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THE STABILITY AND COMPATIBILITY OF $TiH_x/KClO_4$ PYROTECHNICS

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ABSTRACT

The stability and compatibility of pyrotechnic compositions are often significantly affected by variables which may not be adequately controlled during compatibility testing or production processes. The influence of several of these factors was determined for the $TiH_x/KClO_4$ pyrotechnic system. The stability of $KClO_4$ was shown to be affected by the presence of trace quantities of metal oxides, by water vapor, and by compaction. The compatibility of TiH_x fuels is related to the availability of moisture to establish an electrochemical corrosion cell. The affinity of the materials for water, necessary to establish this corrosion cell, was related to the titanium oxides which coat each particle of the powder. Several methods for controlling the influence of these variables were investigated.

INTRODUCTION

The energetic materials in combination with various plastics, adhesives, metals, and ceramics utilized in explosive components comprise complex materials systems which are not easily amenable to scientific investigation. Yet engineering requirements demand that these systems withstand a wide range of adverse environments over a 20 to 25-yr period with no substantive degradation of performance or reliability. In response to these requirements, materials scientists have devised numerous tests to evaluate materials prior to committing them to component use. Perhaps the best known and most widely used test of this type is the chemical reactivity test (CRT) in which stacks of materials of interest are aged at elevated temperatures in closed cells that are then analyzed by gas chromatography (ref. 1). Other advanced analytical techniques that have been applied in these evaluations include Fourier Transform IR, electron spectroscopy, specific ion electrodes, ion chromatography, luminescence techniques, mass spectroscopy, etc. These techniques, while providing significant new information about material properties, still do not adequately address the most serious problem in materials evaluations--the

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necessity of working with poorly defined systems. Production materials used in the fabrication of components are not the ultra-pure, well-characterized chemicals used in research, but represent compromises among cost, availability, ease of handling, and other engineering requirements. Also, these materials are routinely exposed to production environments in which additional contamination can occur. Failure to account for the presence and action produced by impurities or contaminants in materials testing programs can lead to uncontrolled experiments which yield false or misleading results; yet most testing programs do not explicitly identify the effects of these impurities. Combined effects that include the action of impurities are typically measured so that gross reactions are identified but subtle effects may be missed. This paper discusses several impurities that have been identified in the $TiH_x/KClO_4$ pyrotechnic system and their effects on the compatibility/stability of the material.

EXPERIMENTAL

The materials, experimental techniques, and instrumentation used in this study have been previously described (refs. 2-5).

RESULTS AND DISCUSSION

Titanium subhydride/potassium perchlorate ($TiH_x/KClO_4$) is a relatively new pyrotechnic composition for use in actuators and igniters which has the advantage of being sensitive to hot wire or low energy ignition while being insensitive to accidental initiation by electrostatic discharge (ref. 6). The stability of this material, together with the implications of the test results with respect to its compatibility in a component configuration, has been previously reported (ref. 7). Recent studies have shown that trace materials, only partially discussed in the previous study, can influence both the chemical stability and the performance characteristics of the pyrotechnic.

One of the most important of the minor constituents in the pyrotechnic system is the titanium oxides which coat the fuel particles. This coating is responsible for much of the chemistry and many of the performance properties of the pyrotechnic. Titanium powders are easily oxidized, and, in fact, are pyrophoric when fresh metal surfaces are exposed to oxygen. Thus, the titanium oxide coating on the metal particles stabilizes the material by controlling the accessibility of the titanium to the oxygen and is necessary to prevent undesirable oxidation reactions. This oxide coating protects the metal from the oxidation processes to temperatures in excess of 500°C as shown by the differential thermal analysis (DTA) curves in Fig. 1. Thus, the titanium oxide impurity, which is rarely mentioned in writing the pyrotechnic reactions, is essential to the stability of the material.

