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PROCEEDINGS OF THE CONFERENCE ON THE STANDARDIZATION OF SAFETY AND PERFORMANCE TESTS FOR ENERGETIC MATERIALS-VOLUME I

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SEPTEMBER 1977

US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
LARGE CALIBER
WEAPON SYSTEMS LABORATORY
DOVER, NEW JERSEY

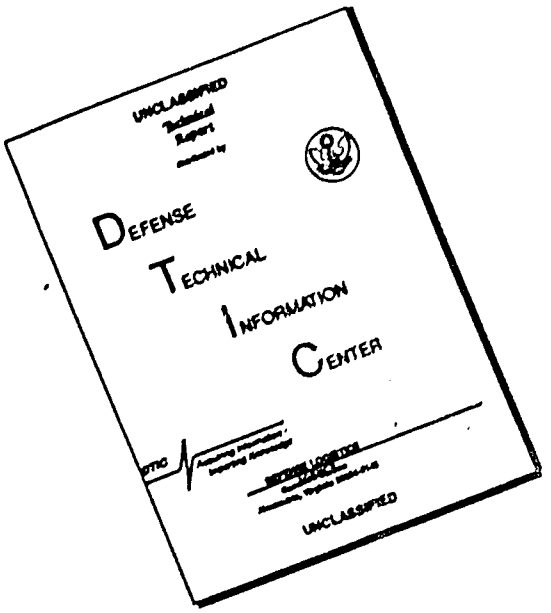
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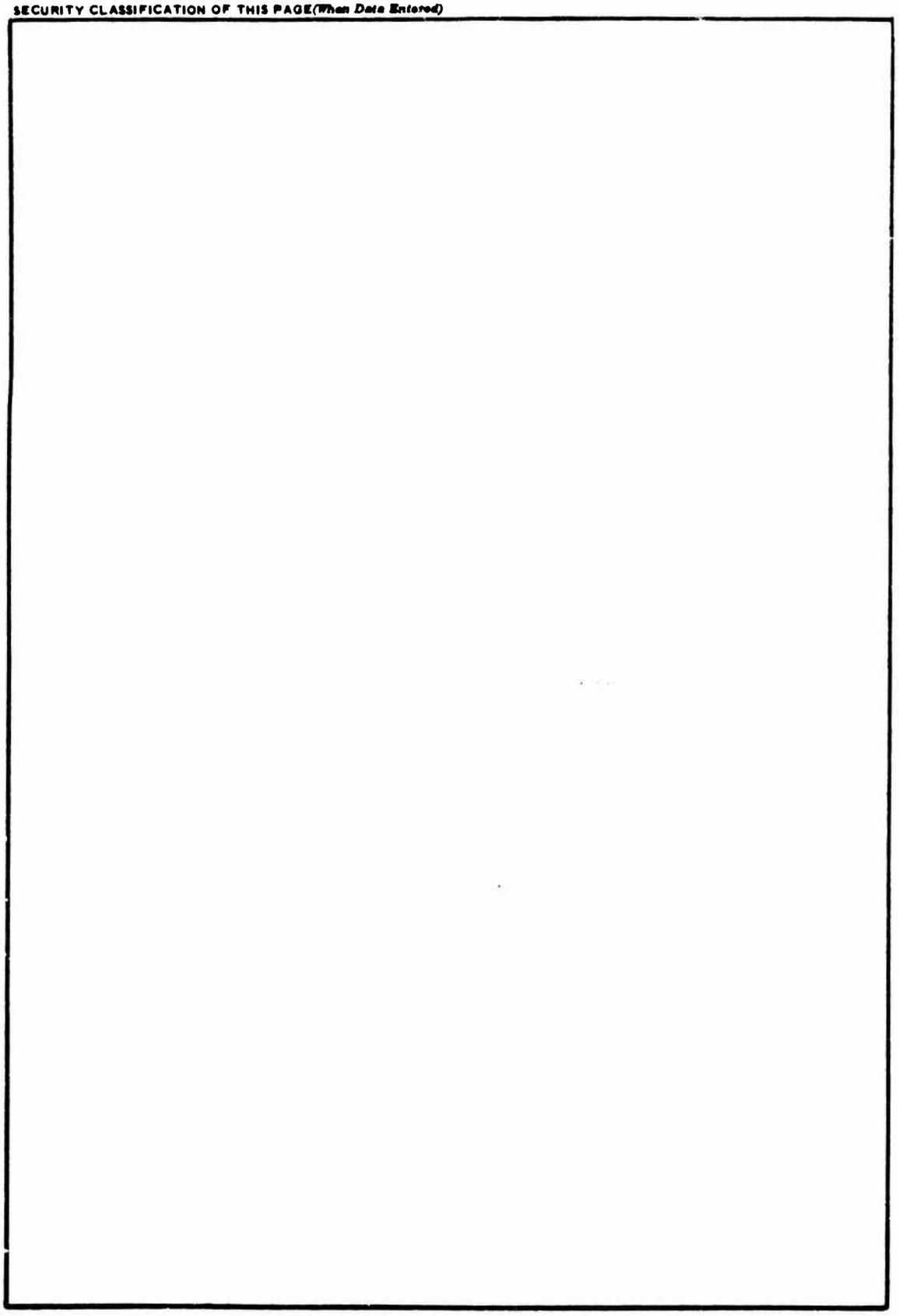
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report is a compilation of the papers presented at the Conference on the Standardization of Safety and Performance Tests for Energetic Materials which was held at ARRADCOM, Dover, NJ on 21-23 June 1977.

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PREFACE

The Conference on the Standardization of Safety and Performance Tests for Energetic Materials was held at the US Army Armament Research and Development Command (ARRADCOM), Dover, New Jersey on 21-23 June 1977 and was sponsored jointly by the Energetic Materials Division, Large Caliber Weapon Systems Laboratory, ARRADCOM, and the Joint Technical Coordinating Group for Munitions Development, Working Party for Explosives (JTCG/MD WPE). The General Chairman was Dr. Raymond Walker, Chief, Energetic Materials Division, LCWSL, ARRADCOM and the Program Committee included Dr. H. J. Matsuguma. Dr. F. Owens and Mr. Louis Avrami. The purpose of the conference was to provide a rational basis for and a coordinated approach to the international standardization of tests for explosives, propellants and pyrotechnics. The term qualification embraces the producibility, hazards, storability, transportation, performance and cost effectiveness criteria that the materials must meet in order to be acceptable for military use. The presentations and discussions were, therefore, directed to:

1. Reviewing the philosophy, methodology, and documentation employed in different agencies and countries for the qualification of energetic materials for military use.

2. Reviewing on-going research and development to provide improved tests and criteria.

3. Developing in an executive session an approach to the evolution of improved standard tests, criteria, and manuals for national and international acceptance.

The participants were welcomed by Major General Bennett E. Lewis, Commanding General, ARRADCOM, who was introduced by Colonel Peter B. Kenyon, Commander/Director, LCWSL, ARRADCOM. The keynote address was presented by Dr. R. F. Walker, EMD, who set forth the theme and objective of the conference. The conference was divided into four sessions as follows:

- Session 1: Chairman - Dr. Harold J. Matsuguma, ARRADCOM (USA)
- Session 2: Co-Chairmen - Dr. B. Zeller, Societé Nationale des Poudres et Explosifs, Centre de Recherches du bouchet, France, and Mr. K. Beedham, Ordnance Board, United Kingdom.
- Session 3: Co-Chairmen - Dr. John Kury, Lawrence Livermore Laboratory, USA, and Mr. Louis Avrami, ARRADCOM, USA.

- Session 4: Co-Chairmen - Dr. W. Schmacker, Bundesamt für Wehrtechnik und Beschaffung, West Germany and Dr. H.J. Pasman, Technological Laboratory TNO, The Netherlands.

On the morning of the last day of the conference discussion groups held parallel meetings and in the afternoon each group reported its findings to the general assembly. The discussion groups were as follows:

- Discussion Group on Requirements and Prospects for Improved Hazard and Storability Tests: Chairman, Dr. T. Joyner, US Naval Weapons Center, China Lake, CA.

- Discussion Group on Requirements and Prospects for Improved Performance Tests for Propellants: Chairmen, Mr. C.B. Dale, Naval Ordnance Station, Indianhead, MD, and Mr. C. Lenchitz, ARRADCOM.

- Discussion Group on Requirements and Prospects for Improved Performance Tests for Explosives: Chairman, Mr. J. Hershkowitz, ARRADCOM.

- Discussion Group on Requirements and Prospects for Improved Performance Tests for Pyrotechnics: Chairman, Mr. T. Boxer, ARRADCOM.

- Discussion Group on Prospects for Standardization of Methodology Among Nations and Commodities: Chairman, Dr. R.F. Walker, ARRADCOM.

Attendance at the conference totaled 150 participants representing nine countries and about 45 different government and commercial organizations. Thirty-two papers were presented and discussed. These papers constitute Volume 1 of the proceedings while Volume 2 will consist of the findings and recommendations of discussion groups as presented in the final assembly. A compilation of the abstracts for the papers was distributed at the meeting.

We wish to extend our thanks to the authors, session chairmen, group discussion chairmen, and all of the participants who made this meeting a success. The need for standardization is clear and the

international interest that was evident at the conference has, we hope, laid the groundwork for continued progress toward international standardization of safety and performance tests for energetic materials.

Raymond F. Walker
General Chairman

Louis Avrami
Harold J. Matsuguma
Proceedings Committee

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CONFERENCE ON THE STANDARDIZATION OF SAFETY AND PERFORMANCE TESTS FOR ENERGETIC MATERIALS

INTRODUCTION

by

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INTRODUCTION

As the individual who perhaps had more to do with the concept of this Conference than anyone else, I feel it is incumbent on me to explain what led up to the concept, what is the objective and what our plan is for the conduct of the Conference. Let me deal with the last two of these issues first. I will then discuss the events that led up to the occasion and, in doing so, provide an introduction to some current local perspectives on the Conference topic.

Simply stated our objective (Fig 1) is to examine the basis on which we might standardize the tests and criteria that determine the acceptability of energetic materials for military use. Many of the tests and criteria will parallel, if not replicate, those used by private industry for mining and civil engineering explosives (Ref 1) In this respect, it is well to remember that military requirements, vast though they appear in the Public image, are but a drop in the bucket of the industrial production capacity for civil explosives. And it is for these reasons that we have invited representatives of the civil industry to participate in our discussions. It is unfortunate that we are unable to welcome here Dr. Per Anders Persson from Sweden, who is President of the old European Commission for the Standardization of Tests for Explosives, now known as EXTEST. He has asked me to draw your attention to the existence of this group and to the recent description of its activities that has been given in the referenced issue of "Propellants and Explosives" (Ref 1). We are able to welcome one representative of EXTEST, namely Dr. Richard Watson from the U.S. Bureau of Mines; and representatives from the Office of Hazardous Materials of the U.S. Department of Transportation. Of one thing we may be sure, sooner or later the Department of Transportation prerogatives overlap and often constrain those of the military, and the continuing debt of the military to the contributions of the civilian industry (including the U.S. Bureau of Mines) date back to the time of Nobel.

We have planned this as a working conference, with the purpose of arriving at some executive decisions which can be used as appropriate for future concerted action. For this reason it has been necessary to limit the scope of the conference and to place even greater constraints on detailed technical discussions. We propose (Fig 2) during the first day to review the methodology and documentation currently used in the qualification of energetic materials. Later today and tomorrow we plan to review quite hurriedly some of the on-going R & D to provide improved tests and criteria. These reviews are by no means exhaustive, and we regret that in our

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A RATIONAL BASIS AND IMPROVED APPROACHES TO THE
INTERNATIONAL STANDARDIZATION OF TESTS FOR ENERGETIC MATERIALS.

Fig 1 Conference objective

1. REVIEW THE METHODOLOGY AND DOCUMENTATION USED FOR THE QUALIFICATION OF MATERIALS FOR MILITARY USE.

2. REVIEW RECENT ATTEMPTS TO DEVELOP NEW OR IMPROVED TESTS.

3. IDENTIFY REQUIREMENTS FOR NEW TESTS AND CRITERIA.

4. EXPLORE THE POTENTIAL FOR A UNIFIED, INTERNATIONAL APPROACH TO THE STANDARDIZATION OF METHODOLOGY, TESTS AND CRITERIA.

Fig 2 Scope of the conference

selection process we have had to reject or consolidate many excellent offerings whose inclusion would deflect us from our purpose. Some of the items that cannot be available as formal presentations will be included in the Proceedings. At this point I should also add that we have specifically excluded from consideration the topic of standard samples and substances. Important though this subject is, it has been considered a secondary issue within the framework of our immediate objective.

Our plan during the first two days is to provide just so much of an overview as to lend perspective to the last day's activities, which we hope will be the high-light of the Conference. On that morning we plan to divide you up into Discussion Groups in accordance with your interests or expertise, and as identified by colored stripes on your badges (Fig 3). These groups will meet in separate Conference Rooms on Thursday morning at locations to be announced.

We will pre-select facilitators and chairmen for these groups; the former will assure that each group has the necessary room, equipment, and guidance to conduct its discussion. The facilitators will also serve as guides for those who for security or other reasons need assistance in arriving at the correct location.

It is our desire that these morning sessions will be brainstorming sessions devoted not to what is being done, but what should or, more importantly, can be done to produce improved methodologies, tests and criteria. The approach to be used must be left to the Chairmen; however, each group must also have a secretary or recorder, because in the afternoon we plan that the groups will reassemble here and that Chairmen will present a synopsis of the Group's conclusions which we can include in the Proceedings along with comments from the audience. I urge you to get in touch with your Chairmen and Facilitators to indulge in as much planning as appears appropriate.

Now let me turn to the events which in my mind at least led up to the idea of holding this conference. Several years ago the U.S. Department of Defense was faced with a serious shortage of its basic high explosives, and in a time of emergency it turned hurriedly to its in-house laboratories and to private industry for ideas for substitute formulations to supplement the materials in short supply. Among others, private industry was frustrated in its attempts to gain acceptance of its offerings because of the diffuse and ill-prescribed criteria to be used in their selection. The actual tests involved were scattered throughout the literature or existed in the recent memories of in-house experts and had never been collected into an agreed compilation for routine or occasional use.

- **HAZARDS AND STORABILITY**

  CHAIRMAN: DR. T. JOYNER, US NAVAL WEAPONS CENTER, CHINA LAKE, CA
  FACILITATOR: W. VORECK, ARRADCOM

- **PYROTECHNIC PERFORMANCE**

  CHAIRMAN: MR. T. BOXER, ARRADCOM
  FACILITATOR: J. TYROLLER, ARRADCOM

- **PROPELLANT PERFORMANCE**

  CHARIMEN: MR. C. B. DALE, NAVAL ORDNANCE STATION, INDIANHEAD, MD
  MR. C. LENCHITZ, ARRADCOM
  FACILITATOR: C. CHRISTOE, ARRADCOM

- **HIGH EXPLOSIVE PERFORMANCE**

  CHAIRMAN: MR. J. HERSHKOWITZ, ARRADCOM
  FACILITATOR: V. SIELE, ARRADCOM

- **STANDARDIZATION OF METHODOLOGY**

  CHAIRMAN: DR. R. F. WALKER, ARRADCOM
  FACILITATOR: H. MATSUGUMA, ARRADCOM

Fig 3 Discussion groups

In response to this deficiency the three U.S. Services jointly agreed to subscribe to a compilation that was already in preparation by the U.S. Navy and which with minor adaptations was acceptable to the Army and Air Force. In 1972 this limited document was approved for use by the Joint Logistics Commanders and responsibility for the oversight of the procedures was assigned to individual service authorities. Despite numerous deficiencies this document (Ref 2) has proved to be highly effective during the last five years in evaluating the merits of the formulations proposed for military use, and in assuring that the formulations meet the minimum standards for military acceptability in the present economic and political climate. By way of introduction let me describe some of the philosophy which has guided the preparation and use of the procedures.

It is possible to distinguish several phases in the process by which energetic materials are evaluated first as isolated materials and subsequently as integral components of systems that have been designated for field use and proven as reliable products in the military stockpile (Fig 4). The key thought I would interject at this point is that materials are not formulated and fabricated in a vacuum; that something more than a vague idea of the intended application of the material is required before formulation and testing can be intelligently commenced.

In fact in today's world, from the moment the formulation work begins an iterative process should be triggered by which a number of issues are assessed at each step of the overall qualification - acceptance debate. In Figure 5 I list these issues as we see them during the first or interim qualification phase. Some or all of those issues have to be addressed during each of the steps outlined in Figure 4. In Figure 6 I have indicated some that relate to Final Qualification.

What our Joint Services Manual has attempted to do is to bring together those tests and criteria that relate to the interim and final qualification of HE which have previously been scattered throughout the literature, or in the minds of individuals. The manual is a very imperfect document in its technical completeness, editorial consistency, and the definitive value of the tests and criteria on hand. For this reason alone, it is part of a methodology which continues to place reliance on the judgement of committees of experts, and by its very deficiencies provides a rational basis for including in our technology-based R and D program, activities to provide new or improved tests and criteria.

1. SELECTION OF THE CRITERIA THAT DETERMINE ACCEPTABILITY.

2. INTERIM QUALIFICATION OF FORMULATIONS AS CANDIDATES FOR SPECIFIC APPLICATIONS.

3. FINAL- OR TYPE-QUALIFICATION OF AN END-ITEM CONTAINING A SELECTION FROM AMONG THE CANDIDATE MATERIALS.

4. QUALIFICATION OF SUB-ASSEMBLIES (SUCH AS FUZES).

5. QUALIFICATION OF SUB-ASSEMBLIES IN COMPLETE MUNITIONS OR SYSTEMS (SUCH AS FUZES IN PROJECTILES).

6. AFTER EACH STEP, A REVIEW AND APPROVAL PROCEDURE BY A COMMITTEE OF EXPERTS.

Fig 4 Steps in the evaluation of energetic materials

- DECISION CONCERNING PROSPECTIVE APPLICATION OF FORMULATION

EG					
	.	ILLUMINANT	.	GUN PROPELLANT	. DETONATOR
	.	DECOY	.	MINES	. PRIMER
	.	SIGNAL	.	DEMOLITION	. BOMB
	.	S.A. PROPELLANT	.	BOOSTER	. SHAPED CHARGE

- LABORATORY-SCALE TESTS ON FORMULATIONS
  - MANDATORY TESTS - SAFETY, PERFORMANCE, STORABILITY, ETC.
  - OPTIONAL, AD HOC OR PROSCRIBED TESTS.
- ASSESSMENT OF PRODUCIBILITY, AVAILABILITY, COST-EFFECTIVENESS
- REVIEW AND APPROVAL PROCEDURE BY COMMITTEE
  - BY LOCAL, SINGLE SERVICE GROUP.
  - BY OTHER SERVICES, AGENCIES FOR JOINT ACCEPTANCE.

Fig 5 Interim qualification of candidate materials

- SAFETY, PERFORMANCE, ENVIRONMENTAL TESTS IN ACTUAL END-ITEM CONFIGURATION
- MANUFACTURING TECHNOLOGY
  - PROCESS DEVELOPMENT
  - FABRICATION
  - LOADING
  - QUALITY ASSURANCE
  - COST ANALYSIS
  - POLLUTION AND ENERGY IMPACT
  - DEMILITARIZATION/DISPOSAL
- IN-PROCESS REVIEWS
  - CHANGES IN FORMULATION REQUIRE REQUALIFICATION AT INTERIM PHASE.
  - FAILURES OF ACCEPTANCE CRITERIA REQUIRE INVESTIGATIONS AT LABORATORY AND MUNITION DEVELOPMENT LEVEL.
- REVIEW AND APPROVAL PROCEDURES

Fig 6 Final- or type-qualification of materials

The economic and political pressures which precipitated the development of the foregoing rationale for HE qualification in the USA argue also for the rationalization of all testing of energetic materials whether for military or civil applications, but particularly among members of the NATO Alliance. In considering the implication of such a trend against the background of the deficiencies which already exist in the HE field the question must inevitably be raised: What is the most effective approach that we can adopt in each of the areas of high explosive, propellant and pyrotechnic materials; primers, igniters and initiators?

When we consider the issues such as hazards and storability which are already common to each of the fields, and consider that current technical thrusts point strongly to a greater interpendence among the fields within the technology base (Fig 7), the question must inevitably arise: To what extent can we reduce the deficiencies that relate to the whole technology base at the same time as we refine those that relate to HE alone?

The question is difficult to answer and not one that can be treated within the confines of narrow commodity interests. It is for this reason that we have endeavored to encourage broad-based participation at this Conference. Some of the potential advantages to be gained by standardization both between commodities and among nations are listed in my final figure (Fig 8). Your comments and suggestions will be most welcome both with respect to the appropriateness of the concept, the institutional mechanisms by which such a goal could be realized, and the new or improved tests that are required to make the international, interservice adoption of reliable tests a living reality.

REFERENCES

1. H. Ahrens, Propellants and Explosives 2, 140 (1977)

2. Joint Service Safety and Performance Manual for Qualification of Explosives for Military Use. JTCG/ALNNO, Working Party for Explosives. 12 May 1972

- USE OF NITRAMINES AS PROPELLANTS; OF NC, NQ IN HE.
- REPLACEMENT OF TNT WITH PU OR PB BINDERS; USE OF POLYMERIC BINDERS FOR PYROTECHNICS.
- INCREASED CONSIDERATION OF CIVIL OR AN-TYPE FORMULATIONS FOR HE.
- REQUIREMENT TO MAKE TRADE-OFFS TO LIVE WITHIN PRODUCTION BASE AND ECONOMIC CONSTRAINTS.
- ADVANCES IN THE UNDERSTANDING OF COMBUSTION/EXPLOSION AND IGNITION/ INITIATION WHICH SUGGEST ESSENTIAL UNITY OF THE THEORIES AND ASSESSMENT PROCEDURES.
- DEMANDS FOR INTERCHANGEABILITY, INTEROPERABILITY AND COMPATIBILITY OF MATERIEL.

Fig 7 Trends pointing greater interdependence of energetic materials selection

- COMPATIBILITY AND INTEROPERABILITY OF MUNITIONS AMONG TREATY NATIONS.
- MINIMUM NEED FOR REPETITIVE TESTING.
- A MEANS TO EXCHANGE INFORMATION BETWEEN GOVERNMENT AND INDUSTRY, THE ARMED SERVICES, AND NATIONS.
- FLEXIBILITY AND INTERDEPENDENCE OF MATERIALS SELECTION.
- MAJOR REDUCTION IN R & D COSTS AND DEVELOPMENT SCHEDULES.
- IMPROVED HAZARDS AND PERFORMANCE ANALYSES THROUGH POOLING OF DATA AMONG TREATY NATIONS.

Fig 8 Potential advantages of a standard methodology

UK PHILOSOPHY AND METHODOLOGY FOR THE QUALIFICATION OF EXPLOSIVES, PROPELLANTS AND PYROTECHNICS FOR MILITARY USE

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ABSTRACT

The philosophy, methodology and documentation employed in UK for the assessment of safety of energetic materials for military use are reviewed. The procedure is described in Annex A to Ordnance Board proceeding 41779 dated 15.2.77, and is common to the three UK Armed Services.

The procedure involves:

a. Selection, from a comprehensive list, of an agreed minimum schedule of tests to be performed on the material, both in powder and in charge form. The tests are designed to provide information on the response of the material to the conditions it could encounter during the manufacture, processing, filling, storage, operational use, and disposal, and

b. Assessment of the test results. Assessment does not involve rigid pass/fail acceptance criteria, but rather judgements based on comparison of the response in a variety of safety tests to that of energetic materials with proven service experience in similar roles.

It is intended to submit the UK procedure to NATO in the near future as a basis for a STANAG, and all steps towards International Standardisation are welcomed.

SUMMARY

The procedure which has recently been adopted on a tri-service basis in the UK for assessing the safety and suitability of a new explosive for service is reviewed. The use of a safety questionnaire to identify an agreed minimum schedule of tests to be performed on the material is described and the philosophy of the assessment of the results is outlined.

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INTRODUCTION

This paper deals primarily with the UK qualification procedures for the safety aspects of a new energetic material proposed for introduction into service. When a new high explosive, initiatory explosive, propellant or pyrotechnic is developed it is necessary not only to establish the performance parameters but also to examine those characteristics which could affect safety and ultimately its suitability in service.

In the UK, tri-service agreement has recently been reached on a uniform procedure to be adopted for an assessment of the safety and suitability of a new explosive whenever one is proposed for introduction into service (Ref 1). This assessment is additional to those procedures which would normally already have been undertaken to establish the hazard classification of the explosive material itself and to devise appropriate techniques for manufacture, transport, storage and disposal although information on the characteristics of an explosive necessary for such a classification may also be relevant to its suitability for service in its intended application.

Before describing the procedure it is useful to explain a number of terms used.

Terms Used

The term explosive is used to describe any energetic material and includes high explosives, propellants, initiatories and pyrotechnics.

The term "new explosive" is taken to encompass:

a. A modification of an existing explosive which has been shown to cause a significant change in the result of a safety test.

b. A new explosive of a type not hitherto in service.

c. A major change in application of an existing explosive.

The term "suitable for service" means that the material will not be unacceptably degraded by the service environment throughout the agreed service life.

The term "sensitiveness" refers to the ease of ignition or initiation of the explosive by prescribed types of stimuli representative of accidents.

The term "explosiveness" refers to the damaging capacity of the resulting explosive event after ignition or initiation of the explosive by prescribed types of stimuli representative of accidents.

PROCEDURE

When a new explosive is proposed for use in the UK, the proposing authority and the Ordnance Board together with their specialist advisers first agree on the minimum requirements for determination of the characteristics of the material on which an assessment of its safety and suitability for service can be made.

A safety questionnaire is used to identify those questions about the characteristics of a new explosive which are relevant to its nature and intended use. In this respect the characteristics of the explosive both in its normal filled condition and after possible degradation due to the service environment are important and would be considered.

Ideally the procedure should be completed before a decision is made to specify the material in a weapon design.

SAFETY QUESTIONNAIRE

The general characteristics of the new explosive are identified as indicated in Table 1. Certain questions relating to the physical and chemical properties are also posed in order to anticipate problems of long term physical or chemical stability.

Questions concerned with the thermal and electrical safety characteristics are listed in Table 2 and standard tests which are in use in the UK to provide experimental data of the response of explosives to thermal stimuli are indicated. Most of these tests are described in a Manual of Hazard Tests (Ref 2) and are divided into those carried out on small samples or samples in powder form and those carried out on charges since the hazards associated with explosive charges cannot yet be predicted with confidence from the results of small scale tests.

Questions relating to the sensitiveness and explosiveness characteristics when subjected to mechanical stimuli are shown in Table 3. Again the standard tests in use in the UK are indicated (Ref 2) and appropriate tests in powder and/or charge form are selected to answer the relevant questions depending on the type and role of the explosive. The physical properties of a charge can be an important factor in determining the response of an explosive to mechanical

stimuli and where these vary widely with temperature this is taken into account when establishing the safety characteristics. Normally tests on initiatory or pyrotechnic compositions are restricted to those on powder samples since this is usually considered to be the most hazardous condition and is considered also to be a guide to the ease of response in the filled (e.g. pressed) state. This is not always so for secondary explosives and it could be that under certain conditions it is not a valid assumption for initiatory and pyrotechnic compositions.

A general point can be made about the tests shown in Tables 2 and 3. The tests listed are not mandatory or exclusive and evidence from other sources or from new tests is accepted provided comparison can be made with the response of standard service composition of a similar type. It is also recognised that in some instances test methods do not exist or have not yet been developed in a standard form for providing direct experimental evidence in respect of answers to particular questions. Depending on the relevance or importance of the question in an overall hazard assessment the development of appropriate test methods would, it is hoped, be stimulated.

ASSESSMENT

The results of the agreed schedule of tests are considered and assessed by the Ordnance Board and their specialist advisers and formally reported to the proposing authority and the prospective service users together with recommendations on safety and suitability for service. Formal pass/fail criteria are not applied but judgement is made by comparison of the overall characteristics of the new explosive composition with those of explosives with known and proven service experience in similar applications.

It is emphasised that recommendation of a new explosive as suitable for introduction into service does not imply acceptance in any weapon system application. The safety of a particular weapon system will need to be demonstrated by appropriate tests. However, prior information on the safety characteristics of an explosive in a system is valuable for anticipating possible problem areas to which special attention can be directed during design, development and in the safety trials of the weapon system. Thus where a new explosive has some characteristic rendering it unsuitable for recommendation for general application, it is not thereby necessarily excluded from consideration for particular applications when it is shown that the undesirable feature can be satisfactorily overcome in the weapon system.

CONCLUSIONS

A national position has been established in the UK for the assessment of the safety and suitability of a new explosive for introduction into service. The procedure involved puts onto a formal basis the effort required to establish the material and safety properties of a new explosive at the time when it is under consideration for service use. The safety questionnaire offers a flexible approach to identifying the relevant questions and enabling suitable tests to be selected on which an assessment of the characteristics of the new explosive can be made.

The UK authorities are very conscious of the need for international standardisation in these matters and a draft NATO Stanag, based on the UK procedure, is being prepared. In these days of collaborative projects and interoperability of allied forces, the consequences of lack of standardisation can be unfortunate and very expensive. It is considered that the first aim should be to reach agreement on the relevant questions which need to be answered about a new explosive, depending on its nature and application, and the types of test which will provide the necessary evidence. Secondly, with interchange of information on the safety tests in use internationally it should further be possible to agree on the mutual acceptance of results from national versions of these types of test. Finally, and perhaps ideally some further standardisation may be possible in the actual test methods (e.g. as has been the case with some charge safety tests of secondary explosives) especially where the tests are considered to provide evidence on questions particularly relevant to the assessment of explosive hazard.

REFERENCES

1. Annex A to OB Proceeding 41779, "Introduction to New Explosives to Service", 15 Feb 1977

2. UK Sensitiveness Collaboration Committee, "Explosive Hazard Assessment", Manual of Tests, SCC No. 3 (in progress)

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Table 1

General characteristics of a new explosive

	Material properties	Information required
1.	What is its composition?	Composition and specification.
2.	What is its intended role and explosive type?	Main warhead filling, booster charge, initiatory, pyrotechnic, propellant, etc.
3.	In what form will it be used in service?	Pressed, cast, extruded etc. Density (also as % TMD)
4.	Is it closely related to other explosives already in service?	Service applications of closely related explosives.
	Physical properties	
5.	Have its mechanical and thermal properties been determined? Are any of these properties likely to affect adversely its suitability for service?	Liability to powdering, cracking, exudation, compaction, etc. in the expected environment. Liability to degradation of properties after storage.
	Chemical properties	
6.	How stable is it?	Appropriate stability results and where applicable consumption of stabiliser in hot storage. Appropriate thermal decomposition data, e.g., DSC, DTA and TGA.
7.	How compatible is it?	Known incompatibilities both physical and chemical. Compatibility of materials likely to be in contact with or near the explosive. Susceptibility to biological attack.
8.	Does it, or do its combustion products present any special new health hazard?	Relevant toxicity data.

Table 2

Thermal and electrical safety characteristics of a new explosive

Sensitiveness and explosiveness properties	Examples of standard tests - selected as appropriate	
	Powder tests	Charge tests
Thermal		
1. How easily does it ignite?	Temperature of ignition. Ignition by flash.	Minimum energy of ignition (by hot wire). Adiabatic compression tests e.g. Spigot test with air gap, RARDE vertical activator test with air gap.
2. How does it react when ignited?	Train test. Bonfire test on boxed material.	Bonfire test on boxed material.
3. How does confinement affect the response when ignited?	ERDE large sealed vessel test.	ERDE large sealed vessel test. ERDE small sealed vessel test. RARDE burning tube test.
4. Is there a possibility of the charge size approaching the critical self heating value?		Heat flow calorimetry (plus DTA/DSC data).
Electrical		
5. How readily does it react to electric sparks?	Electric spark test (including method for sensitive explosives where appropriate)	

Table 3

Mechanical safety characteristics of a new explosive

Sensitiveness and explosiveness properties	Examples of standard tests - selected as appropriate	
	Powder tests	Charge tests
1. How readily does it react to impact where trapped between hard surfaces and what is the response?	Drop weight impact test. Ball and disc test (for sensitive explosives.	Drop weight impact test on sample discs.
2. How readily is it sensitised by adventitious grit and what is the response?	Drop weight impact test with sandpaper or added grit.	RARDE vertical activator test with added grit.
3. How readily does it react to frictional impact and what is the response?	Mallet Test. ERDE emery paper friction test (for sensitive explosives).	Oblique impact test.
4. How readily does it react to explosive shock and what is the response?		Appropriate gap tests. Low amplitude shock initiation test.
5. How readily does it react to attack by high velocity fragments and what is the response?		Fragment attack tests (on bare charges and model sections of warhead, rocket motors, etc).
6. How readily does it react to high velocity impact and what is the response?		Susan Test. 30 mm shell impact test.
7. How readily does it react to intrusion and what is the response?		Spigot intrusion tests.

EXPLOSIVE TESTING AT THE LAWRENCE LIVERMORE LABORATORY - PHILOSOPHY AND PRACTICE

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EXPLOSIVE TESTING AT THE LAWRENCE LIVERMORE LABORATORY - PHILOSOPHY AND PRACTICE

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ABSTRACT

This paper discusses the evolution of explosives testing at the Lawrence Livermore Laboratory. The areas of performance, shock initiation, stability, mechanical properties and safety are addressed with emphasis on the standardization of tests.

INTRODUCTION

The Lawrence Livermore Laboratory (LLL) is a prime contractor of ERDA whose major mission is the design, testing and production engineering of nuclear weapons. High explosives are an important component of nuclear weapons, and LLL became active in this technology area around 1955. At that time a backlog of information had already been developed by the DoD and AEC for several TNT-based formulations, and data were just becoming available for HMX-containing plastic bonded explosives (PBX).

The mission of the newly-formed explosives group at Livermore was two-fold: first, to provide data on existing formulations and to assist in deciding which would best meet the requirements of a specific weapons system, and second, to search for new improved explosive formulations. Explosive testing immediately became an important aspect of our program. Neither our mission nor the importance of testing has changed significantly in the last twenty years. Our approach, however, has. This paper discusses the evolution in approach and presents specific comments on testing in the areas of performance, shock initiation, stability, mechanical properties, and safety including recommendations for standardization of tests.

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EVOLUTION OF EXPLOSIVE TESTING

Progress has been made over the years in the understanding of an explosive's behavior strictly by empirical testing. Drop hammers[1], gap tests[2], sand tests[3], and plate dent tests[4] are a few examples of the many tests which provide relative data on explosives. The explosives community still relies very heavily on this type of screening test. The appeal lies not necessarily in the quality of the information generated but in the relatively low cost and the small amount of explosive used in such tests. Nevertheless, these tests are useful in that they can provide relative information on explosive properties. We use tests of this type to get a "feel" for a new material and to point the way for further testing.

The development of high speed cameras, fast electronics and large computers has lead to an integrated calculational-experimental approach to explosives research. This involves formulating computer models, and verifying and calibrating these models through carefully chosen tests. In general, the tests require an amount of explosive intermediate between that used in small-scale screening tests and an actual weapon proof test. The goal is that data from these tests will permit a quantitative tradeoff of the various properties of candidate explosives thereby minimizing the number of proof tests required. These data should also provide insight on how to develop new improved formulations. *The major payoff from standardization of test procedures and data reporting would be for tests of this type!*

PERFORMANCE (ENERGY TRANSFER) TESTING

Our initial approach to performance testing was strictly empirical starting with Trauzl block[5] and sand tests. Formulations were chosen based on simple heat of explosion calculations - the larger the better. Boron hydride, aluminum, and fluorine-containing additives were all tested. Since weapon designers found it rather difficult to identify with "grams of sand crushed" we graduated to plate dent and both small-scale and large-scale plate push tests[6]. Hundreds of explosive formulations were tested, and the relative rankings were, in general, consistant with other performance test results.

By this time, though, it had become clear that the key to understanding an explosive's performance and exploiting this knowledge lie in obtaining a detonation product equation-of-state (EOS) for use in hydrodynamic calculations. Thermo-hydro codes like BKW[7], RUBY[8], and now TIGER[9], provided the necessary information, but even for standard explosives containing only hydrogen, carbon, nitrogen, and oxygen our absolute predictions of performance would be in error by ∿22%. A

significant shift in elemental composition or the presence of other elements further degraded our ability to predict performance. This is still true today, and as a result we have had to rely on metal acceleration experiments to provide the data necessary to develop an equation-of-state for detonation products.

In particular, we have concentrated on the cylinder test [10, 11]. This test not only provides an accurate indication of relative performance, but also, when combined with detonation velocity and detonation pressure, provides the data necessary to calibrate the JWL equation-of-state[10]. This equation-of-state has proven to be very useful for weapon design, and data are now available for most "ideal" explosives[12].

Multicomponent, "non-ideal" explosives, however, require a more complex description to model accurately the reactive flow that occurs. This description must include both temperature and time. Larger diameter cylinder tests[13] and a recently-developed, underwater test[13] can provide useful information, but much work still remains to be done to develop a model for the behavior of these explosives. In particular, better tests are required for determining parameters such as temperature-time and pressure-time profiles in the detonation products.

In summary, our current practice with new formulations is to use the small-scale plate dent test to verify detonability and then to do a cylinder test. The cylinder test can be instrumented to measure detonation velocity and detonation pressure. If the explosive is "non-ideal", a larger diameter cylinder test and, possibly, an underwater test are carried out. These tests provide sufficient information on the explosive to permit useful warhead design calculations.

Standard cylinder tests are currently being carried out at over half a dozen installations throughout the world with excellent reproducibility. A large data base already exists (over 500 experiments at Livermore alone). We recommend that this test be adopted as a standard and an effort be made to disseminate the detailed results that have been obtained to date.

SHOCK INITIATION TESTING

The shock initiation test most commonly used is the gap test. We have not emphasized this test at LLL. Rather, our approach has been to do tests with realistic mockups when investigating warhead initiation and to rely on more definitive tests when studying fundamental shock initiation phenomena.

We have used wedge tests[14] for sustained pressure pulse studies and a 101-mm gas gun[15] for both sustained and thin pressure pulse studies. Recently we have concentrated on developing electrical flyer plate techniques[16] to determine shock initiation behavior of explosives. Diagnostics for the above tests include, streak cameras, shorting pin switches, piezoelectric probes, manganin and quartz pressure gages, laser interferometer systems, axially symetric magnetic probes, and an Image Converter Camera.

Data from these tests were used to develop the $P^2\tau$ criterion for initiation[17]. This relationship has proven very useful as a design engineering tool and for assessing the shock response of the explosive used in a warhead. We are now developing a phenomenological model for the shock initiation process (See Appendix A). Initial results have been encouraging in that the major features of the experimental observations are reproduced by the calculations.

We feel that a standard shock initiation test would be very useful. The most promising appears to be one involving electrically-driven flyer plates. The test is one-dimensional and generates a well-defined pressure pulse which makes it practical to model. In addition, it involves only a small amount of explosive which permits the testing of expensive or sensitive materials. We recommend that a standard version of this test be developed for use throughout the explosives community. (The test would not be suitable for composite explosives with extremely long reaction zones.)

EXPLOSIVE STABILITY TESTING

A knowledge of the thermal stability of an explosive, both alone and in contact with other materials, is important for the design, production and fielding of safe, useful warheads. Our initial approach to both thermal stability and compatibility testing involved the vacuum stability test[18]. The limitations of this test soon became apparent. For example, portions of the sample under test would distill from the hot zone and only the total amount of gas (not its composition) was measured. This, plus an awareness of the real complexity of the problem, caused us to look for better tests. We have found the Henkin test[19], thermogravemetric analysis, differential scanning calorimetry and hot stage microscopy all to be useful thermal analytical tools.

Currently, we are using three main tests to evaluate thermal stability; a chemical reactivity test (CRT)[20], differential thermal analysis (DTA) and a one-dimensional time to explosion test (ODTX)[21]. The chemical reactivity test (CRT) performs the same function as the vacuum thermal stability tests run at other laboratories. There are

three significant improvements however: the hardware is stainless steel rather than glass, distillation from the hot zone is minimized, and the evolved gases are analyzed both qualitatively and quantitatively by gas chromatography. Preliminary compatibility assessments are also made by testing mixtures of explosive with other materials of interest.

Differential thermal analysis (DTA) is a standard technique that has found wide use in the explosives community. We run DTA's not only on the explosives themselves, but also on mixtures with materials involved in their processing and use, i.e., binders, moid releases, plastics, metals, etc.

The one-dimensional time to explosion test (ODTX) is designed to measure time to explosion as a function of temperature under a precisely controlled set of thermal and physical boundary conditions. The results plotted as the logarithm of time to explosion versus reciprocal temperature generally give straight lines. The slope of the line along with the intercept can be used to predict critical temperatures for the explosive. The test differs from other time to explosion tests in that the geometry is one-dimensional and there is positive containment under pressure. Both spheres and slab configurations are currently being used. The gaseous decomposition products can be totally contained in the apparatus up to a maximum burst pressure of 1500 atmospheres.

The above small-scale screening tests have produced useful results on a relative basis. However, they do not provide the data needed to assess the thermal response of actual warheads using heat transfer codes such as TRUMP[22]. This is not surprising when one considers that the thermal stability of an explosive is not a unique, precisely definable quantity. It is a complicated combination of thermodynamics and kinetics which is system dependent. Moreover, the system must be defined in terms of previous thermal history, physical state of the sample, free volume, heating rates, pressure, containment, and the nature - both chemical and physical - of other materials in proximity to the sample. As a result the intermediate-scale tests we now use are mockups of actual weapon configurations. We follow these with full-scale weapon tests as required.

In summary, we have three excellent small-scale screening tests - all of which are necessary. The CRT looks for instability by gas evolution; DTA looks for instability by heat evolution; and ODTX investigates the effect of confinement. Based on the results we have obtained with ODTX we recommend that a standard version of this small-scale test be developed. We are dubious that a meaningful intermediate-scale, non-weapon-specific test can be developed and, therefore, do not recommend standardization in this area of testing.

MECHANICAL TESTING

Having detailed information on the mechanical properties of an explosive has become more important over the years. From the onset, TNT-based explosives were not considered structural materials so warheads containing these explosives were designed accordingly. However, as stronger plastic-bonded explosives became available they could be used to help distribute the loads the warhead would see in service use. As a result, tests designed to measure stress-strain failure envelopes and creep properties were developed[23].

More recently we have become aware of the importance that mechanical properties play in determining the safety of an explosive. As a result we are paying special attention to high-strain-rate testing and fracture characterization of explosives. A variety of tests is being used. They include universal testing machines[24] (strain rates (R) = 10^{-5} to 10^{-1} per second), a cam-driven uniaxial tester[25] (R = 10^{-2} to 10^{2} per second), a Hopkinson bar[26] (R = 10^{2} to 10^{4} per second) and flying plates[27] (R > 10^{4} per second). Where possible, the degree and mode of fracture are measured by post-examination of the specimens.

Models for describing the stress-strain, strain rate, and fracture behavior of explosive materials are in a very early stage of development. Work is required both on better test methods and more realistic models, however, before test standardization can be considered.

SAFETY TESTING

The three previous sections discussed testing of explosives subjected to a specific type of impulse. The physical and chemical phenomena involved have, in general, been identified. Progress is being made toward developing models which will permit more accurate tradeoffs based on a formulation's shock initiation behavior, thermal and chemical characteristics, and mechanical properties.

All these areas are related to the safety of an explosive. Unfortunately, our efforts in these areas have not permitted an "accurate" assessment of safety for at least two reasons: there are an almost infinite number of possible accident scenarios, and safety assessments involve decisions on the tail of a probability curve.

As a result, the degree of hazard involved in working with a new explosive is determined from a series of empirical tests that have also been applied to common explosives for which we have extensive handling experience. Such tests usually examine thermal and chemical response as well as response to mechanical and shock stimuli. Since the response observed in a specific test depends on a combination of properties, a

variety of tests is used in an effort to avoid leaving out any one important element in the explosive's behavior. The tests really become a search for "traps" or unexpected behavior.

We commonly use three tests of this type to assess new formulations. The small-scale drop hammer test is used to screen materials and place them in one of four broad categories: TNT-like, Comp B-like, PETN-like, or nitroglycerine-like. In spite of all the effort spent on drop hammers we feel this test will never be anything but a guide to laboratory handling practice.

We use the Susan test[28] to evaluate the response of explosives to crushing impact. Results are reported either as relative energy release versus impact velocity or overpressure versus impact velocity. A detailed understanding of the test is required in order to interpret these results in terms of safety. For example, the ignition threshold for sensitive explosives is closely tied to their mechanical strength. A necessary but not sufficient condition for ignition in the Susan test is longitudinal case rupture. Case rupture velocity can vary from about 29 m/s for a water-filled case to about 41 m/s for the strongest PBX. Thus, threshold velocities in this range are determined by the relative dynamic strength of an explosive, including its ability to undergo elongation without fracture. Also, since the size of an event is measured by overpressure gages, comparison between explosives requires that they be in similar geometries at the time of maximum reaction. Reaction details available from test film records are, therefore, required in order to interpret the test results.

We use the skid test[29] to evaluate plant handling characteristics of large bare charges (typically 0.28 m diameter hemispheres that weigh about 15 kg). Again it is our experience that inferring safety, even on a relative basis, from this test requires considerable judgement. For example, threshold heights for impact on the standard sanded-steel surface are not necessarily the lowest heights at which reaction can occur. Some ceramic surfaces have been observed to produce even lower threshold heights. Also, a "no reaction" for a particular drop should be considered a "no test" if the billet is cracked or broken. Impact on a more flexible target could produce substantial reaction. In the same vein, large differences between 14° impact angle results and 45° impact angle results are often due to the sample falling mechanically in the 45° drops, particularly with explosives containing TNT

Of the above tests, the only one that appears suitable for modelling is the skid test. This may also be true for a few other large-scale safety tests. However, these tests can cover only a limited number of accident scenarios. Standardization would certainly increase the

useful data base, but the other safety tests would still have to be done to look for "traps" or for unexpected behavior. It is not clear that this situation will change in the forseeable future.

CONCLUSIONS AND RECOMMENDATIONS

LLL has pursued an integrated calculational-experimental program of explosive research and development. Based on this program we recommend that three tests be considered for international standardization. They are the cylinder test for explosive performance, an electrical flyer plate test for shock initiation, and the one-dimensional time to explosion test (ODTX) for thermal stability. The cylinder test is already widely used and would not require modification. Both the electrical flyer plate test and ODTX are recent developments and could still be modified somewhat to facilitate standardization.

In addition, we recommend that an increased effort be put into the compilation and dissemination of data on the properties of explosives. We recently began the second update of UCRL 51319[30] and would welcome comments and data.

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APPENDIX A

A NEW MODEL FOR SHOCK INITIATION

A two-step reaction model has been developed to simulate shock initiation of detonation. The rate of energy release during initiation is taken as:

$$\frac{dF}{dt} = A(1-F)\frac{d\ln V}{dt} + B(1-F)^{\frac{2}{3}}F^{\frac{2}{3}}\int \frac{d\ln V}{dt} p^n \qquad (1)$$

where F is the fraction reacted, V is the specific volume, t is the time, p is the pressure and both A and B are rate constants. The area of the burning surface is approximately $F^{\frac{2}{3}}(1-F)^{\frac{2}{3}}$. The first term in equation (1) may be considered as expressing the effect of the shock upon the virgin explosive. A plausible postulate is that the shock creates damaged regions and ignites some of these regions as it passes. The factor $\frac{d\ln V}{dt}$ is a measure of the rate of compression. In a finite difference calculation, it is related to the artificial viscosity. Subsequent to the passage of the shock, the explosive burns at a rate proportional to the pressure and the area of the burning surface according to the second term. The exponent n will normally have a value near 1.0 consistent with laminar burning. In addition to the pressure and composition effects, the second term is also assumed to be influenced by the shock strength expressed by $\int \frac{d\ln V}{dt}$ as more ignited surface is produced as the shock strength is increased.

The hydrodynamic model enables us to make calculational predictions for the shock initiation experiments mentioned earlier. Determining the coefficients in the rate law from a single set of experiments should then enable us to predict the other experimental observations and thus test the phenomenological model. Initial results have been very encouraging in that the major features of the experimental observations are reproduced by the calculations.

THE SAFETY AND HAZARD PHILOSOPHY FOR ACCEPTANCE OF GUN AND ROCKET PROPELLANTS IN THE UK

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Abstract

In this paper an attempt is made to discuss in more detail for propellants the hazard appraisal procedures covered in the general papers for all explosives by the Ordnance Board and the Navy authorities.

The philosophy of these procedures involves the use of a range of standard tests, the results of which for new materials may be compared with those for familiar propellants whose characteristics are well known. An overall hazard assessment can then be made.

Small scale tests involving up to a few grams of material are available, in which samples are subjected to the usual range of stimuli (impact, friction, spark etc). These show most propellants - especially those containing nitrocellulose with or without nitroglycerine - as easily ignitable, which is not surprising in view of their function. Nevertheless their manufacture has progressed satisfactorily in spite of this property.

Hazard problems with propellants are concerned more with large charges and with the consequences of ignition, ie their explosiveness, in particular situations.

With gun propellants there are two related principal problems both more acute with higher-performance materials viz whether the propellant presents a fire or an explosion risk for bulk storage and transport, and whether an assurance can be given that it will burn steadily rather than explosively in a high pressure gun chamber.

For rocket propellants relevant problems include also response to spigot intrusion and fragment attack. Here the physical and chemical properties play a large part, a considerable variation being found as regards the minimum amount of intrusion required for ignition, and the consequences of that ignition, particularly when propellants of high frangibility provide an increased surface area for burning. Response to explosive shock must also be considered.

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1 Summary

UK procedures for acceptance of gun and rocket propellants involve the use of a range of standard tests, the results of which for new materials may be compared with those for familiar propellants whose characteristics are well known. Small scale sensitiveness tests, in which up to a few grammes of material are subjected to a range of stimuli (impact, friction etc) show propellants in general as easily ignitable; up to the present time however, manufacture has not presented any intractable problems. The hazards presented by propellant charges or quantities of such charges have, with the exception of classification of propellants in bulk for storage and transport, so far received comparatively little attention in the UK. However, with the increasingly stringent requirements for performance required for present-day applications, such problems as those presented by the dropping of bare charges, intrusion by hard and irregular surfaces, fragment and bullet attack, and response to explosive shock will require consideration in future. Standard tests to simulate these are available and suggestions are made for future developments.

2 Introduction

The manufacture, storage, transport, handling and use of explosives of any type is necessarily accompanied by potential hazards to personnel, equipment, and facilities and even on occasion to the general public. The assessment of such hazards is a difficult problem with many aspects. It is clearly impracticably expensive and time-consuming to carry out full scale trials to simulate every conceivable hazard situation, and recourse is therefore had to a series of standard tests which in most cases are not directly representative of actual hazard situations (though some are more so than others) but which can be relied on to give reproducible results and which can be carried out reasonably quickly and comparatively inexpensively. Explosives may then be ranked in order of response to the several tests and comparisons can be made between the new material whose hazards are in question and more familiar materials whose behaviour is considered to be known. It is of course essential that an adequate range of tests shall be available to cover the various aspects and PERME Waltham Abbey, which exercises a design function for propellants and is capable of manufacturing almost any propellant in or proposed for UK Ministry of Defence service, has developed what, up till now, has been thought to be an adequate group of procedures for this purpose

The tests may be divided into two broad classes, those carried out on a few grammes (or less) of powdered (or at any rate finely-divided)

material, and those concerned with larger charges. Tests in the first class assess sensitiveness, that is, the ease with which the propellant may be ignited by a prescribed stimulus. Tests in the second class may give information on sensitiveness and also on explosiveness, that is, the violence of reaction of the material after ignition, in terms of blast output and/or damage to the surroundings. Explosiveness is dependent not only on the chemical constitution of the propellant, but on such extensive factors as the mass, configuration and degree of confinement of the charge. Hazard assessment clearly requires consideration of both these aspects, though, to anticipate, it may be suggested that the main problems are connected with the assessment of explosiveness in particular situations.

3 Safety Certificate Testing - Outline of Procedures

In the UK the development of gun and rocket propellants takes place very largely in Ministry of Defence Establishments and agencies, and the subsequent manufacture of these materials in Royal Ordnance Factories which also form part of the Ministry of Defence (MOD) organisation. MOD practice requires the provision of a document in standard form, and known as a Safety Certificate, for any explosive material whose manufacture in a Royal Ordnance Factory is proposed. The Safety Certificate provides data on the properties of the material in question, including the results of a series of sensitiveness tests designed to examine the response of a small quantity of the material, ideally in powdered form, to a range of stimuli, and directed towards some of the hazards arising in manufacture or handling.

The Rotter Impact test[1] (Fig 1) was developed for the study of crystalline high explosives, but its use has been since extended to almost all kinds of explosive material. The impact produced by the fall of a 5 kg weight is transmitted through two intermediate components to the base of an inverted brass cup which contains a 0.03 cm^3 sample of the material and fits over the projecting "pip" of a hardened steel anvil (Fig 2). The chamber is sealed during firing and the normal criterion for an ignition is the generation of a minimum gas volume (1 cm^3). The procedure used is the Bruceton staircase method[2], designed to give the best possible value of the median height (ie drop height for 50% probability of ignition) and to avoid possible drifting effects due to wear on the equipment the runs are interlaced with those of a standard, a highly purified RDX with a fairly narrow particle size range, to give a Relative Median Height or RMH (expressed in terms of standard RDX = 80). In development work 50-shot runs are employed, but for safety certificate purposes 200-shot runs are used. The action of the test is of shear flow under compressive stress.

The mallet friction test[1] employs a small sample of the material under test, spread on an anvil and struck a glancing blow with a standard steel-tipped or wooden mallet held in the operator's hand. These mallets weigh about 980 g and 700 g respectively. In the standard procedure, the former is used with mild steel, naval brass and aluminium bronze anvils, and the latter with hardwood (oak), softwood (soft Norwegian pine) and yorkstone anvils, though other combinations, including anvils of plastics materials, are available if required. The standard practice is to attempt a maximum of five strikes at the sample; when an ignition occurs or five strikes take place without ignition, another sample is tested, and ten samples in all are used for each mallet/anvil combination. The results are thus obtained as a number of fires out of ten for each mallet/anvil combination and for safety certificate purposes these are further rounded as follows:

0 fires out of 10	rounded to	0
1 - 6 fires out of 10	rounded to	50
7 - 10 fires out of 10	rounded to	100

The human element in this test is obviously considerable and the action in practice is not entirely frictional in character. A machine designed to overcome this difficulty and obtain more quantitative data is described in the paper for this conference by J F Sumner of this Establishment.

The temperature of ignition test[1] uses a sample of 0.20 g (for initiating compositions 0.05 g) which is heated at 5°C/minute in a standard borosilicate test tube until an event occurs or 400°C is reached; the character of the event and its temperature are noted.

The Bickford fuze (or ease of ignition) test[1] makes use of a length of gunpowder fuze to produce a shower of incendive sparks on a sample of 3 g of the material, also in a borosilicate test tube, at room temperature. If an ignition is not obtained the attempt is repeated and up to five attempts in all are made. The nature of any event is noted.

In the train test[1] a hemicylindrical mild steel trough 300 mm long by 13 mm diameter and 1.5 mm wall thickness is filled flush with the top with the material under test, which is ignited at one end by a gas flame. Again the nature of the event is noted.

The electric spark test[1] uses successive trials with sparks of 4.5 J, 0.45 J and 0.045 J on samples of the material under the confinement provided by 6 mm diameter holes in a 3 mm thick polythene strip,

closed at the bottom by a continuous copper foil electrode 0.08 mm thick and at the top by discrete pieces of similar foil to provide the second electrode. Only one spark is applied to each sample and if no ignition is obtained in 50 trials at any one energy level the trial is discontinued. If ignitions occur at 0.045 J a more searching procedure is required in view of the fact that an operator may acquire an electrostatic charge of up to possibly 0.01 J on his person in extreme conditions in the UK.

It will be seen that the six tests outlined provide information on the response of a small sample of material to situations which represent (respectively) impact leading to shear flow; friction; comparatively slow temperature rise; incendive sparks; naked flame; and electric spark. None of these tests can be claimed to be representative of any particular hazard situation, their value lying in their standard character, the reproducibility of the results, and the fact that they can be carried out adequately by semi-skilled staff. As a result of these factors a many years' accumulation of data is available from which the behaviour of new materials may be assessed through comparison with others whose characteristics are well known.

4 Safety Certificate Testing - Results for Propellants

In practice most attention is given to the results of the Rotter Impact test, which provides numerical discrimination between materials and the results from which should achieve good reproducibility over long periods. Propellants in general give much lower values than high explosives, reflecting their greater ease of ignition; single and double-base propellants give values down to 15 - a result recently obtained for a sample of the familiar SC (Solventless Carbamite) cordite, which has been in service for many years. Lower values may give rise to concern, not so much because of any direct resemblance between the experimental array and any hazard situation as because this is the principal quantitative sensitiveness test assessment available; this is reflected in the term Figure of Insensitiveness (F of I) which is given on the Safety Certificate to the RMH value. It should be pointed out however that propellants do not in general produce their full volume of available gas (~ 20 ml) in the Rotter test, as crystalline high explosives do - gas volumes of 1.5 to 5 ml being typical for the "fires" in the test runs for propellants. Even at drop heights far in excess of the median value the gas volume is often not significantly increased so that the ignition is not fully effective under the conditions of test. Another complication is that composite propellants (which consist fundamentally of ammonium perchlorate with fuel binders of various types) cannot be ground to powder, so it is necessary to test these in the form of discs,

2 mm thick by 4 mm diameter. (Comparative experiments using double-base propellants suggest that this modification of procedure has little effect on the results.) Composite propellants in general give RMH values down to 30, which are considered acceptable.

Up to the present UK hazard appraisal procedures have not required assessment of the sensitising effect of grit on propellants. In terms however of the latest Ordnance Board procedures (discussed in the paper for this conference by K Beedham) this assessment will be called for in the future for the new and modified types of propellants (and other kinds of explosive materials) to which that Proceeding will be considered to apply; the Rotter impact test will be used.

The results of the mallet friction test generally correlate with those of the Rotter test for the class of double-base and single-base propellants as a whole; ignitions are obtained with the steel-tipped mallet (usually 100 on steel, 50 - 100 on naval brass, 50 - 100 on aluminium bronze) and the more energetic or faster-burning propellants give ignitions with the wooden mallet on yorkstone also. Composite propellants in general, give higher friction sensitiveness for similar F of I than double-base materials; values of 100 with the steel-tipped mallet on all three metal anvils are usual, as is a similar result with the wooden mallet on the yorkstone anvil. The latter result is attributed to "hot spot" generation accompanying erosion of the wood of the mallet by the rough surface of the stone, and is thus comparable to sensitisation by grit. Occasional ignitions (leading to a result of 50) with the hardwood anvil are also observed, but ignitions with the soft-wood anvil would give rise to concern.

The temperature of ignition (T of I) test is in effect an accelerated stability test and propellants containing nitric esters (in practice nitrocellulose with or without nitroglycerine) all give values in the general range 155 - 170 C and produce flame. In general materials with measured temperature of ignition less than 140 C are not stable enough for service use. Composite propellants in general give T of I values above 200 C.

In general propellants ignite in the Bickford fuze test (though a few slower-burning composite materials fail to do so) and burn steadily or vigorously in the train test. A material which "exploded" in either of these tests would hardly be suitable for use as a propellant.

The electric spark test shows that with nearly all single and double-base propellants no ignitions are obtained at the maximum energy of 4.5 J, although a few give a result of "ignitions at 4.5 J but not at

0.45 J". All composite propellants so far tested give no ignition at 4.5 J. Nitrocellulose itself, particularly when finely divided can be ignited with sparks of 0.045 J but in general there is no problem with it or with any propellant as far as charged personnel are concerned. However there are two situations in which a hazard can arise. One is the accumulation of charge as a result of moving a large quantity of propellant powder during processing, which may result in available energies well in excess of 0.01 J, and the other is the possibility of ignition of solvent-air mixtures, arising from the solvents used in processing, as a result of such movements or by charged personnel. However graphiting the material reduces the former problem and the use of appropriate clothing reduces the latter.

It will be seen that propellants in general are readily ignited in all these tests except for the last. Since ready and reproducible ignition is a pre-requisite for their functioning in a gun chamber or rocket motor, this is not surprising. Even propellants with the lowest values of F of I and the highest friction figures in the ranges quoted have not been found to produce an unacceptable ignition hazard in service, providing that the store is not designed or handled in such a way that small quantities of the propellant can be subjected to sharp mechanical stimulus (friction or "nipping") between metal surfaces. Manufacture and processing, where a much greater energy density may be applied to the material then during subsequent handling etc may provide a greater hazard, and in at least one process (viz the rolling of sheets of extruded double-base propellant) it may be necessary to accept that occasional fires may occur and to instal drenching equipment. However in other respects procedures may be laid down which if rigidly followed may be claimed to eliminate for all practical purposes the incidence of ignitions during propellant manufacture and processing.

5 Classification for Storage and Transport

For purposes of storage and transport of explosive materials it is necessary to discriminate between explosive risk on the one hand and fire risk on the other ie to assess their explosiveness under these circumstances. Since the quantities involved may be very large it is necessary to devise tests which may be carried out on a comparatively small scale, with compensation for the reduced mass of explosive by means of confinement much greater than that provided by approved explosive packaging (ie a "penalty" test).

The Standard UK classification test is the large sealed vessel (LSV) test[3] of which two types are available. The filling may be cast or extruded into the vessel, or used in granular form, as appropriate. The igniter version (Fig 3) is the more frequently used, since the heated

version (at a rate of 5° C/minute) has been found to be an overtest in the case of materials that have been cast or extruded into the vessel, although it is probably satisfactory for granular materials. The result is assessed by the degree of fragmentation of the vessel and the present practice is that if none of the four firings with igniter type vessels gives more than nine fragments, then the material is classified as a fire risk.

If any one test gives 16 or more fragments, an explosive risk is established. In all other cases, the standard deviation of the mean of the number of fragments is calculated and the upper limit for the mean number is estimated; if this is greater than or equal to 13, the material is taken to be an explosive risk, and if less than 13, a fire risk. This is a somewhat more detailed requirement than that quoted in reference 3.

When trials with boxes are required testing may be carried out either (a) on a single box with an igniter embedded in the contents or (b) on a single box in a standard kerosene or timber fire or (c) as a stack trial with a linear vertical array of three boxes by three in a brick-lined concrete pit, the bottom three boxes containing live material and the remaining six boxes being filled with sand. The contents of the central bottom box are ignited.

Most of the available LSV test results are on gun propellants, and on composite propellants consisting essentially of ammonium perchlorate and binder. Gun propellants of small web size are explosive risks for bulk storage and transport, whereas ones of large web size are fire risks.

All composite propellants of the plastic type have been shown to be fire risks only, provided their rate of burning is not greater than 50 mm/s at 10 MPa and they are stored in standard boxes not greater than four high. In these circumstances composite propellants in particular can lead to the throwing of firebrands. Though few results are available rubbery composite propellants have usually been found to be somewhat less reactive in the LSV test than the plastic ones.

Since the majority of, if not all, double-base rocket propellants of whatever charge design, have a web size much larger than the critical size, they will all be fire risks, unless they are damaged and thus have an increased surface area (see Section 6).

In contrast to the rocket motor situation, it should be noted that the LSV test, involving a bursting pressure appreciably less than that of the chamber of a modern gun, is an under test in that context. Some

thought has been given to designing a stronger vessel which would burst at a pressure somewhat higher than most gun chamber operating pressures.

6 Hazards with Charges

For assessment under this general heading, there are available a number of tests to cover a variety of hazard situations, including those with cased material as well as bare charges. Up to the present time little if any use has been made of these tests in assessing the acceptability of gun and rocket propellants for service use in the UK but in terms of the latest Ordnance Board procedures (discussed in the paper for this conference by K Beedham) results from these tests will be called for in connection with the assessment of future "new explosives".

For example, large bare charges of the more rigid types of propellant have to be handled while being moved from one work area to another, or in preparation for machining; this applies to extruded double-base propellant and, from time to time, to cast double-base propellant. There is then always the possibility of accidental dropping. To assess this, the oblique impact or skid test[4] is available. This test was developed for high explosives and so far has not been used for propellants. Normally if ignition takes place the violence of the ensuing event will depend very much on the damage caused to the charge on impact. If little or no damage is caused, combustion will proceed relatively quietly, since the charge will eventually be burning at atmospheric pressure.

Accidental dropping of an explosive store on to a hard irregularly shaped surface, such that an intrusion is made through the case and into the material inside, is another hazard that has to be considered. To simulate this, some form of spigot intrusion test is employed. The test used at PERME (Fig 4) consists of a steel tube 127 mm long and 40 mm internal diameter, to one end of which a steel plate, 64 mm square and 1.6 mm thick is welded. The tube is filled with the propellant under study and placed on a heavy base with the cover plate facing upwards. A cylindrical spigot 19 mm diameter by 114 mm long fitted to a 45 kg weight is allowed to drop, so that the spigot perforates the plate and enters the charge. Only a few propellants have been tested in this way, and all have shown that under these conditions drop heights in the range of 1 - 2 m (resulting in intrusions into the propellant of 10 - 20 mm) are capable of causing ignition, the charge continuing to burn.

The assessment of the response of propellants, and of cartridges or rocket motors containing them, to attack by bullets or fragments

is clearly of importance, and many ad hoc trials have been carried out against individual stores - rocket motors in particular.

Work is in progress at PERME Waltham Abbey to investigate this problem, both to compare threshold velocities for ignition of a range of propellants under standard conditions, and to look into the effect of variation of parameters (eg tube material and propellant composition) on the violence of the response of a standard model rocket motor subjected to a standard form of attack. It would certainly be premature at present to lay down any criteria for acceptability in this connection, but the results will provide a yardstick against which future candidate propellants can be measured. Little information appears to be available on the fragment or bullet attack of gun propellants.

Another area of hazard is the susceptibility of gun and rocket propellants to explosive shock following accelerating combustion, or from nearby high explosives. For this assessment there are available at PERME Waltham Abbey a number of gap-type tests, including the Low Amplitude Shock Initiation (LASI) test (Fig 5), in which information is given on the threshold pressures for the onset of combustion as well as of detonation to several go/no go gap tests, eg Scale VI (using bare 12.7 mm square cross-section charges 25.4 mm long), Scale F1 (using bare 50 mm diameter charges 76 mm long) and Scale IX which uses cased charges and is virtually identical with the US NOL Large Scale Gap Test. The LASI test, which also is based on NOL work, uses 50 mm diameter charges. It is recognised that there is a potential hazard with double-base rocket propellants since all are detonable (some giving larger outputs than TNT) in relatively small diameters, ie of the order of 20 - 30 mm. They are, however, relatively insensitive to shock, input pressures of say > 90 kb being required for detonation and > 70 kb for onset of combustion (under the conditions of the LASI test). The addition of ammonium perchlorate and aluminium, and of nitramines, increases the sensitivity, the critical pressure for detonation dropping for example to half or one-third of the value for plain double-base compositions on addition of the last-named type of material. Most gun propellants in bulk will also be detonable. On the other hand it is well known that composite propellants based on ammonium perchlorate and fuel-binders are not detonable in diameters less than about 1.5 m, provided their porosity is low.

7 Conclusions and Recommendations

It will be seen that a wide range of tests is available to explore the response of propellants to various stimuli under a range of

conditions. The small scale tests, carried out on virtually every material submitted for examination, lead to the general (and perhaps fairly obvious) conclusion that propellants are readily ignitable (except by electric sparks whose duration appears to be too short) and in fact they must be so in order to perform their proper function. This suggests that there may be merit in the development of a standard test which aims to measure explicitly a minimum energy of ignition, preferably with different rates of application of energy. This concept of minimum energy of ignition has so far received very little attention in the propellant field in the UK. Some kind of inverse correlation with the linear rate of burning may be expected. The need for vigorous control in processing propellants has already been emphasised; while no formal criteria have been laid down, it may well be that materials showing F of I less than 10, and/or ignitions with the wooden mallet on the softwood anvil, would present problems in processing.

When the propellants have been manufactured, it is the explosiveness of large charges or quantities of material which is of concern. Granular propellant, filled to greater than a certain minimum depth, may be expected to burn to detonation on ignition; this hazard can be important for casting powder as well as for finished propellant, and a standard procedure for determining this depth would be very useful.

In connection with solid charges, there is need for more quantitative information on critical diameters for detonation, and such a study is currently proposed at PERME Waltham Abbey.

At the same time, many practical problems are concerned with events which fall short of full detonation of the propellant but which can be very destructive. The mass explosion risk represented by the 1.1 hazard classification for transport and storage is an example of this. So is the high-performance gun problem; it is not necessary for the propellant to burn completely to detonation for rupture of the gun chamber to occur, leading to the loss of the gun and probably the gun crew. The problems presented by the fragment attack of rocket motors are analogous. Both these last are problems with stores, but the behaviour of the propellant itself is fundamental. With the increased performance of modern propellants, in both the gun and rocket fields, there is a penalty in the form of potentially increased hazards, and consequently a need for increasingly careful assessment of the problem.

