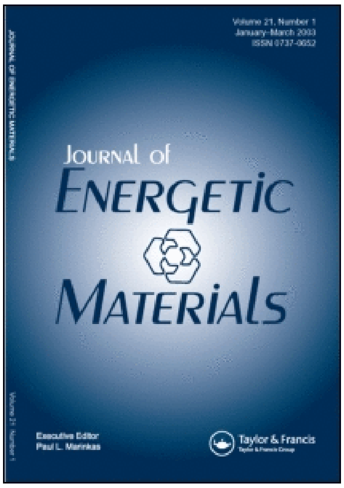

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Workshop report: boron hydrides in very high burning rate (VHBR) applications

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WORKSHOP REPORT: BORON HYDRIDES IN VERY HIGH BURNING RATE (VHBR) APPLICATIONS

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ABSTRACT

A joint JANNAF-ARO sponsored workshop was held to assess the state of knowledge on related chemical, formulation and combustion aspects of boron hydride based VHBR propellants. Workshop elements were laid out in the framework of a series of questions, formal presentations, poster session and discussion periods. Workshop findings are presented in summary form. Workshop recommendations relating to improved test methods, literature analyses and areas needing further study are present.

INTRODUCTION

Boron hydrides, particularly salts of the $B_{10}H_{10}^{=}$ and $B_{12}H_{12}^{=}$ anions, have been a subject of study as burning rate promoters in very high burning rate (VHBR) propellants for the past eight years.[1] Formulations with apparent burning rates of 1 to several hundred meters per second have been reported.[2,3] Related $B_{10}H_{10}^{=}$ based formulations with propagation rates up to 1500 m/s have been marketed under the trade name "Hivelite" and used in thermally insensitive energy transfer and severance devices for the past 20

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years.[4] The rates mentioned above fall intermediate between normal deflagration and detonation velocities.[5] As such, the combustion mechanisms capable of yielding these burning velocities are of great technical as well as practical interest. Among the practical applications currently under study are monolithic propellants,[6] traveling charge,[7] and high rate-low smoke propellants.[8] Applications to in-flight guidance[9], as consumable plugs in tubular projectiles, and in lasers have also been considered. The burning rate enhancing ability of boron hydride salts has been most recently applied to combustion tailoring of ramjet fuels.[9]

The state of knowledge on the combustion aspects of VHBR propellants was reviewed by a JANNAF Combustion Subcommittee Workshop in 1981, as reported by Fifer.[10] In part as a result of recommendations made at that wokshop, a great deal of new information has been developed in this area since then. In addition, several new potential applications have become driving forces in VHBR propellant development.

During the last workshop, strong participation by the DDT community resulted in a number of useful insights into the probable physical processes involved in VHBR burning. In addition, valuable recommendations were made for new combustion experiments. As a result, needed growth has taken place in the combustion diagnostics and modeling areas. As these studies progressed, however, it became clear that combustion diagnostics and modeling were not sufficient to yield the insights necessary for safe development and use of these VHBR materials in their intended applications. Ingredient chemistry, propellant processing conditions, and ingredient particle size effects were all found to significantly influence the combustion behavior of VHBR formulations. Much of the detailed knowledge of these factors remained inaccessible, however. At the same time, several serious accidents involving energetic boron hydride based materials pointed to the need for chemical insights into the hazards posed, either directly or through aging, by these formulations. It was felt that a better integration of information on chemical, formulation, and processing effects as they relate to the combustion and hazard properties of VHBR propellants is necessary. The time, therefore, appeared ripe for a second workshop on VHBR propellants to assess developments in the past five years and to chart directions for future growth.

WORKSHOP ORGANIZATION

The present workshop has sought to lend increased emphasis to chemical and formulation factors affecting VHBR propellant combustion and hazard properties.

