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Titanium Hydride - Potassium Perchlorate: A Spark Insensitive Pyrotechnic Material (U)

W. B. Leslie, R. W. Dietzel

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TITANIUM HYDRIDE - POTASSIUM PERCHLORATE: A SPARK INSENSITIVE PYROTECHNIC MATERIAL (U)

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ABSTRACT (U)

This report is the result of a study of the comparison of titanium hydride-potassium perchlorate and titanium-potassium perchlorate as pyrotechnic mixtures for actuators and squibs. The handling characteristics of the powders and the performance when used in actuators are described. The nearly ideal properties of the hydride mixture are evident.

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TITANIUM HYDRIDE - POTASSIUM PERCHLORATE: A SPARK INSENSITIVE PYROTECHNIC MATERIAL

I. Introduction

The program for the development of the W75 Artillery Fired Atomic Projectile required the use of one or more gas valve actuators in order that at the proper time a mixture of deuterium and tritium under high pressure could be transferred to the weapon pit. For nuclear safety reasons, it was necessary that an inadvertent transfer of gas to the pit could not take place in the event the weapon were involved in an accident involving fire. Because of space limitations, it was essential that the powder used in the actuator be inherently bonfire safe, that is, the autoignition temperature of the powder would be much higher than the main explosive charge of the weapon.

We studied more than 100 explosive and pyrotechnic materials and found that one, titanium-potassium perchlorate (Ti-$KClO_4$), could be used as an actuator powder with the proper firing characteristics. It also exhibited a very high autoignition temperature. Actuators loaded with this material were insensitive to spark initiation, although the loose powder was sensitive.

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In spite of the undesirable characteristic that Ti-$KClO_4$ is spark sensitive as loose powder, it was the only material available for the W75 application. This sensitivity means that Ti-$KClO_4$ is not an ideal actuator or squib powder.

In principle, it should be possible to design an actuator or squib containing a spark sensitive powder that is not hazardous if it has been tested to a standard safety specification and it is installed and used in its final application assuming it is self-contained. However, the hazards of such a component should be examined from a broader viewpoint.

a. First, there are hazards associated with the development and manufacture of the component (handling loose powder, etc.), and often there are hazards in testing.

b. There is a trend toward use of a previously developed component in new systems for a new purpose; however, the precautions that were applicable for the previous system may not be valid for the new system.

c. Design changes (deliberate or inadvertent) can occur during production. Again this can lead to a hazardous situation since the precautions and procedures might not be adequate.

d. Manufacturing defects can occur which circumvent the engineering techniques used for desensitization.

e. The units are handled prior to and during installation.

f. Installed components are removed on occasion for stockpile sampling tests and opened for postmortem examinations.

g. Other agencies frequently handle and use Sandia components (often not in the intended application). Often this is not done in strict accordance with the detailed safe procedures.

In summary, if a component contains a sensitive material it must be regarded as inherently hazardous independent of engineering design and procedures.

Consequently, we have been concentrating our efforts on materials and techniques which are safer, particularly with regard to electrostatic charges generated by the human body. In particular we have examined pyrotechnic powders which have previously been accepted by others as spark insensitive (probably examined only in an actuator or squib configuration) and found that some lots of material are spark sensitive when examined as loose powder, for example Al-CuO and B-$CaCrO_4$.

We also have examined a mixture of titanium hydride-potassium perchlorate (TiH_2-$KClO_4$) and found it to be spark insensitive. Additional tests of a preliminary nature showed that this material should be investigated further as an actuator and squib material. Since we had already studied some of the properties of Ti-$KClO_4$, we believed that a thorough investigation of the two powders conducted in parallel would be worthwhile.

Titanium powder mixed with potassium perchlorate has been used by many workers as an actuator and squib material. The properties of the mixture and titanium powder alone are well documented (for example, see Reference 17).

Titanium hydride, a much lesser known material, is a grey powder of specific gravity 3.76 grams per cubic centimeter.[2] Titanium hydride is not a solid solution of hydrogen in titanium because the metal structure is hexagonal close-packed while the hydride has a face-centered cubic fluorite structure.[3]

A composite phase diagram of the titanium-hydrogen system has been prepared from pressure-composition-temperature measurements taken from several sources.[4]

Titanium hydride may be prepared by the direct union of hydrogen gas and titanium metal. The reaction is exothermic and is carried out at 673 to 873 K (400 to 600°C).[5,6]

Trace impurities in titanium such as oxygen and nitrogen have a marked effect on the rate of attainment of equilibrium in a titanium-hydrogen system. Impurities in the hydrogen used in the production of titanium metal powder (by hydriding and dehydriding) cause the formation of metal that is considerably harder than metal produced with highly purified gas,[7] which further shows the significance of impurities.

The hydride is remarkably stable. For example, it may be heated in 25 percent hydrochloric acid at 373 K (100°C) for 2 hours without significant decomposition.[8] Titanium hydride is also slightly less prone to spontaneous ignition when heated in air than is titanium metal.[9] The hydride probably does not react readily with the halogens, nitrogen, ammonia, or hydrocarbon gases.[10] Reactivity between the hydride and metals is more dependent on the nature of the alloying than on corrosion mechanisms. Since some hydrogen can be liberated, the problem of hydrogen embrittlement with certain metals must be carefully considered.[11]

Procedures have been developed for the quantitative analysis of various impurities in TiH_2 as well as the determination of the Ti and H content.[12,13]

The thermal decomposition of TiH_2 starts at 623 to 653 K (350 to 380°C).[14] The coefficient of thermal expansion of TiH_2 has been reported to be 10.6×10^{-6}.[16]

Titanium hydride has been little used as a pyrotechnic material. Ellern, in his book on pyrotechnics,[17] states that because TiH_2 is more inert than the metal, its lower ignition sensitivity and slower burning rate limit its usefulness.

A gas producing composition has been reported which consisted of a Zr-$KClO_4$-Viton B ignition mixture (hot wire sensitive) and a main charge of TiH_2-$KClO_4$-Viton B.[18] On the basis of our measurements on the above ignition powder, an actuator or squib prepared as described above would be very spark sensitive.

II. Experimental Procedure and Results

The two pyrotechnic mixtures used in this study were prepared as follows. The titanium-potassium perchlorate mixture contained 33 percent (by weight) titanium and 67 percent potassium perchlorate. The proportions were chosen, based upon the reaction:

$$2Ti + KClO_4 \rightarrow 2TiO_2 + KCl$$

The mixture contained a 29 percent excess of potassium perchlorate over the stoichiometric requirement. These proportions were found to be an optimum in the course of a study conducted by Unidynamics, Phoenix, Inc., Phoenix, Arizona for Sandia Laboratories.

The titanium powder was -325 mesh, Grade Z, (Lot No. J-3896A-2) manufactured by Metal Hydrides Corp., Beverly, Mass. (name since changed to Ventron Corp.).

The potassium perchlorate was -325 mesh and was supplied by Mason & Hanger-Silas Mason Co., Inc., Amarillo, Texas.

The details of the procedure for the preparation of the mixture are described in Sandia Laboratories Drawing Number SS287895.*

The titanium hydride-potassium perchlorate mixture contained 26.5 percent (by weight) titanium hydride and 73.5 percent potassium perchlorate. The proportions were chosen, based upon the reaction:

$$4TiH_2 + 3KClO_4 \rightarrow 4TiO_2 + 4H_2O + 3KCl$$

The mixture contained a 29 percent excess of potassium perchlorate over the stoichiometric requirement. This excess was chosen only because the same excess was found best for $Ti\text{-}KClO_4$, as noted above. This may not be a valid extrapolation, however, since commonly used titanium powder may contain as high as 13 percent of titanium hydride (calculated as TiH_2) which could explain the need for excess oxygen.

*The mixture used in this study was designated Lot SC-TP-1 and was prepared by R. J. Buxton, 2516 and T. M. Massis, 2516.

No other ratios of TiH_2 to $KClO_4$ were used in this study.

The titanium hydride powder* was -325 mesh, Lot J-3250A-2, manufactured by Metal Hydrides Corp., Beverly, Mass. (name since changed to Ventron Corp). The potassium perchlorate was the same material used for the preparation of the titanium-potassium perchlorate mixture described above.

The mixing of the two components was done in 20-gram batches by blending the two components on a sheet of paper using a plastic spatula. The mixing was done in a static-free area. Other safety precautions were observed.

Loose Powder Studies

Bulk Density -- The bulk density of the pyrotechnic powders was determined by filling a small container of known volume with powder. The powder in the container was then weighed. Care was taken to avoid compacting the powder while determining its volume. The data obtained are shown in Table 1.

TABLE I

Bulk Density of Loose Pyrotechnic Powders

$Ti\text{-}KClO_4$	0.67 g/cm^3
$TiH_2\text{-}KClO_4$	0.81 g/cm^3

Impact Height -- The impact height of each powder was determined by a standard 2 kg weight drop test using a 20 mg sample for each determination. The anvil and cup were bare steel. The impact threshold was determined as that height at which one initiation was obtained in 10 samples tested. The impact values were as follows (for comparison, PETN gave a value of 35 cm):

TABLE II

Impact Height of Loose Pyrotechnic Powders

$Ti\text{-}KClO_4$	114 cm
$TiH_2\text{-}KClO_4$	114 cm

*The powder contained 3.92 percent hydrogen which corresponds to the formula $TiH_{1.96}$.

Spark Ignition Threshold -- The spark ignition threshold of the loose powder was measured by discharging a 600 pf capacitor from an electrode through a sample of loose powder (approximately 200 mg sample) to a ground plane. A sketch of the test fixture is shown in Figure 1. No resistance was added to the discharge path. Only one discharge was made through each sample.

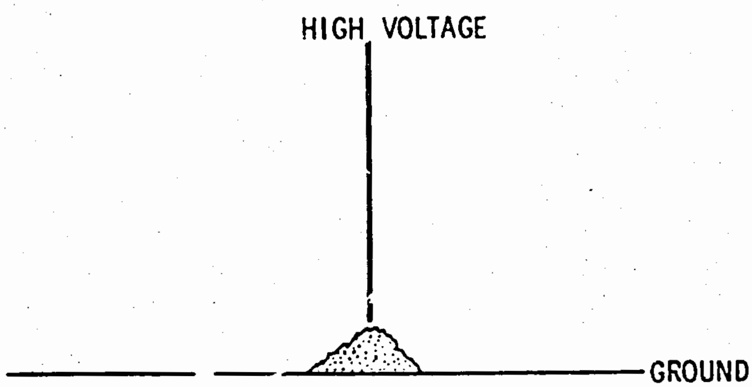

Figure 1. Test fixture for spark ignition of loose powder

The voltage was varied until one ignition in 10 samples tested was obtained or the limits of the test equipment were reached. The energy stored in the capacitor at that voltage level was designated as the spark ignition threshold. The data are summarized below.