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Figures

1 Rotter Impact Apparatus

2 Rotter Impact Chamber

3 Large Sealed Vessel (Igniter Version)

4 PERME Drop (Spigot) test

5 Low Amplitude Shock Initiation Test

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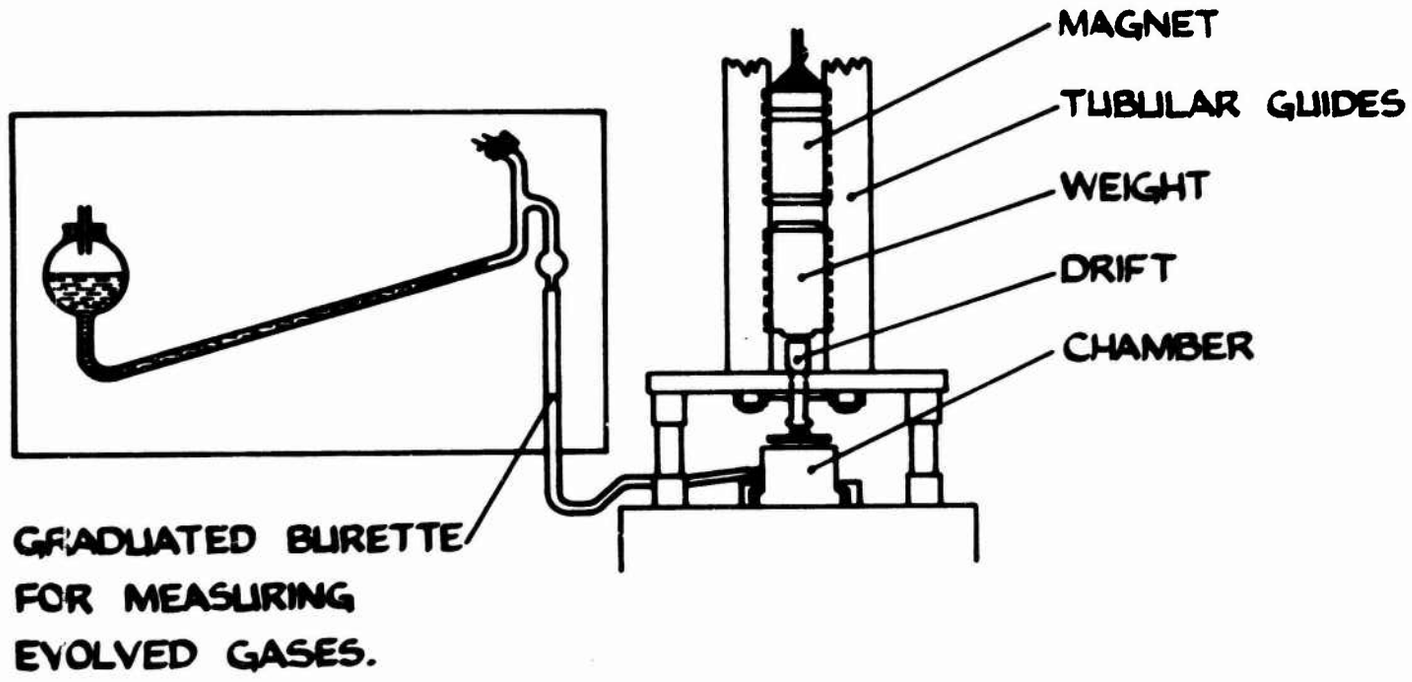


FIG. 1 ROTTER IMPACT APPARATUS

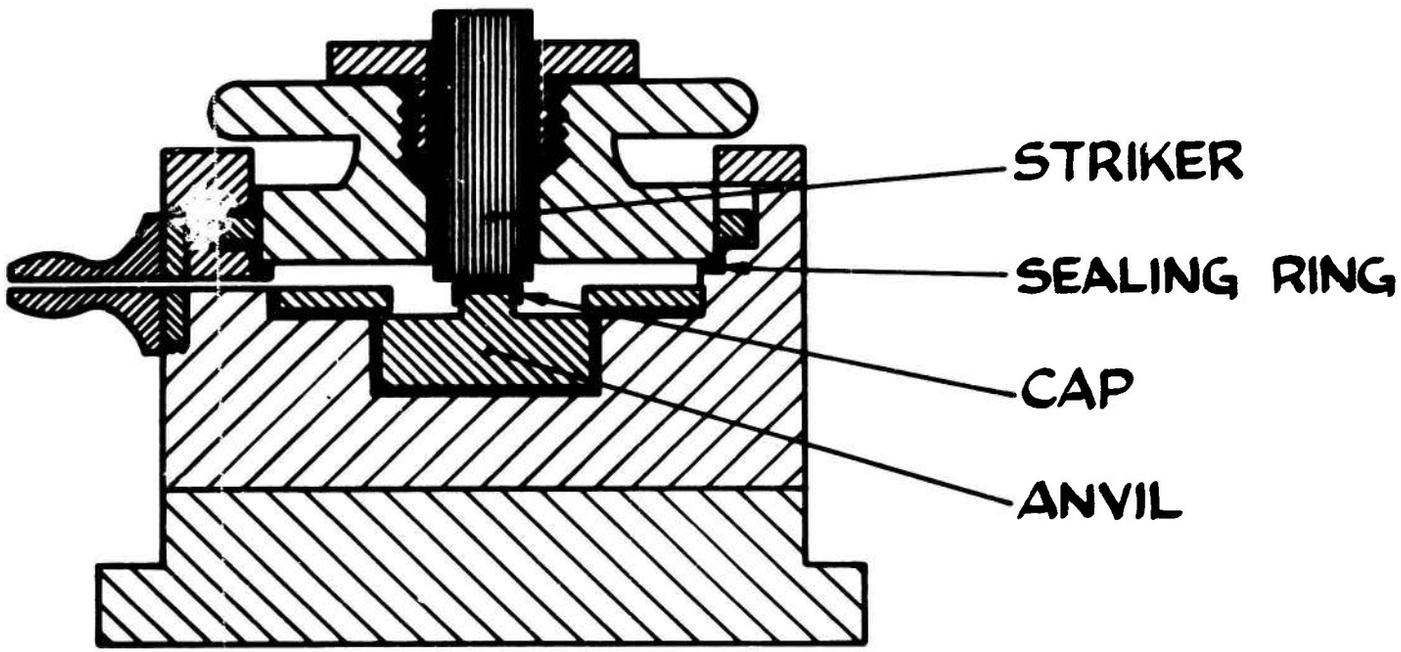


FIG. 2 ROTTER IMPACT CHAMBER

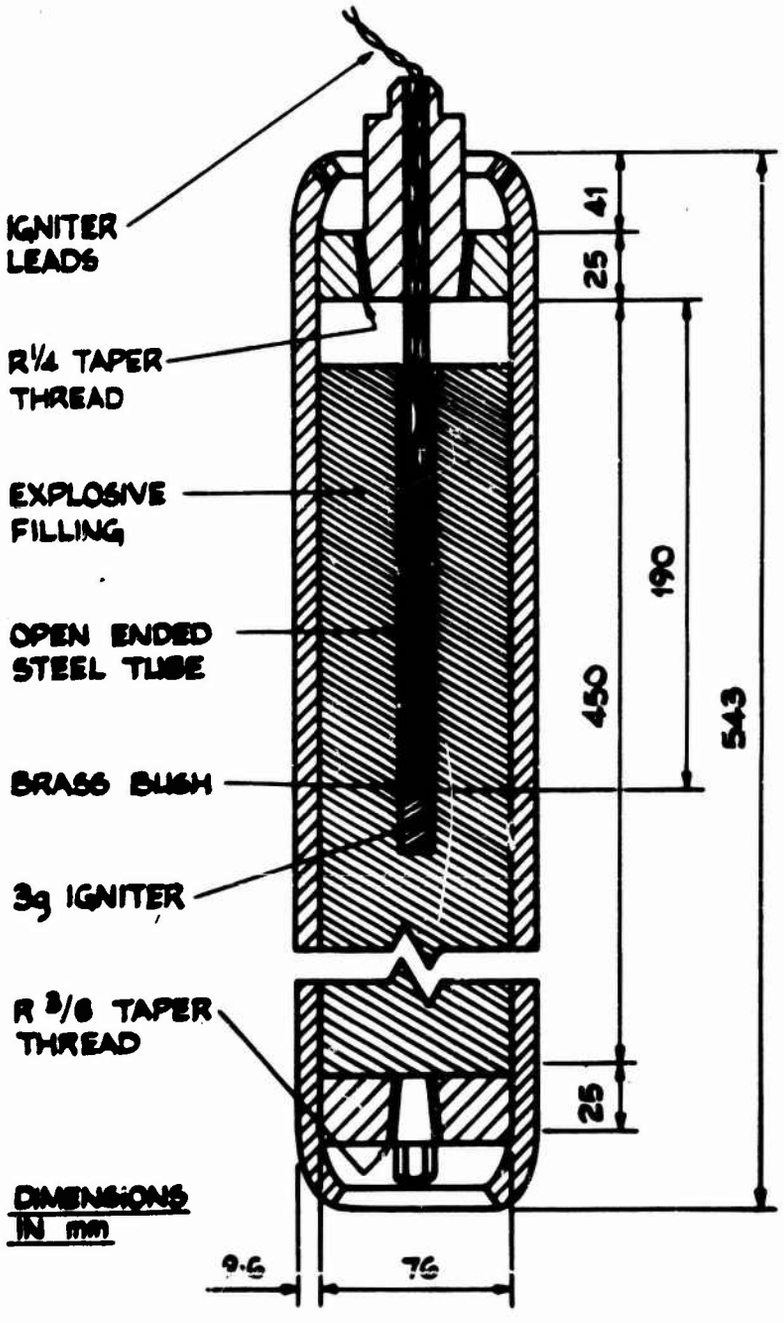


FIG.3 LARGE SEALED VESSEL.(IGNITER TYPE)

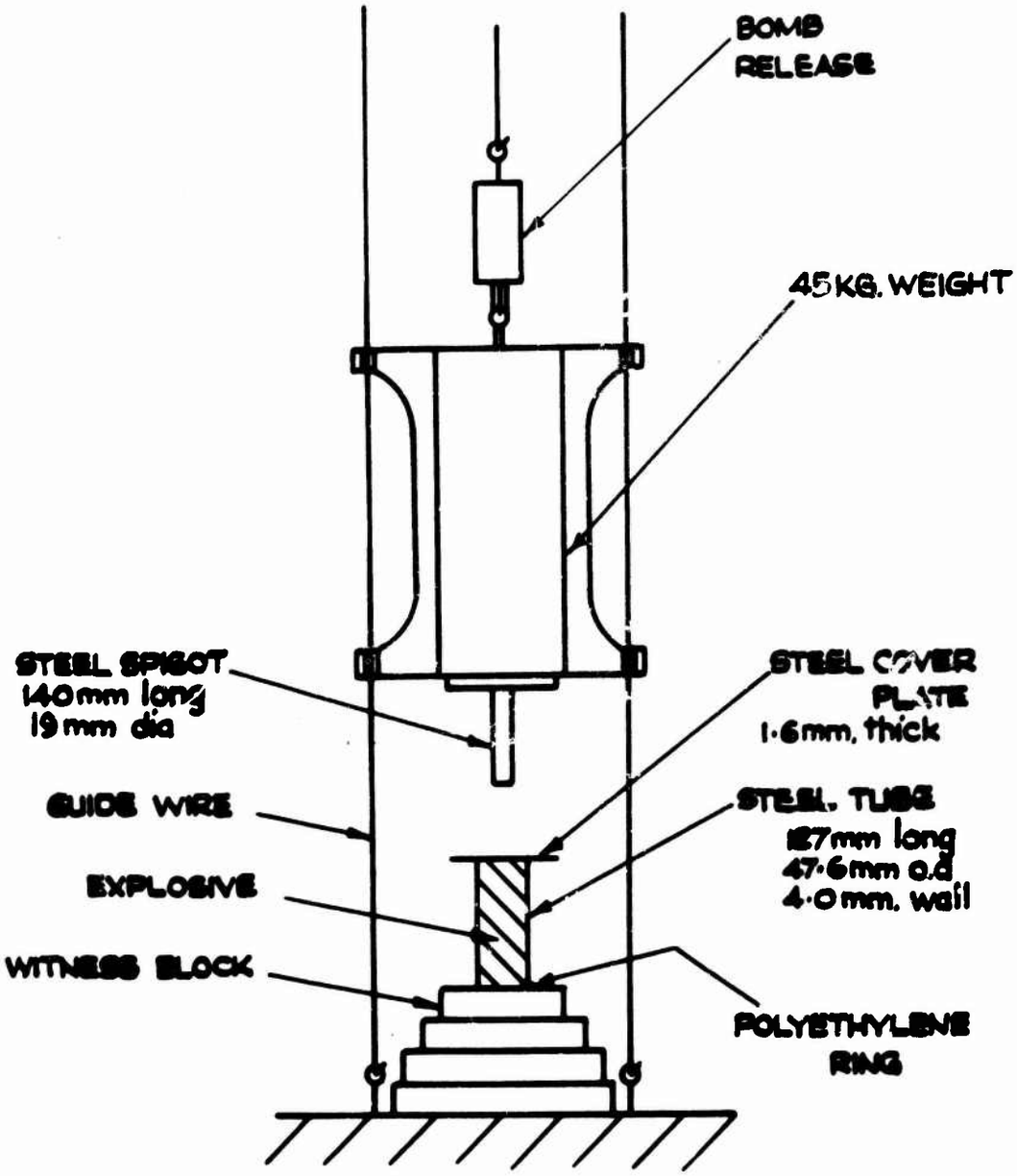


FIG. 4 PERME DROP (SPIGOT) TEST

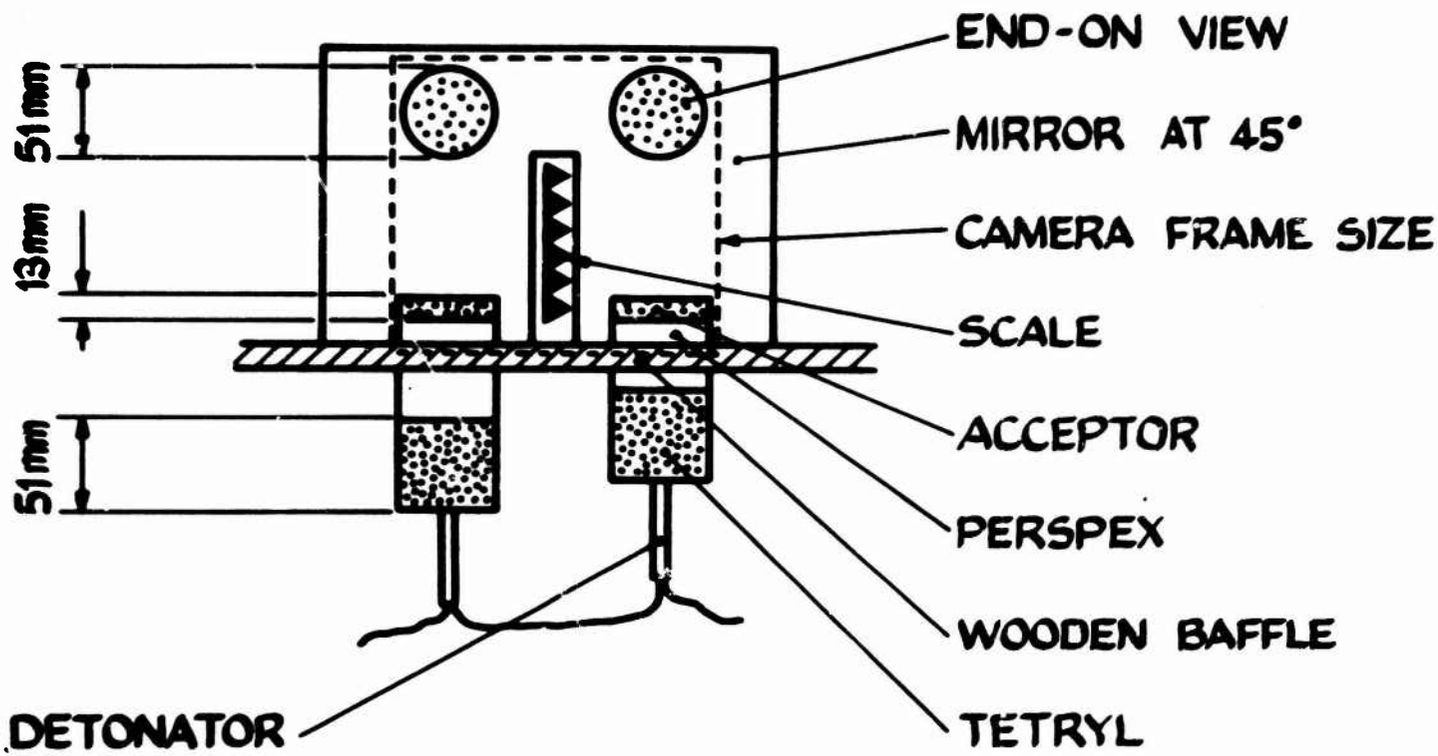


FIG. 5 LOW AMPLITUDE SHOCK INITIATION TEST

GENERAL PRINCIPLES USED AT AWRE FOR CHARACTERISING NEW HE COMPOSITIONS

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ABSTRACT

At AWRE, procedures for assessing new HE compositions have evolved with time. To illustrate the methods and underlying principles, a typical sequence used in the development of a secondary explosive will be described.

First, the required properties of the HE are listed to provide a target. In the development phase, the basic idea is to increase gradually the amount of explosive that can be experimented with at any one time, starting with a purely paper study and finishing with batches weighing tens of kilograms. At each stage, appropriate performance, safety and compatability tests are done and approval to go on to the next stage, using larger amounts of explosive, is only given if the safety and compatability tests are satisfactory.

When a suitable material has been identified in the development phase, characterisation is started. Several large batches of the chosen composition are made and a large number of tests are done to measure its properties during manufacture and as the final charge. Many of these are repeats of tests performed earlier but the duplication is desirable, since the material in the later, larger batches should be more typical of the final product and batch-to-batch variability can be investigated. If unsatisfactory results are obtained during characterisation, further development is done, leading to a different material to be assessed in a new characterisation programme.

In general, to minimise costs, tests involving large amounts of material or expensive facilities are done late in the characterisation sequence.

The characterisation is usually of a general nature. When it is complete, the explosive will be recognised as a composition with well-defined and generally acceptable properties and with a prescribed method of manufacture. When it is used in a weapon development project, further specific tests may be needed to demonstrate its suitability for the particular application.

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INTRODUCTION

During the development of a new explosive composition, the explosive material is continually assessed using a range of tests in order to answer two questions:

(i) Is there any reason to doubt that this composition will be acceptably safe in experimental work, manufacture and Service?

(ii) Is there any reason to doubt that this composition will be functionally satisfactory in its intended role?

Research work is normally started using very small quantities of materials and, as confidence increases, larger quantities are used. In parallel with the increase in quantity, the initial tests are small-scale and the scale of testing, the range of properties tested and the costliness of the test all increase as development proceeds.

At AWRE, procedures for assessing new explosives have evolved with time as new methods and apparatus became available, as the importance of new types of test become apparent and as the safety and performance requirements varied.

It is generally recognised that, while performance tests are quite realistic, since the designer knows how he intends the explosive to work, most safety tests are rather idealised. This is because there is a large, possibly infinite, number of ways of having an accident. For example, even if several powder impact tests are done, there is no guarantee that the explosive has been assessed against all possible stimuli of this type. As an example from a different field, Polson and Hanna (Reference 1) showed that, in special circumstances, lead azide could be several orders of magnitude more sensitive to spark than had previously been thought possible. Thus, the best that can be done is to choose tests which are representative of a hazard class and estimate the likely hazard of a new material by comparing its results with those for established materials whose safety properties are known.

The tests vary with the type of composition under consideration - a main charge explosive is assessed differently from a booster or a detonator material. To illustrate the principles involved, the tests used during the development of a typical powerful secondary

explosive will be described; for other types of explosive, the range of tests will vary but the principles remain the same.

Recently, steps have been taken at AWRE to formalise the programme of tests undertaken during the development phase. The effects of this have been:

(i) to separate the work into definite phases.

(ii) to set limits to the total amount of explosive in existence at any one stage, these limits increase as confidence in the safety of the explosive is gained.

(iii) to specify a minimum set of safety tests which must be done, with satisfactory results, before the next stage can be started.

(iv) to assign responsibility for deciding to move from one stage to the next; the initial decision to start an investigation is taken at a fairly senior level, approval for the next stage can be given by junior scientific grades rising to higher levels as the work proceeds and more explosive is involved.

Inevitably, during the development of a new composition, some candidate materials will be rejected at different stages for a variety of reasons. This means that, instead of the work proceeding steadily to a satisfactory conclusion, the researchers must return to an earlier stage and start work on a new composition. This cyclic progress increases the duration and cost of a development programme and this should be remembered when reading the straightforward sequence described, for simplicity in the following sections.

THE TARGET SPECIFICATION

At the start of an HE development programme, a target specification is written in collaboration with the weapon designers. This specification contains qualitative and quantitative target properties and includes desirable safety and performance features.

In spite of the quantitative data, it is, in essence, largely qualitative, partly because there may be uncertainity about the required values for some of the performance properties, partly because some of the properties specified, eg tensile values, are ways of describing unquantifiables such as machineability and handleability and partly because many safety data are essentially comparative, as was mentioned in the Introduction.

Even allowing for this, the target specification is a useful statement. It constitutes an agreement between the weapon designer and the explosive formulator that the target is desirable and achievable and it gives the latter a set of properties to aim for in his work. A typical target specification is shown in Table 1.

The reasons for specifying most of the properties will be obvious; there are, however, a few which merit some discussion:

(i) The tensile and static compressive strengths are included to give the composition adequate strength in handling and machining.

(ii) The strain at failure in tension is specified to minimise the chances of cracking when HE components are exposed to low Service temperatures in weapons where they are fixed to metal components with lower co-efficients of expansion.

(iii) A maximum dynamic strength is given because there is some evidence that high values of this property are associated with high sensitiveness (critical drop height for an event) and explosiveness (typical size of event) on the oblique impact test.

(iv) Experience has shown that, on the oblique impact test, events for a given explosive do not become more violent with increasing drop height above the threshold. It is thus useful to specify an explosive in terms of both its sensitiveness and explosiveness, since this will tend to limit both the likelihood and size of an event in case of accident.

THE R AND D PHASE

Having decided, by paper study and previous experience, on one or more possible ways of meeting the target specification, the R and D phase starts. In practice, several different groups of components, each consisting of a powerful explosive, such as HMX or RDX, with one or more elastic or plastic materials to make up the binder , are assessed in parallel. Also, for binders which consist of more than one material, or which are synthesised in the laboratory, a related research programme on the properties of the binder alone may be pursued along with that on the composition. For simplicity, in the following description, we will ignore any binder programme (in which the aim is to develop a material with appropriate physical properties, which is compatible with the explosive and typical Service materials) assume that there is only one set of components from which the composition will be formulated and also that, while much may be known about the individual ingredients, little or nothing is known about their behaviour when mixed together.

To begin, very small quantities of the explosive constituents (less than 0.1g) are mixed with the individual components of the binder (the exact proportions are not important at this stage) and samples of about 0.01g or less are examined according to a scheme such as the following:

(i) Allow the mixture to stand at room temperature and watch for signs of reaction: colour change, liquefaction, gassing etc.

(ii) Slowly warm the mixture to about 100°C and note signs of reaction as in (i).

(iii) Heat a small quantity to ignition, note the violence of the reaction and compare it with that of the pure explosive.

(iv) Carry out a DSC scan, note any endotherms or exotherms and compare them with those of the individual materials.

(v) Subject the mixture to impact, eg by placing a small quantity on a steel anvil and striking it with a steel hammer and observe the violence of reaction.

Gradually, by performing tests such as these, with all possible combinations of the inert components with the explosive powder, any ingredients likely to lead to stability or safety problems can be identified and eliminated from the composition.

If the preliminary results are satisfactory, the next stage may be entered. Here, a few grams of the composition are made up in about the proportions that are thought likely for the final composition and, if possible, the ingredients are incorporated by the proposed method.

This mixture is then used to obtain a first estimate of the powder safety characteristics of the composition using standard UK safety tests (see the Appendix for a brief description of these and other tests mentioned in this paper; full details are given in Reference 2 for the safety tests). In some cases, shortened forms of the test are used.

The tests at this stage include:

(i) Rotter impact test using only 10 caps to show whether the F of I (figure of insensitiveness) is greater than or less than 50 (RDX = 80 (standard) HMX = 60).

(ii) Vacuum stability test, using only 1g of material; the standard test uses 5g.

(iii) Mallet friction test, using a boxwood mallet on a yorkstone anvil only; this form of the test gives stimuli of intermediate violence.

(iv) Temperature of ignition.

Having obtained acceptable results in these tests, development work using larger quantities can proceed.

Now, since confidence is increasing, quantities up to 0.5 kg can be used. So far, the "composition" has been a mixture of the proposed components in approximately the proportions which are envisaged for the final material.

Now that larger quantities are being used, the mixtures can be formulated more accurately, using scaled-down versions of the likely incorporation techniques (paste mixing, slurry mixing, etc) and preliminary experiments on the effects of varying the proportions of the ingredients on the properties of the composition can be done.

Safety tests performed at this stage include:

(i) Rotter impact test using 50-200 caps.

(ii) Full-scale vacuum stability test using a 5g sample.

(iii) Several tests used in earlier stages, eg DSC scan, temperature of ignition, mallet friction are repeated on these more representative samples.

These safety tests are not done on all the different mixtures made at this stage, but only on a selection, including extremes, to assess whether varying the proportions of the ingredients within the proposed range has any effect on safety and stability properties.

In addition to these safety tests, preliminary fabrication experiments are done. Most powerful compositions developed at AWRE are pressed isostatically but, to begin gradually, small pellets are die pressed in a 25mm (1.0 in) diameter mould, initially at room temperature but later ones are pressed at typical pressings temperatures (70-100°C depending on the composition). These pellets are used to obtain initial values of physical properties, such as density and strength and some are gap tested to give a rough estimate of shock sensitivity.

Having achieved satisfactory safety and performance results, larger quantities (up to 10 kg) can now be used. Any further experiments needed to define the method of making the moulding powder are done at this stage. Compatability tests, in which the moulding powder is assessed against materials with which it is likely to be in contact at all stages from processing to Service, are begun. Isostatic pressing experiments are started; initially, pressing is limited to small charges but, as experience is gained and the pressing sequence defined, larger charges, up to 177 x 177mm (7 x 7 in) are produced. These charges are used to provide specimens for physical testing (tensile and compressive strength and creep

measurements) and storage experiments at ambient, elevated and cyclic temperatures are started, to assess the variation in physical properties density and chemical stability with age.

More extensive gap testing is done and the powers of one or two compositions are estimated using the cylinder test (Reference 3). Also, a few Oblique Impact Tests are done using Jabroc vehicles (see Reference 4 and Appendix) to assess the charge safety characteristics.

In this phase, many different compositions are made to estimate the effects of formulation variables, such as proportions of ingredients, explosive particle characteristics (fine, coarse, bimodal etc) and fabrication techniques on the final charge properties. Some of these variants are intended only to provide data to show how charge properties of interest vary with composition, while others are definite candidates for the final composition.

As more information is obtained and interest is concentrated on choosing one composition for full characterisation, some compositions are eliminated and more work is done on a few which are definite candidates for Service use. Larger quantities of explosive (up to 100 kg) are made, pressed and subjected to testing. Few, if any, new tests are introduced at this stage; the aim is to obtain more information on properties which were measured earlier and (since several batches of moulding powder are made) to obtain some estimate of the reproducibility of the production process.

The tests on which effort is concentrated include:

(i) Tensile and static and dynamic compressive testing; for all three, ultimate strength, modulus and strain at failure are measured.

(ii) Creep testing.

(iii) Gap testing.

(iv) Cylinder testing.

(v) Oblique Impact Testing using 23 kg (50 lb) hemispheres (see Appendix) to obtain both sensitiveness and explosiveness estimates.

(vi) Pressing tests to define optimum pressing conditions.

When a new composition is brought into production at an Ordnance Factory, it must have a Safety Certificate. The recognised test centre is at RARDE but it is thought worthwhile to perform a preliminary set of tests at AWRE, so that any problems can be identified. Many of the Safety Certificate tests have been done earlier but this stage, late in the development, is a convenient time to go through the whole sequence. The tests are (see Appendix):

(i) Rotter impact (200 caps)

(ii) Mallet friction.

(iii) Vacuum stability.

(iv) Compatibility with a range of materials.

(v) Temperature of ignition.

(vi) Spark sensitivity.

(vii) Trough inflammation.

(viii) Bickford fuze.

From the work done and the results obtained, a composition is chosen for characterisation by comparing all the data with the target specification. Practically all the information collected is of use in making the choice, since data on compositions which are not chosen show how the properties vary with composition and processing variables and, assuming the correlation is good, they lend support to the experimental values for the chosen material.

FULL CHARACTERISATION

In the characterisation phase, about 1000 kg of HE, in batches of 20–100 kg, is made and tested, compared with a total of about 100–200 kg, of the composition finally chosen, in the R and D phase. The aims of the characterisation phase are:

(i) To show, using a wider range of tests and several repetitions of some tests that the chosen composition is safe and suitable for manufacture and Service use,

(ii) To show that satisfactory, reproducible methods of making the moulding powder and fabricating charges have been developed.

Several of the tests used in this phase are repetitions of ones used in the R and D stage but many are new. The tests, grouped under headings are discussed below.

(a) Batch-to-batch reproducibility

Many of the tests listed under the other headings give information on reproducibility since they are done on more than one batch; however, the following are intended specifically to assess reproducibility. The tests are done on at least one sample from each batch.

(i) Rotter impact test.

(ii) Particle size and composition analysis of the moulding powder.

(iii) Measurement of density and composition analysis of small blocks taken from a pressed charge to assess variation of these properties throughout the charge.

By this time, the properties of the individual ingredients of the moulding powder should be well known. Sources of such data include specifications for standard explosive powders and for commercial materials. If such data are insufficient or if some of the materials were developed during the R and D phase, the materials are characterised at this stage, using suitable tests, so that Specifications may be written. In addition, Specifications are drawn up for the moulding powders, pressed charges etc using the data generated during the characterisation phase to define limits.

(b) Powder Safety

A sample is sent to RARDE for Safety Certificate testing.

A burning trial is performed on a bag of moulding powder in a typical wooden storage box to assess the likely fire hazard.

(c) Physical Properties

The physical property measurements performed in earlier stages (static and dynamic compression, tensile and creep tests) are repeated on several batches. Some tests are done at high and low temperatures and thermal conductivity, thermal diffusivity and coefficient of expansion are measured.

(d) Storage Tests

Machined samples are stored on their own and also in contact with appropriate Service materials. Samples are stored for four years or more at ambient and also on a diurnal sinusoidal cycle between 40 and 45°C, which has been found to be a realistic accelerating environment.

(e) Charge Safety

Several tests are done to give more information and a wider survey of charge safety.

(i) Proof machining. Charges are machined, band sawn and drilled at feed rates well above the normal accepted range. Some charges are band sawn while sandwiched between metal plates so that both metal and explosive are cut. A decision on permitted machining methods (close or remote control, wet or dry) is made on the basis of these tests.

(ii) Oblique Impact Test. Several drop using 23 kg (50 lb) HE hemispheres are done. The first tests are at 45° angle of incidence; tests at the more severe 76° incidence are only done if it proves diffioult to obtain events at 45°.

(iii) Spigot Test. Several spigot tests (Referenoe 5) are done to estimate the sensitivity of the explosive to this stimulus. Most tests are done with a 1.6 mm

(1/16 in) air gap between the explosive and the spigot since this condition, in which adiabatic air compression is an important feature, is most likely to cause initiation but one or two tests are also done without an air gap to find out if the material is particularly sensitive to impact and viscous shear processes. Most reasonably insensitive secondary explosives are not initiated in this latter form of the test, even at the maximum drop height, 42.7 m (140 ft).

(iv) Susan Test. About 10 rounds in standard Susan vehicles (Reference 6) are tested at velocities in the range 61 - 275 ms^{-1} (200 - 900 ft s^{-1}) to assess the sensitiveness and explosiveness of the material in a confined state to high velocity impact.

(v) Burning Trial. A typical wooden magazine box containing a charge weighing about 20 kg is burnt to find out how large charges of the material behave in a fire.

(f) Initiation and Performance

Several tests, including the following, are done to obtain information on the shock sensitivity and power of the explosive (see Appendix and Reference 3 for experimental details).

(i) Gap Test. The explosive is tested on the AWRE Scale I gap test and, if insensitive, on Scale II as well.

(ii) Pick up delay. The test explosive is initiated across a copper barrier and the initiation delay measured for a variety of barrier thicknesses.

(iii) Cylinder Test. Several tests are done.

(iv) Plate throw test. Large charges of HE are used to accelerate aluminium plates of various thicknesses. From these results, the C.J. pressure is estimated.

(v) Velocity of detonation. Velocity of detonation is measured in the cylinder and plate throwing tests. Other tests at diameters less than 25mm are done to give an estimate of the variation of velocity with diameter.

CONCLUSION

The tests described in the previous sections are typical of those to which a powerful explosive composition is submitted during development and characterisation. If the results are satisfactory and match the target specification reasonably closely, the composition is accepted by AWRE as being suitable for Service.

It will have been noticed that none of the tests is specifically related to any weapon system. This is deliberate, since the characterisation is intended to be general, because, while the broad class or classes of weapon in which a given HE may find a use may be predictable, it is not often that the detailed weapon design is known during development. Thus, further work is usually necessary to show that the explosive, even though generally acceptable for Service, is actually suitable for a particular new weapon system in terms of performance, safety and stability. Such tests are designed around the weapon system, bearing in mind its proposed range of application and weapon designers, explosives specialists and Ordnance Board representatives are involved.

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TABLE 1

TYPICAL TARGET SPECIFICATION FOR A POWERFUL HE COMPOSITION

Figure of Insensitiveness (Rotter)	:	> 50
Vacuum stability	:	< 5 ml gas at NTP
Temperature of ignition	:	> 250°C
DSC	:	no exotherm below 250°C
Compatibility	:	compatible with typical explosive and non-explosive weapon materials *

Physical properties:

	Strength MPa (lbf in^{-2})	Strain at failure %
Creep (non recoverable) : < 1%		
Tensile	> 3.4 (500)	> 0.5
Static compressive	> 6.9 (1000)	-
Dynamic compressive	< 20.6 (3000)	-

Gap test (Scale I)	:	0.5 - 0.75 mm (20-30 mils)
Cylinder test	:	as powerful as Explosive X †
Oblique impact test	:	no event greater than large partial no event below x metres dropheight
Susan test	:	no worse than Explosive Y †

NOTES: * In an actual specification, some materials might be named.

† In an actual specification, these explosives would be named.

APPENDIX

BRIEF DESCRIPTIONS OF TESTS MENTIONED IN THE TEXT

(i) Rotter test (SCC Test 1/72)

A small sample(about 30 mg) of powered explosive is confined between a steel anvil and a thin cap, a steel drift is placed on top of the cap. A 5 kg weight is dropped on the drift from the selected height and the gas evolved from the explosive is measured using a burette; an event is recorded if more than 1 ml gas is evolved. The drop height is changed, using a Bruceton procedure, in successive tests and the critical height for producing explosions is calculated. In a full test, 200 caps are used.

The Figure of Insensitiveness is calculated thus:

$$\frac{\text{F of I of test material}}{\text{F of I of RDX (= 80)}} = \frac{\text{Critical height of test material}}{\text{Critical height of RDX.}}$$

(ii) Spark test (SCC Test 6/66)

A powdered explosive sample is held in a hole in a thin polyethylene strip sandwiched between metal electrodes. A spark is generated in the explosive by connecting a capacitor, charged to 9.5 kV, between the electrodes. By varying the capacitor, explosive samples are tested at 4.5 0.45 and 0.045j stored energy and the lowest energy which produces explosions is recorded.

(iii) Mallet friction test (SCC Test 2/72)

A small sample of explosive is spread on an anvil and struck a glancing blow with a mallet held in the operator's hand. Mallets of boxwood and steel and anvils of softwood, hardwood, yorkstone, mild steel, aluminium bronze and naval brass are used in various combinations. The numbers of explosions generated in ten strikes on the samples are recorded.

(iv) Vacuum stability and compatibility tests

5g samples are heated in vacuum, at 120°C; the gas evolved between 1.5 hrs and 41.5 hrs is recorded (estimated at NTP). In the compatibility test, 4.75g explosive and 0.25g test additive are used and the gas, in excess of that which would have been evolved by the test materials, if tested separately, is recorded.

(v) Temperature of Ignition (SCC Test 3/66)

An 0.2g explosive sample is heated in a test tube so that the temperature rises at 5°C min^{-1}. The temperature at which inflammation or other violent reaction occurs is recorded.

(vi) Trough inflammation test (SCC Test 5/66)

An unconfined train of material, held in a mild steel trough, 12.7mm wide, is ignited at one end by a naked flame and the behaviour of the sample is recorded.

(vii) Bickford fuze test (SCC Test 4/66)

A 3.0g sample of explosive in a test tube is subjected to the short burst of flame from a length of Bickford fuze, placed in contact with it. The ease of ignition and violence of reaction are recorded.

(viii) Tensile strength test

The tensile strength is estimated using a three-point rupture test on a rectangular bar sample.

(ix) Compressive strength tests

Compressive test are done by axially loading cylindrical samples. In the dynamic test, the load is applied by dropping a weight onto a drift assembly (including a felt smoothing layer) placed on top of the sample. The rate of strain in the dynamic test is about 20 sec^{-1}.

(x) Creep test

Cylindrical specimens are axially loaded at 0.69 MPa (100 lb f in^{-2}) at 60°C for 100 hr. Total and non-recoverable creep are measured.

(xi) Oblique Impact test

Two forms of test sample are used:

(a) A 23 kg (50 lb) solid explosive hemisphere.

(b) A Jabroc (resin bonded, laminated wood) vehicle with an explosive charge, weighing about 1.5 kg and cylindrical in shape but with one face machined to the same radius of curvature as the Jabroc component, inset at the pole; the total weight is 23 kg.

The latter form of vehicle is used, so that tests can be done at an early stage in the programme when less explosive is available.

Test assemblies are dropped from various heights, so that they impact, at 45° or 76° to the vertical, a standard steel plate, onto which sand is stuck using epoxy resin.

Event sizes are assessed subjectively on a scale: no event; small partial, large partial; explosion; high order.

(xii) AWRE gap test (Scales I and II).

The Scale I donor is a 1.7 Mg m^{-3} PETN pellet, 6.0mm diameter, 5.1mm long (0.235 x 0.2 in) initiated by a low density PETN train. The Scale II donor has an additional PETN pellet, 10.2mm diameter, 3.8mm long (0.4 x 0.15 in). The barrier is laminated brass shim and the receptor is a block of HE of minimum size 12.7 x 12.7 x 25.4mm (0.5 x 0.5 x 1.0 in). The assembly is placed on a steel witness block.

Testing is performed according to the Bruceton up-down procedure and the critical gap thickness calculated from the results.

(xiii) Pick up delay

The donor is a cylinder of powerful HE, 31.8 mm diameter, 38.1mm long (1.25 x 1.5 in) initiated by an exploding wire detonator, the barrier is solid copper and the receptor is a stack of discs of the test material 31.8mm diameter, 5.1mm to 25.4mm long as required. Ionisation probes placed between the discs and at the ends record arrival time.

Initiation delays for different barrier thicknesses are estimated from space-time plots.

(xiv) Plate throw test

Cylinders of the test HE, 127mm diameter, 127mm long (5 x 5 in) initiated by a plane wave lens are used to accelerate aluminium plates up to 10mm thick. The plate velocities are measured and used to estimate the C.J. pressure.

AUSTRALIAN TEST PROCEDURES FOR THE ACCEPTANCE OF MILITARY ENERGETIC MATERIALS

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ABSTRACT

Australian procedures for the acceptance of explosives by the Defence Force, the Defence Science Laboratories and the Munition Factories are described. Sensitivity, compatibility and environmental tests are summarised and mention is made of the role of the recently formed Australian Ordnance Council.

INTRODUCTION

The vast majority of energetic materials used by the Defence Force of Australia are closely based on UK or US formulations, although in recent years a growing number of European compositions have been introduced into service. The procedures used for the qualification of these materials are largely derived from UK practices, although each of the old Departments of Navy, Army, Air and Supply had evolved their own acceptance methods and had separate Explosives Regulations. These four Departments were recently combined to form a single Department of Defence and thus enable rationalisation of activities to take place in a number of areas. In the case of explosives, it is hoped that the formation of an Australian Ordnance Council will lead to greater local standardisation of acceptance procedures.

The Australian Ordnance Council, incidentally, is an independent joint service body established "to provide objective advice to appropriate authorities on the safety of explosive stores intended for use by the Australian Defence Force, and on the ability of these stores to remain safe in the Service environment". It is responsible to the Chief, Defence Force Staff and to the Chief Defence Scientist, and comprises members from the three Services and Defence Science.

In practice there are three main reasons why it may be necessary to qualify an energetic material for Australian military use.

Firstly, and most frequently, the Australian Defence Forces buy "off the shelf" foreign weapons which contain energetic materials which have not previously been in Australian service use. In such cases it is customary for the Defence Forces to consider the acceptability of the energetic material as part of a detailed evaluation of the safety and serviceability of the whole weapon system. The qualification tests used by the country of manufacture are considered in this study and it would be most unusual for any Australian tests special to the energetic material to be carried out prior to purchase. The acceptability of the energetic material is decided upon by the Service purchasing the store and each Service has its own approval procedure.

Secondly, weapons of foreign design are made in Australia under licence. It has usually been a requirement of the Defence Forces that energetic materials of Australian manufacture should meet the original foreign specification. If this specification can be met, the foreign qualification tests are accepted and the energetic material is manufactured and filled without any independent Australian qualification. The manufactured material would of course be subject to storability tests. Recently, however, it has become recognised that Australian raw materials, particularly in the case of gun propellants, are not identical to those used overseas and it may consequently be advantageous to permit deviations from the material specification, provided performance is matched. If such a material is not covered by the foreign qualification tests, it has to be tested in Australia to provide it with a Safety Certificate for manufacturing purposes and to provide the data on which service acceptance is based.

Thirdly, weapons are designed and manufactured in Australia. As far as possible, standard energetic materials are used in such designs. It is only where there is a requirement which cannot be met with existing materials that a new formulation is contemplated for service use. It is then necessary to carry out every appropriate test which is available in Australia and, in general, an attempt is made to obtain all the information which would enable the material to be qualified for military use in the UK and US.

The qualification tests currently available in Australia are summarised in the following paragraphs.

SENSITIVITY TESTS

Historically, the United Kingdom was the main supplier of military equipment to Australia and there are still close links between the Defence Forces, the Ordnance factories and the R & D Laboratories of

Britain and Australia. Australian sensitivity tests, and other qualification procedures, are therefore based largely on those of the United Kingdom. The following are currently in use in Australia:

(i) Rotter Impact

(ii) Mallet Friction

(iii) Temperature of Ignition

(iv) Ease of Ignition (Bickford Fuze Test)

(v) Train Test

(vi) Electric Spark Sensitivity

The above tests provide the data for Australian Safety Certificates which closely follow the UK model. An example is appended.

(vii) Ball and Disc Test

(viii) Liquid Explosive Impact Sensitivity (using a modified Rotter machine)

(ix) Shock Sensitivity (using AWRE small scale gap test)

(x) Glancing Blow Test (a modified version of the test which originated at ICI, Ardeer)

(xi) Henkin and McGill Test

(xii) Setback Simulator (Picatinny Arsenal Activator)

(xiii) Technoproducts Drop Weight Test

It can be seen from the above list that all current Australian sensitivity tests are carried out on small samples of material, usually powdered, and are mainly directed towards clearing energetic materials for factory and laboratory use. Large scale tests, such as Spigot, Susan or Oblique Impact, on fabricated specimens of explosive cannot be carried out in Australia and current opinion is that the cost of introducing such tests could not be justified by the small number of explosives which are likely to need to be tested.

STORABILITY

In common with most other countries, Australia uses a vacuum stability test (40 h at 100°C) to assess the stability of explosives and explosive formulations. The same test is used as a routine check

on the compatibility of explosives with other materials. UK procedures, the silvered vessel test and analysis of stabiliser content after prolonged storage (up to 5 years) at 49°C, are employed to assess the stability of gun propellants.

Recently, there has been considerable interest in new methods which might supplement and complement these traditional tests and which might provide a more rapid indication of incompatibility. For example, a modified version of the vacuum stability test is now applied routinely in compatibility studies concerning gun propellants; the test temperature is lower (80°C or 90°C) and gas evolution is monitored over an extended period of 168 hours. Differential scanning calorimetry is used routinely to test for gross incompatibility and consideration is currently being given to the possibility of using changes in the values of kinetic parameters during decomposition in the scanning calorimeter to detect more subtle cases.

The life of Australian designed or Australian manufactured weapons and other military stores containing energetic materials is assessed by the same type of environmental trials as are used in Britain and America (1),(2). In addition, all military stores, both Australian and foreign, undergo surveillance during their service life to ensure that no deterioration takes place. The details of the environmental testing and surveillance programmes are decided by the user Service in conjunction with the Australian Design Authority. In the past there has been little formal co-ordination between the three Services concerning their trial requirements and procedures. It is hoped, however, that the formation of the Australian Ordnance Council will lead to the development of a common tri-service approach to the subject. Furthermore, it is believed that by giving proposed testing programmes wider publication in the form of Australian Ordnance Council Proceedings, there will be a more widespread discussion of the nature and relevancy of particular tests, resulting in a greater assurance that all possible contingencies have been foreseen. The explosive components of a practice bomb were recently the subject of the first AOC Proceeding of this type (3).

It may be of interest to note that in recent years there has been an increasing tendency in Australia for weapons to be kept beyond their original approved storage life. This may be a greater problem than in, say, the US and UK because of the much smaller usage rate and turnover of many stores and because of the greater proportion of foreign weaponry being used. In many cases the country of origin has no interest in extending the service life of their own stores. Australia has therefore to carry out its own re-assessments of permitted service life. Often the replacement of energetic materials is required which

leads to new environmental trials before the refurbished items can be accepted. It is anticipated that trials of this type will also be the subject of Australian Ordnance Council Proceedings.

TRANSPORTATION

Decisions concerning the transportation of military explosives within Australia are made by the inter-departmental Commonwealth Explosives Transport Committee (CETC). The CETC is the closest Australian equivalent to the United Kingdom Explosives Storage and Transport Committee (ESTC) and, where possible, uses ESTC classifications for military explosives. If available, other foreign classifications are used but if none exist, the CETC categorises explosives on the basis of existing information; it would be unusual for Australian testing to be requested.

Australia has decided to adopt the United Nations system for the classification of explosives. In considering how the UN system should be introduced, it became apparent that there was a need for greater co-ordination of activities associated with the storage and transport of explosives. It has therefore recently been decided to establish an Australian Defence Explosives Storage Committee (4) under the aegis of the Australian Ordnance Council. The first major task of the Explosives Storage Committee will be to co-ordinate and oversee the implementation of the UN Classification System within the Department of Defence and at the same time to standardise the three Services' Explosive regulations. It is envisaged that a standardised test procedure will be introduced for items of doubtful classification but details of how this will be implemented have yet to be decided.

CONCLUSIONS

Most military explosives and explosive-filled stores requiring qualification for use in Australia are of foreign manufacture or design and most safety and performance tests and acceptance procedures are of UK origin, even although the items to be qualified originate from an increasing range of countries. Steps are being taken to rationalise acceptance procedures within Australia, for example, as mentioned above, by the formation of an Australian Ordnance Council. However, it would clearly be to the benefit of Australia if there was greater international standardisation of safety tests for energetic materials and wholehearted support is therefore given to the objectives of this Conference.

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MATERIALS RESEARCH LABORATORIES

MARIBYRNONG

EXPLOSIVES SAFETY CERTIFICATE TESTING

REFERENCE:	E.D.G. Composition based on American Photoflash Powder.	E & A: S.C.T. No. 34 dated 13.5.1976

CLAUSE 1 a. DESIGNATION AND GENERAL CHARACTERISTICS

Photoflash Composition

Explosive Pyrotechnic

1 b. COMPOSITION

Potassium Perchlorate	40%
Magnesium Powder, Grade 5B	34%
Aluminium Powder, Grade F, Class 4	26%

Note: Magnesium and Aluminium to American Specification

CLAUSE 2 CLASSIFICATION

a. (i) Sensitiveness to Impact & Friction: Sensitive

(ii) Sensitiveness to Electrostatic Spark: Comparatively Insensitive

b.	Storage and Transport	Group 1
c.	Quantity Distance	ZZ
d.	Fire Fighting	Class 1

Note: 2a. based on Clauses 3, 4A, 4B and 8

CLAUSE 3 SENSITIVENESS TO DIRECT MECHANICAL SHOCK

a. Rotter Impact Test

Figure of Insensitiveness 70 (against RDX = 80)

Mean Gas Volume, cm^3 No gas evolved

b. Ball & Disc Test (Primary Explosives Only)

Height, cm 50% Prob. of Ignition

CLAUSE 4A. SENSITIVENESS TO FRICTION

MALLET TEST (Expressed as percentage)

ANVIL	MALLET	
	Boxwood	Steel
Yorkstone	50	100
Hardwood	0	0
Softwood	0	0
Mild Steel	)	
Naval Brass	) Not tested	
Aluminium Bronze	)	

CLAUSE 4B. SENSITIVENESS TO FRICTIONAL IMPACT

GLANCING BLOW TEST (Minimum Ignition Energy), joule

a.	Steel on Steel	2.9
b.	Brass on Steel	9.7
c.	Steel on Bakelised Cloth	3.9
d.	Brass on Bakelised Cloth	3.3

CLAUSE 5 — TEMPERATURE OF IGNITION (Degrees Celsius)

Not under 400°C

CLAUSE 6 — IGNITION BY FLASH

Explodes

CLAUSE 7 — BEHAVIOUR ON INFLAMMATION

Ignites and supports train vigorously throughout

CLAUSE 8 — IGNITION BY ELECTRIC SPARK

Ignitions at 4.5 joule but not at 0.45 joule

CLAUSE 9 — CHEMICAL STABILITY

Should be satisfactory if kept dry.

CLAUSE 10 — INCOMPATIBILITY WITH OTHER MATERIALS

Avoid contact with acid, alkali, phosphorous, sulphur or mixtures containing sulphur (such as gunpowder).

CLAUSE 11 — ADDITIONAL INFORMATION

Warning is given that Photoflash Composition containing Potassium Perchlorate will develop explosive violence when ignited. From experience in the UK and USA it is essential that all operations of mixing, pressing etc. should be carried out behind adequate shields and by remote control.

REMARKS:

D. J. Pinson

(D.J. Pinson)
HEAD, EXPLOSIVES TESTING GROUP

EXPLOSIVENESS AND HAZARD ASSESSMENT

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SUMMARY

This paper describes the basis for the development of a test for assessing explosiveness, which is defined as the relative level of response of an explosive system to initiation by stimuli insufficient to produce detonation directly. Comparisons of explosiveness have been made for different explosives using systems of widely different size and giving differing levels of confinement.

INTRODUCTION

Accidental initiations of confined explosive charges can be devastating even when the explosive does not detonate but merely deflagrates. Numerous methods already exist for the assessment of the relative ease with which a response in explosive compositions can be initiated by a variety of stimuli. Two examples are the well-known Rotter Impact Test and the Mallet Friction Test.

The aim of the present study is to develop a test procedure for determining the relative "explosiveness" of explosive compositions under a range of confinement conditions. As used here, the term "explosiveness" is defined as the relative level of response of an explosive system to initiation by mechanical and or thermal stimuli insufficient to produce detonation directly.

EXPERIMENTAL CONDITIONS AND RESULTS

The compositions examined are listed, together with some of their composition details, in Table 1.

The test vehicles used for the majority of the investigations were the RARDE Small Burning Tubes. These are mild steel tubes 254 mm long by 32 mm internal diameter having 6 mm thick walls and with screw-on caps having 6 mm thick end faces.

Approximately 350 g of each of 4 propellant and 12 high explosive compositions were confined in such tubes and ignited at one end by means of 1.5 g charges of ballistite propellant. The passage of the burning process along the charge was followed by observing the emission of reaction products from a line of 2 mm diameter holes along the length of the tube. The holes were either drilled through the tube wall only, in which case they extended to the charge surface, or they were extended to the charge centre by means of hollow bolts. A permanent record of each event was obtained by high speed cine photography at 14,000 to 16,000 pps. The relative explosiveness of each composition was assessed from the following measurements (i) the time to tube rupture, (ii) the amount of unconsumed explosive and (iii) the number and type of fragments produced. A longer time to tube rupture, a larger quantity of unconsumed explosive remaining and fewer, larger fragments indicate a lower explosiveness.

The results from experiments using these small scale tubes are presented in Table 1, arranged in descending order of explosiveness.

The results of the small scale burning tube trials possibly tell only a part of the story since no consideration of the effects of scale and confinement has been taken into account.

To examine the effects of scale, the RARDE Large Burning Tubes were designed and constructed. These are mild steel tubes 711 mm long by 102 mm internal diameter with 12.7 mm thick walls and having screw-on caps with 12.7 mm thick end faces.

Approximately 9 Kg of each of 10 explosive compositions were confined in these tubes and initiated at one end by 3 g of ballistite propellant. The relative explosiveness of the 10 compositions studied was assessed using the same 3 basic measurements that were employed in the small scale experiments. The results obtained from these larger scale trials are shown in Table 3 in descending order of explosiveness.

It appears that there are no major differences between the results of the two series of experiments shown in Tables 2 and 3 despite a 30-fold difference in charge mass and a 2-fold difference in tube wall thickness. Thus, although the potential to cause damage increases with charge size, the order of explosiveness, i.e., the relative positions of the different explosive fillings, remains essentially the same.

In order to examine the effects of light confinement, tubes of the same internal dimensions as the Small Burning Tubes, but having a wall thickness of only 1.6 mm were constructed. These tubes had press-on end-caps since the wall thickness was too thin to allow the cutting of screw threads. The end confinement was provided by holding the tubes and end-caps between the heavy, opposed faces of a screw jack.

RDX/TNT 60/40 and TNT were the only compositions studied using this equipment. The explosiveness in each case was found to be extremely low, the deflagration process fading and extinguishing soon after initiation. The results obtained from these experiments under conditions of low confinement are shown in Table 4.

DISCUSSION

The results from both the Small and Large Burning Tube experiments suggest that a range of explosive compositions can be consistently ordered into a table of decreasing explosiveness when under conditions of moderate confinement representative of that found in HE shell or GW warheads. It is found that melt-cast explosives such as RDX/TNT (60/40) Type A, EDC1A, etc, have the highest deflagration

velocities, produce the largest number of fragments and are most completely consumed, i.e., have the greatest explosiveness. Plastic and plastic-bonded explosives tend to have the lowest explosiveness. Pressed waxed compositions are intermediate in behaviour. Added aluminum and terylene or other fibres appear to reduce explosiveness.

An interpretation of these observations is as follows. Differences will exist in the linear rate of burning and the pressure exponent between different explosive compositions similar to those found between different propellant systems. Overlaid on this phenomenon is the effect of the brittleness of the composition. The more brittle and easily cracked a composition is, the easier it will be to create new surface as the initial pressure-pulse from the igniting propellant and explosive passes through it. Increased surface will cause the rate of deflagration to accelerate and the pressure in the container to rise more rapidly. The use of inert fibres will tend to prevent the cracking by acting as reinforcement and the use of plasticizing agents and/or certain inert additives will tend to reduce the brittleness of the explosive. The presence of aluminum in a composition probably also reduces the violence of a deflagration by acting as a heat sink.

The results obtained using the thin-walled small scale burning tubes suggest that there is a lower limit to the confinement below which most secondary explosives cannot sustain significant burning processes. The early loss of confinement by venting through the distorted casing leads to the deceleration and possible extinction of the deflagration reaction. The apparently anomalous results which have sometimes been observed when thin-walled munitions are involved in accident situations are probably due to such a confinement loss. On the other hand, there must be an upper limit to the confinement above which a deflagration to detonation transition may take place. The damage occurring from a non-detonative initiation may then depend on the detonative characteristics of the explosive.

The level of confinement in the case of most, if not all, conventional munitions appears to fall between these two limits and within this regime the hazard order shown in Tables 2 and 3 will remain valid irrespective of charge size.

To date no work has been conducted under conditions of very heavy confinement. However, work carried out to investigate the mechanism of premature initiation of one particular service shell during training firings indicated that, even with the massive confinement afforded by the shell and barrel of the weapon, the 14 kg of RDX/TNT in this base ignited shell merely underwent a rapid deflagration. The fragmentation of the shell was extensive, but was nevertheless typical of a pressure burst.

CONCLUSIONS

The Small Burning Tube experiments form the basis for the development of a standard test in that they have shown that it is possible to construct a scale of relative explosiveness of different explosives under conditions of moderate confinement. This explosiveness scale has been derived from 3 numerical quantities which are not readily amenable to combination into a single parameter.

The explosiveness of an explosive system is a function of (a) confinement and (b) explosive type. The factors controlling the behaviour of different explosive types are their mechanical properties, particularly brittleness and their linear burning characteristics, with the latter being dependent upon confinement.

Under conditions of low confinement the 2 explosive types studied (TNT and RDX/TNT) behaved similarly, the observed events apparently being the result of similar linear burning rates with the confinement having little effect. In contrast, under conditions of moderate confinement the relative explosiveness appears to be controlled by both the properties of the explosive and the confinement. It is unlikely that sufficient confinement exists in present types of shell, bombs, mines or GW warheads to enable a deflagration to detonation transition to occur with the explosives used.

Definite safety benefits can accrue from the choice of an explosive munition filling of low explosiveness without necessarily causing a loss of detonative performance. Plastic explosive No. 4 (PE 4) containing 88% RDX and a desensitising grease made up from liquid paraffin and lithium stearate would make an excellent filling if low explosiveness and high velocity of detonation (8200 ms^{-1}) were the most significant criteria in munitions filling design. However, the safety problems arising from migration of desensitiser in the charge and exudation from it must also be taken into account. Nevertheless the explosiveness characteristics of PE4 indicate a direction which could be taken to improve the safety characteristics of future filling compositions, namely a move towards plasticity and/or high resistance to cracking.

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Table 1

Details of compositions studied

	Explosive	RDX	TNT	HMX	AL	Beeswax	Wax 3	Wax 6	Wax 8	Polyure-thane	DG 29 Grease	NC	Terylene Fibre	Other binders and casting additives
	RDX/TNT 60/40 Type A	60	40			+1								
	RDX/Wax/Al	68			20			12						
	RDX/Wax/Al No 2	71			20			9						
	RDX/Wax 3	90					10							
	RDX/Wax 8	88							12					
100	RDX/Pu	88								12				
	W1	4	25	70		1								
	W2	4	30	65		1								
	W3			95										5
	PBX 9404			94								3		3
	Torpex 2B	42	40		18									
	Torpex 4D	20	55		25									
	Torpex 4D/TF	20	55		25								+0.25	
	PE4	88									12			
	PE6/AL	73			15						12			

Table 2

Small burning tube data

DECREASING EXPLOSIVENESS

Composition	Time to Disruption (m sec)	% of unconsumed charge	Typical No of Fragments	Figure of[a] Insensitiveness (RDX = 80)	Velocity of Detonation ($m\ sec^{-1}$)	Density (Mgm^{-3})
PBX 9404	0.3	-	70		8800	1.84
W2	0.9	0.7	30	110	8127	1.78
TETRYL	0.1	0.7	40	90	7850	1.71
RDX/Wax 3 90/10	2.2	5.0	20	140	8300	1.57
RDX/Wax 8 88/12	1.2	3.0	20	150	8250	1.56
W3	1.9	6.5	20	72	8650	1.78
RDX/TNT 60/40	1.1	3.0	20	140	7700	1.66
TNT	1.7	0.0	6	150	6850	1.60
TORPEX 4D	4.0	10.0	6	140	7200	1.69
RDX/Pu 88/12 Type 1	0.8	36.0	6	100	8300	1.64
RDX/Wax/Al 68/12/20	5.5	25.0	4	140	6800	1.70
F527/433	2.1	51.0	4	-	-	-
MNQF	2.8	76.0	4	30	-	-
HSC	2.0	80.0	4	25	-	-
TRHD	0.0	96.0	1 - 2	-	-	-
PE4	Tube Intact	92.0		150	8250	1.60

(a) Rotter Impact Test, SCC Manual of Tests, Test No 1/72

Table 3

Large burning tube data

DECREASING EXPLOSIVENESS

Composition	Time to Disruption (msec)	% of unconsumed charge	Typical No of Fragments	Figure of[a] Insensitiveness (RDX = 80)	Velocity of Detonation ($m\ sec^{-1}$)	Density (Mgm^{-3})
W1	0.5	12	20	80	8400	1.83
RDX/TNT 60/40	1.1	6	20	140	7700	1.66
TORPEX 2B	2.8	6	20	100	7300	1.70
CW 3	0.7	26	15	120	7725	1.66
TNT	3.3	16	15	150	6850	1.60
TORPEX 4D/TF	1.6	35	12	140	6880	1.76
RDX/Pu 88/12 Type 1	4.1	66	6	100	8300	1.64
RDX/Wax/A1 No 2	3.4	40	3	140	7300	1.65
PE6/A1	23.0	92	2	140	-	
PE4	63.5	95	2	150	8250	1.60

(a) Rotter Impact Test, SCC Manual of Tests, Test No 1/72

Table 4

Light confinement burning tube data

Composition	Time to Disruption (msec)	% of unconsumed charge	Typical No of Fragments	Figure of Insenstiveness (RDX = 80)[a]	Velocity of Detonation ($m\ sec^{-1}$)	Density (Mgm^{-3})
RDX/TNT 60/40	1	80	3,80% of tube intact	140	7700	1.66
TNT	1	85	3,80% of tube intact	160	6850	1.60

(a) Rotter Impact Test, SCC Manual of Tests, Test No 1/72

SAFETY REQUIREMENTS FOR NAVAL ARMAMENT STORES

E.S. Norton
(Presented by Mr. K. Beedham, Ordnance Board, UK)

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ABSTRACT

In the United Kingdom the responsibility for the safety from explosive hazard of all Naval Armament Stores and any explosive stores of other Services embarked on HM Ships or Royal Fleet Auxiliaries is vested in the Director of Naval Ordnance Services (DN Ord S).

To assist in effecting this task DN Ord S has issued a document which incorporates the requirements to be met in order that a formal safety clearance may be issued. Although many of the requirements are common to other publications such as those issued by Design Authorities and the Ordnance Board the manual aims to assemble together all the safety requirements for Naval Explosives stores in one volume.

The subject matter includes explosives, filled explosive stores of all types, guns and mortars and their ammunition, rocket motors and gas pressure generators, packaging, test equipment, environmental testing and the response to fire and fragment attack.

This presentation aims briefly to give a background to the topics mentioned above, to outline the requirements and provide an appreciation of the requirement in terms of the objectives which any particular test or assessment is intended to achieve.

For explosives a number of mandatory tests have been specified largely those aimed at assessing the sensitiveness to various stimulii of small quantities of the powdered explosive. However, the requirement to assess the material in the form in which it will be used in the Service application has also been included as desirable information particularly the assessment of explosiveness.

It is considered essential to assess the compatibility of materials used in explosives stores. Any interactions of either metallic or nonmetallic materials which cause the explosive filling to become unsafe or which degrade the materials (explosive or non-explosive) to a level which cause unacceptable performance are classified as incompatible.

The standards to be adopted in terms of the design, quality, and processing of filled explosive stores are defined.

Requirements specifically dealing with detonators, fuzing systems, electro explosive devices, guns, shells, cartridges, rockets,

gas generators and pyrotechnics are covered for aspects uniquely applicable to such items.

Packaging is considered an important element in the protection from hazard afforded by containers and the design requirements in respect of freedom from static electrical hazards, thermal and mechanical shocks, and marking are included.

The conditions arising during deployment of explosive stores both in storage depots and at sea necessitate the adoption of an environmental trials programme. The schedule specified in the Ordnance Board's Proceedings on this subject have been incorporated.

The hazards caused by fires at sea are particularly dangerous and the assessment of the response of explosives stores which may be exposed to this risk are required to be undertaken.

The safety of explosive stores especially those mounted or exposed on the upper decks of ships and subjected to fragment attack is of concern both in peacetime from the activities of dissidents or saboteurs and in war due to hostile missiles. An assessment of the response to such attacks is mandatory in current Naval Staff Requirements and is included in the DN Ord S safety requirements manual.

SUMMARY

The Safety Requirements for Armament Stores for Naval Use are stated and discussed. The stores considered are all those containing explosives, propellants and pyrotechnics and this paper gives the background to the topics, outlines the requirement and gives an appreciation of the objectives with regard to freedom from hazard which any particular requirement is intended to achieve.

INTRODUCTION

The Director of Naval Ordnance Services (DN Ord S) is responsible for the safety from explosive hazard of all Naval Armament Stores at all times and of the stores of the other Services during such times as their storage or carriage is the responsibility of the Royal Navy. (Vu Foil 1). A new store cannot enter the Naval Service until an explosive safety clearance has been issued by DN Ord S. The overall clearance procedure for the introduction of a new armament store into the Navy is described in the Naval Magazine Regulations (Ref 1).

The requirement is to ensure that appropriate explosive safety standards are incorporated in the design and are not degraded by subsequent modifications to design, by production or by the Service environment. In particular, apparently slight changes to explosive materials or to the materials in contact or close proximity to them, must be carefully reviewed. DN Ord S Safety Requirements are clearly identified (Ref 2) so that Project Directors who are responsible for the procurement of armament stores for Naval use can ensure that the design, production, storage, transport and use safety requirements are met. They have been written in general terms for all armament stores which can be defined as weapons or stores containing explosives, propellants or pyrotechnics.

Although the safety requirements are based on design principles that have been adopted by Design Authorities, published by the Ordnance Board or stipulated in other publications and specifications it is considered necessary to collect together all the relevant requirements in one volume so that those special to the Naval Service are clearly identified and matters not relevant to the safety of Naval Armament Stores are excluded. Generally some background to a particular topic is given, a statement of the requirement made and this is followed by an appreciation of the requirement and a bibliography of related documents.

DN Ord S wishes to acknowledge the assistance given by many sources to the compilation of these Safety Requirements.

SAFETY REQUIREMENTS FOR EXPLOSIVES

These apply to new explosives and novel applications of explosives already in Naval Service. It is emphasized that approval is for an explosive as such and does not cover the weapon designers responsibility to demonstrate the safety and suitability of a particular explosive in a particular weapon. The aim in this instance is to encourage weapon designers to seek approval at an early stage of weapon development and it should be obtained if possible before a firm decision to incorporate a new explosive in a weapon design has been made.

Minimum mandatory data and additional supplementary desirable information provided by certain tests have been established. No pass-fail criteria on acceptability have been laid down for particular tests since it is intended that judgements will be based on comparison with explosives of proven Service experience fulfilling similar roles. The requirements apply to all compositions whether they are primary, intermediary, secondary, propellant or pyrotechnic explosives.

Descriptions of the details of the types of information required and tests used in this instance are included in the paper given by Dr. R.M.H. Wyatt (Vu Foil 2) and largely comprise the results of the small scale sensitiveness tests of the UK Safety Certificate (Ref 3) together with the results from such larger scale assessments as spigot intrusion, gap, oblique impact, Susan, vertical activator, burning tube, fragment attack and large sealed vessel tests (Vu Foil 3).

Appreciations of the indications given by the results of applying the various small scale tests with respect to the stimuli applied are given in the paper by Dr. R.M.H. Wyatt with particular reference to propellants. In general only sensitiveness is assessed. Descriptions of the larger scale tests together with appreciations of the value of the information provided to the assessment of hazard are given in Reference 4. These tests provide a means of assessing explosiveness as well as sensitiveness (Vu Foil 4).

COMPATIBILITY OF MATERIALS USED IN WEAPONS AND STORES CONTAINING EXPLOSIVES

The requirement is aimed at ensuring that the metallic and nonmetallic materials used shall be such that they do not render the explosive filling unsafe or cause unacceptable inferior performance at any time during the life of the weapon or store. An acceptable material is defined as one which does not interact adversely either chemically or physically with the other materials of the design including packaging materials.

All materials which are ingredients of explosive compositions or which come into contact with explosives must be assessed for compatibility. The responsibility for carrying out the assessments lies with the Propellant, Explosive and Rocket Motor Establishment (PERME) Waltham Abbey who must be supplied with the material, its specification and details of the explosive(s) with which compatibility assessment is required.

The test methods used and sentencing criteria depend on the nature of explosive. In general the principle of accelerated degradation is applied by using elevated temperatures and where appropriate high humidities. These methods enable an estimate for the suitability of a material for long term use under service conditions to be made in a relatively short time.

Physical compatibility considerations are not neglected and such changes as melting and resolidification, polymorphic changes and changes of crystal habit which may influence the sensitiveness of explosive fillings must be considered.

SAFETY REQUIREMENTS FOR EXPLOSIVE FILLED STORES

The requirements here are primarily applicable to high explosive fillings although many also apply to solid propellant and pyrotechnic fillings. The aim is to ensure that in the course of its service life when it will be subjected to various environmental conditions which may include, temperature variations, shocks, (including set back in projected stores), vibrations during transport by road, rail, sea or air that the filling will withstand these and retain an adequately low sensitiveness to the stimuli which it may experience in normal use. The basic safety characteristics of the explosive have been dealt with earlier but it is essential to follow this by

an evaluation of the explosive in its Service hardware and environment. The assessment must consist of development and qualification trials incorporating appropriate tests. The selection of tests to be performed may be based on a definition of the real-life service environment (Ref 5). The tests are performed on packaged and unpackaged stores and proposals by the Design Authority for a trials schedule should be made from the comprehensive lists given in Reference 6. For Naval use it is important that the schedule includes drop tests for both packaged and unpackaged stores.

SAFETY REQUIREMENTS FOR DETONATORS, IGNITERS, FUZING SYSTEMS AND ELECTRO EXPLOSIVE DEVICES

These items usually contain sensitive explosive compositions and the requirements include designs to prevent explosive being trapped between adjacent metal surfaces when the device is subjected to shock or vibration, compatibility of all the materials used, avoidance of copper rich alloys in detonators containing lead or silver azide and for fuzing systems compliance with the design safety principles published by the Ordnance Board in References 7, 8 and 9. In addition to the design requirements it is necessary for the devices to be subjected to a series of tests to ensure safety and reliability. The tests are selected from the lists already mentioned above and described in Reference 6. Electroexplosive Devices (EED) are potentially susceptible to the electromagnetic environment and the requirement includes freedom from hazard in the standard Naval radio environment detailed in Naval Weapons Specification No. 6. In addition EED must conform to the principles and requirements of the Ordnance Board and Design Authority given in References 10 and 11.

SAFETY REQUIREMENTS FOR GUNS AND GUN AMMUNITION

The calculation of gun tube strength must be based on the appropriate criterion of elastic failure of the steel. The Pressure Limit must be the maximum pressure the gun can withstand without deforming sufficiently to effect operation or accuracy. In practice this means a circumferential bore strain of 0.07 per cent for smaller calibres and 0.03 per cent for larger calibres. In addition to the design requirements guns must be proved by subjecting them to firings which include pressures 20 per cent above the ballistic design pressure.

The design of the firing arrangements must be such that the striker is "safe" before it is assembled or dismantled from the mechanism and the condition "safe" or "fire" must be indicated. In the

"safe" position it must be shown that the gun cannot fire even when the firing gear is operated, a loaded gun cannot be fired when the striker is being dismantled or assembled, and after firing the striker shall be withdrawn before the bolt or breech block is free to open. For electrical or combined percussion and electrical strikers adequate insulation must be provided. A mechanical means to prevent the gun being fired before the breech is fully closed is required.

Shell and projectiles are required to be designed to withstand the forces to which they will be subjected and in addition must be subjected to trials which demonstrate both the adequacy of the strength of design and the safety in gun of the projectile. Details of the requirements are given in References 2 and 12. Projectiles are subjected to high base loading, high axial and for shell high rotational accelerations and because of this it is necessary to ensure that the body is free from internal defects which if present could result in premature initiation of the filling. The criteria to be used are freedom from (a) imperfections in the internal surface (b) foreign matter and (c) rust. In addition samples of both filled and empty shell must be subjected to sectioning examination and mechanical tests. The stringent requirements for manufacture and inspection of shell are given in Reference 2. The propulsive element of gun ammunition is conveniently considered in terms of the cartridge case, propellant and primer. Safety requirements for cases include providing protection for propellant during storage, transit and handling, withstanding the forces applied during unseating and extraction and supporting and retaining the projectile during storage, handling and ramming. The safety requirements for propellant as such have been dealt with under the heading of explosives. The particular safety requirements relevant to gun propellant are its stability and mechanical strength. The ignition system or primer is required to provide rapid and regular ignition of the charge both to avoid hang fires and misfires and to ensure minimum variation in the time to shot ejection after actuation of the firing mechanism. Primers are required to be subjected to the testing and proof specified in the relevant specifications.

SAFETY REQUIREMENTS FOR ROCKET MOTORS AND GAS GENERATORS

Solid propellant rocket motors must be designed to have adequate strength and stiffness. The mandatory factors must be met in rocket motors for Naval use. The proof of the design factors must be demonstrated by suitable testing. Similar requirements exist for gas generators employed in weapons and the strength requirements as with

rocket motors fall into two categories (A) when failure could injure personnel or damage other parts of the weapon system so as to prejudice subsequent firings and (B) where failure would not injure personnel or damage other parts of the weapon system so as to prejudice the firing of subsequent weapons.

SAFETY REQUIREMENTS FOR PYROTECHNIC COMPOSITIONS

The requirements for explosives with regard to sensitiveness and hazard assessment and compatibility as given previously apply in the case of pyrotechnics. Additional requirements for pyrotechnic stores and devices include designs to prevent nipping of powder or consolidated charges, hermetic sealing to prevent moisture ingress, minimization of segregation when subjected to the service environment and trials to demonstrate that the consequences of credible accidents are acceptable. The complete pyrotechnic store must be subjected to the appropriate environmental tests as determined by and specified in References 5 and 6.

THE RESPONSE OF EXPLOSIVE STORES TO FIRE

Fires are particularly hazardous aboard ship and the more so when explosive stores are involved. New weapons and explosive stores must be so designed that when subjected to a Standard Fuel Fire (Ref 13) they will not explode or detonate. A theoretical assessment of the response to fire must be made at an early stage of Project Definition.

RESPONSE OF EXPLOSIVE STORES TO BULLET OR FRAGMENT ATTACK

An assessment of the response to attack by 7.62 mm AP bullet, Weapons A(1) must be made either by trial or analogy and the need to assess the response to attack by 0.5 inch AP machine gun (A2) 20 mm cannon (B) and 84 mm HEAT (C) shaped charge considered on a case by case basis by the Project Director in association with DN Ord S and the Ordnance Board. The required response to attack by weapon A(1) is that the explosive store shall not detonate or explode. The primary attention should be given to high explosive warheads since detonation of one may lead to sympathetic detonation of adjacent warheads. In general the attack of rocket motors results only in burning and/or deflagration although with certain high energy propellant and the B or C weapons detonation cannot be ruled out.

CONCLUSION

DN Ord S with the support and assistance of the Naval Project Authorities, Research Departments and Ordnance Board has issued a manual (Ref 2) which clearly identifies the Safety Requirements for Naval Armament Stores. It is intended that Project Directors should invoke compliance with these requirements in the procurement of such stores. Any design which falls below the required standard should be identified by a Project Manager and considered in association with DN Ord S as early as possible in the weapon development.

REFERENCES

Any requests for information on the references in this paper should be directed to the author.

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ARMY STANDARD PROCEDURES FOR QUALIFICATION OF PYROTECHNIC FORMULATIONS

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INTRODUCTION

Pyrotechnic formulations are employed in a wide variety of ammunition and ammunition components. Conventionally they provide radiant energy in the visible and infrared regions and are used as illuminants, signals and markers, tracers, night vision aids and decoys. Pyrotechnic formulation research and development require various tests to provide the understanding of the nature of the reactions, define the performance of the formulations, and assess their safety under a given set of environmental conditions.

In this presentation only some key performance tests will be covered. These tests are listed in Table 1 and will be described in the sequence listed.

