SAND96-1469C
CONF-960717--1

THE PROCESSING, PROPERTIES AND USE OF THE PYROTECHNIC MIXTURE- TITANIUM SUBHYDRIDE/POTASSIUM PERCHLORATE

Thomas M. Massis
Senior Member Technical Staff
Sandia National Laboratories
Albuquerque, New Mexico

Abstract

The processing, properties and use of the static insensitive pyrotechnic, titanium subhydride/potassium perchlorate are discussed. Development of this pyrotechnic occurred because of the need for a static insensitive material to meet personnel safety requirements and related system safety issues in nuclear weapon energetic material component designs. Titanium subhydride materials are made by the thermal dehydriding of commercial titanium hydride powder to the desired equivalent hydrogen composition in the titanium lattice. These titanium subhydrides, when blended with potassium perchlorate, meet the static insensitivity requirement of not being initiated from an equivalent human body discharge. Individual material and blend qualification requirements provide a reproducible material from lot to lot. These pyrotechnic formulations meet the high reliability requirements (0.9995) for initiation and performance parameters and have the necessary stability and compatibility to meet long lived requirements of more than 25 years. Various experiences and problems will also be discussed that have led to a mature technology for titanium subhydride/ potassium perchlorate during its use in energetic material component designs.

Introduction

In the early 1970s, a policy decision was made at Sandia National Labs that primary explosives, mainly lead azide and lead styphnate, would not be used in future energetic material weapon designs because of the safety issues associated with such materials. These included personnel safety in regards to the handling/processing of primaries in the bulk and within components, plus safety issues during the use of such materials in loaded devices for nuclear weapon component designs. The main concern was the accidental initiation of these materials by electrostatic discharge (ESD) from a human body.

This decision was followed by an increased use of pyrotechnic mixtures, mainly titanium/potassium perchlorate ($Ti/KClO_4$). Pyrotechnics such as titanium/potassium perchlorate are static sensitive, especially in the bulk powder form, but show reduced static sensitivity when pressed into a component. This is especially true when component static breakdown protection measures are also used such as header bleeder resistors and external spark gaps.

In 1974, it was found that titanium hydride/potassium perchlorate ($TiH_2/KClO_4$) was insensitive to initiation from a human body electrostatic discharge.[1] This included the bulk and pressed forms of $TiH_2/KClO_4$. Human body electrostatic sensitivity was defined as initiation from by an electrostatic pulse from a 600 picofarad capacitor charged to 20 kilovolts and discharged through a 500 ohm series resistance. It is called the standard man ESD test. Subsequent ESD tests with $TiH_2/KClO_4$ using discharge voltages in excess of 40 kilovolts have never initiated this pyrotechnic. The upper voltage or energy for ESD sensitivity is not known.

Initial component actuator and igniter designs with $TiH_2/KClO_4$ found this material to function well, but a number of low-temperature (less than 219°K) ignition failures occurred.[2] In addition, stability and compatibility tests with $TiH_2/KClO_4$ measured an instability of this mixture at higher temperatures that might limit its use for long lived applications in excess of 25 years.[3] Compatibility tests, to be discussed later, in component hardware also indicated that the reaction products from this instability, chloride ions and water, were cause for the potential problems with the header pins and bridgewires.[3]

An experimental program was started to determine if removing hydrogen from the titanium lattice in titanium hydride would still provide ESD insensitivity while providing ignition reliability. Additional stability work with $TiH_2/KClO_4$ found that pretreating the titanium hydride at temperatures of 450°K (177°C) prior to blending improved the stability of the mixture to that approaching $Ti/KClO_4$.[3] Based upon these data, titanium subhydride/potassium perchlorate mixtures were predicted to be stable and compatible. An active development program was started between

---

This work was supported by the United States Department of Energy under Contract DE-AC04-94AL85000.

Sandia and Monsanto Research Corporation, Mound Labs, Miamisburg, Ohio, to produce titanium subhydrides, TiH_x. This work produced titanium subhydrides with equivalent hydrogen concentrations from 0.45 to 1.70 (or $TiH_{0.45}$ to $TiH_{1.70}$). ESD studies with these materials blended with $KClO_4$ measured human body static insensitivity until the equivalent hydrogen concentration dropped to a nominal value of $TiH_{0.60}$.[2] At this nominal TiH_x value, ESD sensitivity dropped rapidly, approaching that of Ti/$KClO_4$. A typical ESD sensitivity curve verses titanium lattice hydrogen concentration is shown in Figure 1. Note the sharp break in the curve from being ESD sensitive to ESD insensitive around the $TiH_{0.60}/KClO_4$ composition.

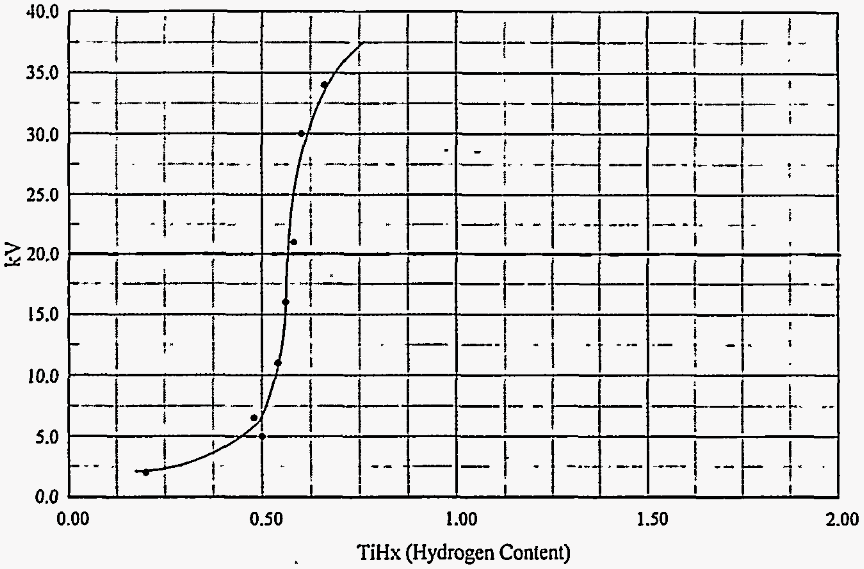

Figure 1: Electrostatic Spark Discharge (ESD) Sensitivity verses Hydrogen Content in Titanium