TABLE III

Summary of Spark Ignition Tests on Loose Powder

	$Ti-KClO_4$	TiH_2-KClO_4
Ignition threshold	<7.5 mJ	> 480 mJ

Flame Ignition -- A train of loose powder, approximately 3 mm wide, 3 mm high, and 50 mm long (0.12 x 0.12 x 1.97 inches) was laid out on an asbestos board. One end of the train was ignited by a small flame of a propane torch. If the train failed to propagate, it was ignited again. This was repeated until the train was consumed.

When a train of $Ti-KClO_4$ was ignited, it burned in a single brilliant flash. A train of TiH_2-KClO_4 was slow to ignite, and when it did ignite it failed to propagate. It required 14 successive ignitions by the flame before being consumed.

Quantitative DTA -- A quantitative differential thermal analysis (DTA) was conducted on samples of the pyrotechnic powders. Nominal 10 milligram samples were heated in closed cups at a rate of 20K (20°C) per minute using the DuPont Model 900 Thermal Analysis System.*

Figure 2 is the record of the temperature difference between $KClO_4$ (the lot used to prepare the pyrotechnic powders) and a reference sample, as a function of temperature. The endotherm shown on the record at approximately 588K (315°C) is caused by a phase change of crystalline potassium perchlorate; the second endotherm at approximately 883K (610°C) is caused by melting of the $KClO_4$. The beginning of an exotherm immediately afterward is probably due to decomposition with evolution of oxygen.

Figure 3 is the DTA record for the titanium metal used to prepare the Ti-$KClO_4$ mixture.

Figure 4 is the record for the TiH_2 used to prepare the TiH_2-$KClO_4$ mixture. The minor exotherms above 773K (500°C) may be caused by reaction of the TiH_2 with small quantities of oxygen gas present in the vicinity of the sample.

Figure 5 is the record for Ti-$KClO_4$. The endotherm at approximately 588K (315°C) is caused by the phase change of the $KClO_4$ in the mixture; the strong exotherm at approximately 783 K (510°C) is caused by the pyrophoric reaction of the two constituents of the mixture. The cause of the mild exothermic reaction over the range 548-613K (275 - 340°C) is not known, but could be due to an early reaction between Ti and $KClO_4$. This exotherm was not present in all samples from the large lot.

Figure 6 is a record for TiH_2-$KClO_4$. The large exotherm at approximately 788K (515°C) is caused by the pyrophoric reaction of the two constituents of the mixture. The mild exothermic reaction observed with some samples of Ti-$KClO_4$, at 548 - 613K (275 - 340°C) in Figure 5, was not observed with TiH_2-$KClO_4$.

A sample of TiH_2-$KClO_4$ was removed from an actuator. The actuator had been stored for 30 days at 373K (100°C) and yielded a record that was not significantly different from the record obtained with an unheated sample (compare Figures 6 and 7).

Experimental Actuators

Actuators used in this study were prepared in a conventional manner as follows (squibs could be fabricated the same way). The body of the actuator was machined from Type 303 stainless steel hexagonal bar stock as shown in Figure 8. Two types of bodies were used, differing in powder cavity volume.

*The analyses were conducted by T. M. Massis, 2516.

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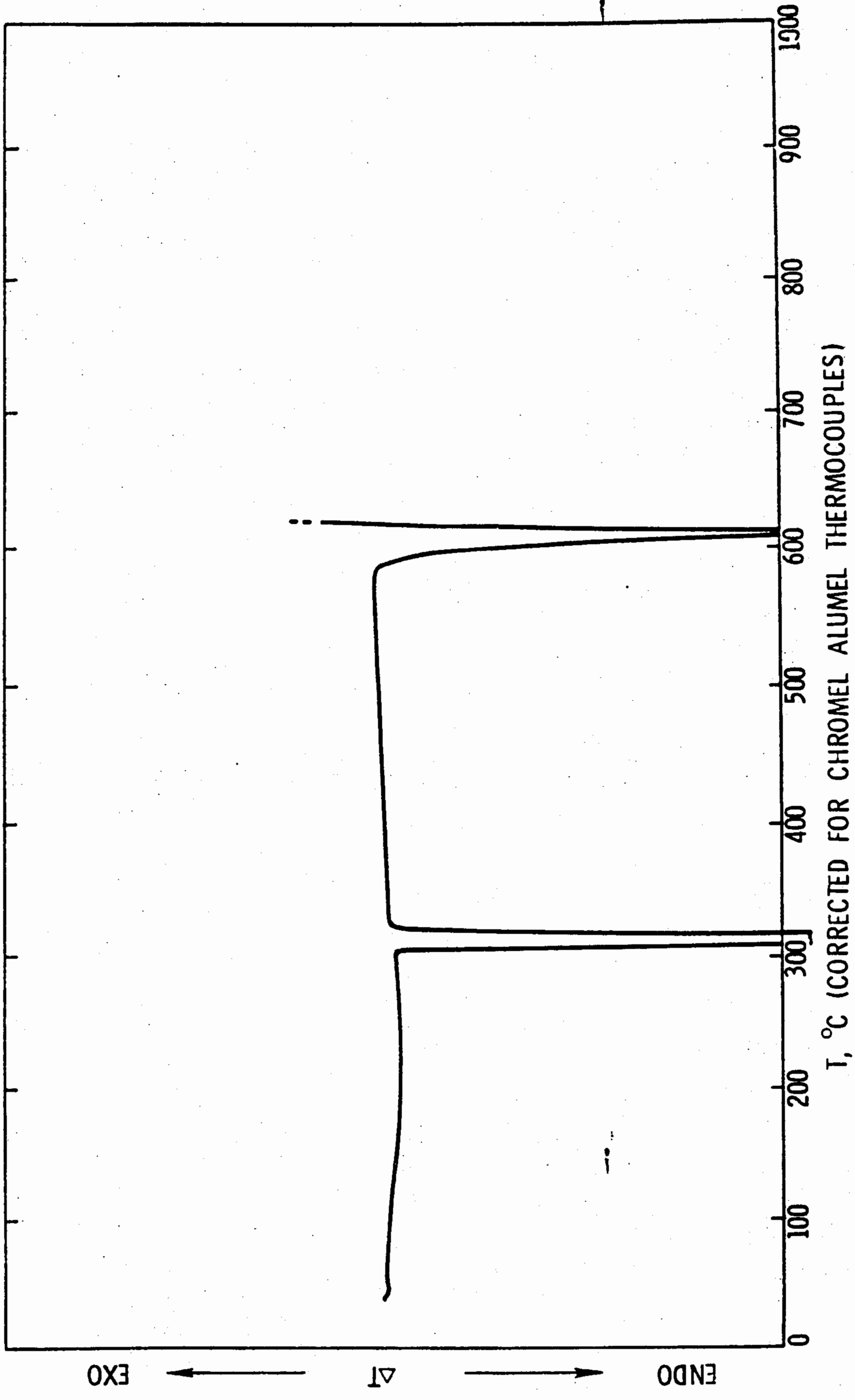

Figure 2. Differential thermal analysis of $KClO_4$

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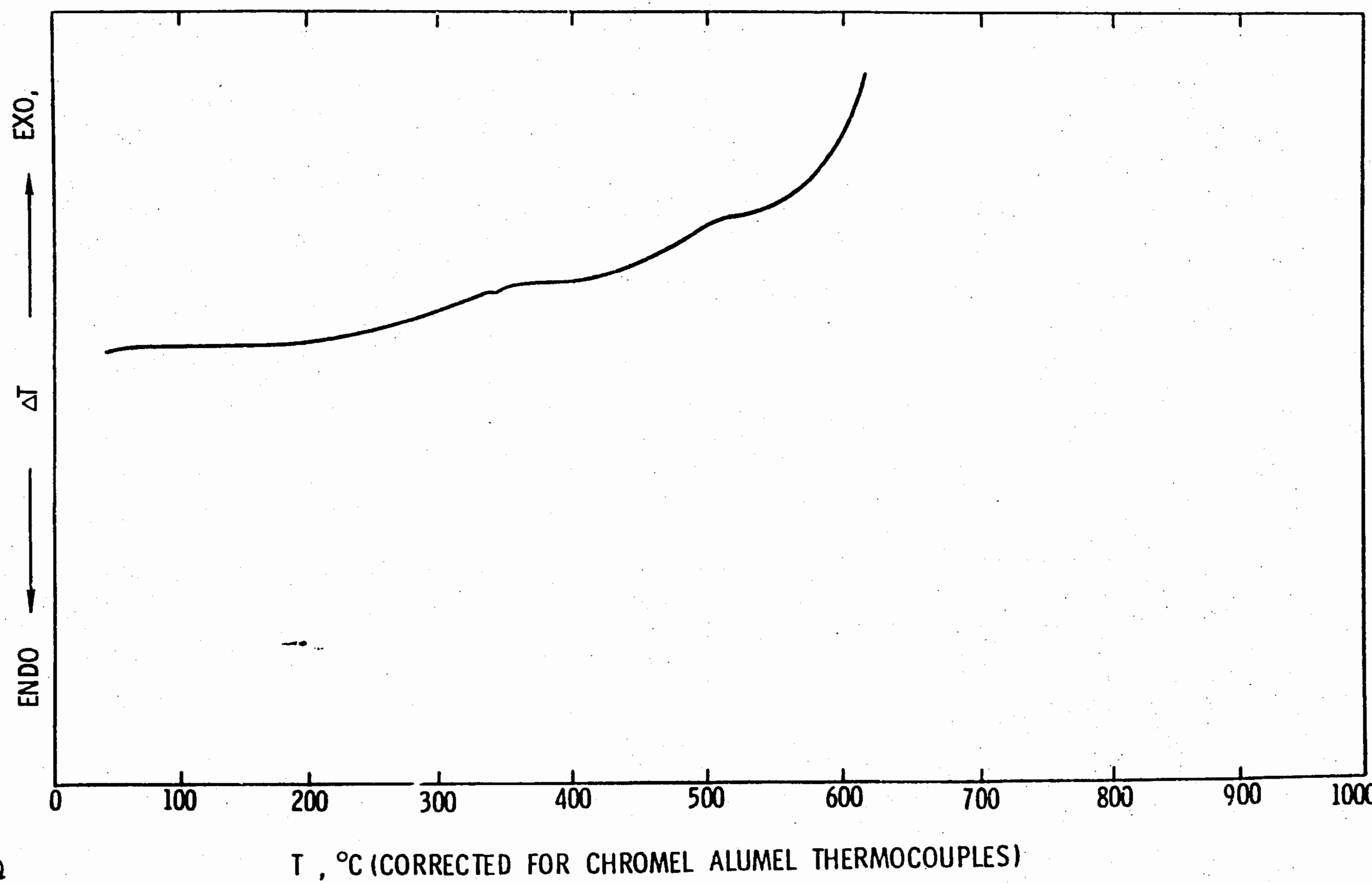