Accordingly, input was actively solicited in these areas as well as in combustion diagnostics and modeling. As in the last workshop, no attempt was made to restrict discussions to formulations incorporating the $B_{10}H_{10}^{=}$ and $B_{12}H_{12}^{=}$ anions. Rather, it was hoped that the focus could be brought on the common beneficial properties of various boron hydride additives. In view of its extensive program in boron chemistry, ARO co-sponsorship of the workshop was sought to help assure strong input in the chemical area. Finally, it was felt that the workshop would benefit from contributions in two additional areas. The first concerned future energetic materials needs for advanced weapons applications. The second concerned an overview of some thirty years of boron hydride/ energetic materials research in general, and the $B_{10}H_{10}^{=}$ and $B_{12}H_{12}^{=}$ systems, in particular. Contributions were sought in these areas as well. A tentative agenda and list of discussion questions were formulated and promulgated to prospective participants. The proposed workshop outline appears below.

I. Advanced Concepts/ Past and Future Perspectives
II. VHBR Propellant Formulations & Properties
III. Combustion Diagnostics & Modelling
IV. Chemical Decomposition & Reactivity Studies
V. ARO Sponsored Boron Hydride Research

Response from the community was favorable. Submissions were received in each of the topic areas above. An agenda was prepared and discussion questions finalized. The workshop was held at the Ballistic Research Laboratory on 28-30 May, 1986. A list of the discussion questions appears in Appendix B.

The workshop was organized with sessions consisting of related presentations, each followed by a short question and answer period. In addition, at the end of each session, time was set aside for a more extended dialog covering the topic area as well as related discussion questions. A separate poster session was devoted to ARO sponsored research on the synthesis and reactivities of boron hydrides. The final portion of the workshop was set aside to reconsider each of the discussion questions in detail. The list of workshop presentations arranged in sessions appears in Table 1.

Two of the presentations, the catalyst effectiveness study by T. Casti and the combustion cinematography work by A. Helmy were impromptu reports sparked by workshop discussions. Regrettably, two important papers relating to the use of VHBR propellants in medium caliber monolithic charges were cancelled at the last minute. Part of that data, however, was subsequently presented at the 1986 JANNAF Propulsion meeting.[11]

DISCUSSION

The discussion section is divided as follows. Initially, the individual sessions are summarized, emphasizing the most significant results of each. This is followed by an overall summary of workshop insights into the combustion of VHBR propellants. The final section is devoted to the workshop recommendations and conclusions.

The first session, on advanced concepts and perspectives, served to focus on the application needs driving the development of very high burning rate formulations as well as some possible chemical tailoring approaches to new materials. In addition, the session served to surface a great deal of information on boron hydride and carborane chemistry which, though familiar to the rocket community, was not known to those in the gun area. A re-examination of some of this information could, very likely, advance some of the applications of current interest. One of the workshop recommendations to be discussed later involves the retrieval of such information. Of special significance to the VHBR effort were hazards and handling data on some of the boron hydrides. Much of this was new information to the gun community. Some of the hazards information is included in Appendix B. An additional workshop recommendation however, involved a followup in the context of the JANNAF Propulsion System Hazards Subcommittee.

TABLE I. Workshop Presentations

Session I. Advanced Concepts/ Past and Future Perspectives

R. Miller, ONR	Advanced Applications for Boron Containing Energetic Compunds
F. Hawthorne, UCLA	Evolution of the Use of Boron Compounds in Enhanced Burning Applications
A. A. Juhasz, BRL	The Traveling Charge Program and VHBR Propellant Development
C. Leveritt, BRL	Perspective on the Use of $B_{10}H_{10}^{=}$ Compounds as Burning Rate Promoters

Session II. VHBR Propellant Formulations and Properties

J. Corney, NSWC	Enhanced Combustion from Boron Hydrides in Solid Ramjet Applications
L. Asaoka, NSWC	Approaches to Tailoring Slow, Medium, and Fast VHBR Formulations
W. Vienna & J. Moniz, NOS	Review of the Indian Head Traveling Charge Formulation, Processing and Safety

