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AFRPL-TR-70-7

DEVELOPMENT OF A LOW COST CATALYST FOR HYDRAZINE (U)

FINAL REPORT

JANUARY 15, 1968 - NOVEMBER 15, 1969

by

Martin Lieberman
William F. Taylor

Prepared under Contract No. F04611-68-C-0044 for

Air Force Rocket Propulsion Laboratory
Edwards Air Force Base
Edwards, California 93523

Esso Report No. GR-7-DCH-70

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Government Research Division
Linden, New Jersey

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FOREWORD

(U) This technical report was prepared for the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Edwards Air Force Base, California by the Esso Research and Engineering Company, Government Research Laboratory, Linden, New Jersey in completion of Contract F04611-68-C-0044. Under this Contract, Esso Research has developed a thermally stable, non-strategically limited catalyst for the monopropellant decomposition of hydrazine fuel. This final report covers all the work conducted on the contract over the period January 15, 1968 - November 15, 1969.

(U) The Air Force Project Officer was Lt. D. Huxtable USAF/RPCL. The Esso Research Program Manager was Dr. M. S. Cohen from January 1968 to June 1969, with Dr. D. Grafstein assuming management after that date.

(U) This report has been assigned Esso Research No. GR-7-DCH-70.

(U) This report contains classified (CONFIDENTIAL) information generated in the program.

(U) This technical report has been reviewed and is approved.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

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1. SUMMARY

(C) An active, highly stable hydrazine monopropellant decomposition catalyst has been developed. This catalyst labeled Esso 500, utilizes ruthenium for its active component and thus does not contain any costly and strategically limited iridium metal. Laboratory and 5 pound thruster studies conducted at Esso Research and Engineering Company and 5 and 25 pound thruster studies conducted at the Air Force Rocket Propulsion Laboratory indicate that Esso 500 is highly active at low ignition temperatures and shows unusually high resistance to loss of surface area during motor firing. Data obtained at both laboratories actually indicated that Esso 500 showed no loss of surface area after up to 24 minutes of pulse mode firing with hydrazine.

(U) A cobalt containing catalyst, called Esso 101, was also developed. This catalyst has much lower activity than Esso 500 for hydrazine decomposition at 5°C. Esso 101, however, is active at higher temperatures and can be employed where short ignition delays at low temperature is not required and where extremely low cost is a desired property.

(U) Results of studies with various cobalt containing catalysts, cobalt-noble metal hybrid catalysts and ruthenium containing catalysts using several different substrate materials are also reported.

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2. INTRODUCTION

(U) The original objective of the work conducted under this contract was to develop a low cost, readily available, active catalyst for the decomposition of hydrazine. At the present time, an active, low temperature spontaneous catalyst does exist for the decomposition of hydrazine--Shell 405. However, Shell 405 derives its activity from the precious metal iridium which is very costly and limited in availability.

(C) In the early stages of this program, we investigated several alumina supported cobalt and cobalt-noble metal hybrid catalysts as hydrazine decomposition catalysts. Though cobalt appeared to be a very active hydrazine decomposition catalyst at high temperatures, it was not capable of affecting spontaneous hydrazine ignition at 5°C. The use of about 10 wt. % of the metals platinum, palladium and ruthenium in hybrid combinations with cobalt improved the low temperature activity. However, decomposition rates were still not great enough to cause spontaneous ignition.

(C) A more detailed study with the metal ruthenium indicated that a dramatic increase in hydrazine decomposition rate could be obtained if the ruthenium was deposited on an alumina substrate containing no cobalt. Subsequent work with ruthenium on alumina showed that properly prepared catalysts at the 30 wt. % ruthenium level had activity approaching that of Shell 405. Ruthenium appeared to offer distinct advantages over iridium as the active hydrazine decomposition catalyst. It is much more widely available and is about one third the cost of iridium. Additional studies with ruthenium based catalysts showed that active ruthenium catalysts with unusually high resistance to degradation in pulse mode hydrazine motor firing could be developed.

(U) This report discusses results of these studies with cobalt catalysts, cobalt-noble metal hybrid catalysts, and finally with supported ruthenium catalysts.

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3. LITERATURE SURVEY

3.1. Active Hydrazine Catalysts

(C) Work conducted by Shell Development Company for the National Aeronautics and Space Administration (Contract No. NAS7-97) indicated that the best possibility for obtaining high activity and stability, without a cost limitation lay in the platinum metals or their near neighbors in the periodic chart⁽¹⁾. Shell workers found that ruthenium, iridium and platinum were more active toward hydrazine decomposition than any other metal with the binary of ruthenium and iridium being the most active of all. Other metals and mixture of metals that were found to be active are listed in Table 1 in descending order of activity.

Table 1

(C) Materials Active for Hydrazine Decomposition^(2,3)

Carbon Carrier	Alumina Carrier
Ru-Ir	Ru-Ir
Ru-Pt	Ir
Ir	Ru
Ru-Rh	Ru-Pt
Ru-Pd	Fe-Co-Ni-Rh
Ru	
Ru-Os	
Ir-Os	
Pt-Ir	
Fe,Co,Ni	
Pt-Os	

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(C) Table I was compiled by Shell workers using liquid phase tests. Both carbon and alumina were used as supports for the various listed catalytic materials. Carbon is one of the most thermally stable materials known. It has a very high surface area and heat of wetting per gram of material. High surface area is advantageous in that it provides an extended support for catalytic promoters. A high heat of wetting helps to affect low temperature ignition. Unfortunately, Shell scientists found that the carbon supports reacted with the hydrogen liberated in hydrazine decomposition to form methane at high temperatures. Alumina was found to be relatively stable at high temperatures and was thus taken to be a more acceptable support. Though alumina has a lower heat of wetting than carbon, it is available in many forms, is substantially inert at high temperatures, and is used as a catalyst support in many industrial processes. After considerable testing, Shell formed two catalyst formulations which were active at 1°C: A 28% wt. metal catalyst with a Ru/Ir ratio of .34 on Harshaw Al-1404 alumina pellets and a 30 wt. % Ir catalyst on Harshaw Al-1404 pellets. The latter formulation was found to be more stable and was later named "Shell 405". This catalyst has been tested by many companies and has compiled an impressive record of stability and long life. However, it is made from extremely costly iridium which is limited in availability.

(C) Other efforts have been made to develop an active hydrazine monopropellant catalyst using more readily available and less expensive transition metals. P. C. Marx, at Aerospace Corporation, found that Girdler T-323 (silica gel treated with 50% pre-reduced cobalt on a Kieselguhr support) was found capable of initiating decomposition of hydrazine at 33°C and restart at 53°C⁽²⁾. However, this catalyst had poor life characteristics, presumably, according to Marx, because of the difficulty in degassing the silica gel at low temperatures.

(C) Hang and Ward found that the combustion of cobalt and copper on activated alumina showed the same catalytic behavior after a repeated number of tests⁽³⁾. Liengme and Tompkins at London Imperial College found that hydrazine could be decomposed on evaporated tungsten films at temperatures from -78 to 0°C⁽⁴⁾. However, no rates were presented. Their efforts were aimed at examining the NH₃/H₂ ratio at different temperatures.

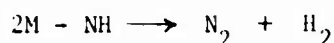
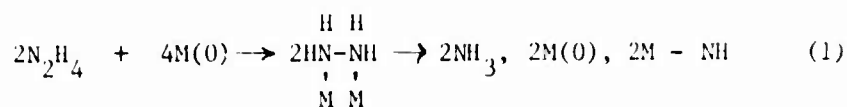
(C) Extensive work by A. F. Grant at the Jet Propulsion Laboratory in the early 1950's produced a series of catalysts using metallic iron, nickel, and cobalt deposited on an alumina carrier⁽⁵⁾. They were active at high temperatures but were not capable of spontaneously decomposing hydrazine at room temperature. Some of these catalysts are readily available from the Harshaw Chemical Co., Cleveland, Ohio, e.g., nickel catalysts Ni-1600S and Ni-1601T.

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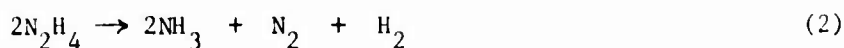
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3.2 Mechanism of Hydrazine Decomposition on Catalytic Surfaces

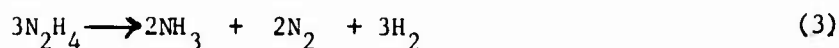
(C) Almost all of the hydrazine heterogeneous decomposition reaction mechanisms presented postulate an electron donor sequence whereby hydrazine donates electrons to vacancies or holes in the catalyst lattice. For example, Eberstein and Glassman postulate a nitrogen donor route which can account for hydrazine decomposition on platinum black at low temperatures and on silica at intermediate and high temperatures (6,7). In this mechanism, hydrazine is chemisorbed on the catalyst by donating electrons from the nitrogen atoms to vacancies in the catalyst lattice (d-band for platinum). Hydrogen atoms then migrate to produce ammonia as well as N_2 and H_2 . This is illustrated by the following schematic equation where M represents metal atoms and O metal d-band vacancies.



The overall reaction is thus



This has been shown to be the mechanism for catalytic decomposition on platinum black on acid supports (8). But this reaction does not account for some experimental results obtained with Raney Nickel. Eberstein and Glassman found that the volume of gas obtained in the presence of Raney Nickel is always greater than that indicated by the above mechanism and more closely agrees with the following overall stoichiometric reaction:



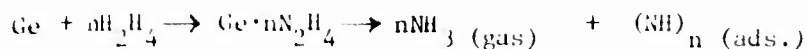
The additional hydrogen produced by the Raney Nickel at low temperatures is believed to be a result of a surface dehydrogenation of adsorbed hydrazine on the catalyst surface. However, the steps in the mechanism of surface dehydrogenation are presently not clear. Both hydrazine dissociative adsorption (reaction 2) and surface dehydrogenation (reaction 3) occur to some degree in heterogeneous catalyzed decompositions. The nature of the catalyst surface will determine which reaction predominates.

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(U) Evidence of changes in the mechanism of the heterogeneous decomposition of hydrazine with very small changes in catalyst composition is found in the work of Voelter and Kuhn⁽⁹⁾. These workers studied the decomposition of gaseous hydrazine on nickel supported by doped MgO. The activation energy for hydrazine decomposition was observed to change from 12 kcal/mole for Ga³⁺ to 16 kcal/mole when Li⁺ was used as the dopant.

(U) Similarly, the Soviet scientist, V. M. Froylov, found that the rate of decomposition of hydrazine on germanium depended on the concentration of antimony dopant in the germanium single crystals⁽¹⁰⁾. Froylov attributes ammonia formation in this study to a reaction mechanism analogous to (1), i.e.,



3.3 Heat, Mass Transfer and Catalyst Bed Design Considerations

(C) A detailed mathematical analysis of the steady-state and transient behavior of hydrazine reactors has been conducted by A. S. Keston at United Aircraft Research Laboratories⁽¹¹⁾. Keston's mathematical model contains a detailed description of the heat and mass transfer processes in the pores of the catalyst pellet. He considers both thermal and catalytic decomposition of reactants, along with simultaneous heat and mass transfer between the free gas phase and the gas within the pores of the catalyst pellets. The results of his steady-state analysis indicate that the steady-state axial temperature in the catalyst bed rises very sharply in the first inch of the bed after fuel injection to a level of about 2200°F and then slowly drops off down the length of the bed. The practical implication of this result is the possibility that a very thin active catalyst bed is required to ignite and sustain hydrazine decomposition. In fact, a long bed appears undesirable because it permits ammonia decomposition which causes the gradual temperature drop in the bulk of the catalyst bed. Experimental data obtained at Rocket Research Corporation agree closely with Keston's theoretical results on axial temperature and gas concentration profiles⁽¹²⁾.

(C) In accordance with these results, J. O. Drake conducted a study to determine whether a practical catalyst bed consisting of a thin layer of spontaneous catalyst (16.5 volume percent Shell 405) could be used in conjunction with a larger less expensive non-spontaneous catalyst (83.5 percent Harshaw HA-3) to produce a workable lower cost spontaneous catalytic system⁽¹³⁾. Tests were run with a fuel containing 63 percent hydrazine, 27 percent water, and 10 percent hydrazine nitrate. The results of Drake's experiments were promising but inconclusive. Spontaneous ignition took place over a wide range of temperatures but not at the very cold -65°F level. Ignition delay times were high; approximately 0.1 sec. Apparently, a higher spontaneous catalyst loading is required for very low (-65°F) ignition. Further work in this area is required to develop the concept. The idea seems even more practical for a pure hydrazine propellant which operates above 3°C.

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4. EXPERIMENTAL EQUIPMENT FOR CATALYST EVALUATION

(U) The basic information required to satisfactorily define the performance of a hydrazine decomposition catalyst includes the isothermal low-temperature activity and the apparent activation energy for the decomposition process. The latter is obtained by measurements of the catalytic activity at several temperature levels and the construction of an Arrhenius plot with this data. The slope of a plot of the log of the rate of decomposition vs. the reciprocal absolute temperature is taken as the apparent activation energy for a given catalyst-reactant system.

4.1 Isothermal Rate Measurement Apparatus and Method

(U) The method used to evaluate the isothermal rate of hydrazine decomposition consists of measuring the change in pressure of a calibrated constant volume container over a period of time during the decomposition reaction. This technique was previously used by the Shell Development Company and was shown to produce reliable results⁽¹⁾. The apparatus used to make the measurements is a replica of the one used by Shell scientists and is depicted in Figure 1. In a typical run, powdered catalyst material is placed in the 5 cm³ glass reactor which contains a Teflon coated magnetic stirrer. The entire apparatus is evacuated, gas collector vessel isolated, and the glass reactor filled several times with helium. A hypodermic needle is used to inject hydrazine into the glass reactor which has been previously chilled with dry ice. The reactor is deliberately kept very cold when the hydrazine is injected to guard against a sudden gas surge with an active catalyst. A temperature for study is chosen, the dry ice bath removed and replaced with a constant temperature bath mounted on a magnetic stirrer. A small charge of catalyst is used in the reactor so that isothermal conditions are approached by active stirring of the catalyst-hydrazine reaction slurry. As gas is formed in the reactor, it passes into the gas riser leg shown in Figure 1 and is discharged into the gas collection chamber. The decomposition is followed by observing the change in gas pressure in the collector vs. time. This technique has been found to yield substantially linear plots of gas formation vs. time for almost all runs. The rate of decomposition of hydrazine at a specific reactor temperature is taken as the slope of this line.

4.2 Five Pound Hydrazine Monopropellant Thruster

(U) Evaluation of a hydrazine decomposition catalyst in an actual monopropellant catalyst engine is required to completely characterize its start-up performance and life. Thus, a 5 lb. thruster was designed

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and constructed for our catalyst evaluation. The basic unit consists of a 1"D x 3"L Type 304 S.S. catalyst chamber instrumented with 1/16" inconel sheathed chromel-alumel thermocouples and Teledyne pressure transducers. Ignition delay and fuel pulse duration is measured by a direct writing oscillograph with a frequency response of 5000 cps. Fuel is stored under nitrogen gas pressure and injected through a 80° cone fuel injector. Nitrogen gas automatically covers the catalyst bed when no fuel (hydrazine) is flowing. The test thruster is not designed for flight operation. Its purpose was to provide a system to measure the comparative performance of several catalysts in adiabatic engine operation.

4.3 Laboratory Adiabatic Spontaneous Decomposition Test

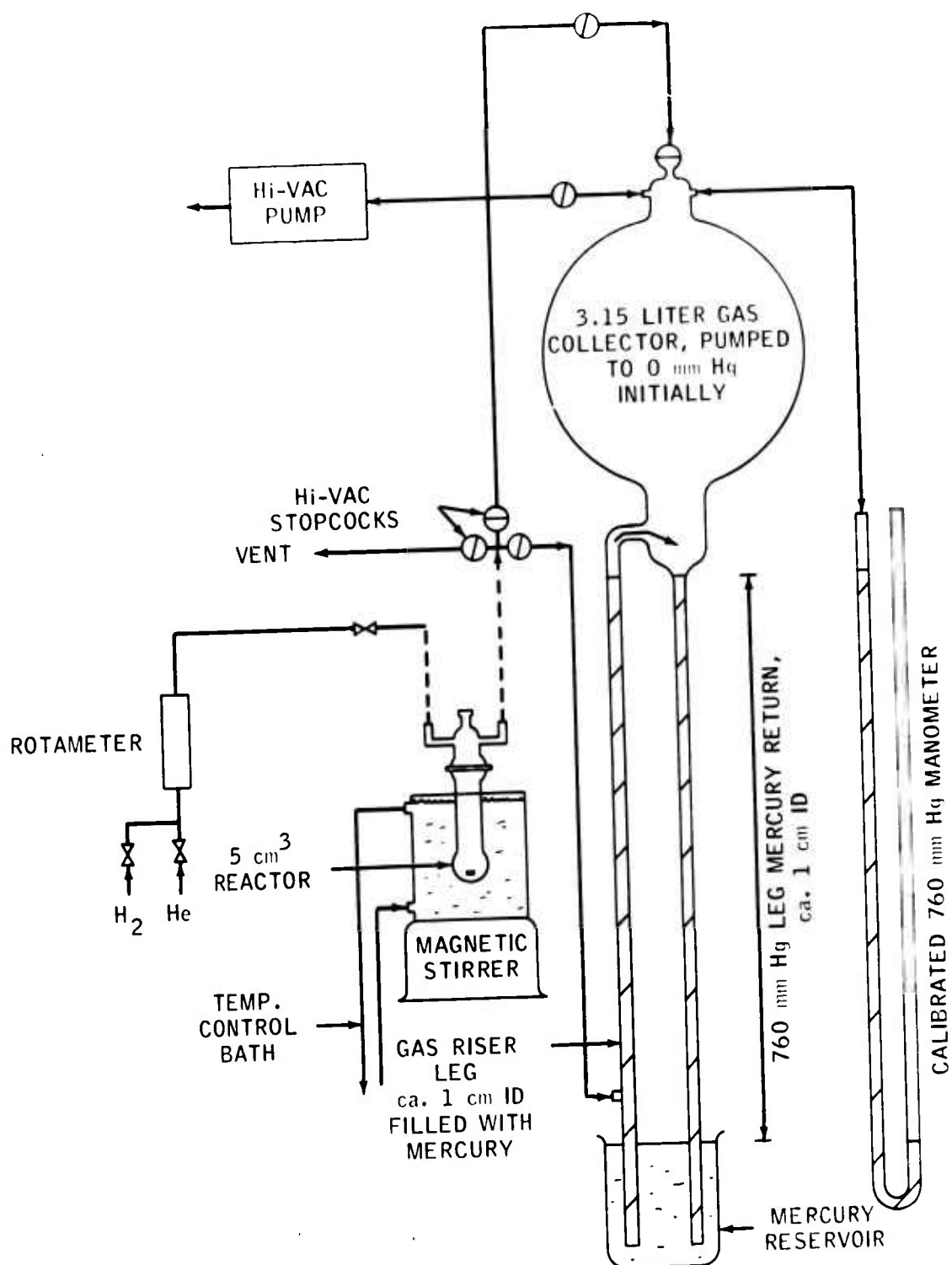
(U) A simple test aimed at simulating monopropellant engine ignition and thereby repeatedly subjecting catalyst pills to high temperatures was constructed and used in our laboratories. This test consisted of partially filling a glass tube with catalyst and charging the tube with cold hydrazine. Observations made during the test included the time required to start the reaction, the duration of the reaction, the physical condition of the catalyst pills after firing and the number of times the high temperature reaction could be sustained. The unit, depicted in Figure 2, provided a convenient and rapid means of determining catalyst relative activity and strength.