Table 1

Key performance tests of chemical formulations

Application	Test
Illumination, night vision, signal, tracer, marker	1. Spectral distribution
	2. Color coordinates
	3. Luminous intensity
Decoy	1. Spectral distribution
	2. Bandpass radiometry

ANALYSIS OF SPECTRAL DISTRIBUTION AND THE COLOR COORDINATES

In the past the performance on pyrotechnic formulations was assessed primarily on bandpass radiometric measurements, though a limited utilization of spectral analysis, especially in the visible spectrum, was done using photographic emulsions as detectors. Radiometric methods are simpler than the more involved and difficult procedures associated with spectral analysis.

Particular difficulties stem from the fluctuations of pyrotechnic flames, generating outputs which are not easily adaptable to conventional single scan techniques. Short scanning times generate spectral distortions caused by the nonsteady-state character of flames. Long scanning times, permitting large electrical time constants to smooth out signal fluctuations, require large items and controlled feeding of the fuel to the flame to generate flame stability. The preponderant dependence on radiometric testing particularly limited the research, as spectral analysis also provides an identification of species and makes possible the prediction and analysis of the chemical reactions taking place. The data analysis required to transform spectrometric waveforms into final spectra was also tedious, extensive and expensive.

With the development of commercially-available digital signal averaging systems, the past shortcomings could be reduced. The OCLI* Model 501 Rapid Scan Spectrometer provides fast sequential spectral analysis, with the period of scanning of the order of one millisecond. This instrument was interfaced with an instrument computer, the NICOLET Model 1080, capable of synchronous addition of sequential scans obtained from the rapid scanner. This addition (averaging) of sequential spectra eliminates erratic fluctuations of single spectra, caused primarily by the in homogeneity of the pyrotechnic material. Reproducible sprectra that reflect the predominant reactions taking place during combustion are obtained.

The arrangement of this instrumental capability is shown in Figure 1, Signal-averaging spectrometric apparatus, showing the spectrometer on the right, and the computer, X/Y recorder and teletype machine next in sequence to the left. Schematic of the spectrometer is reproduced in Figure 2. The optics is a conventional geometry of a grating spectrometer. Rapid scanning is obtained by means of a well-balanced scanning wheel, equipped with multiple corner mirror elements placed on its periphery. The wheel rotates around its axis by means of a synchronous motor and a belt drive to provide separation from 60 cycle AC signals. The passage of each corner mirror across the M_5 mirror sweeps consecutive spectra across each of the two exit slits, resulting in two series of consecutive spectral waveforms, generated by energy sensors placed behind the slits. The lateral displacement of the two slits is so arranged, that the two spectral waveforms correspond to two slightly overlapping wavelength intervals. This geometry, equivalent to two

*OCLI Instruments Company, South Norwalk, Connecticut

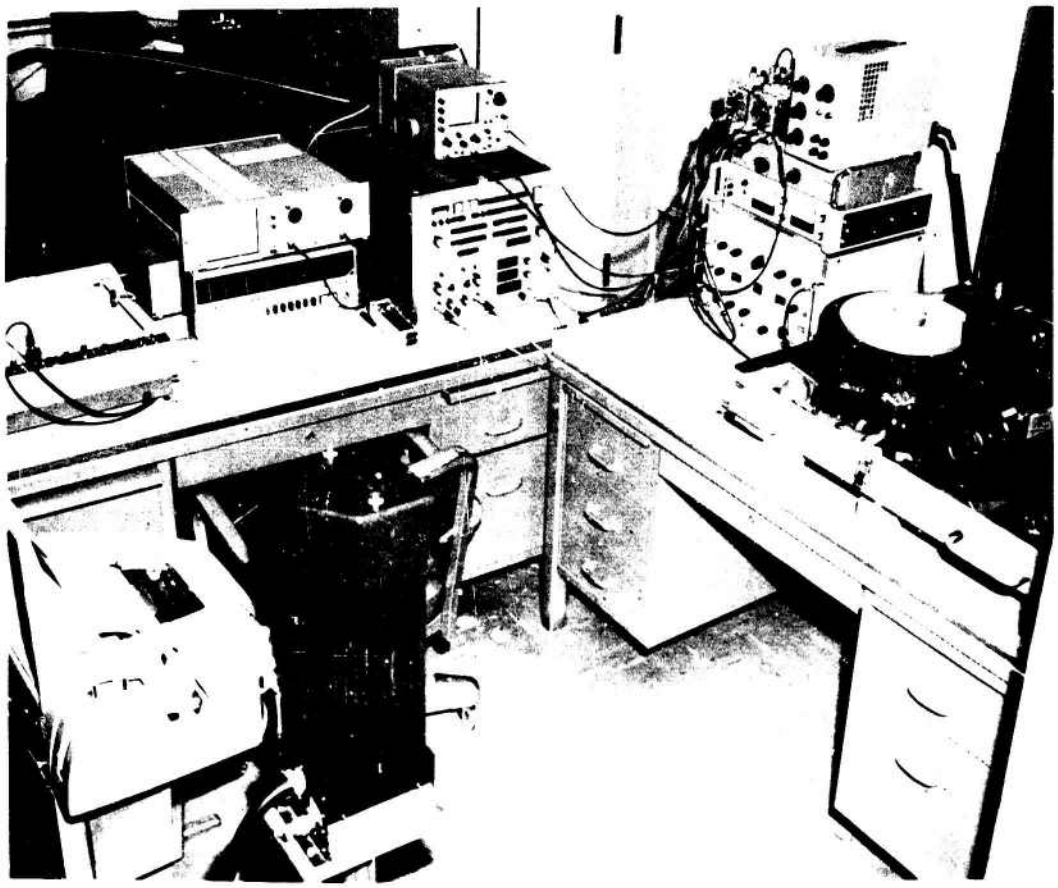


Fig 1 Signal-averaging spectrometric apparatus, showing the spectrometer on the right, and the computer, X/Y recorder and teletype machine next in sequence to the left.

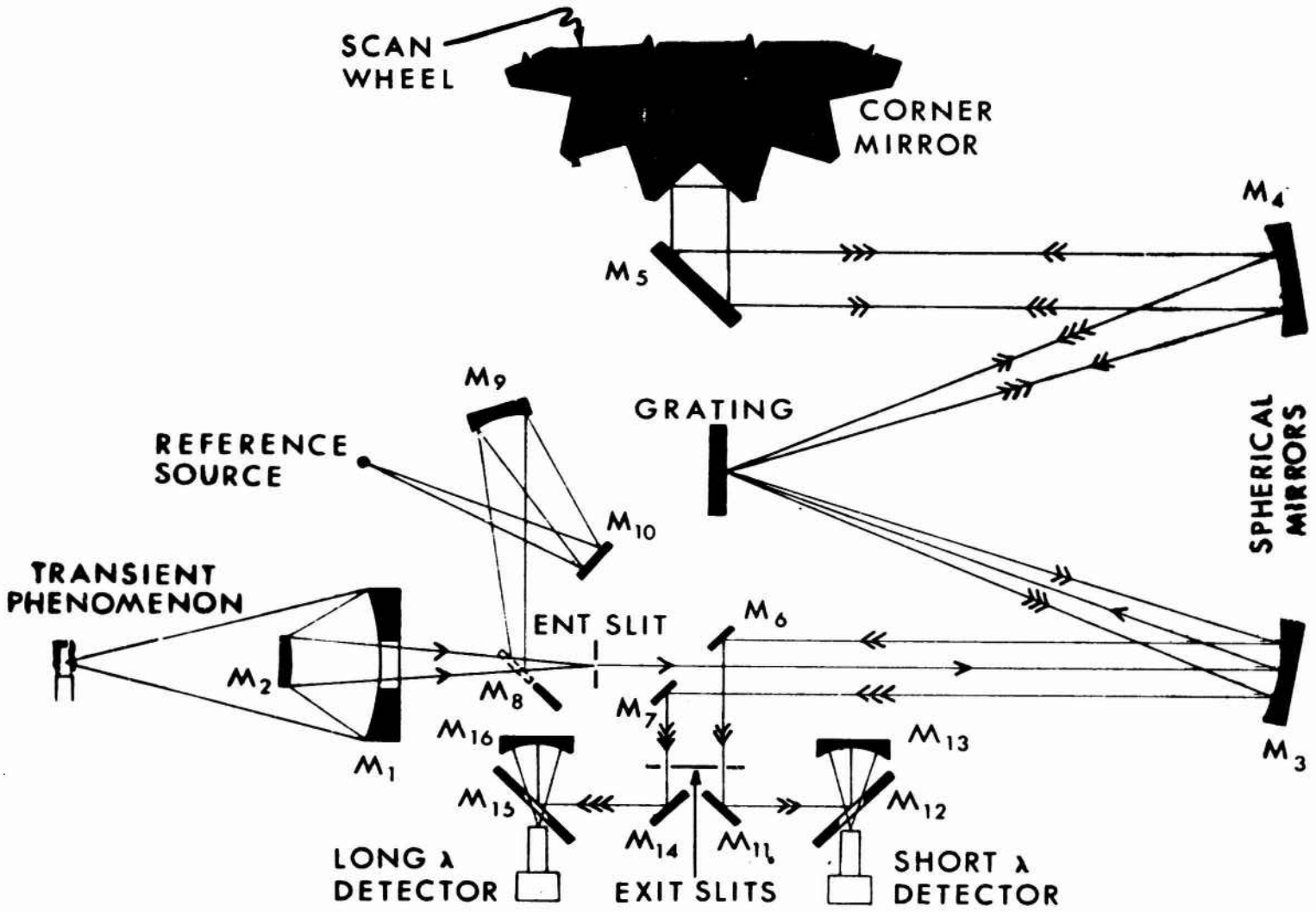


Fig 2 Optical schematic for the OCLI model 501 spectrometer

spectrometer units working in parallel, increases the spectral range of the system by a factor of two. The spectral coverage of the spectrometer is shown in Table 2, which also includes the available scanning times. The original capability of the spectrometer provides for a sequence of short λ and long λ signals, that are displayed on an oscilloscope. This is shown in Figure 3, which is a reproduction of data obtained originally by the manufacturer.

In their original form the signals are not wavelength calibrated. Also because the detectors are not flat, the obtained waveforms do not represent the true spectral contours. True spectra must be recovered from the original data by suitable data analysis. This is done in a real time by digital methods, utilizing the NICOLET Model 1080. By means of this system the two trains of spectral waveforms corresponding to shorter and longer wavelength interval are sequentially added and stored in 20 bit word memory with a resolution of 1000 words for each wavelength interval. The signal stored can be recovered as a print-out, or an X/Y output and available for further data analysis.

To demonstrate the signal averaging capability in a laboratory environment a nonsteady-state source was synthesized by placing in the field of view of the spectrometer two sources, a DC tungsten and an AC mercury discharge lamps. Figure 4 shows an X/Y plot of the memory content corresponding to various numbers of scans averaged, including the waveform of a single scan. Excellent elimination of the signal noise and a recovery of a true average is clearly observable.

The process of signal averaging is followed by an automated data analysis, done under software control, which provides for a sequence of suitable routines, controlling various stages of experimental procedures. Under control of these routines the computer memory is made to accept certain standard information. For each spectral range this standard information comprises the spectral distribution of the standard source and the spectral contour of the spectral sensitivity of the bandpass radiometer, a parallel system, used to evaluate the output of the unknown source. This sensitivity distribution is then utilized to establish the absolute value of the spectrum. This standard information is stored permanently in a separate memory block containing 2000 words. The contents of this memory block, pertaining to the range of the visible spectrum, is shown in Figure 5. It includes the $\bar{y}(\lambda)$ which is the spectral sensitivity of the radiometer measuring the luminous intensity of the source. It also represents one of the three ($\bar{x}(\lambda)$, $\bar{y}(\lambda)$, $z(\lambda)$) color matching functions, all prestored and used later to evaluate

Table 2

Spectral range coverage and scanning speed combinations possible with the OCLI Model 501 spectrometer

Nominal Range (μm)	Blaze Diffraction Grating	Detector
0.40 - 0.61	(0.5 μm)	1P28
.57 - 0.76	300 grooves/mm	4526
.65 - 1.15	(.94 um)	7102
1.10 - 1.79	86 grooves/mm	InAs
1.70 - 3.2	(2.33 um)	InAs
3.0 - 4.7	35 grooves/mm	InSb
4.70 - 7.0	(6.79 um)	Ge:Au
9.0 - 14.0	12 grooves/mm	Ge:Cu

SCANNING SPEED COMBINATIONS AVAILABLE

Repetition Time	Scanning Time
1.25 ml sec	1 ml sec
2.5 ml sec	2 ml sec
6.25 ml sec	5 ml sec
12.50 ml sec	10 ml sec
25.00 ml sec	20 ml sec
62.5 ml sec	50 ml sec
*125.0 ml sec	100 ml sec

*Presently used

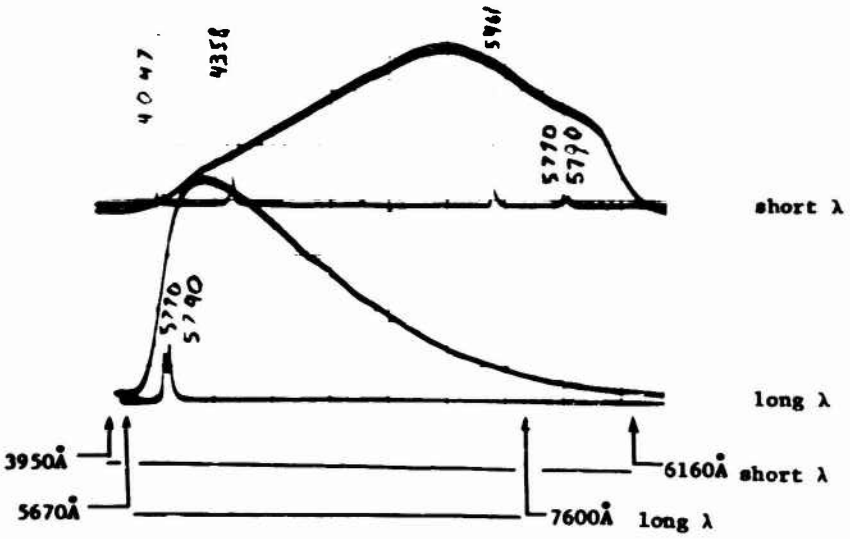
OCLI INSTRUMENTS M-501 AS-30-1

132 WATER STREET, SO. NORWALK, CONN. 06854

(203) 853-2224

Wavelength range coverage with 300 1/mm 5000Å blaze λ grating

Measured with Model 501 Rapid Scanning Spectrometer.



Spectral emission of internal strip lamp source and externally positioned dc mercury arc, to illustrate wavelength coverage achieved with 300 1/mm 5000Å blaze wavelength grating. The upper traces correspond to the short wavelength scan and the lower traces correspond to the long wavelength scan.

Fig 3 Raw oscilloscope data as per manufacturer



Fig 4 Recovery of true signal through signal averaging

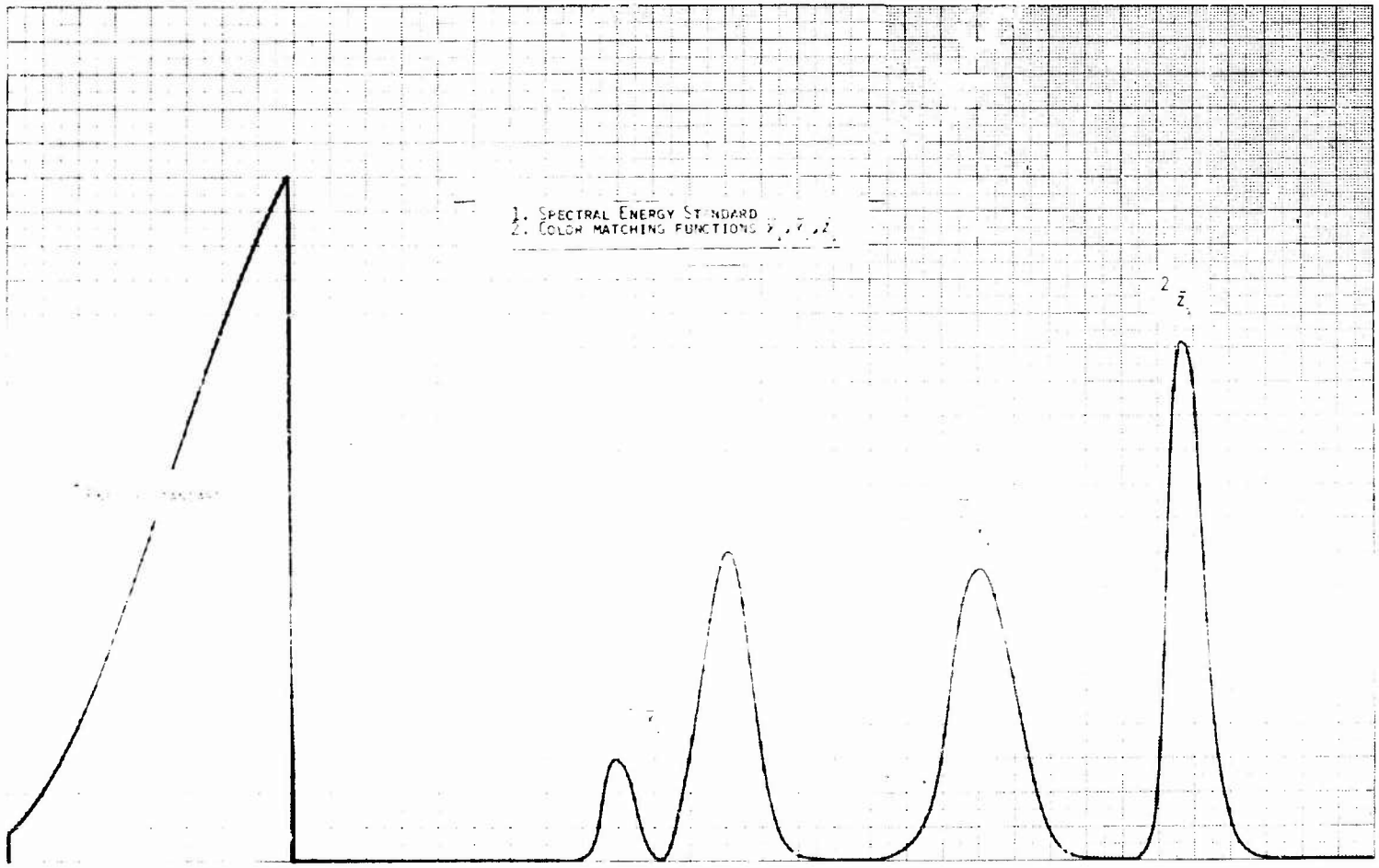


Fig 5 Memory loaded with standard curves

the color coodinates of the source. With system primed with this standard information, a system of additional routines controls all steps of the experimental procedure. The list of routines is shown in Table 3.

Table 3

List of computer routines

Call symbol	Purpose
AST	Array set
RD	Read a standard tape
WVG	Wavelength calibration
CAL	Amplitude calibration
TST	Test
PCL	Plotter calibration
PLT	Plot
ABS	Absolute level set
CUR	Cursor control

By means of these routines the system is primed and calibrated; the unknown signal is accepted and averaged; the system spectral sensitivity is calculated, stored in memory and used to obtain the true spectral shapes; the overlapping, and low sensitivity end segments of the spectrum rejected and the two corrected spectra combined into one. Finally radiometer readings are fed and the final spectrum, absolutely calibrated and a digital printout or an X/Y analog plot generated.

The resultant capability provides a real-time system, where once the system is primed with standard information arrays, the data analysis is essentially instantaneous.

To visualize the transformation of the spectrometer signal into the final spectrum, a single waveform, identical to those shown in

Figure 4 is pictured above the final fully corrected relative spectrum (Fig 6), which at the end of the test routine is stored in computer memory with a resolution of approximately 2000 words/whole spectrum. The continuous base line corresponds to a gray body radiation and the line structure to that of the mercury spectrum. Signal averaging resulted with a complete elimination of the signal noise in the original spectrum.

BASIC MATHEMATICAL OPERATIONS OF SPECTRAL ANALYSIS

Each complete test consists of two basic separate steps. The first step results in an evaluation of the spectral sensitivity at each point of the resulting signals. This is the so-called "Calibration" routine, during which a standard source is viewed by the spectrometer and its signal averaged. The average signals are similar to that shown in Figure 4 with an exclusion of the mercury structure, which would be absent. The spectral sensitivities are defined as

$$S_1(\lambda) = \frac{I_1^*(\lambda)}{W^*(\lambda)} \quad \text{and} \quad S_2(\lambda) = \frac{I_e^*(\lambda)}{W^*(\lambda)} \tag{1}$$

for short λ and long λ parts of the signal. These sensitivities are calculated and stored permanently in the memory block next to the energy standard listing (Fig 7). Here I^* is the spectral current (voltage) of the scan and W^*, the corresponding energy of the standard.

In the next step the actual test is performed, during which the spectrometer views an unknown source and its average waveforms $I_1(\lambda)$ and $I_2(\lambda)$ are obtained. The true relative spectrum are then

$$W_1(\lambda) = \frac{I_1(\lambda)}{S_1(\lambda)} \quad \text{and} \quad W_2(\lambda) = \frac{I_2(\lambda)}{S_2(\lambda)} \tag{2}$$

where $S_1(\lambda)$ and $S_2(\lambda)$ are given by (1).

Cursors are available to properly reject the low signal and segments and the overlapping portions of the two spectra $W_1(\lambda)$ and $W_2(\lambda)$, which then are combined into one continuous relative spectrum $W_r^2(\lambda)$.

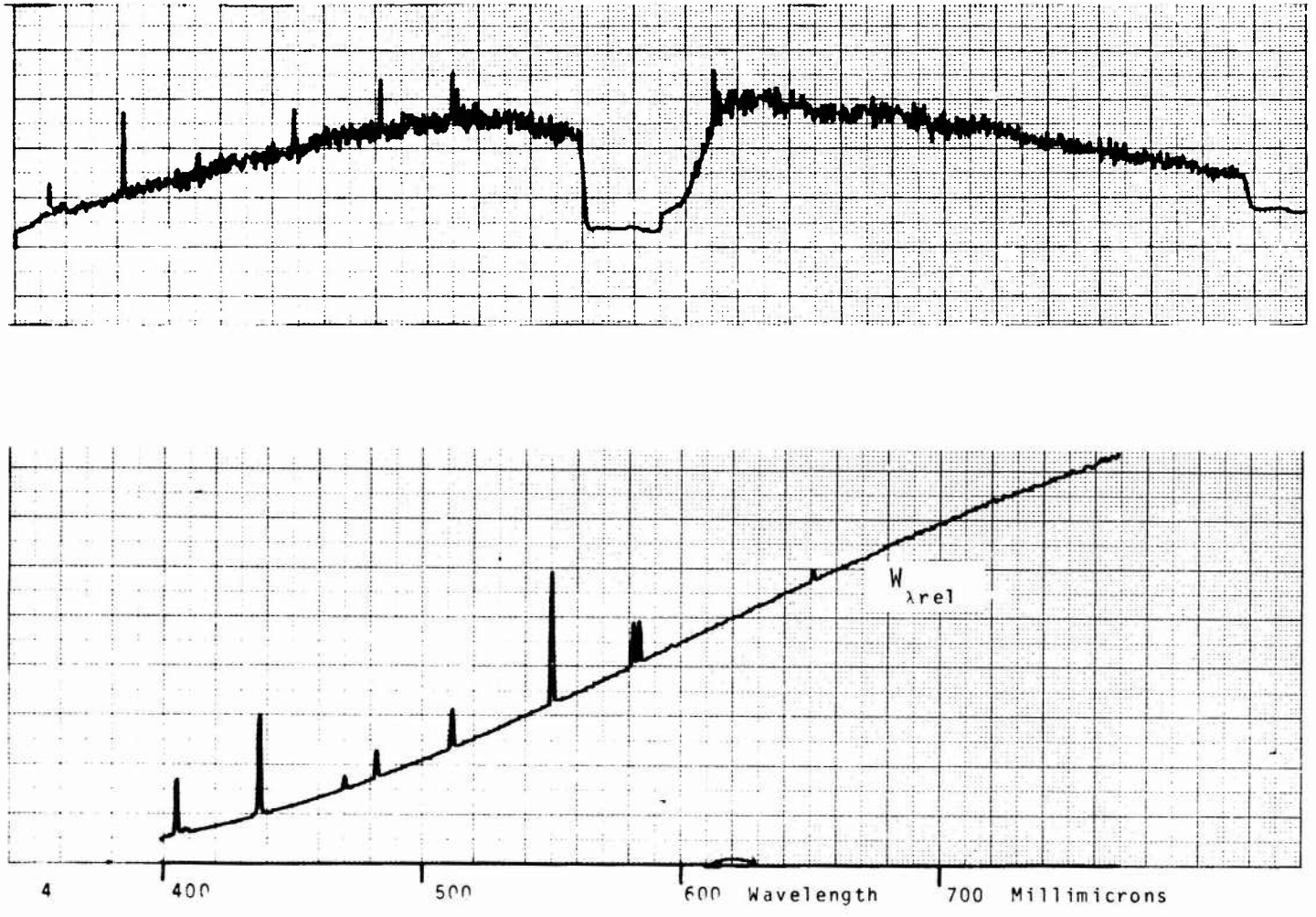


Fig 6 Single waveform and corrected relative spectrum

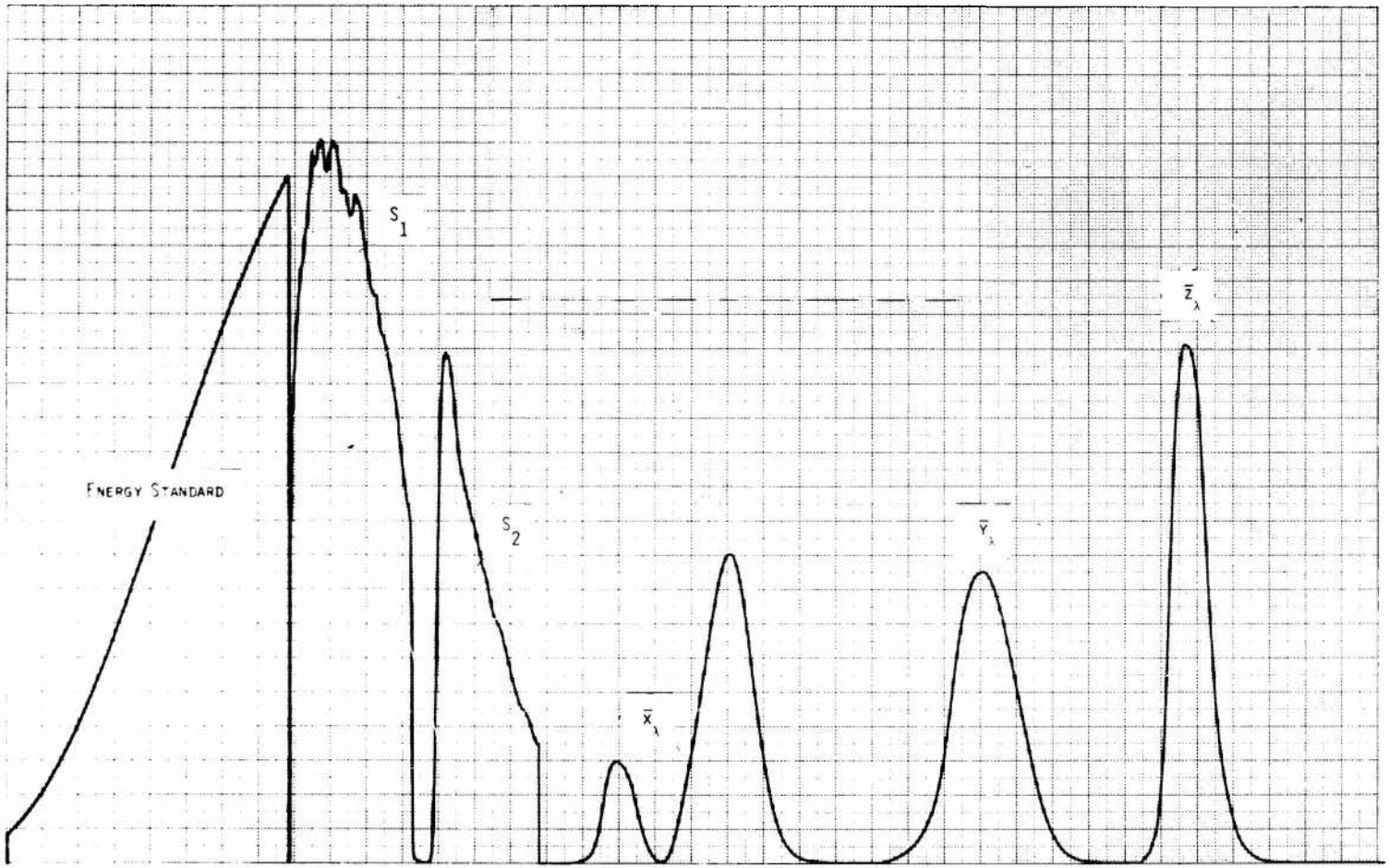


Fig 7 Standard curves and sensitivity curves in memory

The absolute level of this relative spectrum $W_a(\lambda)$ is obtained by means of a separate radiometer which measures the output of the unknown source in a given wavelength interval ΔW between λ_1 and λ_2 assuming a perfectly square filter. The procedure is covered under luminous and infrared radiometry. This output is given by

$$\Delta W = \int_{\lambda_1}^{\lambda_2} W_a(\lambda)\, d\lambda = \int_{\lambda_1}^{\lambda_2} C\, W_r(\lambda)\, d\lambda \tag{3}$$

where

$$C = \frac{\Delta W}{\int_{\lambda_1}^{\lambda_2} W_r(\lambda)\, d\lambda} \tag{4}$$

Therefore the absolute spectrum

$$W_a(\lambda) = C\, W_r(\lambda) \tag{5}$$

DETERMINATION OF COLOR COORDINATES

The color coordinates x,y,z are given by three expressions

$$x = \frac{X}{X + Y + Z} \tag{6}$$

$$y = \frac{Y}{X + Y + Z} \tag{7}$$

$$z = \frac{Z}{X + Y + Z} \tag{8}$$

where

$$X = \int_0^\infty \bar{z}(\lambda)\, W(\lambda)\, d\lambda; \tag{9}$$

$$Y = \int_0^\infty \bar{y}(\lambda)\, W(\lambda)\, d\lambda; \tag{10}$$

$$Z = \int_0^\infty \bar{z}(\lambda)\, W(\lambda)\, d\lambda \tag{11}$$

Here $\bar{x},\bar{y},\bar{z}$ are the ICI tristimulus functions (Fig 5). The available relative spectrum are used to obtain the color coordinates X,Y,Z.

EXAMPLES OF SPECTRA

Examples of spectra, generated by the described Rapid Scan, Signal Averaging Spectrometer are shown. Figure 8 represents the spectrum of the standard source which was viewed by the system as an unknown source. The spectrum represents the gray body contour, expected from the tungsten output. The wavelength is calibrated in millimicrons and the energy in watt/ster/millimicron. Various units can be used, depending on whether point source outputs or the brightness of an extended source are measured. Additionally a digital print-out is obtainable. The print-out of the same energy standard is designated as Table 4. The color coordinates X,Y,Z are calculated and printed (top left corner). Right under the values of the color coordinates is the luminous output, entered into the keyboard as L(Abs) = 1000 lumens. This value is then used by means of Equations (3),(4) and (5) to establish an absolute level of the spectrum. The lower part of the print-out lists the wavelengths and the corresponding energy values.

A sample of a signal averaged flare spectrum is given in Figure 9 and its print-out listed in Table 5. The absolute level was established by a separate luminous intensity radiometer. The measured luminous intensity L(Avg) = 216000 lumens was entered into the teletype keyboard, which established the absolute level of the spectrum. Similar spectra are obtainable in the remaining spectral regions listed in Table 2.

LUMINOUS INTENSITY MEASUREMENTS

The values for luminous intensities and measuring ranges, that are commonly encountered, correspond to large energy fluxes. Therefore the required detectors and electrical circuitry do not have to be optimized for highest signal to noise ratios. Solid state detectors such as the selenium barrier-layer photodiode with a Weston Viscor photopic filter or a silicon photodiode with a suitable photopic filter are used for most of the conventional measurements. These diodes are calibrated against an NBS calibrated tungsten filament lamps. Both the standard and the detector is positioned on an optical bench, equipped with suitable enclosures and baffles. The lamps are the nominal 1000 watt aircraft beacon lamps which

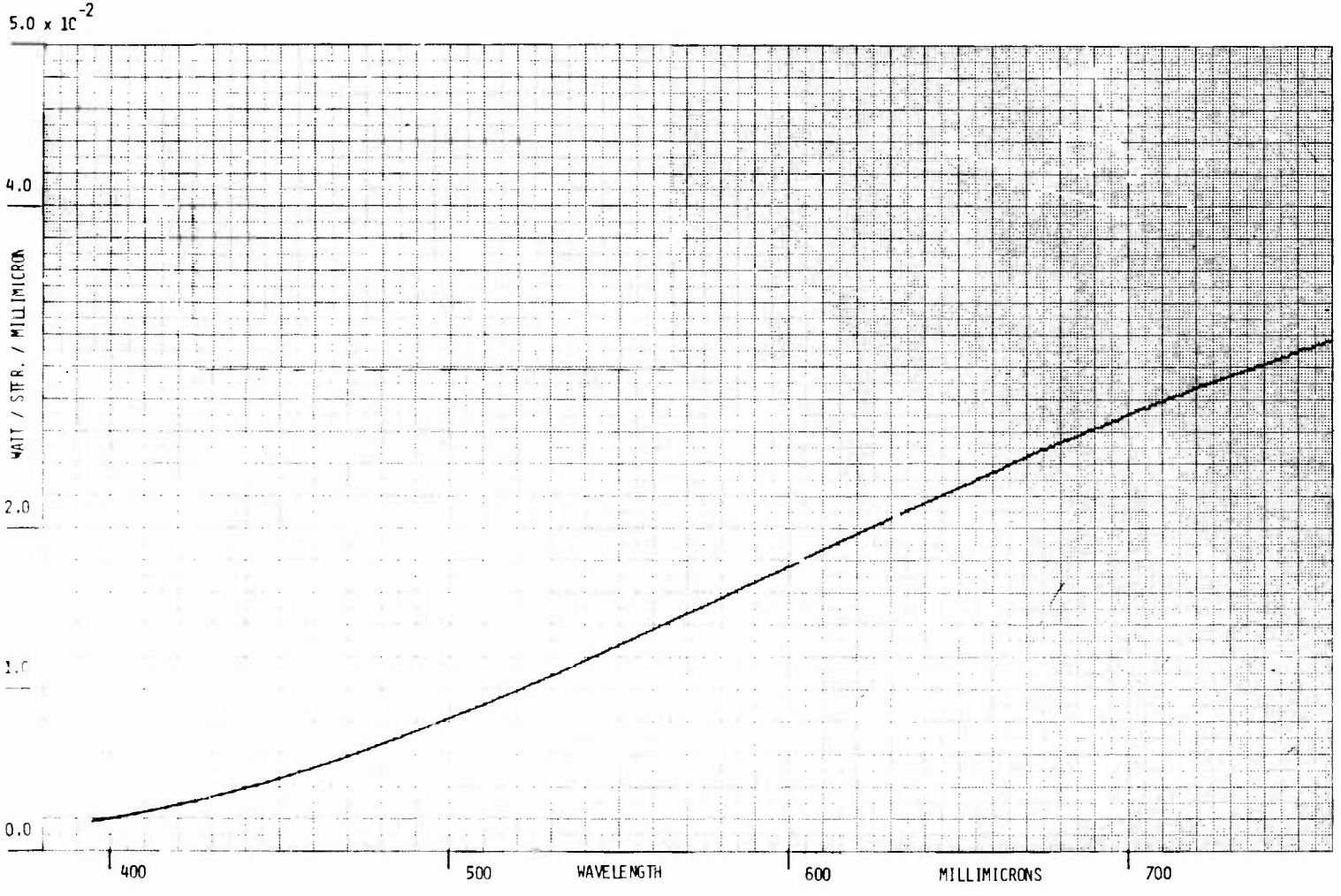


Fig 8 Spectral distribution of an N.B.S. calibrated tungsten coil filament energy standard (color temperature 2854°K)

Table 4

TST Printout of an N.B.S. calibrated coil filament energy standard

X= 4.47409E-1
Y= 4.07833E-1
Z= 1.44756E-1

ABS
L(AVG)= 1000

FACTOR= 1.00000E7

INCREMENT=5

400.00\ 2.01850E-3	405.00\ 2.20140E-3	410.00\ 2.40730E-3
415.00\ 2.64240E-3	420.00\ 2.86540E-3	425.00\ 3.09470E-3
430.00\ 3.36000E-3	435.00\ 3.61570E-3	440.00\ 3.90160E-3
445.00\ 4.22170E-3	450.00\ 4.49520E-3	455.00\ 4.84830E-3
460.00\ 5.13910E-3	465.00\ 5.52420E-3	470.00\ 5.81830E-3
475.00\ 6.20820E-3	480.00\ 6.62830E-3	485.00\ 6.91800E-3
490.00\ 7.34100E-3	495.00\ 7.76610E-3	500.00\ 8.19090E-3
505.00\ 8.63620E-3	510.00\ 9.06100E-3	515.00\ 9.45660E-3
520.00\ 9.90900E-3	525.00\ 1.04029E-2	530.00\ 1.07474E-2
535.00\ 1.11999E-2	540.00\ 1.17884E-2	545.00\ 1.21904E-2
550.00\ 1.27851E-2	555.00\ 1.31875E-2	560.00\ 1.37087E-2
565.00\ 1.42196E-2	570.00\ 1.46290E-2	575.00\ 1.51009E-2
580.00\ 1.58036E-2	585.00\ 1.62258E-2	590.00\ 1.67068E-2
595.00\ 1.71201E-2	600.00\ 1.74941E-2	605.00\ 1.80995E-2
610.00\ 1.84747E-2	615.00\ 1.90377E-2	620.00\ 1.95239E-2
625.00\ 2.01058E-2	630.00\ 2.08172E-2	635.00\ 2.10377E-2
640.00\ 2.16194E-2	645.00\ 2.20185E-2	650.00\ 2.27407E-2
655.00\ 2.28973E-2	660.00\ 2.36281E-2	665.00\ 2.37223E-2
670.00\ 2.41877E-2	675.00\ 2.49070E-2	680.00\ 2.53471E-2
685.00\ 2.56442E-2	690.00\ 2.60790E-2	695.00\ 2.63710E-2
700.00\ 2.69281E-2	705.00\ 2.73530E-2	710.00\ 2.77970E-2
715.00\ 2.80556E-2	720.00\ 2.84273E-2	725.00\ 2.91222E-2
730.00\ 2.93481E-2	735.00\ 2.98594E-2	740.00\ 3.03397E-2
745.00\ 3.08302E-2	750.00\ 3.10383E-2	755.00\ 3.11893E-2

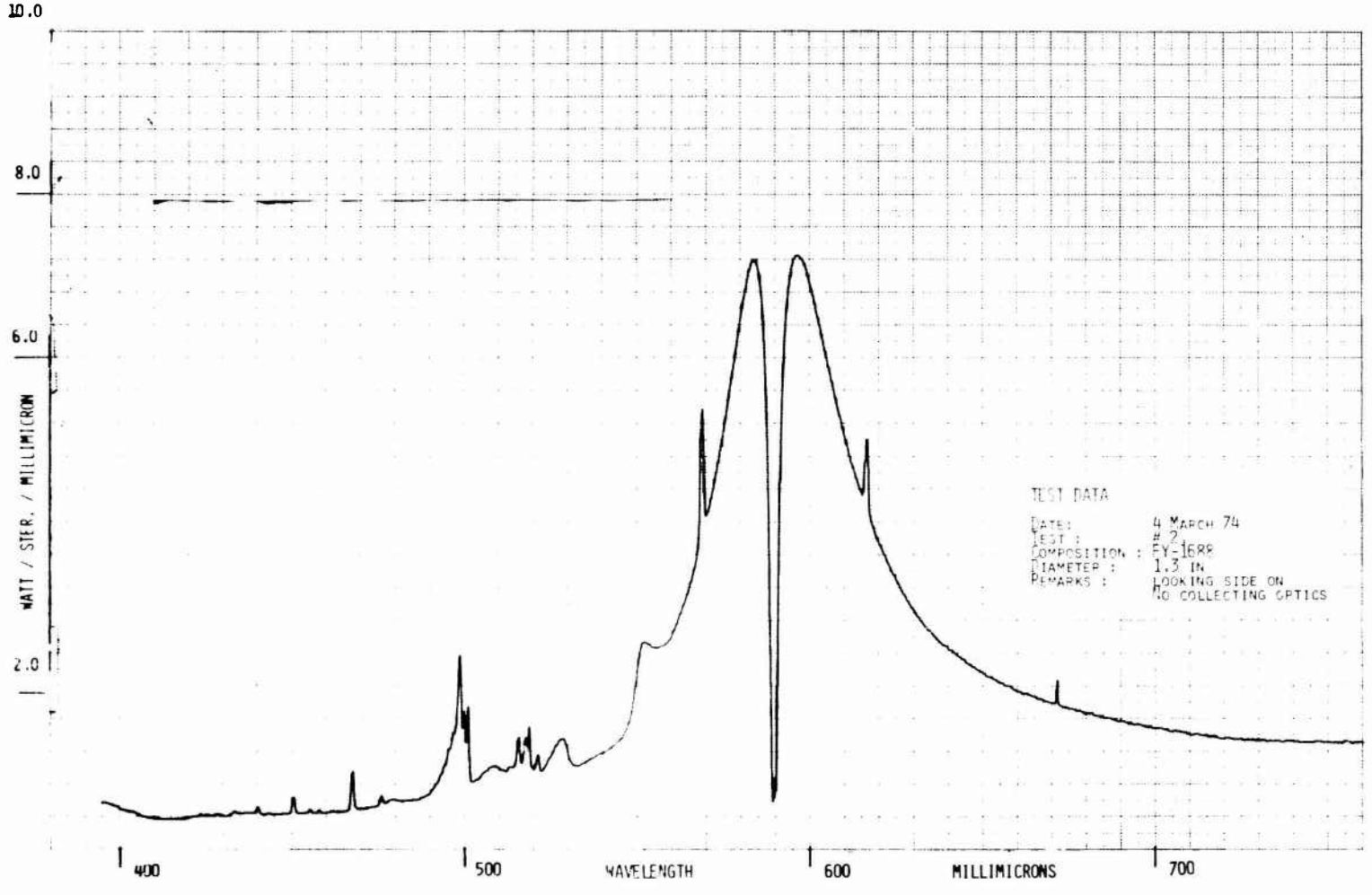


Fig 9 Signal averaged flare spectrum

Table 5

Printout of spectral distribution

.TST

TEST DATA

X= 5.03457E-1
Y= 4.23904E-1
Z= 7.26385E-2

DATE : 4 MARCH 74
TEST : #2
COMPOSITION : FY-1688
DIAMETER : 1.3 IN
REMARKS : LOOKINK SIDE ON
NO COLLECTING OPTICS

ABS
L(AVG)= 216000

FACTOR= 5.00000E4

INCREMENT=5

400.00\ 4.84540E-1	405.00\ 4.21400E-1	410.00\ 3.69100E-1
415.00\ 3.64940E-1	420.00\ 3.77480E-1	425.00\ 4.09840E-1
430.00\ 3.99720E-1	435.00\ 4.28380E-1	440.00\ 4.97880E-1
445.00\ 4.22220E-1	450.00\ 5.76220E-1	455.00\ 4.71500E-1
460.00\ 4.37020E-1	465.00\ 4.47560E-1	470.00\ 4.78960E-1
475.00\ 5.42700E-1	480.00\ 5.81920E-1	485.00\ 5.94500E-1
490.00\ 6.70740E-1	495.00\ 1.09994E0	500.00\ 1.66938E0
505.00\ 8.94320E-1	510.00\ 9.71140E-1	515.00\ 1.08150E0
520.00\ 9.58920E-1	525.00\ 1.12102E0	530.00\ 1.17022E0
535.00\ 1.04664E0	540.00\ 1.15798E0	545.00\ 1.32314E0
550.00\ 2.13230E0	555.00\ 2.44188E0	560.00\ 2.56794E0
565.00\ 3.14186E0	570.00\ 4.04766E0	575.00\ 5.03932E0
580.00\ 6.43866E0	585.00\ 7.10184E0	590.00\ 8.50560E-1
595.00\ 7.10656E0	600.00\ 6.90542E0	605.00\ 5.98116E0
610.00\ 5.05522E0	615.00\ 4.33448E0	620.00\ 3.71084E0
625.00\ 3.26044E0	630.00\ 2.90378E0	635.00\ 2.63270E0
640.00\ 2.41966E0	645.00\ 2.26396E0	650.00\ 2.13042E0
655.00\ 2.01444E0	660.00\ 1.90668E0	665.00\ 1.84288E0
670.00\ 1.76556E0	675.00\ 1.69950E0	680.00\ 1.64434E0
685.00\ 1.59636E0	690.00\ 1.56128E0	695.00\ 1.50190E0
700.00\ 1.46396E0	705.00\ 1.41830E0	710.00\ 1.39250E0
715.00\ 1.36260E0	720.00\ 1.33422E0	725.00\ 1.32886E0
730.00\ 1.31432E0	735.00\ 1.30280E0	740.00\ 1.29858E0
745.00\ 1.28764E0	750.00\ 1.28710E0	755.00\ 1.29324E0

when operating on 110 volts and a current of 8 amps, produce nominally 1500 candles. When used as standards, they are set at color temperature of 2854°K (Illuminant A).

Each complete measurement involves two mathematically identical procedures, that of system calibration, followed by the actual test. In both the current from the photodiode is related to luminous flux at the surface of the detector. Therefore for the calibration

$$\frac{L^*}{4\pi R^{*2}} = k^* I^* \tag{12}$$

and for the test

$$\frac{L}{4\pi R^2} = k I \tag{13}$$

where I is the photo current, R the detector-source distance and k a constant. All symbols with asterisks denote calibration procedure. The unknown luminous intensity is given by combining (12) and (13).

Thus

$$L = L^* \frac{I}{I^*} \frac{R^2}{R^{*2}} \frac{k}{k^*} \tag{14}$$

For routine measurements the ratio k/k^* is assumed to be a unity. The exact calculation is carried out in the Appendix A.

Having obtained the luminous intensity the candlepower is given as

$$C_p = 4\pi L \tag{15}$$

Candlepower measurements are performed statically under laboratory environment in a flare tunnel. The geometry of a flare tunnel is shown in Figure 10. The item is placed in a hearth, equipped with a stack and a fan to exhaust the gasses, and a draft duct under the floor, to permit adequate flow of gasses up stack. The radiometer is placed at an adequate distance for the flame to be an equivalent point source and properly baffled to exclude reflections.

In addition to this static radiometric facility an "Air Drop Simulator" (Fig 11) is used for simulation of dynamic outputs of

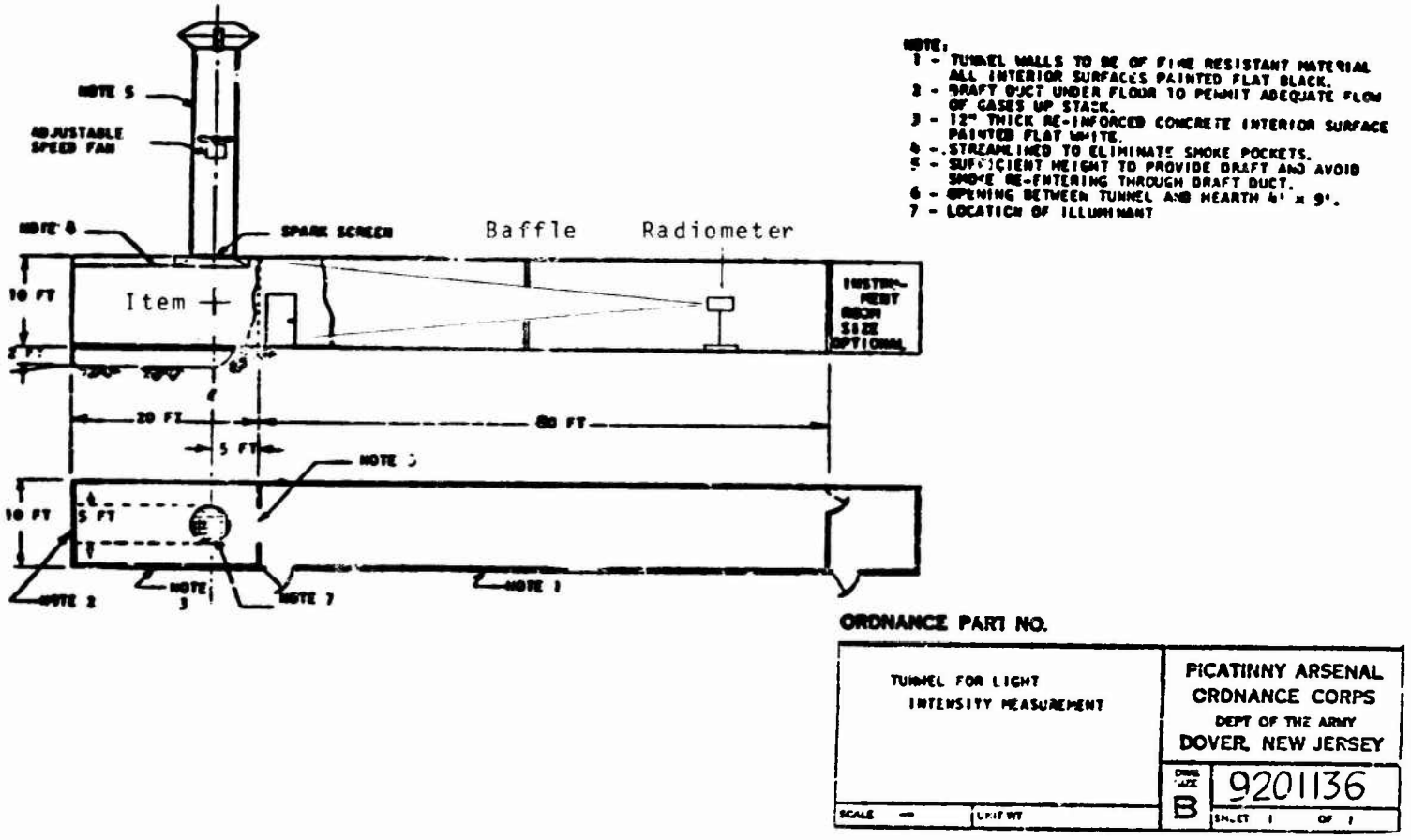


Fig 10 Tunnel for light intensity measurement

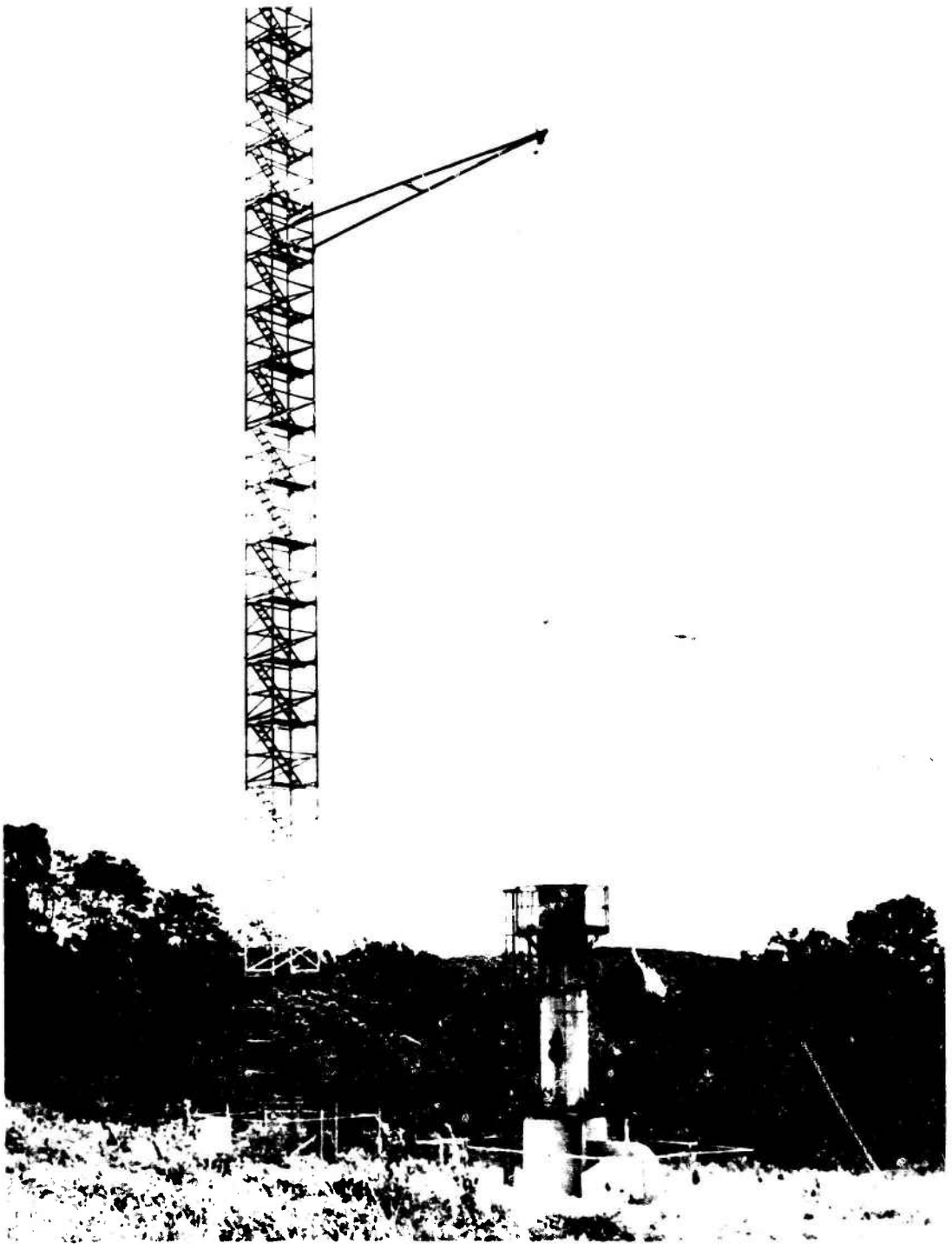


Fig 11 Air drop simulator

parachute flares, descending through the air with their terminal velocities. The flare is suspended by a cable from a steel tower 126 feet high and placed centrally above a stack, 26 feet high and 4 feet in diameter. A maximum 18,000 ft^3/min, variable speed blower provides a collimated air flow, extending approximately 4 feet above the top of the stack so as to produce an air stream of from 5 ft/sec to 20 ft/sec. A system of light detectors is placed in a suitable geometry under the burning flare to record its output.

INFRARED MEASUREMENTS

Infrared measurements are routinely done in a manner, similar to those of luminous intensity, where visible detector-window combination is substituted by appropriate equivalent infrared components. Most of the radiometric work is performed in two spectral ranges of interest, corresponding to sensitivities of the S-1 photocathode and the InSb crystal detector. Similar data analysis to that discussed for candlepower measurement is followed. If one substitutes the photopic sensitivity contour by an idealized 100% square transmission filter, with λ_1 and λ_2, the short and long cut-off wavelengths respectively, then the energies passed through this filter are related to radiometric outputs by two expressions

$$\frac{\Delta W^*}{4\pi R^{*2}} = k^* I^* \tag{17}$$

and

$$\frac{\Delta W}{4\pi R^2} = k I \tag{18}$$

where

$$\Delta W^* = \int_{\lambda_1}^{\lambda_2} W^*(\lambda)\ d\lambda \tag{19}$$

and

$$\Delta W = \int_{\lambda_1}^{\lambda_2} W(\lambda)\ d\lambda \tag{20}$$

The unknown energy in the internal between λ_1 and λ_2

$$\Delta W = \frac{R^2}{R^*} \frac{I}{I^*} \frac{K}{K^*} \tag{21}$$

where

$$\frac{k}{k^*} = \frac{\int_0^\infty W^*(\lambda)\, S(\lambda)\, T(\lambda)\, d\lambda}{\int_0^\infty c\, W(\lambda)\, S(\lambda)\, T(\lambda)\, d\lambda} \tag{22}$$

is a correction factor for the mismatch of the total effective bandpass transmission, given by the product of three spectral terms, the detector sensitivity, the filter transmission and the transmission of the atmosphere. This correction factor is derived in Appendix B and an exact calculation must have its evaluation included.

Very often this term is neglected and as a consequence great discrepancies may result between different infrared tests. These discrepancies are expected when different agencies conduct measurements, utilizing different radiometers (different $T(\lambda)$ and $S(\lambda)$) and different calibration sources (different $W^*(\lambda)$) at different atmospheric conditions and test distances (different $T_a(\lambda)$). Under these conditions one would not expect the two correction terms to be identical.

However, under a skillful choice of test parameters the mismatch term can be made to approach unity. This approach calls for a radiometric evaluation of unknown outputs by a radiometer, whose effective bandpass is placed within the interval of an atmospheric window, and a parallel spectrometric measurements, conducted at close ranges. If the bandpass of the radiometer is suitably smaller than the width of the window and spectral contours of the calibrating source approaches that of the source the mismatch term can be approximated by unity.

Once the time intensity contour is obtained for this narrow bandpass, the time intensity in any other wavelength interval is given by an appropriate scaling of the output. This scaling factor is given by the ratio of areas under spectral distribution curve corresponding to these two intervals.

An example of this type of an analysis is given. Spectral analysis of a certain formulation was found to approximate a gray

body (Fig 12). Radiometric analysis can be performed in two atmospheric windows of 2.0 - 2.5 microns and 3.5 - 4.1 where no structure is observed. If in these intervals the effective contour of the bandpass is flat, then the mismatch term can be approximately by unity.

Radiometric data are displayed on a chart recorder and also recorded on tape. Two time intensity contours for each of two spectra (tests 1 and 2) are shown in Figure 13. Each time intensity contour represents a different spectral band (deleted on contours). Any of these contours can be translated into any other time-intensity curve by amplifying the tape recorded output by a suitable scaling factor, given by the ratio of suitable areas under spectral distribution contour.

The infrared radiometric measurements are done indoors in the same flare tunnel, which is used for indoor candlepower measurements, described previously. To simulate static performance at high altitudes, high altitude facility is utilized, consisting of two 8000 ft^3 vacuum chambers, which can be evacuated to simulated altitudes of over 100,000 feet. These chambers (Fig 14) are 75 feet long with a 15 ft cylinder at the large end, and then tapered to a 5 ft diameter, where they terminate at an instrumentation center. There are large rotary piston pumps, capable of evacuating the tanks to 8 mm of mercury in 20 minutes. Controls of all test instrumentation and pumps are concentrated in the instrumentation center. In addition to infrared measurements these chambers are utilized for photoflash measurements at simulated altitudes. A photograph of the outside view of the high altitude test facility is included in Figure 15, showing the two chambers and the structure on the left, housing the vacuum pumps.

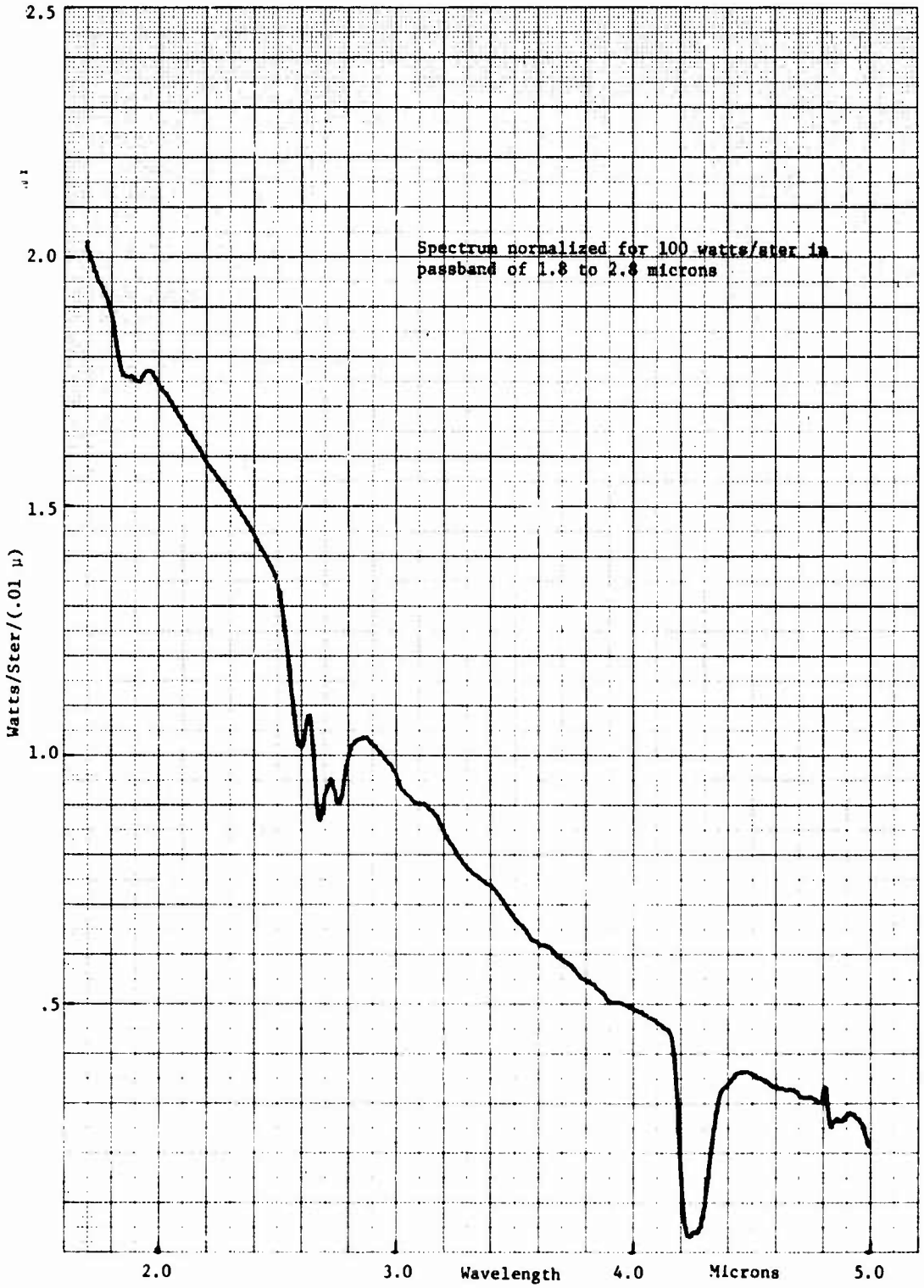


Fig 12 IR flare spectrum approximating a gray body

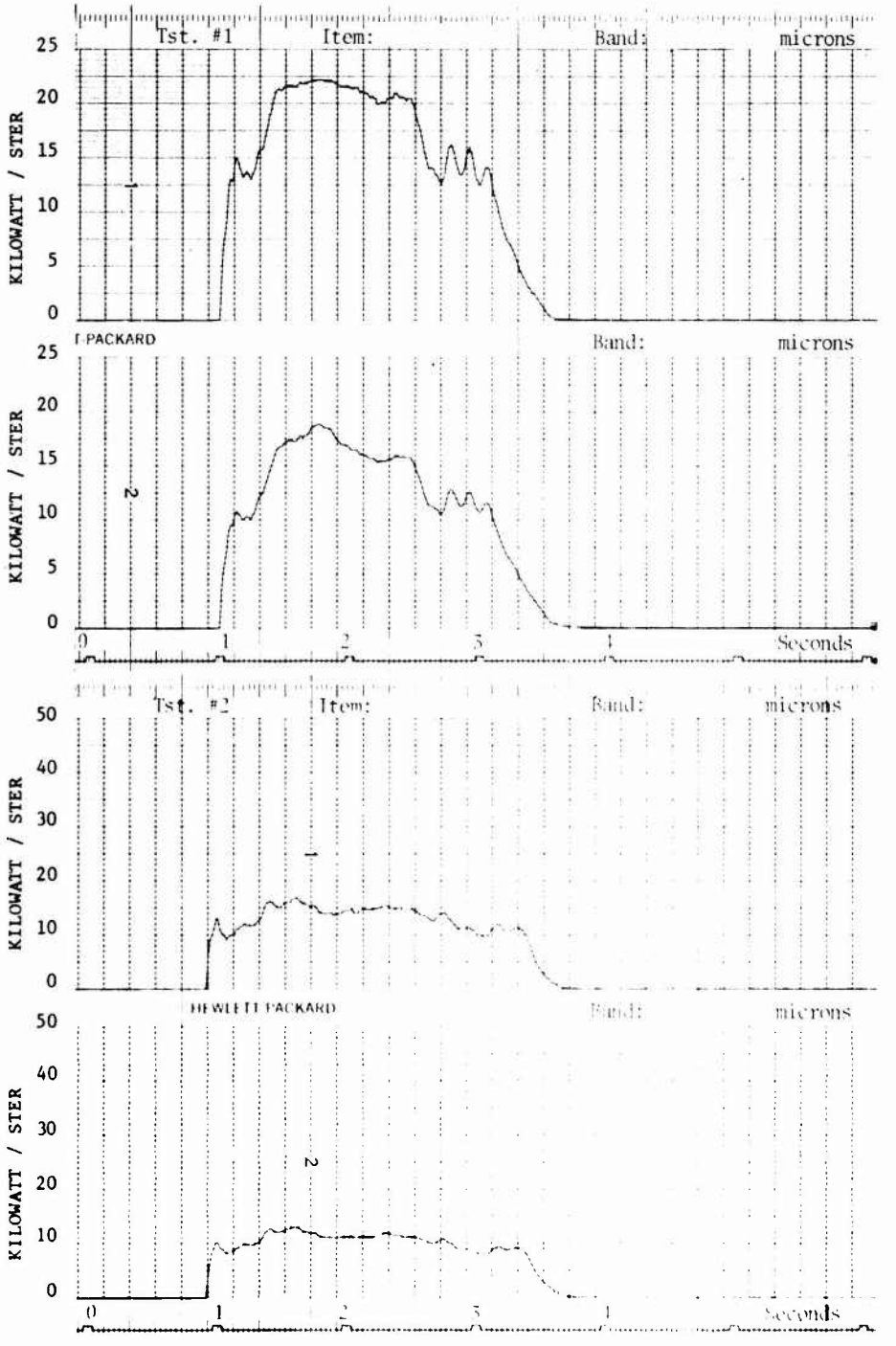
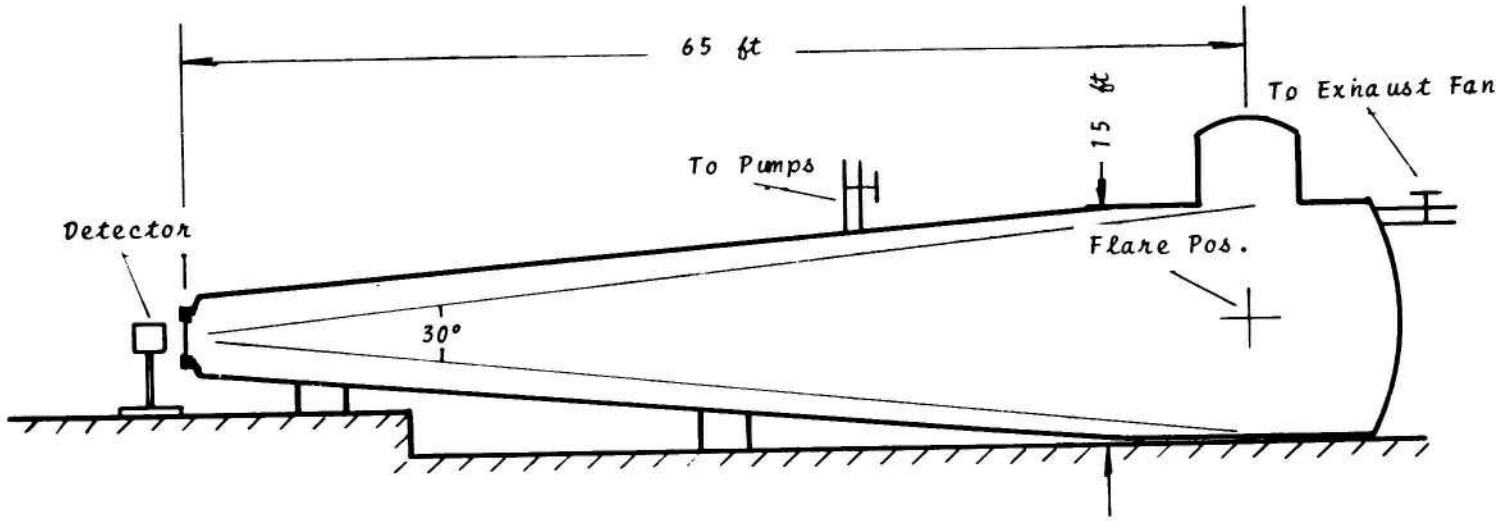


Fig 13 Time intensity contours (tests 1 and 2)



Volume : 8,000 cub. ft
Simulated Altitude: over 100,000 ft
Pumps : 6, rotary piston, capable of evacuating tanks to 8 mm Hg in 20 minutes
Use : Infrared and Photoflash Measurements

Fig 14 High altitude chamber

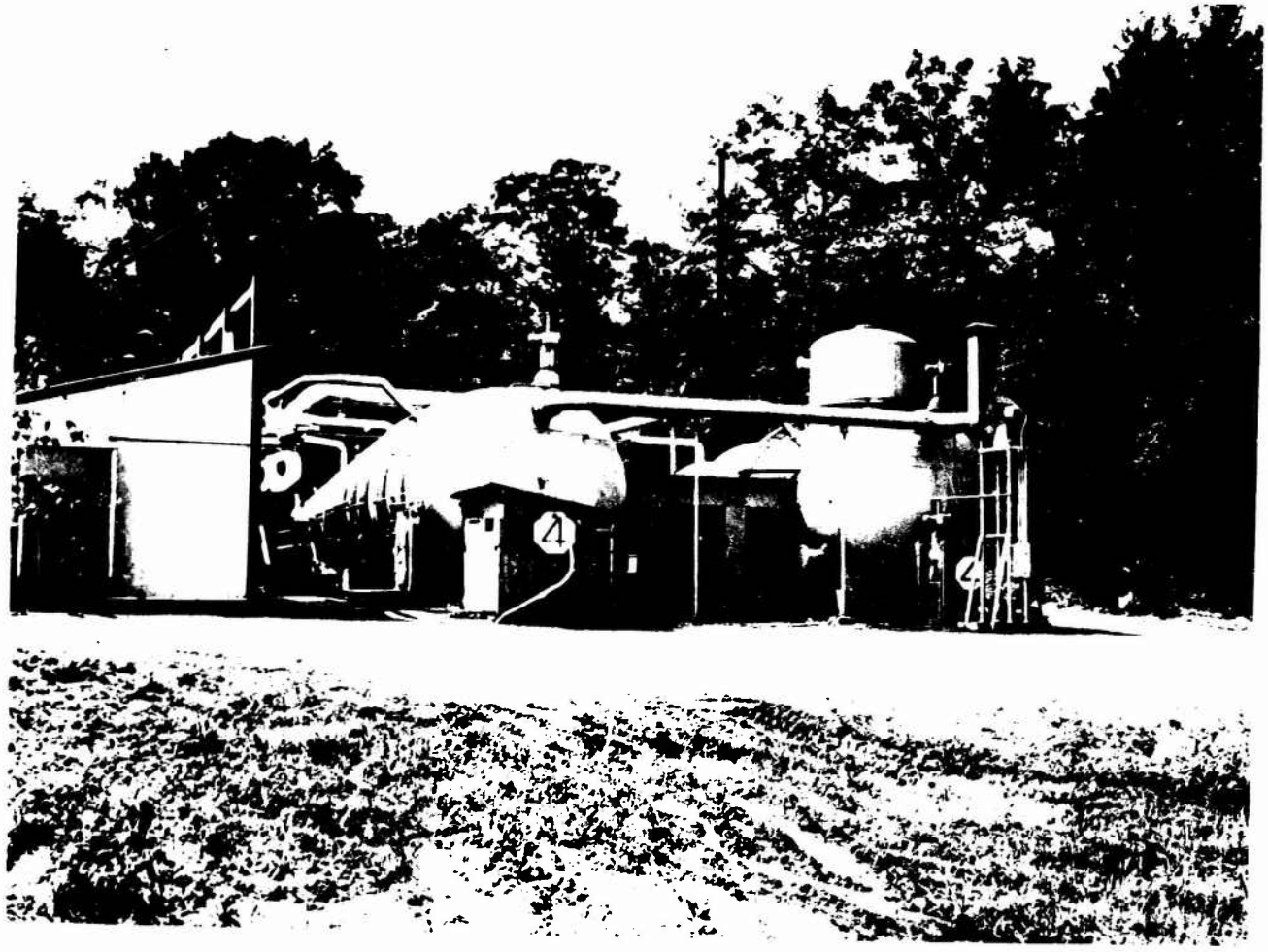


Fig 15 Exterior view of high altitude test chambers

Table 6

Additional performance tests

Composition	Test
Delay	Burning rates and reliability over a range of temperatures and environmental pressures.
Flame	Dispersion, induction time, fire-ball radius, temperature, heat flux, overpressure.
Incendiary	Number and dispersion of fragments and their effectiveness over target initiation.