Characterization Effort

F. Hawthorne, UCLA	Physical, Chemical and Handling Properties of Boron Hydrides
M. Magnum, Hercules	Carboranes as Burning Rate Catalysts for for Solid Rocket Propellants
B. Spielvogel, ARO	ARO Programs in Boron Chemistry
S. Shore, OSU	Higher BH Syntheses from Pentaborane

Session III. Combustion Diagnostics and Modeling

A. Helmy, TMcS	Cinematographic Data on the Ambient Pressure Burning of a VHBR Rocket Propellant
A. Helmy, TMcS	Thermal Decomposition of ropellant Oxidizers With $B_{10}H_{10}^{=}$ Salts
K. White, BRL	Combustion Diagnostics of VHBR Propellants
R. Frey et al, BRL	Flash X-Ray Observations of Burning Hivelite
E. Fisher, Veritay	Thrust Bomb Studies of VHBR Burning
D. Kooker, BRL	Perspective on Combustion Modeling of Boron Hydride Based VHBR Propellants

Session IV. Chemical Decomposition and Reactivity Studies

T. Casti, Hercules	DSC Diagnostics of Catalytic Effects on AP Propellant Decomposition
R. Fifer, BRL	Nitramine-Borohydride Chemical Interactions
M. Schroeder, BRL	Nitramine Interactions
P. Duff, BRL	Studies of the Effects of Hivelite and Other Boron Compounds on Nitramine Decomposition

	by Pyrolysis GC-FTIR
G. Adams, BRL	The New Boron Thermochemistry

Session V. Poster Session on ARO Sponsored Boron Hydride Research

L. Sneddon, U Pa	New Synthetic Routes to Higher Boranes and Carboranes
S. Bauer, Cornell	Rates and Mechanism of $O(^3P)$ Attack on B/H and C/H Fuels
R. Grimes, U Va	Designed Synthesis of New Carboranes and Related Species
S. Shore & J. Wermer, OSU	Pentaborane as a Feedstock for Higher Borane and Carborane Preparations
L. Todd, U of IN	Recent Studies of Azaboranes
G. Kodama, U of UT	Recent Developments of the Chemistry of Lower Boron Hydride Compounds
T. Fehlner, N D U	Ferraboranes

The second session, on VHBR formulations and properties was particularly useful in examining the thinking behind recent formulation developments. Of particular interest here, were questions of ingredient selection, synergistic effects, particle size effects, processing, handling problems, and formulation hazards. The reader is urged to examine the answers to questions 8 and 9 in Appendix B regarding hazards and aging. This session also provided an overview of ongoing research sponsored by the Army Research Office. This, in combination with the ARO investigators' poster session, highlighted a rich menu of compounds for screening as possible burning rate promoters. The contacts made here between synthetic chemists and propellant formulators are one of the important outcomes of the workshop. Questions regarding ingredient evaluation helped to focus on the need for the development of effective small scale screening methodology for ingredients as burning rate promoters. This too resulted in a workshop recommendation.

Session three dealt with recent developments in the combustion characterization and diagnostics of VHBR formulations. At the 1981 workshop, the only available combustion data on VHBR materials concerned low-pressure closed bomb tests and some propagation time measurements under ambient conditions. There has been considerable growth in this area since that time. Cinematographic data presented by Dr. Helmy dramatically showed the effect of a small amount of boron hydride additive on the burning rate of a low-smoke propellant under ambient conditions. Similar observations were reported by BRL for the ambient pressure combustion of a series of formulations with increasing boron hydride content. Observed burn rates increased with increasing percent boron hydride additive. Interestingly, Dr. Helmy's films, taken at ambient pressure, showed no sample deconsolidation. This was in contrast to high speed cinematographic data presented by Dr. White on the burning of VHBR samples under pressure.[12] This data clearly demonstrated a transition to in-depth burning and sample deconsolidation. What is noteworthy here is that the samples in question were at or near theoretical maximum density, with little or no expected gas permeability. White further reported interesting evidence on the effects of hot pressurizing gas on the burning of VHBR samples. High density materials which evidenced low overall burning rates under low pressure closed bomb conditions were found to burn rapidly when pre-pressurized to higher pressures by a conventional booster propellant. Fisher reported differences in the burning properties of VHBR propellant samples depending on whether they were circumferentially bonded into the combustion tube or slipped into the tube with a lubricant.[13] For identical formulations, samples bonded in place had much faster burning properties. Frey, using flash x-ray diagnostics on similar experimental configurations, not only confirmed this observation, but showed that the samples bonded in place burned with breakup while the lubricated samples burned essentially intact.[14] The various observations above appear to be reasonably consistent with each other as well as earlier combustion observations. This will be discussed later.