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Figure 1
ISOTHERMAL RATE STUDY APPARATUS



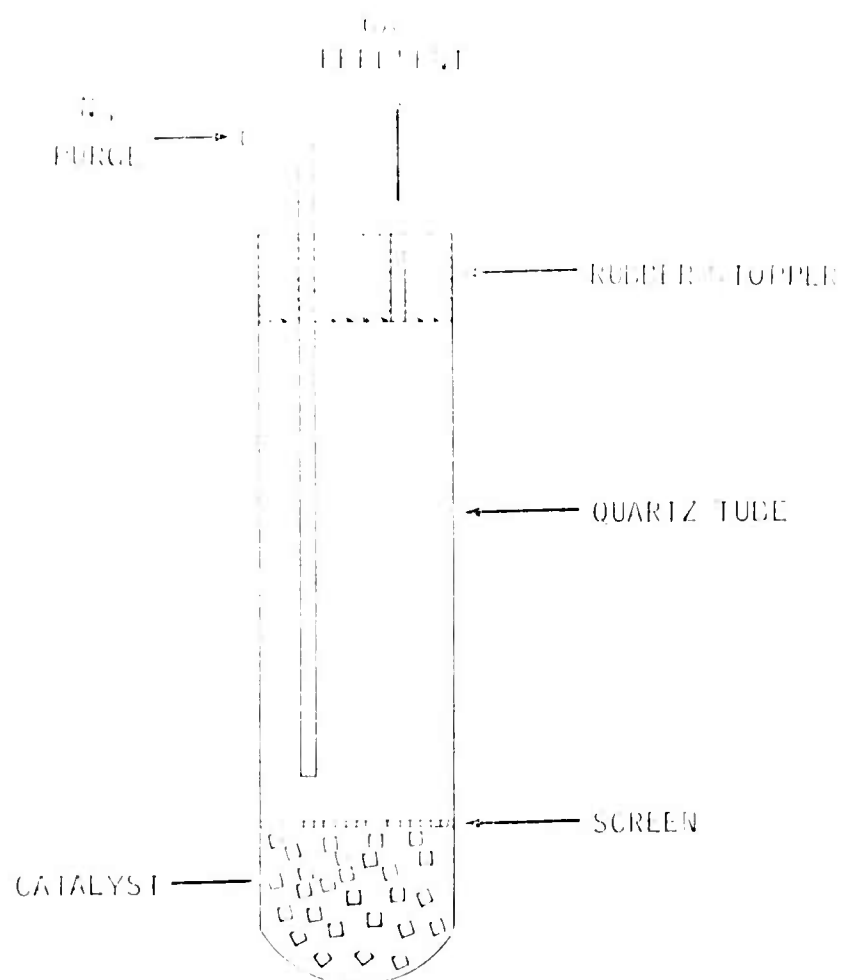
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Figure 2

Laboratory Adiabatic Spontaneous
Decomposition Test



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5. COBALT BASED CATALYSTS - ESSO 100 SERIES

5.1 Catalyst Preparation

(C) The Esso 101 catalyst consists of 60 wt. % cobalt metal and 40 wt. % Al_2O_3 , both co-precipitated from aqueous solution. The co-precipitation technique offers a unique way of dispersing active metal cobalt crystallites in a matrix of alumina, thereby providing a means of preventing cobalt sintering and concomitant loss of active catalyst area. Details of the Esso 101 preparation process are given in Appendix B.

(U) Binary metal compositions used in this study were obtained by introducing the required stoichiometric amount of iron and nickelous nitrate salts, respectively, before precipitation.

(U) The hybrid catalyst metal variations discussed in the next section of this report are fabricated by means of impregnating the Esso 101 catalyst in the "as calcined" stage with noble metals, drying the impregnated catalyst and reducing the mixture as above.

5.2 Isothermal Rate Studies of Esso 101

(U) Isothermal decomposition rate measurements of hydrazine on the basic Esso 101 catalyst powder were made in our glass reactor. As can be seen in Table 2, these measurements indicated that Esso 101 had a much lower room temperature activity than Shell 405.

Table 2

Low-Temperature Activity of Esso 101 Powder		
Catalyst	Hydrazine Decom- position Rate at 23°C cm ³ (STP)/min-gr	Apparent* Activation Energy Kcals/Mole
Esso 101	75	23-28
Shell 405	2,200	17-22

*The term "apparent activation energy" refers to the activation energy displayed by catalyst particles. It includes any effects due to mass transfer through the catalyst pores. The apparent activation energy is obtained by measuring the slope of a plot of hydrazine decomposition activity vs. the reciprocal of the absolute temperature.

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(U) The activation energy, on the other hand, appeared to be somewhat higher than that reported by Shell scientists for Shell 405. Shell's scientists found in the course of their work, that a catalyst must have a minimum activity of 75 cm³/min-gm to be spontaneous. Thus, at low temperatures, Esso 101 would have too long an ignition delay time. Ignition delay measurements on Esso 101 in our 5 lb. thruster confirmed this prediction. Work was thus conducted to improve the low temperature activity of Esso 101. One approach tried at improving low-temperature activity was to increase the cobalt loading of the catalyst.

5.3. Effect of Cobalt Concentration

(C) The basic composition of Esso 101 is 60 wt. % Co -40 wt. % Al₂O₃. To determine whether a change in cobalt concentration would affect the catalytic activity, we prepared catalyst powders with 50 and 70 wt. % cobalt, respectively. These formulations were tested in the isothermal reactor at three different temperatures. The results, depicted in Figures 3 and 4, showed a definite effect of cobalt concentration. The 70 wt. % cobalt formulation was more active than the 60 wt. % formulation; the 50 wt. % formulation had significantly lower activity. Increasing the concentration to 80 and 90% gave further improvement in activity though the relative increase appears to level off at very high cobalt concentrations. Higher cobalt concentrations gave higher catalyst activity, despite the fact that the total BET surface area was lower.

(U) The apparent activation energy for catalyst hydrazine decomposition, on the other hand, was not altered. It, thus, appears that increasing the cobalt concentration in the catalyst formulation could result in some reduction in the low-temperature ignition delay but that this reduction would not be sufficient to yield a catalyst that affected spontaneous hydrazine decomposition at 0°C. Thus, other approaches were tried.

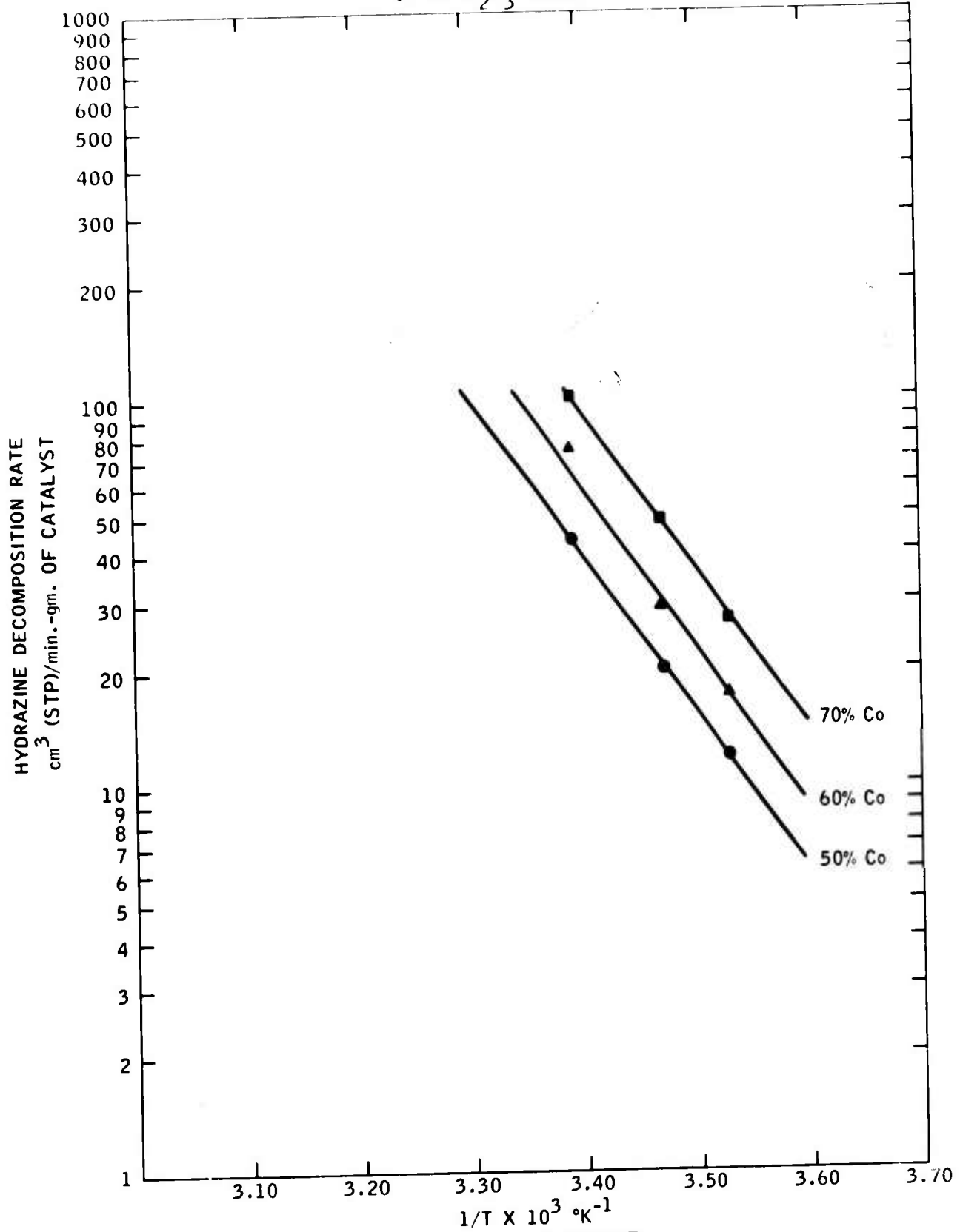
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Figure 3

EFFECT OF COBALT CONCENTRATION
ON ACTIVITY
OF Co-Al₂O₃ CATALYSTS



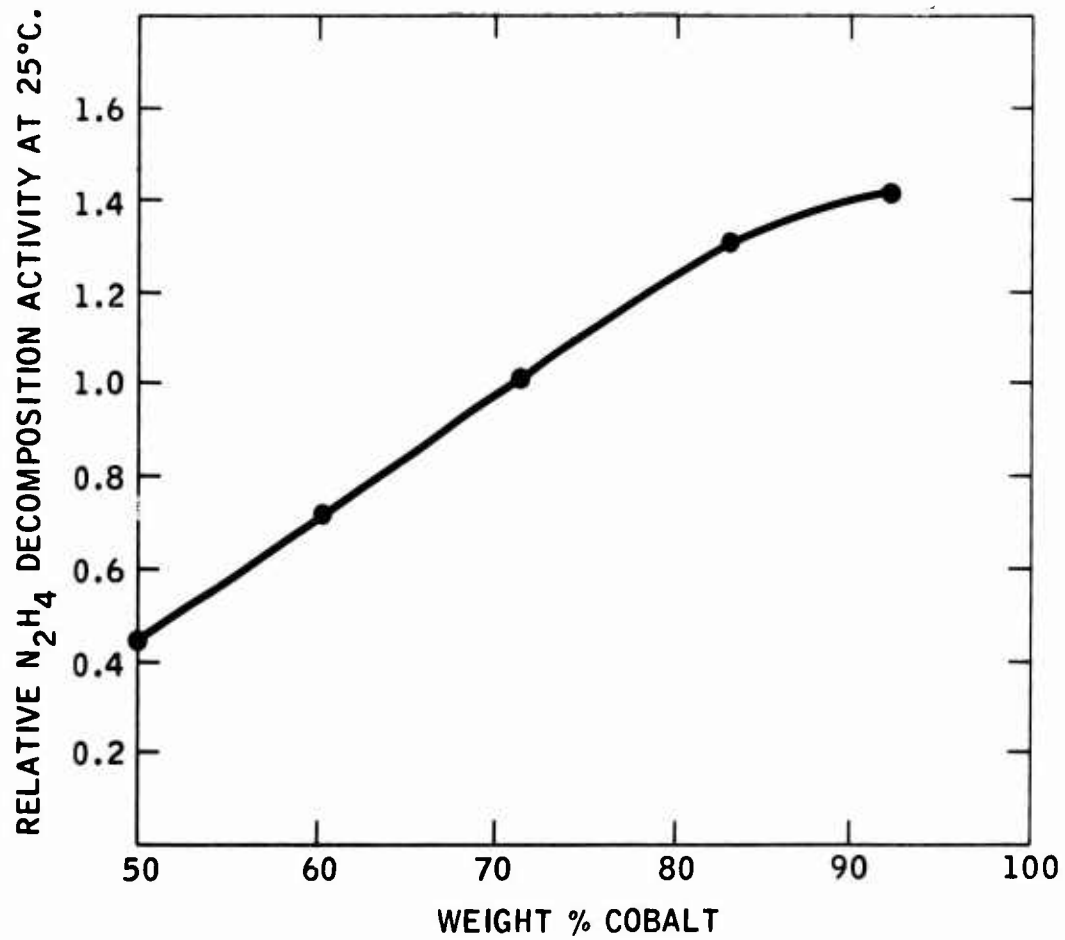
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FIGURE 4

EFFECT OF COBALT CONCENTRATION
ON ISOTHERMAL ACTIVITY



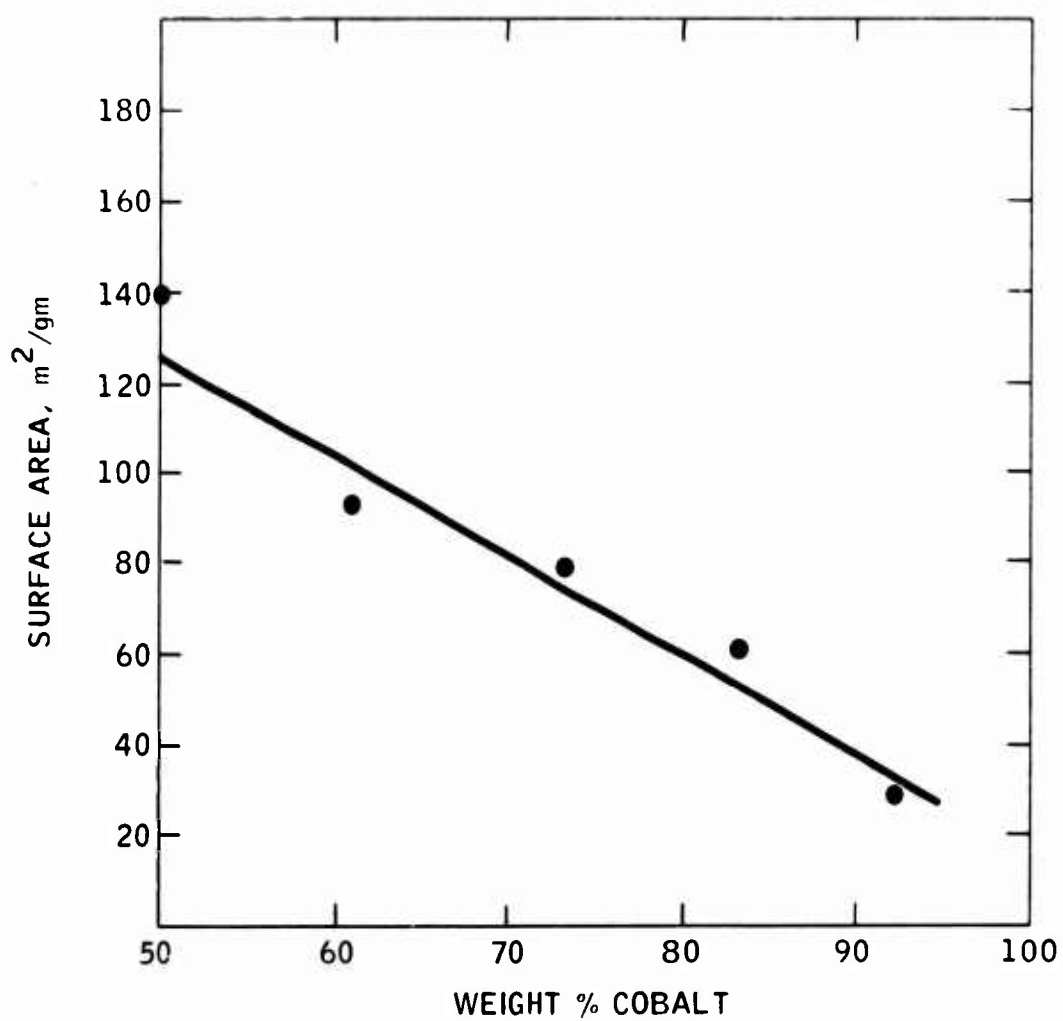
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FIGURE 5

EFFECT OF COBALT CONCENTRATION
ON SURFACE AREA OF CATALYST



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5.4 Effect of Other Transition Metals

(U) Altering the "d band" vacancy of a transition metal catalyst is another means of changing its catalytic activity. In another approach at improving the low-temperature activity of the basic Esso 101 formulation, we attempted to study the effect of introducing the metals, nickel and iron, into the Esso 101 formulation. Modifications containing co-precipitated nickel and iron, respectively, were screened in the laboratory isothermal reactor. The resulting activity of these catalysts are presented in Table 3.

Table 3

(C) Effect of Co-Precipitating Nickel
and Iron with Cobalt

Catalyst Composition	Hydrazine Decomposition Rate at 23°C cm ³ (STP)/min-gm
60 wt. % Co-40 wt. % Al ₂ O ₃ (Esso 101)	80
40 wt. % Co-20 wt. % Ni 40 wt. % Al ₂ O ₃	18
40 wt. % Co-20 wt. % Fe 40 wt. % Al ₂ O ₃	1

(U) Both the nickel-cobalt and iron-cobalt formulations showed much lower isothermal low-temperature activity than the basic Esso 101 formulation. It is difficult to explain this severe loss in activity resulting from binary transition metal formulations. However, the negative results of the preliminary binary transition metal formulation studies did not justify any further effort on this approach with nickel and iron.

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5.5 Effect of Catalyst Preparation Technique

(U) The basic Esso hydrazine decomposition catalyst consists of cobalt and alumina co-precipitated from aqueous solution. The catalyst was originally prepared by dissolution of the nitrate salts of cobalt and alumina followed by the co-precipitation of the oxides of these metals and subsequent reduction of the cobalt oxide to the metal. In the original preparation procedure, precipitation was affected by means of the slow addition of ammonium bicarbonate to a well stirred solution of the nitrate salts at 150°F. The von Weimarn theory of precipitation predicts that high surface area precipitates result from precipitation under conditions that yield a high degree of local supersaturation--rapid addition of precipitating agent, no stirring of solution, low temperature of solution. We attempted to utilize this theory to increase the surface area of the resulting precipitate and hopefully also improve the low temperature activity of the resulting catalyst.

(C) Two variations in the precipitation procedure were tried: (a) the low temperature (0°C) addition of ammonium bicarbonate to a solution which was not stirred and (b) the addition of the cobalt and aluminum nitrate salts to a cold solution of ammonium bicarbonate, i.e., using a mixture of the nitrate salts as the precipitating agent. The results of this experiment are given in Table 4.