Safety tests

Characteristic	Test method - procedure
Impact	Picatinny Arsenal impact test
Friction	Picatinny Arsenal friction pendulum
Electrostatic discharge	Bureau of Mines tester
Heat	Molten metal bath

Safety and Performance

Characteristics	Test method - procedure
Stability and compatibility	100°C vacuum test, storage, surveillance test

These tests were listed to provide a more complete basis for panel discussions.

SUMMARY

A brief analysis of principal test procedures, associated with pyrotechnic composition research was given. Only spectroradiometric measurements, which provide the principal performance characteristics were discussed in a somewhat greater detail.

Difficulties, associated with a conventional single scan spectral analysis of pyrotechnic outputs, were explained as those stemming from an erratic character of combustion, for which single scan techniques result in erroneous spectral signatures, that cannot be associated with predominant chemical reactions or an average performance. This difficulty has suggested an introduction of multiple scanning and signal averaging procedures. Internally developed Rapid Scan, Signal Average Spectrometer system was described in somewhat greater length and its utilization for both the formulations research and engineering analysis and interpretation of radiometric results.

Routine experimental test methods to evaluate luminous intensity and infrared bandpass outputs was covered. The similarity of procedures and analysis of the data was emphasized. Simplified, first approximation data analysis geared for routine gross effect analysis was given. Utilization of spectral signatures was emphasized for a proper choice of test parameters and a valid interpretation of the results. A great sensitivity of the radiometric bandpass results on atmospheric absorption is emphasized and contrasted with a general immunity of candlepower measurement. Correction terms to transform the first approximation into exact formulas were developed for both the luminous intensity and infrared bandpass outputs.

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APPENDIX A

EXACT CALCULATION OF LUMINOUS INTENSITY

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When luminous intensity is expressed in terms of spectral energy expressions (12) and (13) can be written as

$$\frac{680 \int_0^\infty W_a^*(\lambda)\ \bar{y}(\lambda)\ d\lambda}{4\pi\ R^{*2}} = k^*\ I^* \qquad \text{(A-1)}$$

and

$$\frac{680 \int_0^\infty W_a(\lambda)\ \bar{y}(\lambda)\ d\lambda}{4\pi\ R^2} = k\ I \qquad \text{(A-2)}$$

By combining (A1) and (A2)

$$\frac{k}{k^*} = \frac{R^{*2}\ I^* \int_0^\infty W_a(\lambda)\ \bar{y}(\lambda)\ d\lambda}{R^2\ I \int_0^\infty W_a^*(\lambda)\ \bar{y}(\lambda)\ d\lambda} \qquad \text{(A-3)}$$

To evaluate k/k^* we normalize W_a so that

$$\int_0^\infty W_m(\lambda)\ \bar{y}(\lambda)\ d\lambda = \int_0^\infty W_a^*(\lambda)\ \bar{y}(\lambda)\ d\lambda \qquad \text{(A-4)}$$

and assume $R = R^*$. Then

$$\frac{k}{k^*} = \frac{I^*}{I} = \frac{\int_0^\infty W_a^*(\lambda)\ S(\lambda)\ T(\lambda)\ d\lambda}{\int_0^\infty W_m(\lambda)\ S(\lambda)\ T(\lambda)\ d\lambda} \qquad \text{(A-5)}$$

The currents were expressed in terms of the spectral distributions of the standard and the source, the spectral sensitivity of the photodiode and the transmission of the photopic filter.

The normalization of the spectrum can conveniently be accomplished in the "Absolute Level Set" routine by requesting equal luminous intensity for both the standard and the unknown source.

APPENDIX B

EXACT CALCULATION OF INFRARED BANDPASS OUTPUTS

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The correction term is obtained by combining (17), (18), (19) and (20). Then

$$\frac{k}{k^*} = \frac{I^* R^{*2} \int_{\lambda_1}^{\lambda_2} W(\lambda)\, d\lambda}{I\ R \int_{\lambda_1}^{\lambda_2} W^*(\lambda)\, d\lambda} \qquad \text{(B-1)}$$

When we normalize the spectral energy of the unknown source so that

$$\int_{\lambda_1}^{\lambda_2} W_m(\lambda)\, d\lambda = \int_{\lambda_1}^{\lambda_2} W^*(\lambda)\, d\lambda \quad , \qquad \text{(B-2)}$$

place $R=R^*$ and express I and I^* in terms of spectral energies, detector sensitivity and total transmission of the filter plus the atmosphere, then ratio of the constants

$$\frac{k}{k^*} = \frac{\int_0^\infty W^*(\lambda)\ S(\lambda)\ T(\lambda)\ T^*_a(\lambda)\, d\lambda}{\int_0^\infty W_m(\lambda)\ S(\lambda)\ T(\lambda)\ T_a(\lambda)\, d\lambda} \qquad \text{(B-3)}$$

This is the desired correction factor to be introduced into (21) to obtain accurate bandpass outputs. Here $S(\lambda)$ is the spectral sensitivity of the sensor, $T(\lambda)$ the spectral transmission of the bandpass filter, $T_a(\lambda)$ the spectral transmission of the atmosphere, (and the asterisk denotes the calibration symbols). The normalization (23) is obtained in the "Absolute Conversion" routine, the spectral sensitivity $S(\lambda)$ and filler transmission $T(\lambda)$ by a separate spectrometric procedure. However the atmospheric transmission is dependent on the relative humidity, the temperature and the path length and must be interpreted separately for each measurement, or minimized by a choice of a narrow filter that falls into one of the atmospheric windows.

ARRADCOM PROCEDURE FOR QUALIFYING PROPELLANT FORMULATIONS

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ABSTRACT

This paper describes the procedures used to qualify a new propellant composition for a given weapon. After requirements are established (force-flame temperature relationship, erosivity, signature, etc), calculations are performed to assure that the composition will meet the ballistic requirements. Prior to making a pilot-plant lot, small quantities of the ingredients are mixed and a series of compatibility tests are conducted. Pilot plant quantities are then prepared and processing studies are made during preparation.

Laboratory procedures are described for evaluating the finished propellant. These include closed bomb firings, a calorimetric test that assures the correctness of the composition, mortar and large caliber simulators and a laboratory-scale erosion apparatus.

Analog/hybrid computer interior ballistic simulation calculations are used to predict the correct granulation (web) for the new propellant to meet the ballistic requirements for a selected weapon system.

In the final phase sufficient propellant is prepared and actual ballistic evaluation is carried out in a selected weapon system.

DISCUSSION

The importance of universally accepted tests to evaluate propellant formulations cannot be overemphasized. They should form the basis of commonality for assessing all types of compositions on an international level. Without standardized tests, there is always doubt concerning validity and significance of the reported value.

This paper will delineate the tests and criteria that are used by ARRADCOM to evaluate new propellant formulations. For maximum effectiveness these tests are utilized from the inception of a formulation to the final ballistic evaluation.

After selecting the compounds that will comprise the new formulation, it is necessary that thermochemical data be available prior to initiating computer calculations for the desired force-flame temperature relationship. If a new ingredient is to be employed, the required thermochemical data (heat of formation) is obtained from an experimental heat of combustion value, or from calculations based on bond energies. The final thermochemical properties are then calculated by the Hirshfelder-Sherman equations, using more current values as required (Ref 1,2,3 and 4). These equations are computer programmed (Ref 5). The calculated thermochemical properties for three standard propellant formulations are presented in Table 1.

After having established the percentage of each ingredient of the proposed composition to give the desired force-flame temperature relationship, it is required that the compatibility of the formulation be assessed. Toward this end, a 15 to 30 gram batch of propellant is prepared in a small sigma-blade mixer. After the propellant colloid has dried, heat stability tests are conducted in accordance with MIL-STD-286B (Ref 6). For single-base (energetic material is nitrocellulose) propellants, the test is conducted at 134.5°C. For M1, M6 and M14 propellants, the color of the methyl violet test paper must not change to salmon pink in less than 40 minutes and not explode in less than 5 hours. For the M10 propellant the criteria is 60 minutes and five hours. For double-base (energetic materials are nitrocellulose and nitroglycerin) and triple-base (energetic materials are nitrocellulose, nitroglycerin and nitroguanidine) propellants, the test is conducted at 120°C, and the color change and explosion criteria are 40 minutes and 5 hours, respectively (Ref 7). A vacuum stability test at 90°C and 100°C, respectively, for double/triple-base and single-base propellants is also conducted (Ref 6). For these tests, the criteria is that a gas evolution of 11+ ml in 40 or less hours is unacceptable. If the gas evolution is 5 to 11 mils, a border line case is indicated. Anything under 5 ml gas is acceptable. Vacuum stability values for standard propellant formulations are presented in Table 2. At this point, the composition's resistance to heat has been established. It remains to determine its resistance to impact. This is determined by means of an impact tester. Those most commonly employed are the PA and the Bureau of Mines Impact Testers. Typical PA Impact Test values for standard propellant compositions are presented in Table 3.

If the formulation passes all the prior tests, a 3000 gram pilot lot quantity of the composition is prepared for further evaluation. The propellant is processed in the pilot plant in horizontal sigma-blade mixers. During the processing, variables such as the total solvent, solvent composition, solvent ratio and mixing time plus temperature are closely observed for their influence on the formation of a colloid for final extrusion. A portion of the colloid is extruded for strand burning rate and mechanical property studies. The remaining colloid is extruded through a known die assembly into grains from which shrinkage data is determined so that a proper die size may be selected for the desired web. Prior to obtaining the dried grains, a drying cycle is established. For single-base propellant, water drying is the accepted procedure. After air drying for several days to prevent case hardening, the composition is water dried from 7 days to 21 days depending upon the granulation (web) at a water temperature of 58°C (136°F). Final forced air drying is conducted at 55°C (131°F). For double- and triple-base propellants,

air drying for several days is followed by forced air drying for 3 to 8 days at 45°C (131°F) and then raised to 55°C (131°F) for the remaining drying cycle. Prior to removal of the propellant from the dry house, a total volatiles content is determined to ascertain if the propellant is properly dried. If the drying cycle did not achieve this objective, it must be lengthened by whatever time is necessary to give the required value. A high total volatiles content will have an adverse effect upon ballistics because it reduces both the burning rate and the force value. Upon completion of drying, the propellant is thoroughly blended and in some instances, the propellant may be glazed with graphite during this operation.

After manufacture, samples of the new propellant are submitted for laboratory characterization. The total volatiles is the initial test. For the single-base M1 and M6 and the double-base M2 and M5 propellants, the total volatiles is dependent upon the granulation or web size. The total volatiles for M9 flake propellant (for mortar application) is 0.50%, maximum. The maximum total volatiles for the triple-base M30 and M31 propellants are 0.50% and 0.30%, respectively (Ref 7).

The accelerated 134.5°C and 120°C methyl violet paper heat tests along with the 100°C and 90°C vacuum stability heat tests which were discussed during the compatibility phase of testing are repeated. This time, however, the tests are run on the whole propellant grain rather than the colloid. A 110°C Taliani heat test may be run to measure the rate of gas evolution (Ref 6).

80°C (accelerated) and 65.5°C surveillance tests are run on all experimental propellants. For these tests, 45 gram samples are stored in glass stoppered bottles. The appearance of the bottle and its contents is noted daily. The number of days required to cause the liberation of visible reddish fumes of oxides of nitrogen is the reported test value. Typical surveillance test values for standard propellants are shown in Table 4. (It should be noted that these tests cannot be conducted with triple-base propellants, because the decomposition products are not visible.)

Grain measurements are performed in order to generate shrinkage data. The heat of explosion is run to check the experimental value with that calculated during the formulation study. A good agreement will eliminate the need for a complete chemical analysis.

The new compositon and a standard (or reference) propellant are fired at a predetermined loading density in a closed bomb at 70°F, -60°F and +160°F. The closed bomb can be fired up to 100,000 psi maximum pressure. The force and quickness of the new propellant are

determined relative to the standard propellant. The data generated is used to calculate the linear burning rate, $r = bP^n$ at the aforementioned three temperatures (Ref 8).

The specific gravity and gravimetric density is run on the propellant sample to ascertain the porosity of the grain and to determine how much propellant can be placed in a given chamber volume.

The following evaluations have been developed at ARRADCOM for special propellant applications. A standard closed bomb was modified to provide a laboratory scale apparatus for measuring erosion. This method affords a rapid and economical means for studying propellant erosivity and the effectiveness of additives for erosion reduction (Ref 9).

A full-scale laboratory simulator has been developed to study the burning characteristics of the actual component parts of the ignition system for a standard mortar. The simulator can be used to evaluate the individual components, i.e., primers, ignition cartridges and propellant charges for the mortar as well as the completely assembled ignition-combustion train (Ref 10).

A large caliber simulator has been constructed for laboratory scale gun firings. It has been shown that data obtained in the laboratory can be applied directly to the solution of ignition problems with bag charges in a large caliber gun. Again, the laboratory information was obtained at a low cost compared to firings in a gun (Ref 11).

An arc-image furnace is available for specialized laboratory-scale ignition tests. A flame spreading test has been developed to aid in the evalution of low vulnerability propellant formulations. When the propellant is spread on a flat surface and ignited at one point, the flame spreads at a rate which is dependent on such factors as composition, grain size, thickness of layer, bulk density, uniformity of granulation and surface conditions. Therefore, from both a functioning and safety consideration, information on the flame spreadibility or propagation of a propellant is of importance (Ref 12).

Now that our new propellant has been fully characterized, it is time to conduct analog/hybrid computer interior ballistic simulation calculations. Using the closed bomb $r = bP^n$ linear burning rate data, and known parameters for a selected weapon system (i.e., travel, bore area, chamber volume and projectile weight), we can determine the granulation or web, the propellant charge weight, and its loading

density for our new formulation to meet the ballistic requirements for the weapon system. The data obtained from the computer will include (1) pressure, velocity and travel vs time curves (2) point of splintering for multi-perforated propellants (3) point of burnout for all propellants (4) pressure at base of projectile as the shell travels down the gun tube (5) pressure at the muzzle when the projectile leaves the gun tube and (6) exit shock temperature. The last two computer readouts indicate the extent of muzzle blast, and whether the propellant will require a flash suppressor (Ref 13,14,15,16 and 17).

Based upon the data supplied by the computer, sufficient propellant is processed for ballistic evaluation in the selected weapon system. The propellant can either be manufactured at ARRADCOM or at a government owned-contractor operated facility (GOCO plant). The principle outside facility is Radford Army Ammunition Plant run by the Hercules Company at Radford, Virginia. The propellant is usually manufactured in three granulations. One granulation may be 10 to 15 percent smaller than that predicted by computer calculations, the second will be the predicted granulation and the third will be 10 to 15 percent larger than the predicted granulation.

One of the most important phases of the investigation is the actual ballistic evaluation of the propellant in the weapon system. First, the charge weight is established for the optimum propellant granulation required to meet the ballistic requirements for the round of ammunition. These initial firings are conducted at 70^{o}F. Uniformity series are then fired with both a standard propellant and the candidate propellant at 70^{o}F, -60^{o}F and $+160^{o}$F. The propellant is usually conditioned for 24 hours at the two extreme temperatures. Pressure-time traces are taken during the uniformity series firings to ascertain ignition characteristics. Standard deviations for velocity and pressure are calculated as well as the temperature coefficients. Usually, high speed movies are taken to record the flash and smoke characteristics. A visual inspection is made for unburnt propellant at the muzzle of the gun. Gun tube measurements may also be taken to determine gun barrel erosivity.

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Table 1

US gun propellants

Propellant	Single-base[1]	Double-base[2]	Triple-base[3]
Formulation	M6	M26E1	M30
Calculated thermochemicals			
Isochoric flame temp, ^{o}K	2750	3132	3040
Force, ft-lbs/lb	317,000	362,000	364,000
Gas Volume, moles/gm	0.04432	0.04164	0.04308
Heat of explosion, cal/gm	758	977	974
Combustibles, %	62.4	56.2	41.0
Unoxidized carbon, %	6.8	1.6	3.2
Ratio of specific heats, γ	1.2543	1.2384	1.2385
Co-volume, in^3/lb	29.92	28.74	29.26

Notes:

1 Energetic material is nitrocellulose.

2 Energetic materials are nitrocellulose and nitroglycerin.

3 Energetic materials are nitrocellulose, nitroglycerin and nitroguanidine.

Table 2

Vacuum stability heat test values for standard propellants

Propellant	Remarks	Temperature of test	Ml gas in 40 hrs on 5 gm sample
		(^{o}C)	(ml)
M1	Single-base[1]	100	2.86
M2	Double-base[2]	90	4.00
M8	Double-base[2]	90	2.46
M30	Triple-base[3]	90	2.33
M31	Triple-base[3]	90	0.65

Notes:

1 Energetic material is nitrocellulose

2 Energetic materials are nitrocellulose and nitroglycerin

3 Energetic materials are nitrocellulose, nitroglycerin and nitroguanidine

Table 3

PA impact test values on standard propellants

Propellant	Remarks	PA impact values obtained with 2 Kg weight (inches)
M1	Single-base[1]	6
M2	Double-base[2]	3
M5	Double-base[2]	3
M8	Double-base[2]	2
M9	Double-base[2]	2 to 3
M15	Triple-base[3]	7

Notes:

1 Energetic material is nitrocellulose

2 Energetic materials are nitrocellulose and nitroglycerin

3 Energetic materials are nitrocellulose, nitroglycerin and nitroguanidine

Table 4

Surveillance test values for standard propellants

Propellant	Remarks	80°C (accelerated) (days)	65.5°C (days)
M1	Single-base[1]	300 to 350	1800
M6	Single-base[1]	275 to 300	1500
M10	Single-base[1]		500 to 600
M2	Double-base[2]		335 to 365
M8	Double-base[2]		160 to 200
M9	Double-base[2]		200
M26	Double-base[2]		1200

Note:

1 Energetic material is nitrocellulose

2 Energetic materials are nitrocellulose and nitroglycerin

LASL METHODS OF DERIVING MODELS FOR PREDICTING THE THERMAL HAZARDS AND USEFUL LIFETIMES OF EXPLOSIVES

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LASL METHODS OF DERIVING MODELS FOR PREDICTING THE THERMAL HAZARDS AND USEFUL LIFETIMES OF EXPLOSIVES

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Sensitivity, thermal stability, and toxicity are the three major safety factors that must be considered in selecting an explosive for any specific application. At the Los Alamos Scientific Laboratory (LASL) we attempt to obtain quantitative data on these factors at the earliest possible stage in the development of any new explosives system. This paper will consider only the problems associated with thermal stability; some aspects of the LASL philosophy concerning sensitivity will be discussed by L. C. Smith.

Our first goal in studying the thermal stability of explosives was to provide models for predicting thermal hazards. It was desired to be able to sample the first small-scale preparation of a new explosive, make an accurate determination of the kinetics constants for its decomposition, and predict safe handling conditions for fabrication and application. It was presumed that the kinetics methods could also be used to derive lifetime predictive models for systems in which chemical reactions are responsible for the critical degradation processes. We believe that we have been largely successful in attaining our first goal, and we have successfully predicted some long-term degradation rates from small-scale measurements.

When one is attempting to derive a practical, reliable predictive model for the self-heating of an explosive, I consider it imperative that the kinetics measurements be based on heat-evolution rates. Therefore, our preferred method for the determination of kinetics constants uses isothermal differential calorimetry[1-4]. The heat-evolution rates of milligram-size samples are observed with a Perkin-elmer Differential Scanning Calorimeter operated at a series of constant temperatures. Rate constants are obtained from the slopes of plots of signal amplitude versus time, and operational activation energies and pre-exponentials are obtained from Arrhenius plots of the rate-constant data. "Order plots"[2] of the rate data give direct measurements of reaction orders, reveal any complexities, and enable determination of the stoichiometry in mixed systems.

In predicting the thermal safety of any specific size and shape of explosive charge, the critical temperature (T_m) is defined as the

lowest constant surface temperature above which a thermal explosion can result from the self-heating of the explosive. The heat-balance problem involved in the prediction of T_m has been considered[5-7], and the following simple expression allows predictions to be made that are of adequate accuracy for most research and development purposes:

$$\frac{E}{T_m} = R \ln\left[\frac{a^2 \rho Q Z E}{T_m^2 \lambda \delta R}\right] .$$

E is the activation energy of the decomposition reaction, R is the gas constant, a is the radius of a sphere or cylinder or the half-thickness of a slab, ρ is the density, Q is the heat of reaction during the self-heating process, Z is the pre-exponential, λ is the thermal conductivity, and δ is a shape factor (0.88 for infinite slabs, 2.00 for infinite cylinders, 2.72 for a regular right-circular cylinder, and 3.32 for a sphere).

It is obvious from the expression for the prediction of the critical temperature that there is no such thing as a single "autoignition temperature" for an explosive. The temperature at which an explosive can self-heat to explosion will depend very critically on size and shape. Small-scale autoignition tests will give high values for critical temperatures, and explosive devices designed on the basis of such determinations can be dangerous.

Autoignition or time-to-explosion tests can be useful, however, if they can be used to produce an independent experimental value for the critical temperature of any explosive composition. This independent experimental value can be used to test the predictive model derived from kinetics measurements. It is important to recognize, however, that the physical values required for the predictive expression (for example, density, thickness, and shape) must be known for the critical-temperature test assembly.

For practical purposes, the experimental method for the determination of critical temperatures should be adaptable to laboratory operations. It must, therefore, be a compromise between accuracy of definition of conditions and violence of reaction. The method in use at LASL[8] was designed to be as inexpensive as possible and to be used as a routine survey method. It is used to test predictive models, as a control test for explosive quality, and to detect incompatible systems. We have shown that calculated and experimental critical temperatures agree very well[8], allowing predictions for larger systems

to be made with some confidence on the basis of small-scale tests. Complex systems that do not allow successful predictions to be made can be detected with small samples, and suitable care can be exercised in further testing.

Some organic explosives decompose at significant rates only in the homogeneous liquid phase (for example, TNT and TNB), a very few appear to decompose completely in the solid state (the most common being TATB), but most melt with decomposition (for example, RDX, HMX, PETN, and HNS). When the critical temperature of an explosive is below its nominal melting point, it must decompose in the solid state, usually a slow process, until some change allows its decomposition rate to increase sufficiently for it to self-heat to explosion. The critical temperature will be determined by the process showing the maximum rate attainable in a condensed-phase reaction for the explosive in question, but the time to explosion may be largely determined by the low-rate, solid-state reactions. This is an important distinction, because we can usually measure the kinetics constants for the most rapid reaction quite accurately, and, consequently, we can predict critical temperature with some confidence. However, the solid-state reactions involved in time-to-explosion estimations are difficult to measure accurately, and the solid-state rates can vary tremendously with changes in purity and crystal perfection. Attempts to compare systems by use of time-to-explosion tests alone can be misleading.

I believe that the thermal safety of pure explosives and explosive compositions can now be specified with some confidence on an absolute basis. There is no need to standardize relative tests. When the values required for application of the critical temperature expression have been obtained and the accuracy of the derived predictive model for any system has been successfully demonstrated by use of an independent experimental method, objective comparisons among explosives and compositions can be made, safe fabrication conditions can be selected, and the safety of device deployment under different conditions can be predicted.

Safety studies on explosives should consider time-dependent changes in sensitivity, stability, and toxicity. A change in any one of the safety factors that renders a device useless can provide a "critical-lifetime criterion" for the device; however, it should be recognized that many processes other than chemical reactions can cause ultimate failure of a system to function properly or to become too dangerous to use.

When degradation or changes in thermal hazard provide the critical-lifetime criterion, predictive models for lifetime may be derived from thermochemical methods; however, certain precautions must be observed. Predictive models based on solid-state decomposition rates may be unreliable for the same reasons that time-to-explosion calculations are unreliable, heterogeneous reactions may be overlooked as the result of different loading densities in experimental systems compared with production devices, and mechanism changes are likely between service temperatures and thermal test temperatures. Mechanism changes are almost certain when there are phase changes between service temperatures and test temperatures.

I do not believe that a standard procedure can be proposed for the derivation of lifetime predictive models; however, I do believe that standard thermal tests should be used to detect thermal hazards that appear as the result of aging of the explosive or device.

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DEVELOPMENT OF A NEW SURVEILLANCE TEST OF GUN PROPELLANT STABILITY

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ABSTRACT

A typical single-based nitrate ester propellant was subjected to accelerated ageing at 65.5° and 90°. The artificially aged samples were studied by NO + O_3 chemiluminescence for nitrous gas evolution measurement. Thin layer chromatography and heat flow calorimetry were also used to characterize the samples in an attempt to develop a rapid and accurate surveillance test for stability to replace or improve the currently used Abel heat test. Results of these studies show that the chemiluminescence technique shows promise as a method by which the Abel heat test can be put on a quantitative basis.

INTRODUCTION

In order to control the hazard associated with the storage of large amounts of high energy materials in ammunition storage depots, regular surveillance testing of the gun propellants is generally carried out to assess the stability and therefore storability of the propellant. Most countries, including Canada, continue to rely upon the Abel Heat Test as a rapid, easily performed surveillance test. This test is a conservative one in the sense that propellants will fail the test before they are truly unstable. This conservative character has caused some difficulties in Canadian Forces Ammunition Depots (CFAD's) where propellants are sometimes judged unstable by routine surveillance testing only to be requalified for service by the now accepted NATO Stanag 4117 procedure (1).

In an attempt to reduce these difficulties, the Canadian Army tasked DREV to develop a new surveillance test procedure that is at once more reliable than the Abel Heat Test and also sufficiently simple to perform that it could be done in the CFAD's by non-technical personnel.

Tests for propellant stability fall into two categories: direct tests and indirect tests. The NATO Stanag 4117 procedure is an example of an indirect test insofar as the measured quantity is not the decomposition process but rather the propellant stabiliser content remaining after a prescribed period of accelerated ageing at 65.5°. Direct tests, on the other hand, measure the actual rate or intensity of the decomposition process. An example of a direct test is the Heat Flow Calorimetry Method (2) where a propellant is heated to typically 85° and the rate of evolution of heat from the sample arising from the actual decomposition is measured.

Apparatus is now commercially available that permits the reliable measurement of the concentration of NO and NO_2 in the parts per billion range in a variety of carrier gases by exploiting the chemiluminescent reaction between NO and O_3. In the present studies, we have adapted such an apparatus to measure the decomposition rate of gun propellants by the rate of evolution of these nitrous gas products. In this way it was hoped that a direct testing method for gun propellants could be developed where the testing conditions could be better controlled than in the case of the Abel heat test. The sample for the Abel heat test is measured in the presence of air of variable humidity levels and possible atmospheric contaminants whereas in the present procedure the sample is flushed out with high purity argon and the measurement is performed under anaerobic, anhydrous conditions.

The application of the chemiluminescence technique for compatibility measurements has been described by Keller, Jari and Ayer (3) who found the method very satisfactory. In their work, the chemiluminescence apparatus was used to measure the total nitrous gas product after a period of heating and a similar technique has been used in this work with some modification.

Thin layer chromatography and heat flow calorimetry were also used to characterize the samples used.

ARTIFICIAL AGEING

In these preliminary experiments, a study of the degradation of artificially aged samples of a typical single-based gun propellant, FNH/P, was carried out. The FNH/P formulation is the same as the American M1 with potassium salts added for flash reduction and has the nominal composition:

Nitrocellulose (13.1%N)	85%
dinitrotoluene	10%
dibutyl phthalate	5%
diphenylamine (added)	1%
potassium sulphate (added)	1%.

This propellant was aged artificially at 65.5° and at 90° in glass vessels with loosely fitted ground glass stoppers (65.5°) or with corks fit with capillary tubes (90°) to permit slow gas exchange and pressure equalization. Samples of 45 g of the propellant were removed periodically and the residual diphenylamine (DPA) stabilizer in the propellant was measured using the spectrophotometric analytical procedure specified in STANAG 4117 (1). The results of this analysis are presented in Fig. 1 where, for the samples aged at 65.5° and 90°,

we see that the point has been reached where the loss of DPA is accelerating with time, presumably because the sample is approaching autocatalytic decomposition.

From Fig. 1 we observe that, when the time scale is measured in hours for ageing at 90° and in days for ageing at 65.5°, the course of the drop of DPA with time for the two experiments is quite similar. The slopes of the relatively flat portions of the curves before the rate of DPA loss starts to increase are: 90° ageing, 6.8x10-7 %DPA s^{-1} and 65.5° ageing, 2.1×10^{-8} %DPA s^{-1}. This gives an activation energy of 35 kcal mol^{-1} controlling the temperature coefficient of the ageing process over this temperature range.

THIN LAYER CHROMATOGRAPHY

The artificially aged samples were analyzed qualitatively using the thin layer chromatography technique as described by Volk (4). Briefly, this method consists of the extraction of a 2 g sample of the propellant, ground to pass a 20 mesh sieve, with methylene chloride for 16 hours. The extract was evaporated to dryness, then made up to 50 ml volume with acetone and 20 µl samples of this solution were analyzed by two dimensional TLC on 20 cm square glass plates with a silica gel coating. The first development was with benzene:tetrachloromethane: 1,2-dichloroethane = 5:3:2.5 followed by a second development at right angles to the first using ethylacetate:hexane = 20:80 as solvent. The separated compounds were visualized on the plate by examination under UV light, followed by spraying the plate with two agents: p-diethylamino benzaldehyde, 1 g in 100 ml of methanol:conc sulfuric acid = 75:25 followed by potassium bichromate, 0.8 g in 100 ml 60% sulfuric acid. Results of this analysis are shown in Table 1 for the samples aged at 90° and 65°.

Although Fig. 1 shows that the samples aged at 65.5° exhibit a very similar drop in DPA to the samples aged at 90°, examination of Table I shows that the course of the decomposition is quite different, particularly in the case of the higher nitration products (marked "others" in Table 1) which are evident in ageing at 90° at DPA levels below 0.765%, but do not appear in samples aged at 65.5° until the DPA content is reduced to 0.652%. Even more striking is the observation that for samples analyzed by the Stanag 4117 procedure to have about the same DPA content, (for example, 2160 hrs at 65.5° and 96 hrs at 90°) the intensity of spots for DPA by the TLC technique are widely different. For 144 hrs at 90°,

the analysis shows nearly half the DPA remains, whereas this spot is no longer detectable on the TLC plates. This is probably an artifact of the Stanag 4117 analysis procedure, which may convert nitrated DPA derivatives into DPA or compounds measurable as DPA during the digestion in alcoholic KOH. This point should be further investigated by developing a quantitative TLC or high performance liquid chromatography technique and comparing the results of the two methods.

DIRECT MEASUREMENT OF NITROUS GAS PRODUCTS

This method rests on the availability of instruments designed for the measurement of very low concentrations of NO (ppb range) in an inert carrier gas. Such instruments were first developed to allow continuous monitoring of NO_X pollutants in urban atmospheres and are based upon the chemiluminescence produced when nitric oxide reacts with ozone according to the following kinetic system:

$$NO + O_3 \rightarrow NO_2^* + O_2$$

$$NO_2^* + M \rightarrow NO_2 + M$$

$$NO_2^* \rightarrow NO_2 + h\nu.$$

On this scheme, NO_2 represents an electronically excited molecule of nitrogen dioxide and M represents any molecule present in the reaction cell capable of quenching NO_2^* prior to its fluorescence. Analysis of the system shows that the intensity of the emitted light, I, varies according to the expression

$$I = k[NO]\ [O_3]/P,$$

where k is a proportionality constant, [NO] and $[O_3]$ are the concentrations of NO and O_3 respectively and P is the total pressure. Thus, if $[O_3]$ and P are kept constant, the intensity I is proportional to [NO] and the instrument can be calibrated by measuring the response to standard mixtures of NO.

The instrument used in our experiments at DREV was acquired from AeroChem Research Laboratories Inc. of Princeton, N.J.. The operation of the instrument is shown in Fig. 2 which shows a reaction chamber into which flow simultaneously a stream of ozonized air, generated in the instrument, and the sample gas to be measured. These gas streams mix rapidly and react in the field of view of a photomultiplier tube which responds to the filtered chemiluminescence.

As long as the sample gas pressure and gross composition at the source remain constant, the instrument draws a constant flow of sample, i.e. 65 cm^3/min in this case, at one atmosphere pressure.

The apparatus used for sample intreduction is shown in Fig. 3. A 1.5 g quantity of the propellant to be studied was ground to 20 mesh size and then placed in a 0.25 in. O.D. glass tube and connected with Teflon Swagelok fittings into a stainless steel line immersed in a constant temperature bath at 75.2±0.1°. A flow of pure, dry argon was passed through the sample at 65 cm^3/min, the rate demanded by the chemiluminescence instrument. A mercury manometer was provided at the inlet to the instrument to assure a constant pressure of one atmosphere. A 0.5 ℓ ballast volume before the sample facilitated the adjustment of the gas flow rate from the argon cylinder. This ballast was fit with a tap to allow purging out with fresh argon before each experiment.

Since the sample decomposes slowly at 75.2°, nitrous gases are liberated from the nitrocellulose in the sample and these gases must diffuse out of the solid propellant and into the argon stream in order to be measurable. After the artificial ageing process, the sample contains a relatively large residue of gaseous products which were reduced to a minimum by storage overnight under vacuum followed by flushing with pure argon through the sample tube.

If the sample is then immersed in the heating bath and NO and NO_2 measured, a large and variable amount of NO_2 is present initially, but over a period of hours this NO_2 falls to zero and only NO is observed thereafter. Presumably the NO_2 is present in the sample before the start of the measurements and is the result of oxidation of NO to NO_2 by contact with air. The NO, on the other hand, can only be measured in the absence of air and arises during the test where all air is displaced by argon. For all the results reported here, only the NO production is considered.

The rate of NO evolution for each of the samples was measured as a function of time over a period of up to 30 hours. During this period, the generation of NO falls from a relatively high initial rate to a constant steady-state rate as shown in Fig. 4. The initial portion of the curve corresponds to the Abel heat test where a sample is subjected to a temperature of typically 75° and the time required for the generation of sufficient nitrous gas to affect a test paper is measured. The time required is on the order of 10 to 20 minutes for sound propellants which is only a small fraction of the total time in Fig. 4. The final, steady-state generation rate is presumably a measure of the basic rate of nitrocellulose decomposition forming NO in competition with the stabilizer capturing it. If this is so, then the steady-state production rate

should be a function of the residual stabilizer content, and therefore of the condition of the propellant.

The reason for the slow decline to the steady-state generation rate is obscure, but may well be due to a slow drying of the propellant under the test conditions or some solid state gas diffusion process. Other changes also occur during this treatment. For example, analysis by thin layer chromatography of samples before and after the chemiluminescence measurement showed that all of the dinitrotoluene had sublimed out of the powder, while the other components remained.

The steady-state generation rates for the artificially aged samples, as well as for a naturally aged propellant whose %DPA had fallen from 1% to 0.89% over 20 years storage, are shown in Fig. 5. In this figure, the NO concentration in the argon, in parts per million, is plotted against the level of DPA, as measured by the Stanag 4117 procedure, remaining in the propellant sample. First, it is clear that the artificial ageing has increased the rate of NO production but, for the samples aged at 90° there is a maximum in the curve and the production of NO falls off for the longest aged samples. This behavior is quite unexpected. Secondly, there is a difference between the curves for 65.5° ageing and for 90° ageing, showing that the steady-state NO generation rate is not a function of stabilizer concentration alone. Furthermore, the naturally aged sample bears no relationship to the other results.

Since the steady-state rate is approached very slowly, it is difficult to get reproducible results because the end of the drift is hard to judge. In view of this difficulty and of the problematical interpretation of the results, the steady-state generation rate measurement was not pursued further. Instead the rate of NO evolution at the start of the experiment was measured and these results are plotted in Fig. 6. This data is related to the Abel heat test in the sense that the time required to accumulate a quantity of nitrous gases sufficient to affect a test paper should be inversely proportional to the rate at which these gases are given off by the sample. However, the Abel heat test is performed in air of uncontrolled relative humidity, whereas these experiments are conducted in a dry, inert atmosphere.

The initial rate results in Fig. 6 also show an increase in the NO generation upon artificial ageing, as expected. Here again, there is a difference between the 90° ageing and 65° ageing but the difference is not as great. Also, the result for the naturally aged sample (triangle point) is in general accord with the other samples, especially the specimens aged at 65.5°. The rolling off of the points for ageing at 90° recalls the behavior observed in Fig. 5 for the steady-state NO generation, but in this case, the roll-off is less noticeable and cannot be distinguished from simply attaining

a plateau value. In any event, ageing at 90° is a severe process atypical of natural ageing, as we have seen from the TLC experiments, and this is probably why the 90° results do not fall on the same curve as those taken at 65.5°.

In experiments performed on a propellant of very similar composition, Verbeek (5) found that the rate of heat generation, during heat flow calorimetry experiments, decreased with increasing artificial ageing at 65.5°, even though the DPA content fell to nearly zero. Also the Abel heat test time increased from 13 minutes to 25 minutes for one of his samples and from 10 minutes to 15 minutes for the other on increasing the artificial ageing from 300 days to 500 days at 65.5°, where the DPA content had fallen to zero. Perhaps the observed decrease in initial and final NO generation rates in the present work for ageing at 90° is another manifestation of this phenomenon.

HEAT-FLOW CALORIMETRY

The samples of FNH/P propellant aged at 65.5° were studied using a heat flow calorimeter constructed similarly to the instrument described by van Geel (2). Samples weighing 10 g were placed in the calorimeter at 85° in an atmosphere of air and the rate of heat evolution was continuously measured for seven days. The resulting thermograms are shown in Fig. 7 for the propellant lot CAD6272 (manufactured July 1962) artificially aged for 46, 60 and 90 days at 65.5°, as well as for the original sample. Also shown in the figure is the thermogram for the naturally aged sample of FNH/P (lot CAD6231, manufactured July 1957) whose DPA concentration closely resembles that of the 46 days aged sample of lot CAD6272.

Heat flow thermograms can be used in several ways to estimate the condition of the propellant. First, a "safe diameter", D, can be calculated based on the rate of heat released and the ability of the propellant, by virtue of its thermal conductivity, to dissipate that heat. The safe diameter at 85° is calculated from the formula (2):

$$D = (4\delta\lambda RT^2/\rho E q_{initial})^{\frac{1}{2}} = 0.0992/(q_{initial})^{\frac{1}{2}}$$

where δ is a dimensionless, geometrical factor, λ is the coefficient of thermal conductivity, R is the gas constant, T is the temperature, ρ is the bulk density, E is the activation energy for the decomposition process and $q_{initial}$ is the average heat release rate in the first 50 hrs of the experiment.

The safe diameter is the maximum diameter of cylindrical bulk samples of stored propellant that will not exhibit an increasing temperature as a result of their slow decomposition. The integral of the thermogram over the first 36 hr period, divided by the heat of explosion Q_{ex} is $\Delta Q_{ex}(20°)$, where

$$\Delta Q_{ex}(20°) = \frac{\int_0^{36} q\,dt}{Q_{ex}}$$

and q is the heat generation rate per unit mass of propellant and ΔQ_{ex} is typically 3990 J/g. A period of 36 hrs at 85° corresponds to about 10 yrs at 20°, using an activation energy of 25 kcal/mole. It is expected that $\Delta Q_{ex}(20°)$ will correlate closely with the percent decrease in the energy of the propellant after 10 years storage at 20°. The average initial heat generation rate, $q_{initial}$, is defined as

$$q_{initial} = \frac{1}{50}\int_0^{50} q\,dt$$

The results for the samples in question are shown in Table II. The experimental error in measuring the various results is on the order of 10 percent. The three parameters D, $\Delta Q_{ex}(20°)$ and $q_{initial}$ vary regularly for the artificially aged samples of lot CAD6272, however, only $q_{initial}$ and $\Delta Q_{ex}(20°)$ change to a degree clearly outside of the experimental error. The results indicate that CAD6231 is more stable than the original sample of CAD6272. However, at this level of ageing, the naturally aged sample has not varied significantly from the unaged sample. It has not been possible to obtain samples of FNH/P sufficiently aged naturally to exhibit real evidence of instability.

Referring again to Fig. 7, a major change in the shape of the thermograms appears to occur in the case of the artificially aged samples, with the peak of the heat flux moving to earlier times progressively as the samples are aged. Again, the naturally aged lot CAD6231 is more or less similar to the original lot CAD6272 and not the 46 days aged sample that it resembles in DPA content. The most likely explanation for the changes in the artificially aged samples is that the period spent at 65.5° represents a pretreatment equivalent to an initial portion of the calorimetry experiment at 85° resulting in an apparent translation of the curves to earlier times. On the other hand this is not in accord with the time change calculated by applying a 25 kcal/mol activation energy which would

predict much longer translations of the time frame resulting from pre-heating at 65.5°. If the pre-heating hypothesis is none-the-less accepted, this would also explain the progressive changes in the $q_{initial}$ results.

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TABLE I: TLC Analysis of Artificially Aged FNH/P Propellant

	Artificial Ageing at 65.5°					Artificial Ageing at 90°					
time of ageing (hrs)	0	1104	1440	2160	2880	24	48	72	96	120	144
% DPA (Stanag 4117)	1.005	.821	0.785	0.735	0.652	0.894	0.834	0.765	0.721	0.615	0.488
DPA	S	S	M	M	W	S	S	W	VW	VW	-
2-NDPA	_(1)	_(1)	M	M	M	_(1)	_(1)	_	W	W	W
N-NsDPA	W	S	S	S	S	S	S	S	S	S	S
4-NDPA	VW	W	W	W	VW	VW	VW	W	W	W	W
Others	–	–	–	–	1	–	–	1	1	2	3

(1) 2-NDPA cannot be resolved from DPA when DPA is present in large concentration

(2) Numbers in this row correspond to the number of other spots observed. Every sample showed spots for butyl phthalate and 2,4- dinitrotoluene, but these are not included in the Table.

legend: DPA = diphenylamine, 2-NDPA = 2-Nitro DPA, N-NsDPA = N-nitroso DPA, 4-NDPA = 4-Nitro DPA
S = strong, M = medium, W = weak, VW = very weak

TABLE II

Heat Flow Calorimetry Results for Artificially and Naturally Aged FNH/P

Lot No	Ageing at 65.5°C (days)	DPA (%wt/wt)	D meters	$\Delta Q_{ex}(20°)$ (%)	$10^3 q_{initial}$ (W/kg)
CAD6272	0	1.005	0.42	0.18	56.1
mfd July 1962	46	0.820	0.40	0.19	61.1
	60	0.782	0.36	0.23	75.9
	90	0.734	0.33	0.29	88.8
CAD6231	0	0.881	0.45	0.16	49.1
mfd July 1957					

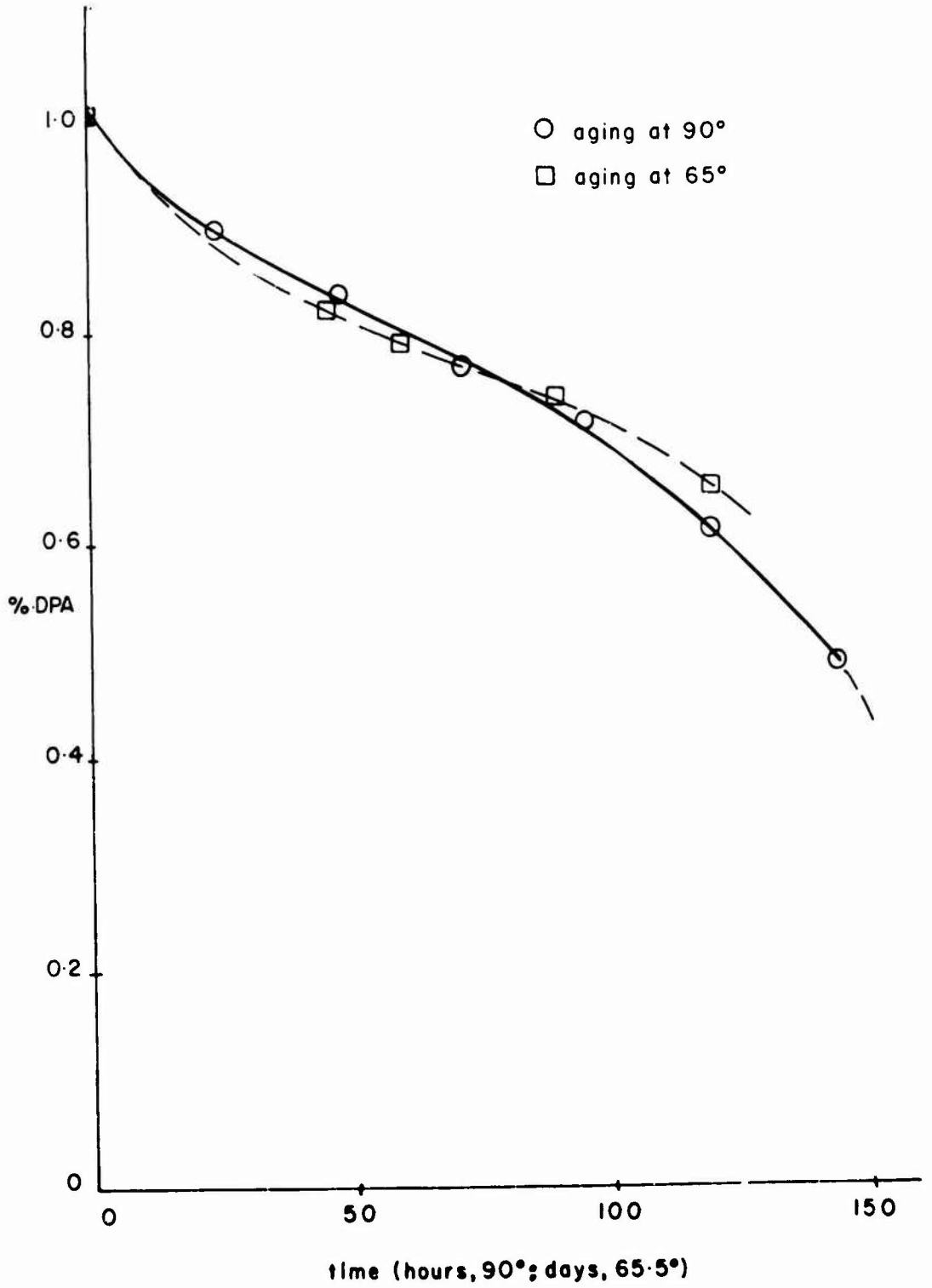


Fig 1 Accelerated ageing at 65.5° and 90°

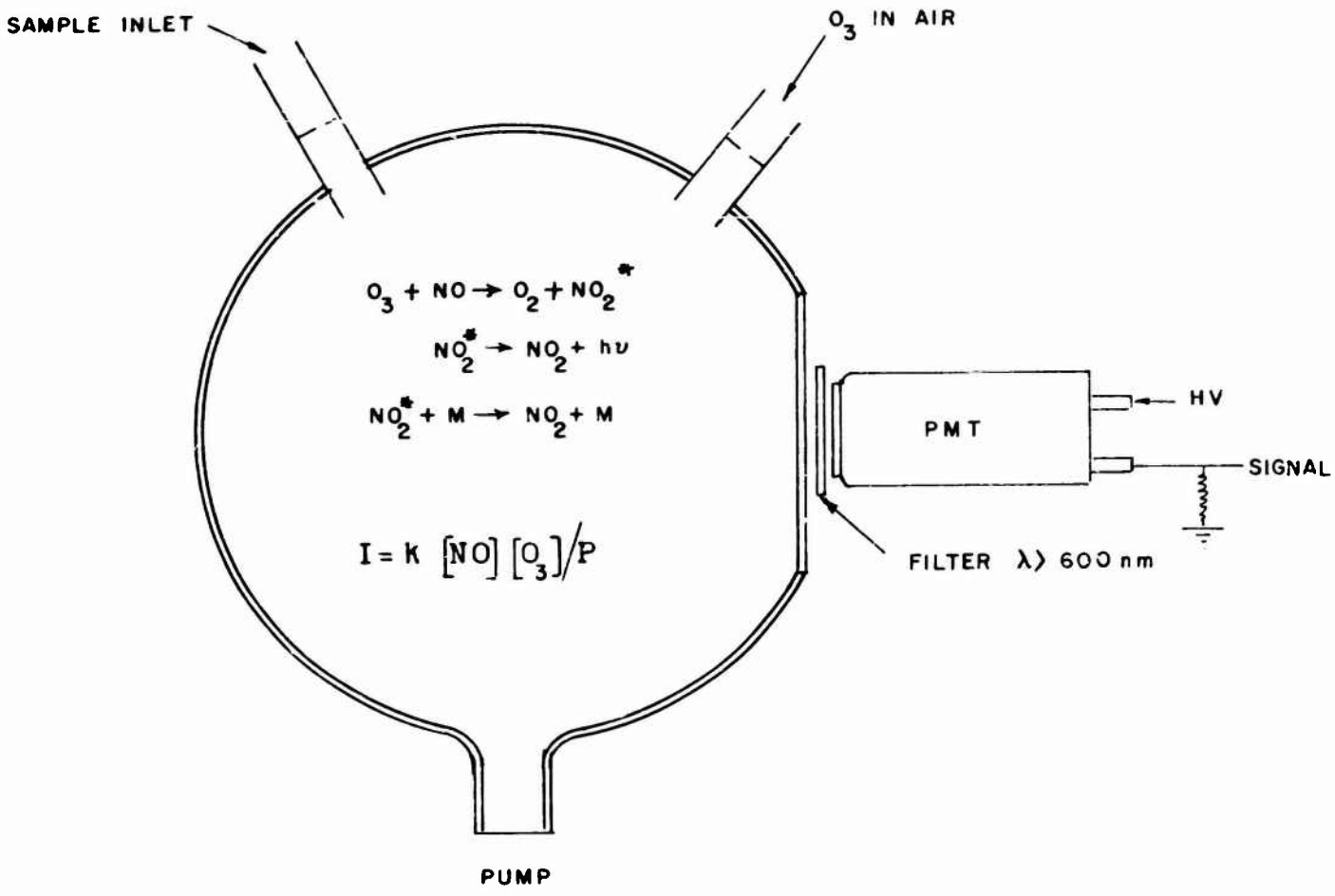


Fig. 2: Chemiluminescence instrument

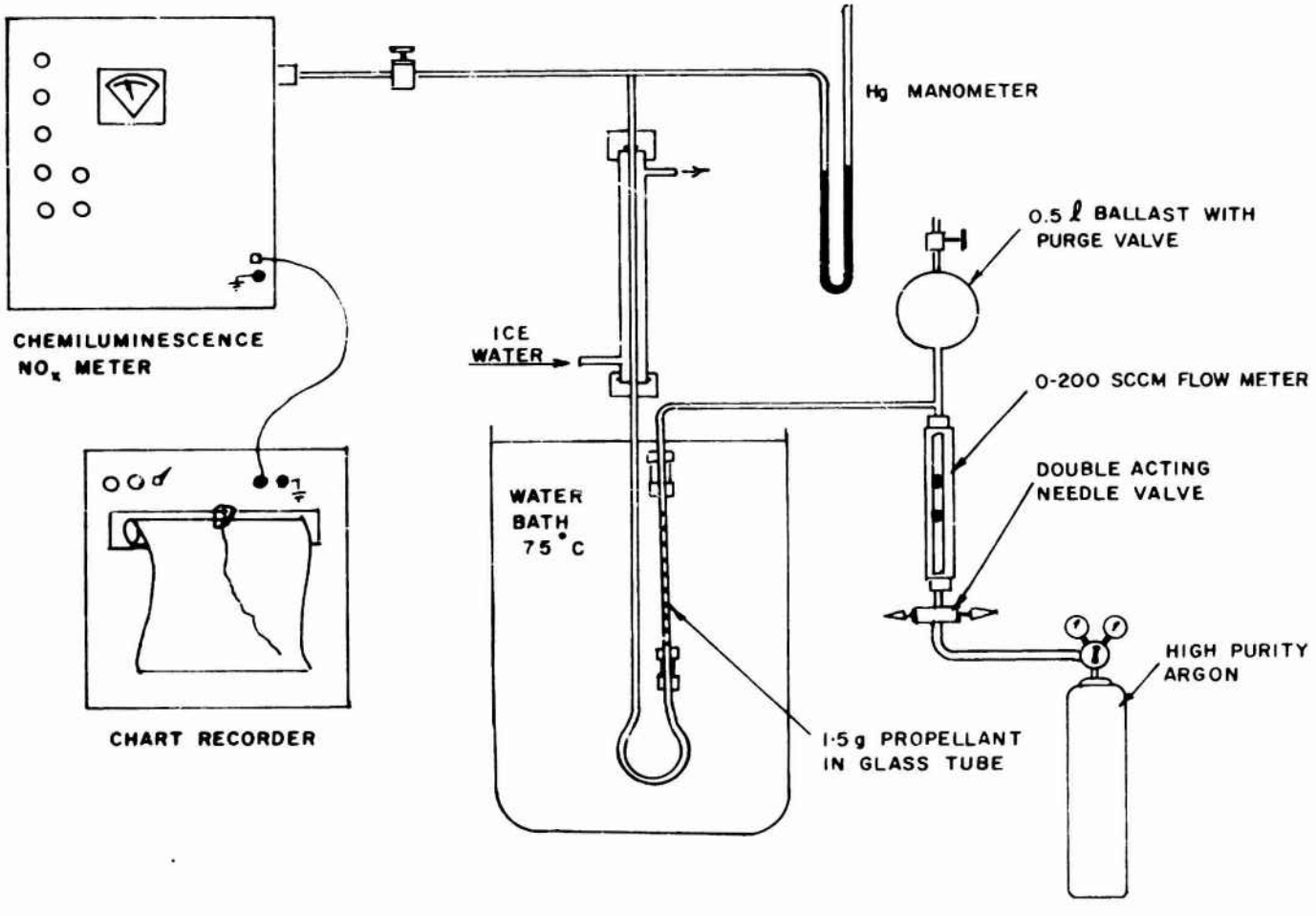


Fig. 3: Propellant testing apparatus

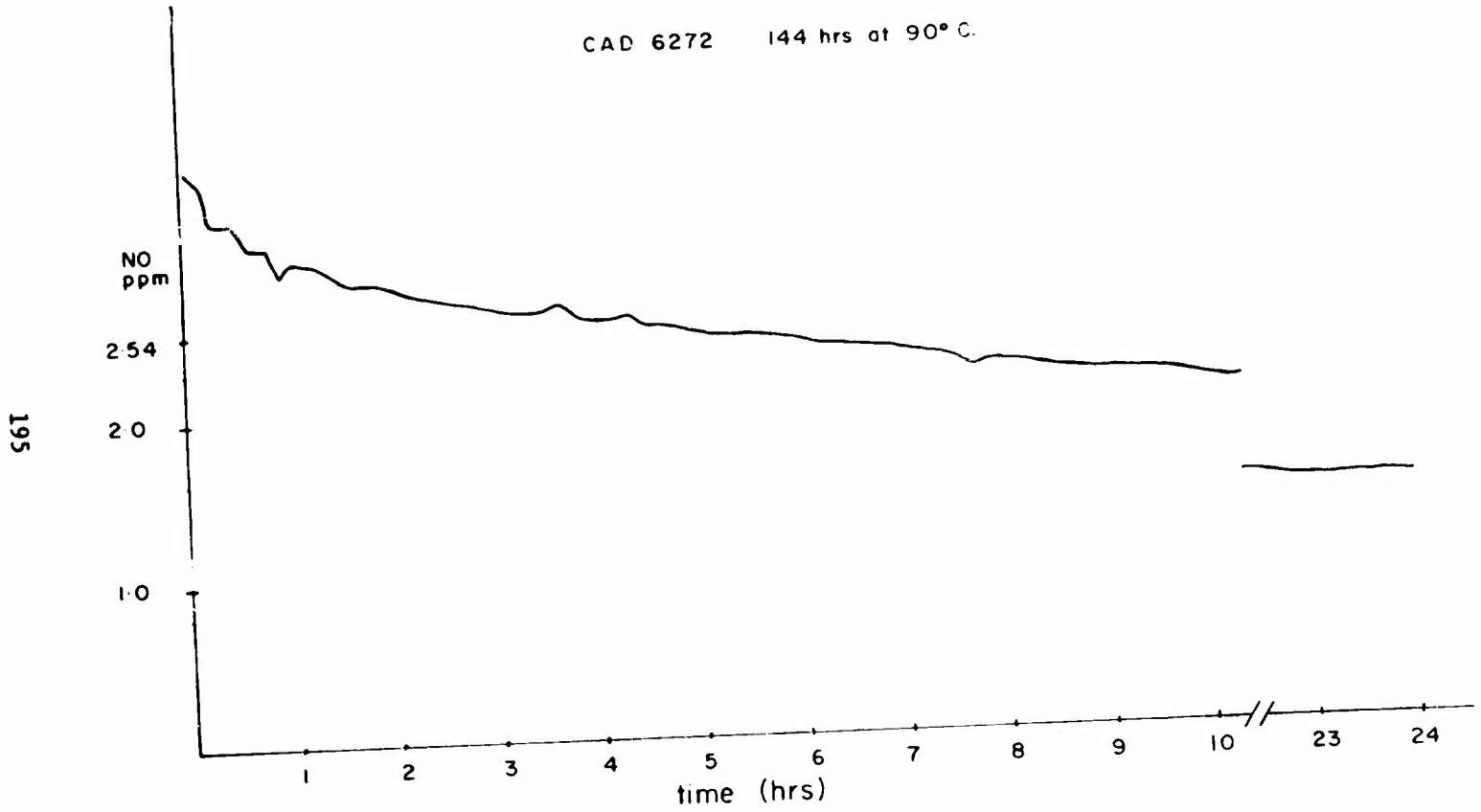


Fig. 4: Approach to Steady-State NO evolution rate

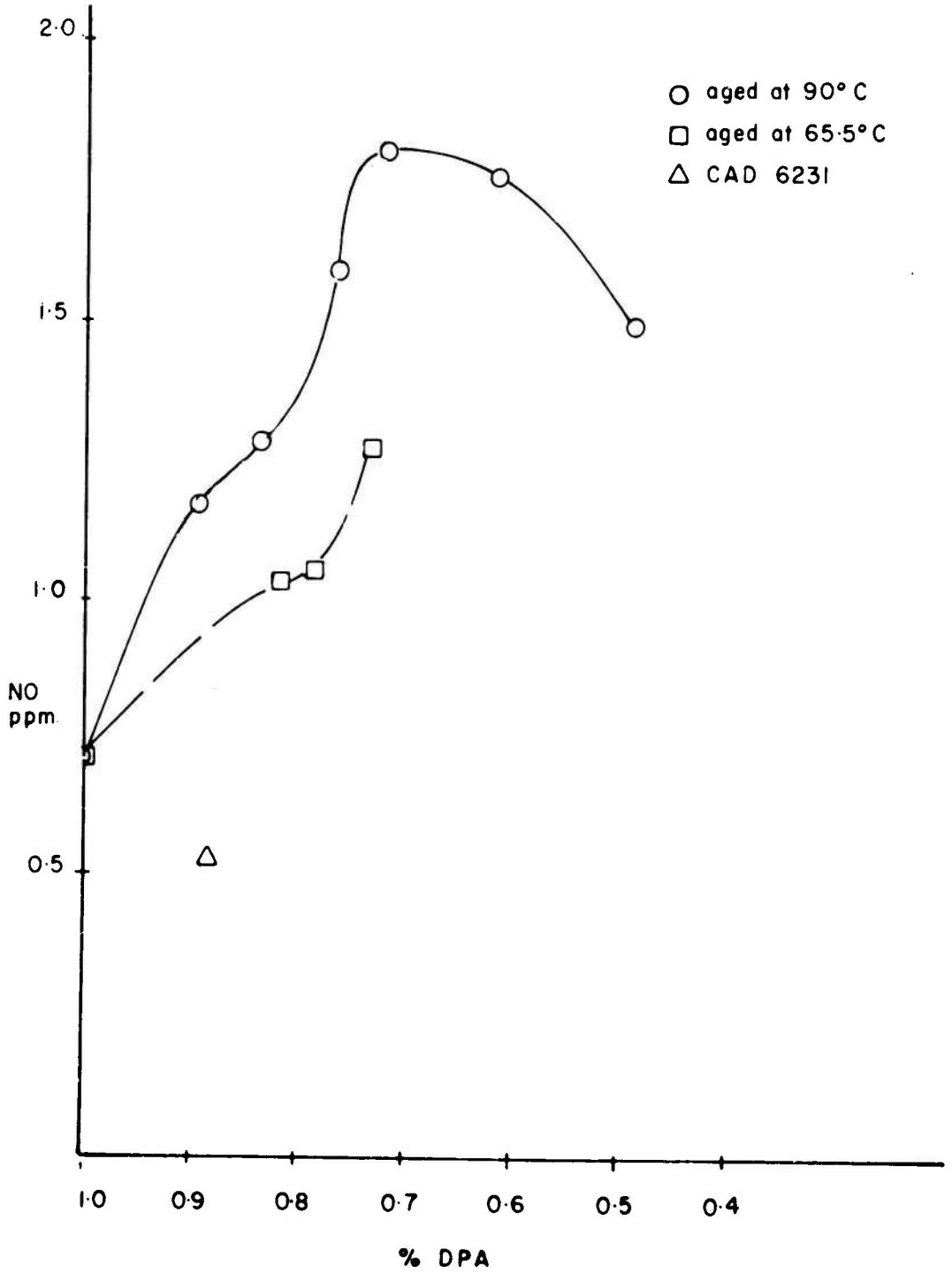


Fig. 5: Steady-state NO evolution rates for artificially and naturally aged propellants

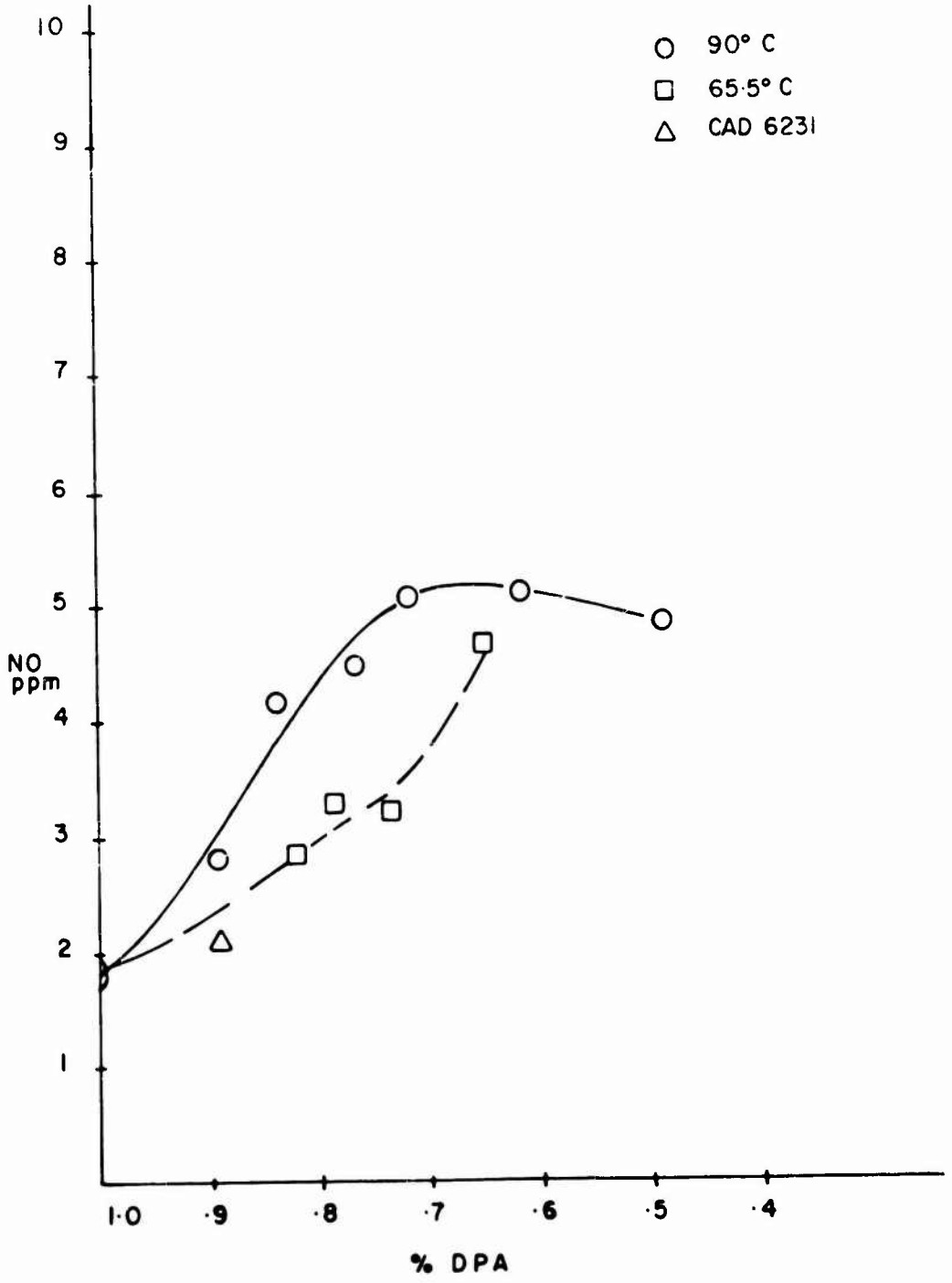


Fig. 6: Initial NO evolution rates for artificially and naturally aged propellants

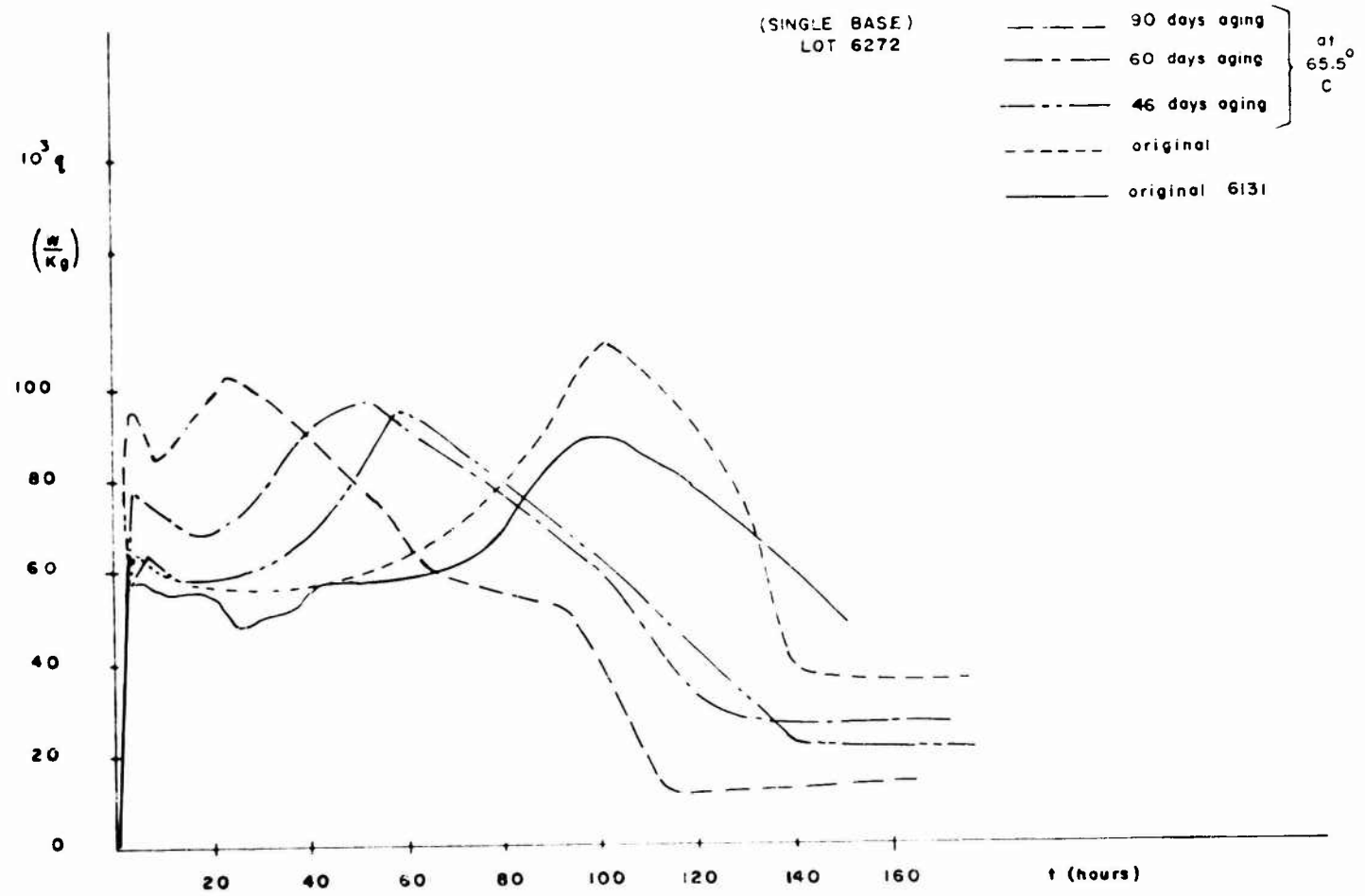


Fig. 7: Heat flow calorimetry thermograms

AN IMPROVED STABILITY TEST FOR NITROCELLULOSE GUN PROPELLANTS

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ABSTRACT

In order to have a good evaluation of nitrocellulose propellants chemical stability, an improved stability test has been developed which consists in keeping propellant samples at 50°C during six weeks and measuring stabilizer content decrease with modern analytical methods.

INTRODUCTION

Safe storability of nitrocellulose gun propellants has been a problem since their development in 1884. As a matter of fact, slow exothermal decomposition of nitrocellulose may raise in some cases propellant temperature up to autoignition. This problem concerns mainly the propellant manufacturer, the department responsible for control and acceptance, and the department responsible for storage. In France they are respectively the SOCIETE NATIONALE DES POUDRES ET EXPLOSIFS, S.N.P.E. (National Company For Propellants and Explosives) and the Division du Contrôle Pyrotechnique, D.C.P. (Pyrotechnical Control Division of the Army Weapon Technical Command).

Acceptance stability tests generally detect suspicious propellant lots but do not give any idea on safe life limits of propellant lots.

At present, the acceptance stability test performed in France on nitrocellulose gun propellants are :

- 108.5°C VIEILLE Test (1) for single base propellants. It consists in heating 10 g of propellant at 108.5°C (227°F) in a special glass tube with a strip of litmus paper. The heating stages are daily and last no longer than ten hours ; they are stopped when the litmus

paper (changed for each stage) is completely red. The test is finished when change in colours happens in less than one hour. The result is the sum of all heating stages, expressed in hours. This sum must be of more than 70 hours for single base propellants without dinitrotoluene and more than 100 hours for single base propellants with dinitrotoluene.

- 120°C Methyl violet paper test (2) for double base propellants.

A 2.5 g propellant sample is kept at 120°C (248°F) in a glass tube (partly closed with a holed cork) with a strip of methyl violet paper. Time of paper colour change and time to red fumes evolution are noted. Requirements depend on the type of double base propellant.

	Colour change	Red fumes
Ball propellants	> 65 mn	> 5 hours
Tubular propellants	> 60 mn	-
Ballistites	> 45 mn	> 1 hour

All acceptance stability tests in western world are performed at temperatures above 80°C and by this mere fact cannot simulate propellant natural ageing because of the complexity of aging mechanism. In many countries, a lot of work has been done in order to improve the knowledge of propellant decomposition mechanism and to be able to predict safe chemical lives of propellant lots.

Many of these investigations have used stabilizer depletion as a criterion. As a matter of fact, experimentations have demonstrated that, below a critical residual stabilizer content, propellant decomposition may accelerate and lead to red fumes evolution and autoignition.

TRANCHANT (3, 4) investigated propellant stabilizer depletion between 60°C (140°F) and 100°C (212°F) and deduced a method giving an idea of chemical safe life. M. ROTH (5) developed a spectrophotometric method for the determination of stabilizer in propellants.

All this work eventually resulted in drafting a Stanag (6), Stanag 4117 approved by N.A.T.O. members. It consists in heating sixty days at 65.5°C (150°F) a sample of the propellant to be tested and determining spectrophotometrically the extracted stabilizer content before and after heating. Requirements to insure a safe chemical life of five or ten years are on final stabilizer content and on stabilizer loss. This test is a real improvement in comparison with what was done before, but it has two drawbacks :

- 65.5°C is too high a temperature and modifies the mechanism observed at normal storage temperatures.