Figure 3. Differential thermal analysis of Ti

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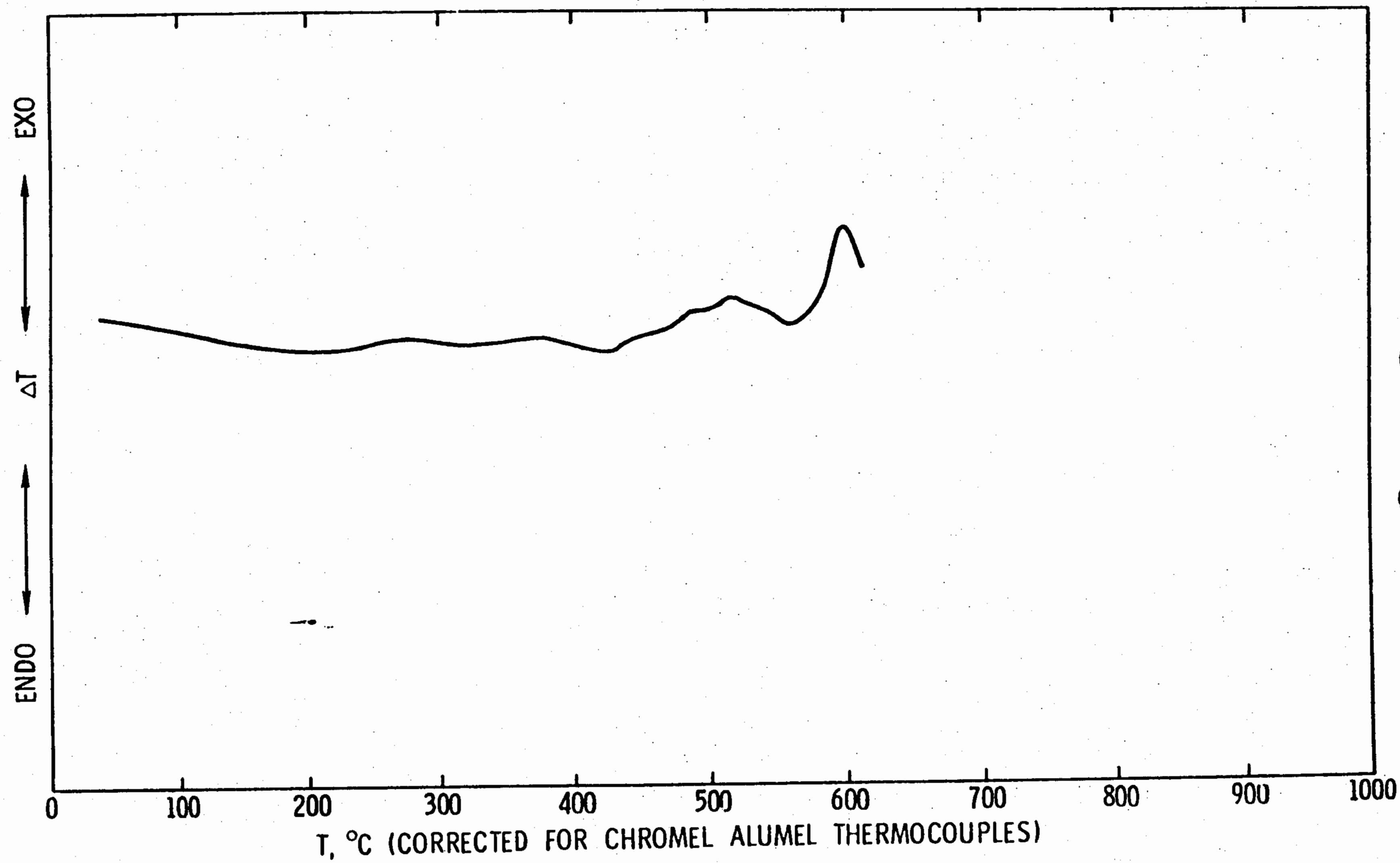

Figure 4. Differential thermal analysis of TiH_2

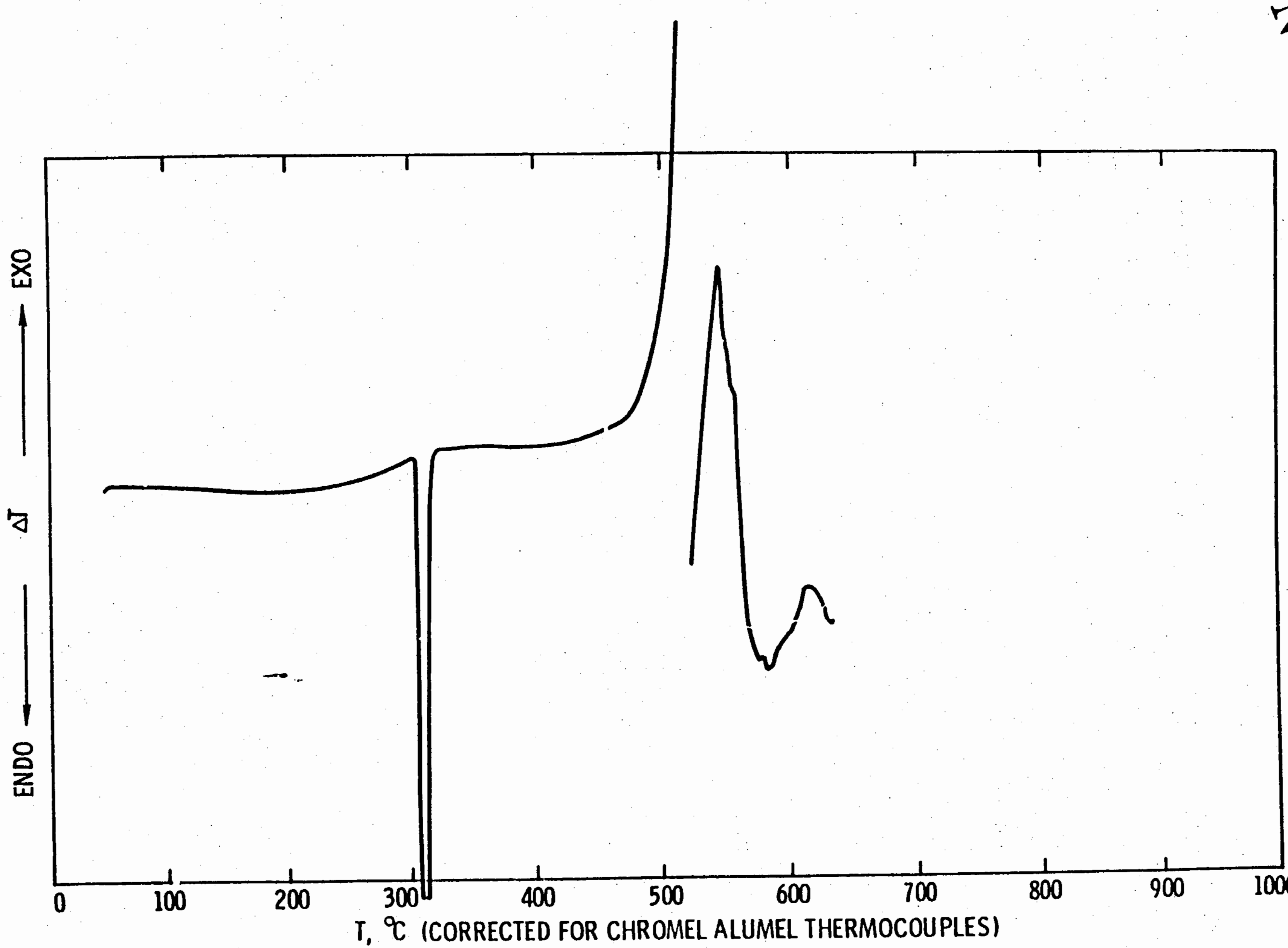

Figure 5. Differential thermal analysis of Ti-$KClO_4$

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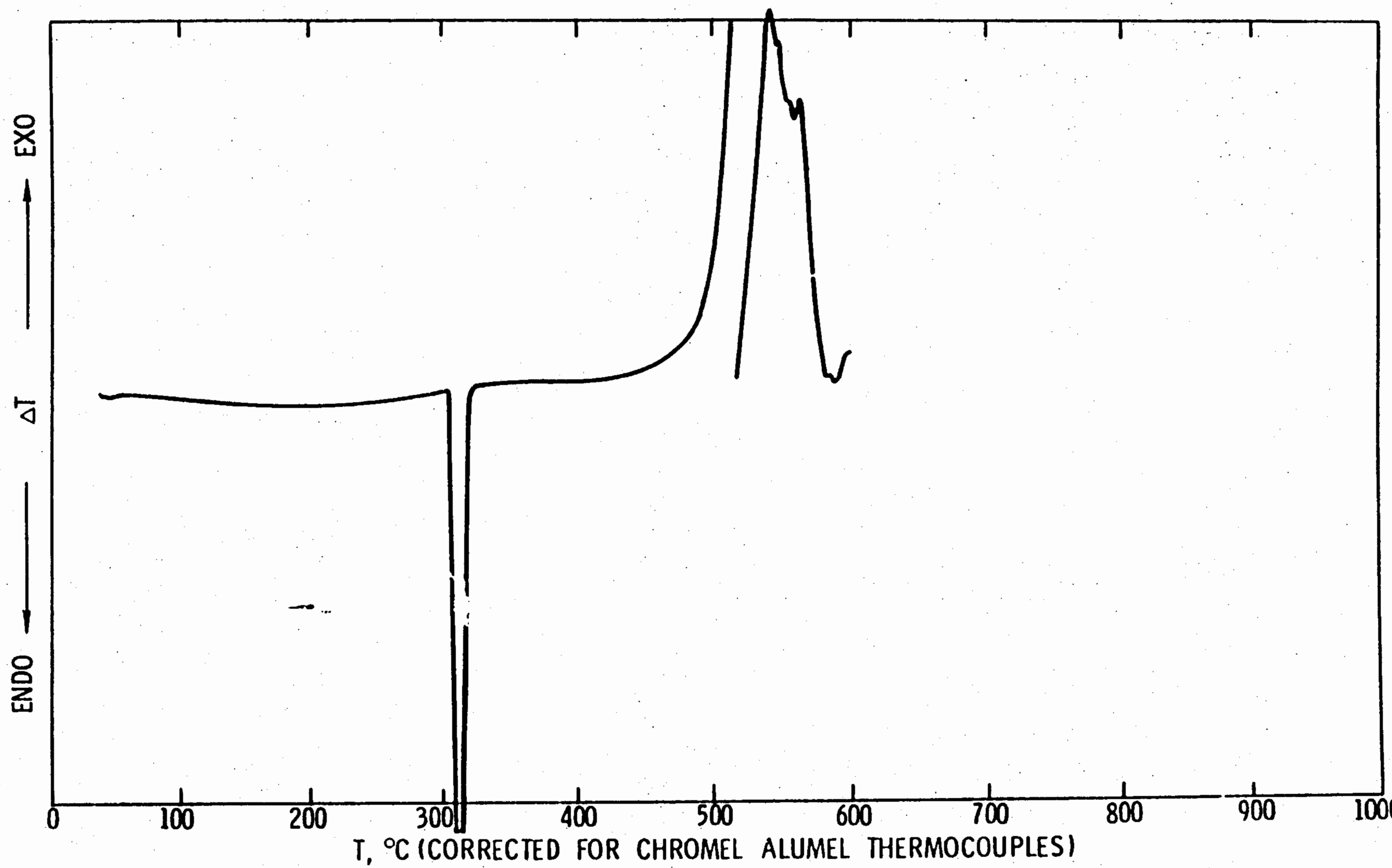