Table 4

(C) <u>The Effect of Precipitation Procedure on the Surface Area of Co-Precipitated Cobalt-Alumina Catalysts (1)</u>	
Procedure	Surface Area m ² /gm
Conventional	61
Low Temperature	100
Low Temperature-Salt Precipitation	129
(1) All preparation procedures resulted in a catalyst composition of 83% Co-17% Al ₂ O ₃	

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(C) Both modifications in the precipitation procedure resulted in increased catalyst surface area. Low temperature precipitation increased the surface area 64% and the low temperature, nitrate salt precipitation more than doubled the surface area when compared with the conventionally prepared catalyst. Unfortunately, the low temperature activity per gram of catalyst was not improved by these modifications in catalyst preparation procedure. This implies that the increase in surface area was mainly due to an increase in the alumina surface area, and not the cobalt. Substantial improvements in the heat of wetting, largely a function of the support surface area, would be expected for the higher surface area catalysts. However, it seemed unlikely that these improvements would substantially improve the low temperature activity of the finished catalysts. Thus, further pursuit of this approach was abandoned.

5.6 Screening of Non-Noble Metal Catalyst Materials

(C) Several non-noble metal and metal oxide catalysts were screened for low temperature hydrazine activity using our laboratory adiabatic screening test, i.e., by observing the presence of any gas evolution when cold hydrazine (2°C) was added to catalyst samples in a test tube reactor. We took advantage of the availability of a wide range of complex inorganic materials which were synthesized in the Esso laboratories for electronic and electrocatalytic applications. These materials included transition-metal phosphides, non-stoichiometric oxides and non-stoichiometric tungstates. The materials tested are presented in Table 5. None showed any sufficient level of activity to warrant further evaluation.

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Table 5

(C) Screening of Potential Non-Noble Metal Catalyst Materials

<u>Material</u>	<u>Hydrazine Decomposition Activity 2°C (1),(2)</u>
Nickel Phosphide NIP	No Activity
Cobalt Phosphide Co ₂ P	No Activity
Titanium Phosphide Ti _x P	No Activity
Chromium Phosphide Cr ₂ P	No Activity
Manganese Phosphide Mn ₃ P ₂	No Activity
Niobium Phosphide NbP	No Activity
Rhenium Metal	Slight Activity
CrWO ₃	Slight Activity
Cr + 1.45 WO ₃	No Activity
Cr ₂ O ₃ ·WO ₂	No Activity
Cr ₂ W ₄ O ₄	No Activity
Cr ₂ O ₃ ·WO ₂	No Activity
Co. _{.263} WO ₃	No Activity
Cr. _{.145} WO ₃	No Activity
Cr ₂ O ₃ WO ₃	No Activity
CrO ₂	Slight Activity
W + WO ₃ + Cr ₂ O ₃	No Activity
Cr ₂ O ₃ + WO ₂	Slight Activity

(1) Test consists of the addition of anhydrous hydrazine at 2°C to powdered catalyst samples and observing the gas evolution.

(2) No Activity - defined as no noticeable effervescence of hydrazine after 5 minutes.

Slight Activity - defined as some effervescence but less than what would be observed with a similar charge of Esso 101 powder.

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6. HYBRID CATALYST STUDIES

(C) Another approach to reducing the low-temperature ignition delay of Esso 101 was to incorporate small quantities of readily reduced transition metals into the catalyst formulation. Small additions of these metals could provide appreciable surface area which would not have any oxide layer resulting from desensitization procedures. Furthermore, low concentrations of readily reduced metals (less than 1 wt. %) such as platinum and palladium have been observed to enhance the activation of nickel catalysts by hydrogen⁽¹⁴⁾. Similar enhancement was expected for cobalt. The cost of incorporating small quantities of these readily reduced transition metals would not be great; e.g., 1 wt. % of a metal costing \$100/troy ounce would add only \$15/lb to the cost of the catalyst. This approach appeared promising and was, thus, studied in the laboratory.

6.1 The Effect of Low Concentrations of Noble Metals

(C) Readily reduced transition metals were added to the basic Esso 101 preparation after the calcining step. Salts of palladium, platinum silver and gold were dissolved and impregnated into different batches of calcined Esso 101, dried, and reduced as described in the standard procedure for fabricating Esso 101 catalyst powder. The various preparations were then individually tested in the isothermal laboratory reactor. The results of these isothermal rate measurements are given in Table 6.

Table 6

(C) Isothermal Rate Measurements of
Esso 101 Catalyst Powders Containing
Small Quantities of Readily Reduced
Transition Metals

Catalyst	Hydrazine Decomposition Rate at 23°C cm ³ (STP)/min-gm
101	80
101 + 1% Pd	100
101 + 1% Pt	55
101 + 1% Ag	42
101 + 1% Au	65

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(C) Only the palladium formulation showed any activity improvement over the basic Esso 101 catalyst at 23°C. On the other hand, formulations incorporating platinum, gold, and silver appeared to be somewhat less active. In terms of these results alone, one would not expect a significant improvement in low-temperature ignition delay performance of the modified catalysts. However, we felt that the advantage of having some metal surface which is unaffected by the passivation step, present in the cobalt catalyst formulation, may not have been clearly seen in the isothermal laboratory reactor tests. We thus evaluated the ignition delay of these preparations in our 5 lb thruster. We also continued screening other readily reduced transition metals.

6.2 Effect of Higher Concentrations of Noble Metals

(C) Initial studies indicated that the incorporation of palladium metal into the cobalt-alumina catalyst formulations, at the 1 wt. % level caused an improvement in low temperature activity. Thus, higher palladium metal loadings were studied. In addition, higher loadings of platinum on the cobalt-alumina catalyst were evaluated. The results of the isothermal low temperature decomposition tests using these and other hybrid formulations are presented in Table 7.

Table 7

(C) Effect of Readily Reduced Transition Metals on the Low Temperature Hydrazine Decomposition Activity of Cobalt-Alumina Catalysts	
Catalyst	Hydrazine Decomposition Rate at 23°C cm ³ (STP)/min-gm
Esso 101	80 (base)
101 + 1% Pd	105
101 + 10% Pd	128
101 + 1% Pt	56
101 + 10% Pt	160
101 + 1% Rb	80
Raney Co-Pt alloy	64
10% Pt	
Shell 405	270 (10°C)

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(C) Increasing the palladium concentration to 10 wt. % resulted in a 60% increase in isothermal activity; increasing the platinum concentration to 10 wt. % yielded a catalyst with twice the activity of Esso 101 at 25°C. These improvements were very encouraging. However, they still were not nearly large enough to affect spontaneous catalyst ignition at 3°C. Some improvement would be expected in the ignition delay of catalysts fired at room temperature. Such was actually observed when a cobalt-alumina catalyst, containing 10 wt. % Pd was fired in a 5 lb thruster.* Table 8 summarizes the results of this test.

Table 8

(C) Ignition Delay of Palladium Cobalt Hybrid Catalyst	
Catalyst (1)	Ignition (2,3) Delay at 23°C msec
Cobalt-Alumina Catalyst	1,200
Cobalt-Alumina + 10 wt% Pd	400
(1) Catalyst consisted of 83% cobalt - 17% Al ₂ O ₃ packed in 1/2" x 1/2" S.S. wire baskets. (2) Runs compared on the 3rd firing in 5 lb thruster. (3) Ignition delay time does not include valve response and fuel flow dead time which is approximately 60 msec in our test system.	

(C) The incorporation of 10 wt. % Pd into the cobalt-alumina catalyst improved the ignition delay of the catalyst after the bed was activated by two initial firings.+ However, this improvement was insufficient to affect spontaneous ignition of the catalysts in the 5 lb thruster.

6.3 Isothermal Evaluation of Cobalt-Ruthenium Hybrid Catalysts

(C) The incorporation of readily reduced transition metals into our cobalt catalyst formulation have improved the low temperature activity and ignition delay of the cobalt catalyst system. The experimental data indicated that the incorporation of platinum and palladium into alumina supported cobalt preparations improved the isothermal

*The Esso 5 lb. thruster does not represent a flight type design. Ignition delay data are thus useful only on a comparative basis.

+Catalyst performance was evaluated on the third firing to avoid any confounding effects of residual oxide.

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activity and ignition delay of Esso 101 type catalysts. This work was extended to ruthenium-cobalt hybrid catalysts. Ruthenium was a particularly attractive transition metal to work with because of its wide availability and reasonable cost. Information made available to Esso Research and Engineering Co., indicated that there is about 150,000 troy ounces of ruthenium/year available, primarily from two sources: the Johnson Matthey and Co. (as a by-product of gold and platinum refining) and the International Nickel Co. (as a by-product of copper and nickel refining). There is also believed to be a substantial backlog of this metal presently available.

(C) Several ruthenium-cobalt-alumina catalysts were prepared by different fabrication techniques. These included 10% ruthenium on oxide sintered cobalt-alumina (prepared by co-precipitation), Esso 201; a structure consisting of 12% ruthenium prepared by co-impregnation of alumina with cobalt ruthenium solution, Esso 202; and a structure consisting of 22% ruthenium prepared by co-impregnating a ruthenium on alumina support with cobalt ruthenium solution, Esso 204. The results of the isothermal hydrazine decomposition tests, using these structures, are presented in Table 9 and Figure 6.

Table 9

(C) ISOTHERMAL DECOMPOSITION RATE OF COBALT-RUTHENIUM HYBRID CATALYSTS

Catalyst	Description	Hydrazine Decomposition Rate at 23°C cm ³ (STP)/min-gm	Apparent Activation Energy Kcals/gm-mole
Esso 201	10% Ru, 75% Co on oxide sintered cobalt-alumina	10	19
Esso 202	12% Ru, 33% Co co-impregnated alumina	25	24
Esso 204	22% Ru, 33% Co co- impregnated Ru-alumina	50	24
Esso 203	12% Ru, 33% Co, 55% Alumina co-precipitated	15	24
Esso 101	70% Co, 30% Alumina co-precipitated	75	26

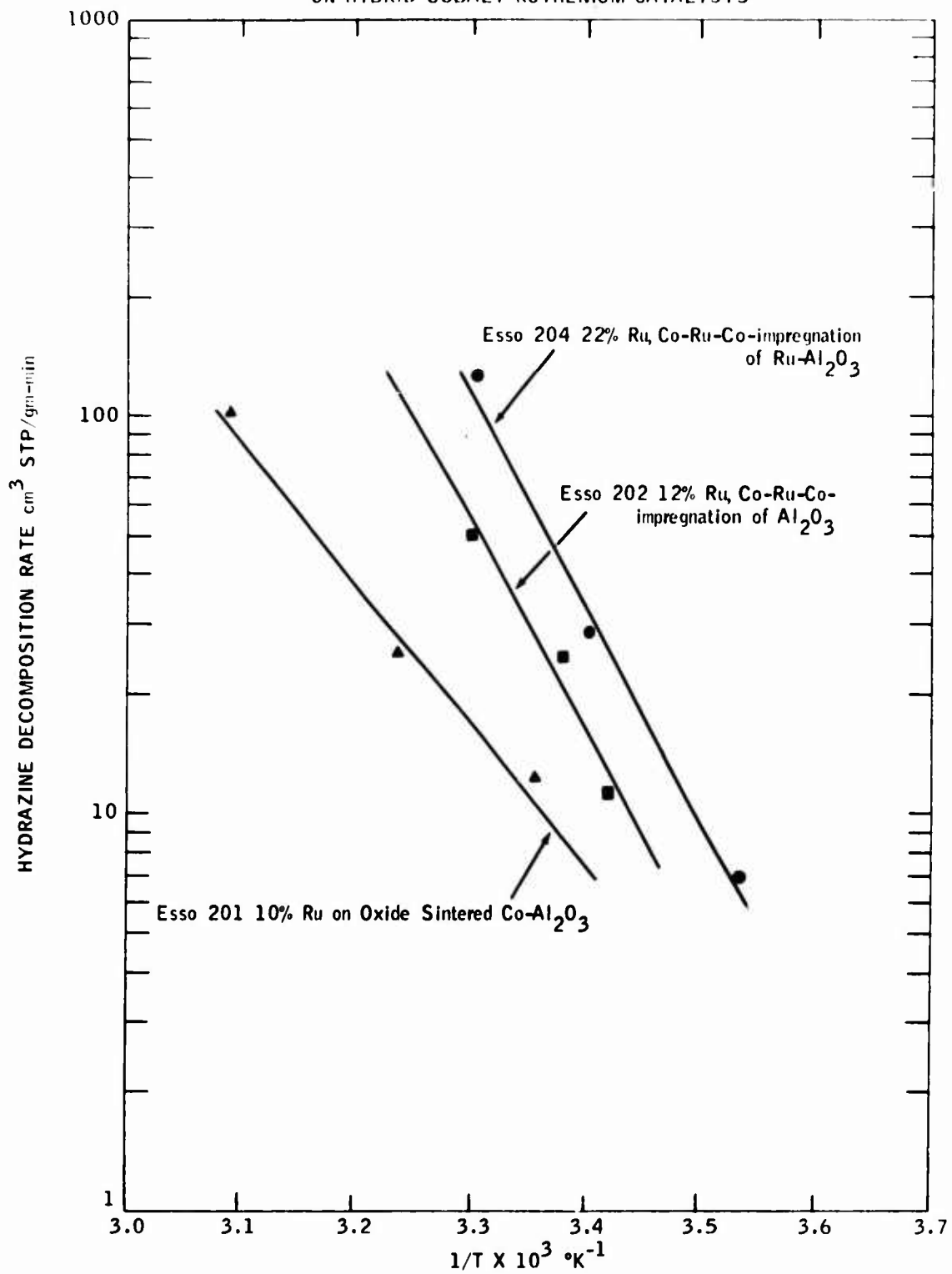
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Figure 6

(C) ISOTHERMAL HYDRAZINE DECOMPOSITION RATE
ON HYBRID COBALT-RUTHENIUM CATALYSTS



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(C) Several interesting observations may be made about the data in Table 8 and Figure 7. First, the isothermal hydrazine decomposition rate of the cobalt-ruthenium hybrid catalysts was less than that of the basic Esso 101 catalyst which contained no ruthenium. Surface area differences were believed to be partly responsible for this difference in activity. Surface area data indicated that the impregnated hybrid catalysts had considerably less surface area than the co-precipitated Esso 101 preparation. However, the magnitude of this surface area difference could not possibly account for the entire activity difference observed. For instance, Esso 201 had about one half the surface area of Esso 101 with comparable cobalt loadings. Yet, the isothermal activity of the Esso 101 catalyst was about seven times greater. This implied that a negative synergistic effect exists for the cobalt-ruthenium catalyst system. Further evidence of this is seen in a subsequent section on the evaluation of ruthenium-alumina catalysts. Despite the poor isothermal decomposition rate exhibited by the ruthenium-cobalt hybrid catalyst preparations, it was important to pursue evaluation of these catalysts in motor firing studies. Significant improvements in ignition delay might still be seen with hybrid catalysts having appreciable noble metal area, not affected by desensitization procedures. This hypothesis was confirmed in subsequent motor firing studies.

(C) The performance of cobalt ruthenium hybrid catalysts appeared to be dependent on the fabrication procedure. Esso 202 and 203 had the same component formulation but different isothermal activity. Surface area differences resulting from different fabrication techniques were held to be a contributing factor. The lower apparent activation energy of Esso 201 compared with other hybrid catalyst preparations was probably also a result of fabrication differences. One possible explanation for this lower activation energy is the increased pore diffusional contribution resulting from the presintering of the substrate used on Esso 201.

6.4 Five Pound Thruster Evaluation of Cobalt-Ruthenium Hybrid Catalysts

(C) The ignition delay of cobalt-ruthenium hybrid catalysts in our 5 lb thruster using hydrazine fuel was measured at several catalyst bed temperature levels. Catalyst pellets 1/8"D x 1/8"L were used in all cases. The results of these studies are presented in Table 10 and Figure 7.

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TABLE 10

(C) IGNITION DELAY OF COBALT-RUTHENIUM
HYBRID CATALYSTS

Catalyst	Description	Ignition Delay at 23°C msec. (1,2)
Esso 101	70% Co, 30% Alumina co-precipitated	>6,000
Esso 202	12% Ru, 33% Co co-impregnated alumina	1,500
Esso 201	10% Ru, 75% Co on oxide sintered cobalt alumina	2,000
Esso 200	12% Ru on cobalt impregnated alumina	750

(C) The incorporation of ruthenium into cobalt-alumina catalyst formulations is seen to dramatically reduce the ignition delay. Furthermore, the degree to which the ignition delay is reduced depends on the mode of preparation of the catalyst. Catalysts 202, 201 and 200 all had approximately the same ruthenium content, but differed in fabrication technique. Esso 200 was prepared by first depositing the cobalt on an alumina support and then depositing the ruthenium on top of the cobalt. In this case, maximum availability of the ruthenium surface was probably achieved. Esso 202 utilized a co-impregnation of cobalt and ruthenium salts. This technique probably resulted in less available ruthenium surface. Esso 201 utilized a ruthenium impregnation of a cobalt alumina support and, thus, should also have readily available ruthenium metal surface. However, the cobalt alumina support was presintered yielding a support with about one half the surface area of Esso 200. This support surface area difference is a possible explanation of the longer ignition delay exhibited by Esso 201 in comparison to Esso 200. Despite the significant improvement in ignition delay resulting from the use of ruthenium in cobalt-ruthenium hybrids, performance had not approached that of Shell 405. Emphasis was thus shifted to the more promising ruthenium on alumina catalysts.

- (1) The Esso 5 lb. thruster does not represent a flight type design. Ignition delay data are thus useful only on a comparative basis.
- (2) Ignition delay time does not include valve response and fuel flow dead time which is approximately 60 msec in our test system.

