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Prediction of Violent Mechanochemical Processes

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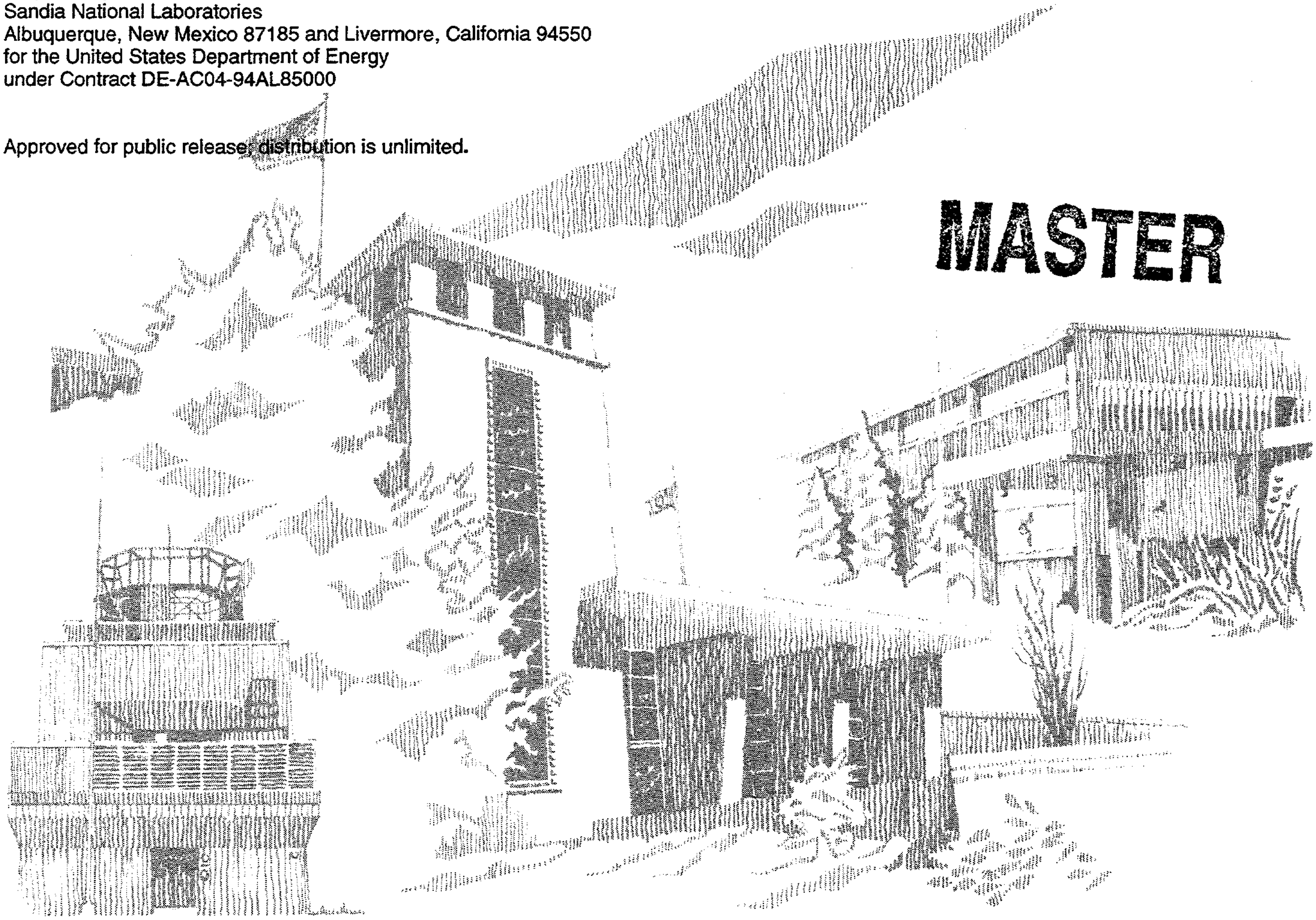

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PREDICTION OF VIOLENT MECHANOCHEMICAL PROCESSES

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Abstract

Energetic materials, such as high explosives, propellants and ballotechnics, are widely used as energy sources in the design of numerous devices, components and processes. Although most energetic materials are selected for safe operation, their high energy densities have the potential for inadvertent initiation and subsequent powerful energy transformations. This potential for damage or injury places a heavy burden on careful analysis of safety issues as part of the design process. As a result, considerable effort has been devoted to empirical testing of initiation conditions, and development of scientific models of initiation processes that have been incorporated into computer models for numerical simulation of initiation of reaction. Nevertheless, in many cases, there is still only rudimentary understanding of the processes of initiation.