Recent studies have shown that the titanium oxide coating also influences the performance characteristics of the titanium based pyrotechnics (refs. 3-5). The

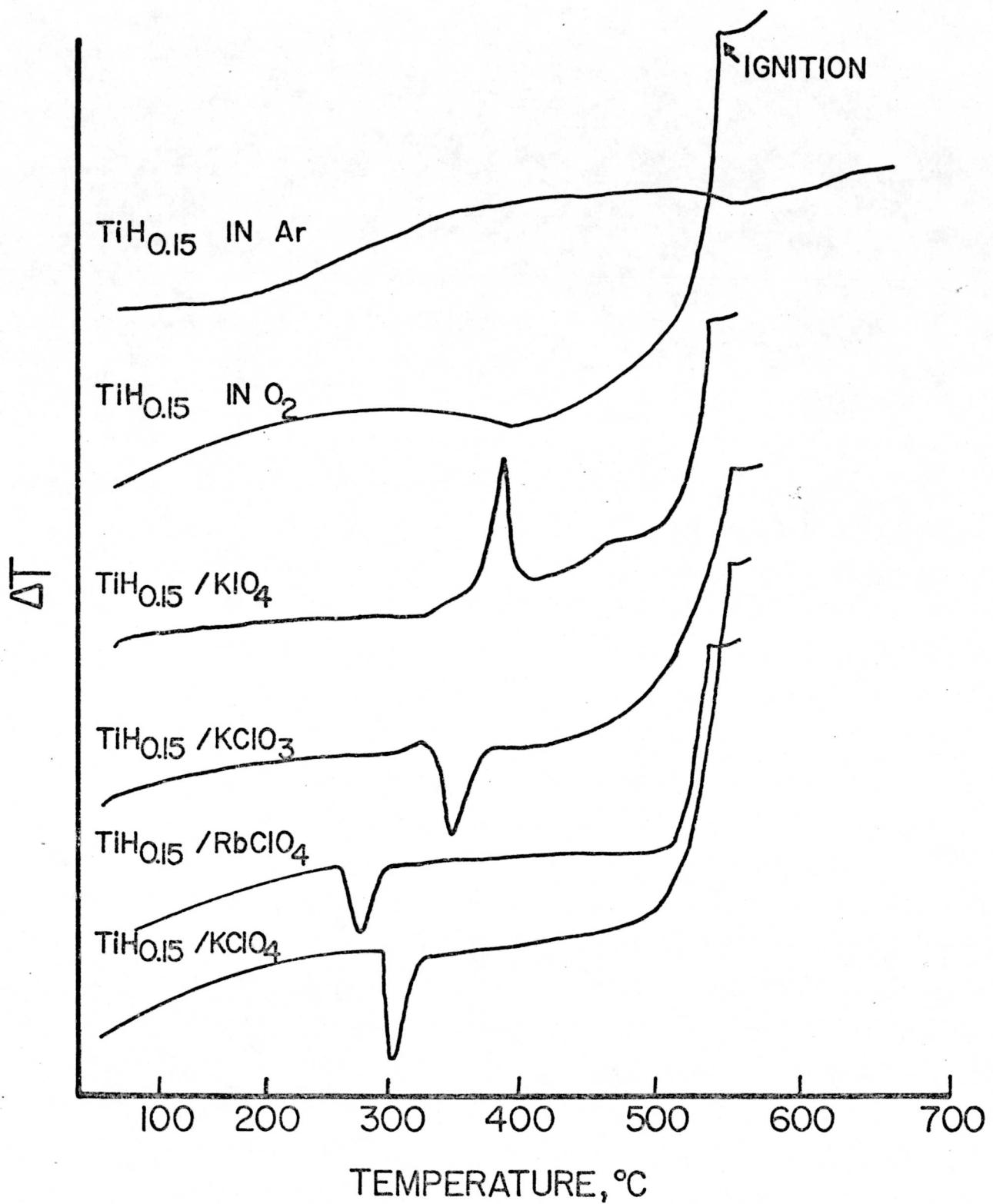


Fig. 1. DTA curves for 10 mg samples of $\text{TiH}_{0.15}$ and $\text{TiH}_{0.15}$ /oxidizer pyrotechnics heated at 20 deg/min in a dynamic atmosphere with a gas flow rate of 80 ml/min. All samples were contained in open platinum pans and argon was used as the flow gas for runs except for the curve for $\text{TiH}_{0.15}$ in oxygen.