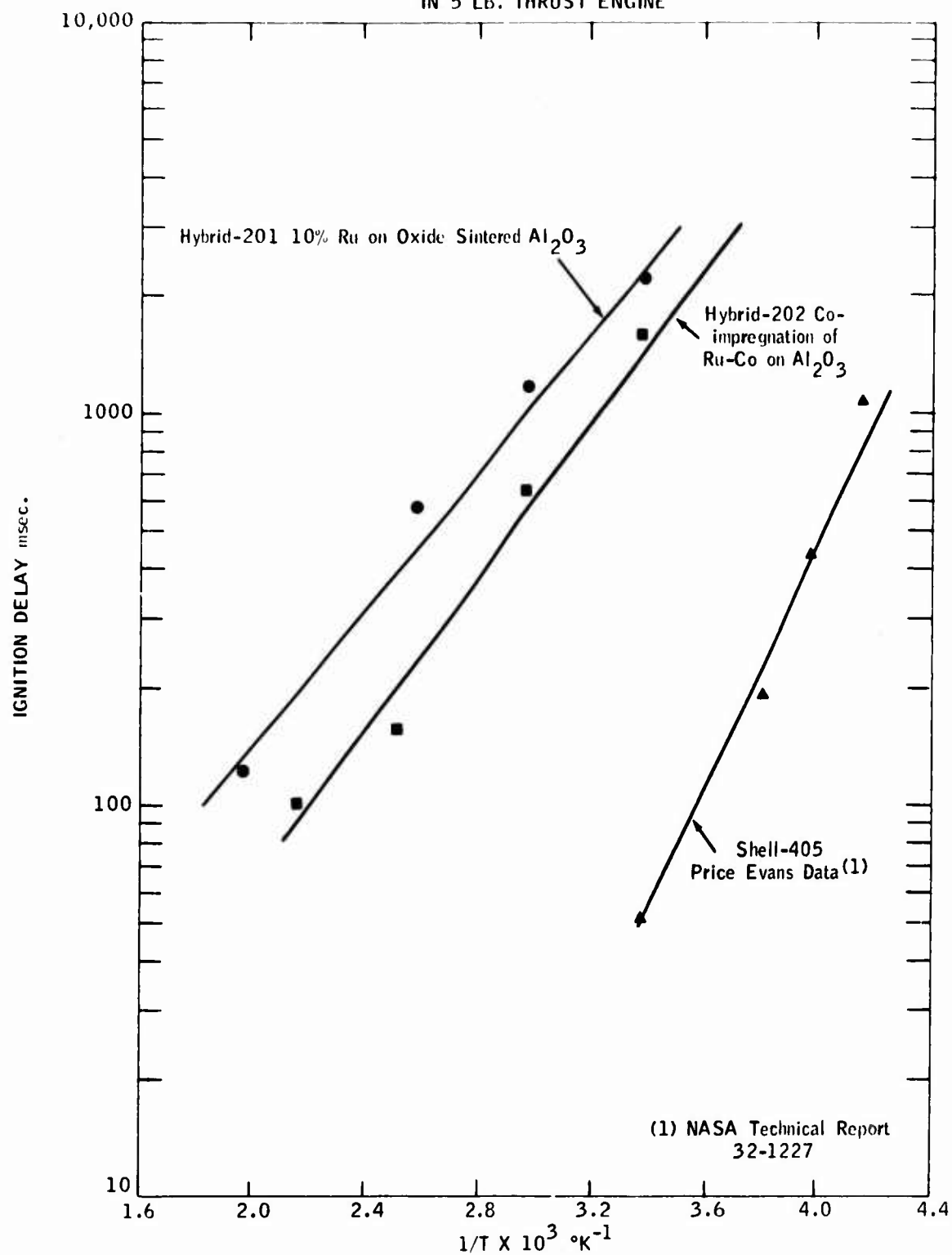
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Figure 7

(C) PERFORMANCE OF COBALT-RUTHENIUM-HYBRID CATALYSTS
IN 5 LB. THRUST ENGINE



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7. (C) RUTHENIUM BASED CATALYST STUDIES

7.1 Isothermal Rate Studies of Alumina Supported Ruthenium Catalysts

(C) A series of ruthenium on alumina catalysts were prepared to determine whether performance could be improved by removing the cobalt from the system. The effect of ruthenium concentration, catalyst support type, as well as the addition of platinum, on catalyst isothermal hydrazine decomposition activity were studied. The results are presented in Table 11 and Figure 8 and discussed in the following paragraphs.

TABLE 11

(C) ISOTHERMAL HYDRAZINE DECOMPOSITION RATE
ON RUTHENIUM CATALYSTS

Catalyst	Description	Hydrazine Decomposition Rate at 23°C cm ³ (STP)/min-gm	Apparent Activation Energy Kcals/gm-mole
Esso 206	12% Ru on Alumina	170	19
Esso 207	23% Ru on Alumina	210	19
Esso 208	36% Ru on Alumina	360	19
Esso 209	33% Ru on Silica- Alumina (6% SiO ₂)	280	19
Esso 210	5% Pt, 33% Ru on Alumina	359	Not Measured

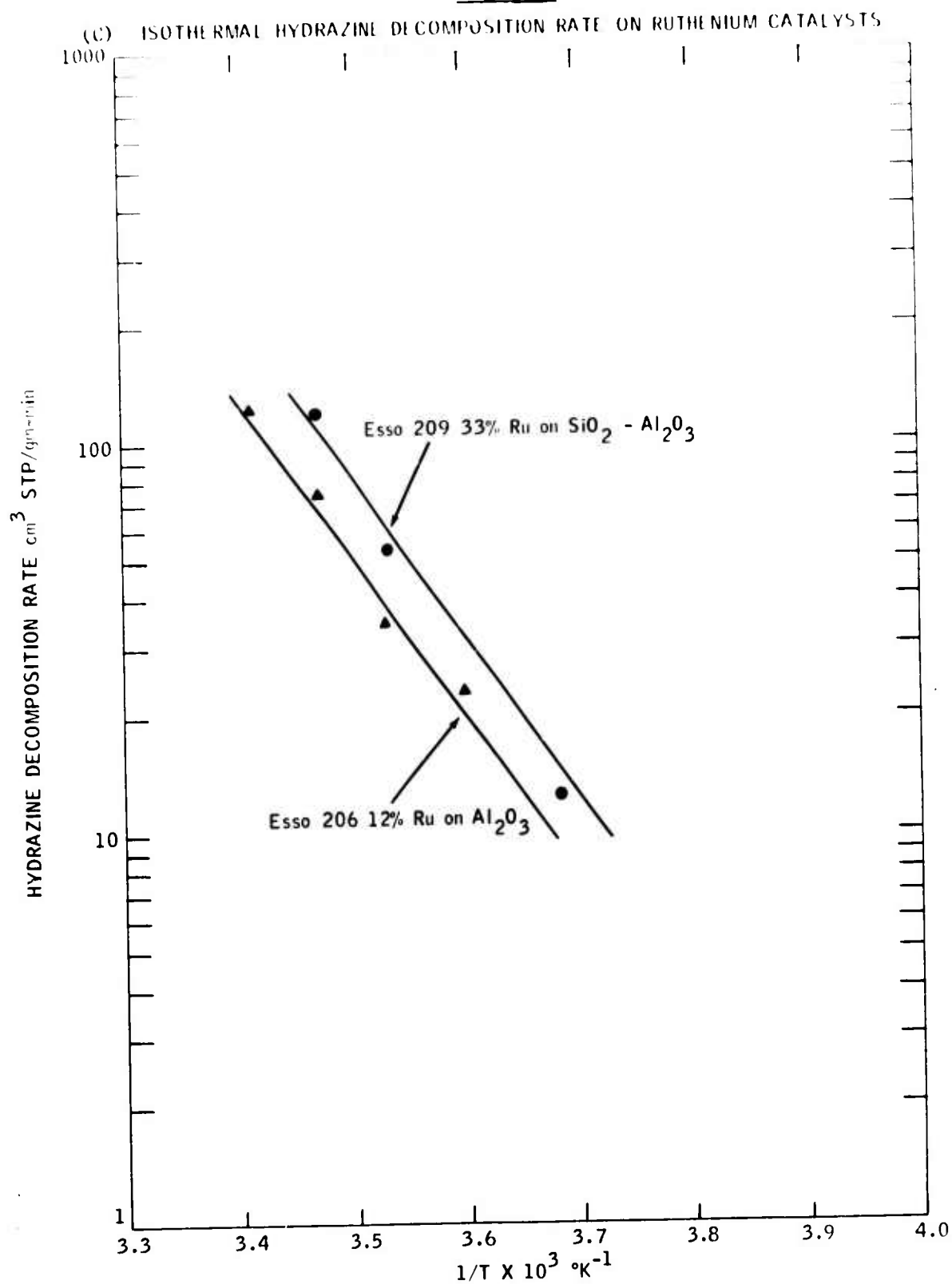
(C) Catalyst isothermal activity increased with ruthenium metal concentration and was more than 5 times as active as Esso 101 at the 36% ruthenium level. The cobalt free, 12% ruthenium on alumina, catalyst was far more active than any of the cobalt-ruthenium hybrids having the same ruthenium content. This data further supported the fact that there was a negative synergistic effect exhibited by cobalt-ruthenium hybrid catalysts toward hydrazine decomposition and that the performance of a ruthenium

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Figure 8



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catalyst depended on the nature of the support used in the fabrication. The relative performance of ruthenium-alumina and cobalt-ruthenium-alumina catalysts in the motor firing studies, discussed in the following paragraphs, gave the same conclusion. The isothermal data suggested that higher ruthenium levels would yield more active catalysts. However, measurements made in the 5 lb. thrust engine indicated that there was a leveling off in the ignition delay as the 35% ruthenium content was approached. The activation energy of ruthenium alumina catalysts was lower than that of the cobalt-ruthenium-alumina hybrids. The hybrids would thus be expected to be more active above 200°C. However, at the adiabatic firing temperature, the reactivity of the catalyst is undoubtedly diffusion limited. The apparent activation energy of the catalysts would then be primarily controlled by pore diffusion effects. The use of a silica-alumina support (Harshaw 1602) did not appear to offer any great advantage over alumina in terms of isothermal activity. The incorporation of 5% platinum into the formulation by co-impregnation appeared to improve the isothermal activity. This improvement was reflected in a very short ignition delay during the first firing of this catalyst in the 5 lb thruster. However, this activity was lost in subsequent 5 lb thrust motor firings.

(C) The addition of 5 wt. % platinum to a ruthenium-alumina catalyst, by means of the co-impregnation of platinum and ruthenium salts, produced a catalyst that gave a very short hydrazine ignition delay for the first firing. This concept was thus explored further. Ruthenium-platinum-alumina supported catalysts were prepared by co-impregnation of the halide salts and subsequent reduction with hydrogen. Catalysts were prepared with ruthenium/platinum weight ratios of 3.0 and 4.5, at a total metals content of 17 and 30 wt. %. Isothermal rate measurements were made using these catalysts. The results are presented in Figure 9 and Table 11. The data show that the incorporation of platinum into the alumina supported ruthenium catalyst reduces the apparent activation energy for hydrazine decomposition. Both 17 and 30 wt. % binary ruthenium-platinum metals catalysts gave activation energies of 14 kcal/g-mole as opposed to 19 kcal/g-mole for the pure ruthenium catalyst. This lowering of the activation energy also meant that the activity of the 30 wt. % binary catalyst was higher at 5°C than that of the 33% alumina supported ruthenium catalyst; the ruthenium-alumina catalyst was, however, still slightly more active at 25°C.

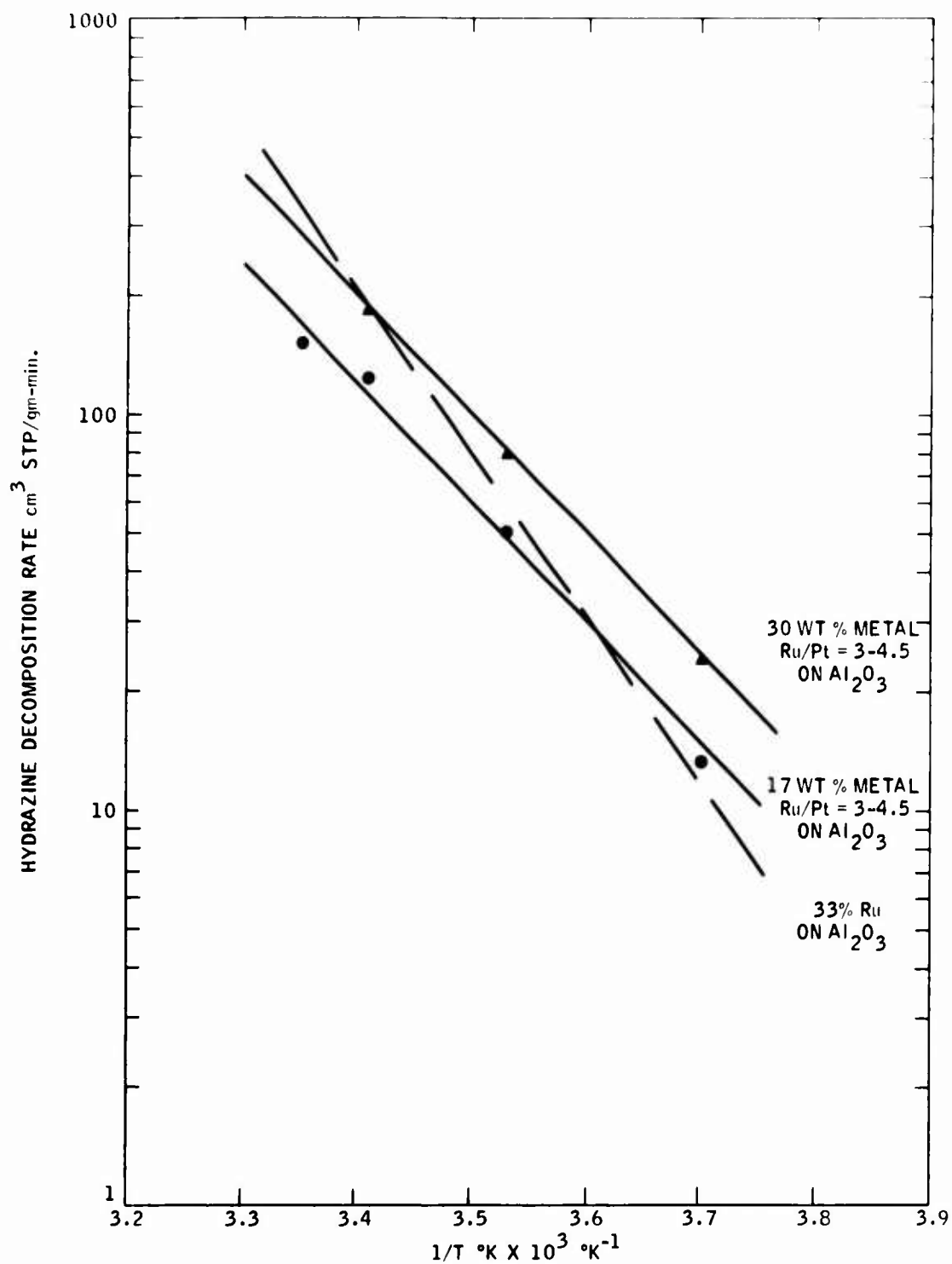
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Figure 9

(C) ISOTHERMAL PERFORMANCE OF ALUMINA SUPPORTED
RUTHENIUM-PLATINUM CATALYSTS



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Table 12

(C) ISOTHERMAL PERFORMANCE OF ALUMINA SUPPORTED RUTHENIUM-PLATINUM CATALYSTS

Catalyst Composition	Temperature °C	Hydrazine Decomposition Rate		Apparent Activation Energy Kcal/g-mole
		cm ³ (STP)/min-cm	cm ³ (STP)/cm ³ -min*	
Ruthenium-Platinum-Alumina 17 wt % Metals Ru/Pt = 3.0 4.5	5	30	78	14
	25	170	440	
	25	170	440	
Ruthenium-Platinum-Alumina 30 wt % Metals Ru/Pt = 3.0 4.5	5	50	130	14
	25	270	700	
	25	270	700	
33% Ruthenium-Alumina	5	30	78	19
	25	350	910	

*Volume of product gas STP per volume of catalyst per minute.

(C) The isothermal data imply that the binary ruthenium-platinum alumina supported catalysts would provide a shorter hydrazine ignition delay at temperatures in the vicinity of 5°C. This is not counting the instantaneous possible hypergolic effect resulting from the presence of platinum oxide. This effect cannot be defined in the isothermal reactor. It can only be detected in catalyst bed ignition studies. We have not tested the start-up characteristics of these new ruthenium platinum-alumina catalysts at 5°C. Our present test facility would have to be modified to do so in a reliable manner. However, preliminary motor firing tests with the 30 wt % ruthenium-platinum catalysts at 25°C did not show any advantage over pure ruthenium-alumina catalysts. In addition, the first start platinum oxide hypergolic effect was much less pronounced than that observed with the 5 wt % platinum, 33 wt % ruthenium on alumina catalyst (Esso 210). Thus, though this area offered further potential to reduce the low temperature hydrazine ignition delay, we felt that we could best utilize our effort by devoting full time to the study of other thermally stable substrates for ruthenium.

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7.2 Five Pound Thruster Evaluation of Alumina Supported Ruthenium Catalysts

(C) The high low temperature isothermal activity of cobalt free ruthenium on alumina catalysts was translated into a significant reduction in ignition delay. Tests on 1/8"D x 1/8"L pellets fabricated by ruthenium salt impregnation of pre-formed Harshaw 1404 alumina gave engine start-up performance which approached that of Shell 405. The results of these tests are presented in Table 13 and Figure 10 and discussed in the following paragraphs.

Table 13

(C) IGNITION DELAY OF ALUMINA SUPPORTED RUTHENIUM CATALYSTS IN 5 LB. THRUST ENGINE

Catalyst	Description	Ignition Delay at 23°C msec. (1,2)
Esso 205	33% Ru on Alumina	120
Esso 206	12% Ru on Alumina	620
Esso 207	23% Ru on Alumina	220
Esso 209	33% Ru on Silica-Alumina 6% Silica	100
Esso 210	5% Pt, 33% Ru on Alumina	5 (first firing) 100

(C) The ignition delay was seen to depend on the ruthenium concentration, decreasing as the catalyst ruthenium content increased. The incremental reduction in ignition delay in going from 23 to 33% ruthenium was much less than that in going from 12 to 23%. Data on a higher ruthenium concentration catalyst further indicated a leveling off of the ignition delay. Thus, very high ruthenium loadings (>50%) are not expected to result in any further significant reduction in ignition delay.

(1) The Esso 5 lb. thruster does not represent a flight type design. Ignition delay data are thus useful only on a comparative basis.

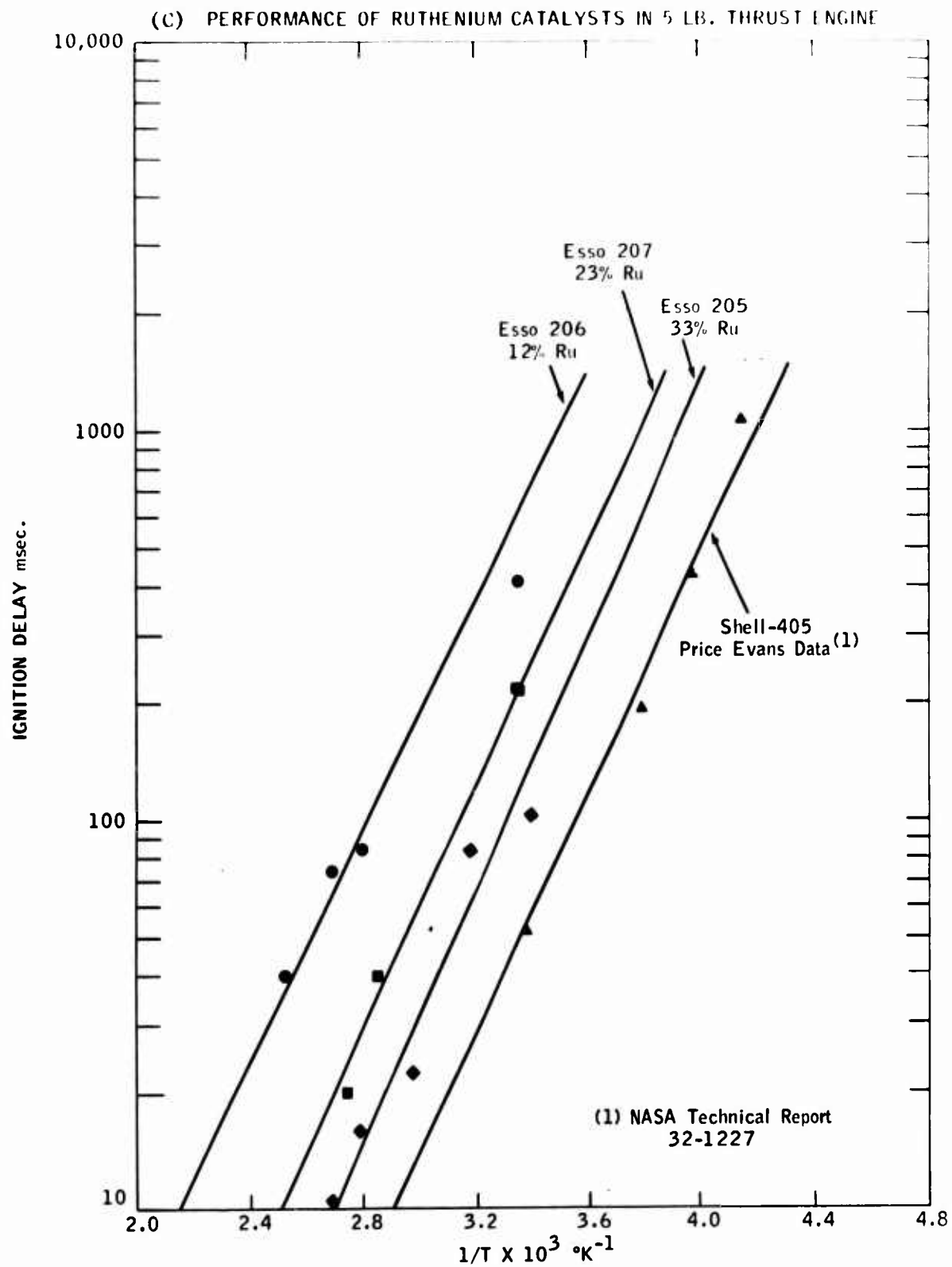
(2) Ignition delay time does not include valve response and fuel flow dead time which is approximately 60 msec in our test system.