Mechanochemical processes are perhaps the least understood of the various excitation mechanisms. In these energy transformation processes mechanical stimuli lead directly to initiation and substantial reaction under conditions not thought to be capable of reaction. There are no established scientific models of the initiation of mechanochemical reactions in energetic materials. Mechanochemical reactions can be initiated by enhanced solid state chemical reactivity, changes in reactant configuration, and localization of initiation energy. Such solid state reactions are difficult to understand, either empirically or scientifically, as they are inherently nonequilibrium processes; scientific models currently used assume equilibrium thermochemical conditions and materials behaviors. The present work was undertaken as a first step in developing a scientific basis for prediction of the initiation of mechanochemical processes in high energy density solids. The work was supported by Sandia Laboratory Directed Research and Development (LDRD) funding and included cooperative efforts with the Los Alamos National Laboratory, as well as with Georgia Tech, New Mexico Tech and North Carolina State Universities. Considerable detail on theory and experimental characterization of mechanochemical processes has been published by the authors as a result of the work. The present report summarizes those publications.

TABLE OF CONTENTS

EXECUTIVE SUMMARY

Energetic materials, such as propellants, high explosives, and ballotechnics, are widely used in modern society. The capability to predict violent chemical reactions from energetic materials is essential for establishing operating limits for components and systems. Principal among the concerns for reliable operation is safety; that is, under what conditions will the materials inadvertently initiate reaction causing the potential for material damage and injury?

Present understanding of initiation of propellants, high explosives, and ballotechnics is largely based on empirical testing or numerical simulation with computer codes based on initiation processes largely *thermo*chemical in character.

Under the extreme mechanical loading conditions often encountered with energetic materials, it is to be expected that *mechano*chemical processes can be significant in the initiation of reaction. There is considerable information on mechanochemical processes in more conventional mechanical loadings, but there is little theory or data describing mechanochemical processes under high-pressure shock compression. Mechanochemistry is truly a neglected, but critical, area of energetic material science and technology.

The present work, sponsored principally by Sandia LDRD funding, and leveraged with cooperative efforts, was undertaken to initiate a science-based capability to understand mechanochemical processes in high explosives and ballotechnics sufficiently well to predict initiation and chemical reaction behaviors. The work has been reported in detail in sixteen scientific papers including both theory-centered and experiment-centered papers which are listed at the end of this report. The published work includes comprehensive review articles. Because the work is documented extensively in the published papers, we restrict the presentation in the present report to the main highlights. The interested reader is referred to the publications for details.

It is found that descriptions of mechanochemical effects in problems of mechanical deformation of highly porous solids are essential to describe deflagration-to-detonation (DDT) and shock-to-detonation (SDT) processes in high explosives, as well as initiation of chemical reaction of ballotechnics.

Data on shock compression of twelve highly porous powders or powder mixtures are reported. The data include both study of physical and chemical characteristics of shock-modified samples as well as nanosecond, time-resolved stress wave measurements on shock-loaded samples. Samples are observed to be strongly modified due to the large plastic deformation and contain unusually large quantities of defects which greatly enhance solid state reactivity. Materials responses under shock loading are found to be strongly time dependent as the porous samples collapse to dense configurations. Initiation of chemical reaction and deformation behavior are found to depend on porosity and powder morphology in complex behaviors not predicted from first-order considerations.

Certain aspects of the theory are incorporated into the Sandia computer code CTH and have been successfully used to interpret wave propagation and chemical reaction in a porous high explosive, HMX, and wave propagation in a two-component mixture. Further, the theory has been successfully used to interpret and describe careful DDT experiments. It has been demonstrated that three-dimensional simulation, as opposed to two-dimensional simulation, is required to properly describe deformation of highly porous solids. In spite of the demonstrated utility of the theory, it is regarded as elementary in substance with much work still to be accomplished to develop a credible predictive capability.