- spectrophotometric analysis of stabilizer is not accurate enough because it does not differentiate initial stabilizer from its nitrosated and nitrated derivatives (case of diphenylamine) appearing during aging.

So, complementary investigations have been undertaken in France.

PRELIMINARY INVESTIGATIONS

Many experimentations have been carried out by S.N.P.E. under sponsorship of Service Technique des Poudres et Explosifs, S.T.P.E. (Propellants and Explosives Technical Service) and in connection with D.C.P.

The aim was to quantify the effect of various parameters on the rate of nitrocellulose propellant decomposition in order to define a new stability test (on the same basis as Stanag 4117) giving more reliable information on propellant decomposition rate during natural aging.

The parameters which were investigated were :
- temperature
- tightness of vessel
- propellant water content

A survey of this work is given hereafter.

Effect of temperature on stabilizer depletion

Experimentations have been conducted mainly on three types of single base, diphenylamine stabilized propellants :

- B 19 T (0.36) C, single base without dinitrotoluene coated with ethyl centralite, used in 30 mm aircraft ammunition

- B 19 T (1.6), single base without dinitrotoluene used in 105 mm tank ammunition

- LB 7 T (1.2), single base with dinitrotoluene and dibutylphtalate, used in 100 mm Navy ammunition

40 g of propellant are introduced in a glass tube closed, but non hermetically, by a stopper (the same as the one used in Stanag 4117) and kept at fixed temperatures. The temperatures are 90°C, 80°C, 65.5°C, 50°C, 40°C (194°F, 176°F, 150°F, 122°F and 104°F), the heating stages being from 30 days to 360 days. The stabilizer is determined either by gas chromatography (G.C.) or by thin layer chromatography (T.L.C.). With the second method, real diphenylamine and its nitrosated and nitrated derivatives are determined separately whereas the first one gives real diphenylamine content plus about one half of N-nitrosodiphenylamine (first D.P.A. derivative observed in aged D.P.A. stabilized nitrocellulose propellants).

Results are given on figures 1 to 5. Hereof it is possible to deduce that :

- diphenylamine depletion (determined by thin layer chromatography) obeys a first order law at every temperature.

- rate constants of these reactions obey Arrhenius laws (see figure 6), the apparent activation energies of which are different when the propellant contains or not dinitrotoluene. The linear regression coefficient obtained when plotting logarithm of rate constant versus reciprocal absolute temperature are better than 0.99 in all cases.

Propellant type	Single base without D.N.T.		Single base with D.N.T.
	B19T(0.36) C	B 19 T (1.6)	LB 7 T (1.2)
Activation energy between 40°C and 90°C	21,6 kcal/mole	23,8 kcal/mole	29 kcal
Correlation Coefficient	0.998	0.990	0.991

As a consequence of these results, it is possible to say that, if at 65.5°C a B and a LB propellant have the same rate of stabilizer depletion, at lower temperatures, LB propellant will deplete comparatively more slowly its stabilizer than the B propellant : *a 65.5°C stabilizer depletion test does not give a good idea of what happens at lower temperatures : 50°C, 40°C or ambient temperature.*

Effect of tightness of test tube :

In order to assess the influence of tightness on stabilizer depletion rate, experimentation have been carried out at 40°C during one year on a single base propellant without dinitrotoluene (B 19 T (0.36)C) kept in

- open tubes
- same tubes as Stanag 4117
- hermetically sealed tubes.

The results (see figure 7) show that the rate of stabilizer depletion is far slower with open tubes than with Stanag 4117 tubes or hermetically sealed tubes. It seems to be due mainly to the elimination by evaporation of propellant residual water : *a stabilizer depletion test must be performed in sealed tubes or at least in closed tubes in order to prevent propellant residual water escape which may alter results.*

Effect of propellant water content :

As a complementary work on tightness effect it was necessary to study the effect of propellant water content on stabilizer depletion rate.

Experimentation has been carried on at 50°C on two samples of a single base propellant without dinitrotoluene (B 19 T (1.6)) with initial water contents of 0.9 % and 2.0 %. Propellant was kept in hermetically sealed or simply stopper closed tubes.

Results (see figure 8) show that :

- even in dry surrounding atmosphere, a high initial water content involves a faster depletion of stabilizer than a low initial water content (propellants kept in stopper closed tubes),
- in hermetically sealed tubes, stabilizer depletion rate also increases with initial water content, *a stability test must be performed on the propellant containing its normal water content and in*

such conditions that water cannot escape during the test.

50°C TEST AND RESULTS

Description of 50°C test :

All the results of the investigations partly above mentioned have led to the definition (common to S.N.P.E. and D.C.P.) of a stabilizer depletion test, known as 50°C test, whose main characteristics are under-mentioned :

- condition the propellant to be tested 48 hours at 20 ± 2°C and 65 % relative humidity,
- heat the propellant (not ground) at 50°C during 42 days (six weeks),
- gas chromatographic analysis of extracted stabilizer before and after heating,
- determination of stabilizer content decrease.

Appendix 1 gives details on the complete method. A duration of 42 days was choosen because it usually corresponds with a stabilizer content decrease large enough to be detected with sufficient accuracy. However, a modified method is investigated in which high performance liquid chromatography is substituted to gas chromatography. This new analytical method which amplifies measurement results is more accurate (7, 8).

RESULTS

The test has already been performed on more than 200 lots and samples of several single base and double base propellants. Four laboratories (three from S.N.P.E. and one from D.C.P.) have taken a part in this work.

As a general observation, it has been established that the results of the 50°C test depend on the family and the type of propellant :

- single base base propellant without dinitrotoluene or plasticizer deplete their stabilizer more quickly than propellants containing these ingredients,
- double base propellants give results similar to single base propellants containing dinitrotoluene (see figure 9).

An evaluation of the significance of the results of this new test has been undertaken in order to know its real meaning and to compare it with other usual stability tests.

Numerous accelerated aging of propellant samples at 50°C during six, twelve and twenty four weeks have demonstrated that the comparative classification of propellants obtained after six weeks (with regard to stabilizer content decrease) was maintained for longer periods. This test, though nos longer than six weeks, allows to have a good idea on future evolution of propellants tested.

A comparison of results obtained on same propellants lots at 50°C test and at 108.5°C VIEILLE Test (French acceptance test for single base propellants) indicates there is no correlation : two lots may give very different 50°C test results though giving same results at 108.5°C VIEILLE Test (see figure 10). In the same way, a comparison with Stanag 4117 results has shown there were no correlation, even for a given propellant type.

It demonstrates the limites of these two tests.

CONCLUSIONS AND RECOMMENDATIONS

Stability tests used in western world are not satisfactory if one wants to predict the safe storability of gun propellants. Investigations conducted on France have resulted in the definition of a new test, derived from Stanag 4117, and consisting in determining stabilizer content decrease of a propellant sample kept six weeks at 50°C. This test has the advantage of being performed at a temperature not far from normal storage temperatures which makes it realistic. It has the drawback of a total duration of about seven weeks, which is too long for an acceptance test. It seems it realizes the best compromize between all the requirements a stability test must satisfy.

Numerous complementary experimentations are in progress in order to establish its real significance. A comprehensive opinion will reliably be reported only after visiting ammunition lots containing propellants tested in 1976 and 1977 (in 1981 - 1982). The problem of fixing requirements on stabilizer content decrease will be approached when sufficient comparisons between results of the test and results of natural aging are available. But now, this test is usually performed on France, either by the propellant manufacturer wanting to know the effect of changing a stage of manufacturing process on propellant stability, or by the Pyrotechnical Control Division wishing to know more about storability of propellant lots.

It is wished that this test be investigated in many countries in order to accumulate a large number of results (obtained preferably by using liquid chromatography). The final aim is to provide a common method giving a good evaluation of propellants stability.

We thank MM. DREYFUS and LEVEQUE (D.C.P.) for giving us a lot of results used in this work.

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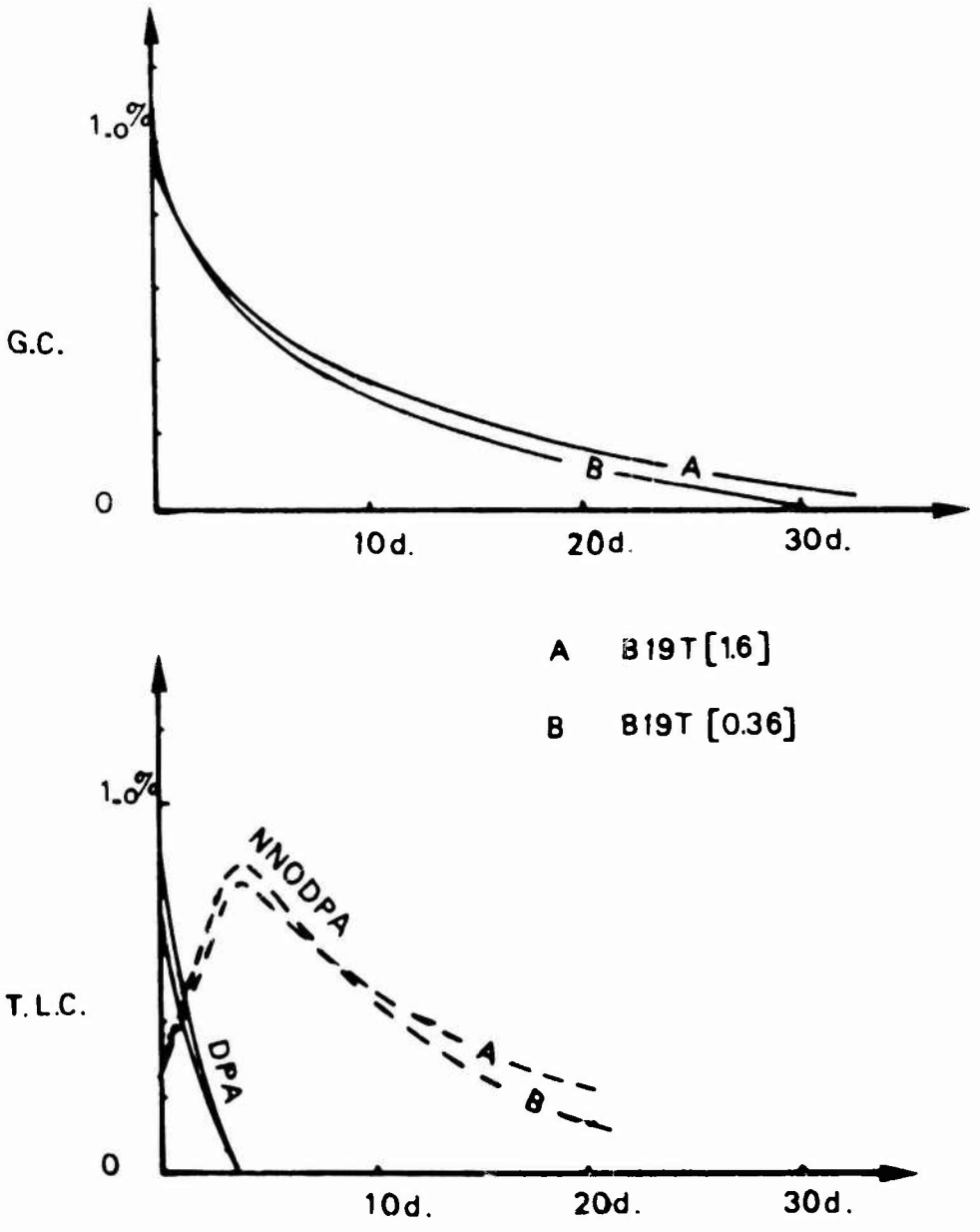
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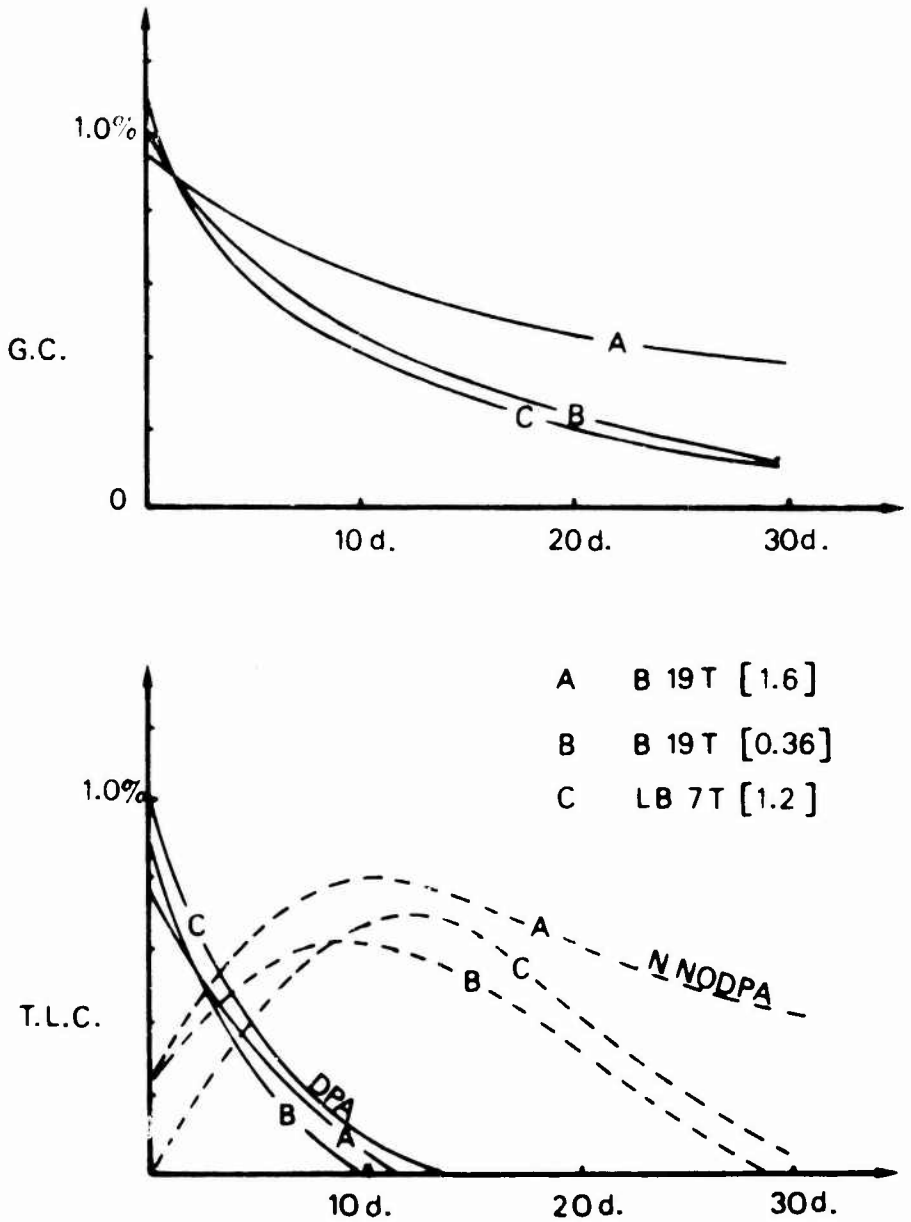
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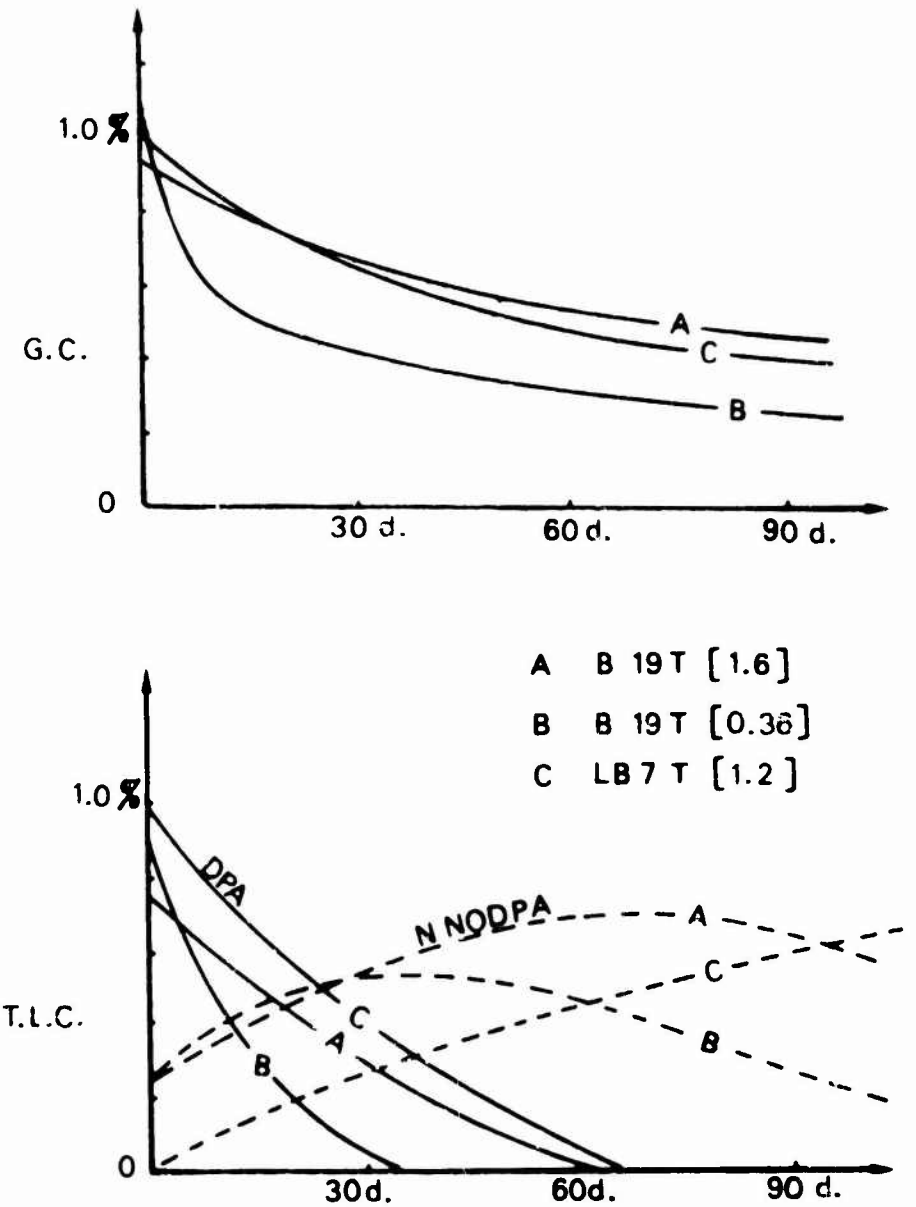
STABILIZER CONTENT AS A FUNCTION OF TIME AT 90°C

Figure 1



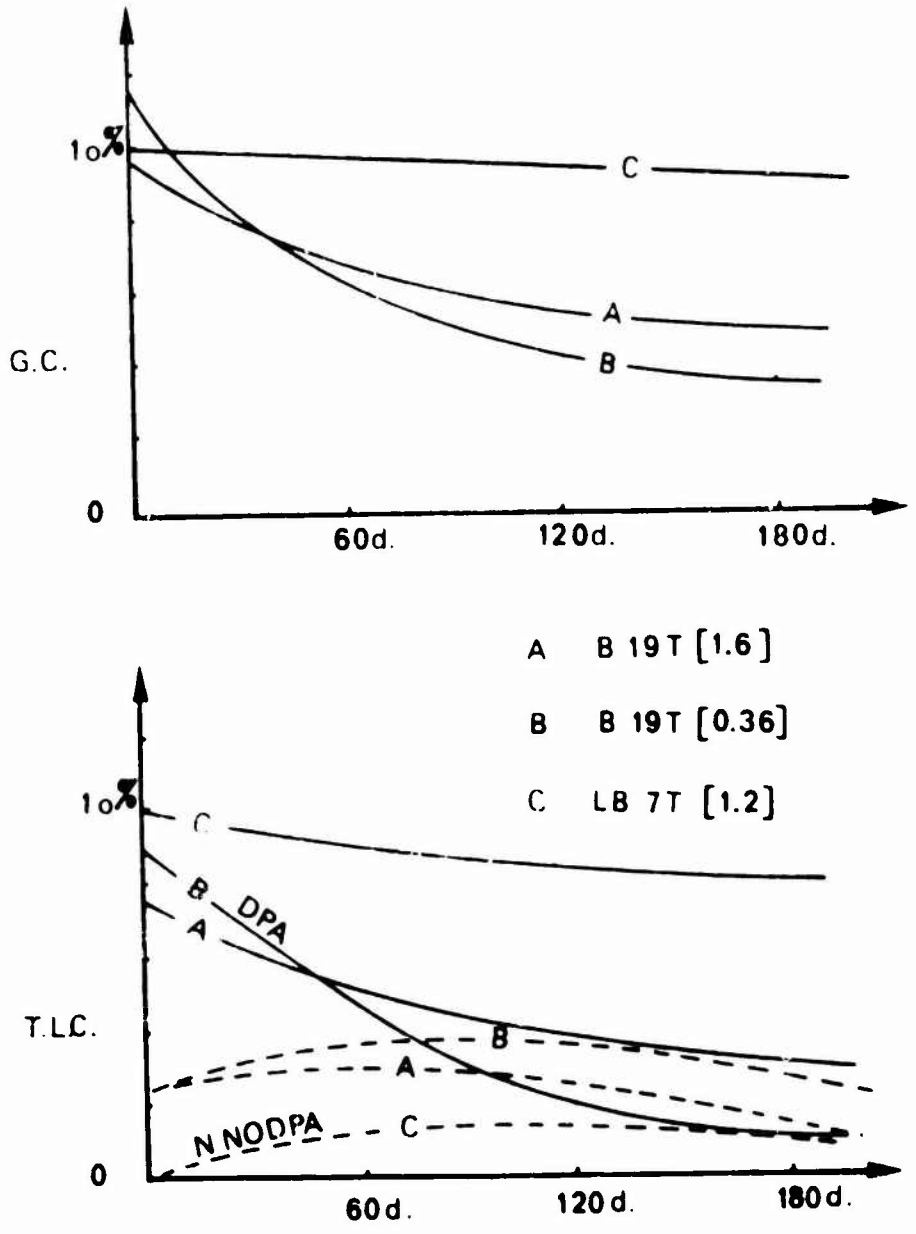
STABILIZER CONTENT AS A FONCTION OF TIME AT 80°C

Figure 2



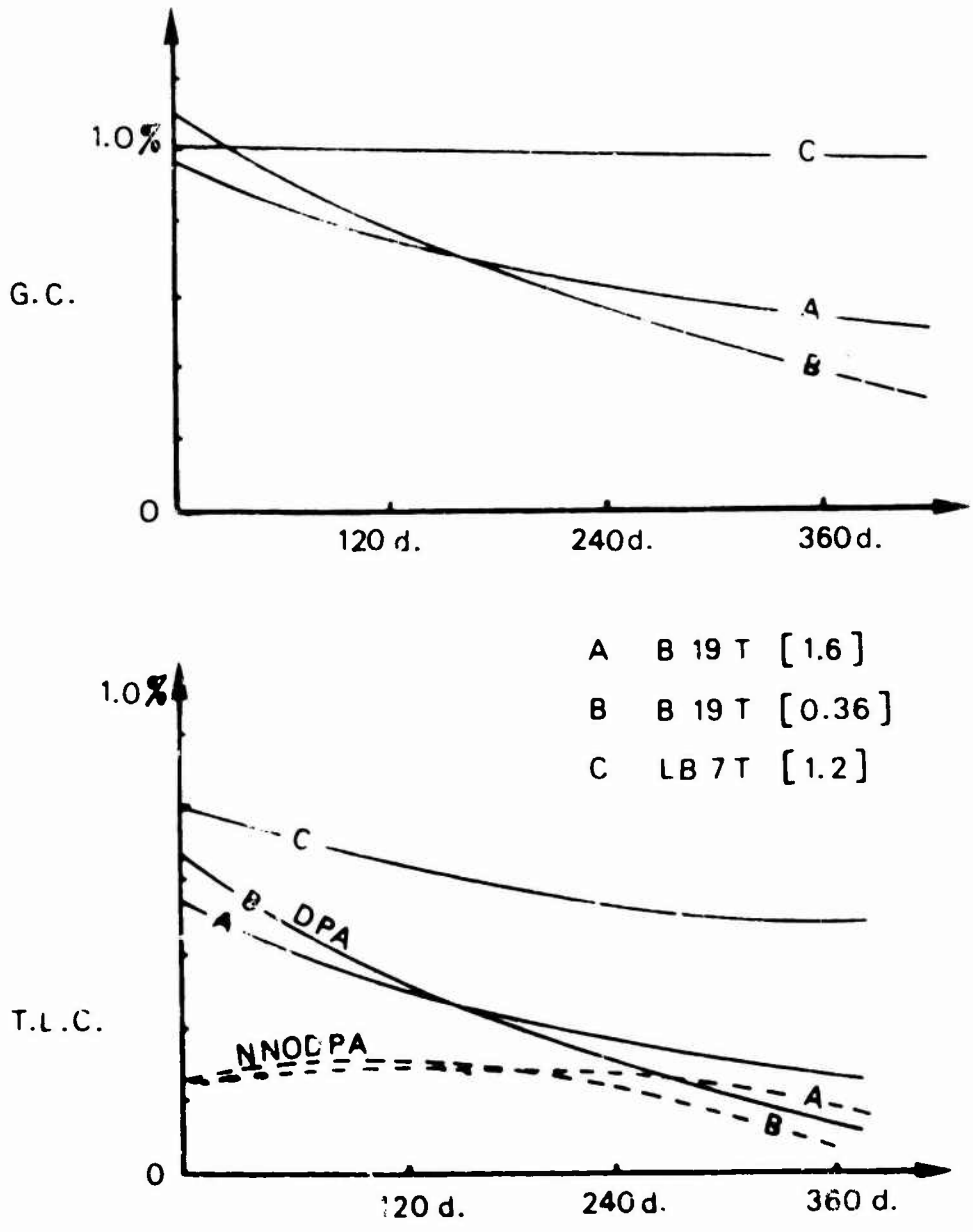
STABILIZER CONTENT AS A FONCTION OF TIME AT 65.5°C

Figure 3



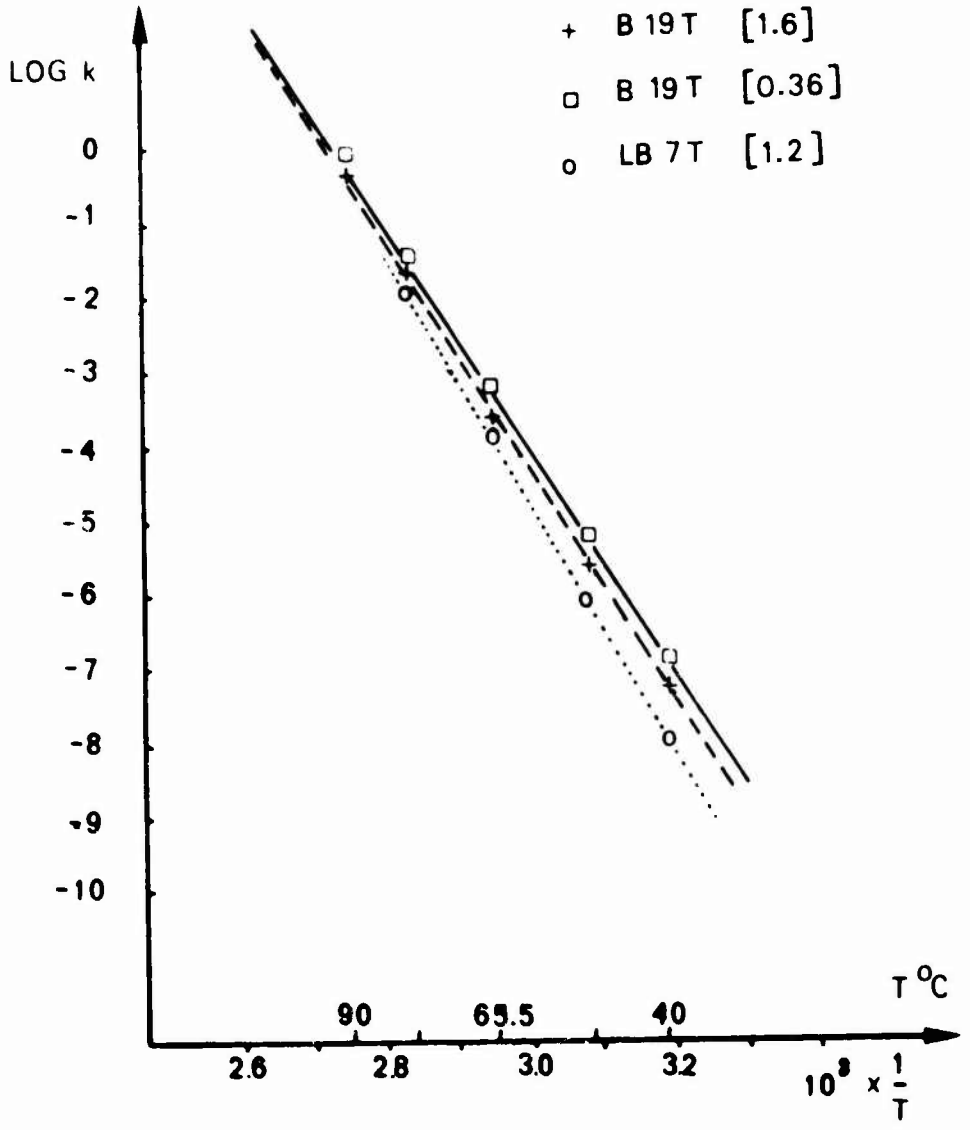
STABILIZER CONTENT AS A FUNCTION OF TIME AT 50°C

Figure 4



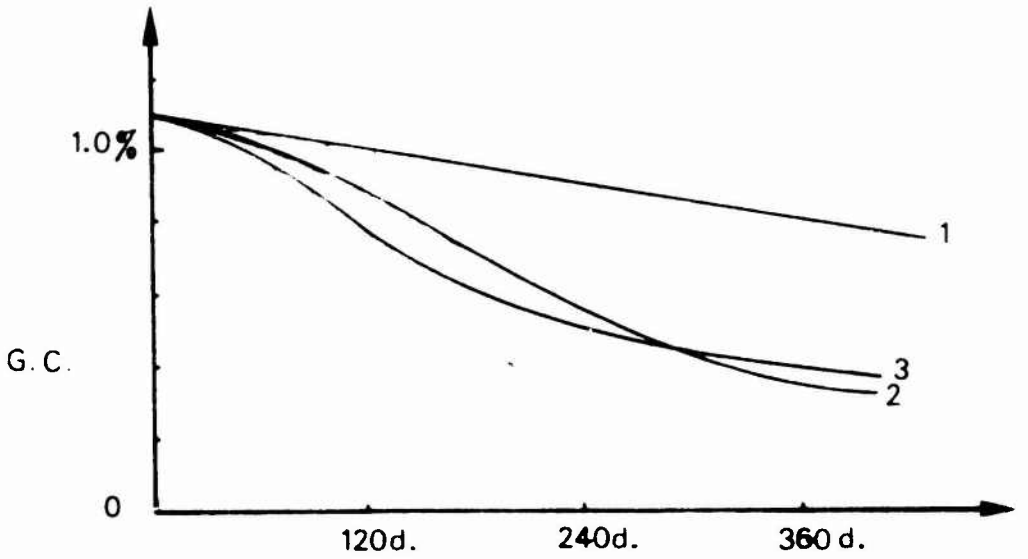
STABILIZER CONTENT AS A FONCTION OF TIME AT 40°C

Figure 5

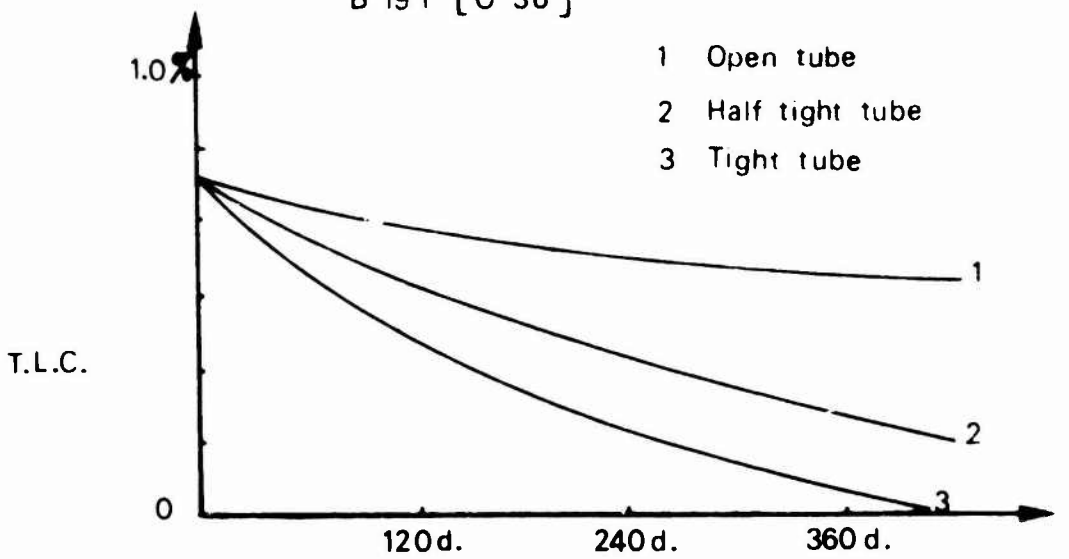


LOG OF RATE CONSTANT AS A FUNCTION OF $\frac{1}{T}$

Figure 6

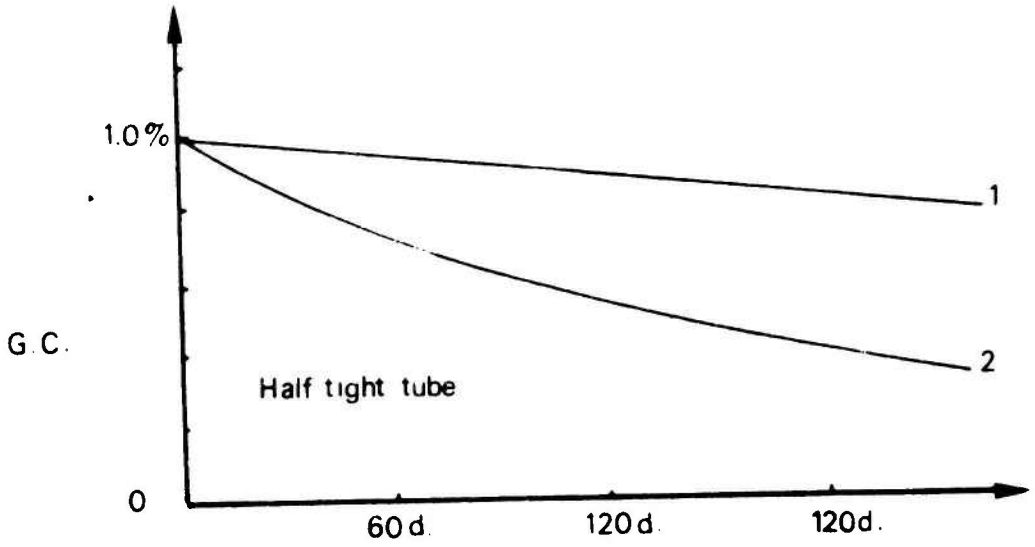


B 19 T [O 36]



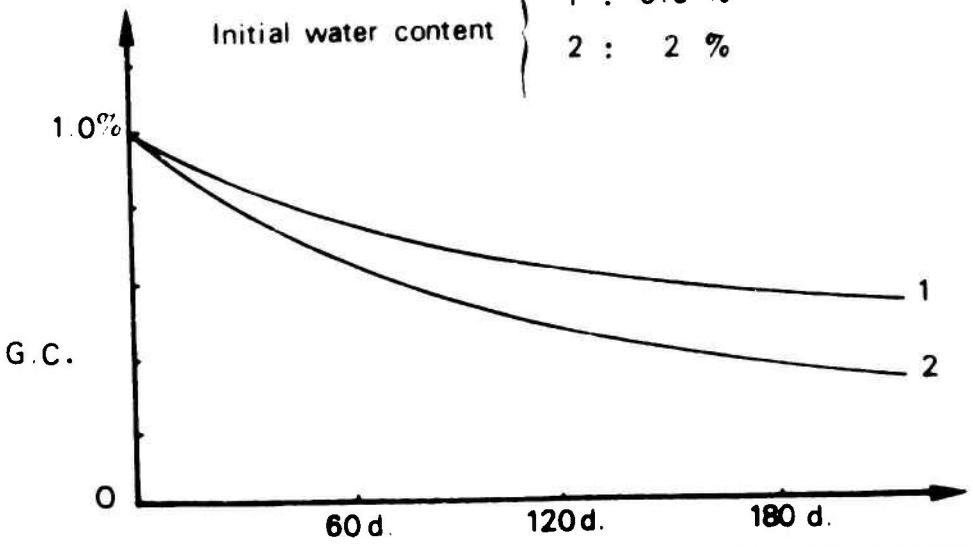
EFFECT OF TIGHTNESS ON STABILIZER DEPLETION RATE AT 40°C

Figure 7



B 19 T [1.6]

Initial water content { 1 : 0.9 %
2 : 2 %



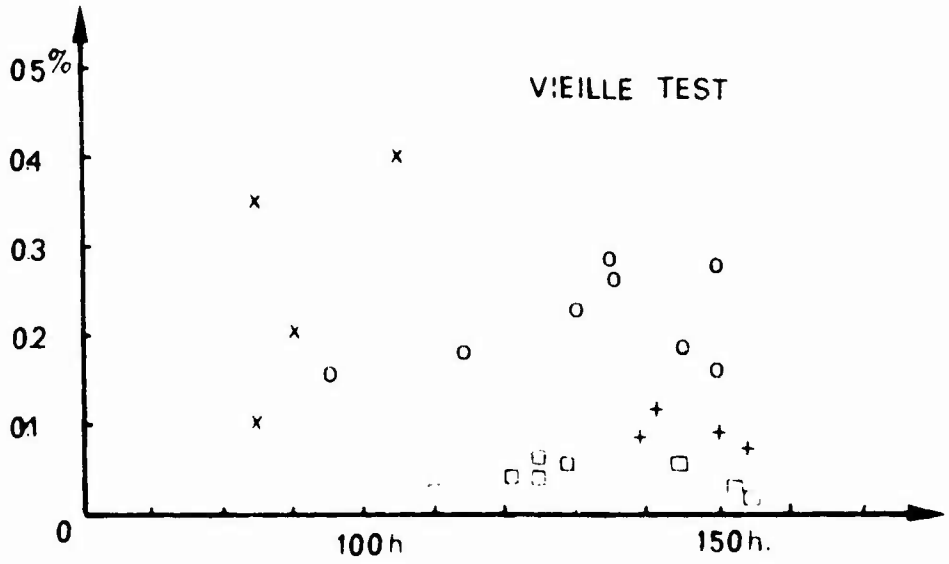
EFFECT OF INITIAL WATER CONTENT ON STABILIZER DEPLETION RATE AT 50°C

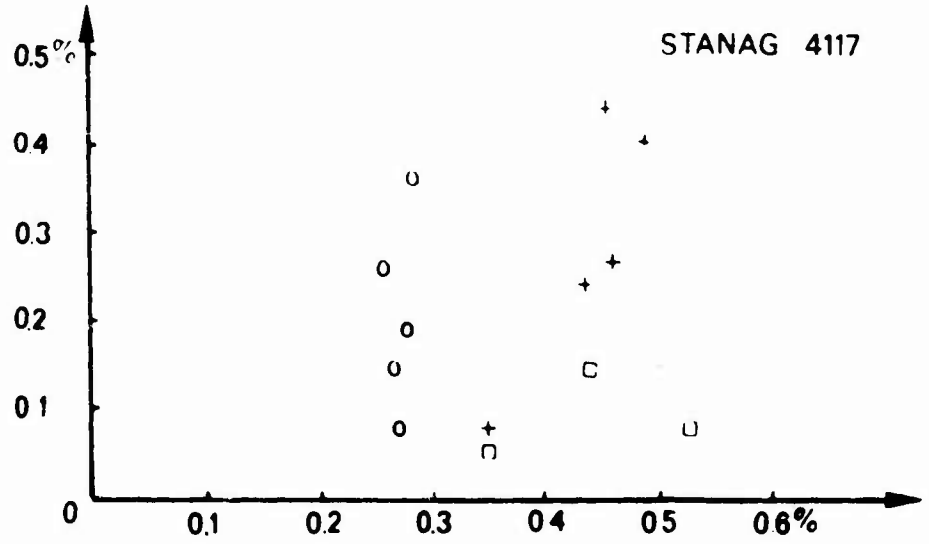
Figure 8

PROPELLANT FAMILY	NAME	NUMBER OF TESTED LOTS	INITIAL STABILIZER CONTENT		FINAL STABILIZER CONTENT		STABILIZER LOSS	
			MEAN	STAND. DEV.	MEAN	STAND. DEV.	MEAN	STAND. DEV.
SINGLE BASE WITHOUT PLASTICIZER OR DNT	B 19 T (1.6)	20	0.94	0.07	0.74	0.10	0.20	0.06
	BTu (0.9) Q	9	1.12	0.07	0.87	0.16	0.25	0.10
SINGLE BASE WITH PLASTICIZER WITHOUT DNT	B7 T (0.4)	9	1.19	0.09	1.10	0.07	0.09	0.03
	BTu (0.9) F	11	0.88	0.09	0.84	0.05	0.04	0.02
SINGLE BASE WITH DNT	LB 19T (1.60)	4	0.97	0.03	0.89	0.01	0.08	0.02
	LBTu (0.4)	8	1.03	0.02	0.97	0.03	0.09	0.03
SOLVENTLESS DOUBLE BASE	GBTu (1.1)	3	0.73	0.06	0.69	0.07	0.04	0.02

Figure 9

RESULTS OF 80°C TEST FOR VARIOUS NITROCELLULOSE PROPELLANTS





RESULTS OF VIEILLE TEST AND STANAG 4117 COMPARED WITH 50°C TEST

Figure 10

A P P E N D I X 1

November 1975 Project CRB - ETBS	50°C STABILIZER DEPLETION TEST	FP 403-C-1 Page 1/3

1 SCOPE :

This method is used for all single base and double base propellants, stabilized with diphenylamine, 2-nitrodiphenylamine or ethylcentralite.

2 PRINCIPE :

A propellant sample is artificially aged 42 days at 50°C in a stopper closed glass tube. The decrease of stabilizer content is measured.

3 APPARATUS :

31 Gas chromatograph equipped with flame ionization
32 Potentiometric recorder
33 1 µl syringe
34 Volumetric flasks
35 Extraction flask
36 Thermostatic block or stove
37 Glass tubes with stopper (see figure)
38 Thermometer ; scale division not greater than 0.2°C

4 MATERIALS (Depending on the type of propellant tested) :

41 Methylene chloride
42 Diphenylamine
43 Ethylcentralite
44 2-nitrodiphenylamine
45 Dipropylphtalate

5 PROCEDURE :

51. Aging

511 Propellant preparation. Condition the propellant before test during 48 hours in an atmosphere of 65 ± 5 % relative humidity at 20 ± 2°C.

Use grains of propellant as they are, when possible. Grind other propellants and keep only 2-5 mm fraction.

512 Aging tubes preparation. Divide the sample into two parts. Keep the first part (25 g) in a tube at 20 ± 5°C ; put the other part into three aging tubes (25 g by tube). Introduce propellant without ramming. Introduce only a whole number of grains for not ground propellants. Close the tube by gently putting the stopper (without grease).

513 Aging. Keep the tubes at 50°C ± 0.5°C during 42 days. Verify temperature with a thermometer inside an empty check tube. When using thermostatic block, the tubes must be fully inside the block.

52. Stabilizer content determination

521 Sample preparation. Grind each sample separately and sieve them through 20 mesh sieve. Determine stabilizer content before and after aging by gas chromatography.

x_o : stabilizer content before aging,

x_i : i = 1, 2, 3 stabilizer content of propellant kept in the three tubes 1, 2 and 3.

Stabilizer content is determined according following methods :

- FP 202 C3 for diphenylamine stabilized single base propellants,
- FP 202 H1 for ethylcentralite stabilized double base propellants,
- FP 202 H2 for 2-nitrodiphenylamine stabilized double base propellants.

6 RESULTS :

61 The differences between stabilizer content of non aged sample and stabilizer contents of the three aged samples are calculated :

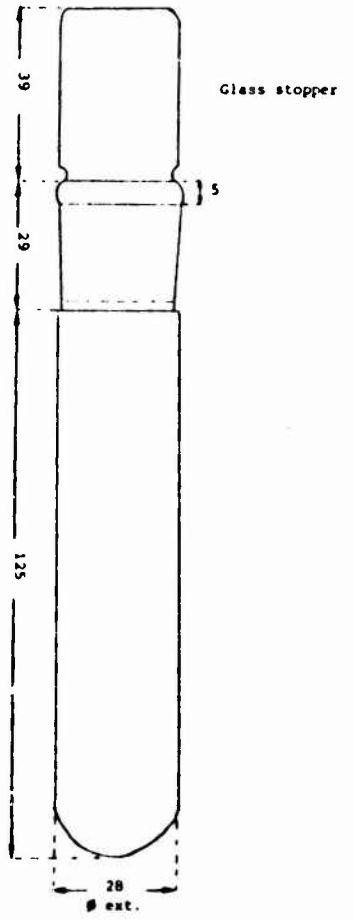
$$\Delta_1 = x_o - x_1$$

$$\Delta_2 = x_o - x_2$$

$$\Delta_3 = x_o - x_3$$

62 The results may also be expressed as a mean decrease on percentage.

$$\Delta\ \% = \frac{\Delta_1 + \Delta_2 + \Delta_3}{3\ x_o} \times 100$$



AGING TUBE

ACCELERATED AGING OF A COMPOSITE EXPLOSIVE

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ABSTRACT

Castable Composite Explosive formulations have been developed at DREV. These composite explosives are mixtures of RDX, HMX, Aℓ and/or $NH_4C\ell O_4$ in a rubbery matrix which is obtained by curing a dihydroxyl prepolymer with a diisocyanate in the presence of a plasticizer, a catalyst and minor additives.

In 1974, a small effort was undertaken to assess the storability of a given formulation by submitting explosive samples to controlled aging at 293, 333 and 353K for slightly over a year. Extensive determinations of mechanical properties were conducted using an Instron Tester. The change of elongation at maximum load can be fitted to an empirical equation. However, although the change of stress at maximum load was found to be a function of temperature, it could not be predicted by a simple relation. Swelling and permeability tests on samples aged at 333K showed that cross-linking increases with time of aging. Infra-red cells were mounted on glass tubes to determine the nature of gases evolved by explosive samples kept at constant temperature in such tubes. It was shown that at 338.5K the N_2O band increased linearly with time of aging.

SYMBOLS

a	constant (h^{-1})
A-2246	2,2'-methylenebis(4-methyl-6-tert-butylphenol)
DEHA	di(2-ethylhexyl) azelate
FeAA	ferric acetyl acetonate
HTPB	hydroxyl-terminated polybutadiene (R-45M)
k	rate of strain change (d^{-1})
RDX	cyclotrimethylene trinitramine
RNB	relative number of crosslinking bonds
T	temperature (K)
t	time of aging (d)
t'	time in gas chromatograph (h)
t_r	retention time
TDI	toluene diisocyanate
V_g	specific retention volume
V_r	retention volume
V_x	volume fraction of polymer in solvent-swollen gel
w	weight of coating (g)

INTRODUCTION

In 1974, a preliminary study was initiated at DREV to characterize the aging of a castable composite explosive based on RDX crystals and polybutadiene binder. Four testing methods were used. These methods included standard mechanical properties measurements to characterize the composite as a whole, gas evolution tests by infrared to follow the evolution of the explosive, the two others, permeability by inverse gas chromatography and swelling to assess binder changes.

Mechanical properties determinations were done on composite samples aged at three different temperatures but for the three other techniques, only samples aged at 333K were used. Furthermore, the tests by infrared and chromatographic techniques were conducted respectively at 338.5K and 373K because no change appeared when conducted at room temperature.

This work describes the formulation of the composite, the oven aging, the procedures used for each testing technique and presents the results obtained.

EXPLOSIVE COMPOSITION AND AGING

Formulation and Processing

The explosive used in this work was a composite material which consists of cyclotrimethylene trinitramine (RDX) crystals supported by an elastomeric binder. The binder used consisted of hydroxyl-terminated polybutadiene prepolymer (R-45M) with di(2-ethylhexyl) azelate (DEHA) as a plasticizer. An antioxidant 2,2'-methylenebis(4-methyl-6-tert-butylphenol) (A-2246) was included in the R-45M at a concentration of 1%. A curing agent, 2,4-toluene diisocyante, was used at a concentration to make the ratio (NCO)/(OH)=1.1. The catalyst was ferric acetyl acetonate (FeAA). Two RDX stocks were used, both supplied by Canadian Industries Limited. One consisted mainly of fine crystals and is designated Class E type B in military specification RDX MIL-P-398C. The other consisted mainly of coarse crystals and is designated Class C type B in the a/m specification. Both stocks were used as received. The detailed composition is given in Table I.

This composite explosive was processed in an helicone vertical mixer with a capacity of 10 gal Model 10CV, manufactured by Atlantic Research Corporation. At the end of the mixing cycle, the composition

was transferred directly, by gravity and under vacuum, into casting molds of about 15 x 13 x 13 cm and cured at 333K for 7 days.

Aging

At the end of the curing period, the composite was machined in slabs of 1.27 cm thick. The slabs were heat aged separately at 293, 333 and 353K in unsealed polyethelene bags.

TEST PROCEDURES AND RESULTS

Gas Evolution by Infrared

Procedure

The infrared method (IR) of studying the accelerated aging of composite explosive is very simple and requires a very small sample for a complete study. It consists in sealing about 3 g of sample, under vacuum, in a test tube which is connected to an infrared cell having a path length of 10 cm and mounted with NaCℓ windows. The test tube is placed in one of the cavities of a metal thermo-regulating block similar to those used for the "Vacuum stability test" of explosive materials. The gases evolved during the heating of the sample at constant temperature (338.5K) are collected through the IR cell which is at room temperature. The cell is taken out from time to time for determining the infrared spectrum of the gases evolved permitting the identification and evaluation of the decomposition products. This method was described in an earlier document (1).

Results

Among the gaseous products evolved from the composite explosive, we noted the presence of N_2O doublets at 2200-2230, 1250-1290 cm^{-1}, CO_2 2330 cm^{-1}, H_2O 3700 cm^{-1}, HCOOH 1075-1095-1100 cm^{-1}, and traces of HNO_2 by the formation of $NaNO_2$ on NaCℓ windows (absorption at 1360 cm^{-1}) after long aging study. N_2O, the major component of the decomposition products, has retained our attention being related directly to the explosive (RDX).

Figure 1 shows the evolution rate of N_2O at 338.5K versus time expressed as one over "t" for a freshly cured composite. During the first 20 days of heating, the evolution of N_2O from the composite is too small to be measurable with this IR cell. Between 20 and 80 days of heating which corresponds to 50 and 12 on the graph (1/t), the evolution is linear meaning that the decomposition is following

a first order process. From 80 to 250 days, 12 to 4 on the graph, the N_2O evolution is again linear with time but the slope is very much increased and probably corresponds to another decomposition mechanism.

Figure 2 shows the normal evolution of N_2O during the heating of RDX at 338.5K under the same conditions. The N_2O evolution rate is slightly smaller than it is for the initial part of the composite explosive curve.

Figure 3 describes the N_2O evolution at 338.5K from composite samples having the same composition but different times of aging. The first one is the same freshly prepared composite while the other three are samples previously aged at 333K for 130, 250 and 375 days. A strong change is noted in the first part of the evolution of N_2O. As shown in Table II, the rate of evolution of N_2O increases regularly with the time of aging. Every sample finally reaches a second stage of rapid evolution of N_2O where all the samples more or less fall on the same line. This behavior could be explained by the action of the binder or its ingredients on RDX decreasing its stability. In the first part of the N_2O evolution curve, the antioxydant neutralizes most of the oxidizing gas, then when the antioxydant is completely depleted, all the samples similarly began showing an increase production of N_2O.

A straight line is obtained in Figure 4 when plotting the slopes of the 'evolution rate of N_2O' versus the 'time of aging' at 333K. This permits to estimate the aged period of the composite explosive at 333K.

Permeability by Inverse Gas Chromatography

Procedure

All the chromatographic measurements were done at 373K on two Vapor Fractometers, Model 154D from Perkin Elmer Co. using thermal conductivity detectors and He as the carrier gas. Turnings from the composite explosive dogbones for mechanical property measurements were put directly into 0.63 cm wide and 30.5 cm long copper columns using normal chromatographic procedures.

Figure 5 compares conventional gas chromatography to the molecular probe, also called inverse gas chromatography. It is noted that in the molecular probe experiment, a known probe, for our purposes nonane or decane, is injected in the flowing carrier gas. The interaction of this probe with the unknown coating (binder) on the inert support (solid explosive) is characterized by changes in the retention times.

The retention time (t_r) is measured from the maximum of the air peak to the maximum of the alkane peak. The flow of the carrier gas is measured to calculate the retention volume (V_r) of gas required to elute the probe. V_r is corrected for the temperature (T) of the gas chromatograph and the pressure drop through the column and transformed to the specific retention volume (V_g) by the following equation:

$$V_g = 273/T \ \frac{V_r}{w}$$

where w is the weight of the coating in g. V_g has the important advantage of being independent from instrumental parameters. The details of this experimental procedure have been published (2, 3).

Results

In brief, the molecular probe test can be taken as the heating in an inert atmosphere of a series of composite explosive samples which have been previously aged in air for various durations. Indeed, it can be expected that any change in the binder will result in a change of permeability of this binder (coating) to the gas probe resulting in variations of the retention volume of the probe.

First, in the gas chromatograph environment, all the samples showed a decrease of the specific retention volume with time (h) in chromatograph which could be plotted as a straight line (Figure 6) using the following equation:

$$\log V_{go}/V_g = a\ t'$$

where a is a constant and V_{go} is V_g at $t' = 0$. Thus, in He, the binder becomes slowly and regularly less permeable to the probe. This form of equation is also characteristic of a first order kinetic process.

However, as can be seen in Table III, the rate of this process changes slightly after 60 days of aging in air. It is obvious that the original sample and the two samples aged for 30 and 60 days at 333K give similar slopes averaging $14.7 \times 10^{-5} h^{-1}$ by the molecular probe while the three samples which were aged for 130, 250 and 375 days gave a second set of similar slopes averaging, $22.8 \times 10^{-5} h^{-1}$. These two sets of slopes indicate that the three samples aged for 130 days and more follow the same trend as the other three but at a slightly faster rate when subjected to heating at 373K under He as in the molecular probe experiments.

Swelling Measurements

Procedure

To check if there was a variation of crosslinking during aging of a composite explosive at 333K, swelling tests were run. Samples of a composite weighing approximately 1.5 g were covered with reagent-grade toluene and sealed in a container for seven days at room temperature. The swollen stock was removed from the solvent and weighed to determine the solvent uptake. After drying the swollen stock under vacuum, the sample was reweighed to obtain the dry weight. From these values, the volume fraction of polymer in the solvent-swollen gel (V_x) excluding filler and the percent gel were calculated by methods described in the literature (4, 5). The relative number of crosslinking bonds (RNB) is approximately proportional to the number of chemical bonds at the branch points and related to the state of cure (6). It is calculated as follows:

$$RNB = V_x^{5/3} \times \text{percent gel}$$

Results

The results in Table IV indicate that the RNB increased from 2.27 to 3.32 as the time of aging increased. This shows that new crosslinking bonds are formed at 333K with time. The low RNB value of 2.36 obtained after 250 days at 333K could not be explained.

Mechanical Testing

Procedure

Each measurement of the mechanical properties at 293K of the heat aged composite explosive was obtained using four JANAF diecut dogbone specimens on an Instron Tester operating at an extension rate of 5.08 cm/min.

Results

Table V displays, for different times of aging, the maximum stress and the corresponding strain and modulus of samples aged at 293, 333 and 353K. From an initial value of 382 kPa after curing, the stress increases as high as 559 kPa for 400 days of aging at 353K when the strain decreases from 20.5% to as low as 3.2%. For approximately the same period of aging at 293K, the maximum stress remains almost unchanged while the strain decreases from 20.5% to 17.5%.

The relative strain $\varepsilon/\varepsilon_o$ and stress σ/σ_o values were plotted against time for the three temperatures of aging (Figure 7). This figure shows that strain decreases monotonicly with time for all temperatures but that relative stress does not. When values of $\varepsilon_o/\varepsilon$ are plotted against 'square root of time', straight lines are obtained (Figure 8) and a constant rate of deterioration (k) can be attributed to each temperature of aging:

$$\varepsilon_o/\varepsilon = k\sqrt[2]{t}$$

where ε_o and ε represent strain at time zero and time t of aging. The values of k tabulated on Figure 8 vary from 0.009 to 0.273 d^{-1} when temperature of aging increases from 293 to 353K.

Using the Arrhenius equation and the aging rate constants, an apparent energy of activation for this aging process was calculated from the slope of the straight line obtained by plotting 'ln k' against 1/T (Figure 9) where T is the aging temperature. The activation energy was calculated to be 48 kJ/mole. From these results, it is justified, within the range of temperatures and period of aging considered, to calculate the equivalences time-temperature: as an example, 1 day at 353K would be equivalent to 30 days at 293K.

CONCLUSIONS

Tensile tests show that the strength of the castable composite explosive developed at DREV increases with time of aging at 293, 333 and 353K. The decrease of the relative strain over one year of aging can be defined by one equation.

Swelling measurements and permeability tests by inverse gas chromatography on samples aged at 333K indicate that the binder crosslinking increases regularly with aging with a break between 60 and 130 days.

Gas evolution by infrared proves that the N_2O emission follows a two stage process: the rates during the first stage increase with time of aging while the rates of the second stage are common to all samples.

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INGREDIENTS	WEIGHT PERCENT	
RDX	85.0	
Class E		25.5
Class C		59.5
HTPB R-45M	7.68	
DEHA	6.75	
TDI	0.57	
ADDITIVES		
FeAA (added)	0.005	
SURFACE AGENTS (added)	0.2	

TABLE I – PERCENTAGE COMPOSITION PER WEIGHT

AGING d	ABSORBANCE RATE N_2O abs · t
0	4.2
130	11.4
250	15.0
375	23.6

TABLE II – N_2O ABSORBANCE RATE AT 338.5K FOR AGED COMPOSITE AT 333K

AGING d	'a' x 10^5 h^{-1}
0	15.0 ± 0.5
30	13.8 ± 0.6
60	15.2 ± 0.7
130	23.0 ± 1.0
250	24.0 ± 1.0
375	21.3 ± 0.5

TABLE III – RATE OF SPECIFIC RETENTION VOLUME DECREASE WITH TIME FOR SAMPLES PREVIOUSLY SUBJECTED TO ACCELERATED AGING IN AIR AT 333K

AGING d	RNP
0	2.27
30	2.27
60	2.74
130	3.16
250	2.36
375	3.32

TABLE IV – RELATIVE NUMBER OF CROSSLINKING BONDS IN COMPOSITE EXPLOSIVE WITH TIME OF AGING AT 333K

TEMP. K	TIME d	STRESS kPa	STRAIN %	MODULUS kPa
293	0	382	20.5	2,715
	40	386	19.0	3,004
	90	396	19.0	2,990
	190	406	17.6	3,300
	390	347	17.5	2,846
333	30	435	17.7	3,466
	60	494	14.0	5,195
	130	493	10.3	6,835
	250	516	7.9	8,578
	375	537	7.7	10,280
353	10	499	13.7	5,133
	25	551	10.5	7,820
	50	544	7.0	10,990
	100	504	5.3	13,828
	200	513	4.2	16,612
	300	505	3.5	18,417
	400	559	3.2	22,744