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Figure 10



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(C) The incorporation of 5% platinum, by means of the co-impregnation of platinum and ruthenium salts, produced a catalyst that showed a very short ignition delay for the first firing. However, subsequent firings did not show any advantage over the platinum free catalyst having a comparable ruthenium content. One possible explanation for the very short ignition delay observed during the first firing of the platinum ruthenium catalyst was the relative ease in which platinum oxide was reduced. All catalysts, prepared by hydrogen reduction, are subsequently exposed to air and, hence, have a thin oxide layer on the surface. This oxide, which is easily reduced, reacts with hydrazine in a bipropellant mode for a fraction of a second giving the system an extra "kick". Platinum oxide is easier to reduce than ruthenium oxide and hence may have accounted for the rapid start. The ignition delay during the first firing of platinum free ruthenium catalysts was usually lower than the next few subsequent firings. The difference, however, was not nearly as great as that observed with the ruthenium-platinum catalyst. Further evidence of surface oxide effects was obtained by re-admitting air into a catalyst bed at room temperature after it had been fired a number of times. A significant reduction in ignition delay, (usually about 50%) and ignition spike pressure was observed in each case in which air was admitted to the reactor bed. However, the shortened ignition delay effect is, again, only present for the initial firing after exposure to air.

7.3 Isothermal Performance of Tungsten Carbide Supported Ruthenium Catalysts

(C) Tungsten carbide possesses several properties which make it an excellent candidate for a high temperature thermally stable catalyst support. It has a much higher melting point than alumina (2780°C as opposed to 2000°C) and thus should be more resistant to sintering than alumina. It has a much higher density than alumina (15.7 gms/cm³ as opposed to 2.6) and thus has the potential to store more active catalyst in a fixed volume. It should be stable in a reducing atmosphere at high temperature. Most synthetic procedures utilize the reaction of tungsten with a hydrocarbon in a mixture of H₂ and N₂ at temperatures ranging from 1,000 to 2,200°C. However, the high temperatures required for the synthesis of WC limit the surface areas that can be obtained with this material. This appeared to be its chief disadvantage. Though the maximum surface area of WC available today is about 10 m²/gm, it was felt that the material possessed enough encouraging properties to warrant investigation. It was felt that Company potential unique technology could be used to increase the WC surface area if ruthenium was shown to be active toward hydrazine decomposition when used in conjunction with a WC support.

(C) Thus, WC supported ruthenium catalysts were prepared at the 10, 23 and 30 wt. % ruthenium level using ruthenium halide impregnation and hydrogen reduction. Samples of catalyst powder were evaluated in the isothermal reactor at several temperature levels. The results are presented in Figure 11 and Table 14.

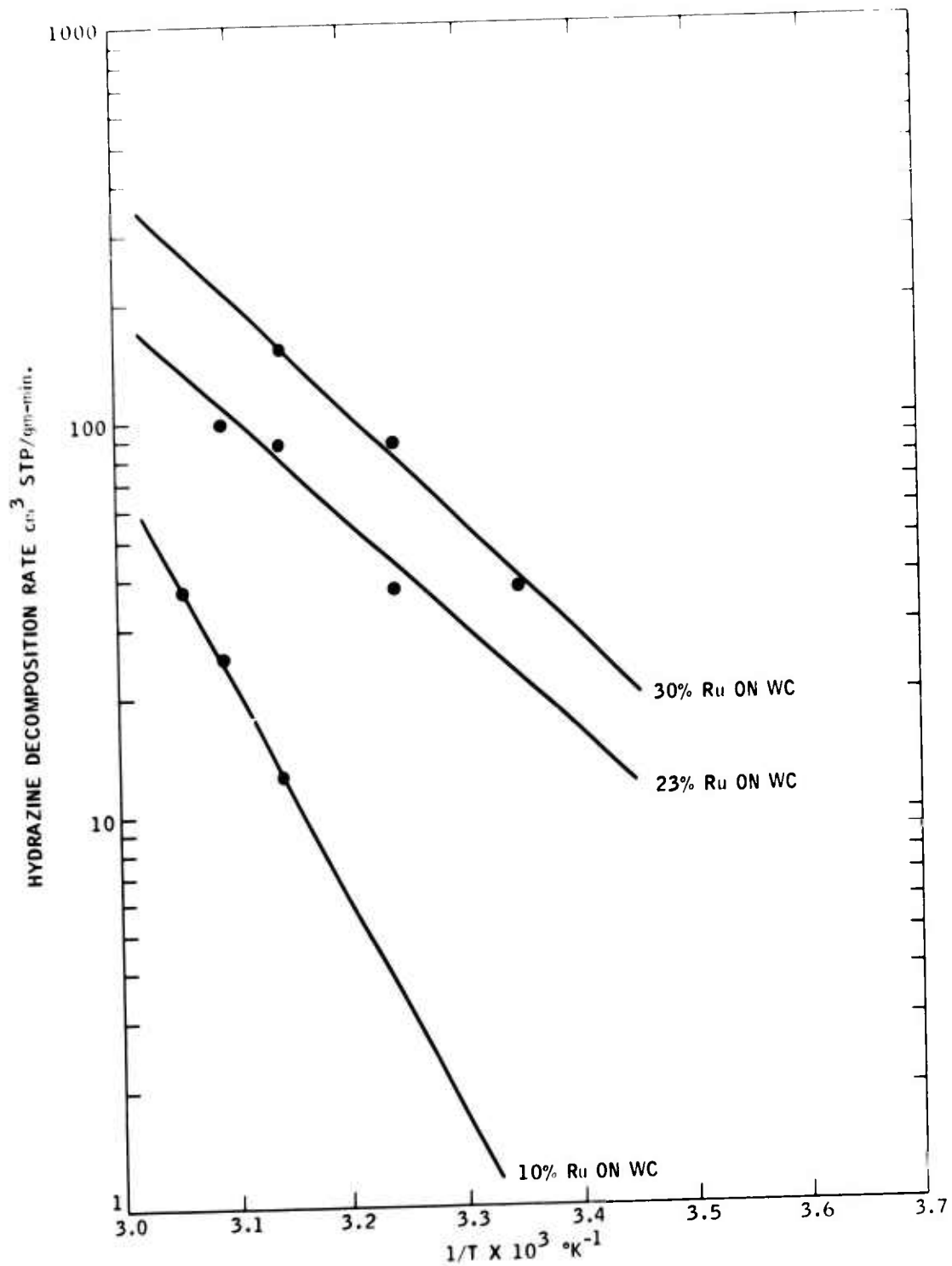
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Figure 11

(C) ISOTHERMAL PERFORMANCE OF TUNGSTEN CARBIDE SUPPORTED RUTHENIUM CATALYSTS



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Table 14

(C) ISOTHERMAL ACTIVITY OF RUTHENIUM-TUNGSTEN CARBIDE CATALYSTS

Catalyst Composition	Apparent Activation Energy Kcals/g mole	Hydrazine Decomposition Rate at 25°C	
		cm ³ (STP)/min-cm	cm ³ (STP)/cm ³ -min*
WC substrate alone		0	0
10% Ru on WC	25	1	16
23% Ru on WC	13	22	345
30% Ru on WC	13	38	596
40% Ru on WC	Not Measured	13	204
33% Ru on Alumina	19	350	910

* volume of product gas STP per volume of catalyst per minute

(C) The data indicated that tungsten carbide supported ruthenium catalysts had considerable activity toward hydrazine decomposition and the decomposition rate appeared to be very dependent on the ruthenium concentration, increasing markedly between 10 and 30% ruthenium and then apparently decreasing at the 40% ruthenium level. The absolute activity of these catalysts, on a mass basis, is not great--only 38 cm³/gm-min as compared with 350 cm³/gm-min for alumina supported ruthenium at about the same 30% metal loading. However, the much higher density of the tungsten carbide support makes this catalyst look much more attractive on a volume basis. Since most potential applications for the hydrazine monopropellant system are volume limited (their design and size are fixed by other factors) a more meaningful comparison of catalysts can be made on a volume basis. High support density cannot fully be translated into catalyst storage savings because of catalyst pill porosity and the bulk density factor. However, the activity per cm³ does appear to be a more practical figure of merit for hydrazine decomposition catalysts. When compared on a volume basis, the activity of the 30% ruthenium on tungsten carbide catalyst at 25°C is less than one half that of the 33% ruthenium on alumina. This is very encouraging in view of the fact that the tungsten carbide support had only 10 m²/gm of surface area. If tungsten carbide supports can be prepared with surface areas of 20-30 m²/gm, the activity of the 30% ruthenium loaded catalyst should be equivalent to that of 33% ruthenium on alumina on a volume basis. It is recommended that further work be conducted on the WC substrate.

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7.4 Performance of PTN Supported Ruthenium Catalysts

(U) Esso Research developed a unique refractory catalyst support material which has both high surface area and resistance to sintering at high temperatures in a humid environment. The stability of this support to sintering in a 80% H₂-20% H₂O at 1100°C environment is shown in Table 15.

Table 15

THERMAL STABILITY OF ESSO PTN SUPPORT

Samples Steamed for 1/2 Hour in 80% H₂-20% H₂O at 1100°C

Support	BET Surface Area m ² /gm		% Decrease in Surface Area
	Before	After	
Esso PTN*	159	121	24
Al ₂ O ₃ (H-1404)	152	70	59
Al ₂ O ₃ -SiO ₂ (H-1602)	211	92	56

*Esso PTN is a specially prepared form of Boron Nitride which was developed under Company-sponsored research.

(U) The very encouraging results achieved in this sintering test for the PTN material clearly made it a potential candidate support for the non-strategically limited ruthenium metal. However, it remained to be seen whether ruthenium would be active on the PTN support and whether catalyst pellets of sufficient strength could be fabricated. Thus, ruthenium was deposited on the surface of the PTN support by halide salt impregnation and hydrogen reduction. Catalysts were prepared at the 23 and 45% ruthenium metal loading. The results of isothermal rate measurements using these catalysts are presented in Table 16 and Figure 12.

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Table 16

(C) ISOTHERMAL ACTIVITY OF PTN SUPPORTED
RUTHENIUM CATALYSTS

Catalyst Composition	Apparent Activation Energy Kcals/g-mole	Hydrazine Decomposition Rate at 25°C		BET Surface Area m ² /gm
		cm ³ (STP)/min-gm	cm ³ STP/cm ³ -min*	
23 wt % Ru on PTN	18	270	600	77
45 wt % Ru on PTN	18	270	600	44
33 wt % Ru on Alumina	19	350	910	73

* volume of product gas STP per volume of catalyst per minute

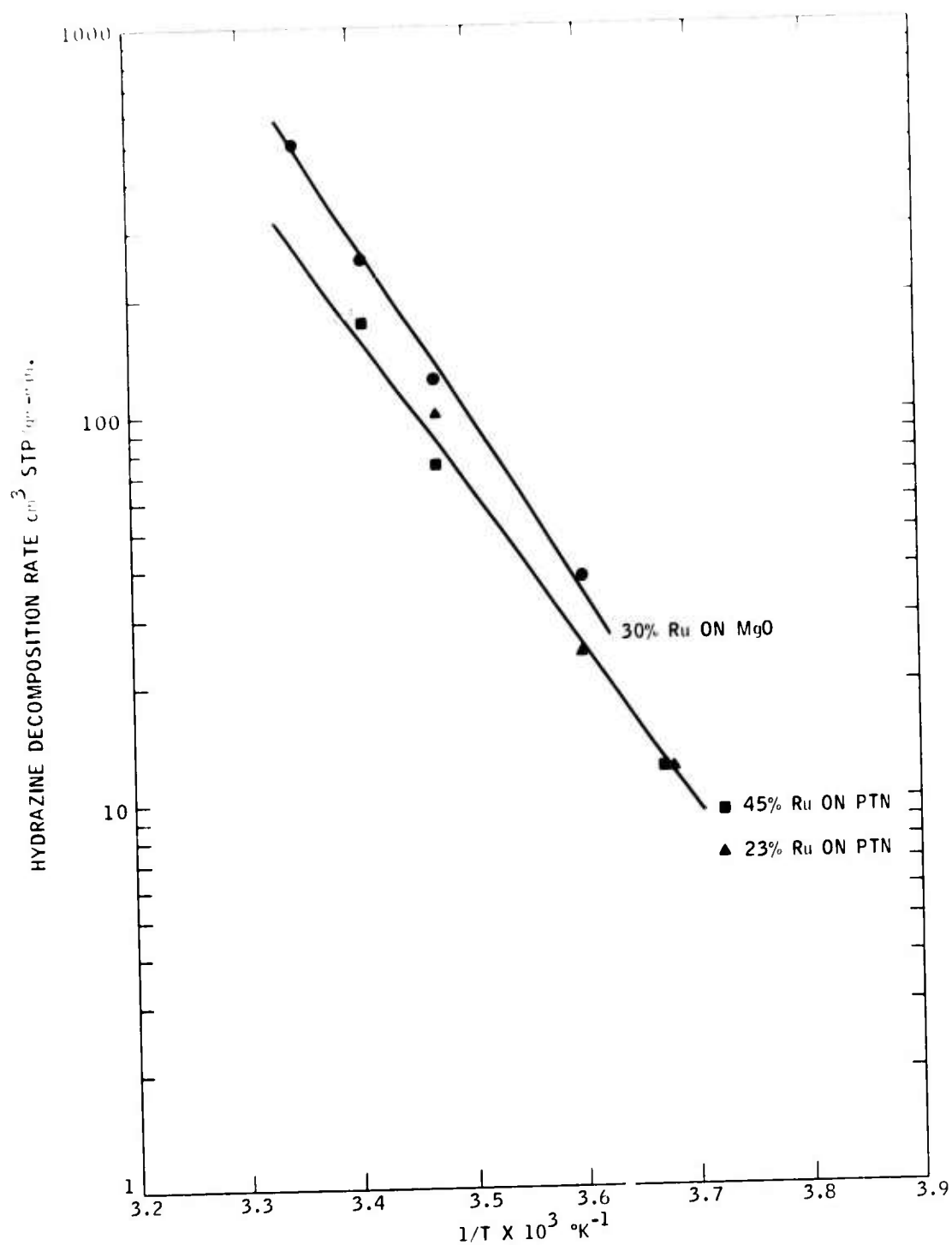
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Figure 12

(C) ISOTHERMAL PERFORMANCE OF PTN AND MgO SUPPORTED RUTHENIUM CATALYSTS



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As can be seen from the data, the PTN supported ruthenium catalyst possesses appreciable activity. Though both the 23 wt. % and 45 wt. % Ru catalysts were less active than the alumina supported 33 wt. % ruthenium catalyst, the high level of activity was still extremely encouraging. Since the surface area of the base PTN support used was low ($80 \text{ m}^2/\text{gm}$), we felt that the activity could be improved. The fact that no noticeable increase in catalyst activity was observed in increasing the ruthenium concentration from 23 to 45 wt. % is partly explained by an apparent loss in surface area. The 43 wt. % ruthenium catalyst had a total BET surface area of $44 \text{ m}^2/\text{gm}$ as opposed to $77 \text{ m}^2/\text{gm}$ for the 23 wt. % ruthenium catalyst. A change in fabrication conditions such as ruthenium halide solution concentration and temperature may offer alternate ways of achieving higher activity at a high metal loading.

(C) The refractory support, PTN, was prepared in a large quantity (100 gms) and was used to fabricate a scaled-up batch of ruthenium-PTN catalyst. As with the earlier small batches, ruthenium metal was deposited on the refractory PTN support by a series of ruthenium chloride impregnations and calcinations followed by reduction with hydrazine. A large batch of PTN supported ruthenium catalyst was prepared at the 40 wt. % metal level and tested in the isothermal decomposition rig. The results are compared with those obtained using catalysts prepared in small quantities in Figure 13.

(C) The scaled-up catalyst preparation showed somewhat higher hydrazine decomposition activity than that of the material processed in small batches. Since very little difference in catalyst activity was observed among small batches containing 23 to 45% ruthenium, the apparent improvement in catalyst activity, observed for the scaled-up batch, was not believed to be due to differences in ruthenium average bulk concentration. Neither was it believed to be a result of differences in catalyst surface area which were substantially the same for large and small batch preparations. A more likely explanation was in the improved dispersion of the metal on the surface of the large batch of PTN material. Much higher solution concentration gradients and high localized deposits of ruthenium can be expected when small batches of catalyst material are processed by a multiple impregnation technique.