In the absence of appropriate descriptions of shock-induced, mechanochemical processes, the foundation of numerical simulation of energetic materials behaviors is seriously in question. Based on fundamental scientific considerations, there is little reason to expect that the presently described thermochemical processes are adequate for realistic prediction of the behaviors of energetic materials.

INTRODUCTION

Energetic materials, such as propellants and high explosives, have become commonplace in modern society. The use of propellants, high-explosive detonators and explosively-actuated bolts and switches are routine in rocket technology. Air-bag technology in contemporary automobiles is based on rapid initiation of chemical reaction of gas-generating, energetic materials. Recent initiatives in this area have been stimulated by deaths resulting directly from air-bag operation. High explosives are widely used in mining and highway construction, in metal processing, and in the synthesis of materials such as industrial diamond. Military use of energetic materials has typically required more detailed knowledge of high explosive performance and safety. The most detailed of scientific and empirical descriptions of explosive performance has resulted from DOE laboratories concerned with nuclear weapon performance and safety.

A new class of energetic materials, called "ballotechnics" has been identified from research at Sandia. Unlike high explosives which are relatively easy to initiate, ballotechnics are difficult to initiate. The starting ballotechnic materials are typically mixtures of powders in a highly porous (perhaps 50% dense) form which can be made to initiate by high pressure shock-wave loading. The controlling initiation processes are thought to be mechanical in character.

All uses of energetic materials require detailed consideration of safety. The overriding issues are the operating environments within which safe and reliable performance can be achieved. The high energy density, powerful nature of the energy source places particular emphasis on safety. Presently two diverse methods are used to establish safe operating conditions. Empirical testing has provided extensive databases of conditions for initiation of chemical reaction or alteration of reliable performance. Nevertheless, the expense and sometimes ambiguous nature of testing has led to the use of computers for realistic numerical simulation of explosive initiation and performance. For the simulations to be effective they must be based on scientific identification of the processes significant to the events, and quantification of the materials behaviors. Very considerable progress has been made in simulation and numerous computer codes are in operation for engineering design.

Of particular interest to Sandia are the phenomena observed in high explosives in which deflagation (burning) is sometimes observed to lead to detonation. Such "DDT" observations are particularly critical in porous solids or in high explosives damaged by mechanical forces. The modeling of such DDT processes is largely based on equilibrium thermochemical effects. Computer codes predicting initiation and propagation of reaction from mechanical shocks ("SDT" observations) are also largely based on thermochemical effects in which the mechanical energy is localized by a void and its collapse results in large local temperatures. Even though present computer models are found to be in satisfactory agreement with certain experiments, there is considerable evidence that the mechanical effects themselves may be significant in initiation of violent chemical reactions.

Mechanochemistry is well known to be significant in chemical reactions in a wide variety of conditions encountered in modest mechanical loadings. Typically, the more severe the mechanical event, the more severe the effect. Thus, the extreme nature of shock loading and the large compressions of deformation of highly porous solids would be expected to enhance mechanochemical effects. The deformations involve the generation and motion of large concentrations of defects at all levels: atomic, mesoscopic, microscopic and continuum. These defects act to greatly enhance solid state reactivity and change the relative location of potential reactants. Large concentrations of defects can lead to local chemical changes even in a fixed composition. Based on the broader picture of effects, there is an obvious need to consider such mechanochemical effects, yet mechanochemistry is a neglected area in energetic materials, both theoretically and experimentally.

The present work was motivated by the need to initiate an effort to develop a predictive capability based on mechanochemical effects in energetic materials subjected to high pressure shock compression. It was intended that the initial effort establish scientific modeling directions and provide experimental data required to identify relevant phenomena and establish a materials behavior database. The effort integrates both theory and experiment to provide a basis, when fully developed over the long term, for scientific prediction of violent mechanochemical reactions.

The work at Sandia was supplemented by cooperative efforts with the Los Alamos National Laboratory, Georgia Tech, New Mexico Tech and North Carolina State Universities.

The present report will first summarize the results of the research as shown in the published works. Results describing the theory-centered publications will be followed by similar experiment-centered publications. The report closes with a general summary, and a full list of publications.

