of thermal stability is quite surprising. However, in view of the fact that water appears to be the most critical impurity as related to thermal stability of ammonium perchlorate, a possible explanation for the high degree of thermal stability is available. The fluid energy mill utilizes in the grinding process high temperature ultra-low humidity air and as a result volatile impurities as well as moisture are near totally eliminated. A sample of the fluid energy milled material has been submitted for moisture analysis in order to confirm the suspicion of a very low water content.

In order to determine whether exposure to high relative humidities would have a similar effect upon the thermal stability of this fluid energy milled ammonium perchlorate as that exhibited by the purified oxidizer,

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samples were subjected to 100%, 75%, 45%, and 15% relative humidities for a period of three weeks. The thermal stability of each sample was then measured. The results are shown in Figure 2. It is obvious that exposure to moisture reduces the thermal stability to a far greater extent with the fluid energy milled unpurified oxidizer when compared with similar data for the prepurified ammonium perchlorate. In fact, the thermal stabilities of the samples of fluid energy milled oxidizer exposed to humidity are no better than "as received" ammonium perchlorate.

A sample of the prepurified ammonium perchlorate will be reduced in particle size in a fluid energy mill and the thermal stability measured not only after grinding but after exposure to the same series of relative humidities. This data will provide evidence for how critical the purity of the ammonium perchlorate is to thermal stability.

Several small samples of freeze-dried ammonium perchlorate were prepared from the prepurified ammonium perchlorate. In each case, the degradation in the thermal stability was related to impurities which were picked up from new equipment. A one-pound batch of the prepurified AP was freeze-dried after the equipment was thoroughly cleaned and the resultant thermal stability at 375°F was in excess of 400 hours (projected). In actuality, the sample remained on the thermal gravimetric balance for 220 hours and had yet to lose one-half percent in weight at 375°F. The particle size of the material, prepared without a coating agent, was 3.2 microns, since some particle size growth did occur in the preparation of the material due to improper temperature control in the sublimator. The formulation studies involving incorporation of this freeze-dried material into prepurified polymers and curing agents is now underway. Following an assessment of the thermal stability of these mixtures, catalysts will be added to the propellant.

Prepurified oxidizer is likewise being reduced in size by ultrasonic fracture and spray-drying and these results will be reported in the next report period.

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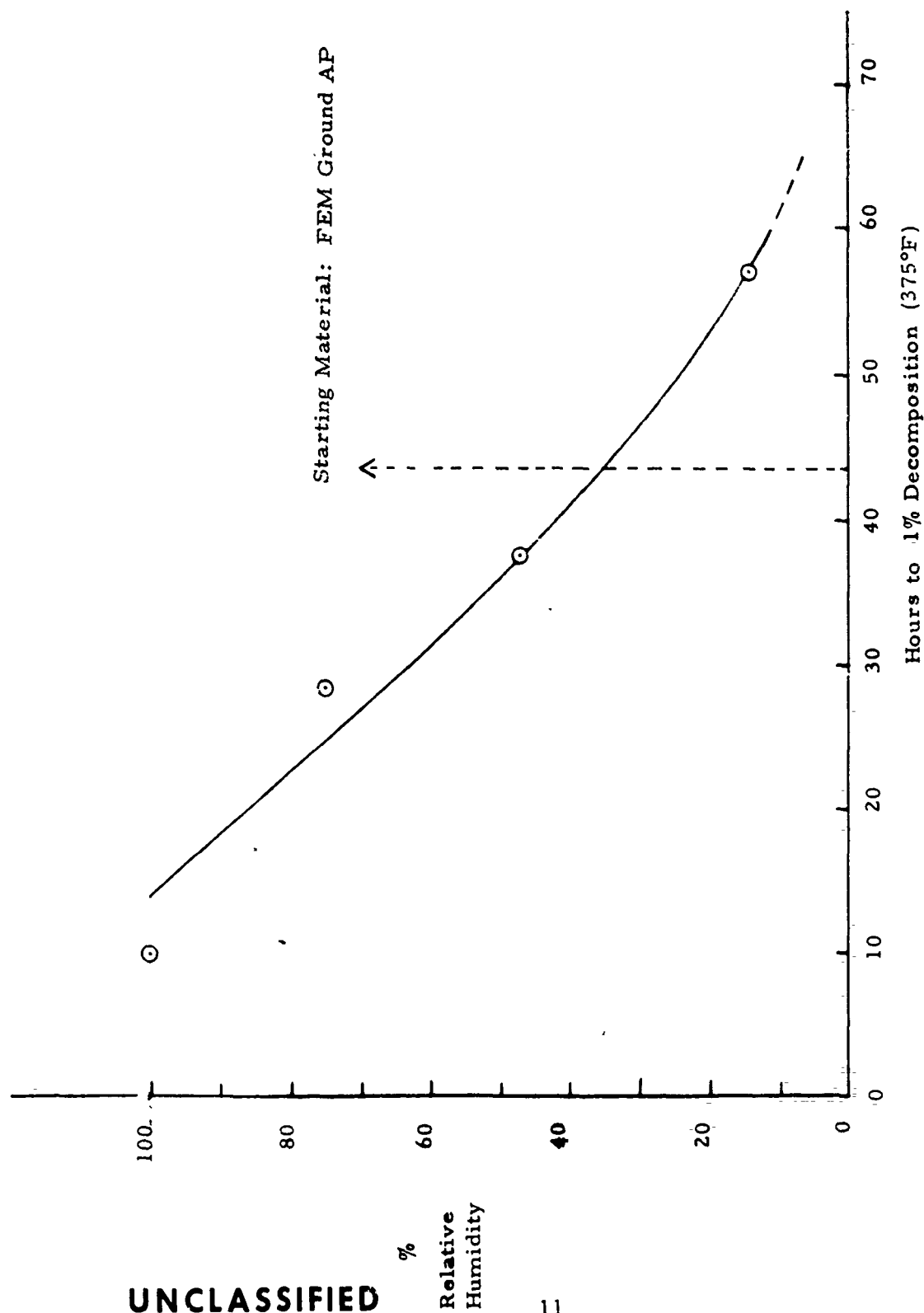


