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INVESTIGATION OF THE THERMAL DEGRADATION OF THE AGED PYROTECHNIC TITANIUM HYDRIDE/POTASSIUM PERCHLORATE*

D. N. Sorensen[1], *A. P. Quebral*[1], *E. E. Baroody*[2] *and W. B. Sanborn*[3]**

[1]Naval Surface Warfare Center, Indian Head Div., NAVSURWARCEN, 101 Strauss Ave, Indian Head, MD 20640-5035, USA
[2]Applied Ordnance Technologies, Inc., 103 Paul Mellon Ct., Waldorf, MD 20602, USA
[3]Pacific Scientific-Energetic Materials, Co., 7073 W. Willis Rd., Chandler, AZ 85226, USA

Titanium hydride/potassium perchlorate (THPP) is a pressure producing pyrotechnic composition consisting of a mixture of titanium dihydride and potassium perchlorate with a small percentage of a Viton binder. The initial phase of the study focused upon chemical analysis of THPP downloaded from parts ranging up to 25 years in age. The DSC curves were too erratic for kinetic analysis; however, high resolution TG curves for the THPP samples revealed a significant difference in the temperature at which the aged materials began displaying mass loss. Isothermal DTA and variable heating rate TG kinetic analysis were employed to determine the activation energy of the THPP.

Keywords: *aging, decomposition, kinetic analysis, potassium perchlorate, pyrotechnic, thermal analysis, titanium hydride*

Introduction

The current trend in the energetics community is to increase the service life of existing components well beyond the life they were originally designed to serve. This is in response to decreasing budgets and increasing procurement and service costs. Some of the current programs have goals to extend service lives to over 30 years for parts that were originally designed for 5 years. In many cases, long-term aging of the energetic materials that were used was not considered beyond the original design lifetime. The designs cannot be changed due to the high cost of re-qualifying the new parts to be used in current military systems; therefore the energetic materials must be re-evaluated for long-term stability. In some rare cases, where a weapons system has been in use for the past 30 years there are residual or returned parts that cover the entire life of the program. This situation provides a unique opportunity to examine ‘real-time’ aging of the components. It also presents some unique challenges. Over the lifetime of the manufacture of the energetics and devices, manufacturing process have changed and evolved, manufacturers have changed, raw material sets have changed, sources for the raw materials have changed, and test methods have evolved. However, much of the original information on the energetic raw materials has been lost or is unavailable and samples of the material do not exist for comparison to current materials. Therefore, all of the typical items used to determine subtle changes in the performance of an energetic material cannot be used to evaluate the trends in the aged family of devices. Some basic assumptions, including that the raw materials and processes are basically constant over time, allow the energetics to be evaluated as a set.

One such opportunity presented itself during the routine surveillance testing of a stockpiled pressure producing pyrotechnic device used on a Navy weapons system. It was noticed that a general trend toward higher output pressure existed with increasing age of the part during the current phase of surveillance testing. The oldest units were trending toward the upper limit of the product specification. The concern was that the older units would eventually fall out of the product requirement. The trend appears to be real since all the original lot acceptance data showed the lots as delivered were ‘nominal’. This trend is unusual in that typical energetic materials will degrade in performance with time rather than become more effective as is the case with this system. This particular device contains two different energetic materials, an ignition and an output powder, separated by an insulating material. The investigation of the phenomena focused on the output material used in the device. The material, THPP, consists of a mixture of titanium dihydride (TiH_2) and potassium perchlorate ($KClO_4$) combined with a small percentage of a Viton™ binder. The initial phase of the study focused upon chemical analysis of THPP from three age groups (1, ~10 and ~25 year-old units) within the population to determine if there were any glaring discrepancies

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** Author for correspondence: bill.sanborn@psemc.com

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Akadémiai Kiadó, Budapest, Hungary
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among the materials. The second phase of the project was to determine kinetic parameters for the pyrotechnic in order to be able to predict appropriate time and temperatures for accelerated aging. The goal of this accelerated aging program is to be able to reproduce the phenomena exhibited in the older devices. Both phases of the program have shown significant advances, but still have tasks underway.