THE PUBLISHED WORK

A list of scientific publications describing the LDRD results and other supporting work is shown in the last section of this report. Sixteen publications are cited, including four that are principally centered about theory and twelve that are principally centered around experiments. The published work includes an overall assessment of the fundamental scientific issues in book form in Reference 5, and a summary of the theory in book form in Reference 4.

The theory-centered work, well described in references 1 through 4, was largely led by M. R. Baer of the *Energetic and Multiphase Processes Department.* Interactions with Professor Y. Horie of North Carolina State University, with his independent efforts, were helpful in alternate development of the concepts.

The effort is largely based on use of the *continuum mixture theory* as initially developed at Sandia by Nunziato and Baer. Processes studied in the present work include the mechanical deformation of highly porous (~59% porous) powders of single- or multi-component composition. Certain of the deformation mechanics of this problem are incorporated in the CTH computer code. Shock-deformation and subsequent chemical reaction behaviors in highly porous high explosive powders are also incorporated into the code in elementary form.

The viscoelastic and viscoplastic behaviors of the polymer, Kel-F, are incorporated in the code and tested with experimental data. This later effort was essential to the overall experimental effort as it is necessary to use polymers in time-resolved, experimental measurements to obtain good mechanical shock impedance matching to the powders. It also represents a further advance in the predictive capabilities for nonequilibrium phenomena in the code.

The capability of the continuum mixture theory as modeled in CTH is well described in reference 3, in which experiments conducted at both Sandia and Los Alamos on highly porous powder samples of the high explosive HMX are interpreted with the theory. Satisfactory agreement can be obtained with the main features of the experimental observations.

The predictive capability is well tested in numerical simulations of typical DDT experiments on ball propellants in long-tube configurations. The numerical simulations predict the principal experimental observations and provide insight into the roles of combustion gasses, grain burning and mechanical compaction waves.

The continuum mixture theory was also successfully used for a first-order description of experimentally observed, time-resolved, wave-profile features of shock-compressed mixtures of aluminum and iron oxide powder samples. In one of the most significant results in work in progress, it has been shown that three-dimensional modeling is required to describe deformation of particles under shock compression. Prior work has typically been limited to two-dimensional analysis.

The experiment-centered work was principally led by R. A. Graham of the *Nanostructures and Advanced Materials Chemistry Department.* There was strong interaction involving students and facilities of Georgia Tech, New Mexico Tech and North Carolina State Universities. Further, there was active cooperation with staff of the Los Alamos National Laboratory.

The published work is based on both preservation and analysis of shock-modified, single- and multi-component, highly porous powders, and time-resolved, stress and stress-rate measurements on shock-loaded powders. The sample-preservation experiments are based on the Sandia "Bear" shock-recovery capability in which experiments are carried out with plane-wave explosive loading. The time-resolved measurements are based on precise impact loading in the Department 1152 facility with stress measurements with the PVDF piezoelectric polymer gauge. A limited number of experiments were carried out with plane-wave high explosive loading at the New Mexico Tech site. The impact and sample preservation capabilities are widely recognized as achieving conditions of unsurpassed quality and fidelity. Such capabilities lend great strength to observations and provide a firm foundation for theoretical development of predictive capabilities.

Sample-preservation experiments centered on simple two-component powder mixtures. Chemical reactions were observed and studied in Ti-Si, Ti-C, Ti-B mixtures as well as in quartz-aluminum powder mixtures. Dissociation and other complex reactions were observed and studied in HgO powder samples.

Typical experimental approaches included applying shock pressure levels both above and below chemical reaction thresholds. It has been observed that samples shocked and preserved without complete reaction are more revealing of mechanochemical mechanisms than those in which full reaction occurs. The typical fully reacted sample is dominated by melting resulting from the heat of reaction of the transition. In the shocked-but-unreacted condition, the configuration of the shocked reactants is shown to be substantially altered as the materials deform by plastic deformation into the voids. Further, there is considerable intermixing due to the high velocity, viscous deformation of materials of different density.