TABLE V – MECHANICAL PROPERTIES AT 293K OF AGED COMPOSITE EXPLOSIVE

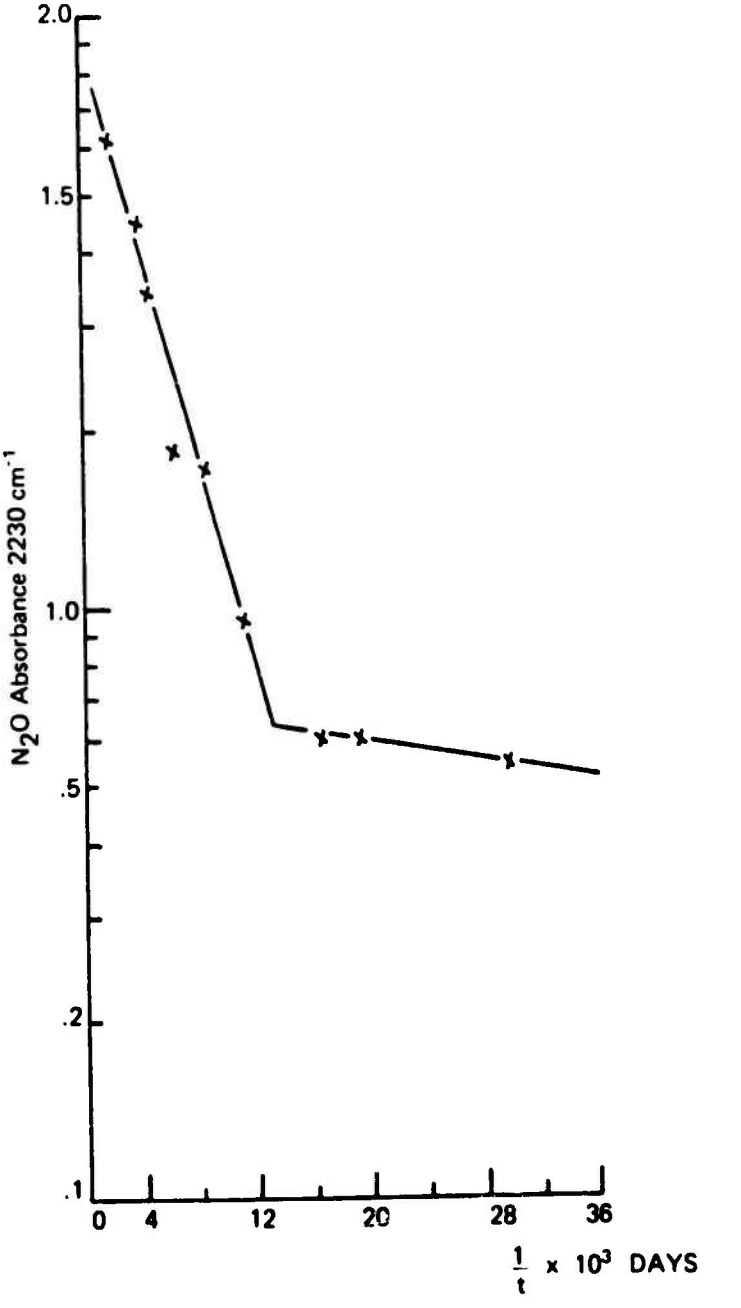


FIGURE 1 – N_2O EVOLUTION FROM COMPOSITE EXPLOSIVE AT 338.5K

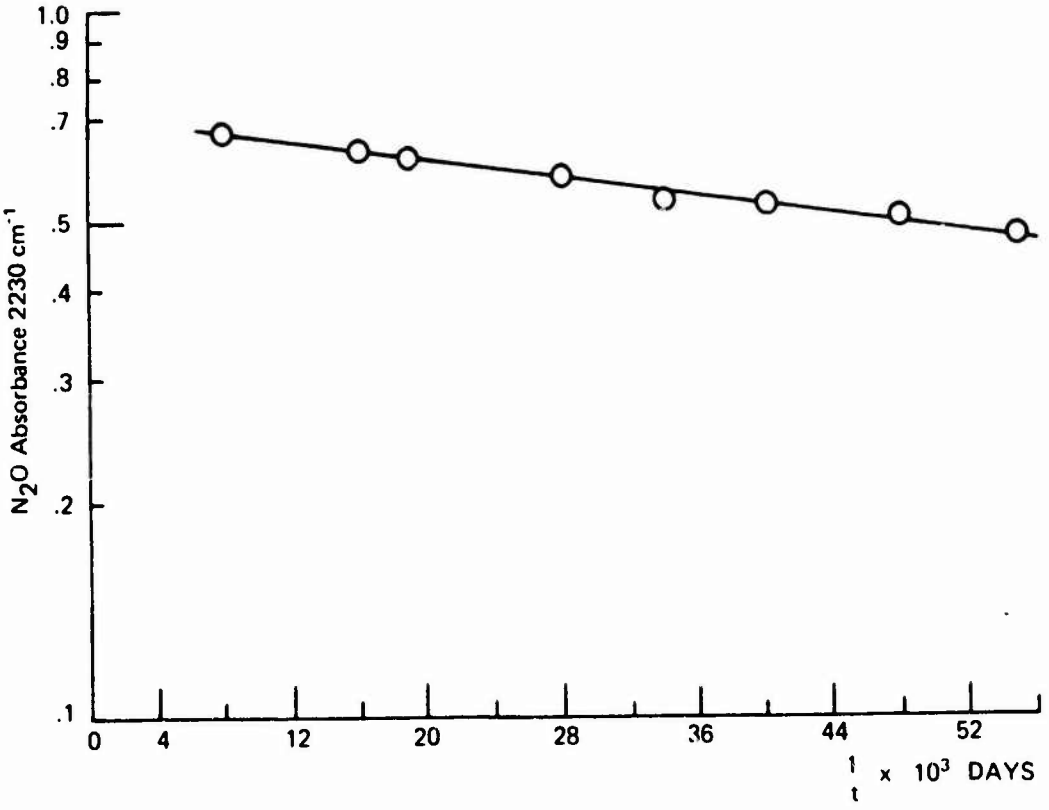


FIGURE 2 – N_2O EVOLUTION FROM RDX AT 338.5K

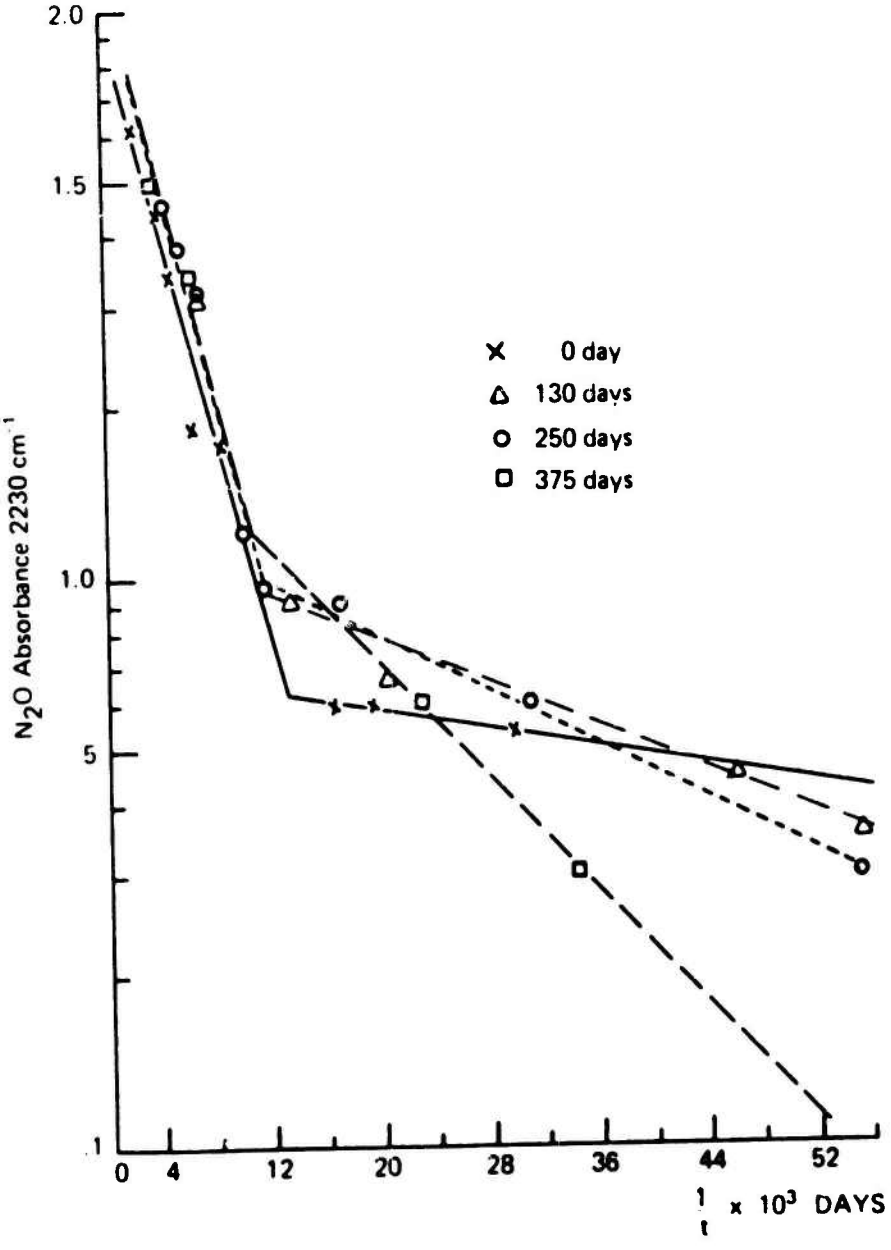


FIGURE 3 – N_2O EVOLUTION AT 338.5K FROM PREAGED COMPOSITE EXPLOSIVE AT 333K

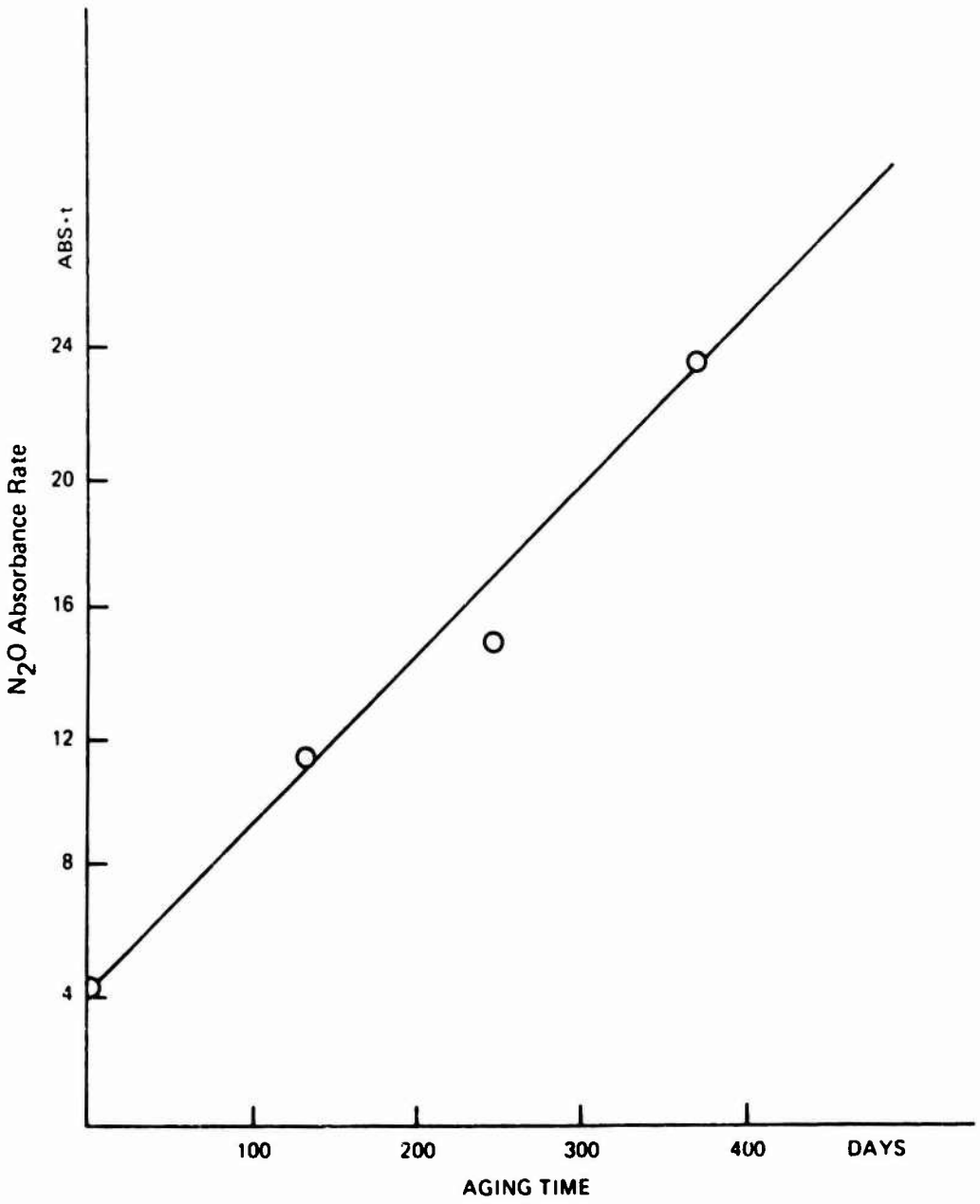


FIGURE 4 – N_2O ABS. RATE AT 338.5K FOR AGED COMPOSITE AT 333K

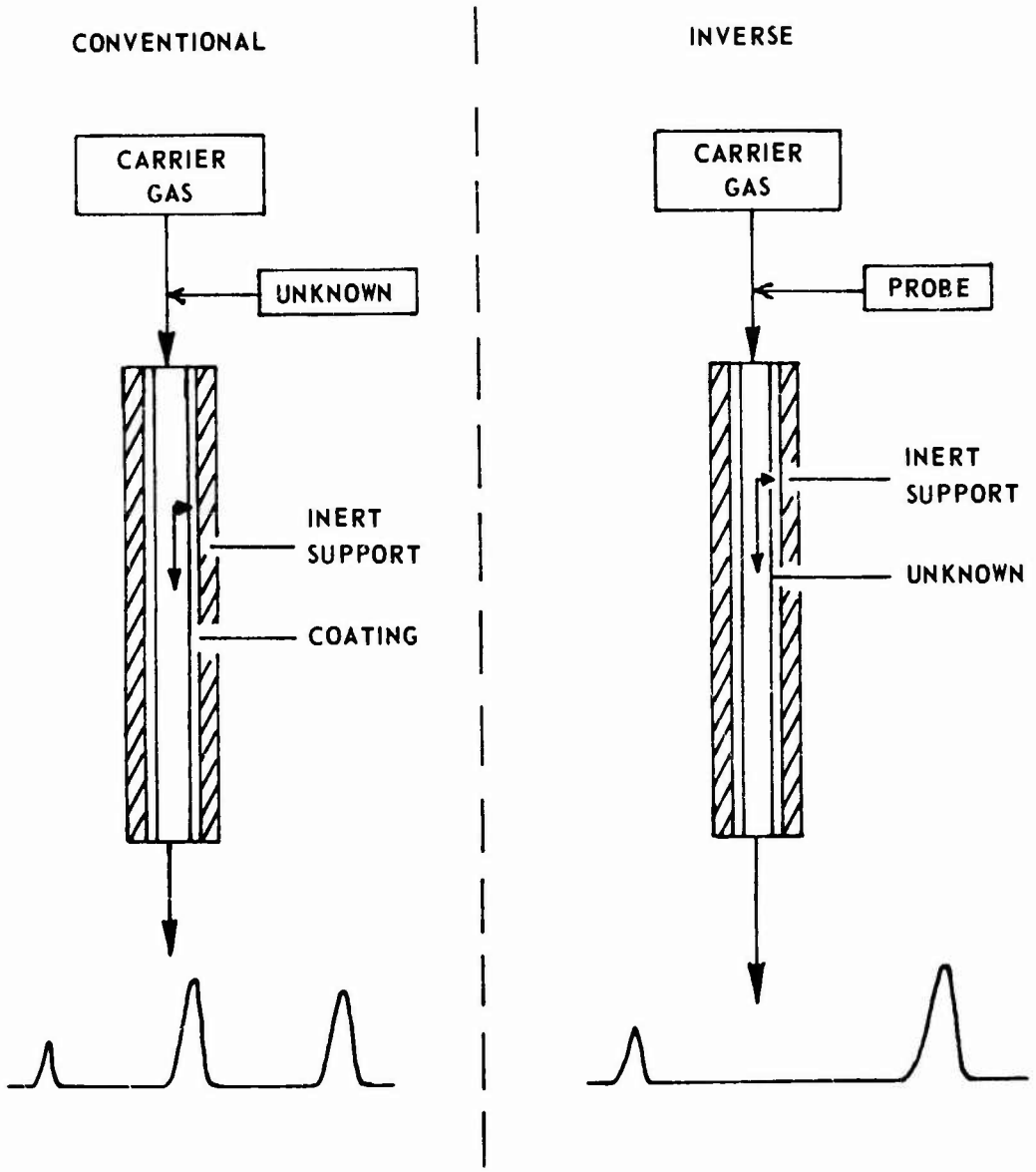


FIGURE 5 – GAS CHROMATOGRAPHY

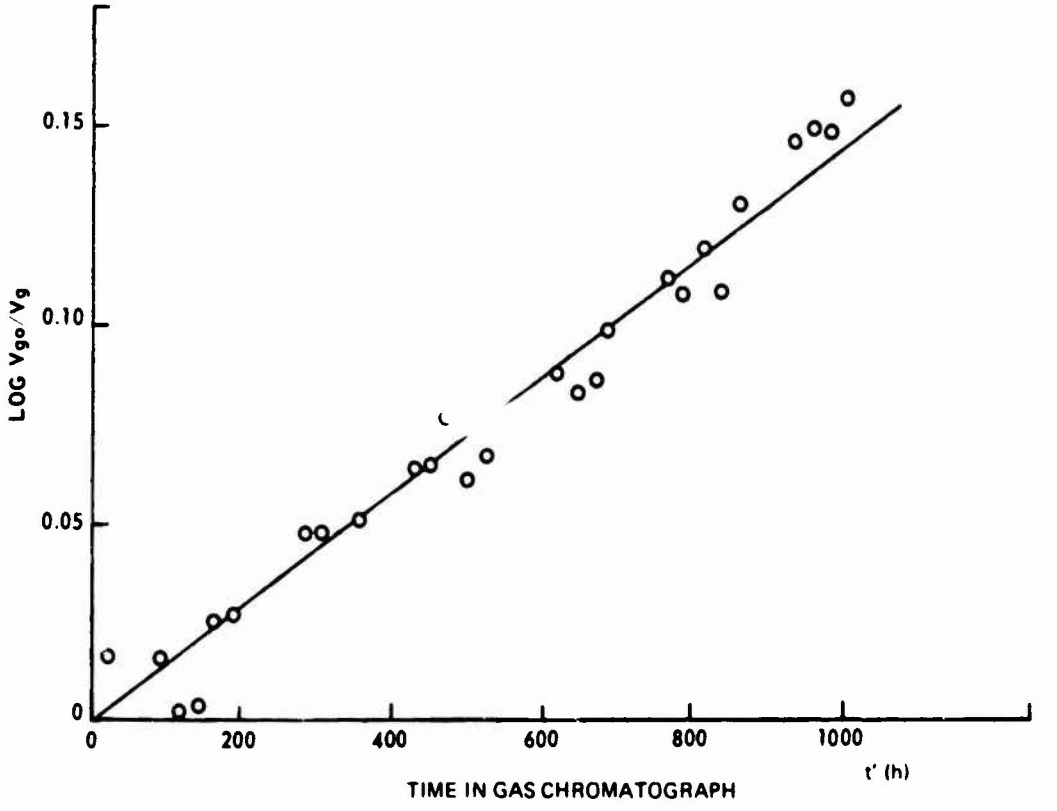


FIGURE 6 – RELATIVE SPECIFIC RETENTION VOLUME WITH TIME IN GAS CHROMATOGRAPH AT 373K

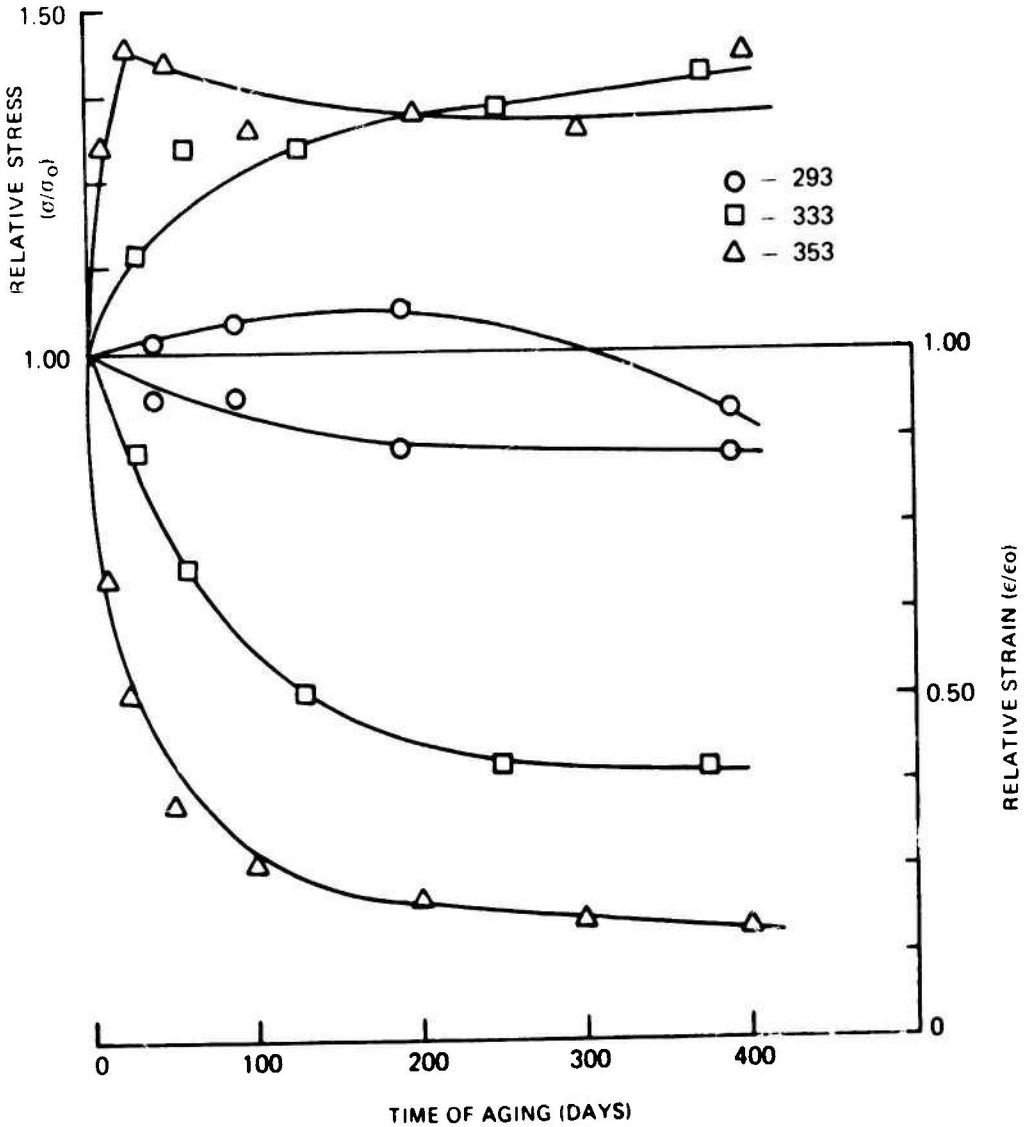


FIGURE 7 – RELATIVE STRESS AND STRAIN WITH TIME OF AGING AT DIFFERENT TEMPERATURES

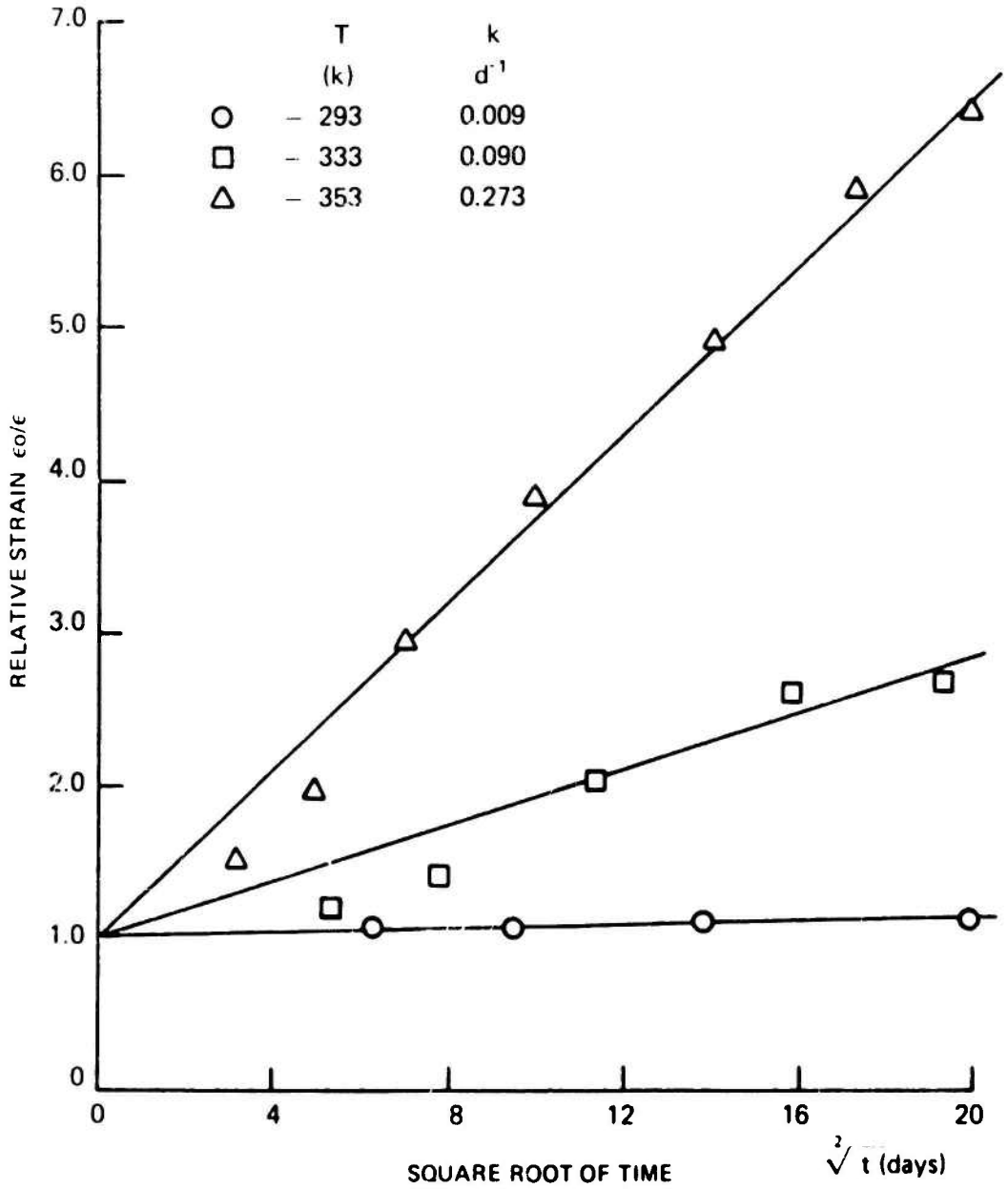
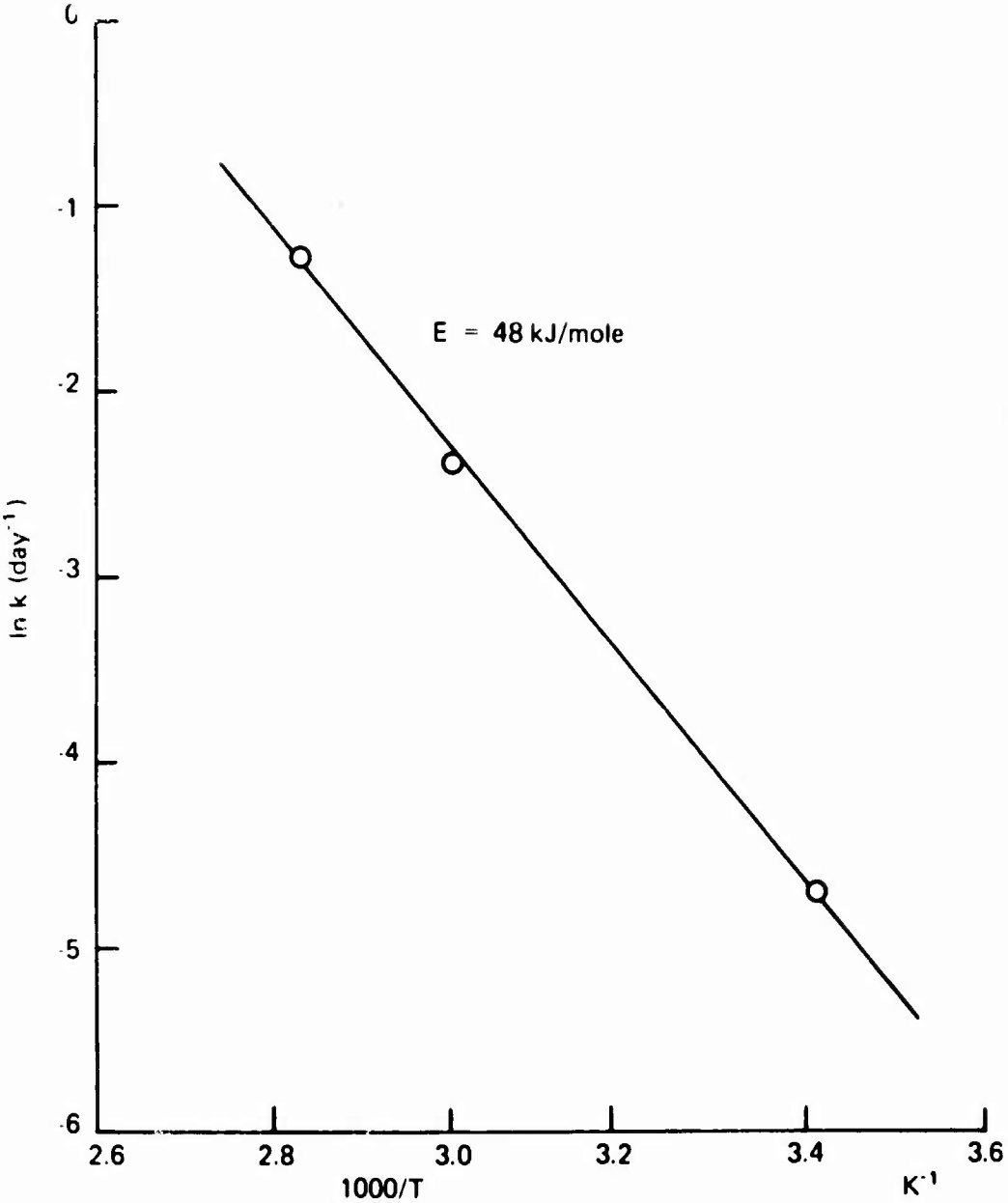


FIGURE 8 – RELATIVE STRAIN WITH TIME OF AGING AT DIFFERENT TEMPERATURES



INVERSE TEMPERATURE OF AGING

FIGURE 9 – ARRHENIUS PLOT OF STRAIN DATA

DETERMINATION OF KINETIC DATA BY THE THERMAL STEP TEST (TST)

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ABSTRACT

In 1968 P.A. Kendall and J.M. Rosen (NOL) published their "Thermal Initiation Apparatus for High Energy Materials". A fluid sample is confined in a stainless steel capillary tube and heated by capacitor discharge up to about 900 K in a few microseconds. Determination of the "delay time to explosion" at different temperatures yields kinetic data of the decomposition of the high energy material, i.e., the activation energy.

By some modifications of the experimental set-up of a comparable test method at the Technological Laboratory TNO, resulting in the so-called Thermal Step Test (TST), it appeared to be possible to test solid materials as well, without previous melting. This has been realized by using a capacitor of a higher value, wider tubes, a strong thyratron and the elimination of self-inductance. However, the activation energies determined by this method do not agree with values obtained from other experimental methods which show values deviating as much as 100 percent in some instances. Therefore, a computer program has been written to compute the delay time to explosion on the basis of geometrical and electrical configuration. So the influence of the time constants in the system can be evaluated and various decomposition mechanisms can be simulated.

INTRODUCTION

In 1968 P.A. Kendall and J.M. Rosen (NOL) published their "Thermal Initiation Apparatus for High Energy Materials" (Ref 1). This test method enables the investigation of the behaviour of thermal sensitive materials in contact with very rapidly heated walls in the temperature range of 600 K to 1300 K. So the experimental input, "stimulus", is a temperature of the wall and the output, "response", is a delay time to explosion. The rapid heating is realized by a discharge of a large capacitor through a steel capillary tube filled with the high energy material under investigation. A further description of the apparatus and the modification developed at the Technological Laboratory TNO, resulting in the so-called Thermal Step Test (TST), is given in the section titled Experimental Set-up.

From the temperature of the wall immediately after the jump and the delay time from the moment of capacitor discharge until temperature increase due to explosion, the pseudo-zero order chemical reaction rate constant and activation energy can be calculated. This problem is treated in the section titled Interpretation of the Experimental Data.

EXPERIMENTAL SET-UP

A scheme of the electric circuit is given in Figures 1 and 2. The capacitor C is charged by a low power high voltage supply through the filled capillary tube R. At the moment when the final voltage V_o or energy $1/2CV^2$ is reached the thyratron is triggered by the trigger unit T, shown in Figure 2, and the capacitor is discharged through tube R. The theoretical maximum temperature of the tube realized in this way is given by

$$(1) \qquad \hat{T}_o = T_\infty + \tfrac{1}{2} CV_o^2 / \{ \rho_2 c_2 l \pi (r_o^2 - r_i^2) \},$$

where T_∞ is the room temperature, ρ_2 the specific mass of the metal of the tube, c_2 its specific heat, l its length, and r_i and r_o the inner and outer radius.

Due to unavoidable self-inductance of the circuit a residual voltage V_∞ occurs, so that equation (1) has to be modified as follows to find the tube temperature after discharge:

$$(2) \qquad T_o = T_\infty + C(V_o^2 - V_\infty^2) / \{2 \rho_2 c_2 l \pi (r_o^2 - r_i^2) \} .$$

It appeared to be feasible to select such dimensions of the circuit that wide stainless tubes could be applied (the tubes tested are

characterized by r_i = 0.15 and 0.7 mm respectively, r_o = 0.3 and 0.9 mm respectively, and l = 50 mm), and solid high energy materials could be tested without previous melting of the substance.

The temperature of the tube can be measured by monitoring the voltage drop V over the tube with resistance R caused by a constant low current i. This current has to be low in order to avoid heating of the tube prior to the discharge of the capacitor. A separate determination of the temperature dependence of the resistance of the tube material enables us to write.

$$T_o = T_{ref} + d_1 \{ R/R_{ref} - 1 \} + d_2 \{ R/R_{ref} - 1 \}^2, \tag{3}$$

where d_1 and d_2 are empirical coefficients of the polynomial giving the temperature dependence of the resistance based on $R=R_{ref}$ at $T=T_{ref}$ and according to Ohm's law.

$$R = V/i_o \ . \tag{4}$$

So the relevant quantities of the TST are the initial voltage V_o of the capacitor, measured by a high voltagemeter, and the value of V/i_o immediately before and after the discharge, monitored on a cathode-ray oscilloscope of UV recorder. A TST sample result is given in Figure 3.

One could wonder which value of T_o, (2) or (3), is the most reliable. Since the resistance of the circuit is low, in particular with our relatively wide tube, the parasitic self-inductance and therefore V_∞ are high, resulting in a low efficiency of the capacitor stored energy. So it is difficult to predict the final temperature T_o on the basis of an adjusted value of the high voltage V_o, because the moment of the explosion cannot be reproduced with an uncertainty smaller than the resonance vibration time of the circuit. An advantage, however, is that the temperature step ($T_o T_\infty$) may be expected to be realized instantaneously.

Kendall and Rosen determine the temperature of the capillary tube by measurement of the electric resistance. However, the temperature dependence of the resistance at high temperatures is not easy to be determined due to radiation losses. The errors in the empirical constants d_1 and d_2 have a great influence by the exponential occurrence of the temperature in the reaction kinetics.

It is useful to correct T_o from (2) or (3) as the contact temperature of two bodies at initial temperatures T_o and T_i, given by

$$(5) \qquad \tilde{T}_o = \frac{\sqrt{\lambda_2 \rho_2 \; c_2}\, T_o + \sqrt{\lambda_1 \; \rho_1}\, T_i}{\sqrt{\lambda_1 \rho_1 \; c_1} + \sqrt{\lambda_2 \; \rho_2 \; c_2}}$$

where λ_i is the heat conductivity, ρ_i the specific mass and c_i the specific heat (i=1 for the body at temperature T_i and i=2 for the substance).

INTERPRETATION OF THE EXPERIMENTAL DATA

Kendall and Rosen (Ref 1) give in their paper a linear relationship between the logarithm of the delay time to explosion τ and the reciprocal of the initial absolute temperature T_o or

$$(6) \qquad {}^{10}\log \tau = A + B/T_o,$$

where A and B are constants. In which way reaction kinetic data such as the activation energy E and the specific heat generation constant $\overline{qk}$ (the product of the specific heat of explosion and the reaction rate constant, which cannot be separated) may be determined on the basis of A and B, is not mentioned by them.

If we suppose that the sample is adiabatically confined in the tube we may use Frank Kamenetskii's formula for the (adiabatic) induction period (Ref 2)

$$(7) \qquad \tau_{ad} = \frac{c_1 R \; T_o^2}{E \; \overline{qk} \; e^{-E/(RT_o)}}$$

(R is the universal gas constant) from which follows the linear relationship

$$(8) \qquad \ln (\tau_{ad}/T_o^2) = E/(RT_o) + \ln \{c_1 R/(E \; \overline{qk})\} .$$

(After substitution of the quantities in this formula by representative numerical values it appears that in general it is not allowed to write this equation in the form of (6).) However, by plotting the measured values of $\ln(\tau_{ad}/T_o^2)$ vs. $1/T_o$ the activation energy E can be computed from the slope and subsequently the quantity $\overline{qk}$ from the intercept.

Now we have to answer the question whether the state of the sample in the capillary tube is really adiabatic. The primarily heated exterior layer will lose its heat to the rest of the sample and, when the temperature of the outside layer is higher than the temperature of the wall by the decomposition of the sample material, also to this wall, since a good thermal contact between the sample and the wall is desired to make adequate heating of the sample possible. The transport to the rest of the sample will be important in the first part of the process and is described by the penetration theory, and the transport to the wall is important in the final part. The exploding layer of the test substance will be situated more to the exterior as the initial temperature T_o is higher.

The concept of the internal heat transport in case of cylinder symmetry has been numerically treated by Merzhanov and Averson (Ref 3) and results in the numerically empirical equation.

$$(9) \quad \ln \{\tau / (T_o - T_\infty)\} = \frac{E}{RT_o} + \ln \left| 0.2\, c_1 \rho / \sqrt{qk} \cdot \{E(T_o - T_\infty)/(RT_o^2 + b)\} \right| .$$

The constant B is equal to 8 in the event of ignition and equa. to 5 for a significant increase in temperature of the sample. (The approximative nature of this formula appears from substitution of $T_i = T_o$, which does not yield the right value of τ, namely τ_{ad}.)

However, considering that the depth of penetration at the moment of the explosion is relatively large and the exploding layer will be near the boundary, we prefer an equation based on heat losses related to the temperature of the metal wall,

$$(10) \quad \rho c_1 V \frac{\partial T}{\partial t} = \rho V \sqrt{qk}\, e^{-E/(RT)} - \alpha S (T - T_o),$$

as a starting point, where T represents the mean temperature of the relevant hot layer of the sample, V its volume, S its surface and α a heat transfer coefficient between this layer and the wall of the tube. When we rewrite (10) as

$$(11) \quad \frac{\partial T}{\partial t} = \frac{\sqrt{qk}}{c_1} e^{-E/(RT)} - F (T - T_o) ,$$

the unknown quantities α, S and V are caught in

$$(12) \quad F = \alpha S / (\rho c_1 V).$$

After some approximations, for instance the Frank-Kamenetskii approximation for the Arrhenius term, we may conclude to

$$\tau = -\frac{1}{F} \ln (1 - F\,\tau_{ad}) \qquad (13)$$

in a pure analytical way, where τ_{ad} is given by (7). It appears that for values of $\tau_{ad} \leq 1/F$ (13) is a false equation. Let us call the initial temperature at which $\tau_{ad} = 1/F$, T_o^*, then we see that T_o^* is a critical or minimum ignition temperature, since τ_{ad} and T_o are negatively correlated. Indeed we have to realize a certain smallest temperature step to cause ignition and so the temperature T_o^* can be determined experimentally.

We suppose that the heat transfer quantity F is independent of the initial temperature T_o and when the adiabatic induction period at T_o^* is given by τ_{ad}^*, it follows that

$$\tau = -\tau_{ad}^* \ln (1 - \tau_{ad}/\tau_{ad}^*). \qquad (14)$$

The ratio τ_{ad}/τ_{ad}^* decreases very rapidly with $(T_o - T_o^*)$ and so we may write in a good approximation (e.g. if $(T_o - T_o^*) > 15$ K)

$$\tau = -\tau_{ad}^* \left(-\tau_{ad}/\tau_{ad}^* \right) = \tau_{ad}. \qquad (15)$$

Hence, the state of the sample may be considered *adiabatic* when the initial temperature T_o differs sufficiently from the critical value T_o^* although this condition is satisfied more quickly at room temperature than at the temperatures of several hundreds of degrees relevant to the TST. This holds even when F is not constant at different values of T_o. Then application of (8) yields the activation energy E and the quantity qk.

COMPUTER MODEL

The caloric behaviour of the tube and its contents is represented by

$$\rho c_p \frac{\partial T}{\partial T} = \vec{\nabla}.\lambda\ \vec{\nabla}\ T + \phi''' \quad , \qquad (16)$$

neglecting convection phenomena in the substance, in which

(17) $\rho = \rho\{r, T(r, T)\}$

is the specific mass (the configuration is supposed to be cylindrically symmetric and the dependence of the radius r serves to distinguish between the properties of the tube and its contents, as a function of the temperature T, varying with time t and place r),

(18) $c_p = c_p\{r, T(r, t)\}$

is the specific heat,

(19) $\lambda = \lambda\{r, T(r,t)\}$

is the heat conductivity, while the heat production density is represented by

(20) $\phi''' = \phi\{r, T(r, t)\}$.

Rearranging the terms yields

(21) $$\frac{\partial T}{\partial t} = \frac{1}{\rho c_p} (\vec{\nabla} . \lambda \vec{\nabla} T + \phi''').$$

It is quite possible to compute with a current and dissipated energy, both varying in time but the relaxation time of the discharging process is about a thousand times shorter than the delay time to explosion and so we are allowed to suppose

(22) $$T(r, t=0) \overset{r}{\equiv} T_\infty + \varepsilon(r - r_i) . (T_o - T_\infty),$$

where $\varepsilon (r - r_i)$ is a Heavyside step function. The chemical heat production density is written as

(23) $$\phi''' = \varepsilon (r_i - r) . \rho \overline{qk} \; e^{- E/(RT)},$$

where $\overline{qk}$ is the specific heat generation constant, E is the activation energy, and R is the universal gas constant.

Equation (22) yields one boundary condition. The other conditions are

$$\vec{\nabla} T\ (r=0,t) = \vec{0} \tag{24}$$

and

$$\vec{\nabla} T\ (r = r_o,t) = \vec{0}, \tag{25}$$

based on neglecting convective and radiative heat losses to the surroundings within the relevant time. So Equation (21) may be solved in a numerical way to compute T(r,t) and the delay time to explosion if ρ, c_p, λ, $\overline{qk}$ and E (physical and chemical constants) are given. A priori the Du Fort and Frankel method (Ref 4) seems to be recommendable, but in practice the Binder-Schmidt method with a fixed distribution of variable steps satisfies better.

EXPERIMENTAL RESULTS

The results of experiments with four liquid and three solid high-energy materials are given in Table 1 and Table 2; application of (3) (no boundary correction as in (5)) in (8) and (9) yields the data shown. So far a determination of τ^*_{ad} and T^*_o is not possible with sufficient accuracy. The last columns in the tables contain values found in literature. Figure 4 shows the plot ln (τ/T_o^2) against $1/T_o$ for one sample.

The effect of corrections of the boundary temperature according to (5) on the calculated activation energy E is limited to only 1%. Variation in the constants d_1 and d_2 in (3) of 5% causes a variation of the activation energy of 2%. Replacement of (3) by (2) as a basis for the initial temperature T_o has an influence on E of 10% at the most except the cases of ethylene glycoldinitrate and the propellant, where 100% difference is encountered.

DISCUSSION

The interpretation of the delay time to explosion τ poses two problems: the initial temperature of the wall of the tube T_o cannot be measured accurately, and it is not easy to correct the induction time τ for non-adiabatic confinement conditions in the tube. A priori we expected to find activation energies of an order

of magnitude of at least 150 kJ/mole, because reaction mechanisms with relative large activation energies may be expected to govern the decomposition process at high temperatures. However, values were found of 20 up to 100 kJ/mole. This discrepancy is confirmed by the fact that substitution E in the computer model of the E-values found experimentally, complemented by literature values for c_i, ρ_i and λ_i (i = 1,2) does not yield an explosion at all. The effect on E of corrections and various computation methods is limited (only a few percent). Nevertheless, the values found by us agree with the experimental results of Kendall and Rosen (Ref 1) and of Wenograd (Ref 8) although these results were obtained by melting the solid materials previous to testing.

It is evident from equations such as (8) and (9) that heat losses due to non-adiabatic conditions give rise to different values of the factor $\overline{qk}$ especially; the influence on the value of E is relatively small.

Possible explanations for the observed discrepancy are: (a) Heating of the sample in contact with the wall is obstructed by a vapour layer, resulting in lower apparent values of the activation energy at high temperatures: as the vapour layer will be thicker at high temperature its insulating effect will be larger. (b) Also, melting and gasification of the substance could influence the decomposition kinetics. (c) Unlike Zinn and Rogers (Ref 9) a bursting criterion of the tube by pressure build-up is not included in the calculation of the time to explosion. (d) Another contributing cause could be electrical skin effect so that most energy stored in the capacitor is dissipated at the outside surface of the capillary tube.

CONCLUSIONS

A preliminary test series with the TST showed experimental results which are in agreement with previous work, but are not well explainable in terms of self-heating theory and known reaction kinetics. Further investigations on this rather direct and relatively simple method on thermal decomposition in the milliseconds domain are planned to reveal additional information on the physics involved. Modifications and improvements may appear to be possible, so that the final goal, viz. data on decompositions kinetics in the high heating rate regime may be obtained.

ACKNOWLEDGEMENT

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Table 1

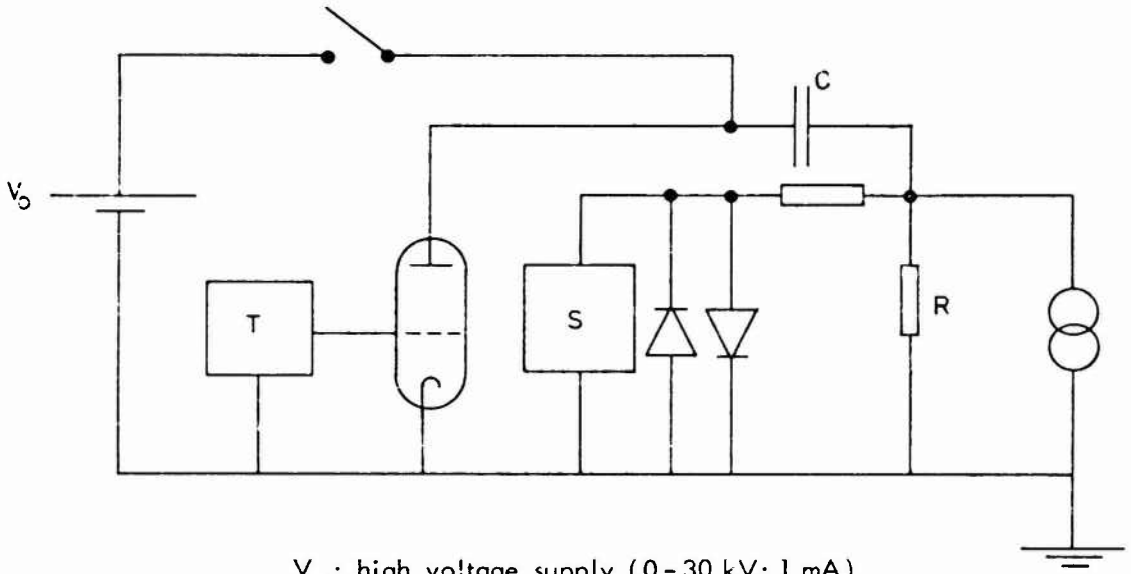
The reaction kinetic data determined by thermal step tests with sample tubes with an inner diameter of 0.3 mm and an outer diameter of 0.6 mm (d_1=1296.64;d_2=525.66).

		Adiabatic induction period formula	Merzhanov's formula (b=8)	Literature values [5]
ethylene glycol dinitrate	$\frac{E}{qk}$ (kJ/mole) (W/kg)	34.39 0.209×10^{13}	33.98 0.149×10^{14}	- -
isopropyl-nitrate	$\frac{E}{qk}$ (kJ/mole) (W/kg)	54.82 0.141×10^{14}	52.99 0.144×10^{15}	- -
nitro-methane	$\frac{E}{qk}$ (kJ/mole) (W/kg)	101.13 0.154×10^{15}	96.08 0.227×10^{16}	206.07 0.728×10^{21}
trichlora-nitromethane	$\frac{E}{qk}$ (kJ/mole) (W/kg)	86.53 0.562×10^{11}	79.59 0.503×10^{13}	- -

Table 2

The reaction kinetic data determined by thermal step tests with sample tubes with an inner diameter of 1.4 mm and an outer diameter of 1.8 mm (d_1=965.540;d_2=988.760)

		Adiabatic induction period formula	Merzhanov's formula (b=8)	Literature value [6,7]
pentaerythritol-tetranitrate (PETN)	$\frac{E}{qk}$ (kJ/mole) (W/kg)	15.34 0.196×10^{9}	14.02 0.424×10^{9}	161.58 0.291×10^{22}
tetryl	$\frac{E}{qk}$ (kJ/mole) (W/kg)	37.08 1.75×10^{10}	35.43 1.07×10^{10}	146.09 0.128×10^{19}
propellant (CBI)	$\frac{E}{qk}$ (kJ/mole) (W/kg)	18.35 0.135×10^{10}	19.88 0.649×10^{10}	140 0.68×10^{18}



V_o : high voltage supply (0 - 30 kV; 1 mA)

C : capacitor (i.c. 5.4 - 21.4 μF)

R : capillary tube (ca 0.03 - 0.14 Ω)

T : trigger unit

S : oscilloscope

Fig 1 The experimental set-up of the thermal step test (TST)

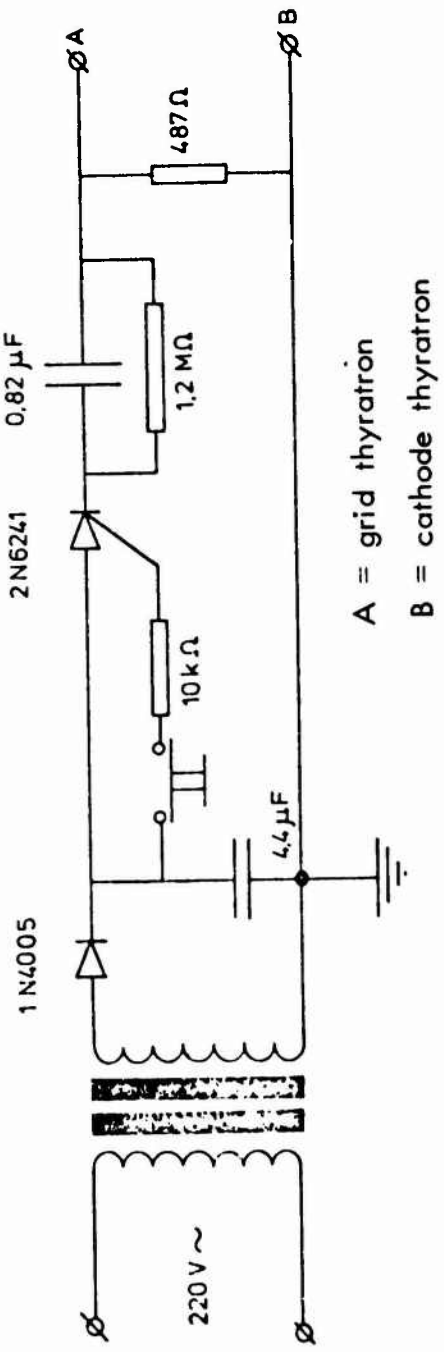


Fig 2 The trigger circuit of the thyratron

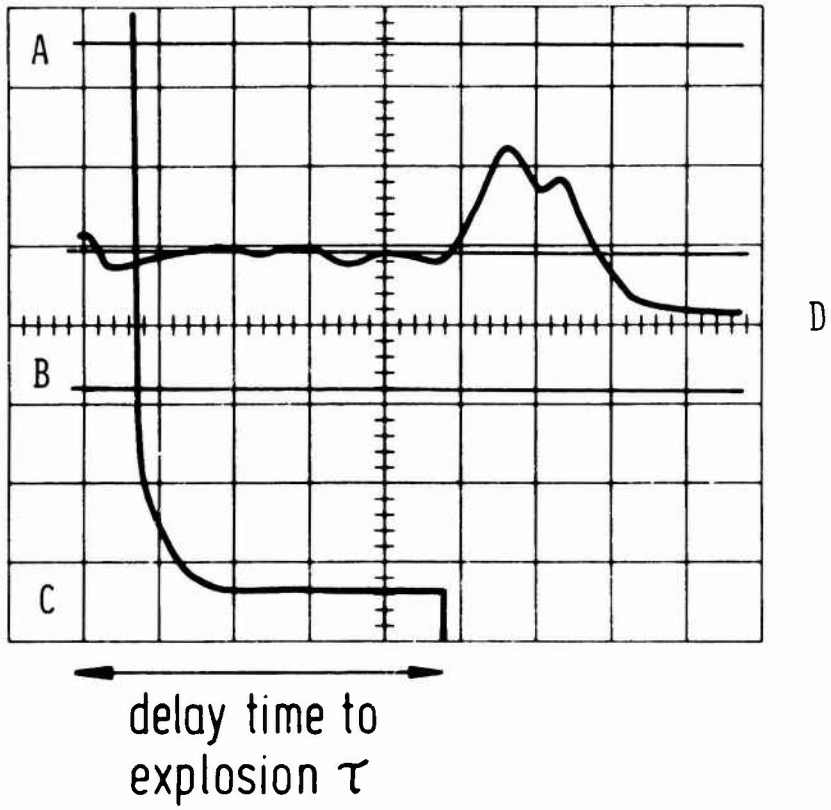


Fig 3 A typical TST sample result, i.c. a (double beam) oscillogram showing (A) the zero reference of the voltage, (B), the voltage due to the constant current i_o at the temperature T_i, (C) the voltage over the sample tube during and after the capacitor discharge and indicating the end of the τ and (D) a microphone signal (with zero reference) of the trigger and the explosion noise (10 mV/div vs 0.2 ms/div)

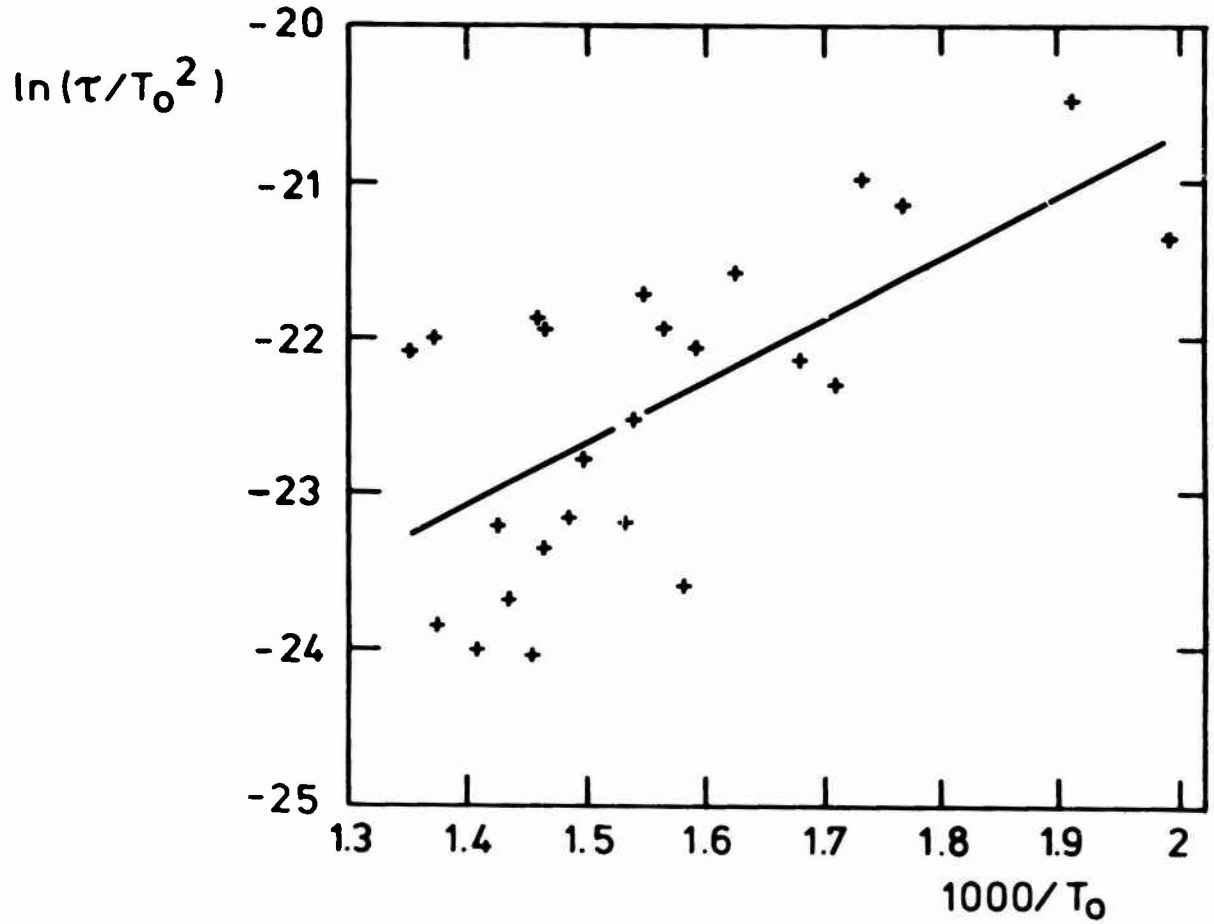


Fig 4 A typical plot of $\ln(\tau/T_o^2)$ against $1000/T_o$, i.c. ethyleneglycoldinitrate (based on (2.3) and (3.3) without (2.5))

A STUDY OF THE THERMAL INITIATION, COOKOFF, OF M30 PROPELLANT

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ABSTRACT

A study has been made of the thermal stability of the triple-base propellant M30. The apparatus employed applied the test specimen for a controlled time interval to a heated copper block with a force adequate to maintain good thermal contact. A GO-NO GO test procedure was followed over the temperature range 200 to 260 °C. A lower contact time limit was observed below which ignition did not occur. A higher limit was also observed above which ignition always occurred. Between these limits, which become narrower with increasing temperature, ignition was variably observed. Contact geometry and contact pressure were also studied. The latter was found to have a significant effect on time to ignition of a single grain with the time to ignition and the variability of observation increasing as contact pressure was decreased. The data are discussed with respect to the problem of propellant cookoff in heated cartridge cases.

INTRODUCTION

Ammunition storage compartments remote from the crew compartment are being designed for developmental armored vehicles. The objective is to lower the vulnerability of the vehicle by reducing the contribution from the ammunition. A problem exists with this approach in that a fire which results from a single cartridge being hit in an encounter may lead to thermal initiation or cookoff of the remaining ammunition.

As part of the Ballistic Research Laboratory (BRL) task to improve the ammunition storage compartment in tanks, a problem arose in reconciling conflicting cookoff test results. A series of tests was conducted by Frey[1], at BRL, in which rounds were wrapped with heating wire and heated

at various rates and the time to explosion and wall temperature at explosion were measured. The results were not in agreement with those from work done at Picatinny Arsenal[2] (PTA) in which a grain of propellant was placed on its side on a hot surface at a known temperature and the time to ignition measured. The times to ignition were much longer for the latter tests.

In order to resolve this discrepancy, a proposal was made to study the thermal initiation of M30 propellant by another technique. Previous work by Strittmater and Holmes[3] employed a hot-plate method to study cookoff and relative thermal sensitivity of propellants. A large copper block was heated to a known temperature and the propellant samples were attached to one end of an electrically-triggered, spring-loaded arm. When the arm was triggered, the sample was rapidly placed in contact with the hot copper block and kept in good surface contact for a preset time. Then, when the spring-loaded arm was electrically released, the sample either continued to burn to completion or extinguished. Results were reported as a visual observation of the GO - NO GO type with respect to sustained combustion after liftoff of the arm. The tests described in this report were conducted with an improved version of the Strittmater-Holmes apparatus.

EXPERIMENTAL METHODS

The original instrumentation used by Strittmater and Holmes[3] was modified to the extent that more precise temperature and time control was possible. The temperature sensor was an iron/constantan thermocouple inserted into the copper block just under the surface and monitored by a Model 1000 Honeywell Differential Voltmeter. The readout scale was adjusted so that the temperature could be read ± 0.1 °C. A similar thermocouple was used as a control in conjunction with a Model 200 F&M Power Proportioning Temperature Controller which was adjusted so that the temperature of the copper block would not vary more than ± 0.5 °C. A Tektronix Type 162 Waveform Generator was used to control the time pulse that initiated the lifting of the sample arm from the hot block; the time could be varied from 0.1 ms to 10 s. The actual time was read on a Model 361-R TSI Universal Counter. A photograph of the instrumentation is shown in Figure 1.

The top of the copper block was covered with silver solder to ensure a surface less prone to oxidation. It was periodically necessary (after 8-12 runs) to clean the surface of accumulated decomposition products. This prevented the forming of a carbonaceous residue which would act as an insulating layer between the sample and the copper block. The force exerted by the spring-arm is given in Figure 2 which shows the force as a function of the fraction of spring compression. The spring was 50-

to 75-percent compressed during a typical run (forces between 820 and 980 grams).

The propellant chosen for this study was M30, a triple-base formulation used in tank rounds and for other BRL tests of vented ammunition compartments. Propellant samples were prepared by cutting standard 7-perforation grains to 6.35 mm (0.25 inch) in length and preparing the ends to ensure complete contact over the whole surface area. This consisted of making sure the end surfaces were as parallel and smooth as possible and that the perforations were cleaned of any particulate matter.

The majority of test samples were 6.35 mm (0.25 inch) in diameter, although some tests were performed on 2.54-mm (0.1-inch) diameter samples. Propellant descriptions are given in Table I. The samples were attached to the spring-loaded arm with double-stick tape. The standard mode was with the grain vertical so that the flat end was applied to the hot copper block. In some cases, the grain was attached horizontally so that the curved outer surface was applied.

A primary question was the effect of the contact pressure between a hot surface and a propellant grain on the ignition limits of the propellant. A series of tests was run in which the sample was simply laid on the hot surface and the time to ignition measured with a stop watch. This technique was analogous to that used by PTA. Test configurations are listed in Table II.

A baffle was placed around the hot plate so that the sample and heated surface would be relatively free from convective cooling by air currents. The studies were always carried out in a laboratory fume hood. There was no confinement of the gaseous products given off during combustion.

RESULTS AND DISCUSSION

The results for the 6.35-mm (0.25 inch) diameter grain in a vertical position are listed in Tables A-I through A-VI, in Appendix A, as a simple GO-NO GO observation for each sample as a function of block temperature and contact time. Each sample is referenced to a set of notes, Table III, that gives a more detailed description of the reactions observed. Only those samples meeting Observations 2A or 2B (sustained combustion) are listed as GO in the tables.

A. Effect of Temperature

The results are given for 10-degree intervals from 210 - 260°C. In runs at 200 and 190°C, ignition did not occur. A gradual softening and mushrooming resulted, eventually forming a "putty-like", amorphous mass. Wisps of smoke occasionally were seen, however, indicating that chemical decomposition was taking place. At 200°C, this process took between 600 and 700 seconds and at 190°C, it took 15 minutes or longer.

From the data in Tables A-I through A-VI a high and low limit were selected. The high limit was that time above which one could always expect sustained combustion and the low limit was that time below which sustained combustion did not occur. A summary of the higher and lower limits is given in Table IV. The relationship between these limits is shown graphically in Figure 3 where the high and low limit times are plotted versus temperature. This clearly shows the increasing time spread during which sustained combustion takes place as temperature is decreased. This is to be expected, for, as the temperature of the hot surface is decreased, the thermal energy imparted to the sample is lower. Slower thermal decomposition and self-heating of the sample result. Therefore, convective and radiative energy loss from the sample becomes more important.

The data in Figure 3 appear to follow an exponential relationship with temperature. Such a relationship would be expected if the surface temperature of the sample is a major controlling factor in determining the time to ignition. This is supported by Arrhenius plots where the log of the reciprocal of the limit time was plotted versus the reciprocal of the block surface temperature. These are shown in Figures 4 and 5 for the high and low limit data respectively. Reasonable first order fits result which give experimental activation energies of 37.8 kcal/mole for the low limit and 39.8 kcal/mole for the high limit. It is likely that the same chemical reactions are controlling at both limits, and thus the difference in activation energies is a measure of the variability in the efficiency of energy transfer in this experiment.

B. Effect of Contact Area and Geometry

To evaluate the effect of contact area and geometry, samples were run at 240 and 250°C in Test Configuration 2. These results are listed in Tables A-VII and A-VIII, respectively. Table V shows the variations in high-low limits for the two test configurations. The low limits are increased somewhat with side contact, but the high limits are variably affected. For the 6.35-mm diameter grain used in the bulk of these studies, the effect of end versus side contact does not appear to have a significant impact on the thermal ignition limits.

C. Effect of Grain Diameter

The effect of grain diameter on the ignition limit was determined. The data are given in Tables A-IX and A-X where 2.5-mm diameter samples were tested at 250°C. If a comparison is made between the two diameters in Configuration 1, the high and low limits are increased by 27 and 64 percent respectively for the smaller diameter. In Configuration 2, the difference between diameters is less than 10 percent with the low limit decreased and the high limit increased for the smaller diameter.

In Configuration 1, the contact area for the 2.54-mm diameter grain is one sixth that of the 6.35-mm diameter grain, and the perimeter to contact area ratio is 2.5 times larger for the smaller grain. This should result in significantly large convective heat losses from the smaller grain, making it more difficult to ignite. This is reflected by the increase in the high and low limits and the increased spread between these limits for the smaller diameter grains. Due to the tangential contact of the samples with the heated surface in Configuration 2, the difference in contact area and exposed perimeter between the two grains is small, and results in the smaller differences observed in high and low limits between the two grains.

D. Effect of Contact Pressure

The method used by investigators at PTA, placing the sample (under its own weight) on the hot surface and measuring the time to ignition, was followed at 210, 240 and 250°C. The results are in Table VII.

The reactions of the samples when laid directly on the hot plate were rather interesting. Those samples placed on the cut ends "danced around," emitted wisps of smoke, and bubbles formed at the edges until ignition occurred. Samples placed on their sides rolled aimlessly all over the hot surface. The movement of these samples can best be explained by the "jet" action of the decomposition gases evolved. Because of this "dancing" movement, the probability of close contact, necessary for effficient conductive heat transfer, was diminished considerably. The large times to ignition for these experiments, compared to the data obtained with the ignition test device, underline the importance of contact pressure in determining heat transfer and therefore ignition.

CONCLUSIONS AND RECOMMENDATIONS

The contact pressure between a propellant grain and a heated surface has a profound effect on the time to cookoff at a given temperature. This can readily be seen by comparing the data in Table IV from the cookoff test apparatus with that from the "hot plate" method shown in Table VII. This explains the aforementioned discrepancies between the experimental data of Frey, et al[1] and the PTA hot plate data[2]. In the former tests, the grains in contact with the heated surface were under the weight of the propellant charge, resulting in a contact pressure similar to those used in the cookoff test apparatus used herein.

Table VIII gives some of the experimental data of Frey, et al[1]. The measured case surface temperature at cookoff and the time elapsed from application of heat to cookoff are listed. The Arrhenius parameters were used to calculate cookoff times for the experimental case surface temperatures. These are also listed in Table VIII. The calculated times appear to be qualitatively similar to the data of Frey. This is shown graphically in Figure 6 for the low limit data. While this required an extrapolation of the test data into a lower temperature regime where ignition was not achieved with the present experimental apparatus, there does seem to be a useful correlation between the fit of the data from the test apparatus and actual cartridge case cookoff data. The agreement is particularly good if one considers that the cartridge case containing the propellant was subjected to a dynamic heating from ambient to the cookoff temperature, while the heated surface of the test apparatus was maintained at a constant temperature and the time to cookoff determined. The time to cookoff in the dynamic runs (with a smaller average temperature) should be larger than in those tests with a preheated, constant temperature surface.

Figure 6 also illustrates the importance of thermal contact in determining cookoff times. The triangles in this data represent the no force applied hot plate data provided by PTA[2]. It can be seen by comparison with the cartridge case and calculated data that if no force is applied, considerably longer times are required to reach cookoff at a given temperature.

While the results herein illustrate the effects of temperature, contact pressure, and contact geometry on cookoff of single propellant grains, there are several aspects of the problem which should be investigated further. These include the effect of propellant composition, the atmosphere and pressure surrounding the propellant, multiple grains, and dynamic heating effects. Further investigations in these areas should make possible a useful laboratory technique for determining the susceptibility of propellants to cookoff. The final step would be the derivation of a predictive model for use in ammunition compartment and vehicle design.

REFERENCES

1. R.B. Frey, et al, "Pressure Measurements in Lightly Confined M456 Cartridge Cases After Primer and Cookoff Ignition," US Army Ballistic Research Laboratory Memorandum Report to be published.

2. S. Bernstein, Picatinny Arsenal, private communication to R.E. Prenatt, Ballistic Modeling Division, US Army Ballistic Research Laboratory.

3. R.C. Strittmater and H.E. Holmes, "Hot Plate Flammability Tests," US Army Ballistic Research Laboratories Memorandum Report No. 2292, May 1973. (AD #762149).

Table I. Propellant Descriptions

Propellant	Lot	Diameter	Web
M30	PA-63557	6.35 mm (0.25 inch)	1.17 mm (0.046 inch)
M30	RAD-E31	2.54 mm (0.10 inch)	0.38 mm (0.015 inch)

Table II. Test Configurations

Configuration No.	Force Applied	Grain Position
1	Standard	Vertical
2	Standard	Horizontal
3	None	Vertical
4	None	Horizontal

Table III. Explanation of Notes for Tables A-I - A-X

1A No sustained combustion and no observable reactions during contact.

1B No sustained combustion but visual evidence of reaction (smoke, evolution of gases) during contact.

1C No sustained combustion but sample undergoes thermal degradation with dimensional changes during contact.

1D Ignited while in contact but no sustained combustion after liftoff.

2A Sustained combustion after loss of surface contact - relatively slow fizz burning.

2B Sustained combustion after loss of surface contact - relatively fast with flame.

Table IV. Summary of Cookoff Data for M30 Propellant (Lot PA-63557)

Configuration	Temp (°C)	Time (s) Lower Limit	Higher Limit
1	260	0.260	0.378
1	250	0.574	0.621
1	240	1.538	2.329
1	230	3.422	4.111
1	220	6.257	7.045
1	210	9.400	18.256

Table V. Comparison of High/Low Limits Between Test Configurations

Test Configuration	Temp (°C)	Time (s) Lower Limit	Higher Limit
1	240	1.538	2.329
2	240	1.956	2.015
1	250	0.574	0.621
2	250	0.585	0.670

Table VI. Comparison of High/Low Limit Data at 250°C for Two Grain Diameters

Test Configuration	Grain Diameter (mm)	Time (s) Lower Limit	Higher Limit
1	6.35	0.574	0.621
2	6.35	0.585	0.670
1	2.54	0.728	1.018
2	2.54	0.541	0.733

Table VII. Summary of "No-Force Applied" Data

Temperature (°C)	Test Configuration	Average Time To Ignition (s)	Notes
210	3	---	1
210	4	---	1
240	3	63.5	2
240	4	63.5	2
250	3	41.5	
250	4	41.0	

Note 1. No ignition occurred up to 10 minutes; merely softening, wisps of smoke, and bubbling.

Note 2. When held very lightly with forceps (just enough force to prevent sample movement) average time to ignition for Configuration 3 was 21 seconds and for Configuration 4, 13 seconds.

Calculated Times to Cookoff For M30 Propellant at Experimental Cookoff Temperatures (Times Calculated From Fit of High and Low Limit Data)

Case Surface Temperatures (°C)	Experimental Time to Cookoff (min.)	Calculated Time to Cookoff (min.)	
		High	Low
159	48	42.6	22.0
176	3.4	7.4	4.2
181	1.5	4.5	2.6
186	1.1	2.8	1.6
194	1.5	1.6	1.0
214	1.1	0.2	0.2

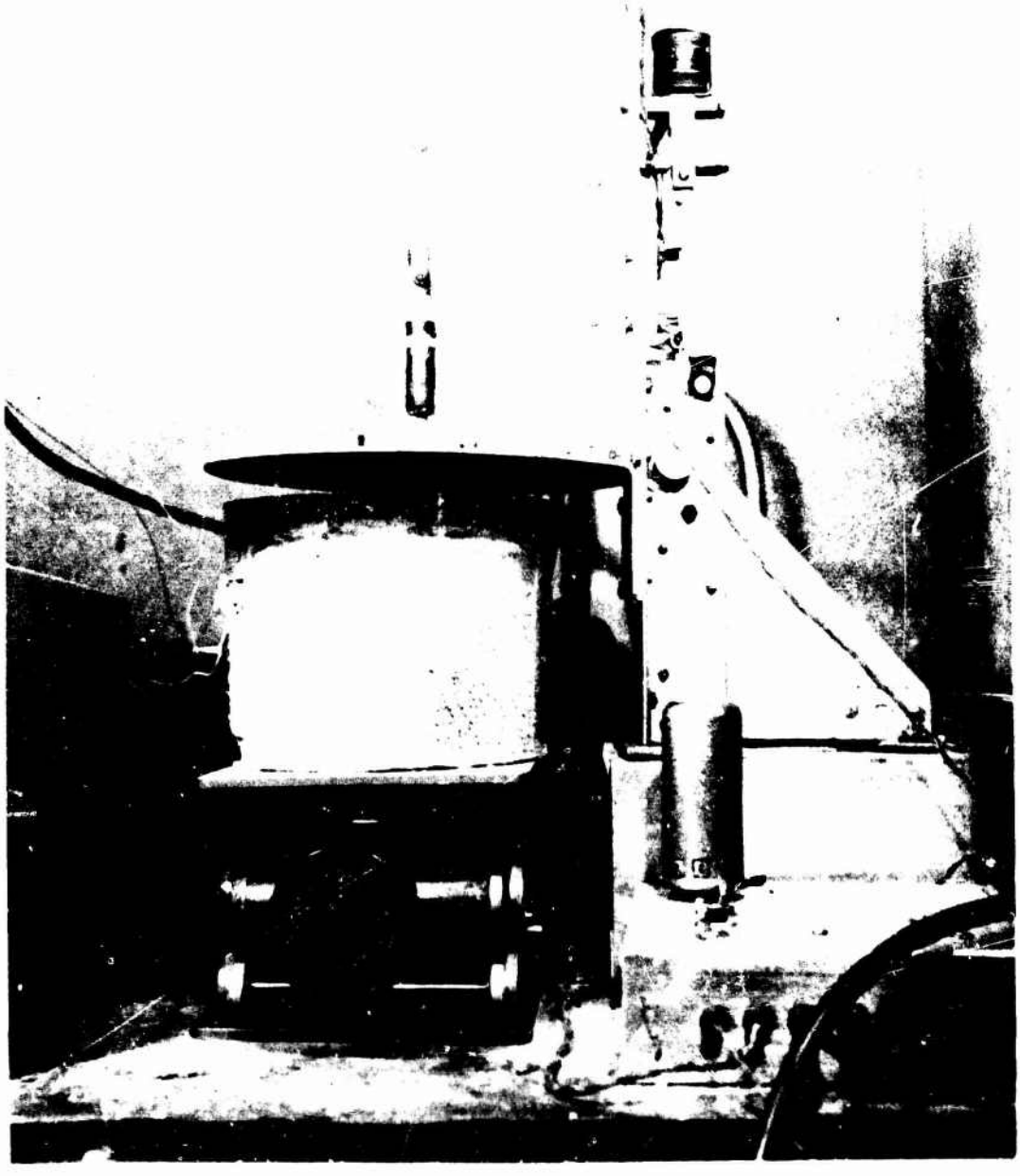


Fig 1 Photograph of instrumentation

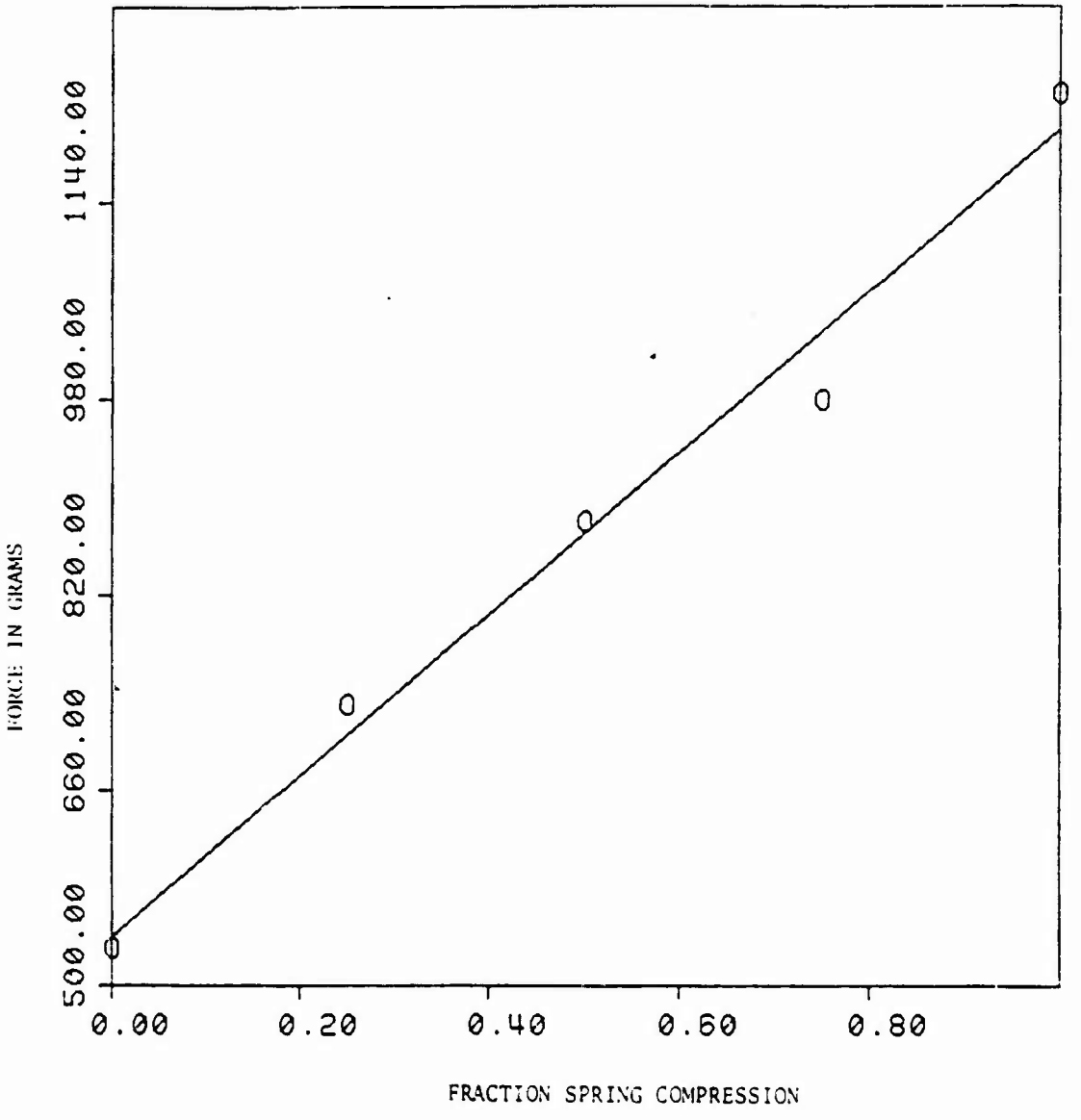


Figure 2. Force Versus Fractional Spring Compression

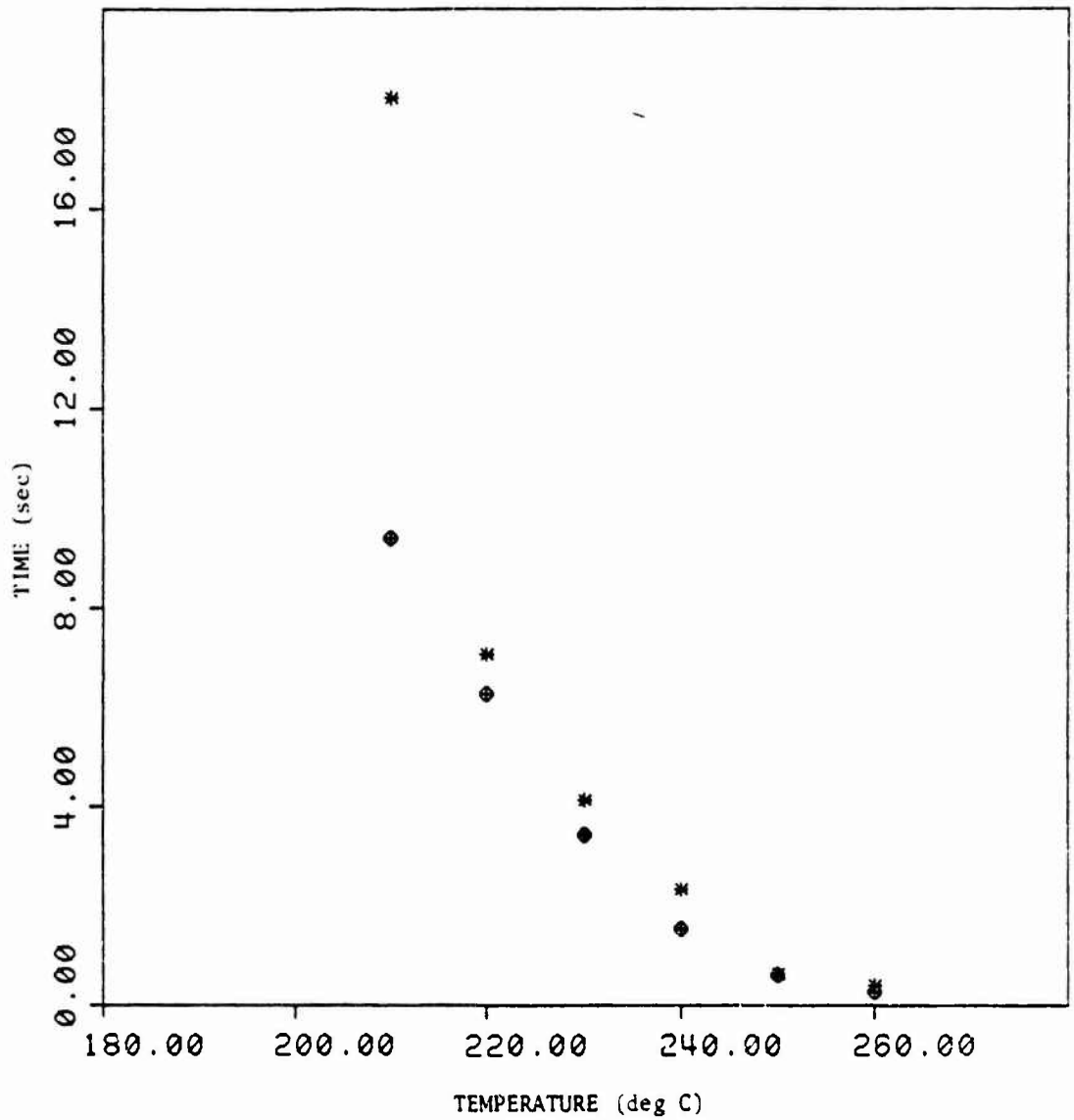


Figure 3 Graphical Summary of Test Configuration 1 Higher and Lower Limit Data

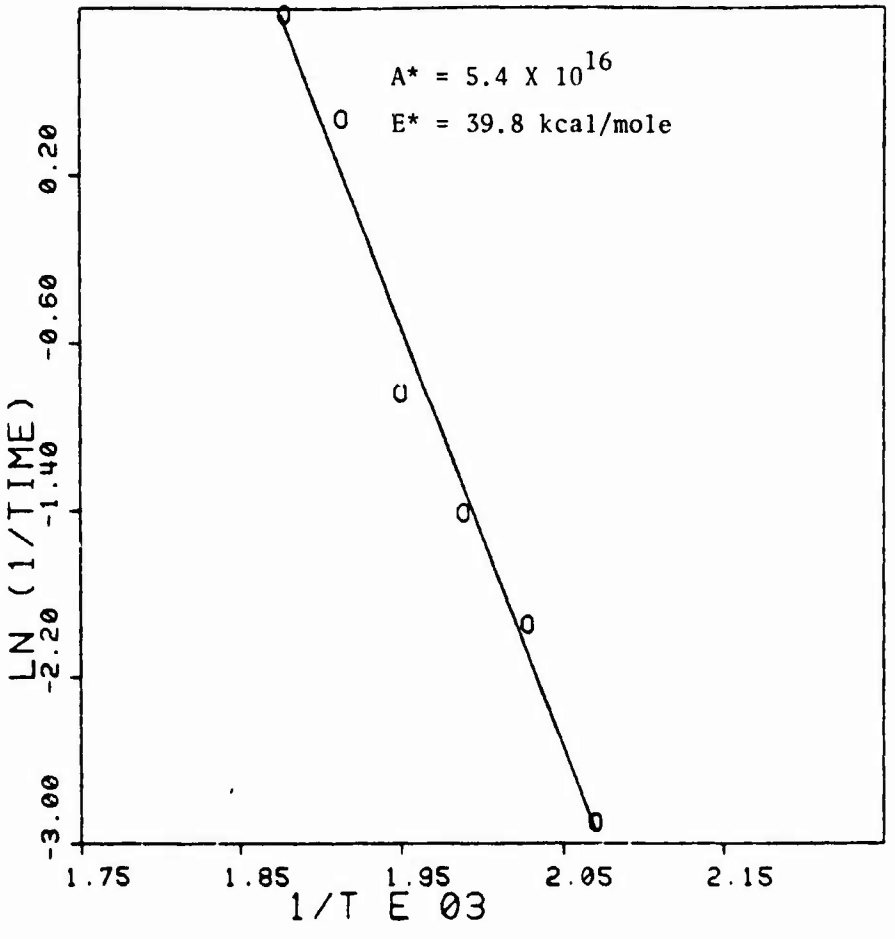


Figure 4. Arrhenius Plot for High Limit Data

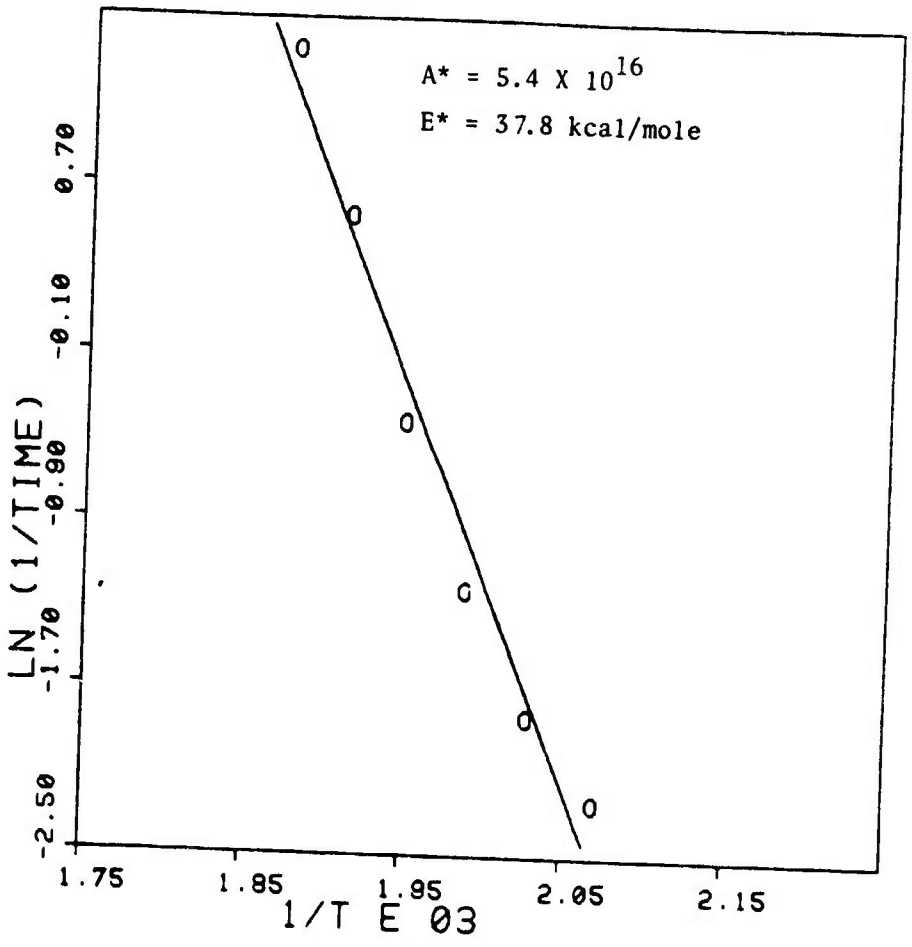


Figure 5. Arrhenius Plot for Low Limit Data

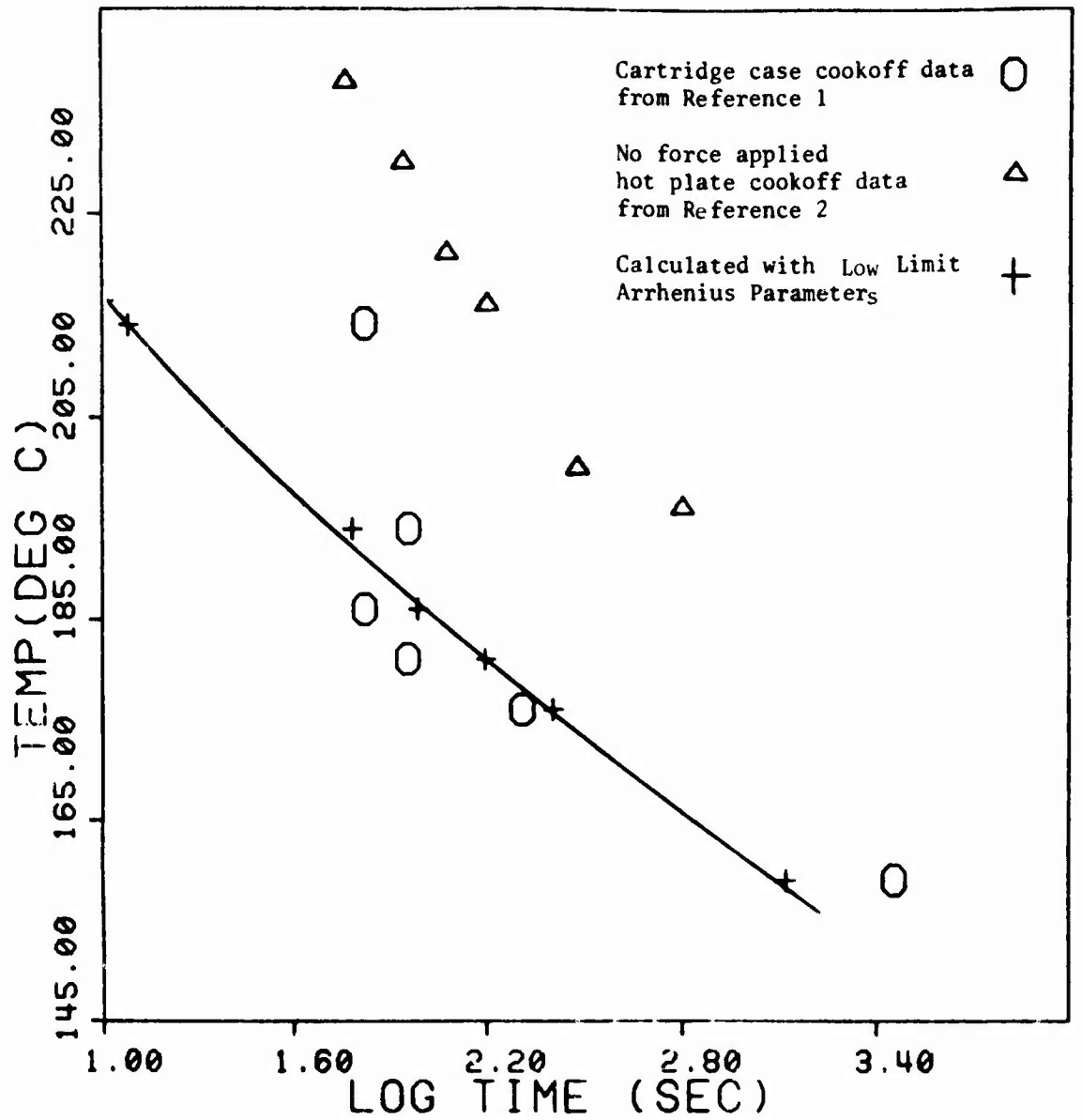


Figure 6. Comparison of Experimental Cartridge Case Cookoff Data with Calculated Data