It was also found with these titanium subhydrides that the thermal stability of the pyrotechnic increased as the of hydrogen concentration in the titanium lattice was lowered.[3] These data are shown in Figure 2. Ignition reliability at low temperatures also improved to meet requirements, while maintaining the same output performance.

Based on this development work with titanium subhydrides, various component designs using $TiH_{0.65}/KClO_4$ have been produced until the present. In the early 1980s, ESD requirements to meet a 0.9995 reliability were imposed on Sandia actuator designs. $TiH_{0.65}/KClO_4$ was near the break point of the ESD curve. It was decided that $TiH_{0.65}/KClO_4$ may not meet this new requirement, especially if the TiH_2 particle size decreased slightly (see later discussions regarding this influence on ESD sensitivity). To meet this requirement, the equivalent titanium hydrogen concentration was increased to $TiH_{1.65}$. This produced a titanium subhydride with the proper phase composition (see later discussions on material characteristics that lead to ESD insensitivity), plus maintained the necessary ignition reliability, output and long term stability necessary for Sandia components. $TiH_{1.65}/KClO_4$ is presently used in all actuator designs at Sandia.

Materials

Titanium Hydride

Titanium hydride used for the dehydriding process was commercially procured powder from the Ventron Corporation, Beverly, Massachusetts. Of the titanium hydride manufacturers, Ventron was the only producer found that met the particle size/surface area requirements necessary for TiH_x production.

In 1994 Ventron sold their titanium hydride process to Chem Metal, Hanau, Germany. Recent use of Chem Metal's titanium hydride as a pyrotechnic fuel with

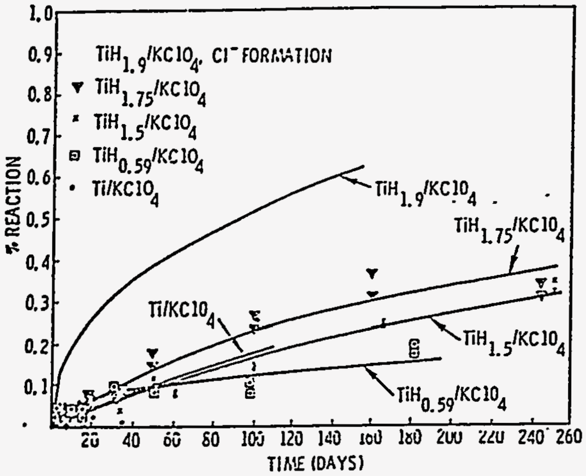

Figure 2: Stability of $TiH_x/KClO_4$
(Chloride Formation at 100°C)

potassium perchlorate in non-DOE applications has resulted in less than satisfactory results.[4] The particle size distribution of Chem Metals product is somewhat larger, and the surface area lower, than Ventron's 2 micron TiH_2. This larger material is questionable for reliable performance as a pyrotechnic fuel (see discussions below).

Titanium hydride was procured from Ventron as their standard 2 micron average particle size powder. Subsequent particle size distribution analyses using the Coulter Counter technique confirmed this material to be 2 micron titanium hydride. It was found that the most important size parameter was not the particle size distribution but the BET surface area of the powder. Similar particle size distributions of various 2 micron TiH_2 powder lots would measure significant differences in BET surface area. Sandia's titanium hydride specification addresses the surface area requirements to produce TiH_x for reliable performance as $TiH_x/KClO_4$.[4]

Titanium hydride surface areas that are too low, less than 2 meters squared per gram (m^2/gm), will produce TiH_x pyrotechnic blends that have low temperature ignition reliability problems. Powders with surface areas too high, in excess of 6 m^2/gm, are potentially pyrophoric when dry and exposed to air. In addition, they off gas hydrogen in small amounts which can present an additional safety hazard. The ideal TiH_2 powder was found to have BET surface areas from 2.5 to 4 m^2/gm.

Supplier manufacturing techniques to produce fine particle TiH_2, grind titanium hydride sponge in an inert liquid to the desired particle size. The resulting morphology is a spherical shaped particle with few if any re-entrant voids that would increase the surface area.

Titanium Subhydride (TiH_x)

All DOE titanium subhydride powders are produced by the thermal decomposition of titanium hydride powder to the desired hydrogen composition. The direct hydriding of titanium powder to the desired TiH_x composition was attempted, but resulted in variable hydrogen compositions throughout the TiH_x powder bed. It appears that the oxygen coating on the titanium powders inhibits the uniform diffusion of hydrogen into the titanium lattice of a powder bed in reasonable lengths of time.

The dehydriding process of TiH_2 to the desired titanium subhydride composition was able to be controlled to +/-0.06 of the "x" composition of TiH_x within a single powder bed.[6,7] Samples are taken "side-to-side" and "top-to-bottom" within a powder tray for each lot produced for hydrogen analyses and are specified to meet the +/-0.06 "x" composition.[6,7] An acceptable bulk TiH_x composition for pyrotechnic production must be within +/-0.03 of the desired hydrogen composition when the powder lot is made uniform by tumbling methods and sampled.