Figure 2. Effect of Humidity on Thermal Stability of AP (after three weeks conditioning)

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TASK II - THERMALLY STABLE CATALYSTS

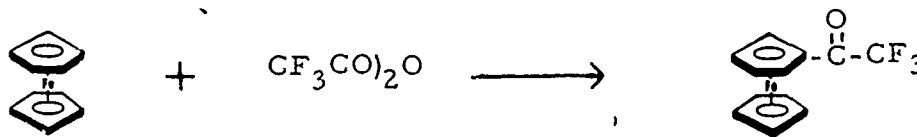
The technical approach to achieving thermally stable burning rate catalyst was initiated with a study of the impurities present in alkyl ferrocenes, and the effects of these impurities upon propellant stability. These experiments showed that there were three critical classes of impurities which should be eliminated in order to improve thermal stability. These classes include the hexane-insoluble components, the volatile components, and the ionic contaminants.

The second part of Task II has been initiated with the completion of the impurities investigations. The current part of the program involves an assessment of those features of molecular structure which are necessary to insure thermal and oxidative stability.

At the present time a number of model compounds are being prepared for evaluation in stability experiments. Those structures which are shown to be most stable in propellants will be utilized in the synthesis of improved catalysts.

Trifluoroacetylferrocene

Trifluoroacetylferrocene has been prepared in very low yield by the reaction of trifluoroacetic anhydride with ferrocene in the presence of aluminum chloride. The initial experiment was done at room temperature and gave both mono- and di-acetylated product in approximately 3% yield. When the reaction was repeated at 0°, the mono substituted compound was prepared in approximately 5% yield. Between 8 and 9% yield was obtained when the reaction was done at -70°C. The product was identified by infrared spectroscopy and fluorine analysis (theory 20.21%F, found 20.77%F). It was not intended that this reaction would provide a model for stability investigation since the vapor pressure would be too high. The reaction was investigated as a possible means of addition of a strongly electron withdrawing group to the ferrocene nucleus. The method does not appear promising.



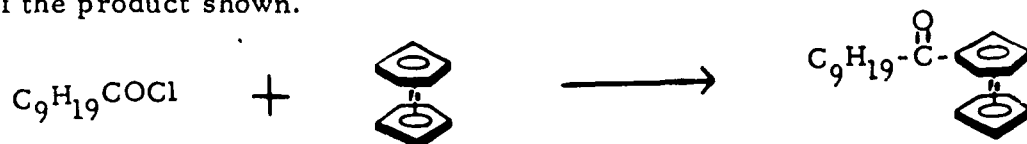
Decylferrocene

In order to provide a non-volatile standard compound for comparison purposes, decylferrocene was prepared. Reduction of decylferrocene with zinc amalgam and hydrochloric acid gave the product in 85% yield.