chemistry of electrostatic initiation was shown to be governed by the presence of titanium metal or titanium suboxide species on the surface of the fuel. Minor changes in these surface species can either negate the safety margin afforded by hydriding or improve the safety of the material, depending on the chemistry of the change. The small changes in the oxide content of the fuel necessary to produce the changes in performance would not normally be detected in compatibility testing since these studies tend to focus on species associated with corrosion or gas production. Also, the distribution of the oxide is as important for compatibility as the quantity of oxide--oxide distributed over the surface of the particles stabilizes the powder while the same quantity of oxide mixed with fresh metal powder produces little effect.

Moisture adsorption by the titanium powder also seems to be related to the properties of the titanium oxides. The presence of water vapor is known to make the titanium pyrotechnics less susceptible to electrostatic initiation as shown by the data in Table 1. According to the recently developed theory of electrostatic initiation, the reactive suboxides on the particle surface have an affinity

TABLE 1

Variation in the electrostatic initiation energy for a $TiH_{0.65}/KClO_4$ blend as a function of the relative humidity in the air atmosphere surrounding the sample at $25^\circ C$

Relative humidity	Nominal sensitivity, mJ
10	40
45	60
65	90
85	250

for water molecules as well as for oxygen. As the water molecules adsorb on the reactive sites, they hinder the reaction of the fuel with oxygen that can be initiated by electrostatic discharge. Thus, a more fully oxidized surface should be less susceptible to electrostatic initiation and also have a lower affinity for water. Both of these conditions are desirable since electrostatic discharge can lead to accidental ignition and water can provide the liquid medium to establish a corrosion cell.

A more complete oxidation of the titanium fuel surfaces was achieved by heating the powder in an oxygen rich atmosphere. The resulting powder showed improved performance characteristics as shown in Table 2. Again, the titanium oxide impurities influenced material properties which are significant to the compatibility of the pyrotechnic.

TABLE 2

Effect of treatment of $TiH_{0.15}$ powder at 300°C in an 80% oxygen atmosphere. No weight gain was detectable for the treated powder

	Untreated	Treated
ESD Sensitivity	1 mJ	10 mJ
Water adsorption at 60% RH (5 days)	0.82 wt %	0.57 wt %

Titanium subhydride fuels also contain other impurities with effects less understood than the effect produced by the titanium oxides. Photoelectron spectroscopy (PES) indicates that carbon is present on the surface of the titanium particles and can persist to very high temperatures as shown by the spectra in Fig. 2. Initially, the carbon is present as an organic entity as shown by the peak for the C-C bond; upon heating, this material is removed or changed through reaction to form a carbide as shown by the peaks at higher temperatures. The influence of this carbon on the compatibility of the material is not fully understood but it has been shown that it can lead to gaseous products. Massis et al (ref 7) used gas chromatography to measure the evolution of carbon dioxide and reported the curves shown in Fig. 3. Formation of this gas could cause problems in certain types of applications.

The stability of the potassium perchlorate oxidizer can also be influenced by impurities such as metal oxides as shown in Fig. 4. As little as 0.01% of metal oxides such as Co_2O_3 can lower the thermal decomposition temperature of $KClO_4$ by as much as 25°C. Titanium oxides can interact with the oxidizer to provide a lower energy pathway for decomposition. There is evidence that this catalytic interaction occurs at room temperature as well as at elevated temperatures and that it influences the performance characteristics of the pyrotechnic. Comparison of mixtures of $TiH_{0.15}$ with $KClO_4$ or with Al_2O_3 shows that the $KClO_4$ desensitizes the $Ti + O_2$ reaction to electrostatic initiation while the inert Al_2O_3 produces no effect on the reaction. The desensitizing effect is clearly shown by the curves presented in Fig. 5. New studies using photoelectron spectroscopy have now directly shown the changes in the chemistry of the titanium oxide layer of the fuel particles upon mixing with oxidizers. These studies will be reported in some detail in a later paper.