$TiH_{0.65}$ and $TiH_{1.65}$ are produced by different dehydriding processes. $TiH_{0.65}$ is produced by the thermal decomposition of TiH_2 under vacuum for 24 hours at a nominal temperature of 430°C .[8] The temperature is then allowed to drop to room temperature for a few additional hours to make uniform the hydrogen composition. The vacuum process is necessary to produce $TiH_{0.65}$. If traditional closed volume PVT procedures are used that measure the amount of hydrogen being evolved to achieve the desired hydrogen composition, the temperature is too high, greater than 450°C, and significant sintering occurs. This increases the particle size, reduces the surface area and renders the subsequent powder useless for pyrotechnic use.

$TiH_{1.65}$ is produced by thermal decomposition procedures using the traditional closed volume PVT method. The dehyriding temperature is low enough to minimize sintering. The dehydriding temperature is similar to that for making $TiH_{0.65}$, a nominal 430°C. The pressure is monitored in a calibrated volume until the predetermined evolved hydrogen pressure is measured indicating the desired TiH_x composition. There are similar stoichiometry requirements for the powder trays within the reactor and the bulk $TiH_{1.65}$ as there are for $TiH_{0.65}$.[7]

Both $TiH_{0.65}$ and $TiH_{1.65}$, following dehydriding, require controlled passivation (oxidation) of the subhydride surfaces. If this is not done, removal of the subhydrides from the reactors and exposing them to atmospheric oxygen will result in thermal ignition of the powders due to the rapid reaction of the exposed titanium surfaces with air. They are pyrophoric if not passivated.

Air is added to the reactor in controlled amounts and the pressure monitored. The pressure will decrease due to the reaction of titanium with oxygen during passivation. Additional controlled volumes are made until there is no further pressure drop. The powders can then be safely removed from the reactor without the hazard of a pyrophoric reaction.

The oxygen content for titanium subhydrides powders is typically 2.5 to 3.0 weight percent. Analysis for total oxygen on the titanium subhydride powders is made for control of the production process, theoretical calorific output calculations of the pyrotechnic compositions and sometimes for performance calculations. All titanium, titanium subhydride and titanium hydride powders are analyzed for total oxygen. Nuclear activation analysis for total oxygen was the most available method but there were other techniques and provided similar results.

Figure 3 is the titanium/hydrogen phase diagram.[9] The subhydride material produced is a mixture of the alpha/gamma phases over the temperature ranges of typical use and interest. After production, the following bulk powder properties are measured for control of the process (Table 1).

Table 1

TiHx Bulk Property Measurements
Hydrogen Content
Oxygen Content
Titanium Assay
Impurity Content
Particle Size Distribution
BET Surface Area
Moisture Content

For both $TiH_{0.65}$ and $TiH_{1.65}$, the combined hydrogen, oxygen and titanium contents must exceed 99%. The impurity content must not be greater than that found in the titanium hydride lot used for the dehydriding process.

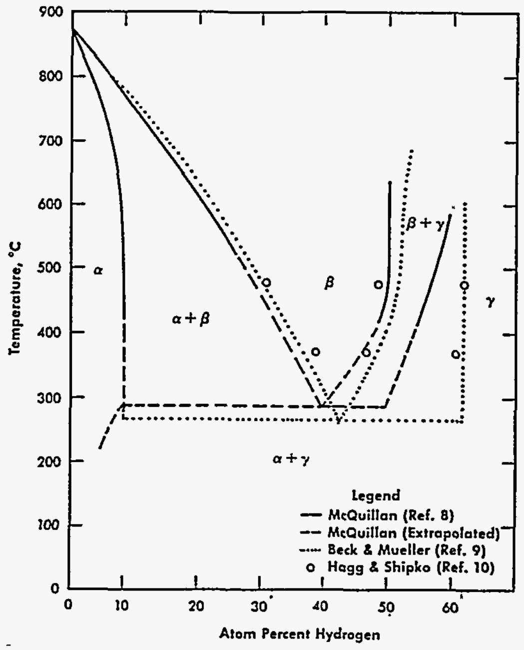

Figure 3
Equilibrium Titanium-Hydrogen Phase Diagram

During dehydriding, slight sintering of the subhydrides occurs. There is a small increase in the particle size distribution and decrease in surface area. For the current lot of titanium hydride used, the initial surface area is a nominal 2.64 m^2/gm while the resulting surface areas are reduced to 1.65 m^2/gm and 2.00 m^2/gm for $Ti_{0.65}$ and $TiH_{1.65}$ respectively.

The produced subhydride powders, are sieved through a 400 mesh (36 micron opening) sieve prior to pyrotechnic use and stored desiccated. Because of their uniform exterior surfaces. less than 0.1% moisture pickup is observed at 90 % relative humidity. Compare this to 2 micron pyrotechnic grade titanium powder that can pickup over 0.6% moisture at 90% relative humidity.

The storage life of the subhydride materials prior to blending with potassium perchlorate is indefinite.

These subhydride powder blends are made in 150 gram lot sizes for DOE applications because there is no need for larger lot sizes. The lot production size of these materials could be scaled up to many kilograms if needed.

Original production of the subhydride materials was made at the Mound Facility in Miamisburg, Ohio, a DOE production facility. They have been available for sale to the DOD and private sector. Mound has subsequently closed all production due to DOE downsizing. A privatization effort in the Miamisburg area has resulted in the following company being formed for the commercial production of titanium subhydrides.

Wheatville Technology, Inc.
Dr. Richard S. Carlson
5265 State Route 122 South
West Alexandria, Ohio 45381

This is the only company known that now produces titanium subhydride materials for pyrotechnic use. Dr. Carlson was the inventor of the TiH_x processes.