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$$\text{C}_9\text{H}_{19}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_6\text{H}_5 \xrightarrow[\text{HCl}]{\text{Zn(Hg)}} \text{C}_{10}\text{H}_{21}-\text{C}_6\text{H}_5$$

The reaction of decanoyl chloride with ferrocene in methylene chloride using aluminum chloride catalyst gave approximately 40% yield of the product shown.



Tridecylferrocene

$$\text{C}_6\text{H}_5\text{CH}_2\text{OCH}_3 + \text{C}_{12}\text{H}_{25}\text{MgBr} \longrightarrow \text{C}_6\text{H}_5\text{C}_{13}\text{H}_{27}$$

Trichloroacetylferrocene

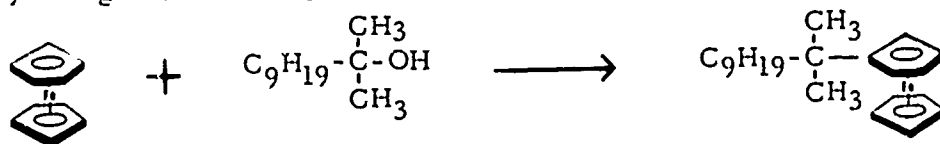
$$\begin{array}{c} \text{C}_6\text{H}_6 \\ \text{C}_6\text{H}_6 \end{array} + \text{Cl}_3\text{C}-\overset{\text{O}}{\parallel}\text{C}-\text{Cl} \xrightarrow{\text{AlCl}_3} \text{Cl}_3\text{C}-\overset{\text{O}}{\parallel}\text{C}-\begin{array}{c} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_5 \end{array}$$

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Branched Ferrocenes

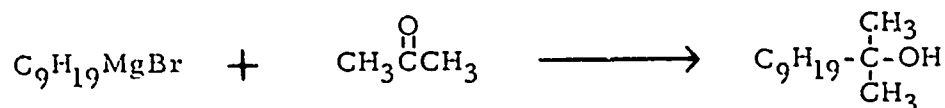
Branching which removes all α -hydrogen atoms appears to be a route to greater stability. For this reason, a number of branched model compounds have been considered.

The reaction of ferrocene with 2-methyl-2-hydroxyundecane in the presence of aluminum chloride gave very little alkylated product. When the reaction was repeated in the presence of polyphosphoric acid a very low yield of mono- and di-alkylated ferrocenes was obtained. These materials are currently being characterized.

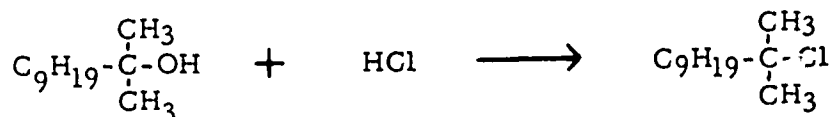


A low yield of mono- and di-alkylated products was obtained by the reaction of 2-chloro-2-methylundecane with ferrocene in the presence of aluminum chloride.

2-Methyl-2-hydroxyundecane was prepared by the reaction of nonylmagnesium bromide with acetone as shown.



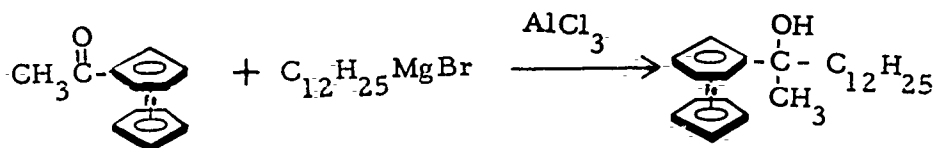
This alcohol was converted by treatment with anhydrous hydrogen chloride to the corresponding tertiary halide.



An earlier attempt using aqueous hydrochloric acid was successful, however the branched chloride was obtained in very high yield by the use of anhydrous HCl.

α -Hydroxy- α -methyltridecylferrocene

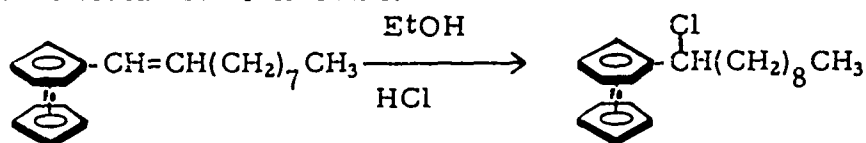
This molecule was synthesized as an intermediate for future synthesis. It was prepared by the reaction of dodecylmagnesium bromide with acetyl ferrocene.