Figure 6. Differential thermal analysis of TiH_2-$KClO_4$

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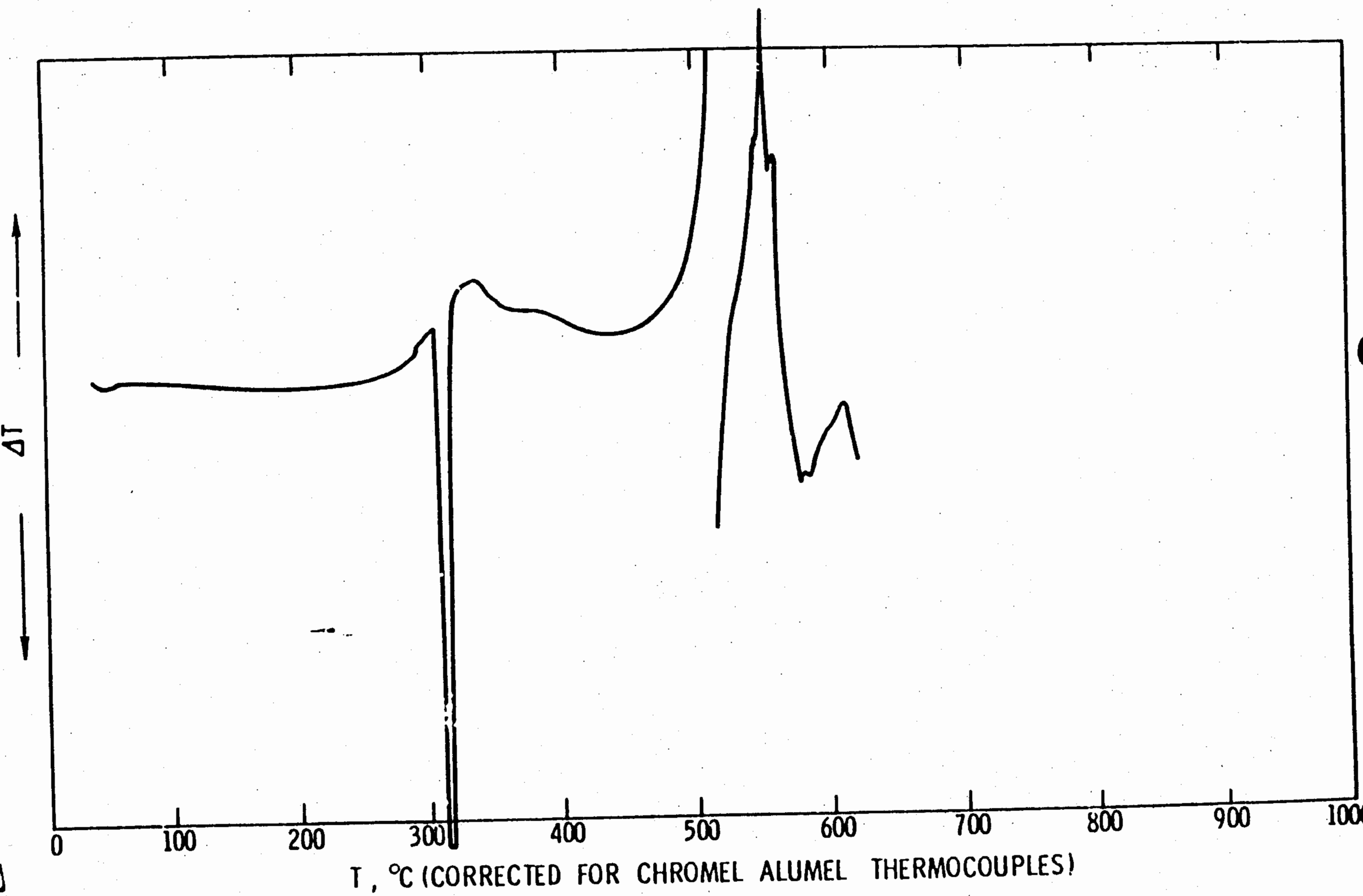

Figure 7. Differential thermal analysis of TiH_2-$KClO_4$ after storage at 373K (100°C) for 30 days

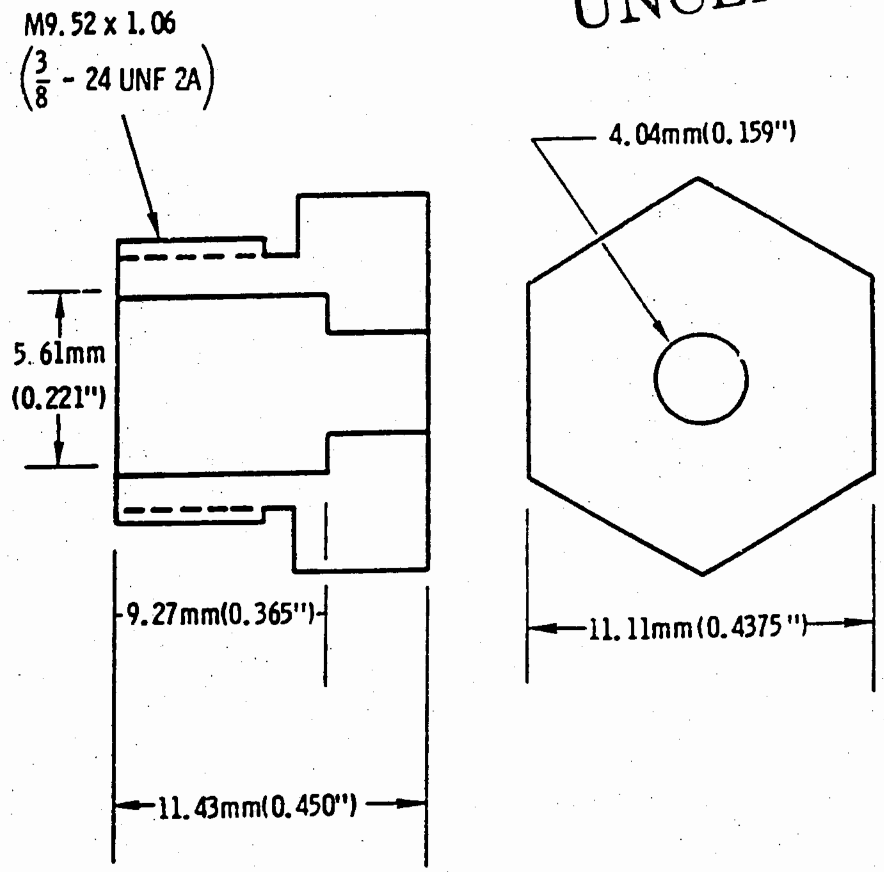

Figure 8. Actuator housing

The header for the actuator was made from glass and Kovar. The connecting pins were spaced 2.41 mm (0.095 inch) center to center. A 0.051 mm (0.002 inch) round, straightened and cleaned Evanohm* wire [655.8 ohms per meter (199.9 ohms per foot)] was resistance welded to the connecting pins. The effective bridgewire length was 1.40 mm (0.055 inch) and the resistance was 1.00±0.10 ohm.

The bridged header was pressed into the actuator body. The assembled actuator is shown in Figure 9. Powder was pressed against the bridgewire at 703 kg/cm^2 (10,000 psi) which filled the remainder of the cavity. Some of the constants for the actuators are listed in Table 4.

---

*Evanohm is a trademark of the Wilbur B. Driver Co., Newark, N.J., for an alloy of the composition 74.5 percent Ni, 20 percent Cr, 2.75 percent Cu and 2.75 percent Al. The wire has a resistance of 800 ohms/circular mil foot, a temperature coefficient of $\pm 3(10)^{-6}$, exhibits high resistance to corrosion and has high tensile strength.

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Figure 9. Actuator housing and header with bridgewire. The assembled actuator is shown on the right.

TABLE IV

Some Actuator Constants

	$Ti-KClO_4$	TiH_2-KClO_4
weight (mg)	175	110
Cavity diameter (mm - inches)	5.61 - 0.221	5.61 - 0.221
Cavity length (mm - inches)	3.79 - 0.149	1.98 - 0.078
Cavity volume (cm^3 - cubic inches)	0.0937 - 0.00572	0.0491 - 0.00300

When TiH_2-KClO_4 was loaded into actuators with the larger powder cavity, the actuator body usually failed at the thread area. For this reason, the studies with this powder were made using the actuator with the smaller powder cavity. All actuators loaded with $Ti-KClO_4$ used the actuator body with the larger powder cavity.

When actuators containing TiH_2-KClO_4 were fired without confinement at the open end of the actuator, the powder usually failed to propagate properly. The actuators fired by bridgewire ignition were assembled using a 7.95 mm (0.313 inch) diameter brass disc [0.41 mm (0.016 inch) thick] firmly held against the powder for confinement. (A few actuators were fired using copper discs, which may have had the added advantage of more tightly sealing the actuator to prevent pressure loss upon firing.)

<u>Bulk Density of Actuator Load</u> -- The bulk density of the powder in the loaded actuator was determined from the weight of actuators before and after loading, and the volume of the actuator cavity. The actuators were loaded with a ram pressure of 703 kg/cm^2 (10,000 psi). The average density of the actuator loads were as follows:

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TABLE V

Bulk Density of Powder in Actuators

$Ti-KClO_4$	1.93 g/cm^3
TiH_2-KClO_4	2.23 g/cm^3

Spark Initiation Threshold -- The spark initiation threshold of the actuators was measured by discharging a charged 600 pf capacitor from the bridgewire of the actuator to the actuator body. Only one discharge was made through each actuator.