Potassium Perchlorate

All pyrotechnic titanium subhydride compositions have used potassium perchlorate ($KClO_4$) as the oxidizing agent. For DOE applications, the $KClO_4$ used is a commercially procured powder at the required particle size distribution.[10] The nominal 50th percentile of the number particle distribution using the Coulter Counter technique has been 6.0 microns maximum. This is approximately 2-3 times coarser than titanium/titanium subhydride particle size data.

KClO4 which is coarser than 6 microns degrades (lowers) pyrotechnic performance. Actuator output will be out of specification when the particle size exceeds the specified distribution.[11] Finer $KClO_4$, (approaching an average 3 micron particle size), results in a material that has handling problems such as static charging and agglomeration.

The $KClO_4$ purity exceeds 99% with a maximum allowable chloride ion impurity of 100 parts per million (PPM). Past and current lots of $KClO_4$ have had chloride contents of less than 40 PPM. Chloride contents have been a source of concern because of a past corrosion problem in an actuator that was attributed to chloride contamination. It was our desire to minimize the presence of chloride containing materials in pyrotechnics.

Any $KClO_4$ can be used and ground to the desired particle size to meet performance requirements. Our quantity needs were minimal. Commercially purchasing the KClO4 at the desired particle size distribution, eliminated another processing procedure. The only supplier to be able to meet our specification requirements has been Barium and Chemicals, Inc., Stubenville, Ohio.[11] Numerous attempts over the years to find another supplier have proved to be unsuccessful.

Titanium Subhydride/Potassium Perchlorate (TiHx/KClO4)

All titanium subhydride/potassium perchlorate ($TiH_x/KClO_4$) pyrotechnic compositions have been blended to a 33/67 weight percent fuel/oxidizer ratio.[12] These pyrotechnics are oxidizer rich by design to insure that the fuels all oxidize during function. This minimizes the chance for metallic fuel residues being deposited between the header pin posts after functioning. Such residues could lead to conductance-after-fire conditions that lead to unwanted power source drawdowns. Mid-1970 output performance measurement techniques also indicated optimization at the 33/67 composition. The 33/67 composition has been used to the present.

Sandia pyrotechnic compositions, including $TiH_x/KClO_4$, have been blended dry and without a binder such as Viton. To maximize pyrotechnic output impulse, it was decided in the beginning not to use a binder. An inert binder, such as Viton, enters in the reaction, burns at a slower rate with potassium perchlorate and does not provide any early impulse advantage (as do the titanium subhydrides) during actuator applications.

Dry blending procedures were used from the beginning though wet blend procedures could have been used. Our process, tumbles the titanium subhydride and potassium perchlorate materials in a ribbed conductive container that interrupts the tumbling action for a better blend. This mixture is then sieved through a 400 mesh sieve and then re-tumbled.

The existing process is totally remote and produces blend lots of 150 grams.[13] It can readily be scaled up if necessary with no upper limit. Over 250 blends have been made and qualified for DOE production use. There never has been a safety incident or accident with these pyrotechnic blends.

Unpublished blend homogeneity studies using scanning electron microscopy (SEM) show the individual potassium perchlorate particles to be uniformly coated with the titanium subhydride particles to less than a bridgewire diameter

(50 microns or 2 mils). There has never been an ignition failure attributed to blend non-homogeneity like chromate containing pyrotechnic devices. Qualification of a blend consists of calorific output, blend ratio composition, chloride ion content, thermal analysis and moisture content.[12]

The calorific output in an inert atmosphere is required to be no more than 100 calories below the theoretical calorific output calculation based upon the following reaction. Calorific output measurements have always been above theoretical calculations and is probably due the oxygen present not totally as TiO_2.

$$2TiH_x + (1+0.25x)\, KClO_4 \longrightarrow 2TiO_2 + (1+0.25x)KCl + xH_2O$$

Table 2 lists the necessary heat of formation data for the theoretical calorific output calculation. For the calculation, the measured oxygen content of the fuel must also taken into consideration. It is assumed to be present as TiO_2 and reduces the available TiH_x content accordingly.

Table 2

Heat of Formation Data for $TiH_x/KClO_4$ Formulations

$KClO_4$	-103.6 kcal/mol
TiH_2	-30 kcal/mol
$TiH_{0.65}$	-11 kcal/mol
$TiH_{1.65}$	-27.9 kcal/mol
TiO_2	-218 kcal/mol
KCl	-104.2 kcal/mol
H_2O	-68.3 kcal/mol

Table 3 lists the typical calorific output measurements obtained for four (4) production lots of $TiH_{1.65}/KClO_4$ qualified and used for production. This shows the blend reproducibility of DOE product.

Table 3

Calorific Output Data for $TiH_{1.65}/KClO_4$

Blend No.	Measured Output (cal/gm)	Theoretical Output (cal/gm)
PC137	1614	1552
PC146	1602	1547
PC148	1617	1544
PC149	1602	1544

The blend composition is determined by actually analyzing for titanium and potassium perchlorate. Limits of the blend composition are 33+/-1% for the fuel and 67+/-1% for the oxidizer.

Sandia philosophy for blend performance has been to analyze for and control the properties of the individual materials prior to blending and analyze for the critical parameters after blending. This has led to reproducible pyrotechnic blends, with much less than one percent blend rejection rates; which meet critical performance requirements for the application required.

Pyrotechnic Properties

Over the years, numerous properties of the $TiH_x/KClO_4$ compositions have been measured to help our understanding these materials. Over 150 publications or presentations have been made regarding $TiH_x/KClO_4$ since its inception in the middle 1970s.