Study of the samples also shows whether the deformation is viscoplastic or elastic with local sample cracking. Such information cannot be determined by time-resolved measurements alone. In most cases it is apparent which component of a two-component mixture carries the bulk of the deformation and flows around the other constituent. Materials behavior show surprising variations. For example, silicon behaves in a brittle fashion in some situations and in a plastic mode in others, depending on the particle size, porosity and substituent. Under some conditions, aluminum is found to flow around iron oxide particles, and in other conditions, the opposite is true. In stresses and porosities in which iron oxide deforms around aluminum particles, it is observed that the same aluminum deforms around tungsten oxide particles. The observed behaviors cannot be described by simple, equilibrium-mixture theory.

Considerable detail was obtained on the Ti-Si samples from experiments on powders of three different sizes. The work is the first to use both sample-preservation and time-resolved stress measurements on the same powders. The strong influence of morphology dominated the observations. Interpretation of the observations requires that the theory incorporate local inter-particle stresses as well as micromechanical intra-particle stresses. As observed in all time-resolved stress measurements, the sample behaviors are dominated by rate-dependent deformation.

Experiments on aluminum and iron oxide (hematite) powder mixtures revealed particularly descriptive observations of deformation behavior of two-component powder mixtures. The experimental observations of wave profiles showed evidence for the individual deformation contribution of each component. Further, the relative importance of each component in controlling total deformation appeared to change with total pressure. In recent, not yet analyzed experiments, the ratio of mixtures was substantially altered with major changes in experimentally observed wave structure. This materials system appears to offer the potential for development and validation of a theoretical model for two-component powder deformation under shock loading.

In a revealing and highly significant experimental advance, the PVDF stress gauge was combined with the VISAR particle velocity system to obtain a simultaneous time-resolved description of the deformation of a shock-compressed, highly porous HMX sample. Both experimental tools have previously been shown to provide detailed information on wave structure, but each provides a fundamentally different description of materials behavior.

The VISAR provides direct information on *compression or volume change.* The PVDF gauge provides direct information on *stress* and, as additional data, *stress-rate.* Rate-dependent materials descriptions may differ significantly depending upon whether the model is strain or stress based. When combined experimentally, a materials response model which fits the data is unambiguous within the experimental errors.

The observations with the combined PVDF-VISAR measurements on a porous HMX powder showed the time-dependent collapse of the powder into the voids in a time of about 150 nsec. The deviation of the materials response from one-dimensional overall conditions due to local-stress interparticle configurations was clearly indicated in the data. Such measurements appear to be particularly powerful for future work developing micromechanical models of materials deformation.

Finally, it should be recognized that development of the precise impact loading, PVDF and VISAR experiments provides a capability for future funding that requires such experimental capabilities

PREDICTIVE CAPABILITIES

It has not been possible in the limited scope of the present work to fully develop the predictive capability to describe mechanochemical processes in energetic materials. Attainment of this objective must be a very long range one, as the phenomena are complex, there are few data upon which models can be built, and materials descriptors and algorithms in models may require major revision. Nevertheless, the work firmly establishes the need to incorporate mechanochemical effects in materials behavior models. The work makes the first, highly significant steps needed to build a more substantive predictive capability.

The work is certainly sufficient, both theoretically and experimentally, to establish that present predictive models, based largely on thermochemical processes, are not fully capable of predicting initiation and propagation of chemical reaction in shock-deformed energetic materials. The failure to include mechanochemical processes represents a major shortcoming of the present predictive capabilities.

PUBLISHED SCIENTIFIC PAPERS OF THE PRESENT WORK

---- Theoretically Centered ----

1. M. R. Baer, *A Mixture Model for Shock Compression of Porous Multi-Component Reactive Materials*, in High-Pressure Science and Technology – 1993, edited by S. C. Schmidt, J. W. Shaner, G. A. Samara and M. Ross, Amer. Inst. of Physics, AIP Conference Proceeding 309, Part 2 (1994) pp. 1247-1250.
2. M. R. Baer, I. S. Hertel and R. L. Bell, *Multidimensional DDT Modeling of Energetic Materials*, in Shock Compression of Condensed Matter (1996), in press, pp. 433-436.
3. M. R. Baer, R. A. Graham, M. U. Anderson, S. A. Sheffield and R. L. Gustavsen, *Experimental and Theoretical Investigations of Shock-Induced Flow of Reactive Porous Media*, in Proceedings 1996 Combustion Subcommittee and Propulsion Systems Hazards Subcommittee Meeting Joint Meeting, Naval Post-Graduate School, Monterey, California.
4. M. R. Baer, *Continuum Mixture Modeling of Reactive Porous Media*, in HIGH-PRESSURE SHOCK COMPRESSION OF SOLIDS - IV: RESPONSE OF HIGHLY-POROUS SOLIDS TO SHOCK COMPRESSION, edited by Lee Davison, Y. Horie and M. Shahinpoor, Springer-Verlag, in press.