Experimental

Sampling

All the pressure producing pyrotechnic devices used for the function testing that established the pressure trend and subsequently lead to the chemical testing were from two slightly different designs. However, these devices have identical internal configurations where the energetic materials reside with only minor housing differences. The history of any single unit was not determined, but all the devices as provided were reported to have similar histories and were not abused. The functional testing utilized in excess of 150 devices of various ages to establish the trend. The majority of the function testing was performed under ambient environments. A total of 16 devices divided among the three age groups were provided for initial chemical testing.

Initial chemical testing

The initial testing on the devices was intended to determine if there were any gross changes evident in the parts or output pyrotechnic. These tests included neutron imaging analysis (N-ray), residual gas analysis, and ion chromatography. The results of the testing will be summarized here, but will not be covered in detail [1]. The device in question was designed with a plenum in the end of the unit of an approximate volume of 29–45 μL based upon design tolerances. The N-ray was to examine if the powder had deconsolidated. If the powder had filled the plenum, the higher surface area of the pyrotechnic would allow for a quicker burn that could account for a higher output pressure. However, no obvious evidence of deconsolidation was observed in the N-ray images.

If there was a significant level of reaction, decomposition or other gas-producing event within the THPP, then either hydrogen or other permanent gases should be present within the device. The presence of the plenum and the hermetic nature of the devices allowed for the sampling of residual gases present within the unit. The testing was developed and performed at Sandia National Laboratories (SNLA) in Albuquerque, NM. The test involves puncturing the device and then purging the plenum with a carrier gas. The effluent is then analyzed on a gas chromatograph. The devices could be tested for either hydrogen or permanent gases, but not both at the same time. A minimum of two devices from each age category was tested for hydrogen and a second set for permanent gases. The permanent gas analysis revealed only nitrogen or other purge gases that accounted for nearly all the STP volume of the plenum, with only a trace of other gases. The most significant other gas was carbon dioxide, but this appeared to be constant over time. Oxygen did not appear to be present in the devices. This is either due to inert purging during the welding operation or reaction with the pyrotechnic materials. The hydrogen analysis provided a trend toward higher levels of hydrogen with age, Fig. 1. However, the worst case for hydrogen content only accounts for a 0.011% decomposition of the THPP.

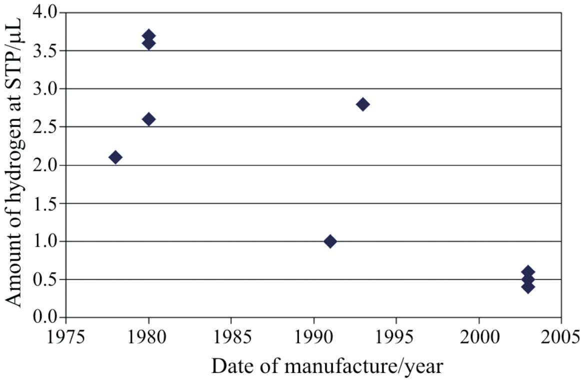

Fig. 1 Hydrogen levels based upon the date of manufacture for the THPP pyrotechnic devices

After the residual gas analysis the six samples used for the permanent gas analysis were downloaded and subjected to ion chromatography at SNLA, Fig. 2. Sandia has a long history with the related pyrotechnic, titanium sub-hydride/potassium perchlorate ($TiH_{1.65}$/KP) and routinely tests these types of materials in their surveillance programs. The ions of most interest are chlorate, ClO_3^-, and chloride, Cl^-, both of which are present in the initial potassium perchlorate, but more significantly are also in the decomposition path of perchlorate, ClO_4^-. Both chloride and chlorate display a typical aging pattern and are not out of the ordinary for what is observed in the related pyrotechnic, $TiH_{1.65}$/KP [2]. It is likely that the observed pattern is influenced more by the initial content of chloride and chlorate in the potassium perchlorate used in the manufacture of the THPP rather than evidence of aging decomposition of the material. Unfortunately, there is no historical record of the ion analyses of the exact raw materials used to manufacture these pyrotechnics or of a single lot of THPP over time, so the interpretation is