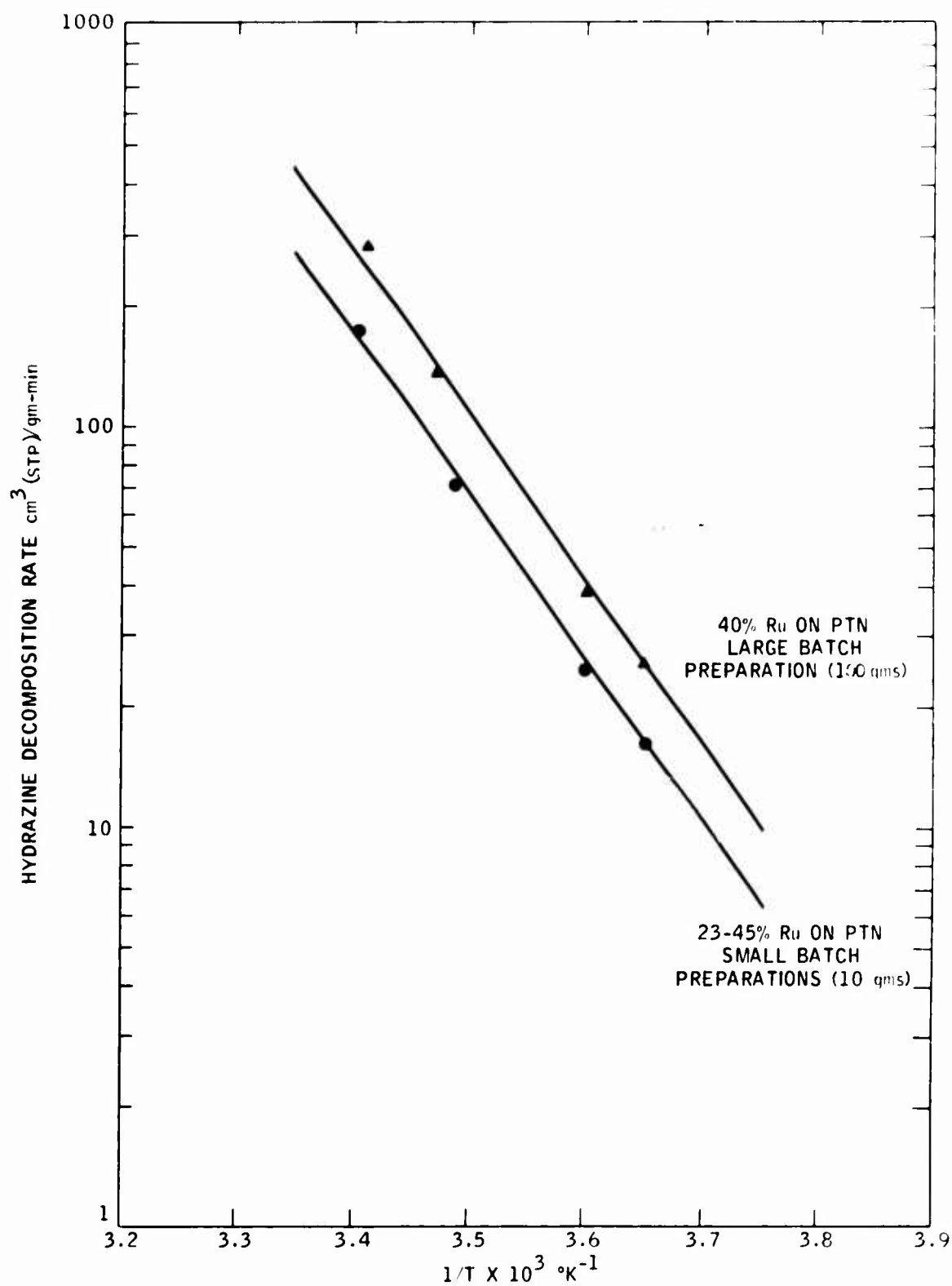
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Figure 13

(C) ISOTHERMAL PERFORMANCE OF SCALED-UP RUTHENIUM-PTN CATALYST



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(U) PTN supported ruthenium catalyst pellets (1/8"L x 1/8"D) were prepared by means of a Stokes Pellet Press. Pellets as formed from the press had low crush strength. Thus, the sinter strengthening technique, successfully employed with the cobalt-alumina catalysts, was applied to the Ru-PTN system. Pellets were subjected to sinter treatments at different temperatures for a specified time in a tube furnace. Argon gas was used to protect the pellets against oxidation. The effect of sintering treatment on catalyst pellet crush strength is shown in Table 17.

Table 17

EFFECT OF SINTER STRENGTHENING ON CRUSH STRENGTH OF Ru-PTN CATALYST PELLETS

Sinter Temperature °C	Sinter Time Mins.	Average Pellet Crush Strength Lbs.*
----- No Sinter Treatment -----		7.5
1200	30	8.5
1300	30	14.0
	120	11.0
	360	5.0

*Average of (10) 1/8" D Pellets

(U) The data in Table 17 indicate that considerable improvement in Ru-PTN pellet crush strength can be achieved through the sinter strengthening technique. Pellets sintered at 1300°F for 30 minutes have almost twice the crush strength as pellets receiving no sinter treatment. Increasing the sinter times, however, produced increasingly weaker pellets. This was contrary to what was expected and observed with cobalt-alumina catalysts.

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7.5 Performance of Refractory Oxide Supported Ruthenium Catalysts

(C) Several refractory oxides have properties that make them potential candidate thermally stable supports for ruthenium. These include tungsten oxide, magnesium oxide, and zirconium oxide. These materials have very high melting points, are chemically stable at high temperatures and can be prepared in high surface area. Thus, several of these materials were impregnated with ruthenium halide solution to the 30 wt. % metals level, reduced with hydrogen and tested in the isothermal rig. The results are depicted in Table 18 and Figure 14.

Table 18

(C) PERFORMANCE OF REFRACTORY OXIDE SUPPORTED RUTHENIUM CATALYSTS

Catalyst	Catalyst Surface Area m^2/gm	Isothermal N_2H_4 Decomposition Rate cm^3 (STP)/min-gm at 25°C
30% Ru on ZrO_2	37	250
30% Ru on WO_3	23	163
30% Ru on MgO	21	500
30% Ru on MoO_3	14	Negligible Activity
33% Ru on Al_2O_3	70	350

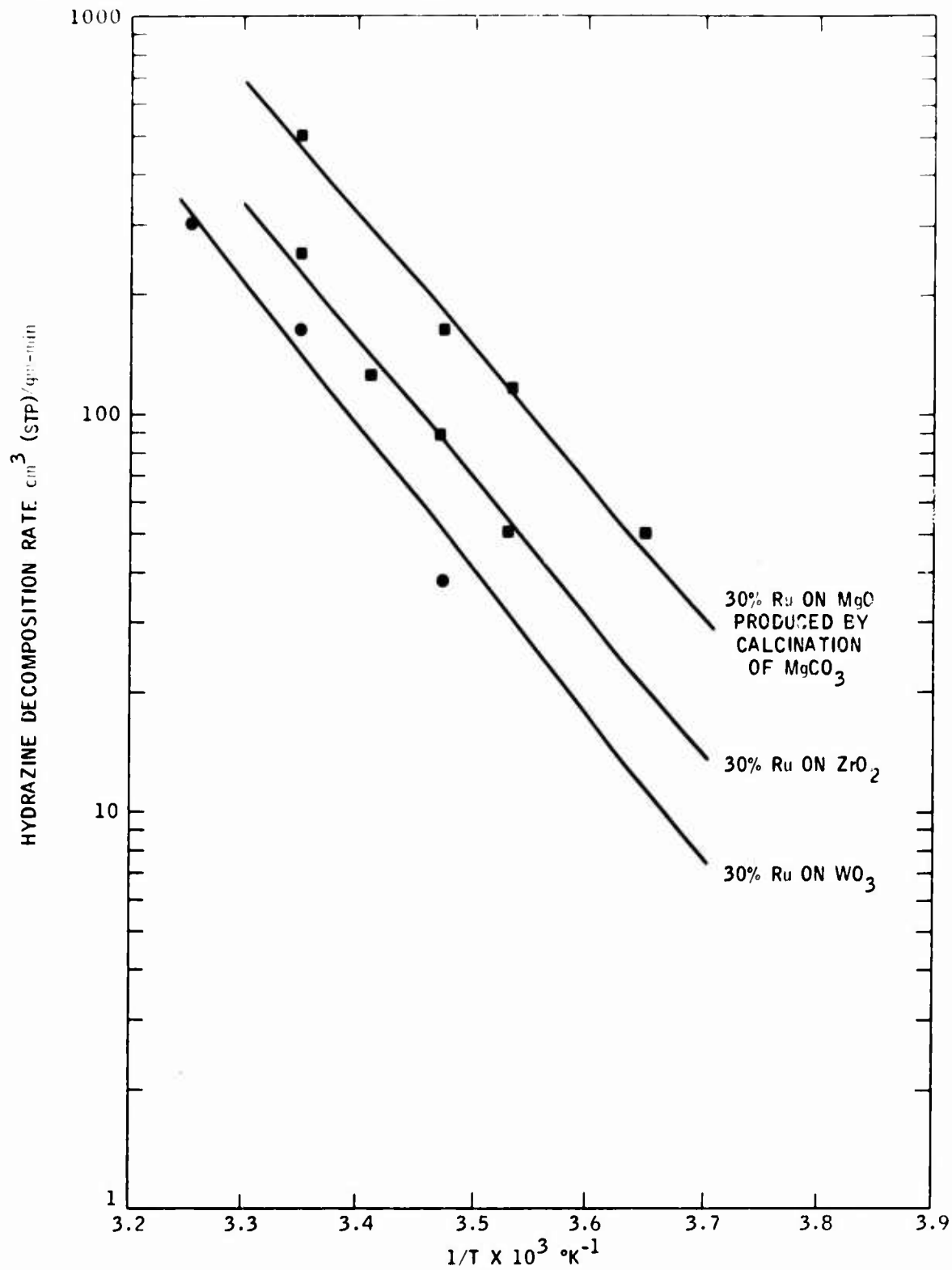
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Figure 14

(C) ISOTHERMAL PERFORMANCE OF REFRACTORY OXIDE SUPPORTED RUTHENIUM CATALYSTS



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(C) Differences in catalyst surface area cannot explain this wide range of results in hydrazine decomposition activity. In fact, the most active hydrazine decomposition catalyst, 30% Ru on MgO, had a surface area of only 21 m²/gm. The results are more likely due to the strong chemical interaction of catalyst and substrate which strongly determines the resulting supported catalyst hydrazine decomposition activity. The isothermal hydrazine decomposition activity of the magnesia supported ruthenium catalyst was high enough to affect spontaneous hydrazine ignition at temperatures as low as 5°C. Thus, it was considered a very promising system for this project and was subjected to further evaluation.

7.6 Preparation and Performance of High Surface Area Magnesia

(U) High surface area magnesium oxide was prepared by calcining MgCO₃ and Mg(OH)₂ under specified conditions. Two temperature levels and two calcination duration periods were evaluated. The BET surface areas resulting from specific process treatments are presented in Table 19.

Table 19

EFFECT OF PROCESS CONDITIONS ON THE SURFACE AREA OF RESULTING MgO SUBSTRATES

Source of Magnesia	Run Identification	Calcining Temperature, °F	Calcining Time, hrs.	Magnesia BET Sur. Area m ² /gm
MgCO ₃	B	1000	2	114
	A	1000	15	216
	D	615	2	62
	C	615	15	90
Mg(OH) ₂	F	1000	2	135
	E	1000	15	85
	Vitro Magnesia			60

(U) The MgO substrates resulting from MgCO₃ decomposition showed surface areas ranging from 62 to 216 m²/gm, surface areas increasing with the severity of treatment. Substrates resulting from Mg(OH)₂ decomposition at 1000°F showed a decrease in surface area with an increase in calcining time. Preliminary tests at 615°F indicated this temperature level was too low to affect significant Mg(OH)₂ decomposition. The lower surface area resulting from the longer calcination period, using Mg(OH)₂ as the source, implies that the H₂O formed during decomposition may have catalyzed sintering. The results of our steam sintering tests discussed later in this section support this theory.

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(C) The process conditions yielding the highest surface area MgO (Run A) was used to fabricate an Ru-MgO catalyst at the 30 wt. % metal level. This catalyst was prepared in a similar manner to the Vitro MgO supported catalyst using multiple ruthenium halide solution impregnation, calcination and hydrogen reduction. Isothermal catalyst activity tests were run on the high surface area MgO-Ru catalyst. The results are compared with the performance of the Vitro MgO supported Ru catalyst in Table 20.

Table 20

(C) PERFORMANCE OF MAGNESIA SUPPORTED RUTHENIUM CATALYSTS

Catalyst	Substrate Surface Area m ² /gm	Temperature °C	Isothermal N ₂ H ₄ Decomposi- tion Rate cm ³ (STP)/min-gm
30% Ru on Vitro Magnesia	60	1	25
		15	125
		25	500
30% Ru on MgO (MgO from Prep. A above)	216	1	50
		15	163
		25	500

The high surface area MgO supported Ru catalyst showed considerably higher activity than the Vitro MgO supported Ru catalyst at low temperatures; no difference in activity was noted at 25°C. The high surface area MgO supported Ru catalyst should be active enough to affect spontaneous hydrazine ignition at 5°C. A large batch of high surface area MgO was prepared and was used in pilling studies. The results of sinter strengthening experiments on 1/8"D x 1/8"L Ru-MgO catalyst pellets were discouraging. Cracks were formed in the catalyst pellets during the sinter strengthening process. One possible explanation for the crack formation was a further decomposition of some remaining MgCO₃ during the sinter strengthening operation. It was felt that an acid treatment might help remove MgCO₃ that has not been completely removed during the calcination step. Acid treatment of the MgO formed from calcination of MgCO₃ or Mg(OH)₂ might also provide additional substrate surface area. The results of an acid leaching treatment are discussed in the following paragraphs.

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(C) MgO substrate samples produced from both $\text{Mg}(\text{OH})_2$ and MgCO_3 sources were treated with 0.05 M phosphoric acid. Phosphoric acid is a good halide free leachant and this treatment of refractory oxides has also been shown to inhibit sintering in a H_2O environment (2). Treatment consisted of equilibrating calcined substrate materials with 0.05 M phosphoric acid, drying at 250°F , and calcining at 750°F for only 1 hour. This procedure was conducted twice with each substrate sample. The resulting change in substrate surface area is given in Table 21.

Table 21

EFFECT OF PHOSPHORIC ACID LEACHING ON
MAGNESIA SUBSTRATE SURFACE AREA

Substrate	Identification	BET Surface Area m^2/gm	
		Before Leaching	After Leaching
MgO (From MgCO_3)	A	216	252
MgO (From $\text{Mg}(\text{OH})_2$)	E	85	252

(C) The data presented in Table 21 show that the leaching treatment produced a significant increase in substrate surface area for both samples. The increase is much greater for the substrate initially produced from $\text{Mg}(\text{OH})_2$ decomposition indicating that this substrate had a greater fraction of the source which was not decomposed by calcination. As in our calcination studies, we wanted to see if the higher surface area produced by the acid treatment could be translated into higher supported ruthenium hydrazine decomposition activity. Thus, a portion of a phosphoric acid treated substrate was used to fabricate a Ru loaded catalyst. A catalyst containing about 30.0 wt % Ru on phosphoric acid treated, MgCO_3 calcined substrate (Run A) was fabricated by the standard multiple ruthenium chloride solution impregnation technique followed by calcination and reduction. The hydrazine decomposition activity of this catalyst was measured in the isothermal test rig. The results are compared with the activity of a catalyst prepared from calcined MgCO_3 which had not been acid treated in Table 22. The acid treated catalysts were found to be less active than catalysts prepared from the calcined substrate.

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Table 22

(C) PERFORMANCE OF ACID LEACHED MAGNESIA SUPPORTED CATALYSTS

Catalyst	Substrate BET Surface Area m^2/gm	Temperature $^{\circ}\text{C}$	Isothermal N_2H_4 Decomposition Rate $\text{cm}^3 (\text{STP})/\text{min-gm}$
30% Ru on Acid Treated MgO	252	1	25
		15	125
30% Ru on as Calcined MgO	216	1	50
		15	163

(C) Magnesium oxide appears to show considerable promise as a support for ruthenium. The activity of the MgO-supported ruthenium toward hydrazine decomposition is quite high and the substrate can be prepared in high surface area. However, several questions exist pertinent to the physical strength of MgO granules and pellets. Further work in this area is required to define the magnitude of this problem.

7.7 High Temperature Stability of Various Hydrazine Decomposition Catalysts and Substrates

(C) Several catalysts and substrates were subjected to high temperature sintering tests in $\text{N}_2\text{-H}_2\text{-NH}_3$ and $\text{H}_2\text{-H}_2\text{O}$ atmospheres respectively. The results of these tests are presented in Tables 23 and 24. Of the substrates tested, the tungsten carbide appeared to show the highest resistance to sintering in both the water free and water containing environment, decreasing less than 10% in surface area during both test periods. The PTN material was the second most stable support tested, though a considerably greater loss in surface area was observed in comparison to our first sinter stability test run on PTN reported earlier in this program. This difference in stability is most likely a result of slight variations in PTN composition from batch to batch and not a result of the difference in the gaseous ambient used in the tests. This is borne out by the fact that the PTN desurfaced about the same amount in both current stability tests in a $\text{H}_2\text{-N}_2\text{-NH}_3$ environment and in the $\text{H}_2\text{-H}_2\text{O}$ environment. The fact that the PTN and WC support were as stable in a gaseous environment containing 20 vol. % H_2O as they were in a H_2O free ambient implies that these substrates may be used with fuels containing hydrazine nitrate.

(C) The PTN supported ruthenium catalyst at the 23 wt. % metal loading was almost as stable as the metal free substrate itself and also showed little difference in surface area loss in both a water free and water rich gaseous environment. The tungsten carbide supported ruthenium catalyst, on the other hand, decreased in surface area considerably in

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both tests with a more drastic loss taking place in the H_2 - H_2O gas test. This loss is believed to be a result of the fact that the high loading of ruthenium deposited on the low surface area WC substrate was probably not well dispersed, allowing ruthenium crystallites to sinter together easily. This is further supported by the fact that the 30 wt. % ruthenium on tungsten carbide catalyst showed much higher initial total BET surface area than the substrate itself, indicating that a good portion of the ruthenium produced was "unsupported" and actually physically mixed with the tungsten carbide.

(C) The refractory oxide substrates and supported ruthenium catalysts showed very poor stability characteristics with the exception of the Harshaw 1602 alumina-silica substrate which was reasonably stable. The very active magnesia supported ruthenium catalysts and the magnesia substrates themselves were notably unstable, desurfacing sharply in both tests, though to a greater extent in the H_2 - H_2O atmosphere. The standard Harshaw 1404 alumina substrate desurfaced considerably in the water free NH_3 - N_2 - H_2 environment and almost completely in the H_2 - H_2O ambient. Catalysts fabricated with Harshaw 1404 alumina will have an extremely short life when hydrazine nitrate is used in the fuel blend. Zirconium oxide and tungsten oxide substrates were also unstable in the H_2O containing environment though considerably more stable than the Harshaw 1404 alumina.

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Table 23

(C) HIGH TEMPERATURE STABILITY OF HYDRAZINE DECOMPOSITION CATALYSTS

Test Temperature - 1100°C

Time - 1/2 hour

Gas Environment - 25 vol % N₂, 25 vol % H₂, 50 vol % NH₃

Catalyst or Substrate	Total BET Surface Area m ² /gm	
	Before	After
WC	2.3	2.1
30% Ru on WC	11.2	1.5
PTN	73.4	38.4
23% Ru on PTN	77.0	24.7
MgO from Calcined MgCO ₃	216	9.3
MgO from Calcined Mg(OH) ₂	85.1	0.1
30% Ru on MgO from MgCO ₃	21.0	1.2
Vitro MgO	60.0	3.2
40% Ru on MgO	11.8	2.6
Vitro ZrO ₂	25	6.2
30% Ru on Vitro ZrO ₂	12	2.0
Vitro WO ₃	38	5.4
30% Ru on WO ₃	12.0	<1.0
Harshaw Sintered Al ₂ O ₃ (1404)	95	12.6
Harshaw Sintered Al ₂ O ₃ -SiO ₂ (1602)	145	46

Table 24

(C) HIGH TEMPERATURE STABILITY OF HYDRAZINE DECOMPOSITION CATALYSTS

Test Temperature - 1100°C

Time - 1/2 hour

Gas Environment - 80 vol % H₂, 20 vol % H₂O

Catalyst or Substrate	Total BET Surface Area m ² /gm	
	Before	After
WC	3.0	2.7
30% Ru on WC	11.2	.3
23% Ru on PTN	77.0	21.8
Vitro MgO	60.0	7.5
30% Ru on Vitro MgO	18.7	6.0
Vitro WO ₃	38.0	1.6
30% Ru on WO ₃	12	1.9
Harshaw Sintered Al ₂ O ₃ (1404)	95	.6
Harshaw Sintered Al ₂ O ₃ -SiO ₂ (1602)	145	45

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8. PROMOTED RUTHENIUM CATALYSTS - THE ESSO 500 SERIES

(C) Considerable evidence is present in the literature to indicate that the incorporation of foreign ions into γ -alumina can substantially improve the thermal stability of this refractory oxide. For example, Krischner, et al. have found that the incorporation of alkaline earth ions into γ -alumina markedly enhanced its thermal stability (15). Similar observations have been made in our Company high temperature petroleum processing catalyst studies. On the basis of this information, and the fact that hydrazine decomposition appears to increase with increased substrate basicity, we prepared a number of "doped" substrate catalysts which we called the Esso 500 series. These catalysts have been extensively tested in our 5 lb. thruster and isothermal reactor and characterized in our laboratories. One of them was evaluated by Air Force personnel in 25 lb. and 5 lb. thrust engines. The results of these tests are discussed in the following paragraphs.