APPENDIX A

M30 TEST DATA

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Table A-I. M30 Test Data at 210°C and Test Configuration 1 for Lot PA-63557

Test No.	Time (s)	GO	NO GO	Note
1	5.276		X	1B
2	5.910		X	1B
3	6.656		X	1B
4	8.402		X	1B
5	8.667		X	1B
6	9.051		X	1B
7	9.400		X	1A
8	9.409	X		2A
9	9.421		X	1B
10	9.439	X		2A
11	9.534	X		2A
12	9.782	X		2A
13	9.802	X		2A
14	9.936		X	1A
15	10.190		X	1B
16	10.224	X		2A
17	10.600	X		2A
18	10.986	X		2A
19	11.880		X	1B
20	12.013	X		2A
21	12.404		X	1B
22	12.678	X		2A
23	12.926	X		2A
24	13.132	X		2A
25	13.356	X		2A
26	14.001		X	1C
27	14.458	X		2A
28	14.733	X		2B
29	15.552		X	1C
30	16.090	X		2B
31	16.496		X	1C
32	17.168	X		2A
33	17.303	X		2A
34	17.550	X		2A
35	17.561		X	1C
36	18.256	X		2A
37	19.602	X		2A
38	19.775	X		2A

Table A-II. M30 Test Data at 220°C and Test Configuration 1 for Lot PA-63557

Test No.	Time (s)	GO	NO GO	Note
1	6.111		X	1A
2	6.181		X	1A
3	6.235		X	1A
4	6.257		X	1A
5	6.387	X		2A
6	6.388	X		2A
7	6.502		X	1A
8	6.640		X	1B
9	6.733		X	1A
10	6.840	X		2A
11	6.998	X		2A
12	7.045		X	1A
13	7.045	X		2B
14	7.497	X		2A
15	7.789	X		2A

Table A-III. M30 Test Data at 230°C and Test Configuration 1 for Lot PA-63557

Test No.	Time (s)	GO	NO GO	Note
1	3.048		X	1A
2	3.194		X	1A
3	3.422		X	1A
4	3.466	X		2A
5	3.522		X	1B
6	3.562		X	1A
7	3.727		X	1B
8	3.813	X		2A
9	3.874	X		2A
10	3.884	X		2A
11	3.926		X	1A
12	4.111	X		2A
13	4.150	X		2A
14	4.194	X		2A
15	5.283	X		2A

Table A-IV. M30 Test Data at 240°C and Test Configuration 1 for Lot PA-63557

Test No.	Time (s)	GO	NO GO	Note
1	1.237		X	1A
2	1.338		X	1A
3	1.457		X	1A
4	1.503		X	1A
5	1.505		X	1A
6	1.530		X	1A
7	1.538		X	1A
8	1.546	X		2A
9	1.571	X		2A
10	1.575		X	1A
11	1.577		X	1B
12	1.649		X	1A
13	1.664	X		2A
14	1.691	X		2A
15	1.697		X	1A
16	1.700		X	1B
17	1.762	X		2A
18	1.895		X	1A
19	1.915		X	1A
20	1.933	X		2A
21	1.940		X	1A
22	1.975	X		2A
23	1.984		X	1A
24	2.085	X		2A
25	2.129	X		2A
26	2.134	X		2A
27	2.136		X	1A
28	2.329	X		2A
29	2.453	X		2A
30	2.621	X		2A

Table A-V. M30 Test Data at 250°C and Test Configuration 1 for Lot PA-63557

Test No.	Time (s)	GO	NO GO	Note
1	0.550		X	1A
2	0.561		X	1A
3	0.569		X	1A
4	0.572		X	1A
5	0.574		X	1A
6	0.586	X		2B
7	0.593	X		2B
8	0.600		X	1A
9	0.600	X		2B
10	0.606		X	1B
11	0.617	X		2A
12	0.620		X	1B
13	0.621	X		2A
14	0.621	X		2A
15	0.642	X		2B

Table A-VI. M30 Test Data at 260°C and Test Configuration 1 for Lot PA-63557

Test No.	Time (s)	GO	NO GO	Note
1	0.197		X	1A
2	0.252		X	1A
3	0.260		X	1A
4	0.262	X		2A
5	0.265		X	1A
6	0.290		X	1A
7	0.297		X	1A
8	0.300		X	1A
9	0.314		X	1A
10	0.322		X	1B
11	0.328		X	1A
12	0.330		X	1D
13	0.332	X		2B
14	0.345	X		2A
15	0.345		X	1A
16	0.346		X	1A
17	0.350		X	1A
18	0.351		X	1A
19	0.359	X		2A
20	0.361		X	1A
21	0.362	X		2A
22	0.371		X	1A
23	0.373		X	1A
24	0.375	X		2A
25	0.376	X		2A
26	0.377	X		2A
27	0.377	X		2A
28	0.378		X	1A
29	0.378	X		2A
30	0.447	X		2A

Table A-VII. M30 Test Data at 240°C and Test Configuration 2 for Lot PA-63557

Test No.	Time (s)	GO	NO GO	Note
1	1.892		X	1A
2	1.911		X	1A
3	1.922		X	1A
4	1.955		X	1A
5	1.956		X	1A
6	1.957	X		2A
7	1.963	X		2A
8	1.987	X		2A
9	1.998		X	1A
10	2.015	X		2A
11	2.052	X		2A
12	2.072	X		2A
13	2.080	X		2A
14	2.136	X		2A
15	2.616	X		2A

Table A-VIII. M30 Test Data at 250°C and Test Configuration 2 for Lot PA-63557

Test No.	Time (s)	GO	NO GO	Note
1	0.487		X	1A
2	0.568		X	1A
3	0.568		X	1A
4	0.582		X	1A
5	0.585		X	1A
6	0.586	X		2A
7	0.586	X		2A
8	0.604		X	1A
9	0.620		X	1A
10	0.621		X	1A
11	0.630		X	1A
12	0.642	X		2A
13	0.645		X	1A
14	0.651		X	1A
15	0.664		X	1A
16	0.670	X		2A
17	0.671	X		2A
18	0.703	X		2A
19	0.704	X		2A
20	0.739	X		2A
21	0.797	X		2A

Table A-IX. M30 Test Data at 250°C and Test Configuration 1 for Lot RAD-E31

Test No.	Time (s)	GO	NO GO	Note
1	0.569		X	1A
2	0.611		X	1D
3	0.639		X	1D
4	0.728		X	1D
5	0.889	X		2A
6	0.914		X	1D
7	0.915		X	1D
8	0.928		X	1D
9	0.998		X	1D
10	1.018	X		2A
11	1.094	X		2A
12	1.171	X		2A
13	1.183	X		2A
14	1.278	X		2A
15	1.299	X		2A

Table A-X. M30 Test Data at 250°C and Test Configuration 2 for Lot RAD-E31

Test No.	Time (s)	GO	NO GO	Note
1	0.526		X	1A
2	0.541		X	1A
3	0.572	X		2A
4	0.575		X	1A
5	0.577	X		2A
6	0.578		X	1A
7	0.590		X	1A
8	0.605		X	1A
9	0.622		X	1A
10	0.624	X		2A
11	0.643	X		2A
12	0.645		X	1A
13	0.664		X	1A
14	0.733	X		2A
15	0.740	X		2A
16	0.749	X		2A
17	0.824	X		2A

TEST METHODS FOR ASSESSING THE THERMAL INSTABILITY OF HAZARDOUS MATERIALS

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ABSTRACT

The collection and evaluation of test methods and test data have been studied from the standpoint of both the decomposition sensitivity and energy release. The minimum amount of thermal excitation necessary to initiate a decomposition reaction identifies the sensitivity of a material. From a fundamental standpoint, this excitation is associated with the rates and mechanisms of the initial reaction process. On the other hand, the energy release of a decomposition reaction is related to the thermodynamic aspects of the reaction and is a function of the initial and final states of the process.

The purpose of this paper is to review some of the available test methods which furnish information about the thermal instability of hazardous materials and indicate which measurement parameters are relatable to fundamental concepts on thermal explosions.

The definition and identification of thermal instability become more difficult as soon as the constraint of quantitativeness is imposed. A solution to the problem of this quantitative definition and identification should be possible with the development of a correlation scheme which includes the appropriate thermal, kinetic, and transport parameters. Ideally, such a correlation should be able to rank all substances between nitroglycerine and sand according to their thermal instability. The correlation should have a good theoretical foundation and not be solely empirical. The proper combination of parameters necessary to provide a ranking for a thermal instability scale should be found within the theory of thermal explosion.

From a study of experimental investigations of hazardous materials and the concepts of thermal explosion theory, a calorimetric experiment offers a promising route to obtain data from which an unambiguous reactivity scheme could be developed. Parameters which are embodied in this theory are derivable from calorimetric measurements. These parameters include: heat evolved from the self-heating process, activation energy required to initiate self-heating, pre-exponential factor, heat transfer coefficient, the temperature above which a runaway reaction cannot be controlled by heat leakage to the surroundings, and the induction time prior to explosion or rapid runaway.

INTRODUCTION

The need to find a clear definition and a more quantitative identification of the property known as thermal instability (self-reactivity) of chemical substances was the goal of the efforts put forward in the Physical Chemistry Division of the National Bureau of Standards (NBS) over the past few years [1, 2, 3]. This need is acknowledged by groups within various sectors involved in the production, handling, and transport of hazardous materials. The Office of Hazardous Materials Operations of the U. S. Department of Transportation (DOT) has supported this investigation as part of its own program to review the hazard classification system, to re-examine regulations for hazardous cargoes, and to implement an emergency response system.

An evaluation of the literature which reported explosive sensitivity test methods and test data comprised part of our efforts for DOT. Previous attempts [1] to determine whether a correlation could be made between test data and various thermochemical and kinetic parameters which would allow the establishment of a ranking of substances on the basis of their chemical reactivity provided only qualitative relationships.

Although a large array of test methods and test data were found as a result of performing the literature survey, we were not able to establish a reliable reactivity ranking which could be applied to chemical substances as a whole. Some of the test methods and test data are empirical in nature, however, others could be linked to fundamental concepts involving thermal explosion theory. The broad spectrum of data required to cover the range of reactivity from nitroglycerine to sand were either unavailable or were present in a form which could not be merged easily with other related information.

It appears that a calorimetric approach has the promise of providing part of the necessary information and support for concepts from which a reactivity scheme could be developed. A firmer foundation for a definition of thermal instability and for a method to rank chemical reactivity could be obtained from the theory of thermal explosion. The calorimetric approach offers the advantage of permitting simultaneous determination of thermochemical, kinetic, and heat transfer parameters from experimental measurements performed on a specific thermal decomposition process. The need to calculate these parameters from the same reacting system, thus providing a common base for comparison, appears to be an important feature. The fact that the calorimetric approach should provide the parameters embodied in the theory of thermal explosion suggests that a ranking for chemical reactivity could be developed from such investigations.

TEST METHODS

The sensitivity of a material can be related to the minimum amount of thermal excitation necessary to initiate the process. In more fundamental terms, this concept can be associated with the rates and mechanisms of the initial reaction process. In the case of bond-breaking processes, the bond dissociation energy and the activation energy are equivalent, and are useful estimates of material sensitivity for decomposition. On the other hand, the total energy release of a decomposition reaction is related fundamentally to the thermodynamic aspects of the reaction, and is a function of the reaction's initial and final states.

A variety of thermal stability tests are listed below. An attempt has been made to provide some identification of the physical property which is being measured or the parameter being sought by means of the measurement. A brief description of the conditions under which the sample is subjected in the test method is also furnished.

a. JANAF Thermal Stability Test No. Six for Liquid Propellants[4]

Maximum temperatures are determined to which thermally unstable liquids can be subjected for short periods of time without danger of explosive decomposition. Under confinement in a microbomb a liquid sample is either heated rapidly and held at a pre-determined temperature for an arbitrary time interval, or heated at a constant rate until evidence of rapid decomposition appears.

Rates of decomposition can be estimated from plots of the sample temperature vs. time, and from plots of the temperature difference between the sample and bath vs. time.

From a plot of the logarithm of the self-heating rate of the sample vs the reciprocal of the temperature, a linear slope proportional to the activation energy is obtained.

b. ASTM Standard Method of Test E-476-73 [5]

Thermal Instability of Confined Condensed Phase Systems (Confinement Test)

The temperature at which a chemical mixture will begin a reaction is measured. Appreciable heat or pressure can be liberated when subject to a programmed temperature rise. This method applies to solids or liquids in a closed system in air or some other atmosphere present initially under normal laboratory conditions. The sample to be tested is confined in a closed vessel equipped with a burst diaphram, pressure transducer, and thermocouple. The apparatus is equilibrated in a bath at room temperature and subsequently heated at a constant rate. The temperature difference between the bath and sample, the pressure in the closed vessel, and the bath temperature are recorded continuously during the course of the test. Examination of the rate of temperature rise of the sample and rate of temperature rise of the bath, allows an evaluation of kinetic parameters.

c. Self-Heating Adiabatic Test [6, 7, 8]

The thermal decomposition of poorly conducting materials (i.e. wood) is monitored under conditions such that heat exchange between the sample and its surroundings is kept to a minimum (i.e., adiabatic conditions). A furnace is designed with such controls so as to keep the furnace temperature as close to the temperature at the center of the sample as possible. After a sample had been brought into thermal equilibrium at a given temperature, the furnace temperature control system is changed automatically to allow the sample to self-heat up to a temperature of 500°C with minimal heat exchange to the surroundings inside the furnace.

The time to thermal runaway as a function of temperature is measured. The runaway times so measured will correspond to the predicted behavior of actual materials in the limit of perfect insulation or of very large size.

d. Vacuum Thermal Stability Test [9]

The explosive character or tendency toward decomposition of materials at elevated temperatures (200° to 350°C) are determined in vacuum in a storage environment.

This test measures the amount of gas evolved by a sample at a fixed temperature using a mannometric method.

e. Thermal Surge Test [10]

The thermal surge test supplies data on explosion temperatures which represent conditions of minimal heat transfer. The discharge of a capacitor across a thin-walled tube provides the thermal stimulus to initiate explosive decomposition. The time-temperature profile of the decomposition is obtained from oscillographic records. Although the tubes are thin-walled, they have considerable strength and provide a state of heavy confinement for the explosive or unstable material.

The test is particularly suited to liquid material but solids can also be accommodated by melting prior to their insertion into hypodermic needle tubing. Materials are subject to temperatures in the range of 260° to 1100°C and delay times of 50msec to 50μsec.

f. Explosion Temperature Test [11]

The temperature at which a material explodes, ignites, or decomposes is determined after a five second immersion in a Wood's metal bath.

This test gives an estimate of how close the explosion temperature is to ambient condition for a material, and, hence, provides a measurable indication of thermal instability. Explosion temperature data as a function of time serve as useful indicators to assist in maintaining safe thermal condition during handling and transport.

g. Adiabatic Storage Test [12]

The time interval or induction period is determined during which the gradual increase of temperature due to self-heating will result in explosion of the material under test.

A temperature-time profile is obtained for a substance from a pre-selected starting temperature until rapid exothermic decomposition results. An indication is provided of what constitutes an unfavorable storage environment under adiabatic conditions.

h. Isothermal Storage Test [12]

The heat generation rate as a function of time is measured and an estimate of the induction period at a given temperature for a material is obtained. A sample begins to self-decompose and to generate heat inside an aluminum block held at a constant temperature. The heat flow from the sample to the block takes place via a Peltier element which produces an electric signal. The rate of heat generation as a function of time is observed. Test can be made with a large variation in sample size (up to 50 grams). The critical radius of the sample can be calculated from the results. This test also allows one to examine the degree of self decomposition as a function of time at a constant temperature.

i. Exothermic Decomposition Meter Test [12]

The self-heating of a sample is determined at small to moderate heat generation rates as a function of temperature or time. A cylindrical aluminum block contains a cavity which has a Peltier element attached at the bottom and a sample is placed on the Peltier element. Heat flow from the block to sample is measured by means of the Peltier element which provides an electrical signal to a recording device. From a plot of the heat generation of the sample vs. the reciprocal of the absolute temperature, kinetic parameters can be calculated.

j. Self-Heating Test for Organic Peroxides [13-17]

The minimum ambient temperatures for the self-heating to explosion of thermally unstable compounds is investigated in charges of specified shape but varying size. The thermal decomposition of organic peroxides is observed from studying temperature-time plots to obtain the critical temperatures for explosion, heat transfer coefficient data, and apparent activation energies.

k. Differential Thermal Analysis (DTA) Test [18-27]

Exothermic and endothermic reactions are measured as heat is applied at a particular input rate. The material under test and a stable reference material are heated simultaneously at the same rate. Exothermic and endothermic traces are measured using a recorder providing a temperature-time plot of the reaction process. From the exotherms and endotherms of the DTA curve, decomposition temperatures corresponding to various rates of temperature rise can be obtained. Kinetic parameters can be calculated as a result of properly varying the heating rates and assuming a constant degree of conversion of reactant. When the temperature sensors are placed in the path of the heat flow the DTA apparatus can measure the enthalpies of processes such as heats of decomposition or transition.

l. Shock Tube Test [28]

The expected linear relationship between the ignition delay time required to detonate fine dusts or sprays of explosives and the reflected shock temperature is investigated. Liquid or finely divided solid samples are instantaneously subjected to very hot gaseous environments of known composition. The sample is dispersed by the hot flow behind the incident shock and the particles thus formed are ignited with a measurable time delay by the twice-shocked gases behind the reflected shockwave.

Only a few tests are required to characterize a given sample which needs to be available in only milligram quantities. Environment desensitization may be studied using this technique by studying test responses with a variety of channel gases. The shock tube data are shown to correlate well with impact test data.

The sensitivity tests discussed so far deal with the ease of initiation, hence fundamentally with chemical kinetics. Another aspect of the hazards problem is the magnitude of energy release. While the sensitivity tests present a more crucial aspect of the problem, because the objective is to avoid the release of any energy accidentally, the energy release problem should also be considered briefly because a large energy represents a relatively high hazard. The problems of energy release and sensitivity are coupled in the sense that materials having high exothermicity (relative to their heat capacity) can self-heat to high temperatures and thereby represent an enormous hazard, once initiated.

There are a great many explosives tests designed to evaluate the energy release (sometimes also the rate of energy release) under detonative conditions. These tests almost invariably give a measure of energy release by the effect on the surroundings: size of crater or dent in a plate generated by detonation, displacement of a target, or generation of a blast wave in air. Some of the more important energy release tests are described in references [29-36].

THERMAL EXPLOSION THEORY

In 1928, Semenov [37, 38] presented the first quantitative treatment of the theory of thermal explosion. In this treatment, the heat generated by a self-reacting material competes with the heat lost from the exothermic process due to transfer to the surroundings. As the temperature of the surroundings increases in a linear fashion, the rate of heat production from self-reaction increases, exponentially, until a temperature is reached above which equilibration is not possible and decomposition takes place rapidly with ignition or explosion.

The theoretical treatment of Semenov provides for the calculation of the critical conditions in excess of which ignition or explosion will take place. Assumptions basic to this treatment state that (1) the self-reacting material maintains a uniform temperature during decomposition, and (2) the Arrhenius rate law is obeyed. Heat transfer to the surroundings is not limited to any one mode. The exact solution of the equations generated in Semenov's model is not possible without making some approximations. Necessary data for certain thermodynamic, kinetic, or heat transfer parameters are also required before an actual solution can be obtained. In the absence of data, estimates are usually made.

In 1939, Frank-Kamenetskii [39, 40] developed the Semenov model to accommodate a distribution of temperatures within the self-reacting material and limited the heat loss process to conduction only. In many instances, the Frank-Kamenetskii model is a closer approximation to the actual situation.

Various refinements have been introduced into the mathematical treatment of the theory of thermal explosion. Articles by Chambre [41], Todes [42, 43], Rice, et al. [44, 45], Zinn and Mader [47] and Enig [48] should be consulted. Thomas [46] compared the Semenov and Frank-Kamenetskii models and showed that both are special cases of a more general model. Useful reviews have been provided by Merzhanov and Dubovitskii [49], and Gray and Lee [50].

In order to facilitate a clearer understanding between the theory of thermal explosion and hazards caused by thermally unstable materials, we shall describe some features of a thermal explosion process. Let us imagine a test tube (constructed of a high thermal conductivity metal), containing an hazardous material, which has been immersed in an oil bath initially at some low temperature, T_o. A thermocouple imbedded in the material allows a temperature-time record to be taken. (This situation is analogous to one for the Explosion Temperature Test described earlier). In the first test, the temperature of the material will be observed to rise to the bath temperature, then slightly surpass the bath temperature, and proceed to level off back down to the bath temperature. During this time, the material undergoes decomposition, and if the reaction products are gaseous, has disappear completely. As the bath temperature is increased in successive steps, a critical temperature will be attained, which will be the maximum temperature for maintaining a steady-state process. At temperatures above the critical temperature, a steady-state cannct be maintained, and ignition, rapid decomposition, or explosion results.

The phenomenon of the induction periods begins to emerge at this point. This period is the time interval between immersion of the material in the bath and explosion.

We shall now examine the rate processes taking place during heat generation and heat loss. The self-reacting material produces heat at the rate dq_1/dt, or $\dot{q}_1$, given by:

$$\dot{q}_1 = QV\rho A\exp(-E/RT)$$

where Q is the heat of decomposition. V and ρ are the volume and density of the material, respectively, A is the pre-exponential factor, E is the activation energy, R is the gas constant, and T is the temperature of the material.

The material loses heat to the surrounds at a rate according to Newton's law of cooling:

$$\dot{q}_2 = dq_2/dt = hS(T-T_o) \text{ where}$$

h is a heat transfer coefficient, S is the surface area of the material, and $(T-T_o)$ represents the temperature difference between the material, T, and its surroundings, T_o.

At the critical temperature, a steady-state is reached when the rate of heat generation and heat loss are equal.

$$QV\rho A\exp(-E/RT) = hS(T-T_o)$$

The heat generation rate of the self-reacting material, plotted as a function of temperature, is shown in Figure 1. The heat loss rate corresponds to three straight lines marked as the bath temperatures at 200, 208, and 210 °C. There are three different relationships which are possible between the exponential curve representing the heat production rate, dq_1/dt or $\dot{q}_1$ and the straight lines depicting the heat loss rate, dq_2/dt or $\dot{q}_2$. The net rate at which heat is generated in the self-reacting material is the sum of $\dot{q}_1$ and $\dot{q}_2$, and the rate of temperature rise will be expressed by this sum divided by the heat capacity, C.

$$dT/dt = (\dot{q}_1 + \dot{q}_2)/C.$$

The first relationship in Figure 1 shows the curve cutting the straight line at two points. Here, the heat generation rate of the material for a bath temperature of 200°C is greater than the heat loss rate up to point A, where both are equal. This corresponds to a material temperature of about 202°C. Beyond point A, the heat loss rate exceeds that of heat generation and rapid decomposition or explosion does not take place.

In the second situation, the bath temperature is 208°C, which is the critical temperature, T_{cr}, for the material. The curve is tangent to the straight line at point B. The material temperature reaches about 221°C at point B afterwhich sufficient heat loss to the surrounds takes place and no explosion results.

The bath temperature is at 210°C in the third situation. The curve representing heat production via self-reaction of the material and the line representing heat loss do not meet. This temperature, 210°C, is above the critical temperature, T_{cr}, hence, ignition or explosion takes place.

A temperature-time plot for the self-reacting material is shown in Figure 2 for various bath temperatures. Variation in the induction period can be seen as the bath temperature rises above T_{cr}. The induction time prior to explosion is very short as the bath temperature, T_o, exceeds the critical temperature, T_{cr}. The amount of material reacted during the induction period is small. About 4 percent of the material decomposes before explosion when T_o is 210°C and about 2 percent when T_o is 220°C.

If C = mc where m is the mass of material, and c is its specific heat, and if m = ρV, then the rate of temperature rise is given by:

$$CdT/dt = QV\rho A\exp(-E/RT) + hS(T-T_o).$$

No exact analytical solution is available for the above equation under any boundary conditions because of the nonlinearity of the term describing chemical reaction. Consequently, various approximations are introduced into the model of a thermal explosion to obtain solvable expressions for the critical temperature, critical size of the self-heating material, and the time to thermal runaway. The expressions are as follows:

Critical Temperature under Steady-State Conditions dT/dt:

$$T_{cr} = \frac{(E/R)}{\ell n(QEa^2\rho A)/(\lambda RT_{cr}\delta_{cr})}$$

where a is the half-thickness of a slab, or the radius of a sphere or cylinder, and δ is the critical shape factor (0.88 for infinite slabs, 2.00 for infinite cylinders, 3.32 for spheres).

Critical Size under Steady-State-Conditions dT/dt:

$$a_{cr} = \frac{\lambda R(\delta_{cr})T_o \exp(E/2RT_o)}{\rho QEA}$$

Time to Explosion for Adiabatic Heating T=T_o:

$$t(explosion) = \frac{CRT_o^2 \exp(E/RT_o)}{QEA}$$

CALORIMETRIC STUDIES ON HAZARDOUS MATERIALS

During the course of examining the literature for thermal test methods, a large number of articles were encountered which used calorimetric measurements to characterize the self-reactivity of various materials. Some articles were studies designed to examine or expand various concepts in thermal explosion theory while others reported only thermochemical or kinetic data on a particular decomposition reaction. Many investigators used differential thermal analysis (DTA), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). Some researchers have employed the more standard calorimetric or kinetic methods. These articles supplement those mentioned earlier under TEST METHODS.

Rogers [25-27] has shown that the activation energy and pre-exponential factor can be determined for the decomposition process of many explosives using DSC methods. Critical temperatures can be determined on a routine basis using the method described. Agreement between experimental and calculated values is good for most explosives.

Aleksandrov, Bufetov, Pastukhova, and Tukhtaev [51] reviewed the application of pulsed calorimetry to the determination of thermochemical and kinetics parameters of various explosives. References to studies on the decomposition of nitrocellulose, nitroglycerine powder, ammonium perchlorate, dinitroxydiethylnitramine (DINA) and polymethylmethacrylate were provided.

The thermal stability of tetramethylphosphonium perchlorate, nitrate, and picrate was determined using DTA and TGA techniques by Nambiar and Jain [52]. The thermal stability of these compounds was found to be in the order: perchlorate > nitrate >picrate. The explosive sensitivity of the compounds was determined from explosive delay measurements and indicates the same order as the thermal stability.

Merzhanov, Abramov, and Abramova [53] reported a method, based on the heat balance equation, for calculating kinetic constants from a differential thermogram in which non-isothermal kinetic data are reduced to isothermal conditions. The method is demonstrated using the decomposition of tetryl and the polymerization of styrene.

An experimental investigation of the effect of gas removal on the critical conditions for thermal explosion was performed by Samoilenko, Abramov, and Merzhanov [54]. Experiments were performed on compressed pyroxylin samples. Gas removal conditions were varied by changing the pressure of nitrogen in the system. The authors found that as the pressure of the gas over the sample was raised, the critical temperature for thermal explosion fell sharply.

V. V. Aleksandrov and N. S. Bufetov, [55] carried out a calorimetric determination of the thermal decomposition of a nitroglycerine propellant in vacuum over the temperature range from 70 to 280°C.

Heat capacities and phase transitions were determined for cyclotetramethylenetetranitramine (HMX) by Rylance and Stubley [56] using DSC methods.

The kinetics of thermal decomposition of diethylnitramine dinitrate (DINA) and related heat transfer studies, were conducted by various investigators [57-62] under a variety of experimental conditions.

From an examination of thermal explosion theory and experimental studies of hazardous materials by various methods, we felt that a calorimetric approach offered some reasonable promise of providing the necessary information and support for concepts from which an unambiguous reactivity scheme could be developed. A test procedure for ranking materials consistent with such a reactivity scheme should be derivable which has a strong relationship to the theory of thermal explosion. Properties of materials which are embodied in this theory, are obtainable from calorimetric experiments. Moreover, the calorimetric approach has the advantage of permitting the simultaneous derivation of such properties from the experimental measurements performed on a specific decomposition process. The need to calculate thermochemical parameters (such as the energy of decomposition) and kinetic parameters (such as the activation energy of decomposition) from the same reacting system, thus providing the common base for comparison, cannot be overemphasized. This common base has been lacking for most materials. The promise of the calorimetric method to supply the needed ranking for chemical reactivity is based upon its provision of parameters called for by the theory of thermal explosion. One can anticipate further that if self-reacting systems (decomposition and polymerization) are adequately described by this approach, extension to combustion processes should also be possible.

CONCLUSIONS AND RECOMMENDATIONS

Thermal tests which provide information about the critical conditions for thermal explosion are valuable because they give quantitative data identifying the limit of thermal stability for a specified material. Examples of such thermal tests are: the JANAF Thermal Stability Test, the ASTM E-476-73 Confinement Test, the Thermal Surge Test, and the Explosion Temperature Test. The adiabatic and isothermal storage tests are useful in estimating the induction time prior to explosion for a material.

From an examination of reports of experimental investigations of hazardous materials and the elements of thermal explosion theory, a calorimetric experiment appeared to offer a more likely and reasonable recourse to obtain data from which an unamgiguous reactivity scheme could be developed. We feel a test procedure for ranking materials consistent with such a reactivity scheme should be derivable having a firm relationship to thermal explosion theory. Properties of materials which are embodied in this theory (such as the enthalpy of decomposition, activation energy, pre-exponential factor, heat transfer coefficient, the temperature above which violent decomposition will take place, and the time to thermal runaway) are derivable from scanning calorimetric measurements. The calorimetric approach has the advantage of permitting the simultaneous derivation the above-mentioned properties from the experiments performed on a specific decomposition process.

The properties of materials which are considered to be of prime importance are the critical temperature, critical size, and time to thermal runaway. The latter is perhaps most important of all because from a knowledge of the time to explosion, an opportunity may be available to take some sort of corrective action which can preserve both property and life.

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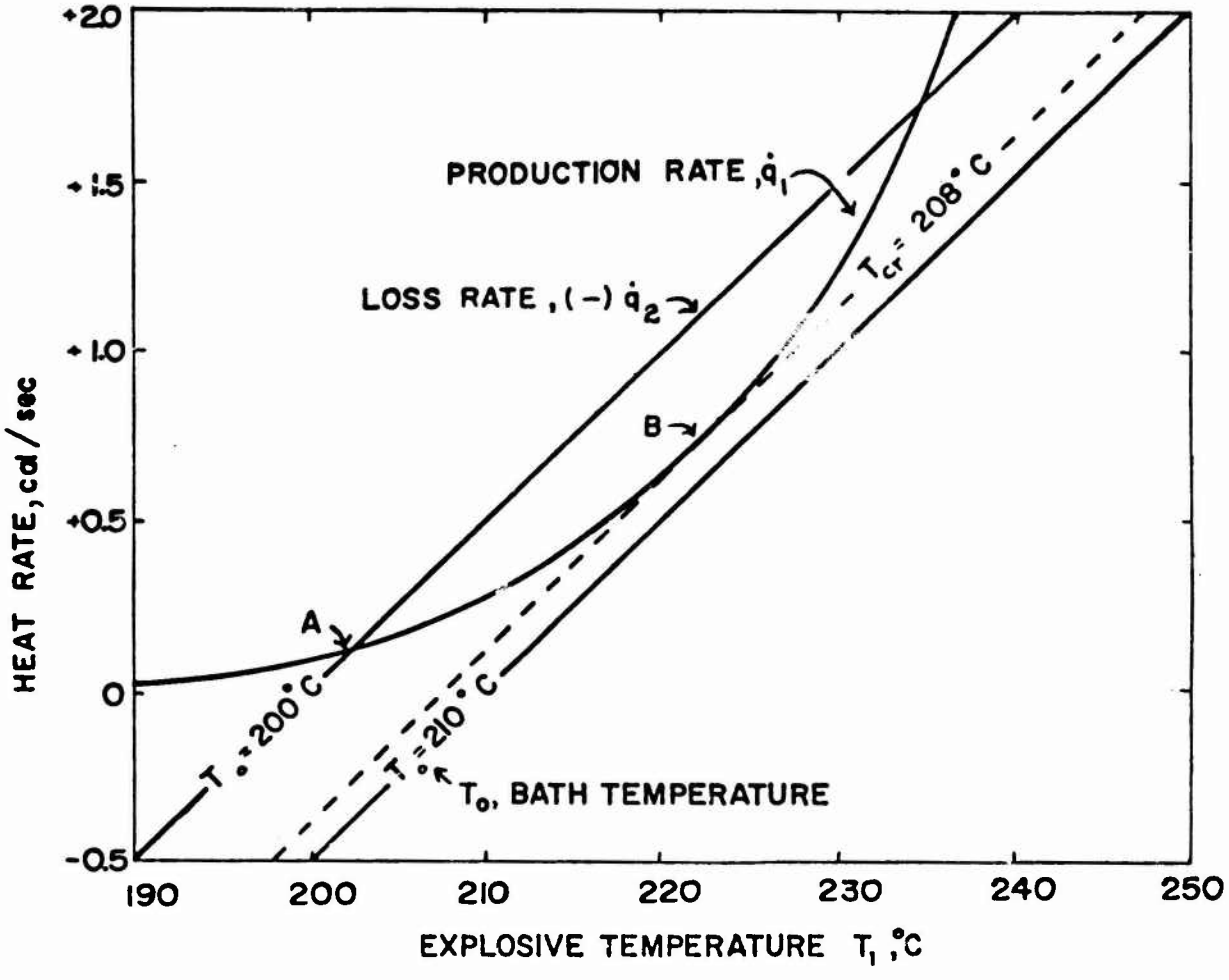


Figure 1 Heat Production and Heat Loss Rates for a Self-Reacting Material

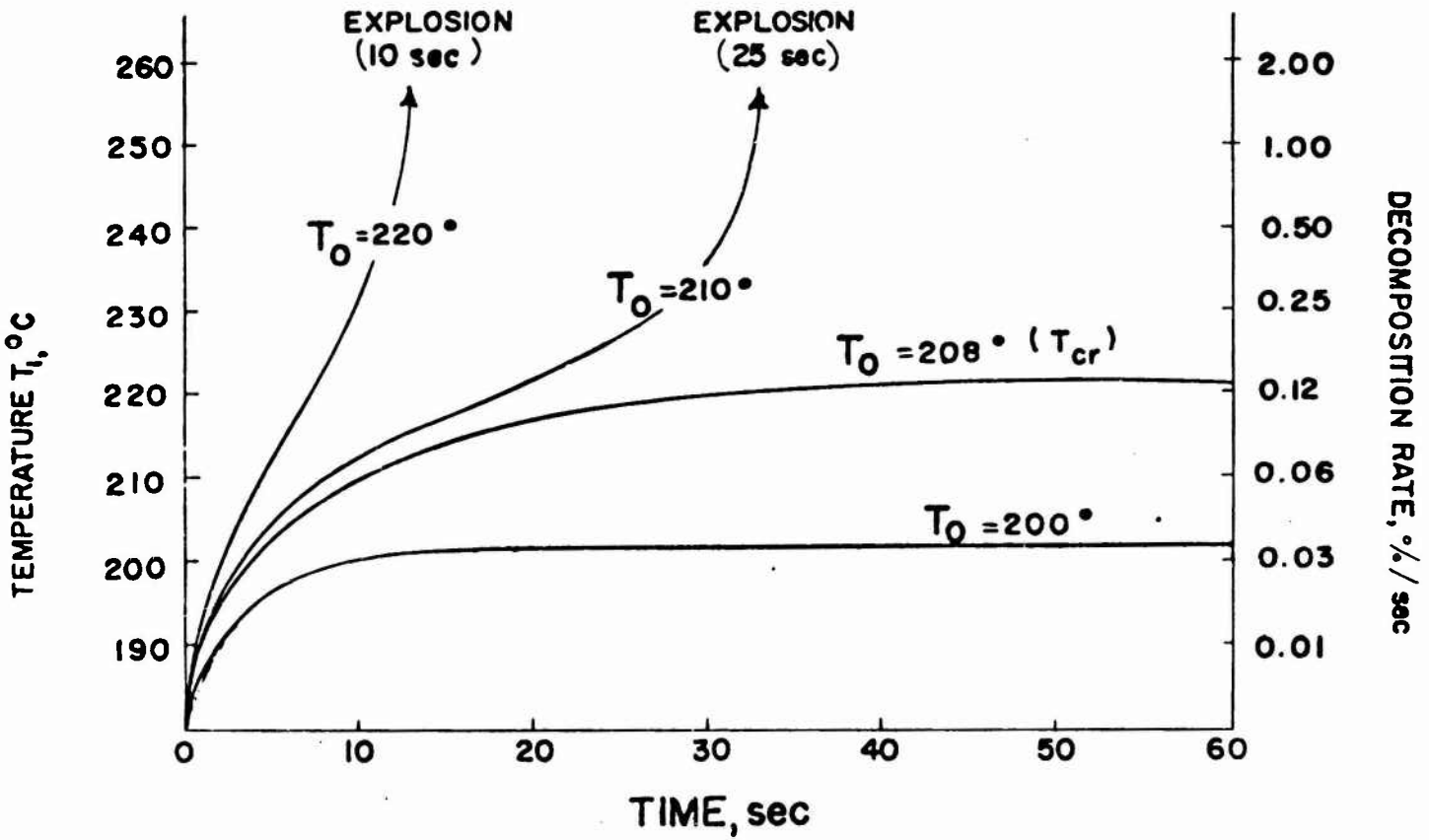


Figure 2 Heating Curves (Temperature - Time Curves) for a Self-Reacting Material

CRITERIA FOR THERMAL EFFECTS OF BURNING AMMUNITION AND EXPLOSIVES

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ABSTRACT

The Department of Defense Explosives Safety Board has not promulgated detailed standards for protection from thermal effects of explosives. In addition, DoD Explosives Safety Standards do not indicate the level of thermal radiation which can be accepted for inhabited buildings and other resources. The practical thermal effects guidelines and a future development plan for the thermal effects standards will be presented which were designed to quantitate and differentiate the intensity of thermal effects inherent in explosives and ammunition placed in DoD hazard class 1, divisions 3 and 4. The thermal effects standards are to be comprehensive in coverage of all phases in the manufacture to end use or disposal sequence and suitably supplement blast and fragment hazard criteria which now exist. The need for these new standards is indicated by the wide disparity in heat output from various ammunition items in the stockpile or R&D phases which are currently covered by a single quantity-distance table which may not provide an adequate degree of safety for all situations.

SUMMARY

New thermal effects safety standards are needed which quantitatively define the rate of heat generation by fire and radiant emission from convection columns. The safety standards must also provide the means for interpretation of test results and in distinguishing between ammunition items. The new standards are needed since the Department of Defense Explosives Safety Board (DDESB) has approved standards for protection against blast and fragment effects, but has not similarly established standards for protection against the thermal flux and firebrands produced by burning ammunition.

BACKGROUND INFORMATION

In past years, experimental work has been largely devoted to observation of the effects of heat flux on various targets. In present DoD Explosives Safety Standards, the acceptable level of thermal radiation to inhabited buildings and other targets is not specified. Thermal effects documentation on burning ammunition which would permit irradiance hazard prediction is generally unavailable. In addition, the present standards do not provide an adequate means for distinguishing between ammunition of DoD hazard class 1, divisions 3 and 4, both of which are basically fire hazards of different intensities. With these requirements in mind, the Chairman, DDESB established a working group[1] representing the military departments to formulate recommended thermal effects standards for submittal to the DDESB for its formal approval and publication. The new Thermal Effects Safety Standards and the information which will be derived from conducting proposed tests are also needed for future revision of DoD standard explosives hazard classification procedures.

The criteria used by the DoD Thermal Effects Standards Working Group in the conceptional development of the new thermal standards and in their proposed test plan to provide needed thermal data will be provided in this paper. A test plan is being recommended to DDESB for contractual accomplishment in FY 77 and 78.

DISTINGUISHING THERMAL AMMUNITION DIVISIONS

Ammunition in DoD class 1, division 3 will be distinguished from ammunition of class 1, division 4 by the inherent property of presenting major effects by projection of firebrands (fragments) in addition to severe radiation hazards. The firebrands of class 1, division 3 materials may reach distances exceeding the radiation hazard of the burning

source material. By definition a firebrand is a projected burning or hot fragment whose heat capacity is transferred to a receptor. The magnitude of thermal energy transferred determines the class of the firebrand; e.g., Underwriters Laboratories firebrand classes A, B, and C approximate 8900, 2200, and 40 kilogram calories of energy equivalent to these values for fuel. In contrast, thermal radiation hazards for ammunition of DoD hazard class 1, division 4 are restricted to those thermal hazards from the burning source.

DATA REQUIREMENTS

Three major categories of data currently unavailable for selected "worst-case" ammunition are needed to develop the new standards:

Radiation Fields

The data to be derived will be used to establish the intensity, duration, and spatial characteristics as functions of material, size of combustion zone, and burning rate, all of which extend to the distance representing that required to obtain a thermal energy value of 0.3 calories/square centimeter/second from the source material. This value accepts first degree burns on an individual in a relatively long duration fire and who takes turning evasive actions. This value has been determined by measurement of burn effects on humans and on combustible resources.[2]

Firebrands

The data to be derived will be used to establish the spatial distribution (number per unit area), thermal capacity, and size of the emitted brands as functions of material and fire characteristics.

Ammunition Thermal Effects on Standard Construction Materials

The data to be derived will be used to relate the thermal threat of ammunition firebrands and Underwriters Laboratory (UL) firebrands on standard construction materials.[3]

RESEARCH APPROACH

The Thermal Effects Standards Working Group recommended that the contractual effort be divided into two phases. Phase I involves tests using relatively large quantities of ammunition to determine quantitative thermal effects data. The information obtained in these quantification tests will become the reference standards upon which the quantity-distance tables will be established. Phase II involves tests using small quantities of ammunition to determine quantitative thermal effects data. The information obtained and the test procedures used will become the reference standards upon which the hazard classification tests for new ammunition items will be established.

TEST AMMUNITION

Review of the ammunition items in DoD hazard class 1, divisions 3 and 4 by the working group resulted in the selection of the "worst-case" ammunition items. In the contract effort these "reference-materials" will be tested in their standard-storage configuration and in their shipping containers. In addition, all tests in phases I and II are to be conducted when the wind speed is five miles per hour or less in the absence of precipitation or dust storms. The following "reference-materials" will be used in phases I and II based upon their availability:

1. Ammonium nitrate
2. Smokeless powder, single, double or triple base gun propellant (granulation and composition to be selected later).
3. Bombs, photoflash, M22 without burster; document destroyer; or illuminating projectiles.
4. M3, M5, or M30 rocket motor.
5. AGM-12B liquid bullpup fuel and oxidizer.

THERMAL AMMUNITION TESTS

Phase I - Thermal Flux Tests

The recommended ammunition sample sizes are to be 200, 400, 1600, and 6400 pounds net combustible weight (NCW). NCW is the total weight of combustible material; e.g., ammunition item, shipping container, and packing materials. Peripheral ignition of the ammunition will be accomplished with a standardized igniter so as not to perturb the thermal measurements.

It is anticipated that the temporal and spatial characteristics of the radiation field will be measured with a series of foil-type radiometers - Gardon-type radiometer, with a range which includes 0.3 calories per square centimeter per second. A minimum of three radiometers will be used in a line from the source in at least two directions at a 90° angle. The size of the thermal source and the combustion zone will be documented by time-lapse color photography. In addition, the burning rate will be determined by a weight-loss method; e.g., load cells which are designed to provide data based upon time and weight.

Phase I - Firebrand Tests

The same test conditions as specified for the thermal flux test will be used simultaneously for the firebrand tests except for the instrumentation which may use infrared scanners or the determination of firebrand effects using the melting of plastic sheet or charring of wood. The firebrand tests shall be designed so that the data will provide a means to determine the equivalence between ammunition firebrands and UL class A, B, and C firebrands (figure 1). The equivalence will be expressed in a convenient term, such as weight, and will be based on the effects produced by burning firebrands on UL class A, B, and C construction materials. In addition, the firebrand effects are to be documented in the horizontal and elevation views from the burning source material.

Phase II - Direct Radiation Measurement Tests

One of the tests will use a 2-inch cube (8-cubic inches) of bulk-reference material. For the assembled reference items, the test specimen to be used will represent the standard storage configuration for that item or the configuration specified in TB 700-2, NAVORD Instruction 8020.3, and TO-11A-1-47, OSAR 8220.1. The standard test apparatus will be designed in such a manner that only one surface is ignited by preventing ignition of the other surfaces. The test apparatus should not be massive so as to avoid the possibility of confinement leading to explosion or pressure rupture, and to the formation of fragments. Direct radiation measurements will again be determined using a foil-type radiometer with a range which includes 0.3 calories per square centimeter per second. The thermal radiation as a function of the distance from the thermal source and the burning rate as determined by the weight-loss method will be determined using controlled ignition of a 2-inch cube.

Single item external fire, STANAG[4], tests will be conducted using a controlled ignition on one or more items as determined by their normal

storage configuration. The data to be derived from the tests shall provide quantitative thermal radiation values in relation to the distance from the thermal-source material.

Phase II - Firebrand Tests

Single item external fire, STANAG[4], tests will be conducted using a controlled ignition on one or more items in their normal storage configuration. The data to be derived from the tests shall provide quantitative thermal radiation values in relation to the distance propelled, and number and size of the firebrands.

CONCLUSIONS

New Department of Defense Thermal Effects Standards will be derived from the test data listed below. These data will be used to establish thermal effects table distance values offering the equivalent thermal protection as is now provided for inhabited building, intraline, public traffic route, and intermagazine distances[5].

a. Quantification Tests - Thermal Flux:

(1) Information which indicates the quantity-distance relationships which approximate 0.3 calories per square centimeter per second.

(2) Information which indicates the burning rate as related to the material quantity.

(3) Information which indicates the size of the combustion zone as related to the material quantity.

b. Quantification Test - Firebrand:

(1) Information which indicates the spatial distribution, thermal capacity, and size of firebrands emitted from the source material.

(2) Information on the maximum distance the firebrands are emitted from the source material.

c. Hazard Classification Test - Direct Radiation Measurement

(1) Information which indicates the thermal energy released from test material as related to the thermal energy released from reference material.

(2) Information which indicates the distance required to obtain a thermal energy value of 0.3 calories per square centimeter per second from the source material.

(3) Information which indicates the burning rate of the source material.

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UL Firebrand Class	BTU	Weight (Grams)	Kilogram Calories	Rounded
A	35200	2000	8870	8900
B	8800	500	2237	2200
C	163	9	41	40

Figure 1. Heat Equivalence of Firebrands (UL) Using Fir and Pine Wood Samples and Assuming 8000 BTU/lb (1 gram = 2.2×10^{-3} lbs.)

AN IMPROVED ELECTROSTATIC SENSITIVITY APPARATUS AND TEST PROCEDURE FOR CHARACTERIZING ENERGETIC MATERIALS

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ABSTRACT

The need is discussed for a single, standardized electrostatic sensitivity test apparatus and procedure for characterizing energetic materials. An improved, approaching-needle apparatus and operating procedure are described, which have been proposed to the Joint Service Committee for adoption as a standard. The apparatus is simple, safe, and capable of yielding meaningful and reproducible results. The proposed test procedure is divided into two parts; a screening test to distinguish between primary and booster or main-charge explosives and a test to rank or compare energetic materials in the primary explosive category. In the screening test, the test materials are assessed by using an oscillatory discharge. The energy for this test is fixed at 0.020 J. There is no electrostatic distinction made between booster and main-charge explosives. Those materials which are ignited at the 0.020J level are relatively sensitive and are placed in the primary explosive category. In the ranking test, the sensitive materials are assessed using oscillatory, spark, and contact discharges. The contact portion of the test is optional.

The time-dependent gaseous discharge characteristics of the approaching-electrode apparatus are also described. It is shown that the addition of resistances in series with the gap changes the nature of the discharge from an oscillatory discharge to a unidirectional one. It is also shown that the magnitude of the current, which is affected by the series resistance, can determine the form of the unidirectional discharge. For currents larger than about 0.3 A, the discharge is essentially an arc, characterized by a low (30-100 V) voltage drop across the gap. For currents less than 0.1 A, the discharge is essentially a spark discharge characterized by a voltage drop of approximately 300-400 V across the gap. The efficiency of energy delivery from the storage capacitor to the gap is profoundly affected by the form of the discharge. The efficiency for arc discharges is approximately 3-6% and the efficiency for spark discharges is approximately 15-25%. The energy of initiation of energetic materials in the primary explosive category as determined by gaseous discharges is a strong function of the energy delivery rate. The minimum initiation energy values are considerably less in the spark mode (long duration discharge) than in the oscillatory or arc modes (short duration discharges).

INTRODUCTION

Electrostatic sensitivity tests are used to assess the electrostatic hazards associated with processing and handling energetic materials. There is, however, no standard electrostatic test because those in current use were independently designed and fabricated by government or private laboratories for their internal purposes. At present, there are four different electrostatic sensitivity apparatuses and test procedures specified in the Joint-Service Manual (Ref 1) for use in qualifying primary, booster, and main-charge explosives. Here at ARRADCOM, there are at least five additional, different apparatuses. Although, in principle, the tests are similar, the parameters of the equipment are different. Consequently, widely, varying minimum initiation energy values have been reported for a single substance such as lead azide. As can be seen in Table 1, values varied from 2×10^{-2} to $<6 \times 10^{-8}$ and 1×10^{-1} to 2×10^{-5} J for RD1333 lead azide and dextrinated lead azide, respectively. It is also possible to change the relative order of sensitivity of primary explosives with the same apparatus by altering the test parameters or the rate of energy delivery. In Table 2, it can be seen that dextrinated lead azide is more sensitive than tetracene when no resistance is in series with the gap (oscillatory discharge). However, when a 100-kilohm resistor is in series with the gap (spark discharge), tetracene is more sensitive. Nevertheless, electrostatic sensitivity tests can provide an important measure of the hazards associated with processing and handling energetic materials. The nature of the test and interpretation of the results are key factors.

In this paper, I will first describe the time-dependent gaseous discharge characteristics of the improved approaching-needle apparatus, which has been proposed to the Joint-Service Committee for adoption as a standard. Then I will describe the apparatus and the recommended operating procedure.

Gaseous Discharge Characteristics

For a better understanding of the electrostatic sensitivity data and to improve the tests, it is important to recognize that when a charged capacitor is discharged through a gas (spark gap), several different modes of discharge can occur depending upon the value of the series resistance in the discharge circuit. Figure 1 shows the current waveforms for several values of series resistances when a 1176 pF capacitor charged to 3000 V is discharged to ground through the discharge circuit containing a 0.18 mm preset gap. With no series resistance in the discharge circuit, the current and voltage of the gaseous discharge vary in an oscillatory (underdamped) manner due to the inductance inherent in the circuit.

Addition of resistance to the circuit damps out the discharge and results in an overall shortening of the discharge time and a decrease in the current amplitude. The discharge time reaches a minimum when the added resistance results in a critically damped circuit. Further increases in resistance results in unidirectional (overdamped) discharges of longer duration. With large series resistances (hundreds of kilohms) the discharge is no longer continuous but takes the form of bursts of sparks due to relaxation oscillations. Representative current and voltage waveforms for a relaxation-oscillation discharge is shown in Figure 2.

It is also important to recognize that unidirectional discharge can occur as arcs or sparks. Both modes may occur in a single discharge, depending primarily on the resistance in the discharge circuit and to a lesser extent on the initial voltage. An arc is a post-breakdown discharge in which thermionic emission from the cathode is responsible for sustaining the discharge. The most characteristic features of an arc are the low post-breakdown voltage drop across the gap, which is usually of the order of tens of volts (30-100 V), and the high current flow, larger than 0.3-0.5 A. An arc may be formed for series resistances as large as 10-20 kilohms, for gaps as large as 1.3 mm, and is not necessarily associated with touching electrodes. A spark discharge on the other hand, is a post-breakdown regime in which the discharge is maintained by secondary emission of electrons from the cathode by ion-bombardment. The voltage drop across the spark is typically 300-400 V and the current is in the milliampere range. Representative current and voltage waveforms for an arc and a spark are shown in Figure 3 for resistances of 2, 10, 100 kilohms. Figure 3A represents an arc discharge. It can be seen that the voltage across the gap, which is initially sufficiently high to break down the gap (greater than 1400 V), rapidly decreases to the low post-breakdown voltage of approximately 30-100 V (region a) and remains at this low voltage until the discharge ceases. The voltage across the gap then increases to the value of the voltage remaining on the storage capacitor (region b), since there is no longer a voltage drop across the series resistor. The current (dashed line) decreases as the storage capacitor discharges in a conventional capacitor discharge pattern from several amperes to below a minimum sustaining value (point c), at which time the discharge ceases.

With the 100-kilohm resistor (Fig 3C), a spark discharge is obtained. The parameters are the same as for Figure 3A except for the higher series resistor. The behavior is similar to that of the arc (Fig 3A) except that the post-breakdown voltage is higher,

approximately 300-450 V, and the peak current is lower, about 30 milliamperes. For an intermediate resistance (10-kilohms) (Fig 3B), the waveforms show that there is a transition during the discharge from an arc to a spark. The gap voltage during the discharge jumps abruptly from 100 V (arc) to 350 V (spark) with a change in the slope of the current waveform. In the transition range the nature of the discharge can be different for repetitive tests. These gaseous discharge characteristics are very similar to those observed for the fixed-gap, parallel-plate apparatus (Ref 2,3).

Efficiency of Energy Dissipated in the Gap

Another effect of adding series resistance is to change the fraction of the energy stored in the capacitor that is dissipated in the spark gap. The energy dissipated in the gap may be written,

$$E_{gap} = \int V_g(t) I_g(t) dt \qquad (1)$$

where

$V_g(t)$ = instantaneous gap voltage

$I_g(t)$ = instantaneous gap current

The voltage waveforms (Fig 3) show that the voltage drop for either an arc or a spark is approximately constant. Thus, Equation 1 may be rewritten,

$$E_{gap} = V_g \int I_g dt$$

$$= V_g Q_g \qquad (2)$$

where Q_g is the total charge passing through the gap. The total charge in microcoulombs (μC) was determined by measuring the final voltage, V, across a one microfarad capacitor, C, in series with the gap,

$$Q_g = CV \qquad (3)$$

The total energy available in the storage capacitor, E_{cap}, is,

$$E_{cap} = 1/2\ C_o V_o^2 \qquad (4)$$

where

C_o = capacitance of the storage capacitor

V_o = voltage to which the capacitor is initially charged

The efficiency is the fraction of the total energy in the storage capacitor which is dissipated in the gap containing the sample; thus,

$$\frac{E_{gap}}{E_{gap}} = \frac{2Q_g V_g}{C_o V_g^2} \qquad (5)$$

The efficiency for arc discharges is approximately 3-6% and the efficiency for spark discharges is approximately 15-25%. The efficiency for an oscillatory discharge is assumed to be about 90%.

Improved Apparatus for Assessing Electrostatic Hazards

To meet the need for a single, standardized electrostatic sensitivity test apparatus and procedure for characterizing energetic materials, an improved, approaching-needle apparatus was proposed to the Joint Service Committee for adoption as a standard test. It is simple, safe, and capable of yielding meaningful and reproducible results. In particular, it distinguishes between primary and booster or main-charge explosives, as well as ranks the electrostatic sensitivity of an energetic material in the primary explosive category.

The electrostatic sensitivity apparatus consists of a charging circuit and an approaching-electrode assembly. The approaching-electrode assembly (Fig 4) is a spring-operated device in which the upper electrode (needle) is rapidly lowered to a preset distance above the base electrode and immediately raised again to its initial position. Adjustments in the gap length is made by raising or lowering the lower (cathode) electrode by means of a micrometer, which is connected to the lower electrode and is located outside the firing chamber. The firing chamber can be made smaller than a 30 cm cube.

A schematic diagram showing the principle of operation of the approaching-electrode assembly is given in Figure 5. The needle electrode is raised to the cocked position when the handle "D" is pulled to the left position. The spring "F" is under maximum tension at this point. The release rod "H" is engaged. When the release rod is pulled, the spring contracts, thereby rapidly lowering the needle to its lowes

position and immediately raising it again to its initial position. Handle "D" must be pulled to the left again to cock the device for another trial.

At present, for booster, main-charge, and some primary explosives, it is difficult to determine whether ignition actually occurred, or whether the smoke observed was just finely divided particles of the explosive dispersed by the discharge. In the proposed apparatus, a special sample holder was designed which allows the reproducible detection of a limited amount of reaction in the sample. The sample holder confines the explosive for a time long enough to allow a self-sustaining reaction to get underway. The upper portion of the lower electrode (cathode) is a detachable, solid cylinder of hardened steel, which serves as the explosive holder (Fig 6). The holder consists of a 0.9-1.6 mm thick nylon or polyethylene washer (3.2-4.8 mm i.d.) fastened along the sides with double adhesive tape to the top of the steel cylinder, leaving a space 3.2-4.8 mm by 0.9-1.6 mm high to contain the explosive. Electrical insulating tape (0.19 mm thick) placed over the opening provides adequate confinement. In using the sample holder, the steel needle punctures the tape and a discharge occurs through the interstices of the powder. A minimum reaction is indicated by a severed tape, whereas no reaction is evidenced by a punctured but otherwise intact tape.

A schematic of the charging circuit is shown in Figure 7. The circuit is designed so that the apparatus can be used both as a screening test to characterize energetic materials and as a test to rank sensitive materials. In the screening test, a 0.002 mfd capacitor is charged to 4.5 kV. No resistance is in the discharge circuit, thus the test materials are assessed by using an oscillatory discharge. The energy for the test is 0.02 J, which is the charge energy that an ungrounded person can accumulate. There is no electrostatic distinction made between booster and main-charge explosives. Those materials which are initiated at the 0.02 J level are relatively sensitive and are placed in the primary explosive category. A second test is then used to rank the sensitive materials.

The sensitive materials are assessed using oscillatory, spark, and contact discharges. The contact discharge portion of the test can be optional. The unit is designed to provide a discharge at any voltage up to 5 kV from any capacitance from 250 pF to 0.01 mfd. To obtain an unambiguous measure of the relative sensitivity to the spark mode, the series resistance is 100 kilohms, which limits the peak current to less than 0.1 A. A detailed description of the apparatus and operating procedure are given in Reference 4.

The charging circuit is designed so that the storage capacitor is connected to the high-voltage source only when the approaching electrode is in the raised position. As soon as the approaching electrode starts to move downward, the high voltage contact is broken, thus disconnecting the high side of the capacitor from the charging source during discharge. For safety, a high-voltage, double-pole, double-throw pressurized relay (switch) is included to discharge to ground any residual voltage remaining in the discharge circuit after the discharge operation is completed. The relay also prevents the capacitor from being recharged when the electrode is in the raised position until the reset button is pushed. The door of the firing chamber is provided with an interlock switch, which, when the door is opened, automatically disconnects the high-voltage power supply from the storage capacitor and shorts to ground the charged capacitor and the approaching-electrode assembly.

Reproducibility

Two series of tests were carried out at the 50% firing point to determine the reproducibility of the approaching-needle apparatus. One of the tests was with RD1333 lead azide and the other test was with dextrinated lead azide. The results, summarized in Table 3, show very good reproducibility. The spread of the 50% firing points are well within the range generally observed for sensitivity measurements.

Screening and Ranking Test Results

The screening test results for a number of explosives commonly used are given in Table 4. As can readily be seen, primary explosives fired, whereas booster and main-charge explosives did not. The ranking of the sensitivity of five primary explosives are shown in Table 2. It should be noted that dextrinated lead azide is more sensitive than tetracene to an oscillatory discharge, but is less sensitive to a spark discharge. The 50% firing point values were used to rank the very sensitive primary explosives.

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Table 1

Lead azide minimum initiation energies

Azide	Energy (J)	Reference
RD1333	2×10^{-2}	5
	4×10^{-3}	6
	4×10^{-4}	4
	3×10^{-6}	7
	$<6 \times 10^{-8}$	8
Dextrinated	1×10^{-1}	9
	2×10^{-2}	5
	2×10^{-3}	10
	4×10^{-4}	11
	2×10^{-5}	7

Table 2

50 Percent initiation points of primary explosives

Explosive	Energy (10^{-7} J)	
	Oscillatory discharge (R = 0 ohms)	Spark discharge (R = 100 kilohms)
Basic lead styphnate	3,400	1,000
NOL-130	3,350	900
RD1333 lead azide	23,600	9,000
Dextrinated lead azide	31,500	18,400
Tetracene	62,500	11,100

Table 3

Reproducibility of determinations using
RD1333 lead azide & dextrinated lead azide
(50% firing point)

Date test	Oscillatory discharge (R = 0 ohms, C = 625 pF)		Spark discharge (R = 100 kΩ, C = 1176 pF)	
	V (kV)	E (10^{-7} J)	V (kV)	E (10^{-7} J)
		RD133 lead azide		
4/25/77	3.02	25,000	2.77	9,000
5/04/77	2.48	17,300	2.71	8,600
5/11/77	3.15	28,000	2.98	10,400
		Dextrinated lead azide		
4/15/77	3.30	30,500	4.09	19,700
5/12/77	3.50	32,500	3.75	16,500

Table 4

Screening test results
(Energy: 0.02J)

Explosive	Fire/no fire
Lead styphnate	Fire
RD1333 lead azide	Fire
Dextrinated lead azide	Fire
Tetracene	Fire
Composition B	No-fire
Tetryl	No-fire
PETN	No-fire
RDX	No-fire
HMX	No-fire
TNT	No-fire

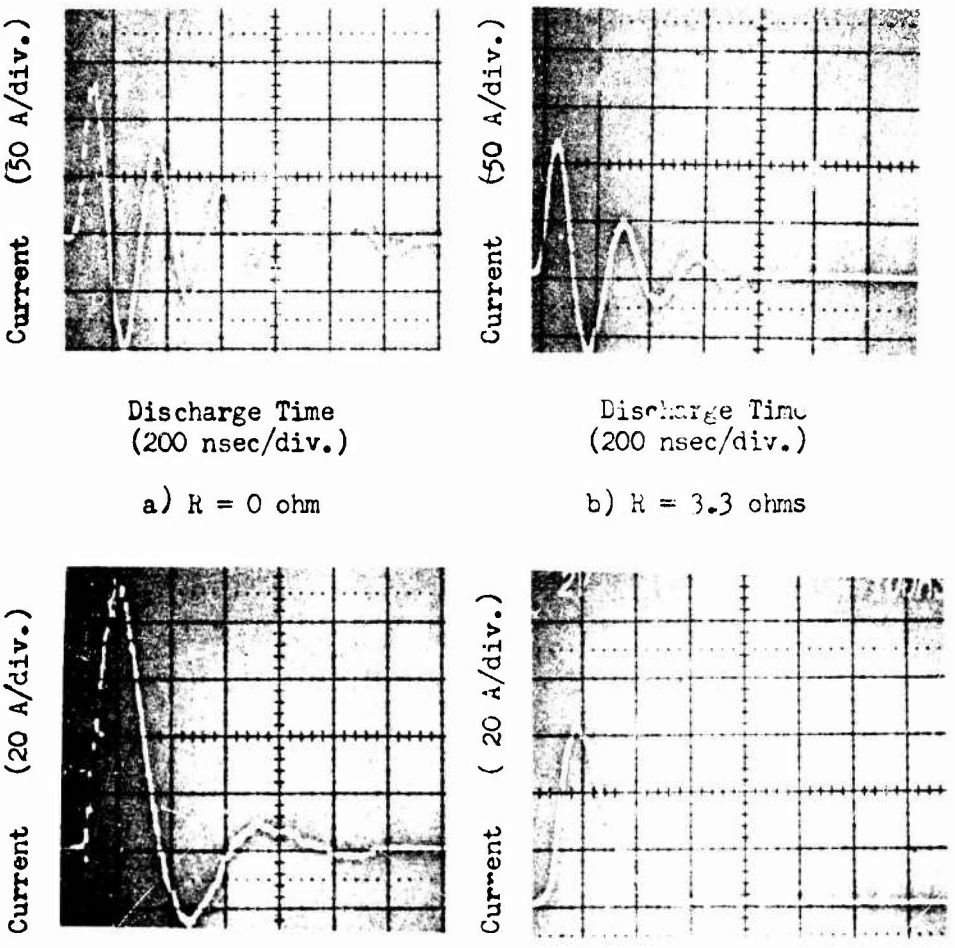
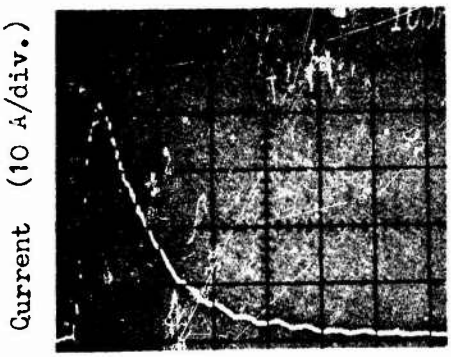


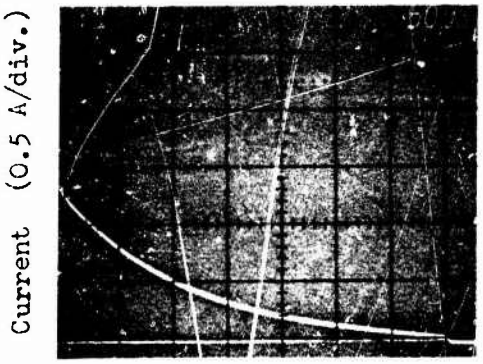
Fig 1 Typical current characteristics

(1176 pF capacitor charged
to 3,000 V)



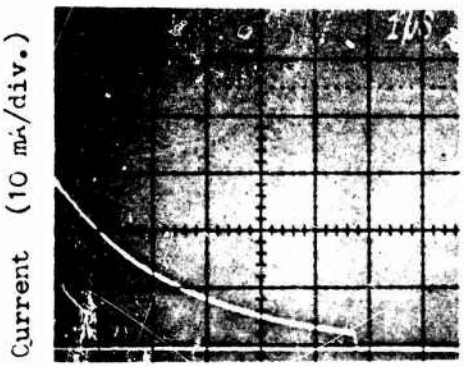
Discharge Time
(100 nsec/div.)

e) h = 100 ohms



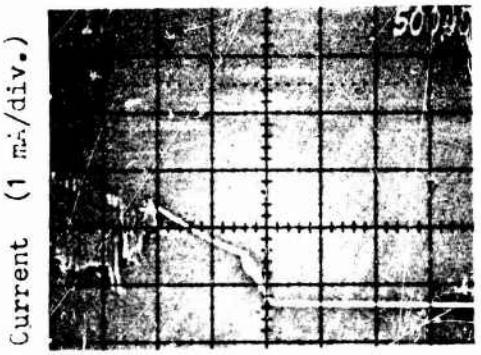
Discharge Time
(1 μsec/div.)

f) h = 2 kilohms



Discharge Time
(50 μsec/div.)