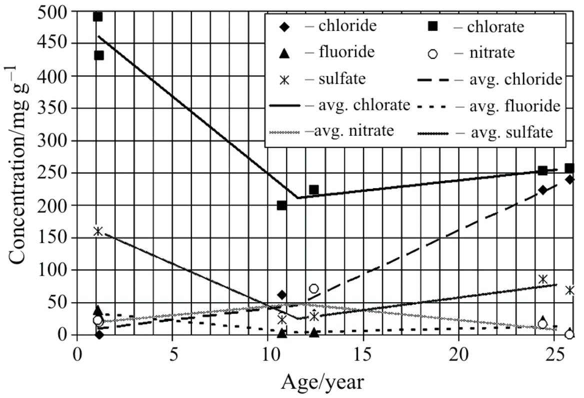

Fig. 2 Aging trends of the ion chromatography results for the downloaded THPP

speculative. The fluoride levels basically remain constant, which indicates that the Viton™ does not appear to be breaking down over time.

Overall, the chemical testing did not reveal any gross decomposition trends within the samples. However, as indicated in the introduction, the trends and variation may be influenced by factors other than aging of the materials. Regardless, work in this area is continuing with additional chemical tests.

Initial thermal analysis

The aim of the thermal analysis testing at Pacific Scientific was initially to examine the decomposition kinetics of the aged materials to determine if there was fundamental difference in how the materials decompose. The idea behind this is if the aged material burns faster than the newer materials, then the pressure difference can be explained and a useful life attached to the part. If the decomposition kinetics are constant within the aged samples, then the pressure increase is probably not due to changes in the THPP. The second aim of the thermal analysis testing was to use the derived decomposition kinetic parameters to establish guidelines for accelerated aging of parts or powder to reproduce the behavior in younger devices.

Differential scanning calorimetry (DSC)

Due to the limited quantity of material available for the kinetic testing of the downloaded THPP, the ASTM E698 method of determining the kinetic parameters was attempted since it required the least sample per test [3]. The differential scanning calorimetry instrumentation used was a TA Instruments (TAI) MDSC 2910 operating in the DSC mode purged at 29 mL min^{-1} with argon. Scan rates of 2, 5, 10 and 20°C min^{-1} were used to evaluate the applicability of the technique for THPP. The samples were prepared in air and sealed into hermetic aluminum pans in the maximum volume configuration with an approximate volume of 20 μL. The pan and lid configuration are typically about 55–60 mg and have a maximum pressure rating of about 0.4 MPa under ideal conditions. The data was analyzed using the TAI Thermal Advantage software.

Due to the energetic nature of the materials, small sample sizes are required to maintain the integrity of the sample pans. For the slower scan rates, slightly larger sample sizes can be utilized as the gas production rate is slow enough to not exceed the pressure limitations of the sample pan and will slightly offset the loss of signal amplitude normally encountered in DSC when reducing the scan rate. Typical sample sizes for these analyses ranged from 0.15 mg for faster scan rates to 0.54 mg for slower scan rates. These samples are small enough that self-heating effects normally encountered in larger samples are insignificant. A representative example of two sets of data is depicted in Fig. 3. Two features are constant for the data set. The first is the solid-state rhombic to cubic phase transition of the potassium perchlorate (KP) and the second is the KP decomposition. The other features, unfortunately, were either weak or inconsistent among the samples. This may be due to a combination of sample size and pan volume allowing the constituents to decompose independently rather than as a homogenous mixture. These phenomena create a situation where it is impractical to apply an ASTM E698 analysis under these conditions. An alternate sample container may resolve the situation. The KP decomposition kinetics likely could be analyzed, but were considered of little value in assessing the pyrotechnic as a whole and was not pursued.