Compaction can also affect the stability of $KClO_4$. Pai Verneker and Rajeshwar (ref. 8) have shown that mechanical stress can significantly alter the thermal stability of potassium perchlorate. This effect has been further investigated by storing $KClO_4$ samples in KBr minipresses of the type commonly used in IR spectroscopy at elevated temperatures after torquing to known pressures. These

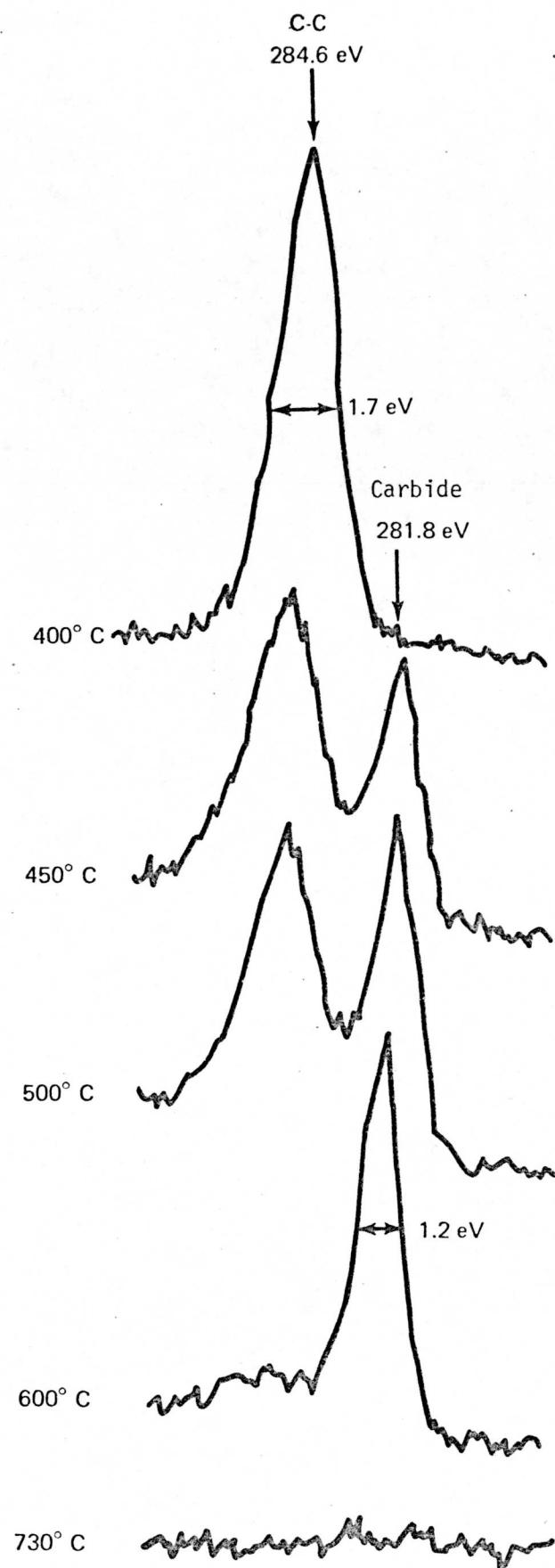


Fig. 2. C_{1s} spectra of titanium obtained by ESCA at various temperatures.