8.1. Characterization of the Esso 500 Series Catalysts

(C) The Esso 500 series catalysts have been characterized in our laboratories. Their approximate compositions are as follows*:

Esso 500	- 5% SrO,	5% SiO ₂ ,	60% Al ₂ O ₃ ,	30% Ru
501	- 5% CaO,	5% SiO ₂ ,	60% Al ₂ O ₃ ,	30% Ru
502	- 5% La ₂ O ₃ ,	5% SiO ₂ ,	60% Al ₂ O ₃ ,	30% Ru
503	- 5% BaO,	5% SiO ₂ ,	60% Al ₂ O ₃ ,	30% Ru
504	- 10% BaO,	5% SiO ₂ ,	55% Al ₂ O ₃ ,	30% Ru
505	- 10% CaO,	5% SiO ₂ ,	55% Al ₂ O ₃ ,	30% Ru
506	- 10% La ₂ O ₃ ,	5% SiO ₂ ,	55% Al ₂ O ₃ ,	30% Ru
507	- 10% SrO,	5% SiO ₂ ,	55% Al ₂ O ₃ ,	30% Ru

Data have been obtained on catalyst surface area, substrate surface area, ruthenium crystallite size and catalyst isothermal activity. These data are presented in Table 25.

*See Appendix for detailed procedure for preparing the Esso 500 series catalysts.

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Table 25

(C) PROPERTIES OF ESSO 500 SERIES CATALYSTS

Catalyst	BET Surface Area m^2/gm		Isothermal Activity cm^3 (STP)/min-gm at 25°C	As Fabricated Crush Strength lbs.	Metal Crystallite Size Å
	Substrate	Catalyst			
Esso 500	182.4	128.0	490	40	135
Esso 501	178.0	131.5	420	41	124
Esso 502	185.6	128.5	455	41	124
Esso 503	184.7	123.1	385	36	111
Esso 504	175.8	116.8	630	41	126
Esso 505	181.8	118.0	420	41	165
Esso 506	166.2	117.0	530	46	145
Esso 507	173.4	117.5	420	43	140
Conventional Supported Ruthenium Catalyst	144.6	91.4	350		

*Based on 1/8" x 1/8"D Pellets

(U) The properties of the Esso 500 series catalysts, given in Table 25, are seen to be superior to those of the conventional alumina supported ruthenium catalysts. Both substrate and final catalyst surface area are considerably higher than those of the conventional supported ruthenium catalyst. Isothermal hydrazine decomposition activity of the Esso 500 series catalysts is seen to range from 10 to 80% higher than the conventional alumina supported ruthenium catalyst. Additional data on metal crystallite size and on surface areas and activity after motor firing are presented in the following paragraphs.

8.2. Performance of Esso 500 Series Catalysts In Esso's 5 lb. Thruster

(U) Eight different Esso 500 Series catalysts were fabricated in 1/8" x 1/8" pellets and tested in our instrumented static 5 lb. thrust engine. Propellant grade hydrazine was supplied to the engine at 25°C using pulse mode propellant injection cycles of 1 second on 5 seconds off. Reactor chamber pressure and degree of catalyst attrition during engine firing were recorded. The results are presented in Table 26.

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Table 26

(C) PERFORMANCE OF ESSO 500 SERIES
CATALYSTS IN A 5 LB. THRUST ENGINE⁽¹⁾

Catalyst	% Change in Bed Pressure Drop	Catalyst Loss Wt %/Sec.
Esso 500	None	0.15
Esso 501	None	0.17
Esso 502	None	0.13
Esso 503	None	0.12
Esso 504	None	0.052
Esso 505	None	0.078
Esso 506	None	0.038
Esso 507	None	0.083

(1) Ignition program - 1 sec. on-5 secs. off - 40 total pulses.

(C) As can be seen from the data in Table 26, the Esso 500 series catalysts all performed very well in the pulse mode operation of our 5 lb. thruster. All catalysts showed excellent mechanical strength and resistance to attrition during engine firing as indicated by the low level of catalyst lost and bed pressure drop stability. These very encouraging results using the Esso 500 series catalysts prompted us to request that the Air Force evaluate one of them in actual flight type hardware. We believed that such a test was essential before studies in this area were pursued further.

8.3. Air Force Engine Firing Evaluation of Esso 500

(C) About 50 gms of Esso 500 1/8" x 1/8" pellets and 25 gms of Esso 500 20-40 mesh granules were sent to Edwards Air Force Base for motor firing evaluation in a 25 lb. thrust flight type monopropellant engine. The Air Force test results using a bed composed of about 10 vol. % granules, the remainder pills, were extremely encouraging. Esso 500 was found to give ignition delays comparable to Shell 405 with propellant grade hydrazine at 30°F and 100°F. Furthermore, no steady-state performance degradation in engine chamber pressure was observed during 350 secs. of hydrazine fuel burn using 2000 pulses of fuel injection. Low catalyst attrition was observed during this firing program and the catalyst was observed to have very good strength properties.

8.4. High Stability of the Esso 500 Series Catalysts

(C) The promoted substrate and final catalysts for the Esso 500 series have extremely high stability. Catalyst surface area, isothermal activity and pellet crush strength all showed little or no change after four

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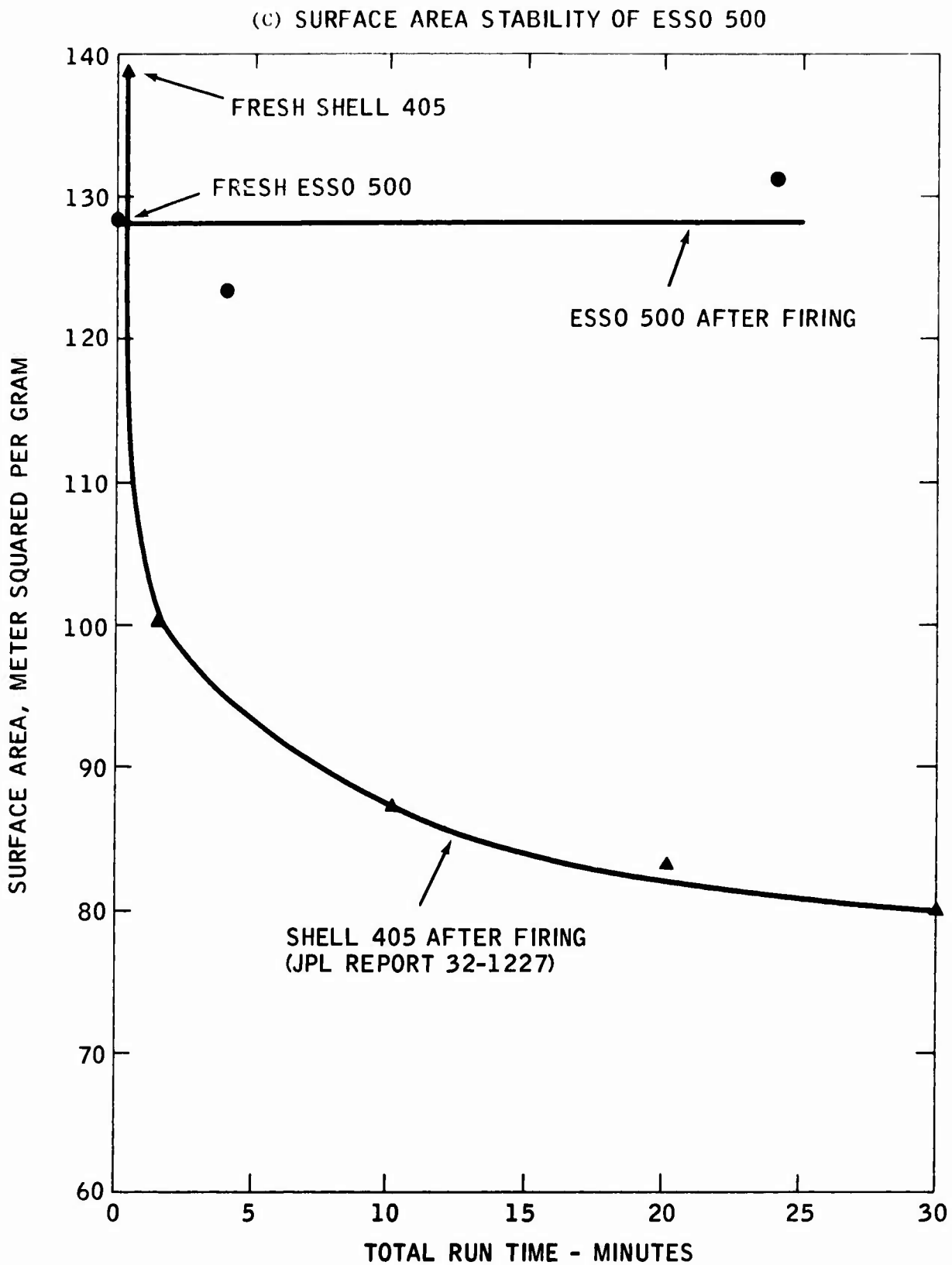
minutes of firing; the catalyst evaluated by the Air Force, and which received 24 minutes of total firing, also showed no loss in surface area. This data is presented in Table 27 and in Figure 16 which depicts the remarkable surface stability of Esso 500 in contrast to Shell 405. Esso 500 is seen to maintain its original "as fabricated" surface area during 24 minutes of total firing time. Shell 405, on the other hand, drastically desurfaces during the first 5 minutes of firing. This unique surface area stability of Esso 500 is a property associated with its unusually stable promoted substrate. It is suggested that surface area stabilization may be affected by the alkaline earth ion retardation of the transformation of γ -alumina to α -alumina.

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Figure 15



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Table 27

(C) STABILITY CHARACTERISTICS OF ESSO 500
SERIES CATALYSTS(1)

Catalyst	BET Surface Area N^2/gm		Catalyst After Firing	Isothermal Activity $cm^3 (STP)/min-gm$ at $25^\circ C$ (2)		Crush Strength lbs*	
	Substrate	Catalyst Before Firing		Before Firing	After Firing	Before Firing	After Firing
Esso 500	182.4	128.0	123.3 131.0 (2)	490	490	40	35
Esso 501	178.0	131.5	132.7	420	455	41	36
Esso 502	185.6	128.5	135.6	455	490	41	36
Esso 503	184.7	123.1	129.4	385	420	36	32
Esso 504	175.8	116.8	123.2	630	560	41	36
Esso 505	181.8	118.0	122.4	420	420	41	35
Esso 506	166.2	117.0	118.9	630	630	46	40
Esso 507	173.4	117.5	105.0	420	420	43	41

(1) All "After Firing" data apply to catalysts run for 4 minutes in hydrazine pulse mode fuel burn.

(2) After 24 minutes of firing.

*Based on $1/8" \times 1/8" \times 1/8"$ L pellets

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APPENDIX A

(C) CATALYST FIRING DATA - 5 LB. THRUST ENGINE

Catalyst No. 428-73
(Esso 200)

Description: 12% Ruthenium on 33% Cobalt
Impregnated Preformed 1404 1/8"
Alumina

	Run No.					
	1	2	3	4	5	6
Fuel Temp., °C	24	24	60	70	60	60
Bed Start-up Temp. °C	158	310	240	235	245	230
Bed Inlet Steady Temp. °C	158	300	760	915	915	915
Bed Center Steady Temp. °C	0	spike	180	162	150	145
Bed Inlet Steady Pressure, psig	0	spike	115	115	115	122
Bed Outlet Steady Pressure, psig	--	--	65	47	35	23
Bed Pressure Drop, psi	not recorded					
Ignition Spike Pressure, psi	4,000	7,800	1,000	500	400	700
Ignition Delay msec.*	3.2					
Wt. % Catalyst Loss and Fines/Cold Start	2	2	15	15	15	15
Pulse Duration, sec.						
Remarks						

*Ignition Delay time does not include valve response
and fuel flow "dead" time which is approximately 60 msec
in our test system.

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(C) APPENDIX A

Catalyst No. 428-74
(Esso 201)

Description: 10% Ruthenium on CO-
Precipitated Oxide Sintered
Cobalt Alumina (75% Cobalt)

	Run No.							
	1	2	3	4	5	6	7	8
Fuel Temp., °C	----- 25 -----							
Bed Start-up Temp. °C	25	60	65	65	65	116	240	25
Bed Inlet Steady Temp. °C	375	510	220	850	900	235	240	205
Bed Center Steady Temp. °C	385	635	845	850	860	830	830	830
Bed Inlet Steady Pressure, psig	25	27	120	105	105	95	110	105
Bed Outlet Steady Pressure, psig	20	25	80	100	100	90	95	90
Bed Pressure Drop, psi	5	2	40	5	5	5	15	15
Ignition Spike Pressure, psi	----- not recorded -----							
Ignition Delay msec.	4,500	1,100	900	1,000	1,100	550	120	2,100
Wt. % Catalyst Loss and Fines/Cold Start	----- 0.5 -----							
Pulse Duration, sec.	2	2	15	15	15	5	5	2
Remarks								

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(C) APPENDIX A

Catalyst No. 428-80
(Esso 202)

Description: 12% Ruthenium, 33%
Cobalt CO-impregnated on
1404-1/8" Alumina

	Run No.									
	1	2	3	4	5	6	7	8	9	10
Fuel Temp., °C										
Bed Start-up Temp. °C	25	57	100	25	100	190	117	130	166	25
Bed Inlet Steady Temp. °C	155	50	240	180	240	190	182	240	212	--
Bed Center Steady Temp. °C	155	445	240	815	845	845	915	880	915	--
Bed Inlet Steady Pressure, psig	10	25	97	65	80	98	113	114	120	--
Bed Outlet Steady Pressure, psig	10	25	92	65	72	80	95	100	100	--
Bed Pressure Drop, psi	--	--	5	0	8	18	18	14	20	--
Ignition Spike Pressure, psi	not recorded									
Ignition Delay msec.	4,700	600	250	1,500	200	100	150	150	100	1,500
Wt. % Catalyst Loss and Fines/Cold Start	0.6									
Pulse Duration, sec.	4.5	4.8	4.8	4.9	4.9	4.9	15	15	15	--
Remarks										

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(C) APPENDIX A

Catalyst No. 428-78
(Esso 205)

Description: 32% Ruthenium on
Preformed 1404-1/8"
Alumina

	Run No.						
	1	2	3	4	5	6	7
Fuel Temp., °C	----- 25 -----						
Bed Start-up Temp. °C	25	25	25	40	60	80	100
Bed Inlet Steady Temp. °C	220	210	210	210	215	215	215
Bed Center Steady Temp. °C	900	845	845	845	845	845	840
Bed Inlet Steady Pressure, psig	112	110	110	110	122	117	113
Bed Outlet Steady Pressure, psig	110	110	107	107	112	100	110
Bed Pressure Drop, psi	2	0	3	3	10	17	3
Ignition Spike Pressure, psi	----- not recorded -----						
Ignition Delay msec.	200	100	160	60	20	15	10
Wt. % Catalyst Loss and Fines/Cold Start	----- 1.7 -----						
Pulse Duration, sec.	----- 5 -----						
Remarks	---- Half Bed Used with 1404-1/8" Filler ----						

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(C) APPENDIX A

Catalyst No. 428-83-A
(Esso 206)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	Run No.													
Fuel Temp., °C								25						
Bed Start-up Temp. °C	25	40	60	80	100	100	120	25	25	120	100	80	60	40
Bed Inlet Steady Temp. °C	230	225	225	225	--	230	230	230	240	240	280	940	775	910
Bed Center Steady Temp. °C	880	880	880	845	--	860	860	860	790	790	845	835	815	830
Bed Inlet Steady Pressure, psig	--	98	115	123	--	123	123	135	--	136	145	145	145	145
Bed Outlet Steady Pressure, psig	--	--	100	107	100	100	107	115	138	113	120	120	117	118
Bed Pressure Drop, psi	--	--	15	16	--	23	16	20	--	23	25	25	27	27
Ignition Spike Pressure, psi	not recorded													
Ignition Delay msec.	40	80	80	85	--	75	40	260	340	20	25	45	75	150
Wt. % Catalyst Loss and Fines/Cold Start	0.62													
Pulse Duration, sec.	5	5	5	5	5	5	5	5	1	1	5	5	5	5
Remarks														

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(C) APPENDIX A

Catalyst No. 428-83-A
(Esso 206)

	15	16	17	18	19	20	21	22	23	24	25	26	27	28
	Run No.													
Fuel Temp., °C	25													
Bed Start-up Temp. °C	60	80	100	120	60	80	100	120	40	60	60	80	40	100
Bed Inlet Steady Temp. °C	915	220	205	205	185	185	180	205	180	--	220	265	205	205
Bed Center Steady Temp. °C	790	770	780	775	760	790	790	710	680	--	845	845	840	845
Bed Inlet Steady Pressure, psig	132	132	132	135	125	139	139	123	97	--	118	118	117	125
Bed Outlet Steady Pressure, psig	110	110	110	130	106	113	113	117	90	--	112	112	112	117
Bed Pressure Drop, psi	22	22	22	5	19	26	26	15	7	--	6	6	5	8
Ignition Spike Pressure, psi	not recorded													
Ignition Delay msec.	85	60	55	45	35	45	45	45	100	35	25	50	130	45
Wt. % Catalyst Loss and Fines/Cold Start	0.62													
Pulse Duration, sec.	5	5	5	5	2	5	4.3	4.3	2.5	2.5	2.5	2.5	2.5	2.5
Remarks														

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(C) APPENDIX A

Catalyst No. 428-83-B
(Esso 207)

Description: 23% Ruthenium on
Preformed 1404-1/8"
Alumina

Run No.												
1	2	3	4	5	6	7	8	9	10	11	12	13
----- 25 -----												
25	80	88	100	25	120	80	127	260	166	85	25	40
250	250	240	245	250	240	240	245	320	245	240	205	205
940	940	940	1000	910	940	1050	930	940	915	850	845	845
128	130	130	130	130	130	130	130	130	130	125	125	118
118	125	125	128	120	120	123	120	120	120	120	114	114
10	5	5	2	10	10	7	10	10	10	5	5	5
335	335	335	335	335	335	335	335	335	335	350	200	350
100	45	20	10	22	5	40	5	45	45	20	100	45

Fuel Temp., °C

Bed Start-up Temp. °C

Bed Inlet Steady Temp. °C

Bed Center Steady Temp. °C

Bed Inlet Steady Pressure, psig

Bed Outlet Steady Pressure, psig

Bed Pressure Drop, psi

Ignition Spike Pressure, psi

Ignition Delay msec.

Wt. % Catalyst Loss and Fines/Cold Start

Pulse Duration, sec.

