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TECHNICAL REPORT ARBRL-TR-02166

WORKSHOP REPORT: FUNDAMENTAL REACTIONS
IN SOLID PROPELLANT COMBUSTION

Robert A. Fifer

May 1979

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US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
BALLISTIC RESEARCH LABORATORY
ABERDEEN PROVING GROUND, MARYLAND

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) (meg) This report summarizes the results of a JANNAF workshop held 26-27 July 77 at the Ballistic Research Laboratory. The purpose of the workshop was to access our current understanding of the fundamental chemical and physical processes involved in the ignition and combustion of nitrate ester and nitramine propellants. A brief review is presented of the nitramine slope break and nitrate ester catalysis phenomena. The workshop discussions are summarized. Specific discussion questions are listed, together with some of the ideas and recommendations that resulted from the workshop.		

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I. INTRODUCTION

This report summarizes the results of a workshop dealing with the fundamental processes involved in the combustion and ignition of solid gun and rocket propellants. The workshop was sponsored by the Workshop Committee of the JANNAF Combustion Working Group, and was held on 26-27 July 1977 at the Ballistic Research Laboratory.

The subject matter of the workshop was limited to nitrate ester and nitramine propellants. It was considered worthwhile to consider both types of propellants together for the following reasons. First, there might be similarities in the chemistry of these two types of propellants, since they both apparently involve decomposition of the solid into formaldehyde and nitrogen oxides, which subsequently undergo a reaction in the flame zone. Secondly, the types of experimental measurements that have been carried out in the past on the two propellant types are in some cases different, and it was felt that it might be useful to consider whether some of the experiments that had traditionally been performed with one of these propellant types might profitably be applied to the other. Finally, this approach brought together in a few cases researchers who were not previously acquainted with each other's work.

An attempt was made to deal only with the results of experimental and theoretical research that can be related to, or discussed in terms of, the fundamental chemical and physical processes involved in the thermal decomposition, ignition and combustion of this class of propellants. Interest centered on the chemical mechanisms and kinetics of these processes, although it was recognized that chemical and physical processes must be intimately tied together in processes as complex as ignition and combustion. The goals of the workshop were to assess the present state of fundamental knowledge of the reactions of these propellants, to identify those areas where information is currently lacking, and to stimulate ideas for promising new techniques and experiments.

The type of subject matter considered included the following:

- I. Composition/Ingredient Chemical Effects
 - A. Propellant-catalyst interactions
 - B. Propellant-binder interactions
 - C. Comparisons with linear (aliphatic) amines and esters
- II. Propellant Ignition/Combustion Properties
 - A. Thermal decomposition rates and products

- B. Ignition mechanisms
- C. Isolation of primary reactions
- D. Chemical interpretations of pressure exponent changes/
plateau burning phenomena
- E. Solid phase, surface, gas phase reactions
- F. Phase transitions: melting, vaporization, polymorphs
- G. Flame structure and diagnostics; species concentrations/
temperature profiles

III. Modeling (involving chemistry): Potential and Prospects

The first half of the one-and-a-half day workshop involved informal presentations by a number of the participants, with interspersed discussion. The second half was devoted to discussion of particular questions or problems, most of which were presubmitted by the participants and distributed prior to the date of the workshop.

The workshop was attended by 22 invited participants, plus a number of observers (see Table I). The workshop was organized and coordinated by the author of this report.

Due to the length of time that has lapsed since the workshop, no attempt will be made to summarize new results presented by the participants at the workshop. (Much of this has since been published; some of it was presented at the 15th JANNAF Combustion Meeting, and will be summarized in the proceedings of this meeting.) Rather, the rest of this report will be devoted to: a) a brief review of the nitramine slope break and nitrate ester catalysis phenomena, to which most of the discussion was directed, including a few representative references that might be a useful starting point for reviewing the literature of these subjects; b) a general summary of the workshop discussions; and c) a more specific listing of some of the formal presubmitted discussion questions, together with some of the ideas and recommendations that arose in discussing them; and d) a conclusion.

II. BACKGROUND

Brief Review of Nitramine Slope Break and Nitrate Ester Catalysis Problems.

1. Slope Breaks in Nitramines

Figure 1 illustrates the slope break phenomena typically observed for HMX* in strand burner measurements with inert or mildly energetic

* - cyclotetramethylenetetranitramine.