Output

The confined burn temperature of $TiH_x/KClO_4$ compositions is around 4000°K.[14] At these temperatures the products of reaction are solid oxides of titanium, gaseous potassium chloride and gaseous water. The primary contribution to gaseous output is the potassium chloride. In a closed, zero volume condition, pressures in excess of 100Kpsi are generated from a 100 milligram charge in an actuator configuration.[14] Potassium chloride melts at 776°C and boils around 1500°C.

Functional output such as the ability to function a valve, stroke a piston, drive a knife blade or ignite a pyrotechnic train is not strongly influenced by "x" in the titanium subhydrides.[2] Particle size or surface area is the property parameter for performance, both ignition reliability and output.

Accurate burn rate measurements in an application have not been determined for all fuel compositions in the same design and conditions. Work by Hingorani-Norenburg, which has application to actuators, indicated that the burn rate of $TiH_{1.65}/KClO_4$ was around 700 meters per second in a packed column tube at 70% theoretical density.[15] It is known that open burning of these pyrotechnics measured burn rates of $Ti/KClO_4$ to be 4-5 times faster than $TiH_{0.65}/KClO_4$ and about 7-8 times faster than $TiH_2/KClO_4$.[1,16,17] Function times for 100 milligram actuator designs are less than 500 microseconds from bridgewire pulse to peak pressure output in a limited free volume.[14,18]

General postulations of burn rate studies indicate that the burn rates of $TiH_x/KClO_4$ decrease with increasing hydrogen content with the function times for most applications less than 500 microseconds for a 100 milligram actuator design.

Electrostatic Discharge Sensitivity

Previous paragraphs, discussed introductory remarks regarding ESD sensitivity of $TiH_x/KClO_4$ materials. ESD sensitivity is influenced by a number of material properties. The first is the microstructure of TiH_x (Figure 3). Healy and Lieberman showed that near x=0.65, the Ti-H system exhibits a eutectoid structure where excess alpha titanium exists.[19] Above 0.65, excess of the gamma titanium phase exists. It has been established that static sensitive materials are those that contain excess of the alpha titanium phase and the opposite for static insensitive materials.

The second property that influences static sensitivity is the particle size/surface area of the TiHx. The smaller the particle size or higher the surface area, the greater the ESD sensitivity.[2] This shift is quite significant. $TiH_{0.65}/KClO_4$ with a $TiH_{0.65}$ surface area of 2-3 m^2/gm has an ESD sensitivity in excess of 30 kilovolts whereas the same material with a surface area of over 6 m^2/gm has an ESD sensitivity of around 8 kilovolts.[2] The particle size of the $KClO_4$ does not influence the ESD sensitivity.

Previous work by Collins, has shown that ESD sensitivity was primarily a function of the partial pressure of oxygen around the titanium and titanium subhydride.[20] The lower the partial pressure of oxygen, the more ESD insensitive the pyrotechnic. This was the main influence on static sensitivity. The presence of potassium perchlorate was found to inhibit the sensitivity of the TiH_x materials. TiH_x by itself was more ESD sensitive than the mixtures with $KClO_4$. This work by Collins helps explain the reduced static sensitivity of pressed of ESD sensitive materials such as $Ti/KClO_4$ and $Zr/KClO_4$..

In recent years, Sandia has adopted a second test model for ESD testing. This procedure, called the Sandia severe man test or Fisher test, simulates a body/hand ESD discharge model. A much faster rise time of the ESD pulse occurs, followed by a slower pulse that closely matches the standard man test previously mentioned. Table 4 compares the parameters of each test.

Table 4

Comparison of the Sandia Standard Man
and
Fisher or Severe Man ESD Models

	Standard	Fisher
Voltage	20 kv	25 kv
Resistance	500 ohms	360 ohms
Capacitance	600 pf	410 pf
Inductance	NA	0.6 µhenries

Production $TiH_{0.65}/KClO_4$ and $TiH_{1.65}/KClO_4$ pyrotechnic blends were found to be ESD insensitive when tested to the Fisher model as well as the standard man model.

$TiH_x/KClO_4$ materials with x>0.60 are ESD insensitive and offer advantageous safety properties when used. Compare this to materials such as $Ti/KClO_4$ and $Zr/KClO_4$ where ESD voltages of much less than 5 kilovolts will readily ignite and function these materials. Note, that zirconium hydride and its subhydrides are also static insensitive.

Ignition Sensitivity

All $TiH_x/KClO_4$ materials have been found to have reliable ignition sensitivity if powder density and contact are maintained at the bridgewire/powder interface. Current Sandia actuator designs have a functional reliability requirement of 0.9995. Typical all-fire current levels to meet this reliability are 3-3.5 amps from a 28 volt source.

As previously mentioned, early designs had low temperature ignition failures with $TiH_2/KClO_4$. A later design also had low temperature ignition failures during mechanical testing to high "G" environments. Investigations showed that the powder pulled away from the bridgewire interface leaving no contact at this interface. It left a low density area that lowered ignition reliability.

If the proper powder density cannot be maintained at this interface, low temperature failures will occur.[21] This is due to a major mismatch in coefficients of expansion (or contraction) between the powder and all the other materials of construction that can lower the density and/or cause gaps in the bridgewire/pin interfaces. See discussions below (mechanical properties) on this subject of coefficient of thermal expansion.