Two different tests were performed: a) the capacitor was charged to 20 kV and then discharged through the actuator with a 500 ohm resistor placed in the discharge circuit; the number of ignitions in 10 units tested was recorded. b) the capacitor was charged to a specific voltage and then discharged through the actuator with no resistance added to the discharge circuit. the voltage was varied until one initiation was obtained in 10 units tested at one voltage level, or until 10 units were tested at the maximum voltage of the tester. The energy stored in the capacitor at that voltage level was designated as the spark initiation threshold. The test data is summarized below.

TABLE VI

Summary of Spark Initiation Tests on Actuators

	Actuator Type	
	$Ti-KClO_4$	TiH_2-KClO_4
No. of initiations @ 600 pf-20 kV - 500 ohms	0	0
Initiation threshold (600 pf-0 ohms	>370 mJ	270 mJ

Spark initiation tests were also made with a different type of actuator that contained two bridgewires connected in series. The inside diameter of the actuator was 5.0 mm (0.201 inch) and contained 162 mg of TiH_2-KClO_4 pressed at 703 kg/cm^2 (10,000 psi). The internal arc path (from bridgewire to case) was 1.0 mm (0.040 inches). The actuators were tested while assembled into the Mini-Flipper (see section II-B-6). A 600 pf capacitor was charged to 35 kV and discharged through the actuator, from pins to case. with a 500 ohm resistor in the discharge circuit. A layer of oil, approximately 3 mm (0.120 inch) deep, covered the top of the actuator to prevent external arcing from leads to case. There were no initiations in 10 units tested. Based on current models and on our experience, there is strong evidence that these actuators would not be initiated by a discharge from the human body.

<u>Autoignition Temperature</u> -- The autoignition temperature of experimental actuators was determined by assembling the actuator into the Mini-Flipper[19] test device and heating the assembly in a vertical-tube electric furnace. A thermocouple and recorder were used to monitor the internal temperature of the assembly. The assembly was heated at a rate of 13.9K (13.9°C) per minute by controlling the rate at which it was lowered into the preheated furnace. When the autoignition temperature was reached, the record showed a strong exotherm caused by ignition of the powder.

A brief description of the operation of the Mini-Flipper is given below in "Actuator Output," Page 23.

The autoignition temperatures of the two types of actuators are listed below.

TABLE VII

Autoignition Temperature of Actuators

$Ti\text{-}KClO_4$	748K (475°C)
$TiH_2\text{-}KClO_4$	793K (520°C)

<u>No-Fire Current</u> -- The no-fire test was conducted by assembling an actuator into a Mini-Flipper test device and passing a one ampere DC current through the bridgewire for a five minute period. To pass this test, the actuator must not fire. Tests were conducted at both ambient temperature and 347K (74°C or 160°F). Actuators loaded with $Ti\text{-}KClO_4$ or $TiH_2\text{-}KClO_4$ passed tests at both temperatures.

<u>Minimum Current for Ignition</u> -- The minimum current for ignition of the actuators was determined by passing a constant current through the bridgewire of the actuator and determining if the powder ignited within a fraction of a second (units that did not fire were not used in subsequent tests). The current level was lowered until a minimum level was reached. The lowest current level that produced ignitions in four out of five units tested is listed below.

TABLE VIII

Minimum Current for Actuator Ignition

$Ti\text{-}KClO_4$	1.7 A
$TiH_2\text{-}KClO_4$	1.3 A

Time to Bridgewire Burn-Out -- The time required to burn-out or melt the bridgewire in a loaded actuator was determined by passing a 3.5 ampere constant DC current through the wire. The current magnitude was monitored with an oscilloscope and a 0.1 ohm current-viewing resistor. The elapsed time from the start of current flow to a sudden decrease in current value was read from a photograph of the oscilloscope trace (see Figure 10). Average values are listed below.

TABLE IX

Time to Bridgewire Burn-Out

$Ti-KClO_4$	2.8 ms
TiH_2-KClO_4	4.2 ms

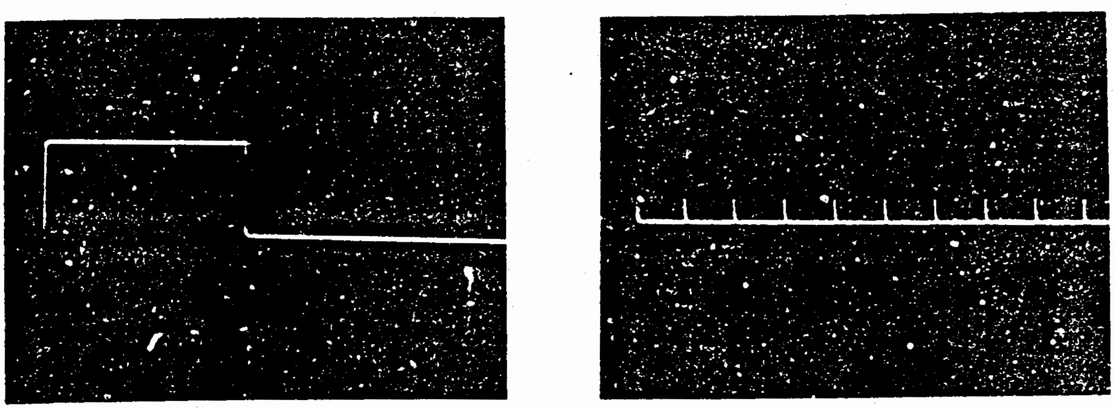

Figure 10. Oscillogram of 3.5 ampere current pulse throug·· an actuator containing TiH_2-KClO_4. (Current amplitude is displayed on the vertical axis. The oscillogram on the right is a display of calibrating time marks at one millisecond intervals.)

Actuator Function Time -- The function time of an actuator is defined as the elapsed time between the start of current flow in the actuator bridgewire and the arrival of the propagation front at the output end of the actuator.

The beginning of the current pulse through the bridgewire was used to trigger the sweep of the oscilloscope. The time of arrival of the propagation front was recorded by a pulse generated by an electronic switch located at the output end of the actuator. The elapsed time was read from the photograph (time marks from a calibrated electronic clock were also recorded on the photograph or on a separate photograph). A typical oscillogram is shown in Figure 11.

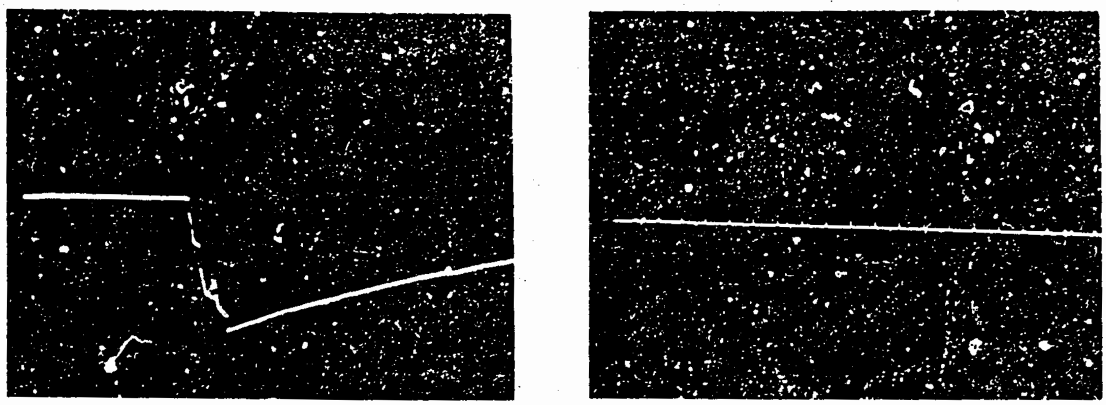

Figure 11. Oscillogram of the function time of an actuator containing $Ti-KClO_4$. (The sharp drop in the oscilloscope trace is caused by the arrival of the propagation front.) One millisecond calibration time marks are shown on the photo to the right.

The range of values and the average value of actuator function times are given below, when six actuators were initiated by a 3.5 ampere, constant DC current.

TABLE X

Actuator Function Times

	Range	Average	Sigma
$Ti-KClO_4$	2.4 to 8.1 ms	4.5 ms	2.231 ms
TiH_2-KClO_4	4.1 to 4.6 ms	4.4 ms	0.222 ms

Actuator Output -- The ability of the actuator to do useful work was measured with a test device called the Mini-Flipper. A cross section of the device is shown in Figure 12. When the vehicle is used, the firing of the actuator drives a piston a short measured distance down a barrel. The piston strikes an annealed brass target and comes to rest. The deformation of the target can be measured with a micrometer and is a measure of actuator output. Also, meaningful electrical measurements can be made during actuator firing.

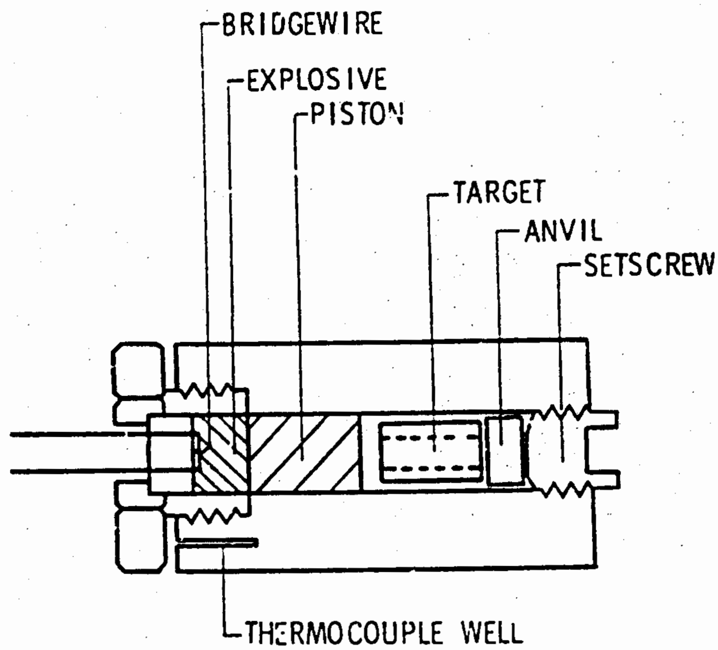

Figure 12. Cross section of Mini-Flipper

A graph illustrating the relationship between target deformation and the quantity of $Ti-KClO_4$ loaded into an actuator is shown in Figure 13 (the data for the preparation of the graph was taken with actuators with powder cavities of varying volume). The figure also shows similar data for TiH_2-KClO_4.

Average values of target deformation for the powder loads given in Table IV are shown below.