The fourth session, on chemical decomposition and reactivity studies, represented the strongest growth area since the 1981 workshop. At that time no chemical decomposition studies were reported relating either to ingredient screening for burning rate enhancement applications or to the chemical mechanisms of burning rate enhancement. Since then, serious efforts at BRL and Hercules have begun dealing with these issues. Casti reported some extremely interesting correlations between the effectiveness of various metal ion and boron hydride burning rate "catalysts" and their effects on the DSC decomposition curves of the propellant oxidizer. Fifer, Duff and Schroeder reported on different aspects of BRL work on the pyrolysis of nitramines and other propellant ingredients in the presence of boron hydride additives.[15, 16] The boron hydrides were shown to affect the pyrolysis product profiles, generally in the same direction as increasing reaction temperatures. Further, new pyrolysis products were also noted from the boron hydride catalized samples. These experiments should cast light on the effects of hydrides on the pyrolysis pathways of oxidizers and other energetic propellant ingredients. Both techniques show promise as possible future micro scale "catalyst" screening tools. Many of the suggestions dealing with possible chemical mechanisms of burning rate enhancement by boron hydrides came from this session.

Up to this point, the discussion has centered on summaries of the individual sessions. The principal objective of the workshop, however, was to examine ramifications relative to the combustion of VHBR propellants. The following paragraphs represent an attempt to provide a generalized overview of the various chemical and physical insights gained into the burning of VHBR propellants.

The term, VHBR Propellant, has been applied to composite propellant formulations consisting of salts of $B_{10}H_{10}^{=}$ or $B_{12}H_{12}^{=}$, oxidizer and binder. Hivelite[4] formulations fall into this category as well. An important consideration impacting combustion related questions is whether these systems are unique or they fall into a larger pattern. Carboranes, specifically n-hexyl carborane and carboranylmethyl propionate, have a well-documented history as burning rate promoters. The burning rates of propellants made with these materials are considerably lower than those reported for VHBR formulations, however. The carboranes, nevertheless, are effective burning rate "catalysts." Professor Hawthorne, reporting on carboranylmethyl acrylate propellants, indicated that some of these formulations had still higher burning rates. The suggestion was made during the workshop that carboranes may influence burning rates by some in-depth effect on the condensed phase reaction zone.[17] If this is so, the similarity in burning rate promoting activity may be more than coincidental. Fifer,[18] studying the effect of a group of lower boron hydride salts on the closed bomb burning of HMX, reported large increases in gasification rates depending on the nature and amount of boron hydride additive. The boron hydrides acted as burning rate promoters to the HMX. This is all the more significant, since burning rate "catalysis" of nitramine systems has, in the past, been difficult. In all, it seems reasonable to expect that there is some chemical similarity in the mode of action of the various boron hydrides as burning rate promoters. This activity is probably related to their potential as sources of hydrogen as well as the ability of boron atoms to be oxidized either by oxygen or nitrogen. It was suggested during the workshop that the combination of thermal stability coupled with high electostatic sensitivity properties exhibited by many VHBR formulations may indicate a hydrogen free-radical initiation mechanism. This seems plausible and may account for the similarities in the burn rate accelerating behavior of various boron hydride compounds. One of the workshop recommendations deals with an experiment to examine this postulate.