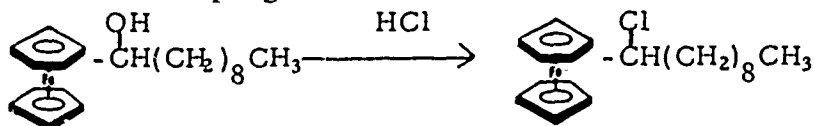
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α -Chlorodecyl Ferrocene

In an attempt to prepare α -chlorodecyl ferrocene, decenyl ferrocene was refluxed in ethanol-aqueous HCl (2:1). A material other than starting material was obtained. However, an analysis of this material indicates that it contained no chlorine.

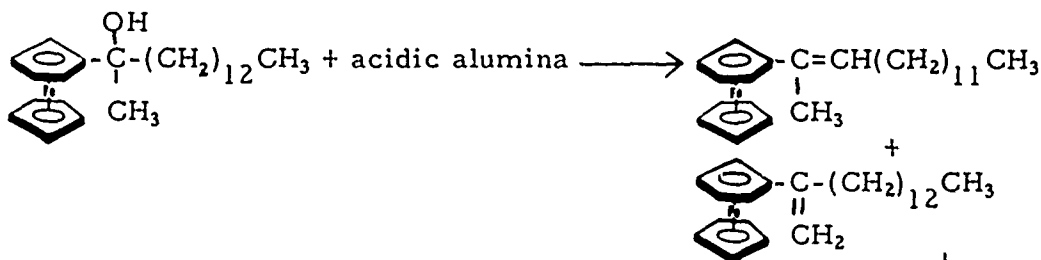
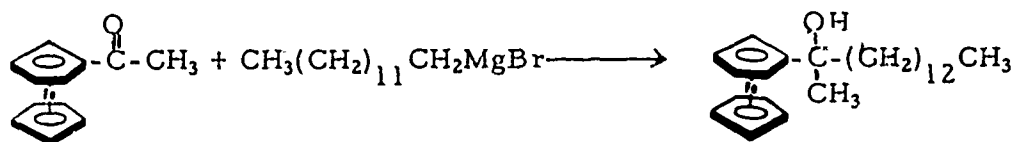


An attempt to prepare α -chlorodecyl ferrocene from α -hydroxydecyl ferrocene is in progress.



α -Chloro- α -Methyltridecyl Ferrocene

Due to the difficulty of preparing a branched alkyl ferrocene with no hydrogens, the synthesis of α -chloro- α -methyl alkyl ferrocene was undertaken.



The Grignard addition to acetylferrocene went smoothly. The alcohol was dehydrated with acidic alumina. The nmr spectrum indicates that the olefin is a mixture of the two isomers.

Addition of HCl to the double bond is not readily accomplished. Conversion of the tertiary alcohol to the halide is being investigated as a route to the chlorinated product.

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Purification

In order to accurately assess the structured effects upon thermal and oxidative stability, impurities must be removed. The critical impurities were identified in Part I of Task II. These impurities fall in three classes: hexane insoluble components, volatile components, and ionic components.

The hexane insoluble materials are being removed from the model compounds by extracting the crude material with hexane, leaving the insoluble material behind. Volatile materials are removed simply by heating the material under high vacuum. Ion exchange resins are being used to eliminate ionic impurities. A solution of the material to be purified is passed through both anionic and a cationic exchange columns. In addition to the above methods, recrystallization, distillation and column chromatography are used as needed.

Model Compounds

Five of the model compounds have been prepared and are being investigated. These include decylferrocene, a reference standard; tri-decylferrocene for comparison of synthetic routes to simple alkyl compounds; decenylferrocene for evaluation of the olefinic bond; decanoylferrocene for evaluation of the carbonyl group; and benzoylferrocene for carbonyl and aromatic effects. All of the models have been purified to remove critical impurities and initial thermal stability measurements are currently being made on pure compounds and in propellant.

Future Plans

During the next period, models containing multiple ketone groups, halogens, and branches will be made. These compounds will be assessed to provide structural guidance and improved catalysts will be synthesized based upon the results.