TABLE I. JANNAF Workshop Participants and Observers

PARTICIPANTS

George Adams	BRL
John Barker	SRI
Richard Beyer	BRL
Thomas Brill	U. Delaware
Leonard Caveny	Princeton
Richard Field	ARRADCOM
Robert Fifer	BRL
Joseph Flanagan	Rocketdyne
Berge Goshgarian	AFRPL
Thomas Hall	NSWC
Edward Johnson	George Washington U.
Mortimer Kamlet	NSWC
Joseph Lannon	ARRADCOM
Joseph Levy	George Washington U.
Raymond McGuire	Lawrence Livermore
James Pfau	BRL
Robert Powers	AFATL, Eglin
Channon Price	NWC
Joseph Rocchio	BRL
Ron Rosher	Hercules, Magna
Harold Sandusky	NSWC
Robert Shaw	Lockheed

OBSERVERS (+BRL)

Richard Biddle	Thiokol, Elkton
Winston Brundige	Thiokol, Elkton
Thomas Christian	CPIA
Frank Goetz	U. Delaware
Lee Harris	ARRADCOM
Richard Miller	ONR
Steve Sergio	U. Delaware
Ludwig Stiefel	ARRADCOM

binders.¹ At low pressures the larger particle size propellant exhibits burning rates significantly lower than that of the pure nitramine. At about 20 MPa (2900 psi), a sudden increase in the pressure exponent occurs, and the burn rate rapidly approaches that of the pure nitramine. A second discontinuity then occurs, and thereafter the burn rate appears to follow that expected for the pure nitramine.² Fine particle propellant, on the other hand, exhibits higher burning rates at low pressure, a much milder slope break at pressures higher than the coarse particle slope break, and thereafter a burning rate that approaches that of the pure nitramine only at very high pressure, if at all. RDX* and many other nitramines^{3,4}, including linear nitramines, show behavior similar to that of HMX.

Increasing the binder energy (and therefore the burning rate) to a value closer to that of the nitramine increases the low pressure burn rate and thereby minimizes the magnitude of the large particle slope changes.⁵ Bimodal HMX (i.e., mixture of coarse and fine) propellants behave very much like the propellants containing fine HMX only.⁶ Burning rates of HMX propellants at low pressures are

* - cyclotrimethylenetrinitramine.

1. N.S. Cohen, "Combustion of Nitramine Propellants", 11th JANNAF Combustion Meeting, CPIA Publication 261, Vol. I, pp. 267-283, December 1974.
2. (a) T.L. Boggs, J.L. Eisel, C.F. Price, and D.E. Zurn, "Burning Rates of Cyclotetramethylenetetranitramine (HMX)", 15th JANNAF Combustion Meeting, Newport, RI, September 1978; (b) T.L. Boggs, C.F. Price, D.E. Zurn, R.L. Derr, and E.J. Dibble, "Temperature Sensitivity of Deflagration Rates of Cyclotetramethylenetetranitramine (HMX)", 13th JANNAF Combustion Meeting, CPIA Publication 281, Vol. I, pp. 45-56, December 1976; (c) also same authors, "The Self Deflagration of Cyclotetramethylenetetranitramine (HMX)", AIAA/SAE 13th Propulsion Conference, 11-13 July 1977, Orlando, FL, Preprint No. 77-859.
3. J.E. Flanagan, "Relationship of Nitramine Combustion Phenomena and Chemical Structure", 13th JANNAF Combustion Meeting, CPIA Publication 281, Vol. I, pp. 69-74, December 1976.
4. R.L. Simmons, "New Nitramines for Gun Propellants", 15th JANNAF Combustion Meeting, Newport, RI, September 1978.
5. N.S. Cohen and L.D. Strand, "Nitramine Propellant Research", 13th JANNAF Combustion Meeting, CPIA Publication 281, Vol. I, pp. 75-88, December 1976.
6. (a) K.P. McCarty, "Mechanism of Combustion of HMX Propellants", 14th JANNAF Combustion Meeting, CPIA Publication 292, Vol. I, pp. 243-258, December 1977; (b) also K.P. McCarty, "Effect of Formulation Variables on HMX Propellant Combustion", 15th JANNAF Combustion Meeting, Newport, RI, September 1978.

increased by materials such as lead compounds^{6,7}; catalysis is considered to be yet another way to minimize slope break effects. Of the three ways to minimize slope breaks (binder-propellant matching, use of small particle sizes, and low pressure catalysis), binder-propellant matching would appear to be the most effective. For many applications, however, the use of a fast burning binder will result in a propellant that is too hot; burning rate pressure exponents may also be too high, even though slope breaks have been eliminated.

The slope breaks with nitramine propellants occur at pressures higher than the operating pressures of most rocket motors, and therefore represent a problem only insofar as they stand in the way of the trend to operate rocket motors at increasingly higher pressures. The problems with nitramines for gun applications are more complex, and have been the subject of two workshops^{8,9} and a number of papers.¹⁰⁻¹² Burning rate exponent shifts may not even manifest themselves under the rapidly-rising pressure environment of a gun chamber. In one closed bomb study with HMX/inert binder propellants¹³, no slope breaks were observed with bimodal 2/10 μ HMX, but breaks were observed with class E ($\sim 15\mu$) HMX. Rather, the ballistic variability observed with nitramine propellants is probably due to the generally higher pressure exponents for nitramine propellants.