A differentiating factor between the activities of individual compounds may be the variation in reactivity characteristics of certain hydrogens. As suggested above, the combustion of boron hydride based VHBR propellants may involve a free-radical initiation mechanism. If this is the case, compounds with more active hydrogens should lead to faster burning. The two apical hydrogens in the $B_{10}H_{10}^{=}$ anion, for example, are considerably more reactive than the rest. Salts containing this anion have been found to have becter burning rate promoting activity than salts of $B_{12}H_{12}^{=}$ which has no such reactive hydrogens. In view of this, it may be interesting to see how the reactivities of hydrogens on some of the carboranes and lower boron hydrides mentioned above compare with the B10 and B12 systems. A review of literature data in this regard would be useful.

What accounts for VHBR burning behavior with formulations of some compounds and normal "catalized" burning with others? One factor which may play a significant role in both the burning and sensitivity properties of such energetic formulations is the proximity of oxidizing and reducing functionality. An admittedly extreme example, the double salt of cesium nitrate and cesium $B_{10}H_{10}^{=}$, in which both the boron hydride and nitrate anions occupy centers in the crystal lattice, is well known for its high electrostatic sensitivity as well as its fast burning properties. Such intimacy at the molecular level is not necessary, however. Close physical blending of the boron hydride salt and oxidizer, especially in the presence of energetic binders, has also been successful in obtaining very high burning rate properties. It has been found that the efficiency of boron hydride burning rate promoters increases as particle size decreases. Typically, in current formulations these particle sizes are in the range of 5 microns and below.[19]

An additional approach used by formulators for increasing burning rates involves increased solids loading of formulations. In this case, less binder would be available to separate the oxidizer from the boron hydride.

Increased solids loading, however, also increases the overall energy of the formulation, another factor leading to faster burning.

Certain factors known to increase the burning rates of conventional propellants are also used in preparing VHBR formulations. Triaminoguanidinium nitrate (TAGN) as an oxidizer or co-oxidizer is known to promote faster burning properties. The same is true for energetic binders, especially glycidyl azide polymer (GAP). Both of these are currently in use. Increasing the overall energy of a formulation, as mentioned above, tends to increase its burning rate. For a sample of fixed solids loading, this may be done by means of energetic binder/plasticiser combinations. Unfortunately, hazard properties also tend to increase with overall energy. Asaoka,[20] however, has shown that stability increases with decreasing boron hydride content, though burning rates also decrease. Nevertheless, this opens the door to interesting tradeoffs. An interesting counterpoint to the rapid burning of energetic binder formulations is the polyethylene glycol (PEG) binder system. Though this is a nonenergetic binder, many of its formulations exhibit very rapid burning in the closed bomb, especially at elevated pressures. It is thought that this is due to the weak bonding between binder and solid fillers (oxidizer and hydride). Finally, it is well known that large particle sizes of the nitramines HMX and RDX promote faster burning at low pressures. Such burning is accompanied by large slope changes as the pressure increases. Evidence seems to indicate that large nitramine crystals and their agglomerates tend to produce in-depth burning.

A further factor influencing VHBR burning is physical rather than chemical. Porosity or frangibility would be expected to result in in-depth burning. One study, for instance, involving samples of identical chemical composition but decreasing density showed that closed bomb burn times are inversely related to porosity.[12] Highly frangible samples have also generally tended to have faster burning properties than samples with a "rubbery" consistency. Nevertheless, low porosity, rubbery samples with energetic binders have exhibited very rapid burning properties under some closed bomb conditions.

The manner of burning can significantly influence the burning properties observed for VHBR samples. Early experiments involving cigarette burning of bare and circumferentially confined samples showed an increase in apparent burning rate with confinement. Further experiments since then have also demonstrated that the interface between sample and its circumferentially confining element can also affect burning behavior, see discussion for session three. Samples bonded into a tube with epoxy burned much faster than identical samples slipped into the tube with a lubricant. Flash x-ray studies indicated that the former burned with breakup while the latter moved down the tube essentially intact. High speed photographic studies of high density VHBR samples have indicated that rather than flamespread between the sample and the confining wall, the reaction appears to propagate through the sample. For a sample bonded into a transparent tube and ignited at one end initial reaction is observed at the front of the sample. Thereafter discrete luminous regions appear along the length of the sample, followed by complete combustion/deconsolidation. White further studied the effects of ignition pressure on the burning of VHBR samples.[21] In a specially designed closed bomb, the VHBR sample could be pre-pressurized with hot combustion gases form a conventional booster prior to ignition. The burn time of the sample was strongly related to the booster pressure. Doubling the booster pressure decreased burn time by as much as one order of magnitude.