In a hot wire design, bridgewire/powder contact can be measured by the electrothermal response (ETR) test procedure.[22] This technique measures the thermal decay of a low energy pulse (below all-fire requirements to the bridgewire). ETR is considered a nondestructive test. Comparison of this thermal decay characteristic of unloaded headers to known loaded units can be used as a guide for powder contact at the bridgewire/powder interface.[23]

Mechanical Properties

All $TiH_x/KClO_4$ materials have a large coefficient of thermal expansion (CTE) compared to the usual materials of construction used in hot wire designs. Table 5 lists some of the CTE's for typical materials used in header designs as well as $TiH_x/KClO_4$.[21,24]

Table 5

Coefficient of Thermal Expansion (CTE)
(CTE X 10^{-6}/°C)

Material	CTE (0-50°C)
$KClO_4$	65
$TiH_x/KClO_4$	42
Ceramic	5
Epoxy Charge Holder	20
Header Glasses	<10
Stainless Steel	17
Inconel	11
Hastelloy C	11

$TiH_x/KClO_4$ expands and contracts at much greater rates during thermal cycling than the usual hot wire device materials of construction. During the contraction phase, $TiH_x/KClO_4$ has been shown to loose contact with the bridgewire and lead to ignition problems.[21] This can occur with all $KClO_4$ pyrotechnics especially at low temperatures. This problem has been so severe at times that the entire pressed powder bed has freed itself from the charge holder walls and moved away from the header to the exterior closure disk.

To correct this problem, various measures have been employed to prevent this from occurring. A one-way washer design which contacts the charge holder walls and is imbedded in the powder, was the original correction to the powder decoupling problem. Current designs use a thin elastomeric disk between the end of the powder column and the closure disk. The disk is under compression by making the closure disk dimple or compress against the elastomeric disk during its welding to exterior header case. This keeps the powder bed under compression at all times.

$KClO_4$ pyrotechnics also have low physical contact and frictional characteristics with the usual charge holder materials which compounds the potential powder decoupling problems that can occur.

Stability, Aging and Compatibility

Stability and aging were addressed in the introduction. Chemical stability of $TiH_x/KClO_4$ compositions is usually determined by the rate of increase of the chloride ion from the reaction or decomposition of $KClO_4$.[3] Stability studies, aging programs and surveillance programs have shown that $TiH_x/KClO_4$ compositions are stable for long periods of time. This includes $Ti/KClO_4$ compositions.

As previously mentioned, even $TiH_2/KClO_4$ is stable if the starting TiH_2 is thermally pretreated.[3] This appears to drive off small amounts of easily evolved hydrogen. This hydrogen then reacts with $KClO_4$. In these studies, pure hydrogen, H_2, was shown not to react with $KClO_4$ or $TiH_2/KClO_4$ mixtures. An activated hydrogen species, when evolved, reacts with the $KClO_4$. Both chloride and water were measured at the same reaction rates.

Active Sandia surveillance programs for over fifteen years with production components have found the stability of all $TiH_x/KClO_4$ materials to be less than 0.01% reaction per year.[25] Currently all Sandia production components using $Ti/KClO_4$ and $TiH_x/KClO_4$ have been certified for requirements related to stability, compatibility and reliability for 25 year lifetimes. Some designs with these materials are currently being certified for lifetimes in excess of 40 years.

No compatibility problems with typical hot wire materials of construction have been found with $TiH_x/KClO_4$ materials.[26] This includes amine cured epoxy materials which are used as inert charge holder materials and adhesive compositions. Contrast the compatibility of amine cured epoxy materials with organic explosives where problems are found.

Standard cleaning agents for headers and charge holders which include organic solvents such as chlorinated materials, CFC freons. alcohols, ketones, aliphatic hydrocarbons, aromatic hydrocarbons and water soluble detergents have all been found to be compatible with $TiH_x/KClO_4$ compositions.[26]

Modern-day cleaning agents used to replace many chlorinated, CFC and organic materials have also been found to be compatible. These include such solvents as d-limonene liquids and specially formulated alkaline cleaners.

The only compatibility problem with $TiH_x/KClO_4$ materials has been when the powder has not been properly dried or when the powder has been exposed to moisture in non-hermetically sealed designs. Moisture in these powders can initiate corrosion reactions at the header pin/ bridgewire/powder interfaces (Ref. 27, 28). The combination of moisture, $TiH_x/KClO_4$ and metallic header materials triggers corrosion and instability of these materials at these interfaces. The saying, "Keep your powder dry," applies to $TiH_x/KClO_4$ loaded devices as well all other $KClO_4$ containing pyrotechnics.

General Material Properties

This section briefly discusses and lists some of the other materials properties for $TiH_x/KClO_4$ compositions. Table 6 is a listing of the energetic material hazard properties for $TiH_x/KClO_4$.[16,29]

Table 6

Energetic Material Properties
for
$TiH_x/KClO_4$ Compositions

Material Property	$Ti/KClO_4$	$TiH_{0.65}/KClO_4$	$TiH_{1.65}/KClO_4$
Friction	6.3 kg	7.2 kg	15.8 kg
Impact	225 kg-cm	>250 kg-cm	>250 kg-cm
ESD	<5 kv	>40 kv	>40 kv
Autoignition	500°C	500°C	500°C

Friction sensitivity testing was conducted with a BAM friction tester, impact sensitivity with a Technoproducts drop weight tester, ESD by the standard man test, and autoignition by thermal analysis and component device thermal ignition procedures.

Figure 4 is a plot of the density of $TiH_x/KClO_4$ over the entire concentration range of hydrogen in titanium.[9] Table 7 lists the density for the various $TiH_x/KClO_4$ materials used at Sandia. Unpublished helium pycnometry measurements with these materials confirm these data.