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7. G.E. Herriott and R.L. Foster, "Ballistic Modification of Minimum Smoke Propellants", 15th JANNAF Combustion Meeting, Newport, RI, September 1978.
 8. L. Stiefel, "Review of Workshop on the Combustion of Nitramine Propellants for Guns", 10th JANNAF Combustion Meeting, CPIA Publication 243, pp. 199-216, December 1973.
 9. R.L. Simmons, "Workshop Report on Nitramine Gun Propellant Combustion", 13th JANNAF Combustion Meeting, CPIA Publication 281, Vol. I, pp. 1-8, December 1976.
 10. R.L. Simmons, "High Pressure Ballistics of Nitramine Gun Propellants", 9th JANNAF Combustion Meeting, CPIA Publication 231, Vol. III, pp. 41-59, December 1972.
 11. O.K. Heiney, "Advanced Gun Propellants", J. Nat. Defense, Weapons Technology, pp. 152-157, September-October 1973.
 12. R.W. Geene, J.J. Rocchio, I.W. May, and R.W. Deas, "Results of Recent Theoretical and Experimental Studies of Nitramine Gun Propellant Performance", 13th JANNAF Combustion Meeting, CPIA Publication 281, Vol. I, pp. 9-20, December 1976.
 13. A.A. Juhasz and J.J. Rocchio, "High Pressure Burning Rates of Nitramine Propellants", 14th JANNAF Combustion Meeting, CPIA Publication 292, Vol. II, pp. 81-89, August 1977.

Various explanations for the slope break behavior of nitramine propellants have been proposed, including a) crystal fracture; b) change from condensed phase to gas phase control when the thickness of the thermal wave approaches the crystal dimension¹⁴; c) change in chemical mechanism; d) particle dewetting; e) condensed phase reaction at the binder nitramine interface¹⁵; f) in depth particle-to-particle burning when the melt layer disappears⁵; and g) an ignition delay for the nitramine crystals, which becomes unimportant for higher pressures.⁶ The last two of these involve rather well-developed scenarios that attempt to explain most of the observed features of nitramine propellant burning, and are based, respectively, on the observations that the melt layer becomes thinner with increasing pressure and vanishes at pressures near those where the slope break appears¹⁶, and that quenched samples show large HMX crystals protruding from the binder matrix for low pressure burning.⁶ None of these mechanisms has received general acceptance, however, and most have difficulty explaining all of the observed features of nitramine propellant combustion.

Modeling of nitramine propellant combustion has received considerable interest in recent years.¹⁷⁻¹⁹ Results are generally insensitive to the model employed since unknown variables in the models are usually "fit" to available burning rate data.¹⁷ Most current modeling efforts^{18,19} involve extensions of the BDP (Beckstead-Derr-

14. J.J. Rocchio and A.A. Juhasz, "HMX Thermal Decomposition Chemistry and Its Relation to HMX-Composite Propellant Combustion", 11th JANNAF Combustion Meeting, CPIA Publication 261, Vol. I, pp. 247-266, December 1974.
15. R.N. Kumar and L.P. Strand, "Combustion Problems of Nitramine Propellants", AIAA Paper 75-239, AIAA 13th Aerospace Science Meeting, Pasadena, CA, 20-22 January 1975.
16. J.W. Taylor, "The Burning of Secondary Explosive Powders by a Convective Mechanism", *Trans. Faraday Soc.*, **58**, 561-568 (1962).
17. M.W. Beckstead and K.P. McCarty, "Calculated Combustion Characteristics of Nitramine Monopropellants", 13th JANNAF Combustion Meeting, CPIA Publication 281, Vol. I, pp. 57-68, December 1976.
18. C.F. Price, T.L. Boggs, and H.H. Bradley, "Modeling the Combustion of Monopropellants", 14th JANNAF Combustion Meeting, CPIA Publication 292, Vol. I, pp. 307-324, December 1977.
19. M.W. Beckstead, "A Model for Solid Propellant Combustion", 14th JANNAF Combustion Meeting, CPIA Publication 292, Vol. I, pp. 281-306, December 1977.

Price) model²⁰ of composite propellant combustion, although other approaches have been taken.²¹ Thermal decomposition chemistry of HMX and RDX is also an active area now, with several new contributions appearing each year. Most of these are directed at establishing the initial steps in the decomposition mechanism of the nitramine molecule. Most of the earlier work has been summarized in Reference 22. Several papers on this subject were presented at the 15th JANNAF Combustion Meeting, and these can be consulted for references to other recent papers. Comprehensive reviews and bibliographies are currently being prepared for publication.

2. Catalysis of Nitrate Ester Propellants

Catalysis of nitrate ester (e.g., nitrocellulose) propellants, unlike slope break phenomena with nitramine propellants, is a deliberately induced effect to improve the combustion of rocket and gun propellants. Figure 2 shows the type of behavior that results when one or two percent of catalyst (usually a lead salt) is added to a nitrate ester propellant. The low pressure burn rate is enhanced, resulting in what has come to be called the "super rate", "plateau" and "mesa" regions. At higher pressures the burn rate approaches that of the noncatalyzed propellant. The plateau and mesa regions have very low pressure exponents, and this, together with the low sensitivity to initial temperature in these regions²³ (not shown in Figure 2) makes the catalyzed propellants ideal for rocket motor applications. "Platonized" propellants have also been considered for gun applications as well.

A fundamental understanding of the site and mechanism of the catalytic activity would be desirable, since it would permit rational design of propellants having the desired burning properties, and minimize the need to resort to costly trial-and-error procedures.