TABLE XI

Average Values of Actuator Output

	Target Deformation in Millimeters (Inches)
$Ti-KClO_4$	3.07 (0.121)
TiH_2-KClO_4	1.50 (0.059)

Resistance-After-Fire -- Resistance-after-fire (RAF) is the resistance measured across the two bridgewire leads of the actuator, beginning immediately after the actuator has been fired. In this study, RAF was measured for a total time of one minute, beginning at the start of current flow in the bridgewire. Two oscilloscopes and a high-impedance input strip-chart recorder were used to measure RAF over three different time intervals. One oscilloscope was used to record RAF during the first 20 ms and another oscilloscope for the first second. The recorder measured RAF for the full minute. A RAF record for the first 20 ms for an actuator is shown in Figure 14.

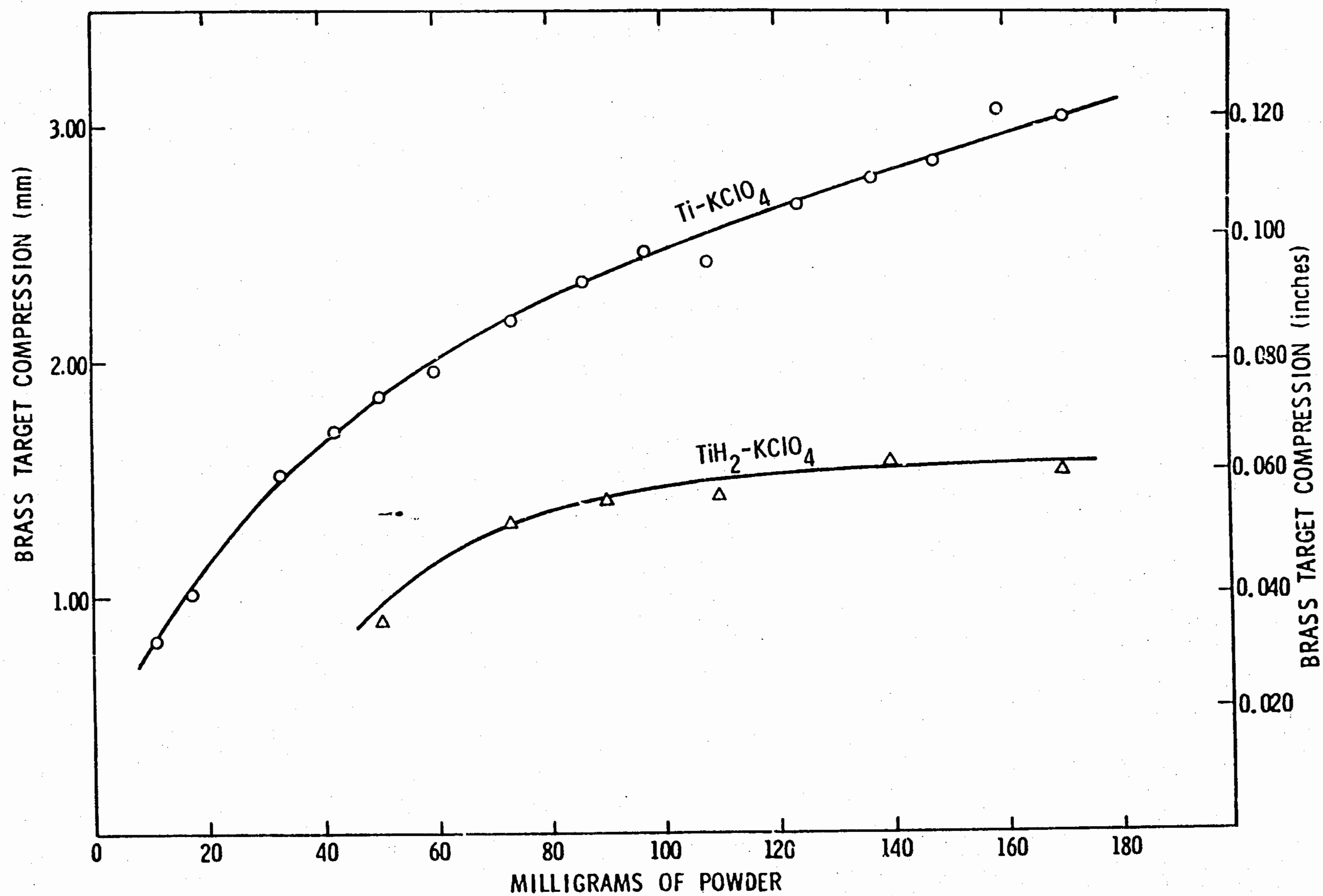

Figure 13. Target compression vs. weight of powder

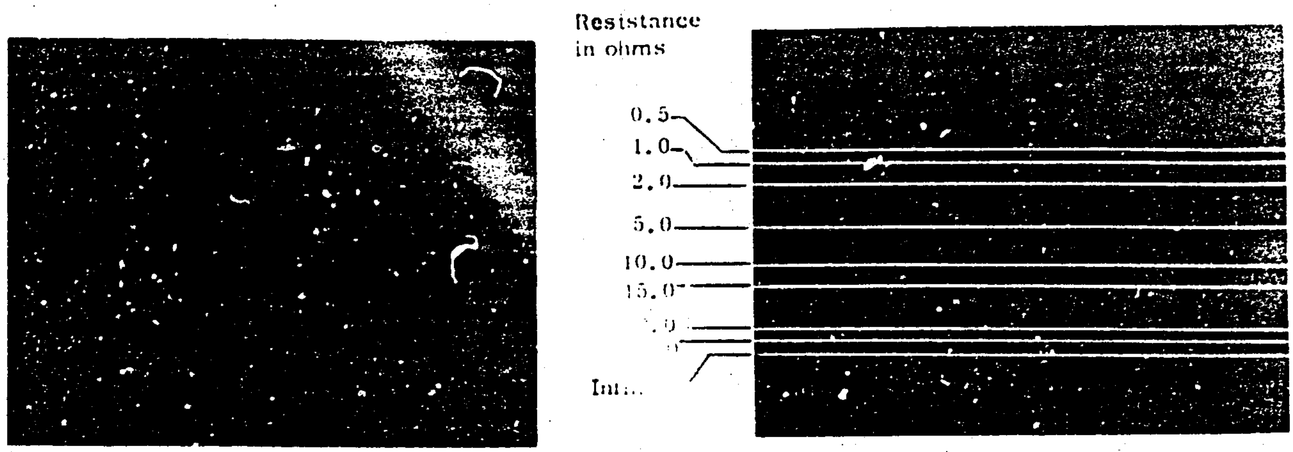

Figure 14. Resistance-after-fire (RAF) reco[illegible] an actuator containing TiH_2-$KClO_4$. (The oscillogram co[illegible] the first 20 milliseconds of the RAF record. The height of th[illegible]e above the base line is a measure of resistance. The flat por[illegible] of the record during the first 4-5 ms is a measure of bridge[illegible] resistance-one ohm. The photo to the right is the resistance ca[illegible]tion record. The photograph of calibration time marks is not [illegible]wn here).

The actuators were fired from a 3.5 ampere direct current so[illegible]. Twenty actuators of each type were tested. The minimum resistance observed for each gr[illegible] is given in Table XII.

TABLE XII

Minimum Resistance-After-Fire

Ti-$KClO_4$	0.01 ohms
TiH_2-$KClO_4$	2.0 ohms

Storage at Elevated Temperature -- One approach to the s[illegible] of the accelerated aging of a pyrotechnic powder is to hold the powder at elevated temperat[illegible] and then test for signs of degradation.

Loaded actuators were assembled into Mini-Flippe[illegible] and the assemblies were heated in a temperature test chamber at 373K±1K (100°C±1°C) for [illegible]ys (the assemblies were not hermetically sealed). The assemblies were then fired at ambient t[illegible]erature using a 3.5 ampere direct current source. Actuators containing Ti-$KClO_4$ or TiH_2-[illegible] fired properly and yielded a satisfactory output.

Powder removed from actuators conta[illegible] TiH_2-$KClO_4$ was tested for spark sensitivity as loose powder. The threshold for ignition w[illegible] found to be greater than 480 mJ. Thus the heating had not measurably increased the spark se[illegible]sitivity.

Thermal Output -- The thermal output of the powder in actuators was measured by firing the actuator by an electrical pulse while the actuator was assembled in a Mini-Flipper. Before ignition, the assembly was placed inside a Parr Adiabatic Calorimeter pressurized with argon. Temperature was measured by a quartz oscillator thermometer.* The data obtained, based upon a small number of measurements, is given in Table XIII.

TABLE XIII

Thermal Output of Actuators

	cal/g of Powder
Ti-$KClO_4$	1530 - 1700
TiH_2-$KClO_4$	1410 - 1750

Leads to Case Resistance -- The actuator internal resistance was measured by applying a constant DC voltage between the actuator leads (leads joined together) and the case. The voltage was increased in 50-volt increments, and maintained at each voltage for 15 seconds. Current flow was monitored by a 0-100 milliampere meter. During the test, the actuator was installed in a Mini-Flipper to maintain confinement of the powder.

When the above test was performed with TiH_2-$KClC_4$, two actuators ignited immediately upon application of 200 volts and two ignited immediately upon application of 250 volts. Four actuators loaded with Ti-$KClO_4$ fired upon application of 10 volts.

Experiments on High-Density Columns

Resistivity -- The resistivity (the resistance of a one cm cube measured across two opposite faces) of high density columns of powder may be determined by employing the relationship:

$$\rho = A\left(\frac{R}{\ell}\right)$$

where ρ is the resistivity, A is the cross sectional area of a column, R is the resistance of the column measured between the two ends, and ℓ is the length of the column.

The resistance of several different column lengths was measured using the technique sketched in Figure 15. The ohm meter used was one with a high impedance input. The column diameters were 5.61 mm (0.221 inch); column lengths were up to 10 mm (0.39 inch).

*Bomb calorimetry measurements made by T. M. Massis, 2516.

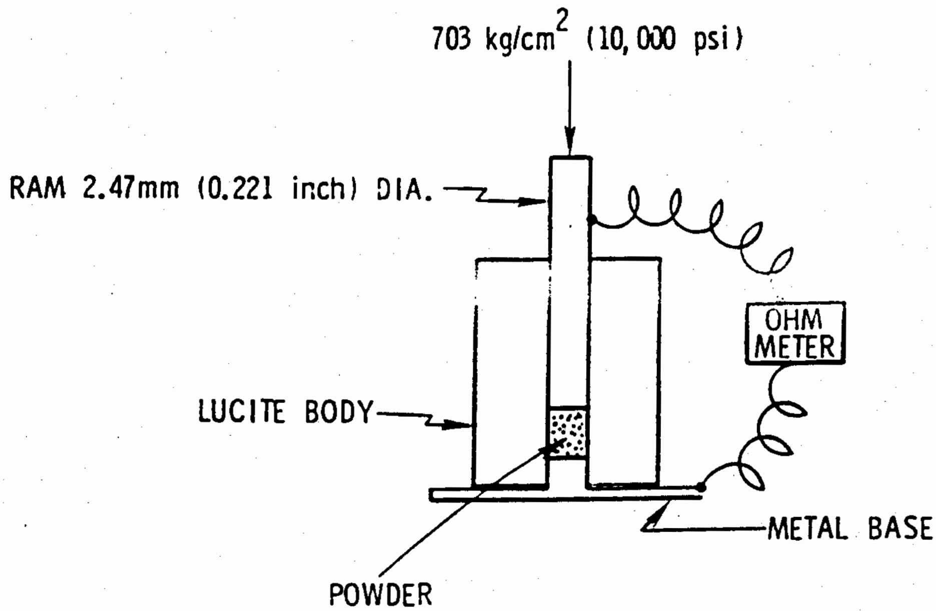

Figure 15. Apparatus for the measurement of resistivity

Average values of resistivity found are shown in Table XIV.