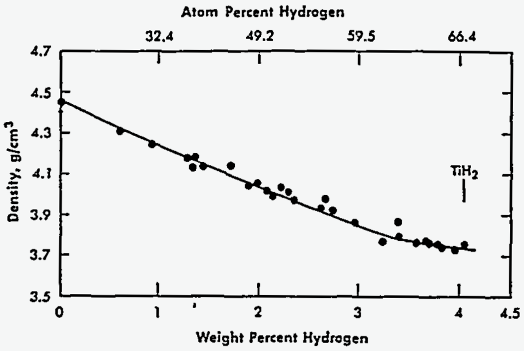

Figure 4
Density verses Hydrogen Content for TiH_x

Table 7

Density of $TiH_x/KClO_4$ Materials

$KClO_4$	2.524 gm/cm3
Ti	4.45 gm/cm3
$TiH_{0.65}$	4.17 gm/cm3
$TiH_{1.65}$	3.82 gm/cm3
TiH_2	3.78 gm/cm3

The following equation can be used to calculate the density of a composite blend.

$$\text{Density of Mixture} = \frac{1gm}{\frac{M_A}{P_A} + \frac{M_B}{P_B}} \qquad (1)$$

where M is the mass fraction of the constituent and P is the density of the individual constituent.

Table 8 summarizes the other properties of interest.[16,30]

Table 8

General Properties if $TiH_x/KClO_4$

Heat Capacity: $Cp=2.48 \times 10^{-4} + 0.163T$ (-50 to 150°C)
(TiH_x=0 to 2)
Hygroscopicity: <0.05% at 50 percent RH
(TiH_x=0.65 to 2)
>0.5% at 50 percent RH
($Ti/KClO_4$)
Detonation: $TiH_x/KClO_4$ mixtures do not detonate
Deflagration-to Detonation Transition (DDT):
$TiH_x/KClO_4$ mixtures do not DDT
Thermal Stability Weight Loss: >0.1 % to 150°C

All $TiH_x/KClO_4$ mixtures are conductive due to the metallic fuel. Studies by White, et al, measured the resistivity of $TiH_x/KClO_4$ from -180°C to 500°C including varying numerous parameters such as density, stoichiometry and powder surface area and are reported as a series of curves.[31]

Toxicity/Environmental Issues

The published toxicity criteria for titanium and $KClO_4$ are described and have been used to imply the toxicity of $TiH_x/KClO_4$ materials.[32]

Titanium Metal: Health hazard none, it is physiologically inert.

$KClO_4$: It is moderately toxic and irritating to the skin, mucous membranes and respiratory track. It may effect the kidneys. Direct contact with $KClO_4$ should be avoided. The probable lethal dose for human beings is 50-500 mg/kg.

Titanium Dioxide (TiO_2): This is a reaction product from $TiH_x/KClO_4$. TiO_2 is inert and not a health hazard. TiO_2 is a major constituent in consumer paint formulations.

Potassium Chloride (KCl): This is also a reaction product from $TiH_x/KClO_4$. KCl is an inert material and is not considered toxic. KCl is sometimes is used as a table salt substitute.

As with all fine particulate matter, a health hazard exists if inhaled.

$TiH_x/KClO_4$ compositions are as close to a "green", environmentally benign energetic material as exists. In the ground, they will decompose to inert materials, TiO_2, KCl and water. After functioning, the reaction products are the same.

$TiH_x/KClO_4$ Uses

The primary use of $TiH_x/KClO_4$ pyrotechnic mixtures has been in actuator designs to function valves and open gas bottles. Their reliability to function has been 0.9995. In recent years, there has been imposed a 0.9995 ESD reliability requirement to not function from a human body discharge. This was the primary reason in switching the fuel from $TiH_{0.65}$ to $TiH_{1.65}$ in actuator designs. As long as care is made to ensure no conductive path to case is made before external spark breakdown measures can take place, these designs can meet this ESD requirement. Personal safety is also enhanced in handling the bulk materials prior to loading.

Ignition of $TiH_x/KClO_4$ has been achieved by a variety of methods and includes ignition by a hot wire, through bulkhead function from thermal and detonation sources, percussion primer ignition, and semiconductor bridgewire (SCB) initiation.

Numerous igniter designs have been developed and, in many cases, put into production for DOE applications. These include hot particulate igniters for thermal batteries, igniters for ignition and high pressure output of reefing line cutters, next assembly igniters for high temperature materials such as thermite and titanium/boron mixtures and percussion actuated igniters.

There are currently commercial uses of $TiH_x/KClO_4$ and $TiH_2/KClO_4$ as igniters for automobile air bag igniter designs. Note, the enhanced ESD safety of such designs over the traditionally used $Zr/KClO_4$ materials.

Other uses have been output mixtures for reefing line cutter designs, special low energy ignition materials for DDT detonators and unusual designs for space applications.

Conclusions

Currently $TiH_x/KClO_4$ materials and applications have been developed to the point where it can be considered a mature technology. $TiH_x/KClO_4$ materials meet the needs of an ESD insensitive material that can meet high reliability design requirements but still be ESD safe from a human body discharge. Low temperature ignition problems have been understood and solved. Output characteristics are sufficient to meet specified design criteria.

These materials are considered to be the most "environmentally friendly" of the energetic materials now in use.

One problem outside of DOE use, would be the scale-up to many kilograms the dehydriding process. The technology has been developed, it just needs scaling up. Another troublesome problem that has developed in the last few years has been the commercial non-availability of a 2 micron TiH_2 that has a surface area over 2 m^2/gm. There is no source within the United States. The European vendor produces a slightly larger TiH_2 that has led to ignition failures.