Nevertheless, neither the mechanism nor the location of the catalytic activity can be considered to be known. Proposed theories cover almost the whole range of conceivable sites: a) direct chemical interaction between lead salt and nitrocellulose molecule,

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20. M.W. Beckstead, R.L. Derr, and C.F. Price, "The Combustion of Solid Monopropellants and Composite Propellants", 13th Symposium (International) on Combustion, The Combustion Institute, pp. 1047-1056, 1971.
 21. M. Benreuven, L.H. Caveny, R.J. Vichnevetsky, and M. Summerfield, "Flame Zone and Sub-Surface Reaction Model for Deflagrating RDX", 16th Symposium (International) on Combustion, The Combustion Institute, pp. 1223-1233, 1976.
 22. K.P. McCarty, "HMX Propellant Combustion Studies", AFRPL-TR-76-59, December 1976 (available from DDC as AD B017527).
 23. N. Eisenreich, "Abhängigkeit der Abbrandgeschwindigkeit von der Anfangstemperatur bei Festtreibstoffen", Institut für Chemie der Treib- und Explosivstoffe, May 1975.

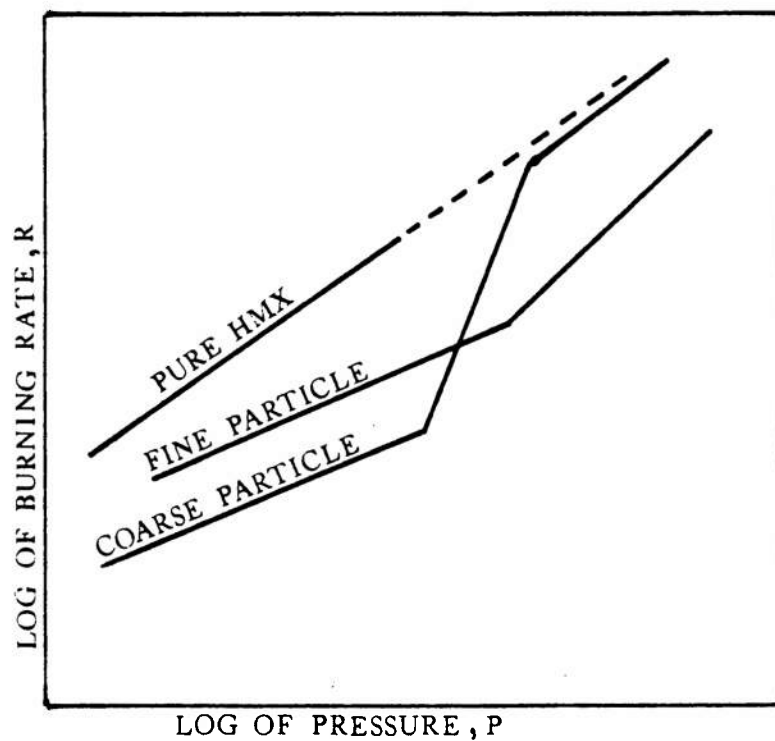


Fig. 1. Burning rate characteristics of pure HMX and HMX-inert binder propellant

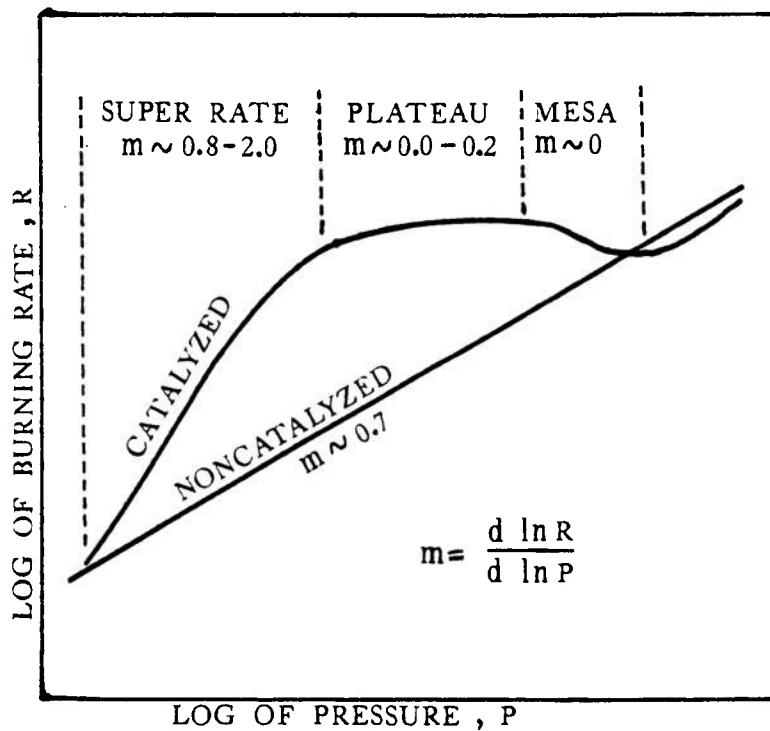


Fig. 2. Burning rate characteristics of catalyzed double base propellant

resulting in enhanced rate of unimolecular dissociation²⁴; b) modification of secondary chemical steps in the solid phase or at the surface, leading to an increased solid phase heat release and surface temperature, which in turn results in acceleration of the subsequent gas phase reaction²⁵; c) no change in solid phase heat release, but increased heat release²⁶ or reaction rate²⁷⁻²⁹ in the "fizz" zone (the first, very thin gas phase reaction zone just above the propellant surface), resulting in increased heat transfer back to the surface; d) increased ultraviolet radiation from the "secondary" flame zone (the luminous flame zone separated from the burning surface by the thin "fizz" zone and much thicker "dark" zone), leading to photochemical acceleration of subsurface reactions.³⁰ The original references should be consulted for a more complete and accurate description of the proposed mechanism involved in each case.

Observations relevant to double base propellant catalysis include the following: catalytic behavior is very similar, no matter what

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24. N.P. Suh, G.F. Adams, and C. Lenchitz, "Observations on the Role of Lead Modifiers in Super-Rate Burning of Nitrocellulose Propellants", *Combustion and Flame*, 22, 289-293 (1974).
 25. R.A. Fifer and J.A. Lannon, "Effect of Pressure and Some Lead Salts on the Chemistry of Solid Propellant Combustion", *Combustion and Flame*, 24, 369-380 (1975).
 26. D.J. Hewkin, J.A. Hicks, J. Powling, and H. Watts, "The Combustion of Nitric Ester-Based Propellants: Ballistic Modification by Lead Compounds", *Combustion Science Tech.*, 2, 307-327 (1971).
 27. (a) N. Kubota, T.J. Ohlemiller, L.H. Caveny, and M. Summerfield, "The Mechanism of Super-Rate Burning of Catalyzed Double-Base Propellants", 15th Symposium (International) on Combustion, The Combustion Institute, pp. 529-540, 1974; also (b) *AIAA J.*, 12, 1709-1714 (1974); also (c) Princeton U., AMSR No. 1087, AD-763 786, March 1973.