---- Experimentally Centered ----

5. R. A. Graham, *Comments on Shock-Compression Science in Highly Porous Solids*, in HIGH-PRESSURE SHOCK COMPRESSION OF SOLIDS - IV: RESPONSE OF HIGHLY- POROUS SOLIDS TO SHOCK COMPRESSION, edited by Lee Davison, Y. Horie and M. Shahinpoor, Springer-Verlag, in press.
6. N. N. Thadhani, R. A. Graham, T. Royal, E. Dunbar, M. U. Anderson and G. T. Holman, *Shock-Induced Chemical Reactions in Ti-Si Powder Mixtures of Different Morphologies: Time-Resolved Pressure Measurements and Materials Analysis*, submitted, J. Appl. Phys., 1996.
7. V. S. Joshi, N. N. Thadhani and R. A. Graham, *Mechanistic Study of Shock-Induced Solid-State Chemistry in Ti- and Ta-Based Carbide and Boride Systems*, in Schmidt, et al, eds., (1994) loc. cit., pp. 1299-1302.

8. M. U. Anderson, R. A. Graham and G.T. Holman, *Time-Resolved Shock Compression of Porous Rutile: Wave Dispersion in Porous Solids*, in Schmidt, et al, eds., (1994) loc. cit., pp. 1111-1114.

9. E. Dunbar, R. A. Graham, G. T. Holman, M. U. Anderson and N. N. Thadhani, *Time-Resolved Pressure Measurements in Chemically Reacting Powder Mixtures*, in Schmidt, et al, eds., (1994) loc. cit., pp. 1303-1306.

10. G. T. Holman, Jr. R. A. Graham and M. U. Anderson, Shock Response of Porous 2Al + Fe2O3 Powder Mixtures, in Schmidt, et al, eds., (1994) loc. cit., pp. 1119-1122.

11. T. E. Royal, N. N. Thadhani and R. A. Graham, *Shock-Induced Reaction Behavior of Ti-Si and Ti-B Powder Mixtures*, in Metallurgical and Materials Applications of Shock-Wave and High-Strain-Rate Phenomena, edited by L. E. Murr, K. P. Staudhammer and M. A. Meyers, Elsevier (1995) pp. 629-636.

12. E. L. Venturini, P. P. Newcomer, B. Morosin, G. T. Holman, R. G. Dunn and R. A. Graham, *Shock-Induced Changes in HgO Powder*, in Murr, et al, eds. (1995) loc. cit. pp. 739-746.

13. B. Morosin, E. L. Venturini, G. T. Holman, P. N. Newcomer, R. G. Dunn and R. A. Graham, *Shock-Induced Defects in HgO*, in Shock Compression of Condensed Matter - 1995, edited by S. C. Schmidt, W. C. Tao, Amer. Inst. of Physics, AIP Conference Procedings 370, Part 2, (1996) pp. 733-736.

14. V. S. Joshi, N. N. Thadhani, R. A. Graham and G. T. Holman, *Shock Compression of Quartz and Aluminum Powder Mixtures*, in Schmidt, et al, eds., (1996) loc. cit., pp. 689-692.

15. M. U. Anderson and R. A. Graham, *The New Simultaneous PVDF/VISAR Measurement Technique: Application to Highly Porous HMX*, in Schmidt, et al, eds. (1996) loc. cit., pp. 1101-1104.

16. W. H. Holt, W. Mock, Jr., M. U. Anderson, G. T. Holman and R. A. Graham, *Effect of Particle Morphology on Input and Propagated Stress Wave Profiles for Two Highly-Porous Polytetrafluoethylene Powders*, in Schmidt et al, eds., (1996) loc. cit., pp. 573-576.

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