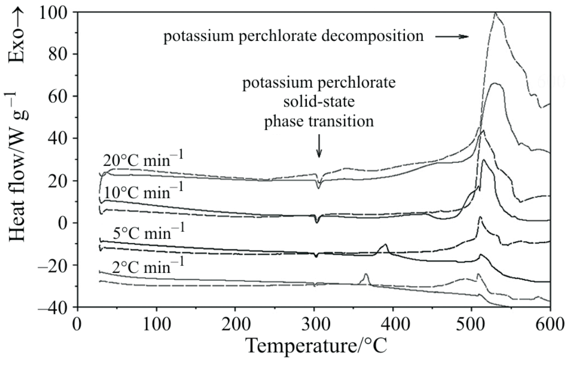

Fig. 3 Overlay of representative DSC curves for THPP downloaded from a 1 year old unit (solid) and a 20+ year old unit (dash)

Thermogravimetric analysis (TG)

Due to the erratic nature of the DSC data, the samples were next investigated using thermogravimetric analysis. The samples were analyzed using a TAI TGA 2950 operating in the HI-RES™ mode. Due to the limited nature of the sample, the high resolution method would provide the analysis option using the least sample. The instrument was purged at 100 mL min^{-1} with argon. Each test used approximately 10 mg sample in a platinum pan. The baseline heating rate was 5°C min^{-1} with a resolution setting of 4 and a sensitivity of 1. The data was analyzed using the TAI Thermal Advantage software. The results are depicted in Fig. 4. The ~1 year units began significant mass loss at around 350ºC, the ~10 years units at about 250ºC and the ~20 year units at about 150ºC. KP decomposition was evident around 500ºC. The exact nature of the source of the mass loss has not been determined. The loss may be due to dehydridation of the titanium hydride, binder decomposition, or most likely a combination of the two. If the loss of hydrogen is complete in the composition, then a 1.16% mass loss is expected. Since the data has mass losses in excess of this, loss of binder during the TG analysis is likely.

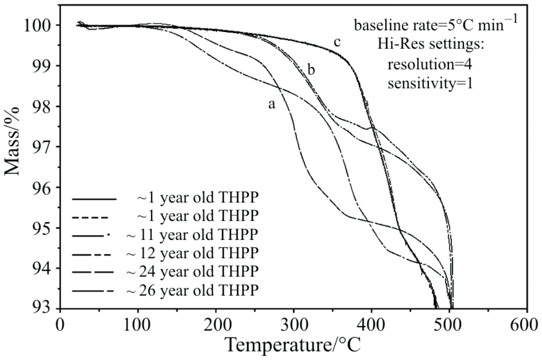

Fig. 4 Overlay of the mass loss curves for six THPP samples downloaded from aged units obtained using high resolution TG. The curves represent two samples from each of the three age groups; a – 20+ year-old, b – ~10 year-old and c – ~1 year-old

Kinetic thermal analysis

After establishing that the downloaded aged and recent THPP samples display significantly different thermal behavior, one path of the investigation was to establish if the difference was from thermal aging of the material. In order to accomplish this, fresh THPP would need to be accelerated aged to reproduce both the thermal behavior and function in devices that were exhibited by the real-time aged units. The 'rule of thumb' guidelines normally used for the accelerated aging of organic based materials typically do not apply for inorganic pyrotechnics. Therefore, a better understanding of the decomposition kinetics of the THPP was required in order to better estimate accelerated aging times and temperatures to make the aging process more efficient. A sample of newly manufactured THPP was sent to Naval Surface Warfare Center, Indian Head Division (NSWC-IH) for larger scale kinetic testing to determine the kinetic parameters.

Differential thermal analysis (DTA)

The DTA system consists of a predrilled aluminum-heating block with four sample holes and a block thermocouple control hole. Heating of the aluminum block was performed at a rate of 1°C min^{-1} via an Omega 4420 controller until the desired preset maximum temperature. DTA samples were prepared by adding approximately 1 g of the THPP into a 15 mm OD test tube. Aluminum oxide was used as a reference standard. A T-series thermocouple was introduced into the powder sample via a glass capillary through pierced FiberFrax plugs. Glass wool was used as insulation between the two plugs. Upon reaching the preset maximum temperature, the data collection continues until the THPP decomposed. After initial experimentation using a 1°C min^{-1} linear ramp survey scan to determine the working region, the isothermal kinetic analysis was accomplished at 252.5, 262.5, 271.6, 281.8, 286.7 and 291.6°C. In all but the lowest two temperature cases, decomposition was significantly energetic to destroy the sample, test tube and thermocouple. Thus, the critical temperature for 1 g of material was bracketed as between 262 and 272°C. The initial data reduction followed the guidelines presented in [4, 5] with some minor modifications. Since the decomposition of 1 g of material is significant enough to destroy the entire test system, the extrapolated onset from the baseline to either peak or data loss was chosen for the endpoint. The zero time for each system was obtained from the point where the reference temperature first reached a steady maximum. The difference between these two points is the reaction initiation time (RIT) in minutes. To obtain a kinetic equivalent, the rate was assumed to be 1/RIT. In a typical Arrhenius fashion, the natural log of the rate is plotted *vs.* the inverse absolute temperature. The activation energy is determined via a least squares fit on the slope of the plotted points according to:

$$\text{activation energy (J mol}^{-1}\text{)} = -\text{slope}\cdot 8.314\ \text{J mol}^{-1} \quad (1)$$

The calculation of the global data set yields an activation energy of 222.7±10.8 kJ mol^{-1}. Analysis of the curve in Fig. 5 shows minor curvature not consistent with typical Arrhenius behavior. Two explanations are readily posed in [6]: competitive reactions of differing energy and the general form of kinetics near the critical temperature. In addition, the 1°C min^{-1} linear ramp survey scans do show endothermic behavior prior to auto-ignition. Therefore, the argument of homogenous/heterogeneous behavior may apply based on the known rhombic to cubic phase change of the KP. Analysis of the three high temperatures yields activation energy of 384.3±1.3 kJ mol^{-1} (cubic) while the (rhombic) reaction derived from the four lowest temperatures is much lower at 186.4±4.7 kJ mol^{-1}. It

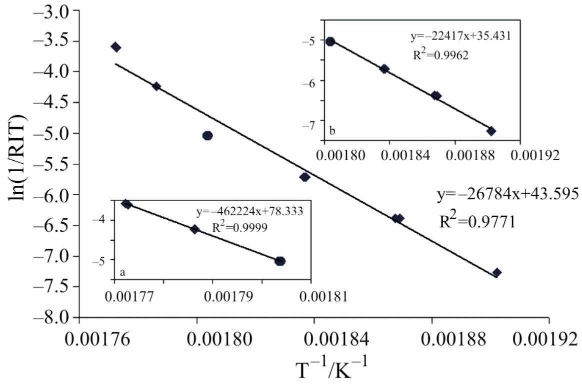

Fig. 5 Arrhenius plot for the DTA data from the thermal decomposition of THPP: insets – a – 281 to 291°C data, b – 252 to 281°C data

is unknown whether this lower temperature event coincides with a mechanism of slow evolution of hydrogen from the sample. From the least-squares fits to the data, the crossover temperature between two reaction mechanisms is 281.8°C.

Thermogravimetric analysis (TG)

TG testing was performed on a TAI TGA 2950 using nitrogen at 50 mL min^{-1} as the purge atmosphere. Samples were placed in closed aluminum pans that had been pin-holed to allow for escaping volatiles. Approximately 20 mg of THPP was used in each test in order to avoid mass effects. The samples were subjected to four heating rates: 0.2, 0.5, 0.75 and 1°C min^{-1}. Data analysis was performed using the TAI Specialty Library program for TG kinetics, which is based upon ASTM E1641 [7]. A representative mass loss plot is shown in Fig. 6. Figure 7 depicts an overlay of the plots for the four heating rates over the range of 150–400°C where the first significant mass loss occurs and the conversion levels. It is hypothesized the mass loss is due to Viton™ volatilization/decomposition as the overall mass change coincides with the rough percentage of that material in the overall composition. Figure 8 shows the log rate plots as a function of reciprocal temperature. There is some spread to the calculated parameters for the lower percent reaction owing to the relatively small mass transition being studied: 1 of a <5% overall mass change is a change of less than 10 μg. A summary of the kinetic results for activation energies as well as the Arrhenius pre-exponential factor (*Z*) appears in Table 1.