 28. N. Kubota, "Determination of Plateau-Burning Effect of Catalyzed Double-Base Propellants", 17th Symposium (International) on Combustion, Leeds, UK, August 1978.
 29. G. Langelle, J. Duterque, C. Verdier, A. Bizot, and J. Trubert, "Combustion Mechanisms of Double-Base Solid Propellants", 17th Symposium (International) on Combustion, Leeds, UK, August 1978.
 30. L.A. Lee, T.D. Austin, and A.T. Camp, "A Photochemical Combustion Mechanism for Mesa and Plateau Burning Double-Base Propellants", 11th JANNAF Combustion Meeting, CPIA Publication 261, Vol. I, pp. 293-306, December 1974.

compound of lead is used. Copper compounds, as well as compounds of certain other metals, also produce accelerated burning at low pressures. Catalytic effects are much smaller for hotter (and therefore faster burning) propellants, or for propellants with more highly nitrated nitrocellulose. Product analysis for low pressure (flameless) combustion²⁵ shows that there is a higher ratio of CO₂ to CO in the "fizz" zone products for catalyzed propellants, and perhaps greater reduction of NO to N₂. Catalytic effects with pure nitrocellulose are similar to those for double base (nitrocellulose-nitroglycerine) propellant.²⁵ Photographs of burning platonized propellants show a thick layer of carbonaceous char on the propellant surface in the super rate region; this diminishes in the plateau region and is no longer apparent at still higher pressures. Metallic lead particles may also form on the surface and be ejected into the flame, which is much more luminous for the catalyzed propellant. Photographs also indicate that the decrease in dark zone length (flame standoff) with increasing pressure is similar for catalyzed and uncatalyzed propellants, and that the flame continues to approach the surface with increasing pressure in the plateau region, even though the burning rate remains essentially constant.^{27,28,31} Experiments with imbedded microthermocouples indicate that surface temperatures for a catalyzed propellant are either slightly higher²⁷ or approximately the same²⁸ as those for the uncatalyzed propellant, and that the final "fizz" zone temperature is not significantly different for the catalyzed propellant.^{27,28} The "fizz" zone temperature gradients, dT/dx , for the catalyzed propellant are significantly higher in the super rate region than for the unmodified propellant,²⁷⁻²⁹ and this temperature gradient remains roughly constant in the plateau region.

Reference 27c is a useful summary of the combustion characteristics, thermal decomposition chemistry and modeling of double-base propellants. The thermal decomposition of nitrocellulose-based propellants is not presently being widely studied. This is probably due to the greater interest in nitramines at this time, and also because the polymeric structure of nitrocellulose and the much greater extent of reaction in the solid phase make it more difficult to determine the initial decomposition steps from the thermal decomposition products. (Final product type molecules such as CO, CO₂ and H₂O are found among the major products even for slow decomposition under vacuum conditions.)