REFERENCES

1. Leslie, W. B. and Dietzel, R. W., Titanium Hydride-Potassium Perchlorate: A Spark Insensitive Pyrotechnic Material, Sandia Laboratories, Albuquerque, NM, SAND74-0220, 1974.
2. E. A Kjeldgaard, "Development of a Spark Insensitive Actuator/Igniter", Fifth International Pyrotechnics Seminar, Vail, CO, 1976.
3. Massis, T. M., Morenus, P. K. and Merrill, R. M., Stability of the Pyrotechnic Mixture Titanium Hydride (TiH_x)/Potassium Perchlorate ($KClO_4$), Sandia Labs, Albuquerque, NM, SAND75-5889, 1975.
4. Personal communication between T. M. Massis and R.S. Carlson, Wheatville Technology Co., Miamisburg, OH.
5. Sandia Specification, SS376045, "Titanium Hydride for Titanium Subhydride Production".
6. Sandia Specification, SS323203, "Titanium Subhydride Powder ($TiH_{0.65}$)"
7. Sandia Specification, SS371477, Titanium Subhydride Powder ($TiH_{1.65}$)".
8. R. S. Carlson, "A Process for Reproducibly Preparing Titanium Subhydride", U. S. Patent No. 4309230, 1981.
9. Mueller, W. M., Blackledge, J. P. and Libowitz, G. G., Metal Hydrides, Academic Press, New York, 1968, p. 337, 368.
10. Sandia Specification, SS308214, "Potassium Perchlorate".
11. Unpublished findings on the "Failure to Meet Requirements for the MC2949A Actuator".
12. Sandia Specification, SS308278, Titanium/ Titanium Subhydride Potassium Perchlorate.
13. R. L. Parks, "Remote Handling: Blending of Energetic Materials," ADPA Compatibility Conference, Blacksburg, VA, October 13, 1980.
14. Burchett, O.L. and Allen, L. C., "Component Characteristics and Development Report-MC3753 Actuator", SAND86-0669, Sandia National Labs, 1986
15. S. L. R. Hingorani-Norenburg, "Experimental Study of the Burn Rate of $TiH_{1.65}/KClO_4$ Pyrotechnic Under Confinement", SAND-88-2393, Sandia National Laboratories, Albuquerque, NM, 1988.
16. Memo, dtd. April 3, 1984, T. M. Massis, Sandia National Laboratories, Albuquerque, N. M. to R. Weinheimer, Lockheed Missiles and Space Co., Sunnyvale, CA, subject-Information and Properties Related to $TiH_{0.65}/KClO_4$.
17. J. A. Holy, "Burn Rates of $TiH_2/KClO_4$/Viton and Output Testing of NASA SKD26100098-301 Pressure Cartridges", EG&G Mound Applied Technologies, Miamisburg, OH, NASA-CR-188357, 1993.
18. J. A. Holy, "Pressure Dependent Burn Rates of $TiH_x/KClO_4$ (x=0.2, 0.65, 1.65)", 11th International Pyrotechnics Seminar, Vail CO, 1986.
19. Healy, J. T. and Lieberman, M. L., "Effect of Fuel Structure on Spark Sensitivity of 33/67 $TiH_x/KClO_4$ Blends", 6th International Pyrotechnics Seminar. Estes Park, CO, 1978.
20. L. W. Collins, "Thermal and Electrostatic Initiation of TiH_x Based Pyrotechnics", 7th International Pyrotechnics Seminar, Vail, CO, 1980.
21. Massis, T. M., Morenus, P. K. and Steele, B. R., "The Simulation of Powder Decoupling Phenomena in Electro-Explosive Devices by Thermomechanical Analysis (TMA)", Sandia National Laboratories, Albuquerque, NM, SAND82-0064C, 1982.
22. Rosenthal, L. A. and Minichelli, V. J., "Nondestructive Testing of Insensitive Electroexplosive Devices by Transient Techniques," JPL Report 32-1494, 1970.
23. Strasburg, A. C., "Methodology for Computation of Interface Parameters of a Hot Wire Explosive Device form the Electrothermal Response Analog," Sandia Laboratories, Albuquerque, NM, SLA-73-1034, 1973.
24. D. R. Lide, ed., Handbook of Chemistry and Physics, 74th Edition, CRC Press, Boca Raton, FL
25. Sandia Quality Assurance, ed., Sandia Surveillance Activities, Sandia National Laboratories, Albuquerque, NM, 1979-present.
26. Sandia National Laboratories, Published and Unpublished Compatibility Studies Related to Energetic Materials.
27. Final Report, "MC3004 Actuator Task Force", Sandia National Labs, Albuquerque, NM, 1982.
28. Massis, T. M., Healey, J. T., Huskisson, D. H., Perkins, W. G., "Corrosion Problems in Titanium/ Potassium Perchlorate Loaded Devices When subjected to Humidity Environments", Journal of Hazardous Materials, vol. 5, 1982, p. 335-351.
29. Wang, P. S. and Hall G. F., "Friction, Impact and Electrostatic Discharge Sensitivities of Energetic Materials", MLM-3252, Monsanto Research Corp., Mound Facility, Miamisburg, OH, 1985.
30. Memo dtd. March 22, 1982, Klassen, S. E. and Massis T. M., Sandia National Laboratories, Albuquerque, NM, to Distribution, subject-Heat Capacity Measurements on $TiH_x/KClO_4$, X=0 to 2.
31. White, K. Reed, J. W., Love, C. M., Glaub, J. E. and Holy, J. A., "Electrical Resistivity of TiH_x and $TiH_x/KClO_4$", MLM-2589, Monsanto Research Corp., Mound Facility, Miamisburg, OH, 1979.
32. AMCP 706-187, Military Pyrotechnic Series, Part 3 Properties of Materials Used in Pyrotechnic Compositions. U. S. Army Material Command, October, 1963.