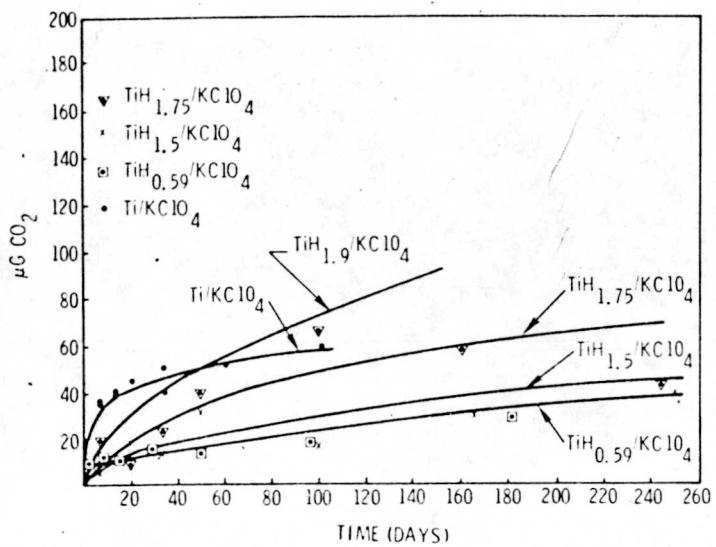


Fig. 3. Effects of TiH_x concentration on rate of CO_2 formation at 373 K.
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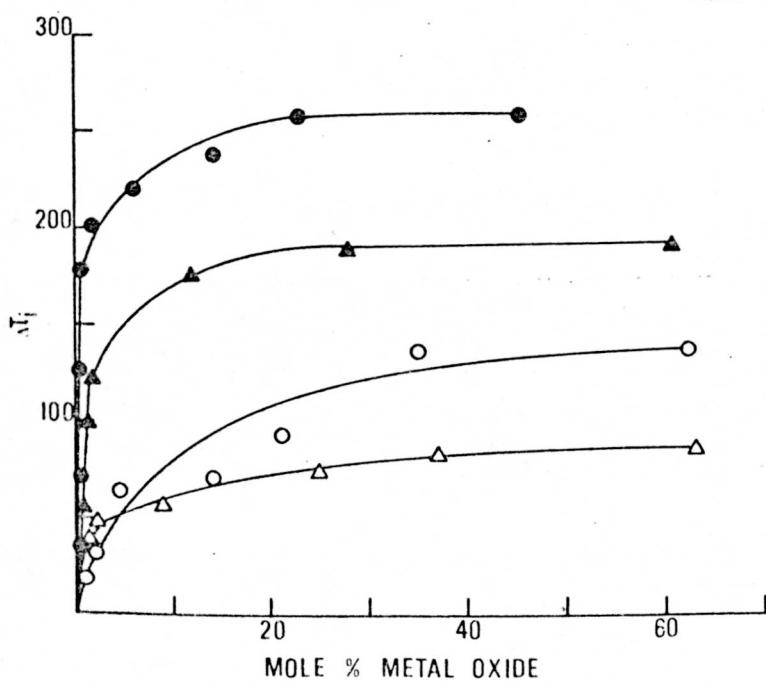


Fig. 4. Change in decomposition temperature of potassium perchlorate as a function of Co_3O_4 (●), MnO_2 (△), ZnO (○), and TiO_2 (Δ) concentrations.