III. GENERAL SUMMARY OF WORKSHOP DISCUSSION

Considering the topic of the workshop, there was very little discussion of specific chemical mechanisms involved in the ignition or combustion of the solid propellants. This indicates, it would

31. N. Eisenreich, "A Photographic Study of the Combustion Zones of Burning Double Base Propellant Strands", Propellants and Explosives, 3, pp. 141-146 (1978).

seem, the primitive state of our understanding of the fundamental processes involved. This state of affairs is a result of the fact that diagnostic techniques have not yet been found that would make it possible to probe the condensed phase, surface or early (close to the burning surface) gas phase reactions of a burning propellant. Consequently, there is no direct information available (e.g., concentration profiles) about the fundamental processes that occur in these regions. No new ideas that might change this situation came up at the workshop, although there is widespread hope that one of the new laser diagnostic techniques will eventually prove successful in probing the early gas phase reaction zone.

For the present, all our information comes from indirect sources. Thermal decomposition experiments are a prime example, since they are presently being carried out in so many laboratories with nitramines. There was a lot of discussion at the workshop concerning which experimental techniques would be expected to most closely simulate the solid phase kinetics and mechanisms operative under actual combustion conditions. Although it appears to be possible to approach the temperatures (e.g., 300-1000°C) and heating rates ($\sim 10,000$ - $50,000$ deg/sec) of the solid in combustion, compromises are inevitably involved. For example, it may be impossible to avoid gas phase reactions, even in an initial vacuum, for conditions of very rapid decomposition; also it is not obvious that a sample under such conditions will experience the temperatures assumed if it is a material that easily vaporizes (e.g., RDX) or sublimates (e.g., HMX). Nevertheless, there was general agreement that thermal decomposition experimentalists should be on the lookout for possible temperature, pressure and heating rate effects in analyzing and comparing results. The effects of these variables are not yet well understood. When they are, it will be possible to better assess the relevance of thermal decomposition studies to propellant combustion. For the gas phase processes, even indirect studies have been almost totally neglected, to the extent that kineticists in the propellant field do not even try to formulate a plausible mechanism for the important gas phase flame reactions of the solid propellants! Some ideas were developed at the workshop for indirect studies involving investigation of model gas phase systems (based on the products observed in thermal decomposition experiments); such studies have, since the workshop, been begun in several research laboratories. Ultimately, this may turn out to be the most important result of the workshop.

There was a divergence of opinion concerning the prospects for detailed modeling of the fundamental processes of ignition and combustion. One group felt that modeling in such detail would never be feasible, and even if feasible, would be of no particular value to the propellant formulator or user -- that the current type of modeling, involving engineering correlations or parametric representation of complex processes would always be sufficient. The other group pointed out recent advances in the combustion community in developing the capability

to model in detail processes such as flame propagation through flammable gases. This group felt that such modeling techniques could be applied in some way to propellant combustion, and that such modeling might ultimately be the only way to gain an understanding of the relative importance of -- and interaction between -- the various chemical and physical processes involved in ignition and combustion.

There was much discussion concerning the possible role of chemical changes in the nitramine slope break phenomenon. In fact, this topic evoked the most lively discussions of the workshop. Perhaps improperly, the discussion began as an either/or proposition: Why can't the slope break behavior of nitramine propellants be due to a change in chemical mechanism rather than, as usually assumed, a physical effect? The mechanism-change hypothesis is as follows: Suppose the pure nitramine normally decomposes by an "autocatalytic" mechanism, for example by decomposing into NO_2 , which in turn reacts with the propellant in such a way as to enhance the rate of decomposition (this is really acceleration by products, not autocatalysis). In a propellant, however, binder decomposition produces species (for example formaldehyde) which react with the NO_2 , thereby suppressing the autocatalysis. Above a certain pressure, binder suppression of autocatalysis becomes ineffective (perhaps due to slower diffusion) and the burning rate increases to that of the pure nitramines. As with many of the other slope break interpretations, it is difficult with such a scheme to explain the lower burning rate of the larger particle propellant at the low pressures.

In any case, the following arguments were brought up in favor of a chemical explanation: a) HMX and RDX behave similarly, even though they have quite different physical properties, b) other composite propellants with similar physical properties do not exhibit such phenomena, and c) some homogeneous nitramine propellants reportedly exhibit slope breaks. This last point, if correct, is extremely important; data showing clear slope breaks for homogeneous nitramine propellants were not available, however, and could not be assessed. Arguments for a physical explanation include: a) the observed particle size effects suggest a physical effect, b) scanning electron microscope pictures of extinguished samples show changes in surface characteristics (melt layer or particle protrusion) at pressures near those where exponent changes are observed, and c) physical changes can be rapid, taking place over a temperature range of a few degrees or less. (The surface temperature probably doesn't change much over a small pressure range.) It might be thought that correlation of the behavior of different binders would provide the most insight. Unfortunately, the effect of different binders seems to correlate best with the thermodynamic properties of the binders, and not with their physical or expected chemical properties.