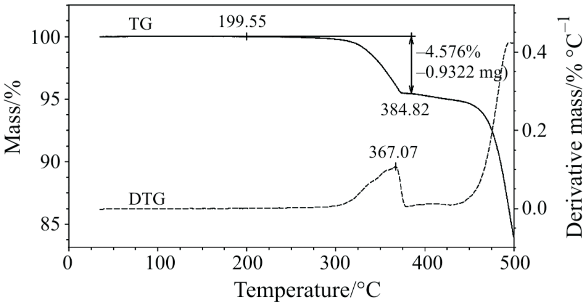

Fig. 6 TG and DTG curves of the decomposition of THPP at 1°C min^{-1}

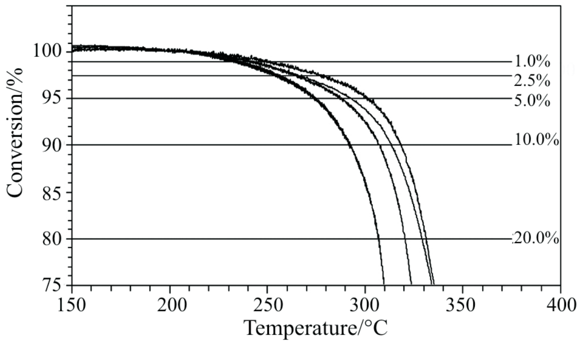

Fig. 7 Overlay of the plots for the four heating rates (left to right: 0.2, 0.5, 0.75 and 1°C min^{-1}) over the range of 150–400°C for the first significant mass loss (<5% of total mass) and the conversion levels of this first mass loss

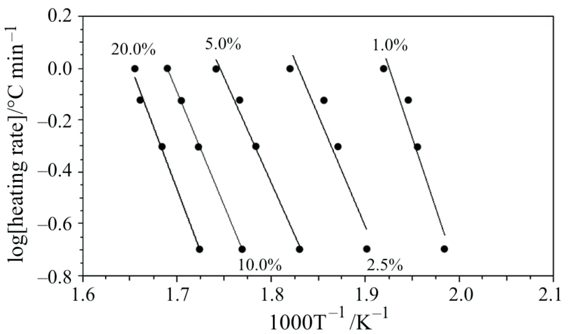

Fig. 8 Log heating rate *vs.* 1/*T* plot for the thermal decomposition of THPP

Table 1 Summary of TG Arrhenius kinetic parameters

Conversion/ %	E_a/ kJ mol^{-1}	log*Z*/ min^{-1}	60 min half-life temp./ °C
1.0	180.5	15.05	281.8
2.5	141.0	10.63	313.1
5.0	132.2	9.46	332.5
10.0	159.9	11.90	330.5
20.0	178.9	13.58	329.1

Conclusions

The observation that a family of pressure generating pyrotechnic devices is producing higher pressures as they age has created concern that the devices may eventually fail the design requirements. In order to better understand the phenomenon that defies convention has given the opportunity to examine real time aged materials. In order to better understand these materials this study examined the thermal activity of the THPP with a variety of techniques. Hi-resolution TG determined that indeed the aged materials behave differently than newly manufactured powder. The next phase is to artificially age fresh THPP to determine if the aged behavior can be reproduced. If it can, then the event is an aging phenomenon and can be accounted for in the estimated service life of the part. In order to efficiently artificially age the powder, the Arrhenius kinetic parameters of the decomposition needed to be determined. One of the assumptions of any determination of this nature is that the mechanism responsible for the higher device output pressures is the same as the one responsible for reaction used to generate the kinetic parameters. The DTA results indicate the possibility of a mechanism shift near 280°C, and this is supported by the phase diagram for the material that indicates solid-state phase transitions near this temperature [8]. However, both the TG results and the lower temperature DTA results will create a good basis for estimating accelerated aging times and temperatures for THPP. The accelerated aging study is scheduled to begin in the near future.

A previous study on the stability of binderless THPP, based upon chloride and water generation, has suggested that it may not be suitable for applications over 25 years [9, 10]. However, degradation of the material in this study does not explain the pressure increase, nor is it supported by the ion analysis. One potential explanation is that the fundamental nature of the bonding of the hydrogen has changed, allowing for a solid solution of the hydrogen rather than classical hydride bonding. This would allow for either higher reaction rates or reaction temperatures that could account for the pressure rise. Studies on the potential mechanisms are also in progress.

Acknowledgements

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