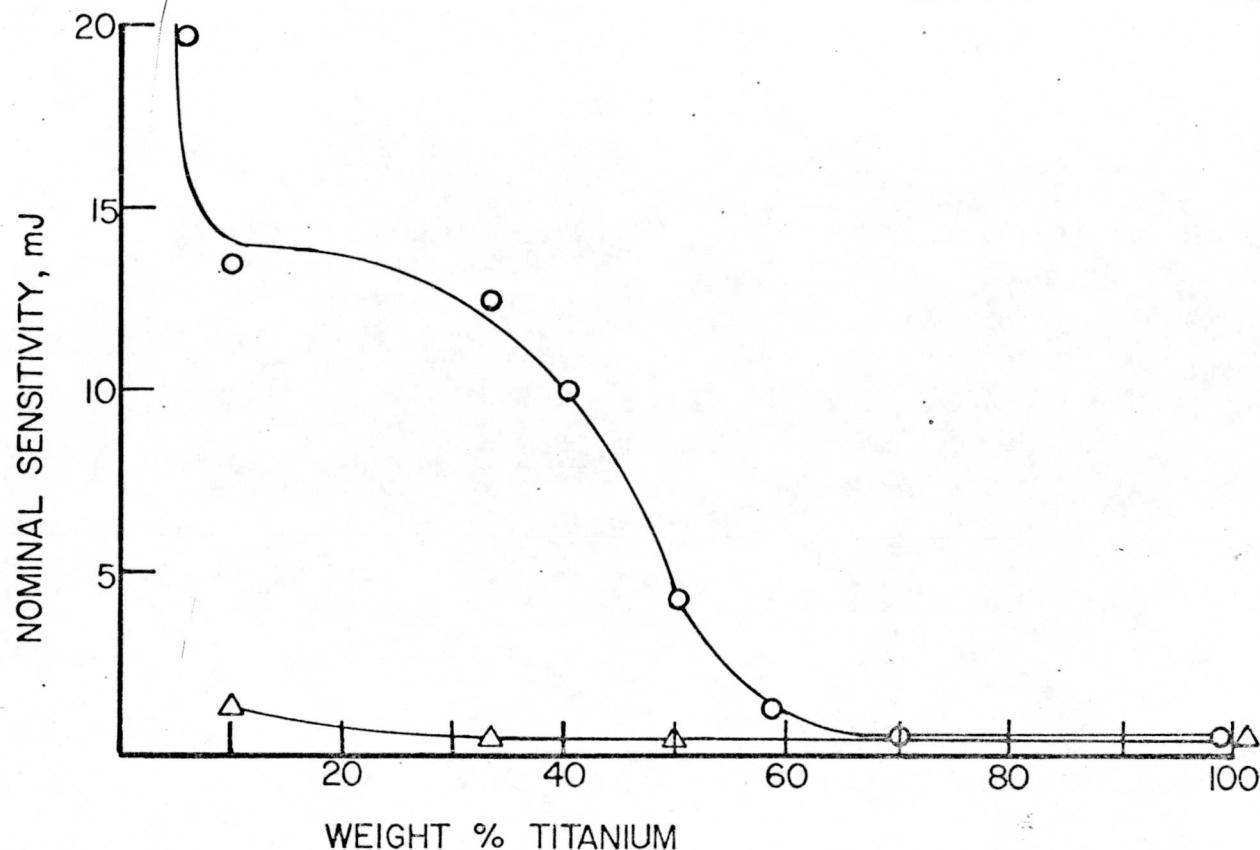


Fig. 5. The relationship between blend ratio and the nominal electrostatic energy required for initiation of $\text{TiH}_{0.15}/\text{KClO}_4$ (○) and $\text{TiH}_{0.15}/\text{Al}_2\text{O}_3$ (△) blends in an atmosphere of 50% O_2 /50% Ar.

samples were then analyzed for chloride ion after one day of storage and the results are given in Table 3. These data indicate that moisture is necessary for the accelerated formation of the chloride ion. Since the minipresses were not hermetically sealed, the elevated temperature removed the moisture present in the sample so little chloride was formed at the higher temperature. However, the data indicate that the combination of mechanical strain and moisture can accelerate the formation of chloride which can lead to corrosion problems.

TABLE 3

Effect of compaction on the formation of chloride ion in potassium perchlorate

Torque applied	wt % Cl^-	
	Room temperature	110°C
0 ft-lb	0.039	0.038
30 ft-lb	0.043	0.039
60 ft-lb	0.051	0.040

SUMMARY

Characterization of the $TiH_x/KClO_4$ pyrotechnic compositions has revealed several impurities which interact with the pyrotechnic constituents to influence either stability or performance. While the nature of the interactions is now better understood, the effect of these interactions in a component configuration still cannot be predicted a priori. However, knowledge of these effects would be explicitly considered in a compatibility problem evaluation and perhaps lead to a rapid diagnosis and solution. Consideration of synergistic effects which might adversely affect component compatibility also allows better product specifications to be written.

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