Actually, the whole question of "chemical-vs-physical" is perhaps somewhat artificial and oversimplistic. For example, the chemical-mechanism change hypothesis must invoke binder-oxidizer flame diffusion effects in order to explain the low pressure suppression of the pure nitramine burn rate, and this can be considered a physical (mixing) process. On the other hand, a physical interpretation based on a change of phase at the surface would have to include the quite likely possibility that the chemical mechanism, or at least the rate of reaction, might be different in the two phases; likewise, disappearance of an ignition delay could certainly be considered to be, at least partly, a chemical change. Therefore, it seems quite appropriate that no consensus of opinion was achieved on this question at the workshop. Nevertheless, the question of the role of chemistry in nitramine propellant behavior is valid and important, since, if chemical processes play a role, the possibility exists for chemical modification and control.

The area of propellant catalysis was also discussed at some length. In the case of nitrocellulose-based propellants, catalysts have been successfully used for several decades and there has been considerable interest in recent years in determining the mechanism of the process. The nitramine community, on the other hand, is still looking for good catalysts, and has not devoted as much effort to determining how they function. An attempt was made by the workshop participants to compare the known behavior of catalysts in nitrate ester and nitramine propellants. Contrary to reports in previous years, it now appears that nitramine burn rates can indeed be significantly increased at low pressures by catalysts; moreover, the best nitrate ester catalysts (e.g., lead compounds) are also among the most effective for nitramine propellants. (The common use of nitrocellulose binder certainly makes the interpretation more difficult, however!) Other similarities, or differences, are not yet apparent; the effect of catalysts on the nitramine propellant combustion chemistry has not yet been measured, and it is not yet clear whether nitramine propellants exhibit plateau and mesa burning similar to that for double-base propellants.

The problem of determining the site and mechanism of catalysis in nitrocellulose-based propellants remains unresolved. There appears to be no firm evidence to support a direct interaction between the additive and the undissociated propellant molecule. The observed pressure dependence of the flame standoff does not support the photochemical model. A very basic difference of opinion exists as to whether the site of catalysis is in the condensed phase or in the "fizz" zone. Thermocouple measurements, together with a solution of the energy balance equations, suggest that the solid phase heat release is probably unchanged by the catalyst, implying that catalysis occurs in the gas phase "fizz" zone. Surface carbon formation, on the other hand, suggests that the condensed phase reaction and heat release are altered. Some experiments were suggested that might resolve this question. For example, if the rate of rapid thermal decomposition

under flameless conditions could be shown to be significantly greater for the catalyzed propellant for the same heat input, this would indicate catalysis of a condensed phase process. (Laser augmented flameless regression would be one of many possible experimental techniques with which to make this comparison.)

IV. SPECIFIC DISCUSSION QUESTIONS, IDEAS, AND RECOMMENDATIONS

The following are a few of the specific questions submitted by the workshop participants for discussion, together with some of the resulting ideas and recommendations.

1. Can an experimental test be designed to distinguish whether the pressure break phenomenon observed with nitramine propellants is due to a chemical (i.e., change of mechanism) or physical (i.e., change of phase or surface structure) effect?

No simple experimental test was suggested, but it was considered that the following types of experiment would be useful: a) thermal decomposition and burn rate data for samples in atmospheres of specific gases or doped with chemical sources of reactive species (e.g., HCHO, NO₂, etc.), including, where appropriate, use of isotopically substituted molecules; b) definitive strand burner data for homogeneous and liquid nitramines; c) systematic studies with binders that would be expected to produce widely varying decomposition products; and d) burn rate measurements for single crystals of HMX at pressures as high as possible to confirm, as currently assumed, that HMX itself exhibits no slope breaks (published single crystal data only extends to about 20 MPa [2900 psi]). Pressed strands of pure HMX do undergo a sharp slope change at sufficiently high pressures, but this is generally assumed to be due to in-depth burning (surface area increase) when the melt layer disappears.

2. Where does catalytic activity influence HMX decomposition/combustion (solid, liquid, or gas phase)? Nitrocellulose decomposition/combustion?

Recommend that experiments include: a) thermal decomposition studies with catalyzed propellants. If the rate of thermal decomposition is increased by the additive, solid phase control would be indicated since no flame would be present; b) DSC/DTA comparisons for catalyzed and uncatalyzed propellants; c) burning rate measurements for pressed strands of binderless HMX with catalyst, to determine if the nitramine decomposition, or that of the binder, is enhanced by the additive in nitramine propellants and; d) a controlled set of experiments with nitrocellulose and nitramine propellants to determine if the chemical effects are similar for both types of propellant.

3. To what extent do slow and fast decomposition experiments produce the same products as high pressure combustion?

As already mentioned, such questions are prompted by the large number of thermal decomposition studies that have been published and are underway, especially for the nitramines. Those not involved in the area quite naturally ask questions such as: "To what use can the results of thermal decomposition studies be put? How do the results of the different studies compare and what is the justification for doing even more studies of this kind?" It is recommended that a critical review of the thermal decomposition literature be undertaken, and that an attempt be made to correlate the available data in terms of the results obtained and the conditions under which the experiments were run. It was felt that such comparisons might bring to light any variations in thermal decomposition chemistry with such variables as pressure, temperature and heating rate, and in addition would make it possible to assess the relevance of thermal decomposition results to the chemistry of burning propellants. Several difficulties were foreseen that might make such a task difficult. These include the following: Different diagnostic techniques measure different species, making comparisons difficult. Many studies have resulted in only qualitative, not quantitative, results, or are poorly documented. Finally, different studies have used different propellants. In order to alleviate this situation, it is recommended that future studies be better documented, make use of simple, well-characterized samples, cover a wide range of rates, and if possible involve analysis by standardized techniques and procedures.