The evidence for some form of in-depth burning mechanism for VHBR formulations is compelling. The difference between "fast" and "slow" formulations may simply be a function of the thickness of the in-depth zone. The "faster" the formulation, the thicker the reaction zone. That is, slower burning may be caused by a near- laminar, thin reaction zone while faster burning would involve a larger in-depth zone. Since many 100 percent TMD samples evidence VHBR properties, some form of self-induced porosity governs the burning of these samples. This may be related to inherent flaws or to some peculiar ability of the boron hydrides to generate reactions in depth. The hydrogen radical initiation mechanism suggested above is one attractive possibility. These considerations suggest an overall mechanism as follows; sample ignition begins at the propellant geometric surface, where gassification rates are controlled by formulation chemistry in a conventional way. The depth of the condensed phase reaction zone increases due to the action of the boron hydride, with reaction centers extending deeper into the sample at discrete paths. The rate at which the reaction front propagates is a function of ambient pressure as well as the chemistry of the formulation. The exothermic, gas forming reactions in-depth generate internal pressures and shear forces which break the sample apart. The large surface area of the broken fragments is responsible for the rapid gas generation rates observed.

CONCLUSIONS

Examining the problem of VHBR burning from multiple perspectives was a valuable exercise. Developments in the combustion diagnostics area have yielded a much more complete physical picture of the VHBR combustion process than was available five years ago. The chemical decomposition studies undertaken since the last workshop promise to provide much needed insight into the chemistry of VHBR burning. This work may also yield valuable micro scale screening tools for new materials. Discussions of formulation technology have helped to systematize the various techniques in use to obtain VHBR burning. The focus on boron hydride chemistry has served to generate a postulate for the mechanism of action of the boron hydride additives, point out some possibly exploitable chemistry for new formulations, and to provide data on potential hazard with these materials.

RECOMMENDATIONS

A number of recommendations resulted from workshop discussions. These are listed below.

1) Use of x-ray cinematography to gain further detailed insight into the physical processes of VHBR combustion.

2) Deuterium isotope effect studies to examine the free radical initiation hypothesis for VHBR burning.

3) Examination of alternate boron hydrides as burn rate promoters. Consider both existing work and new tailored boron hydride systems.

4) Develop new chemical and micro scale bomb tests for ingredient evaluation.

5) Prepare a white paper on the hazard properties associated with BH based formulations. Forge a link with the JANNAF Propulsion System Hazards Subcommittee.

6) Accompany formulation development efforts with aging studies to flag safety problems early.

7) Project "Gum Shoe." This is a literature evaluation proposal aimed at preserving information generated over the last 30 years on the use of boron hydrides in energetic applications.

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APPENDIX A

DISCUSSION QUESTIONS

1. What evidence is there for the effectiveness of boron hydrides in promoting VHBR behavior and what differences have been observed in the burning rate promoting behavior of various boron hydrides?

2. What is the relationship between sample density/ porosity and chemical composition in promoting VHBR behavior?

3. What chemical compounds appear to do the best job in promoting VHBR behavior?

4. What chemical properties can be correlated with differences in VHBR promoting tendencies?

5. Are there alternate ways of incorporating boron hydride functionality into VHBR formulations?

6. Are there synergistic effects between certain binders, oxidizers and catalysts with respect to boron hydrides in promoting VHBR behavior?

7. What formulation, fabrication and curing problems are there attendant to the use of boron hydrides in VHBR formulations?