TABLE XIV

Resistivity of High Density Columns

$Ti\text{-}KClO_4$	1.0 ohm-cm
$TiH_2\text{-}KClO_4$	2500 ohm-cm

Propagation Velocity -- The propagation velocity of high density columns of powder was determined by measuring the time required by the propagation front to travel between two points in the column.

The powder was pressed into brass cylinders with an inside diameter of 5.61 mm (0.221 inch) and a wall thickness of 1.96 mm (0.077 inch). The powder was pressed in increments at a ram pressure of 703 kg/cm^2 (10,000 psi). A header with a one ohm Evanohm bridgewire was pressed into one end of the brass cylinder in order to initiate the column. A diagram of the apparatus devised for the propagation velocity measurements is shown in Figure 16. A small hole, 1.07 mm (0.042 inch) diameter was drilled through one wall of the cylinder, about 2 mm (0.08 inch) from the bridgewire. The hole was drilled before pressing the powder. The purpose of the hole was to allow light to escape when the propagation front passed this point along the column length. A portion of the light was collected by one end of a 0.64 mm (0.025 inch) diameter glass optical fiber located approximately 10 mm (0.39 inch) from the hole. The optical fiber conducted the light pulse to a photomultiplier tube which converted the light pulse to an electrical pulse (Figure 17). Thus, the electrical pulse announced the time of arrival of the propagation front at a specific point along the powder column. This technique is a modification of the photoelectric method for the measurement of the arrival of a detonation front in an explosive.

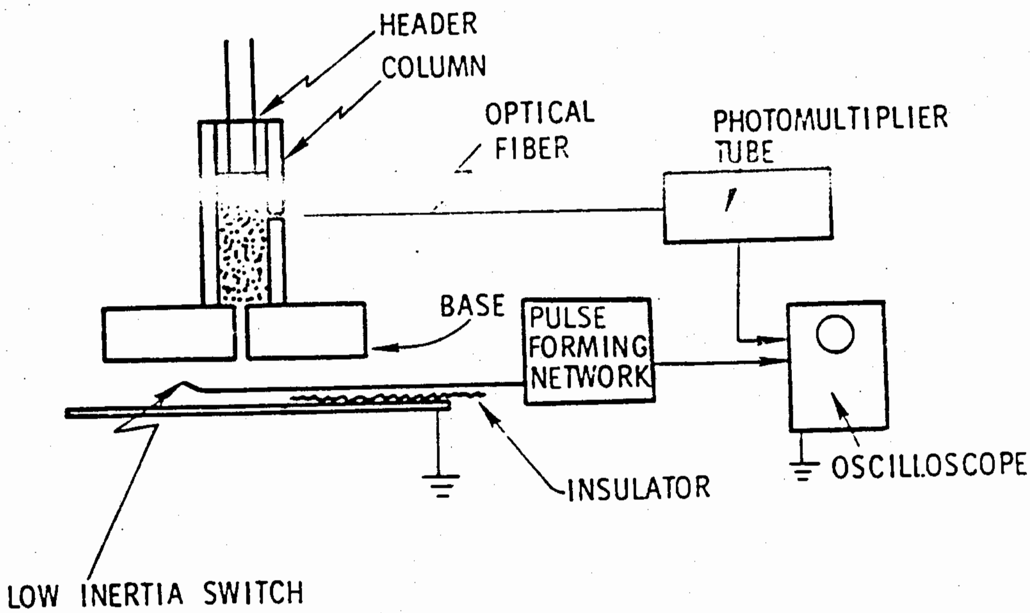

Figure 16. Apparatus for propagation velocity measurements of high density columns

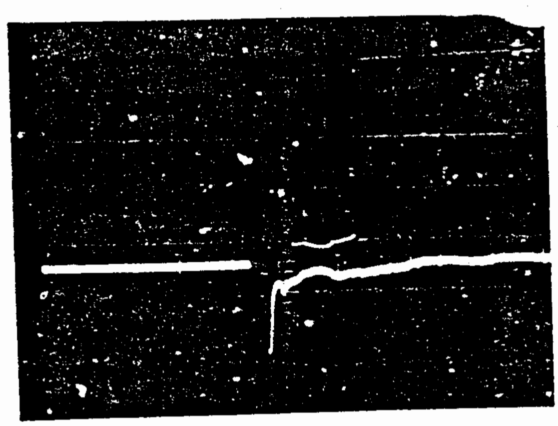

Figure 17. Oscillogram of a pulse from the photomultiplier (the pulse is generated by a light burst from the propagation front in the apparatus shown in Figure 16)

A low inertia electrical switch was located near the end of the powder column. The switch was closed by a jet of high pressure gas that escaped from a small hole at the end of the column when the propagation front reached that point. The closure of the switch generated an electrical pulse. The elapsed time between the photomultiplier pulse and the switch pulse (read from the oscilloscope record) was used to calculate the average velocity of the propagation front as it travelled through a measured length of column.

The entire assembly [illegible], column, [illegible] was tightly clamped together to maintain confinement during the burning of the powder.

Average values and ranges of propagation velocity measured on six 5 and 17 mm (0.200 and 0.669 inch) long columns are tabulated below.

TABLE XV

Propagation Velocity of High Density Columns

	Range	Average	Sigma
$Ti\text{-}KClO_4$	0.104 to 0.899 mm/µs	0.414 mm/µs	0.276 mm/µs
$TiH_2\text{-}KClO_4$	0.0370 to 0.200 mm/µs	0.117 mm/µs	0.057 mm/µs

Dent Tests -- To determine whether high density columns of powder propagate by a burning process, or by detonation, a series of tests were performed.

Columns of pyrotechnic powder were prepared by incremental pressing into 19.05 mm (0.750 inch) long brass sleeves having an inside diameter of 5.61 mm (0.221 inch). The wall thickness was 1.96 mm (0.077 inches); the pressure applied to the powder was 703 kg/cm^2 (10,000 psi). The columns were initiated by (a) a hot-wire actuator, or (b) a shock wave from an exploding wire detonator.

a) Hot-Wire Initiation -- A column of high density powder was placed on end on an aluminum block (Brinell 95-100; 500 kg weight).* An actuator (prepared as described in "Experimental Actuators," page 11) was placed against the opposite end of the column. The assembly was securely clamped together to maintain confinement during the burning of the powder. A sketch of the assembly is shown in Figure 18. The actuator (prepared with the same powder as used for the column) was initiated with a 3.5 ampere direct current pulse. After firing, the depth of the dent produced in the aluminum block was measured.

---

*Initial experiments performed with columns of $Ti\text{-}KClO_4$ and $TiH_2\text{-}KClO_4$ showed that the wall thickness of the brass sleeves was not adequate to maintain confinement during burning of the long column. Therefore, for these hot-wire initiation tests, the brass sleeve was slipped into a close-fitting brass sleeve of 25.4 mm (1.00 inch) outside diameter.

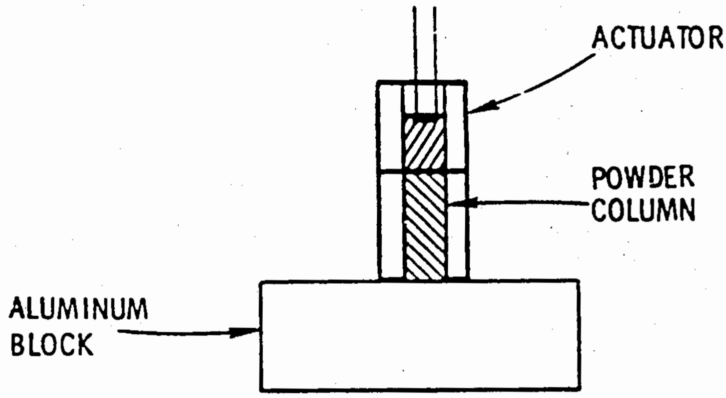

Figure 18. Apparatus for dent measurements of high density columns

TABLE XVI

Hot-Wire Initiation of High Density Columns

Powder	Column Density (g/cm^3)	Dent in Aluminum (mm-inches)	Type of Propagation Through Column
$Ti-KClO_4$	1.93	0.79* - 0.031*	burning
TiH_2-KClO_4	2.23	1.40* - 0.055*	burning
NLS	2.40	0.33 - 0.013	detonation

*These values are not the depth of the usual dents observed in explosive diagnostic studies, but are the depth of annular cavities that were eroded by high pressure-high temperature gases escaping from the confined sleeve. A photograph of a cavity is shown in Figure 19; a usual type dent is shown in Figure 20.

b) Shock Wave Initiation -- A column of high density powder (prepared as described in "Dent Tests," page 30) was placed on end, on an aluminum block (Brinell 95-100; 500 kg weight) or on a mild steel block (Brinell 153-156; 3,000 kg weight). A PETN exploding wire detonator containing a high density tetryl output pellet [7.6 mm (0.300 inch) diameter] was placed against the opposite end of the column. The assembly was held together using pressure sensitive tape. The assembly was similar to that shown in Figure 18. The detonator was initiated with a high voltage capacitor discharge firing system. After firing, the depth of the dent in the aluminum or steel block was measured. For comparison purposes, tests were also made with normal lead styphnate (NLS) and PETN. Measurements also were made with an inert column (Ti-KCl) to measure the degree of transmission of the shock wave from the tetryl pellet through the confined high density column.

A data summary is given in Table XVII.

Figure 19. Annular cavity eroded in aluminum by high temperature-high pressure gases from the burning of a confined column of TiH_2-$KClO_4$. (The cavity is approximately 14 mm [0.56 inch] in diameter).