Remarks

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(C) APPENDIX A

Catalyst No. 428-83-B
(Esso 207)

Description: 23% Ruthenium on
Preformed 1404-1/8"
Alumina

	Run No.													
	15	16	17	18	19	20	21	22	23	24	25	26	27	28
Fuel Temp., °C														
Bed Start-up Temp. °C	80	100	25	40	60	80	25	40	60	80	25	25	25	25
Bed Inlet Steady Temp. °C	205	205	205	200	200	190	205	200	205	205	195	190	180	180
Bed Center Steady Temp. °C	845	845	845	835	835	835	845	845	845	845	760	760	730	760
Bed Inlet Steady Pressure, psig	125	125	122	115	115	118	125	120	120	112	104	114	108	110
Bed Outlet Steady Pressure, psig	120	120	118	115	115	118	120	114	114	112	104	114	100	110
Bed Pressure Drop, psi	5	5	4	0	0	0	5	6	6	0	0	0	8	0
Ignition Spike Pressure, psi	350	350	350	117	117	117	325	325	325	325	350	180	60	93
Ignition Delay msec.	<5	<5	220	65	5	<5	200	60	<5	<5	180	100	45	75
Wt. % Catalyst Loss and Fines/Cold Start	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	1.5	1.5	1.5	1.5
Pulse Duration, sec.														
Remarks														

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(C) APPENDIX A

Catalyst No. 428-83-B
(Esso 207)

Description: 23% Ruthenium on
Preformed 1404-1/8"
Alumina

Run No.													
29	30	31	32	33	34	35	36	37	38	39	40	41	42

Fuel Temp., °C

Bed Start-up Temp. °C

Bed Inlet Steady Temp. °C

Bed Center Steady Temp. °C

Bed Inlet Steady Pressure, psig

Bed Outlet Steady Pressure, psig

Bed Pressure Drop, psi

Ignition Spike Pressure, psi

Ignition Delay msec.

Wt. % Catalyst Loss and Fines/Cold Start

Pulse Duration, sec.

Remarks

25													
25	26	27	28	29	30	31	32	33	34	35	36	37	38

180	180	180	180	180	180	170	170	155	145	170	145	170	170
700	790	770	850	760	760	770	760	770	815	760	810	275	880
106	110	110	113	109	106	106	106	106	119	112	115	106	114
106	106	105	107	100	100	100	100	100	112	107	107	95	100
0	4	5	6	9	6	6	6	6	7	5	8	11	14
240	150	255	270	270	75	165	80	240	310	306	310	300	300
140	105	150	170	150	70	110	80	160	180	160	180	170	150

1.5	1.5	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----

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(C) APPENDIX A

Catalyst No. 428-83-B
(Esso 207)

Description: 23% Ruthenium on
Preformed 1404-1/8"
Alumina

	Run No.														
	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58
Fuel Temp., °C	----- 25 -----														
Bed Start-up Temp. °C	----- 25 -----														
Bed Inlet Steady Temp. °C	135	170	170	170	170	170	170	145	145	170	170	170	170	170	170
Bed Center Steady Temp. °C	205	205	680	500	205	240	240	425	280	355	205	205	200	200	200
Bed Inlet Steady Pressure, psig	107	110	115	115	115	115	110	100	115	112	130	103	165	165	165
Bed Outlet Steady Pressure, psig	100	105	107	107	107	107	105	95	100	95	95	88	88	88	88
Bed Pressure Drop, psi	7	5	8	8	8	8	5	5	15	17	35	75	77	77	77
Ignition Spike Pressure, psi	180	75	250	325	163	73	119	257	335	120	350	108	0	0	0
Ignition Delay msec.	110	60	110	130	90	60	95	150	190	140	255	70	85	125	140
Wt. % Catalyst Loss and Fines/Cold Start															
Pulse Duration, sec.	----- 2.0 -----														

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(C) APPENDIX A

Catalyst No. 428-82-C
(Esso 208)

Description: 36% Ruthenium on
Alumina

Run No.															
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
----- 23 -----															
25	40	60	80	100	25	40	60	80	100	25	40	60	100	80	
200	195	195	195	195	195	220	195	184	220	205	205	205	195	205	
815	815	815	845	815	815	800	815	815	790	815	815	815	815	815	
118	110	110	110	110	120	115	110	110	110	115	115	115	115	115	
103	100	97	97	100	107	102	100	100	100	107	100	100	104	104	
15	10	13	13	10	13	13	10	10	10	8	15	15	11	11	
58	25	18	0	0	150	45	0	0	0	192	40	0	0	0	
90	50	40	30	<5	150	70	20	20	5	185	75	50	75	20	
----- 0.78% -----															

Fuel Temp., °C

Bed Start-up Temp. °C

Bed Inlet Steady Temp. °C

Bed Center Steady Temp. °C

Bed Inlet Steady Pressure, psig

Bed Outlet Steady Pressure, psig

Bed Pressure Drop, psi

Ignition Spike Pressure, psi

Ignition Delay msec.

Wt. % Catalyst Loss and Fines/Cold Start

Remarks

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(C) APPENDIX A

Catalyst No. 428-82
(Esso 209)

Description: 33% Ruthenium on
Silica Alumina

	1	2	3	4	5	6	7	8	9	10	11	12
	Run No.											
	----- 23 -----											
Fuel Temp., °C	25	40	60	80	100	25	40	60	80	100	25	40
Bed Start-up Temp. °C	200	195	195	195	195	195	220	195	185	220	205	205
Bed Inlet Steady Temp. °C	815	815	815	845	815	815	800	815	815	790	815	815
Bed Center Steady Temp. °C	118	110	110	110	110	120	115	110	110	110	115	115
Bed Inlet Steady Pressure, psig	103	100	97	97	100	107	102	100	100	100	107	100
Bed Outlet Steady Pressure psig	15	10	13	13	10	13	13	10	10	10	8	15
Bed Pressure Drop psi	58	25	18	0	0	150	45	0	0	0	192	40
Ignition Spike Pressure psi	90	50	40	30	<5	150	70	20	20	<5	185	75
Ignition Delay msec	----- 0.67 -----											

Wt. % Catalyst Loss and Fines/Cold Start

Remarks

----- each pulse duration - 2 secs. -----

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(C) APPENDIX A

Catalyst No. 428-82
(Esso 209)

Description: 33% Ruthenium on
Silica Alumina

	Run No.											
	13	14	15	16	17	18	19	20	21	22	23	
Fuel Temp., °C												
Bed Start-up Temp. °C	60	100	80	25	40	60	80	100	25	25	25	
Bed Inlet Steady Temp. °C	205	195	205	205	205	205	205	205	190	195	205	
Bed Center Steady Temp. °C	815	815	815	790	790	790	815	815	790	815	815	
Bed Inlet Steady Pressure, psig	115	115	115	115	107	115	107	115	110	110	117	
Bed Outlet Steady Pressure psig	100	104	104	97	95	97	97	97	100	95	105	
Bed Pressure Drop psi	15	11	11	18	12	18	10	18	16	15	12	
Ignition Spike Pressure psi	0	0	0	350	0	0	0	0	107	72	350	
Ignition Delay msec	50	5	20	175	25	20	7	7	135	110	235	
Wt. % Catalyst Loss and Fines/Cold Start	0.67											
Remarks	each pulse duration - 2 secs.											

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(C) APPENDIX A

PERFORMANCE OF ESSO 500 SERIES CATALYSTS IN THE 5 LB. THRUSTER

Data Code

P_1 = Hydrazine Tank Pressure, psig

P_2 = Upstream Reactor Chamber Pressure, psig

P_3 = Downstream Reactor Chamber Pressure, psig

ΔP = Bed Steady State pressure drop, psi

$T_{(Bed)}$ = Bed ignition temperature, °C

T_1 = Upstream Reactor Chamber Temperature, °C

T_2 = Downstream Reactor Chamber Temperature, °C

Spike - Ignition spike pressure - Reactor Chamber pressure, psi

DUR = Hydrazine pulse duration, secs.

DT = Ignition Delay*, msec.

*Ignition Delay time does not include valve response and fuel flow dead time which is approximately 60 msec in our test system.

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(C) APPENDIX A

Catalyst - Esso 500
Date Run - 8/1/69

Run	1	2	5	10	15	19	20	21	22	23	24	25	26
P ₁	400	400	400	400	400	400	400	400	400	400	400	400	400
P ₂	60	65	70	85	93	87	75	88	95	97	97	97	97
P ₃	60	62	70	85	95	85	72	90	100	100	100	100	100
ΔP	0	3	0	0		2	3						
T (Bed)	25	--	--	--	--	--	25	25	204	882	882	882	882
T ₁	--	--	--	--	--	--	193	204	890	927	927	927	927
T ₃	649	788	815	815	815	848	632	699	848	882	882	882	882
Spike	10	0	0	0	0	0	100	70	0	0	0	0	0
DUR	.920	.940	.940	.940	.940	.940	.940	.885	.910	.900	.900	.900	.900
DT	50	50	50	50	50	50	75	70	<5	<5	<5	<5	<5

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Run	27	28	29	30	31	32	33	34	35	36	37	38	39	40
P ₁	400	400	400	400	400	400	400	400	400	400	400	400	400	400
P ₂				90					105					83
P ₃				95					103				103	85
ΔP									2					
T (Bed)				882					861				861	25
T ₁				913					913				960	182
T ₃				890					890				890	681
Spike													0	110
DUR				.910					.905				.900	.900
DT				<5					<5				<5	<5

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(C) APPENDIX A

Catalyst - Esso 501
Date Run - 7/30/69

Run	1	2	3	4	5	6	7	8	9	10	11	12
P ₁	400	400	400	400	400	400	400	400	400	400	400	400
P ₂	62	75	76	80	80	80	67	82	93	100	95	100
P ₃	60	73	78	80	80	80	65	82	92	100	95	100
ΔP	2	2	2	0	0	0	2	0	1	0	0	0
T (Bed)	25	74	127	142	218	290	25	25	567	751	815	815
T ₁	182	182	204	237	263	274	182	193	927	944	913	913
T ₃	649	649	681	681	699	708	590	751	848	882	882	882
Spike	0	0	0	0	0	0	47	60	0	0	0	0
DUR	.880	.900	.900	.885	.890	.890	.868	1.280	1.285	1.290	1.290	1.290
DT	50	<50	<5	<5	<5	<5	90	90	<5	<5	<5	<5

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Run	13	14	15	16	17	18	19	20	25	30	35	37	38
P ₁	400	400	400	400	400	400	400	400	400	400	400	400	400
P ₂	100	100	95	98	90	70	60	80	87	85	90	87	67
P ₃	100	100	95	100	90	68	60	80	85	87	92	90	68
ΔP	0	0	0	--	0	2	0	0	2				1
T (Bed)	815	843	816	102	180	25	25	668	829	802	815	816	25
T ₁	882	913	913	204	898	193	180	858	946	946	848	848	180
T ₃	882	882	882	751	847	590	649	816	848	863	882	882	629
Spike	0	0	0	0	0	48	60	0	0	0	0	0	70
DUR	1.275	1.280	1.280	1.280	1.285	0.840	.940	.940	.950	.940	.940	.970	.950
DT	<5	<5	<5	<50	<50	100	60	<5	<5	<5	<5	<5	100

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Catalyst - Esso 502
Date Run - 8/20/69

[illegible]

Run	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
P ₁	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400
P ₂	70	80		85					--						--				--	
P ₃	70	80		85				85							100					
LP	0	0		0				--							--				--	
T (Bed)	25	154		848				832							848				832	
T ₁	182	182		882				882							882				890	
T ₂	590	788		816				816							832				848	
Spike	70	0		0				0							0				0	
DUR	.890	.900		.920				.910							.900				.910	
DT	70	<50		<5				<5							<5				<5	

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(C) APPENDIX A

Catalyst - Esso 503
Date Run - 8/14/69

Run	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
P ₁	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400
P ₂	82	80	92	100	100				103	103					97			100	87	
P ₃	82	82	93	103					107						100			105	85	
ΔP	0	0																	2	
T (Bed)	25	25	671	816					816						830			848	25	
T ₁	204	193	913	913					927						882			913	193	
T ₂	708	618	816	848					882						863			890	654	
Spike	0	0	0	0					0						0			0	60	
DUR	.890	.895	.895	.910					.905						.900			.900	.895	
DT	50	50	<5	<5					<5						<5			<5	65	

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Run	21*	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
P ₁	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400
P ₂	--	87			92				97						95			87	87	
P ₃	--	85			92				100						92			90	87	
ΔP		2			0										3					
T (Bed)	25	316			848				848						798			704	25	
T ₁	121	913			913				882						882			913	182	
T ₂	262	755			865				848						848			848	644	
Spike	0	0			0				0						0			0	87	
DUR		.895			.890				.895						.900			.900	.905	
DT	--	50			<5				<5						<5			<5	70	

*Faulty Fuel Valve;
No pressure buildup

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(C) APPENDIX A

Catalyst - Esso 504
Date Run - 9/12/69

Run	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
P ₁	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400
P ₂	60	60	70		90				98						105			103		70
P ₃	60	60	73		95				98						108			108		75
ΔP	0	0							0											
T (Bed)	5	25	482		730				788						802			788		25
T ₁	204	182	832		865				848						848			848		193
T ₂	662	590	816		848				865						882			882		560
Spike	0	0	0		0				0						0			0		20
DUR	.880	.910	.910		.915				.920						.905			.910		.900
DT	100	50	<5		<5				<5						<5			<5		90

Run	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
P ₁	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400
P ₂	70	85			88				95						100			100		72
P ₃	73	85			90				95						100			100		73
ΔP		0							0						0			0		
T (Bed)	25	454			816				788						788			788		25
T ₁	193	816			848				832						832			832		193
T ₂	601	787			802				832						832			832		590
Spike	0	0			0				0						0			0		13
DUR	.900	.910			.915				.910						.915			.915		.900
DT	70	<5			<5				<5						<5			<5		85

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(C) APPENDIX A

Catalyst - Esso 505
Date Run - 8/22/69

Run	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
P ₁	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400
P ₂	75	87	100		98				105						98				105	80
P ₃	73	85	100		100				105						100				110	80
ΔP	2	2	0						0											0
T (Bed)	25	25	554		788				788						816				788	25
T ₁	204	204	913		913				890						882				882	193
T ₂	662	681	848		848				848						848				882	632
Spike	0	35	0		0				0						0				0	30
DUR	.890	.890	.900		.900				.900						.900				.900	.910
DT	50	80	<5		<5				<5						<5				<5	70

Run	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
P ₁	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400
P ₂	95	85	95		95				95						93				95	70
P ₃	95	85	95		93				95						93				95	70
ΔP	0	0	0		2				0						0				0	0
T (Bed)	25	25	282		816				832						816				802	25
T ₁	204	193	316		890				890						882				882	193
T ₂	708	681	848		848				863						848				865	618
Spike	60	35	0		0				0						0				0	20
DUR	.895	.910	.910		.915				.920						.910				.910	.910
DT	80	60	<50		<5				<5						<5				<5	100

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(C) APPENDIX A

Catalyst - Esso 506
Date Run - 9/15/69

Run	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
P ₁	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400
P ₂	70	70	87		98				95						90					90
P ₃	70	70	87		102				100						90					90
ΔP	0	0	0												0					0
T (Bed)	5	25	304		751				788						816					816
T ₁	193	193	343		882				882						882					865
T ₂	662	649	816		832				848						848					816
Spike	0	13	0		0				0						0					0
DUR	.890	.900	.915		.920				.915						.920					.915
DT	200	35	<50		<5				<5						<5					<5

Run	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41
P ₁	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400
P ₂	75	70	98		100				98						92					92	80
P ₃	75	70	100		100				98						95					92	80
ΔP	0	0							0						0					0	0
T (Bed)	25	25	454		816				816						848					832	15
T ₁	182	193	882		890				890						882					865	182
T ₂	618	708	816		848				848						882					832	590
Spike	25	20	0		0				0						0					0	20
DUR	.910	.905	.915		.920				.920						.925					.920	.905
DT	95	65	<50		<5				<5						<5					<5	95

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(C) APPENDIX A

Catalyst - Esso 507
Date Run - 8/29/69

Run	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
P ₁	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400
P ₂	72	75	88	97					105						95				95
P ₃	72	73	85	98					105						95				95
ΔP	0	2	3						0						0				0
T (Bed)	+5°C	25	601	788					816						816				816
T ₁	193	193	882	882					865						865				865
T ₂	681	590	832	848					848						848				848
Spike	15	25	0	0					0						0				0
DUR	.900	.910	.910	.915					.925						.930				.925
DT	200	35	<5	<5					<5						<5				<5

Run	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38
P ₁	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400
P ₂	88	75	98		100					100					100				85
P ₃	90	72	100		100					100					100				85
ΔP		3			0					0					0				0
T (Bed)	25	25	704		816					832					848				85
T ₁	182	193	890		890					882					882				85
T ₂	618	662	848		882					882					882				85
Spike	35	40	0		0					0					0				0
DUR	.915	.900	.900		.915					.910					.910				.910
DT	30	95	<5		<5					<5					<5				120

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(C) APPENDIX B

CATALYST PREPARATION PROCESSES

Process for Preparing Esso 101 Hydrazine Decomposition Catalysts

Basis 100 gms of Final Catalyst

- Add 443 gms of $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ and 229 gms of $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ to 1000 cm^3 of distilled H_2O .
- To this solution add 120 gms of NH_4HCO_3 .
- Allow to stand overnight.
- Heat solution to 150°F.
- Add an additional 175 gms of NH_4HCO_3 .
- Filter solution in a Buchner Funnel.
- Dry filtrate for 18 hours at 120°C.
- Calcine for 4 hours at 750°C in air.
- Press into 1/8" D cylindrical pills.
- Reduce at 950°F for 6 hours in hydrogen.
- Passivate by slow, careful drying in methyl alcohol.

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(C) APPENDIX B (Cont'd)

Process for Preparing Esso 500 Spontaneous Hydrazine Decomposition Catalysts

- High purity silica-alumina is heated to 1800°F for 5 hours in air to stabilize the substrate lattice.
- A solution of "dopant" salt is prepared by dissolving 50 gms of an alkaline earth nitrate salt in 1 liter of deionized H₂O.
- The stabilized silica-alumina is saturated with the dopant solution, dried in air at 250°F for 2 hours and calcined at 750°F in air for 5 hours. This procedure is repeated until the desired dopant level is reached.
- A ruthenium trichloride solution is prepared by dissolving 25 gms of RuCl₃ in an isopropyl alcohol-H₂O mixture (90 vol. % isopropyl alcohol).
- The doped substrate is saturated with the ruthenium trichloride solution, dried at 250°F for 2 hours and calcined at 750°F in air for an hour. This procedure is repeated several times until the desired metal level is reached. 30 wt % Ru in the Esso 500 series.
- The calcined catalyst is reduced in flowing hydrogen for 5 hours at 1000°F.

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13. ABSTRACT (C) A low cost, active, highly stable hydrazine monopropellant decomposition catalyst has been developed. This catalyst labeled Esso 500, utilizes ruthenium for its active component and thus does not contain any costly and strategically limited iridium metal. Laboratory and 5 pound thruster studies conducted at Esso Research and Engineering Company and 5 and 25 pound thruster studies conducted at the Air Force Rocket Propulsion Laboratory indicate that Esso 500 is highly active at low ignition temperatures and shows unusually high resistance to loss of surface area during motor firing. Data obtained at both laboratories actually indicated that Esso 500 showed <u>no</u> loss of surface area after up to 24 minutes of pulse mode firing with hydrazine. (U) A cobalt containing catalyst called Esso 101 was also developed. This catalyst has much lower activity than Esso 500 for hydrazine decomposition at 5°C. Esso 101, however, is active at higher temperatures and can be employed where short ignition delays at low temperature is not required and where extremely low cost is a desired property. (U) Results of studies with various cobalt containing catalysts, cobalt-noble metal hybrid catalysts and ruthenium containing catalysts using several different substrate materials are also reported.		

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