4. Can nitramines burn in a "fizz" burning mode and do they have a dark zone?

It is apparently not clear whether nitramines exhibit the same multiple flame zone structure, and incomplete burning at low pressure, as nitrate esters. The reason for this lack of information is apparently the fact that the nitramine flame is difficult to see at lower pressures. Two types of experiments were suggested: Microthermocouple measurements of temperature as a function of distance above the burning propellant surface should establish the flame zone structure for the nitramines, and also provide useful heat release information for the modelers. Calorimetric measurements and product analysis for low pressure combustion should indicate if incomplete burning occurs, and if so, provide valuable information about the early gas phase chemistry. Both of these techniques have already been successfully applied to nitrate ester propellants.

5. Why are the burning rates of pure HMX and RDX similar?

At low temperature, the thermal decomposition of RDX is much faster than that of HMX, either due to the lower melting point of RDX (decomposition from a melt is considered to be faster than solid

phase decomposition) or because vaporization is an important process. Nevertheless, in combustion they both burn at approximately the same rate, despite the large difference in melting points and vapor pressures. This suggests either that vaporization and/or melting are not important processes in the high pressure combustion, or that the surface temperature of burning HMX is much higher than that of RDX. (Another possibility is that the rate constant for HMX decomposition is much higher than that for RDX, or perhaps melting is important but vaporization is not, and the rate constants for decomposition from the melt are approximately equal at high temperature.) It is recommended that comparative surface temperature measurements be made for burning HMX and RDX in order to determine what processes are important under combustion conditions.

6. What effect might a pressure-induced phase transition to a polymorph other than δ -HMX have on the pressure slope break during combustion?

The possibility of a polymorphic transition being responsible for the slope break phenomenon was considered. No evidence for such an effect is apparent. Contrary to observation, such an effect would probably be expected always to occur at the same pressure, and would be expected for pure HMX as well. Nevertheless, it is recommended that the high pressure polymorphs of HMX and RDX be determined. It was also felt that there should be a critical review of available theory and data related to the kinetics of phase transitions (including melting). In other words, under what conditions will a phase transition not have time to occur, even though the temperature is above the equilibrium transition temperature? Such considerations may play a significant role in future modeling efforts with nitramine propellants.

7. Can a technique be developed for measuring the thermal conductivity of explosives and propellants at high temperatures and pressures?

Thermal conductivities for the solid at temperatures up to those of the burning surface are required in most combustion models, but are not in general available. The problem is that there is no technique available to measure the conductivity above the decomposition temperature since, in general, decomposition will be accompanied by self-heating. Moreover, if a high temperature phase transition (including melting) occurs, it is not even possible to extrapolate low temperature data to the conditions of interest. Clearly, a transient experimental technique of some kind is required. No suggestions were made as to how this might be done.

8. To what extent does the kinetics of the gas phase reactions above the surface determine the combustion rate?

This topic developed into a discussion of possible flame diagnostics to probe the gas phase reactions near the surface of the burning propellant. The difficulty lies in the fact that the "fizz" zone of nitrate ester propellants is extremely thin -- perhaps 100 microns even at very low pressures. Surface irregularities on the burning propellant are much larger than this, making most optical techniques out of the question. For nitramines, the situation may or may not be different, depending on whether they have a flame structure similar to that of the nitrate esters. It was suggested that non-transmission optical techniques (e.g., fluorescence, Raman) might be successful. It was also suggested that some useful experiments might be done with thin film propellant samples burning edgewise. For such a configuration the reaction zone of interest would not be obscured by surface irregularities. The outer flame zones pose much less of an experimental problem, although the chemistry there probably does not significantly influence the burning rate of the propellant. (Some limited success in probing the outer flame zone of double-base propellants has already been achieved, most notably with rapid scan i.r. spectroscopy.)

It became evident in this discussion that our knowledge of the important gas phase chemical processes will of necessity come from indirect sources, at least for the immediate future. Several model systems were recommended for experimental study. Suggested experiments included: a) shock tube studies of the high temperature pyrolysis of nitramines in the gas phase, b) measurement of species concentration profiles for burner flames of aliphatic nitrate esters and nitramines and, c) characterization of flames, and ignition limits, of the known propellant decomposition products (e.g., $\text{HCHO} + \text{NO}_2/\text{N}_2\text{O}/\text{NO}$).

V. CONCLUSION

The workshop provided a useful assessment of our current state of understanding of the fundamental chemical reactions involved in the combustion of double-base and nitramine propellants. At present, our knowledge is still very primitive. Some recommendations have been made for research that should provide more detailed information about these processes.

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