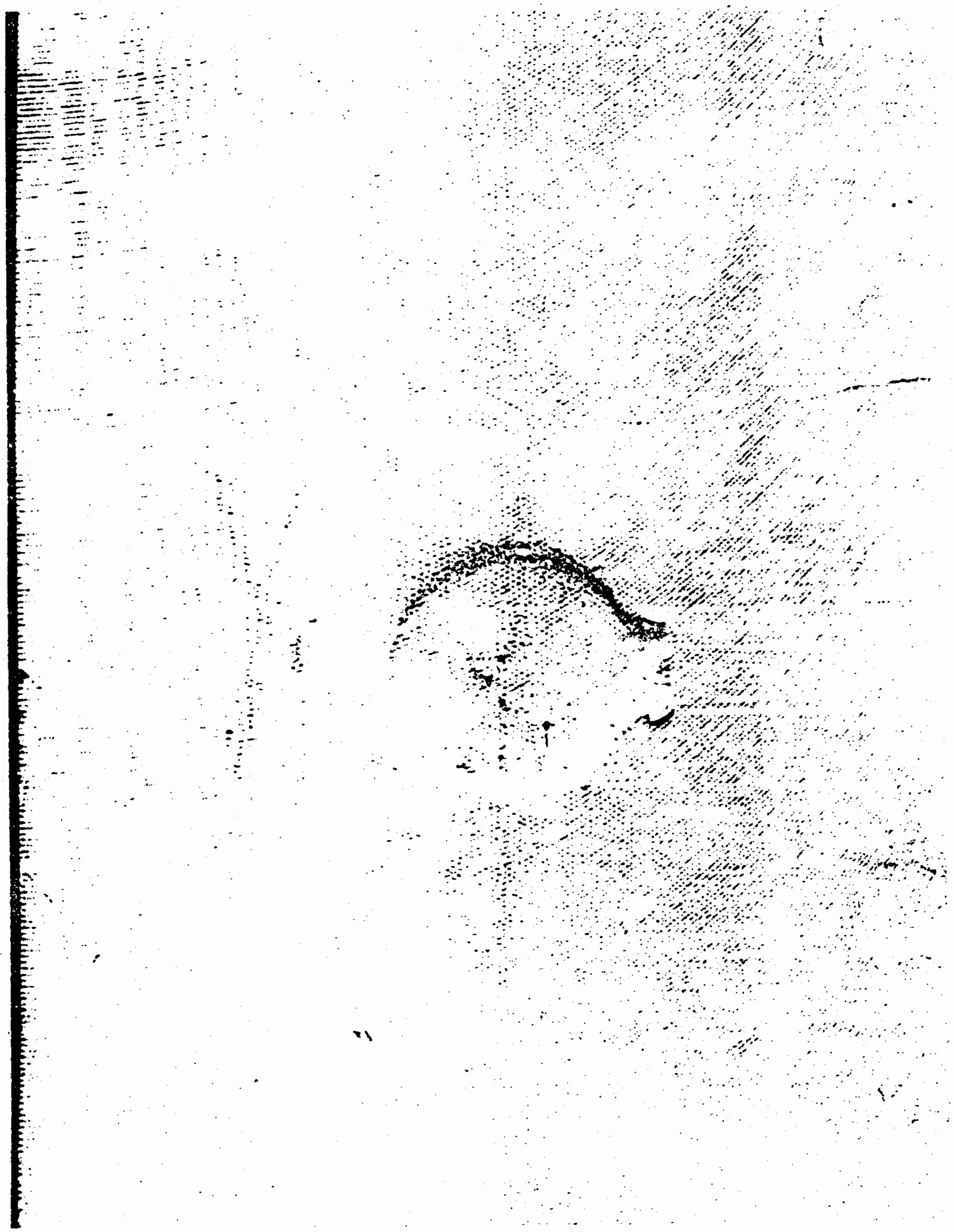

Figure 20. Dent in aluminum produced by a detonating column of normal lead styphnate. (The dent is approximately 6 mm [0.24 inch] in diameter.

TABLE XVII

Shock Wave Initiation of High Density Columns

Powder	Column Density (g/cm^3)	Type of Block	Dent in Block (mm - inches)	Type of Propagation Through Column
Ti-KCl	1.83	Aluminum	0.13 - 0.005	inert
$Ti-KClO_4$	1.93	Aluminum	0.61 - 0.024	detonation
TiH_2-KClO_4	2.23	Aluminum	0.28 - 0.011	detonation (*)
NLS	2.40	Aluminum	3.05 - 0.120	detonation
PETN	1.60	Aluminum	4.06 - 0.160	detonation
NLS	2.40	Steel	0.97 - 0.038	detonation
PETN	1.60	Steel	1.73 - 0.068	detonation

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III. Discussion

Titanium hydride-potassium perchlorate as an actuator or squib loading powder is similar to Ti-$KClO_4$ in performance. The outstanding difference is the fact that TiH_2-$KClO_4$ as loose powder is very insensitive to initiation by static electricity, while Ti-$KClO_4$ can be initiated by a few millijoules. Both mixtures have a very high autoignition temperature. Another difference is that TiH_2-$KClO_4$ has less output energy than Ti-$KClO_4$ (about 58 percent of the output of Ti-$KClO_4$ for actuators containing 110 mg of powder).

The combination of spark insensitivity and high autoignition temperature could make TiH_2-$KClO_4$ a very useful actuator material. If this material has a disadvantage when compared to other materials it is that it must be well confined in order to propagate properly. The confinement can be attained by the addition of a suitable closure disc at the output end of the actuator. It actually may be possible to make use of this disadvantage in designing a new type of safing system for the actuator, that is, the actuator could, (1) be rendered safe or disabled by removing confinement, or (2) be armed by adding confinement to a normally unconfined unit.

Another possible disadvantage is that the actuator can be initiated by 200 volts continuously applied between bridgewire and case. This could probably be eliminated by the insertion of an insulating sleeve in the actuator cavity.

Both Ti-$KClO_4$ and TiH_2-$KClO_4$ are powders that are easily loaded into the pressing die and press smoothly without binding or galling the pressing fixture.

Both Ti-$KClO_4$ and TiH_2-$KClO_4$ appear to be stable materials at temperatures above ambient as judged from the modest experiment involving storage at 373 K (100°C) for 30 days and the DTA measurements. It has been reported that TiH_2 begins decomposing at 623 to 653 K (350 to 380°C).[14,15]

The minimum resistance-after-fire (RAF) of an actuator containing TiH_2-$KClO_4$ appears to be considerably better than an actuator containing Ti-$KClO_4$ judging from the data presented in this report. This may seem surprising when it is considered that the reaction products are probably the same for both actuators (in the case of TiH_2-$KClO_4$, water also is formed which might cause RAF to be lower). However, the value of RAF obtained when an actuator is fired depends not only upon reaction products, pin spacing, header materials, etc., but also upon chance. It will be necessary to measure a large number of actuators before a lower limit for a value of RAF can be stated with confidence. The values of RAF reported here are maximum values of the lower limits.

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The values of resistivity in this report are of interest since they are not usually determined for actuator materials. The technique devised gave very exact values of resistivity for each instantaneous measurement. However, as constant pressure was maintained on the column, the value of resistance displayed by the ohm meter slowly changed (usually toward a larger value) and sometimes suddenly shifted to a lower value. When the pressure was released and immediately reapplied the resistance value was usually higher.

The decrease in resistance could be explained by the fact that friction between the column and the wall of the die as well as internal friction between grains of powder was being overcome. This resulted in a column of slightly higher density. The increases in resistance might be explained by chemical changes produced at particle boundaries by the current applied to the column by the ohm meter, even though the current was only a few milliamperes. The values of resistivity reported are the average of many readings.

The values of resistivity were an early indication that Ti-$KClO_4$ filled actuators would have low leads-to-case resistance and that TiH_2-$KClO_4$ actuators would be marginal. A common requirement for actuators in weapon systems is that the powder resistance must not be less than 10, 000 ohms when 500 volts DC is applied between bridgewire and actuator case. The tests conducted in "Leads to Case Resistance," Page 27, showed that actuators filled with either powder could not meet this requirement.

We believe that the technique developed for the measurement of the average velocity of a propagation front through a high density column of powder gave values that are valid to at least three significant figures. However, a spread of velocity data was obtained when the measurement was made several times (see Table XV). As a model, one might visualize a propagation front originating at the bridgewire when a column is ignited and then progressing uniformally along the column until the column is consumed. Such a model would be similar to the accepted model for a movement of a deflagration front along a column of propellant. Perhaps a more realistic model might be that a propagation front originating at the bridgewire generates high temperature-high pressure gas which seeks an outlet through fissures and local low density areas in the column as well as lower flow resistance areas at the column-brass cylinder interface. Such jets would ignite unburned powder as they travel forward thereby aiding their progress by the local generation of even higher pressures. These jets might reach the end of the column before all of the powder is consumed, and the measurement of propagation velocity then really would be a measurement of the progress of jets through and along the side of the column. This progress could be a random and nonuniform event and therefore yield the varying velocity data observed. The fact that high pressure-high temperature gas is generated by the burning of Ti-$KClO_4$ and TiH_2-$KClO_4$ is evident in Figure 19 as well as in other experiments not reported here.

The aluminum and steel block dent tests described in "Dent Tests," Page 30, were conducted to determine under what conditions the actuator powders could be caused to detonate. The data show that neither Ti-$KClO_4$ nor TiH_2-$KClO_4$ in highly confined high density columns detonated when initiated by a hot wire. However, when a column of Ti-$KClO_4$ was initiated by a shock wave, the dent produced in an aluminum block indicated that the column did detonate. However, because the dent produced under the same test conditions with TiH_2-$KClO_4$ was not markedly deeper than the dent caused by the pressures transmitted by an inert powder (Ti-KCl), one should not conclude that TiH_2-$KClO_4$ detonated, nor conclude that it will not detonate.

Because normal lead styphnate (NLS) is a common actuator material and because there is controversy among those who work with actuators whether or not NLS detonates when initiated by a hot wire, this material was also included. It is known that NLS will detonate under proper conditions since a detonation velocity of 4.90 mm/μs (d = 2.6 g/cm^3) has been reported.[21]

The dents produced in the tests described here show that NLS can detonate under these conditions when initiated by either a hot wire or a detonation wave.

PETN was included in the test series since it is a standard reference explosive.

In conclusion, the data obtained from this study show that Ti-$KClO_4$ and TiH_2-$KClO_4$ are very similar actuator and squib powders in performance but with the outstanding difference that TiH_2-$KClO_4$ is remarkably less sensitive to spark initiation, and based on current models and on our experience, the test data are strong evidence that it would not be initiated by static electricity from the human body. It is recommended that TiH_2-$KClO_4$ be investigated further, (1) to determine the optimum ratio of titanium to hydrogen in the titanium hydride to be used, (2) to determine the optimum ratio of hydride to potassium perchlorate, (3) to determine optimum particle size of TiH_2 and $KClO_4$, and (4) to establish firmly its almost ideal properties for an actuator and squib material. As mentioned earlier, if TiH_2-$KClO_4$ is to be used in a development program, attention must be given to the potential problem of hydrogen embrittlement.

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