8. What chemical ingredients have proven hazardous, i.e. appear to be responsible for high sensitivities in formulations?

9. What compatibility problems have arisen in terms of short and long term stabilities?

10. What safety characterization methodology is used at the various installations and how do the results compare? How well do these techniques characterize the real hazards associated with the handling and storage of these materials?

11. What are the differences in the burning mechanisms of meter per second and hundreds of meters per second VHBR propellant formulations?

12. What are the underlying mechanisms in the ignition (initiation) and burning of boron hydride based VHBR formulations?

13. What developments have taken place in the combustion diagnostics area since the 1981 workshop?

14. What improvements have occurred in our understanding of the mechanisms of boron hydride action in promoting faster burning and in the mechanism of VHBR burning since the last workshop?

15. What new ideas can we apply to improve our understanding of VHBR combustion?

APPENDIX B

HAZARDS

One of the workshop recommendations concerned a compendium of hazards information. This effort is expected to take some time. Certain points, however, which came up during workshop discussions are noted here in the interest of safety.

8. What chemical ingredients have proven hazardous, i.e. appear to be responsible for high sensitivities in formulations?

Historically, the cesium and potassium "double salts" of $B_{10}H_{10}^{=}$ and nitrate ions have been extremely sensitive to electrostatic and friction initiation. It would be reasonable to assume that similar double salts of the $B_{12}H_{12}^{=}$ ion would behave the same. In addition, as mentioned in the first workshop report, certain cobalt complexes of these materials are also quite hazardous. Care needs to be exercised as well in the handling of the hydrazinium and dimethyl hydrazinium salts of the $B_{10}H_{10}^{=}$ system, as they are very sensitive to shock and electrostatic initiation. Most probably similar cautions are in order for the $B_{12}H_{12}^{=}$ system. The free acid form of $B_{10}H_{10}^{=}$ is extremely shock sensitive. A great deal of care must, therefor, be taken to keep $B_{10}H_{10}^{=}$ salts in neutral or slightly basic environment. This point has special significance to the long term stabilities of certain formulations, see question 9.

In regard to ingredient hazards, the gun community is by-and-large not aware of the dangers posed by some of the boron hydride ingredients. The experience of the academic and rocket communities is highly valuable in this regard. It was suggested that a hazards compendium be prepared on boron hydride systems, possibly in the context of the JANNAF Propulsion System Hazards Subcommittee.

9). What compatibility problems have arisen in terms of short and long term stabilities?

Those having experience in the $B_{10}H_{10}^{=}$ propellant system suggest that nitrocellulose may have serious compatibility problems with these salts. Indications are that formulations exhibiting acceptable stability on manufacture may become hazardous in 90 days. Though no hard and fast data are available, there are indications that the sample involved in the incident at BRL in 1980 may have suffered from aging effects. This was a nitrocelluose/ $B_{10}H_{10}^{=}$ salt system with TAGN oxidizer.

Prof. Hawthorne mentioned that there could be serious problems if the $B_{10}H_{10}^{=}$ ion were to become acidified, see Question 8. Further, nitroso and nitronium ions apparently form an impact sensitive red material with the $B_{10}H_{10}^{=}$ ion. As a matter of fact, the $B_{10}H_{10}^{=}$ ion seems to be a very effective scavenger for electrophiles. Indications are that $B_{10}H_{10}^{=}$ could preferentially react with nitrogen oxides in preference to normal stabilizers which may be present in a NC binder propellant.

On the other hand, available data on the compatibility of $B_{12}H_{12}^{=}$ salts with nitrate ester systems including BTTN and NC/NG in low smoke ammonium nitrate propellants has not uncovered any incompatibility problems to date. Although mixtures such as BTTN/$B_{12}H_{12}^{=}$ salt are highly sensitive, formulations may be made if the nitrate ester and boron hydride salt are not mixed first.

Dr. Parry cautioned that prudence would dictate that some form of surveillance studies accompany any of the new formulations prepared for combustion studies in this area. This is existing practice at some installations but not at others.