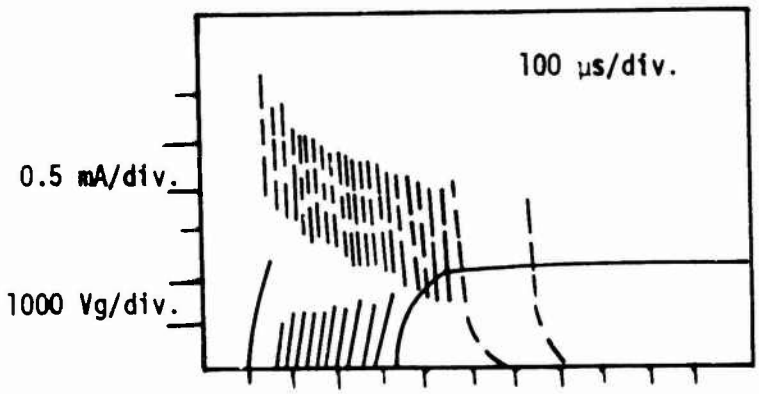
g) h = 100 kilohms



Discharge Time
(500 μsec/div.)

h) h = 1 megohm

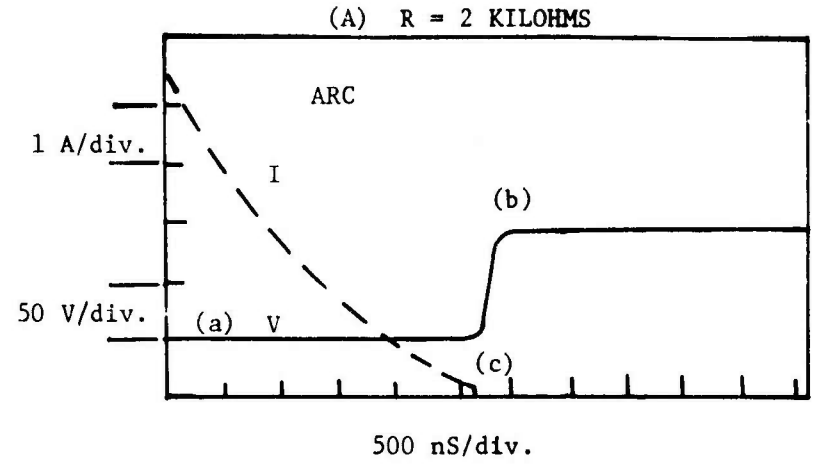
Fig 1 (continued)

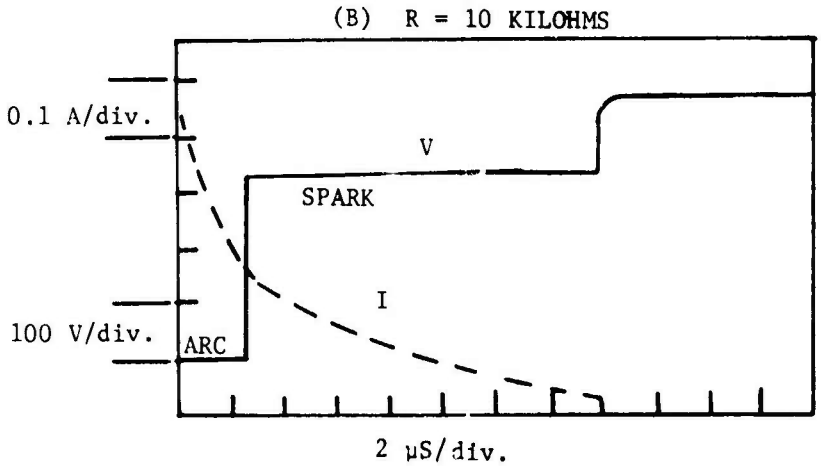


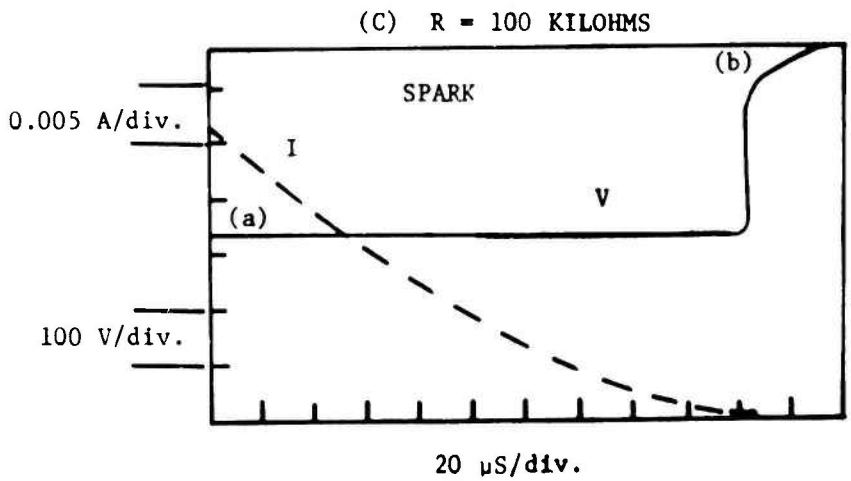
Dashed L ıe: Current vs Time
Solid Line: Voltage vs Time

C=500 pF R=1.2 megohms

Fig 2 Relaxation oscillation discharge







Dashed line: Current vs. Time Solid line: Voltage vs. Time

Fig 3 Representative current

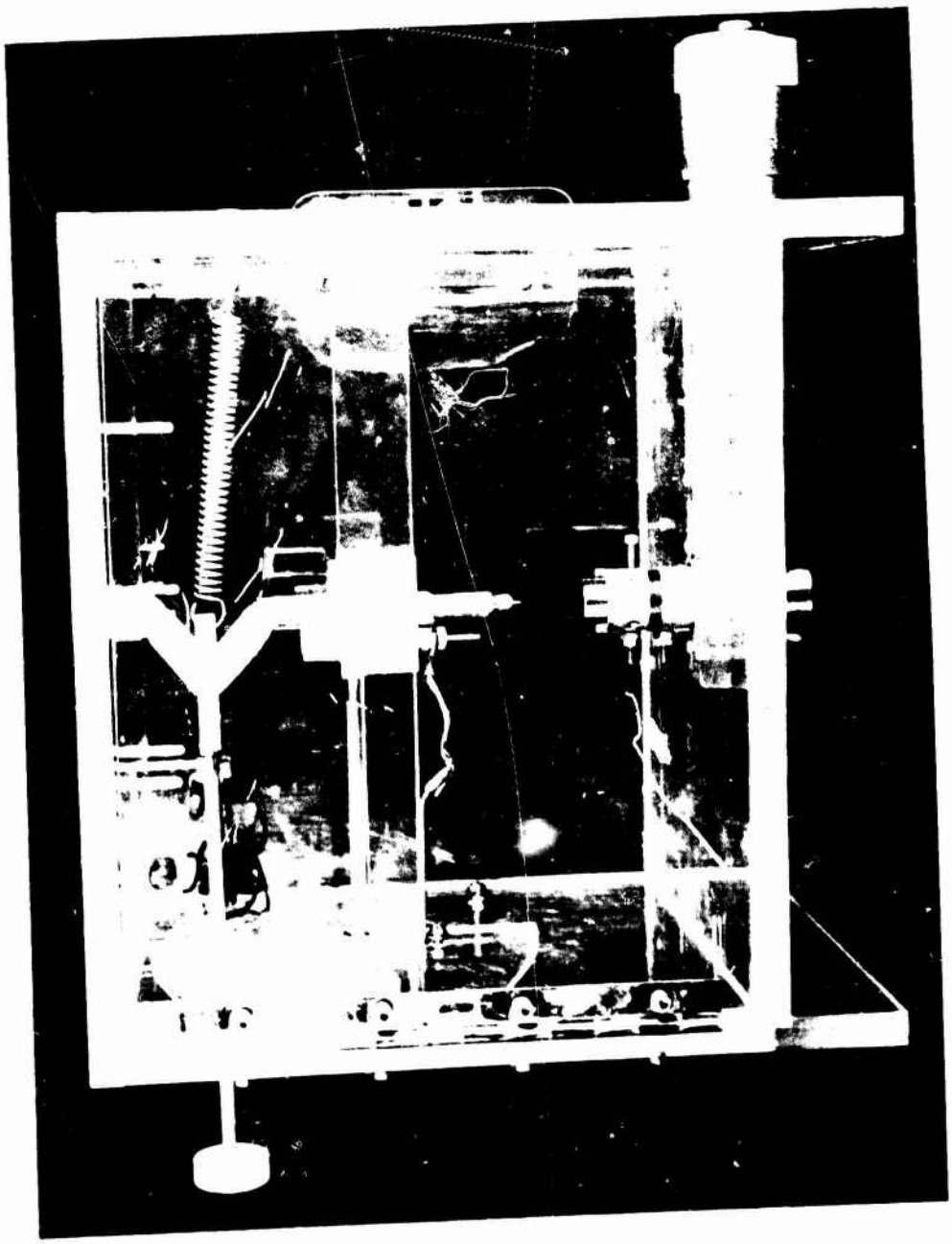


Fig 4 Approaching-electrode assembly

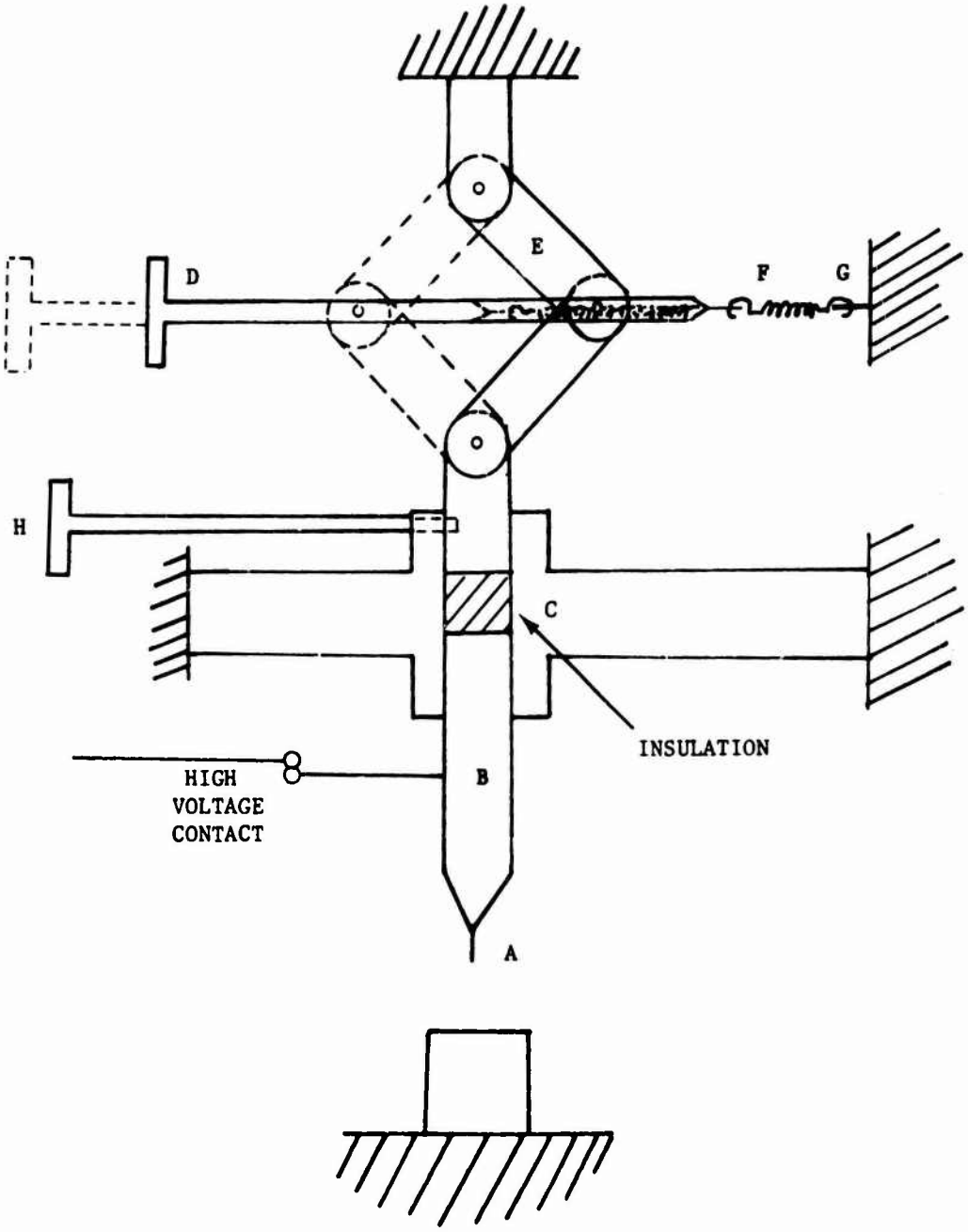


Fig 5 Schematic showing operation of approaching assembly

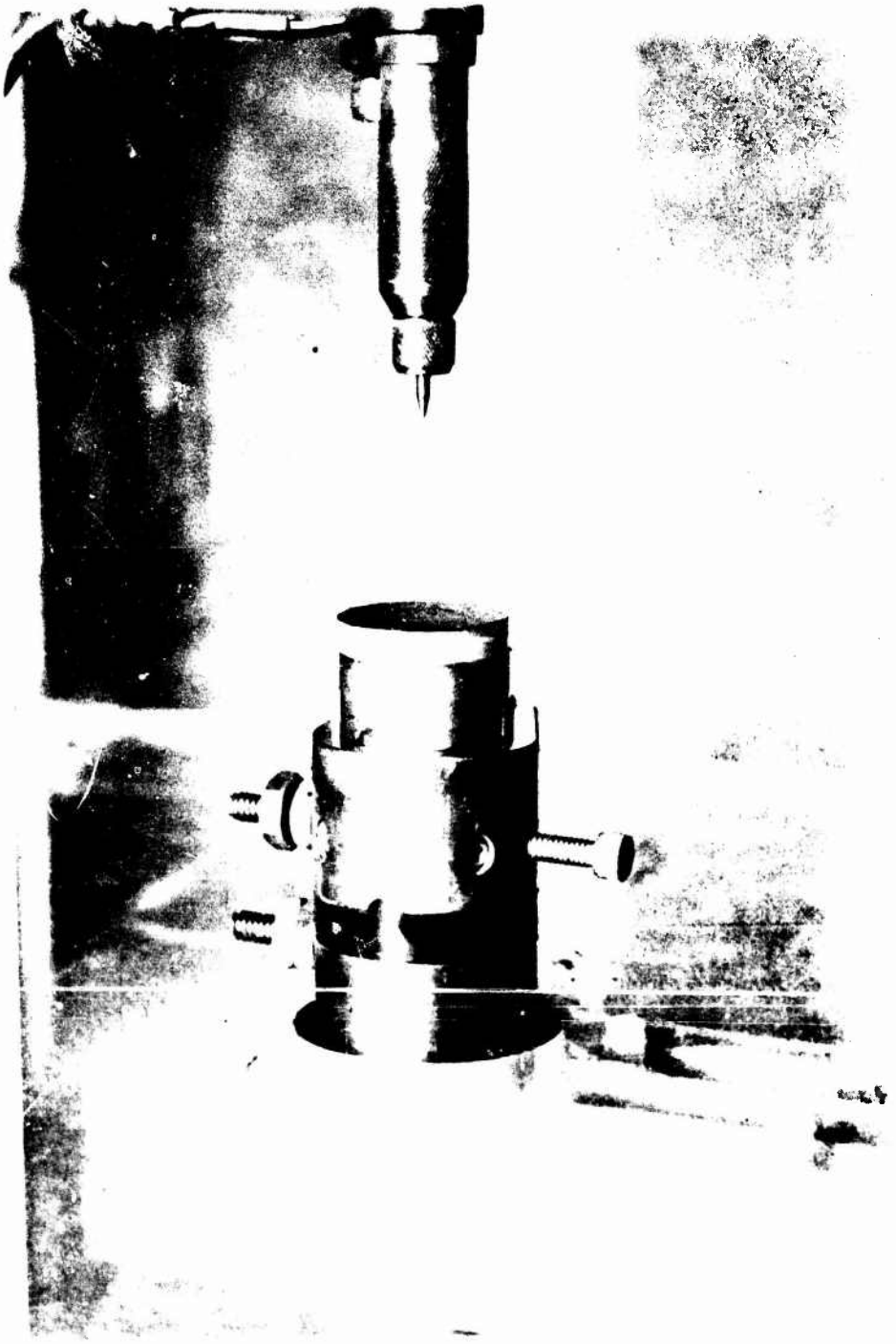


Fig 6 Sample holder

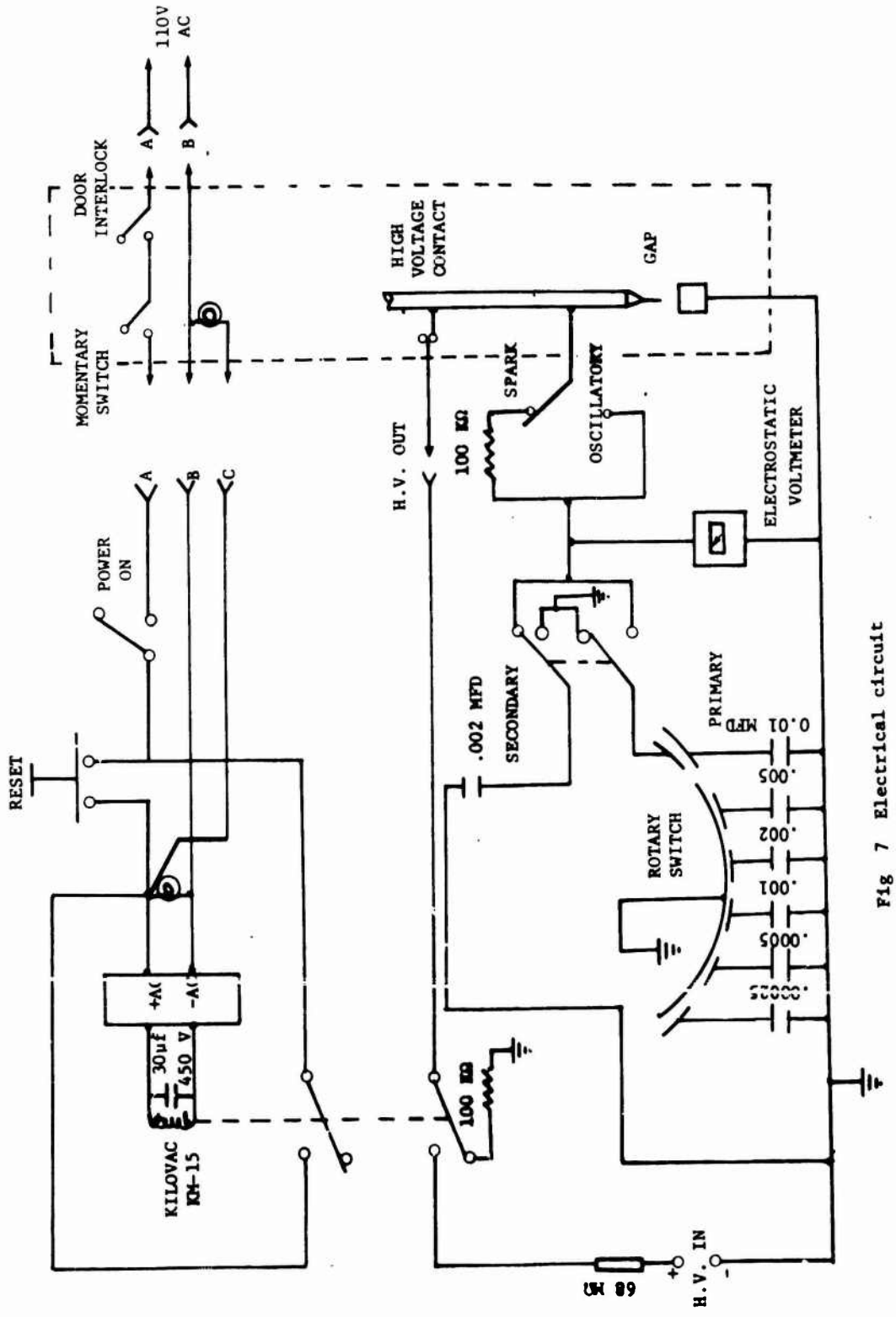


Fig 7 Electrical circuit

A ROTARY FRICTION SENSITIVENESS TEST FOR EXPLOSIVES

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ABSTRACT

A machine with a rotary action has been developed to assess the sensitiveness of explosives to friction between metal surfaces. To provide a reasonably reproducible source of hot spots, the two surfaces confining the explosive should first be in stationary contact under a fixed load, then one surface is moved a fixed distance at some suitable velocity, after which the surfaces are separated.

The load is applied to the underside of a flat steel block which supports a thin layer or sliver of the explosive material in contact with the curved surface of a steel wheel. The latter is moved at a predetermined velocity, by engagement with a fly-wheel, through one-sixth of a revolution. The load and velocity are the normal working parameters of the test, while the strike length, finish (prepared by grit blasting) and hardness of the surfaces are normally kept constant. The standard procedure at present is a 50-shot up-and-down run, varying the velocity for each shot and keeping the load constant.

The machine is capable of covering the range of friction sensitiveness shown by primary explosives at one end to TNT at the other. RDX and PETN have given quite reproducible results, whereas HMX gives a wider spread. TNT ignitions are difficult to discern. Several composite propellants and pyrotechnics have also been studied. Very reproducible results have been obtained with lead azide, silver azide and lead styphnate and their sensitisation by grit has been demonstrated.

In the case of RDX and PETN, a relationship of the form MV^2 = constant has been found, where M is the load and V is the velocity for 50 per cent ignitions. It is hoped that this will form the basis of a scale to cover the whole sensitiveness range.

A few surfaces other than steel have also been studied.

SUMMARY

A mechanically operated test for the friction sensitiveness of explosives has been developed to replace the UK mallet friction test. The hardness and finish of the working surfaces together with the load and strike length are all kept constant, the latter by driving a wheel through a fixed angle, the explosive sample being held between the periphery of the wheel and a flat block. The velocity remains constant during the strike, but is varied from shot to shot following the well-known "up and down" procedure. The results are analysed to give the velocity for 50% ignitions.

This new test covers the whole range of sensitiveness from primary explosives through propellants and pyrotechnics to high explosives. The product of the load and the square of the velocity for any explosive is shown to be sensibly constant suggesting that this value can be used as a measure of the friction sensitiveness over this wide range. Although normally operated with the sample between steel surfaces, other materials can be used if required.

INTRODUCTION

Of the many mechanical sensitiveness tests for explosives, those depending on friction for the generation of heat and its transfer to the explosive sample generally give rise to many more problems than those dependent on impact or an electrostatic spark, since the rate of production of heat energy is much slower than in the latter tests. As would be expected therefore, any friction sensitiveness test will depend largely on the operating velocity and the thermal conductivity and geometry of its working surfaces. Of the many attempts to compromise these various factors and produce a useful test those of Alleghany Ballistics Laboratory[1] and the US Naval Ammunition Depot[2] have met with some success in the fields of propellants and pyrotechnics, while the friction sensitiveness test of the Bundesanstalt fur Materielprufung[3] has been used by a number of European countries. The UK however has continued to rely on the mallet friction test[4] for comparison of explosives for both military and civil use.

From a knowledge of the operating characteristics of the above tests a new test described as the Rotary Friction Sensitiveness Test has been devised. This was aimed at producing comparative values for the friction sensitiveness of explosives ranging from the most sensitive primary explosives to the relatively insensitive high explosives. The hardness, surface finish, contact area and length of strike are kept constant and with a fixed load on the sample the results are determined as the velocity required for 50 per cent ignitions. The principle of operation is to hold the thin sample of explosive between the prepared surfaces of a flat strip and a cylinder or wheel, under a given load. The wheel is then rotated by means of a drive from a heavy flywheel and striking mechanism at a more or less constant velocity after which the surfaces are separated. Each material is subjected to a 50-shot "up and down" run following the procedure described by Dixon and Mood[5] to determine the velocity for 50% ignitions for a given applied load.

EXPERIMENTAL

The sample of explosive is either cut as a sliver or spread by means of a spatula so that its thickness is no more than about 0.1 mm on a flat strip of steel, diamond hardness 200, whose surface has been prepared by gritblasting to a finish of 1.5 to 2.0 μm (60 to 80 μ inches). This strip is shown at A (Fig 1) and is held by means of the compressed air cylinder B under the predetermined load in contact with the periphery of the wheel C. The latter has the dimensions:

Diameter	68 mm
Thickness	9.5 mm
Surface finish	1.5 - 2.0 μm

and is of steel of diamond hardness 470 ± 30. The wheel is mounted on spigots on the end of a rotor the other end of which holds a pivoted latch operated by a relay switching mechanism in the circuit of a solenoid. When the firing switch is operated this latch is moved into the path of a striker on the periphery of a heavy flywheel which drives the rotor and therefore the roughened wheel through 60° after which the friction surfaces are separated by means of a cam on the rotor and a push rod operated by the loading cylinder. The three eccentric spigots determine the section of the wheel subjected to the strike so that each wheel can be used for six strikes, three from each side, before resurfacing. This is done by gritblasting as with the flat surfaces, the geometry of which enables each metal strip to be used for eight strikes each on a fresh surface.

The load used is usually 72 kg for explosives and propellants, or 9 kg for primary explosives, and is controlled by a regulator in the air line. The striking velocity can be varied from 0.4 m/sec to 8.0 m/sec by controlling the speed of the motor which drives the flywheel. This speed is therefore set at a suitable starting value according to the explosive being tested and the first shot fired, the occurrence of ignition being detected usually by a report or flash. In some cases however only a little smoke may be seen or even just a blackening of the smear left on the friction surfaces, any of these observations being counted as a "fire". According to the "up and down" procedure the velocity is increased for a failure or reduced for a fire, by about 10 per cent of the previous velocity, and so forth until 50 shots have been done. The proportions of fires at the successive levels are then submitted to a computer for Probit Analysis,[5] from which an optimised value of the velocity for 50 per cent ignitions is obtained, together with the standard error of this velocity. The slope of the probability regression can also be obtained, but for this purpose it is an advantage to provide some additional experimental values to those obtained by the simple up and down procedure, and some work in this direction is now being carried out.

RESULTS

Crystalline explosives were the first to be examined with this test and these materials were first sieved through an 80 mesh sieve to

allow a suitably thin layer to be spread on the flat strip. Since both load and velocity can be varied some of these materials were tested with different loads with a view to establishing some correlation between these parameters. It was found that for a particular explosive the load M times the square of the velocity V is constant and this may be regarded as a figure of merit for that explosive, Table 1.

RDX and PETN probably attract the greatest interest since these are often accepted as standards for comparison of most explosives. The figures for TNT and HMX are given for comparison but should be accepted with some reserve. In the case of TNT evidence of ignition was only seen as a partial blackening of the smear of explosive, and the low melting point of this explosive means that this must exert a lubricating action. The HMX was tested as the β-form and although an apparently satisfactory figure for 50 per cent ignitions was obtained the probability of ignition varied only a little with the velocity of strike probably due to phase changes during the strike.

The very much greater sensitiveness of the primary explosives lead styphnate and lead and silver azides is well illustrated. In addition the effect of adding 2 per cent grit to the lead azide reduces the velocity for ignition by a factor of three to 0.43 m/s which is about the lowest working velocity of the system and indicates an extremely hazardous material. Even at this level the standard error is still quite small, in relation to its parent value, which is highly satisfactory. Other mixtures of crystalline powders which have been tested are pyrotechnic compositions and these have also given useful results.

Propellant compositions have been tested as thin slivers cut with a microtome or knife and spread or pressed to a layer of not more than 0.1 mm using a rolling pin specially profiled for the purpose. A typical result for a plastic propellant was 2.5 m/s $\pm$ 0.2 with an applied load of 72 kg. This same material was also tested on flat strips of carbon fibre block, which had a diamond hardness of about 50, and gave rise to a value of 4.7 m/s for the velocity.

DISCUSSION

The values of the standard errors shown in column 3 of the table are usually not more than about 5 per cent of the values they qualify and this is regarded as a very satisfactory discrimination factor for the test, especially when considered in relation to the wide range of

sensitiveness coverage. In fact the test has been used with some success to monitor changes of sensitiveness resulting from climatic storage trials on a variety of materials on the one hand and small changes in composition during the development of particular propellants on the other.

The "figure of merit" for any explosive as shown by the value of MV^2 in Table 1 is, as might be expected, an energy term. It would be unwise however to regard it in any way as absolute since only a very small proportion of the energy extracted from the flywheel in a single shot is seen by the explosive. It is appreciated that a fuller understanding of the action of the test may be achieved by measuring the loss of energy of the flywheel during a strike and correlating this in turn with the amount of metal ground out of the flat strip and with the transfer of heat from this region to the explosive. It has been found also that this metal to metal contact is an essential pre-requisite to ignition in this test, and ignitions due to friction between the metal surface of the wheel and the explosive alone would require several times the velocities used in this test.

CONCLUSIONS AND RECOMMENDATIONS

The Rotary Friction Sensitiveness Test fulfils a long awaited requirement for assessing the friction sensitiveness of various explosives in terms which can be used by engineers to design processing equipment to minimise hazards either in normal functioning or in the event of excessive friction due to fault development. The analysis of the results has hitherto been made on the basis of a normal arithmetic probability distribution which is as far as a 50-shot "up and down" run would permit. A more extensive investigation would be required to establish the validity of a logarithmic probability distribution from which it may be possible to extract more definite information in the low incidence region of sensitiveness.

The essential dimensions of the working surfaces have been indicated with values for the hardness and surface finish. It is feasible to change the materials of the wheel and flat strip for other relevant hard materials and a very limited amount of work has already been done in this direction. The importance of using the same surface finish in each test is also realised and the method of achieving this to the usual tolerances is described in the Appendix.

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1	Richardson R H et al	Annals of the New York Academy of Sciences 1968, 152, Art 1, 269
2		US Naval Ammunition Report RDTR No 60 11 June 1965
3	Koenen H R, Ide K H and Swart K H	Explosivestoffe, 1962, 9, 30
4		UK Sensitiveness Collaboration Committee: Explosives Hazard Assessment Manual of Tests SCC, 1966, Test No 2
5	Dixon W J, Mood A M	J Am Statist Ass, 1948, 43, 109
6	Finney D J	Probit Analysis, Second Edition, Cambridge University Press, 1964

DETAILS OF WORKING SURFACES

The flat surface is normally of mild steel, diamond hardness = 200 $\pm$ 10 and is prepared by gritblasting as for the curved surfaces see below but the surface finish is not quite so critical. However, the friction test makes a groove approximately 0.001 in deep and the strip must first be ground flat again by some suitable means before gritblasting.

The curved surface of each wheel is cleaned and prepared by gritblasting with 46 alumina grit using a quarter inch diameter boron nitride nozzle at a distance of about one inch from the surface. The feed pressure is about 70 to 90 psi, and two or three minutes is sufficient to refurbish a set of wheels.

The surface finish should be checked either visually against a standard prepared by the same method or using a profile measuring instrument. The finish should be 1.5 to 2.0 μm (60 to 80μ inch).

TABLE I

Explosive	Load M Kg	Velocity V_{50} M/S	V_{50}^2	MV_{50}^2
PETN	18	3.6 ± 0.1	13.3	240
	36	2.8 ± 0.2	7.9	282
	54	2.3 ± 0.1	5.3	286
RDX	36	5.1 ± 0.1	26.3	948
	54	4.3 ± 0.1	18.6	1000
		4.4 ± 0.2	19.1	1031
		4.5 ± 0.2	20.3	1097
	72	3.8 ± 0.1	14.4	1020
		4.0 ± 0.1	16.0	1172
HMX	36	3.1 ± 0.2	9.4	335
	72	2.1 ± 0.1	4.4	317
TNT	72	3.7 ± 0.3	13.7	980
LEAD AZIDE	9	1.3 ± 0.1	1.7	15
	18	0.8 ± 0.1	0.6	11
LEAD AZIDE + 2% GRIT	9	0.4 ± 0.04	0.16	1.4
LEAD STYPHNATE	9	2.1 ± 0.1	4.4	40
SILVER AZIDE	9	1.7 ± 0.4	2.9	26

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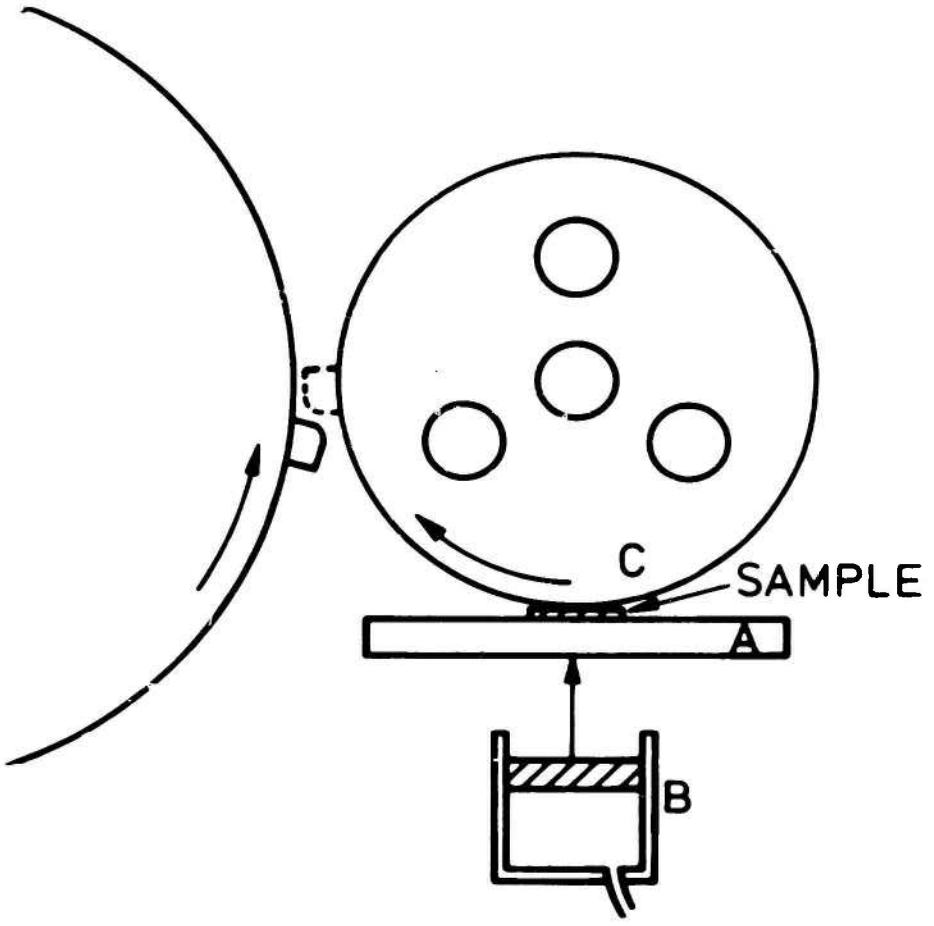


FIG. 1 ESSENTIAL ACTION OF ROTARY FRICTION SENSITIVENESS TEST

A FUNDAMENTAL APPROACH TOWARD AN IMPROVED STANDARD FRICTION SENSITIVITY TEST

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ABSTRACT

Research is underway on a new approach toward an improved standard friction sensitivity test which is based upon the measurement of interfacial temperatures generated by friction in explosives. The temperature rise is produced by sliding frictional stress at the contact area between a fixed solid explosive loaded against a rotating sapphire disc. A new instrument, which incorporates an infrared microscope, torque sensor and balance arm has been developed to obtain simultaneous measurements of temperature, apparent optical contact area, torque, angular velocity and normal force. Deformation theory and Archard's theory of the surface temperature of rubbing surfaces are used to calculate the elastic and plastic contact areas and the theoretical temperature rise from the physical properties of the explosive and sapphire, the normal force, the sliding speed, the coefficient of friction and the contact geometry.

Results are presented for Comp B. It was found that (1) Surface temperature rise increases with sliding speed, normal force and frictional heat input to the contact area, (2) The change of state of Comp B from solid to liquid was observed at the melting point by a decrease in torque, (3) The apparent contact area and the elastic contact area and the plastic contact area of the spherical surface of the explosive on a sapphire disc increases with load, and (4) Correlation is obtained between the experimental surface temperature rise and the theoretical temperature rise calculated using either the plastic contact area or the apparent optical contact area.

Using this technique, it is expected that the effects of composition, lubrication, contact geometry and method of manufacture upon the surface temperature and hence upon hazard can be determined.

INTRODUCTION

Understanding of the interfacial mechanisms involved in the initiation of energetic materials is required in order to provide a rational basis for a new approach toward an improved standard friction sensitivity test. Therefore, a new technique has been developed to measure interfacial temperatures produced by friction in energetic materials and to understand the role of the real contact area. The temperature rise is produced by sliding frictional stress at the contact area between a fixed solid explosive loaded against a rotating sapphire disc. A new instrument, which incorporates an infrared microscope, torque sensor and balance arm, has been developed to obtain simultaneous measurements of temperature, apparent optical contact area, torque, angular velocity and load. Deformation theory and Archard's theory of the surface temperature of rubbing surfaces are used to calculate the elastic and plastic contact areas and the theoretical temperature rise from the physical properties of the explosive and the sapphire, the normal force, the sliding speed, the coefficient of friction and the contact geometry.

This new technique provides a method to quantify fundamental properties of energetic materials such as surface temperature as a function of load, sliding speed and coefficient of friction. Using this method it is expected that the effects of composition, lubrication, contact geometry and processing on friction sensitivity of explosives can be determined. This new technique, used in conjunction with this data base, will provide a rational basis for the further development and establishment of standard sensitivity tests to evaluate hazards associated with energetic materials in development, manufacture, loading and field use. The ultimate objective is to minimize the hazards due to friction sensitivity of energetic materials through an understanding of their significant physical and chemical properties and thereby improve safety in production and field use.

APPARATUS

A schematic of the rotating disc sliding contact friction instrument is shown in Figure 1. An explosive specimen mounted on one end of a balance beam is loaded against a sapphire disc by placing weights in a bowpan pivoted at the other end. The specifications of the sapphire disc are thickness: 1mm, diameter: 2.54 cm, flatness: 10 waves, surface: 1 microinch, parallelism: .0025 cm. The applied force at the contact area is approximately one and one-half times the force of the weights since the balance beam is pivoted to provide a 3:2 load ratio. The frictional stress and interfacial temperature rise at the contact area between the explosive and the sapphire disc is produced by rotating the disc at a constant angular

velocity in the 600-7000 RMP (.6-7 M/s) range by means of a synchronous motor in conjunction with a variable frequency power supply.

The temperature rise at the interface between the explosive and the sapphire is measured with the IR microscope as follows. The radiance emitted at the contact area is transmitted by the sapphire disc and measured with the indium antimonide detector in the microscope. Either the temperature or the emissivity can be determined from the radiance if the other parameter is known. The emissivity is the ratio of the radiance of the explosive to the radiance of a black body at the same temperature. Therefore, the emissivity of the explosive, heated to a known temperature, is first measured with the IR microscope so that the radiance data taken during the tribology experiment can be converted to a measured temperature.

The torque which results from the frictional stress at the contact area is measured with a rotating shaft torque sensor and provides a value for the coefficient of friction. The angular velocity of the rotating shaft is measured with a speed sensor, an integral part of the torque sensor, and provides a value for the sliding speed at the contact area. The air bearing provides low rotational friction and low axial and radial yield in the instrument. The operation of the friction and infrared measuring system is summarized in the block diagram in Figure 2.

Temperature Calculation

The mean temperature rise, θ_m, of the contact area between the explosive and sapphire disc is calculated according to Archard's theory (Ref 1) which assumes that the heat is generated at the true contact area and is conducted away into the bulk of the rubbing members. The model used in this theory is shown in Figure 3 (Ref 1). The spherical surface of the explosive, E, forms a circular contact area on the flat surface of the sapphire disc, S.

Both elastic and plastic deformation are considered. The Hertz equation (Ref 2,3) is used to determine the radius of the elastic contact area

$$A = \pi a^2 \tag{1}$$

$$a_e = \left[\left(\frac{1 - \nu_S^2}{Y_S} + \frac{1 - \nu_E^2}{Y_E} \right) \frac{3}{4} W R \right]^{1/3} \tag{2}$$

where

ν_E = Poisson's ratio of the explosive

ν_S = Poisson's ratio of sapphire

Y_E = Young's modulus of the explosive

Y_S = Young's modulus of sapphire

W = Normal force at contact

R = Undeformed radius of the explosive

For plastic deformation the contact area

$$A_p = \frac{W}{P} \tag{3}$$

where P = hardness of the softer body. Thus the plastic contact radius (Ref 1)

$$a_p = \left(\frac{W}{\pi P}\right)^{1/2} \tag{4}$$

The frictional heat, Q, generated when the explosive moves across the sapphire disc is the rate of heat supply from area, A, per second. Therefore the explosive receives heat from a stationary heat source and the sapphire disc receives heat from a moving heat source. In Archard's theory the temperature rise of the explosive, Θ_E, and the sapphire, Θ_S, is first calculated assuming that all of the frictional heat

$$Q = \mu W v \tag{5}$$

where

μ = coefficient of friction

v = sliding speed at contact area A

is supplied to it. The sliding speed

$$v = \frac{2 \pi r \quad V}{60} \tag{6}$$

where

r = radius of contact from the center of sapphire disc

V = angular velocity of rotating shaft.

The coefficient of friction

$$\mu = \frac{T}{W \quad r} \tag{7}$$

where

T = torque measured at contact area.

Then the mean temperature of the contact area, Θ_m, is calculated from (Ref 1)

$$\frac{1}{\Theta_m} = \frac{1}{\Theta_E} + \frac{1}{\Theta_S} \tag{8}$$

which determines the proportion of total heat flowing into each body by the requirement that each body has the same average temperature over the contact area.

The heat is supplied to a fixed contact area on the explosive and a steady state temperature

$$\Theta_E = \frac{Q}{4 \; a \; K_E} \tag{9}$$

where

K_E = thermal conductivity of the explosive

is reached.

Archard uses a dimensionless parameter, developed by Jaeger (Ref 4), called the Peclet number

$$L = \frac{v \;\; a \;\; d_S \;\; c_S}{2 \;\; K_S} \tag{10}$$

where

d_S = density of sapphire

c_S = specific heat of sapphire

to account for the effect of sliding speed on the temperature rise.

When the sliding speed of the sapphire disc at the contact area is sufficiently small, $L < 0.1$, there is ample time for the temperature distribution of a stationary contact to be established in the sapphire and

$$Q_S = \frac{Q}{4 a K_S} \tag{11}$$

At higher speeds the temperature for a moving heat source falls below that for a stationary heat source because there is not sufficient time for the temperature distribution of the stationary heat source to be achieved in the moving contact.

For moderate speeds, $.1 < L < 5$

$$Q_S = \frac{\alpha Q}{4 a K_S} \tag{12}$$

where α is a function of L which can be obtained from Figure 7 of Jaeger (Ref 4).

At high speeds, $L > 5$,

$$\theta_S = \frac{.31Q}{K_S a} \left(\frac{1}{2L} \right)^{1/2} \tag{13}$$

Temperature Measurement

The temperature rise of the contact area is measured by the IR microscope as follows. The IR microscope has been equipped with a 15X reflecting objective which provides spot size resolution of 3.56×10^{-5} M (0.0014 in.). The radiation from this spot plus that from a related solid angle between the spot and the detector is focused onto a liquid nitrogen cooled indium antimonide detector with a spectral response of 1.8-5.5 microns.

The various sources which emit the radiation received by the detector from an arbitrary spot in a contact formed by a load which produces deformation of the explosive sample are shown in Figure 4.

The radiation consists of contributions from the explosive, N_E, the sapphire disc, N_S, and the ambient background, N_o. The variables N_E, N_S, and N_o refer to the non-attenuated radiation which would be measured if each source could be observed separately. The term ambient background refers to radiation from the room which reflects off the spot and into the detector. The sapphire is transparent and will absorb a very small amount of the IR. In addition, the total quantity of radiation will be affected by fresnel reflection losses at each interface between different media. These attenuations are represented by the attenuation factors η_E, η_S, and η_o. They include losses due to reflection and absorption and are defined as the ratio of the radiation from a particular source reaching the detector to the radiation that would reach the detector without attenuation.

The total radiation collected by the detector is given by

$$N_T = \eta_E N_E + \eta_S N_S + \eta_o N_o \tag{14}$$

The total non-attenuated explosive radiation

$$N_E = \epsilon_E N_{BB} (T_E) \tag{15}$$

where

ϵ_E = emissivity of the explosive

$N_{BB}(T_E)$ = black body radiation intensity at temperature of explosive.

The explosive radiation attenuation (Ref 5)

$$\eta_E = \tau_S (1 - \rho_{I-S}) \tag{16}$$

where ρ_{I-S} = reflectance at normal incidence at sapphire air interface

τ_S = sapphire transmissivity.

The reflectivity at normal incidence of the sapphire air interface (Ref 6) is

$$\rho_{I-S} = \frac{(n_{I-S} - 1)^2}{(n_{I-S} + 1)^2} \tag{17}$$

where n_{I-S} is the average of the refractive index of sapphire relative to air in the 1.8-5.5 micron region.

The sapphire transmissivity

$$\tau_S = e^{-\beta_S x_S} \tag{18}$$

where β_S = absorption coefficient of sapphire

x_S = thickness of the sapphire disc

τ_S can be calculated using available values (Ref 7) of the absorption coefficient for sapphire. Secondary reflections have been neglected by an order of magnitude analysis because the primary fresnel reflection losses are small.

The intensity of incident ambient radiation

$$N_o = N_{BB}(T_o) \tag{19}$$

The ambient radiation attenuation (Ref 5)

$$\eta_o = \rho_{I-S} + \tau_S^2 (1 - \rho_{I-S})^2 \rho_{E-S} \tag{20}$$

where

ρ_{E-S} = reflectivity at normal incidence at the explosive-sapphire interface.

The explosive reflectivity at normal incidence at an explosive-air interface

$$\rho_{E-I} = 1 - \varepsilon_E \tag{21}$$

assuming that the emitting surface of the explosive is opaque. It is assumed that $\rho_{E-I} = \rho_{E-S}$ in the absence of any information on the value of n_E in the 1.8-5.5 micron region.

The non-attenuated sapphire radiation intensity

$$N_S = \varepsilon_S N_{BB}(T_S) \tag{22}$$

is small because the sapphire emissivity is small and T_S is less than T_E (Ref 8). Therefore the sapphire contribution to the total radiation intensity has been neglected.

Substituting equation 15 into equation 14 the total radiation collected by the detector is given by

$$N_T = \eta_E \varepsilon_E N_{BB}(T_E) + \eta_o N_o \qquad (23)$$

The radiance measured by the microscope is

$$N = N_T - N_o. \qquad (24)$$

Substituting N_T from equation 23 into equation 24 and solving for the radiance of a black body at the temperature of the explosive surface $N_{BB}(T_E)$ gives

$$\frac{N - (\eta_o - 1)\ N_o}{\eta_E \varepsilon_E} = N_{BB}(T_E) \qquad (25)$$

The temperature of the explosive surface is then determined from the IR microscope calibration of black body radiance as a function of temperature.

RESULTS

An example of the experimental data obtained is shown in Figure 5. A .377 inch diameter spherical surface of Comp B is loaded against the sapphire disc with a normal force of 7.9 newtons which corresponds to a weight of 500 grams on the pan. The shaft is rotated at an angular velocity of 2048 RPM. Using equation 6 the sliding speed at the contact area is about 2 meters/second since the radius of rotation is .01 M. The upper curve is the torque as a function of time. The larger peak at the beginning is the starting torque of the instrument. The lower curve is the radiance as a function of time. When the shaft stops rotating the torque decreases to the initial level and the explosive cools to ambient temperature.

At one minute the running torque is .5 volts which corresponds to a torque of 5-ounce-inches or .035 newton-meters; using equation 7 the coefficient of friction is .4. Using equation 5 the frictional heat input to the contact area is 7.4 J/s. At one minute the radiance is .08 volts which corresponds to a radiance of 12.4 milliwatts/cm^2 - steradian or a temperature of 80°C, the melting point of Comp B. The temperature rise produced by the frictional heat input is 57.5°C since ambient temperature was 22.5°C. The measured radiance is converted to a temperature using equation 25, the values of emissivity measured with IR microscope (see Table 1), and the IR microscope calibration.

The change of state of Comp B from solid to liquid has been observed at a normal force of 7.9 newtons when the sliding speed was increased. Curves of radiance and torque versus time for a .377 inch diameter spherical surface of Comp B sliding on sapphire at angular velocities of 664 RPM and 2019 RMP are shown in Figure 6. After two minutes of sliding at the initial speed of .7 M/s, the Comp B has been heated to a temperature of 60°C. The temperature rise produced by the frictional heat input is 37.5°C. The torque is 8.5 ounce-inches (.06 newton-meters) which corresponds to a coefficient of friction of .8. The frictional heat input is 4.2 joules per second.

At 2.2 minutes the angular velocity is increased to 2019 RPM, a sliding speed of 2 M/s. The torque drops to 4.5 ounce-inches (.03 newton-meters) which corresponds to a coefficient of friction of .4, but the frictional heat input to the contact area increases to 6.7 J/s. The ratio of the sliding speeds increases more than the ratio of the coefficients of friction decreases. Therefore the temperature rises to 82°C. The torque dropped because the Comp B melted and lubricated the interface. Thus the accuracy of the IR temperature measurement is demonstrated.

Temperature rise is plotted as a function of the product of friction coefficient and normal force for Comp B sliding on sapphire at various conditions of load and speed in Figure 7. The lower line represents a sliding speed of .7 M/s. The upper line represents a sliding speed of 2 M/s. Therefore temperature rise increases with sliding speed for Comp B.

Temperature rise is plotted as a function of the product of friction coefficient and sliding speed for Comp B sliding on sapphire at various conditions of load and speed in Figure 8. The upper line represents a normal force of approximately 8 newtons. The lower line represents a normal force of approximately 2 newtons. Therefore temperature rise increases with normal force.

Temperature rise is plotted as a function of the frictional heat input for Comp B sliding on sapphire at various conditions of load and speed in Figure 9. The temperature rise increases linearly with the frictional heat input. The slope of the line obtained from a least square fit of the data is 8.03 with a coefficient of determination of .94.

DISCUSSION

Deformation theory has been used to calculate the elastic and plastic contact radii of the .377 inch diameter Comp B on the sapphire disc as a function of load. Values of Young's modulus and Poisson's ratio used to calculate the elastic contact radius are given in Table

2. A value of hardness for Comp B was estimated using the approximation (Ref 9) that the hardness is about three times the uniaxial stress to produce plastic yielding. Since Comp B is not an ideal elastic-plastic material the value of compressive rupture stress has been used in the above approximation. Values of hardness of sapphire and compressive rupture stress for Comp B used to determine the plastic contact radius are given in Table 2. The apparent optical contact radius measured with the IR microscope is compared with the calculated values of the elastic and plastic contact radii as a function of load in Table 3. The apparent contact radius, the elastic contact radius and the plastic contact radius increase with load. The apparent optical contact radius is larger than the elastic or plastic contact radii at all except the largest load because the real area of contact is independent of the apparent area of contact (Ref 10). The stress (load/apparent area) at the contact area is the same order of magnitude as the compressive rupture stress of Comp B. Therefore it appears that the deformation is plastic, particularly at the loads applied during the friction experiments.

Archard's theory of the surface temperature of rubbing surfaces has been used to calculate the temperature of the Comp B - sapphire interface from the contact area, frictional heat input to the interface, the thermal conductivity of Comp B and sapphire, and the density and specific heat of sapphire. Values of thermal conductivity, density and specific heat for Comp B and sapphire are given in Table 2. The experimental temperature rise is plotted versus theoretical temperature rise for Comp B in elastic contact with sapphire in Figure 10. The solid line indicates a condition of perfect correlation. The theoretical temperatures are consistently larger than the experimental temperatures. Lack of correlation also indicates that the deformation is not elastic.

The experimental temperature rise is plotted versus theoretical temperature rise for Comp B in plastic contact with sapphire in Figure 11. Improved correlation is obtained because plastic deformation occurs. The experimental temperature rise is plotted versus theoretical temperature rise calculated using the apparent optical contact area for Comp B on sapphire in Figure 12. At the large loads applied in the friction experiments the real contact area is approaching the apparent optical contact area. Therefore improved correlation is also obtained when the apparent optical contact area is used to calculate the theoretical temperature rise.

The relationship between interfacial temperature rise due to frictional stress and time to explosion will provide a basis for a tri-service friction sensitivity test. This relationship can be obtained as follows. The relationship between temperature rise and friction heat input to the contact area can be obtained with the

instrument and technique described herein. The relationship between time to explosion and frictional heat input can be obtained with the instrument described herein or any instrument which measures the friction coefficient, sliding speed and load of a contact such as the PA rotary friction tester. Both relationships combine to provide the required relationship between time to explosion and temperature rise at the contact.

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NOMENCLATURE

Symbol	Definition	Units
A	area of contact	M^2
a	radius of circular area of contact A	M
c	specific heat	J/Kg-°C
Y	Young's modulus	N/M^2
g	acceleration due to gravity, 9.80 M/s^2	M/s^2
K	thermal conductivity	J/s-M-°C
P	hardness	N/M^2
Q	rate of heat supply from area A per second	J/s
μ	coefficient of friction	dimensionless
d	density	Kg/M^3
R	undeformed radius of curvature of explosive	M
V	angular velocity	RPM
v	sliding speed	M/s
r	radius of contact from center of disc	M
W	normal force at contact	N
Θ	temperature rise of the contact above ambient temperature	°C
ν	Poisson's ratio	dimensionless
L	Peclet number	dimensionless
N	radiance measured by IR microscope detector	watts cm^{-2} steradian^{-1}
N_T	total radiation intensity measured at some location in the contact	watts cm^{-2} steradian^{-1}

N_I	non-attenuated air interface radiation	watts cm^{-2} $steradian^{-1}$
N_o	non-attenuated ambient radiation intensity	watts cm^{-2} $steradian^{-1}$
N_E	non-attenuated explosive radiation intensity	watts cm^{-2} $steradian^{-1}$
N_{BB}	radiation intensity from a black body source	watts cm^{-2} $steradian^{-1}$
N_S	non-attenuated sapphire radiation intensity	watts cm^{-2} $steradian^{-1}$
T	temperature	°C
β	absorption coefficient of a material	mm^{-1}
x	thickness of a material	mm
η_I	attenuation factor for radiation from air interface	dimensionless
η_o	attenuation factor for ambient radiation	dimensionless
η_E	attenuation factor for explosive radiation	dimensionless
η_S	attenuation factor for sapphire radiation	dimensionless
ρ	reflectivity	dimensionless
τ	transmissivity	dimensionless
ϵ	emissivity	dimensionless
n	refractive index	dimensionless

Subscripts

m	mean
e	elastic
p	plastic
o	ambient temperature

E	explosive
S	sapphire
BB	blackbody
I	air
T	total

Units

M	meter
N	newton
J	joule
Kg	kilogram
s	second
RPM	revolutions per minute
mm	millimeters
m	minute

TABLE 1

Emissivity of Comp B

Temperature (°C)	Cast	Pressed Powder
38	.96	.92
50	.98	.95
65	.99	.98

Table 2

Physical properties of Comp B and sapphire

Material	Comp B	Reference	Sapphire	Reference
Young's Modulus (10^{10} Newton/Meter^2)	.76	15	36.5	14
Poisson's Ratio	.3	15	.25	13
Thermal Conductivity (Joules/Second-Meter-°C)	.262	11	41.8	14
Specific Heat (10^2 Joules/Kilogram-°C)	12.6	12	4.18	14
Density (10^3 Kilogram/Meter^3)	1.65	12	3.98	14
Hardness (10^{10} Newton/Meter^2)	-	-	1.9	14
Compressive Rupture Stress (10^7 Newton/Meter^2)	1.2	16	-	-

Table 3

Apparent, elastic and plastic contact radii for comp B on sapphire .377" diameter comp B surface

Mass (KG)	Load (N)	Apparent a (10^{-5} M)	Elastic a (10^{-5} M)	Plastic a (10^{-5} M)
.000	.5	11.7	6.1	6.7
.010	.7	13.2	6.6	7.6
.050	1.2	17.5	8.2	10.4
.100	2.0	18.8	9.5	13.2
.500	7.9	27.4	15.1	26.2
1.000	15.2	34.0	18.8	36.5

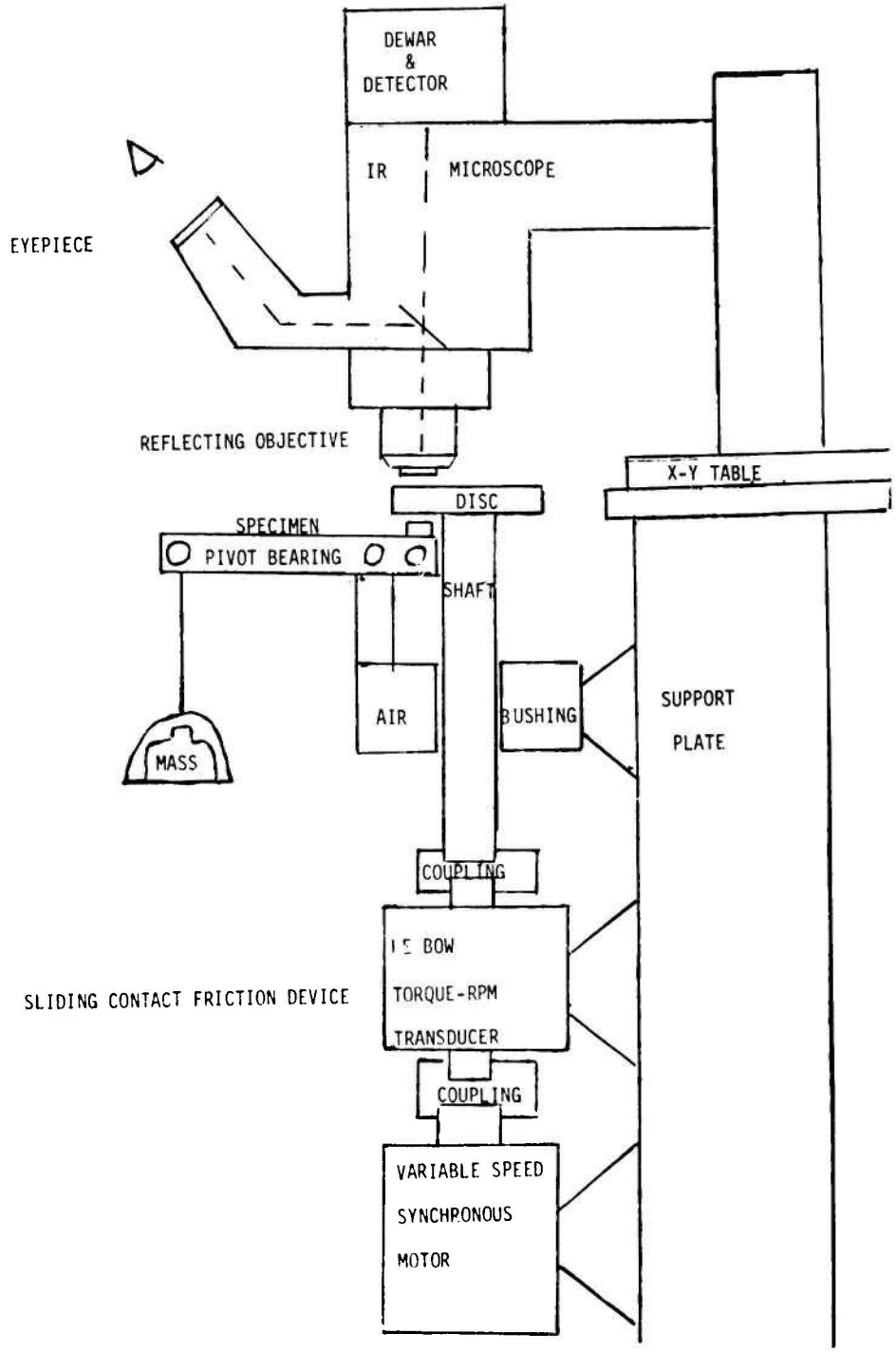


Fig 1 Sliding contact friction device

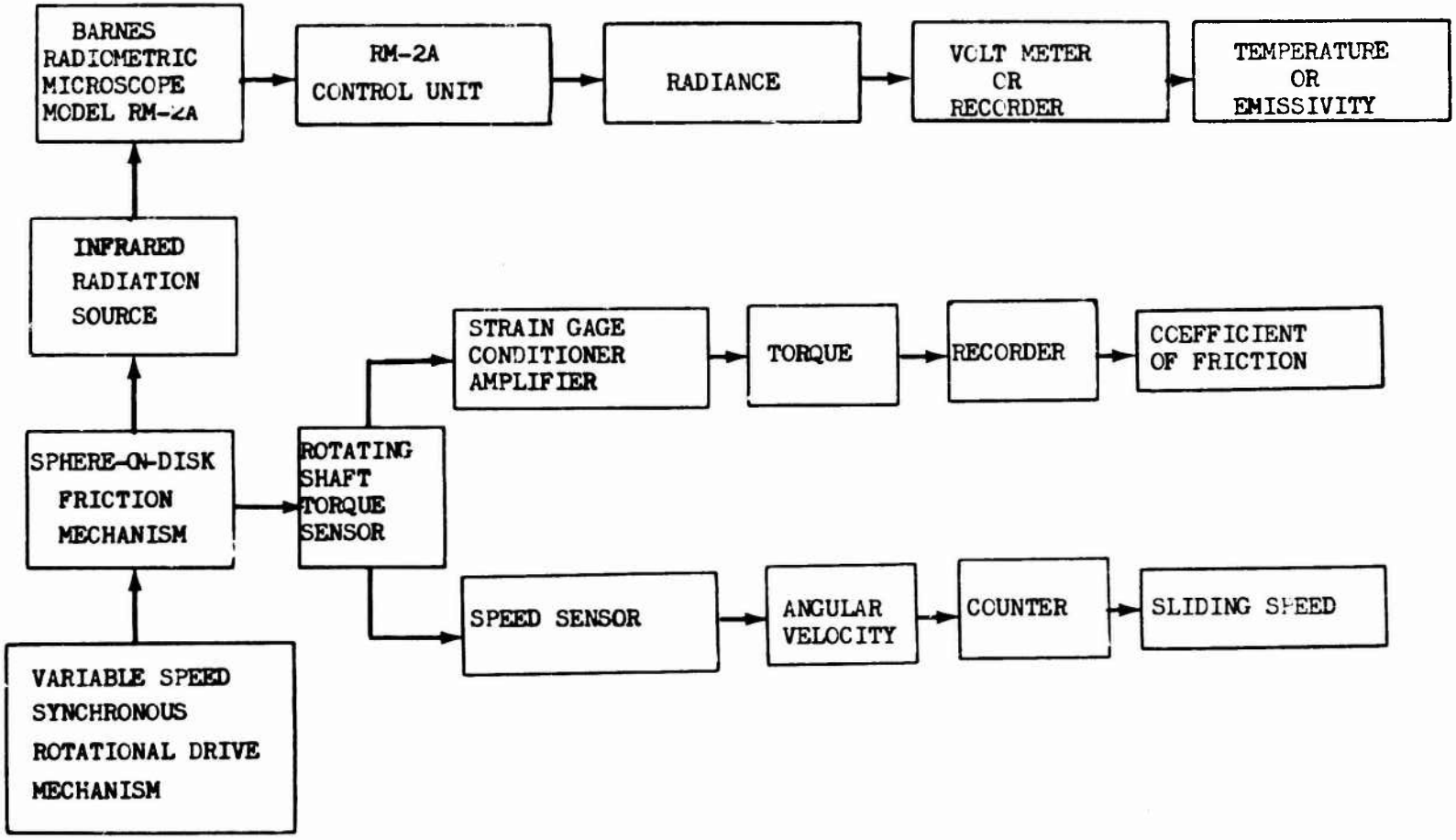


Fig 2 Block diagram of the friction and infrared measuring system

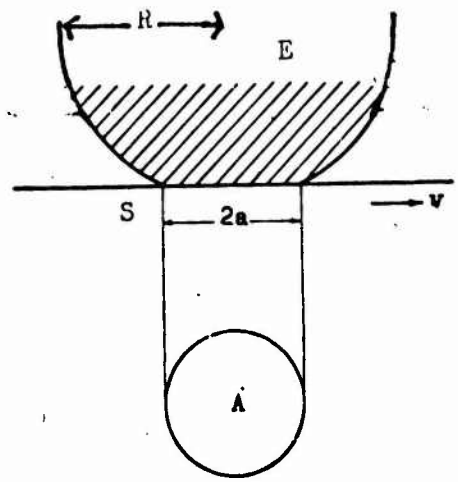


Fig 3 Archard model for temperature of rubbing surfaces

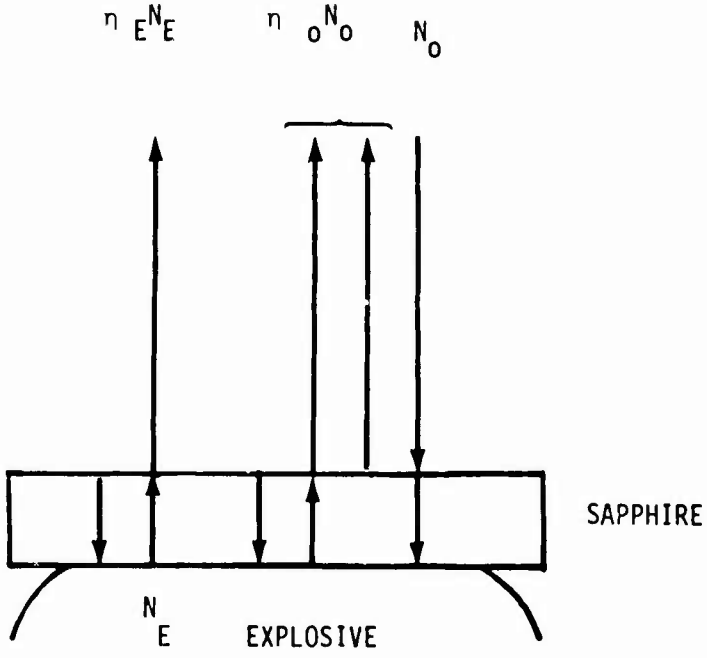


Fig 4 Sources of IR radiation emitted from an arbitrary location in a contact formed by a load which deforms the explosive surface

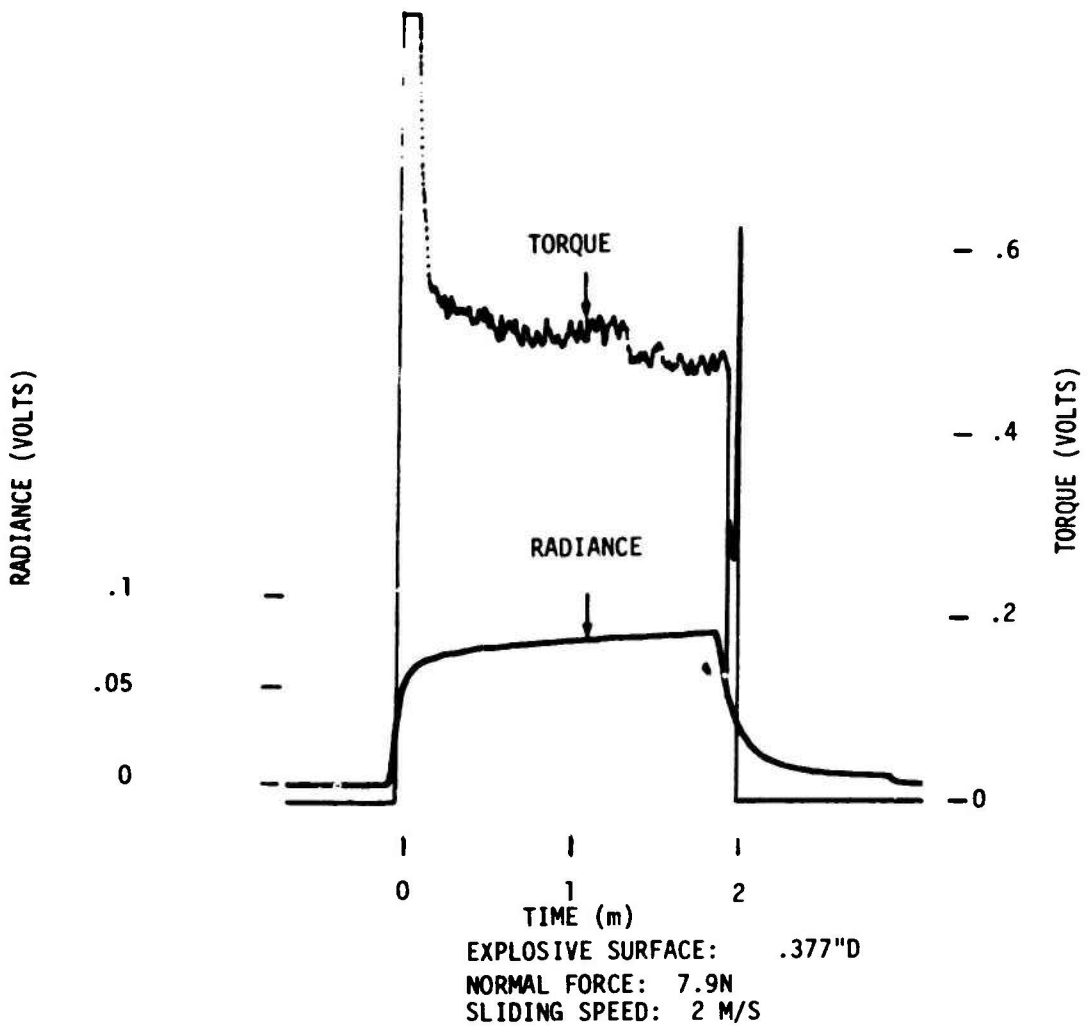


Fig 5 Radiance and torque versus time for comp B on sapphire

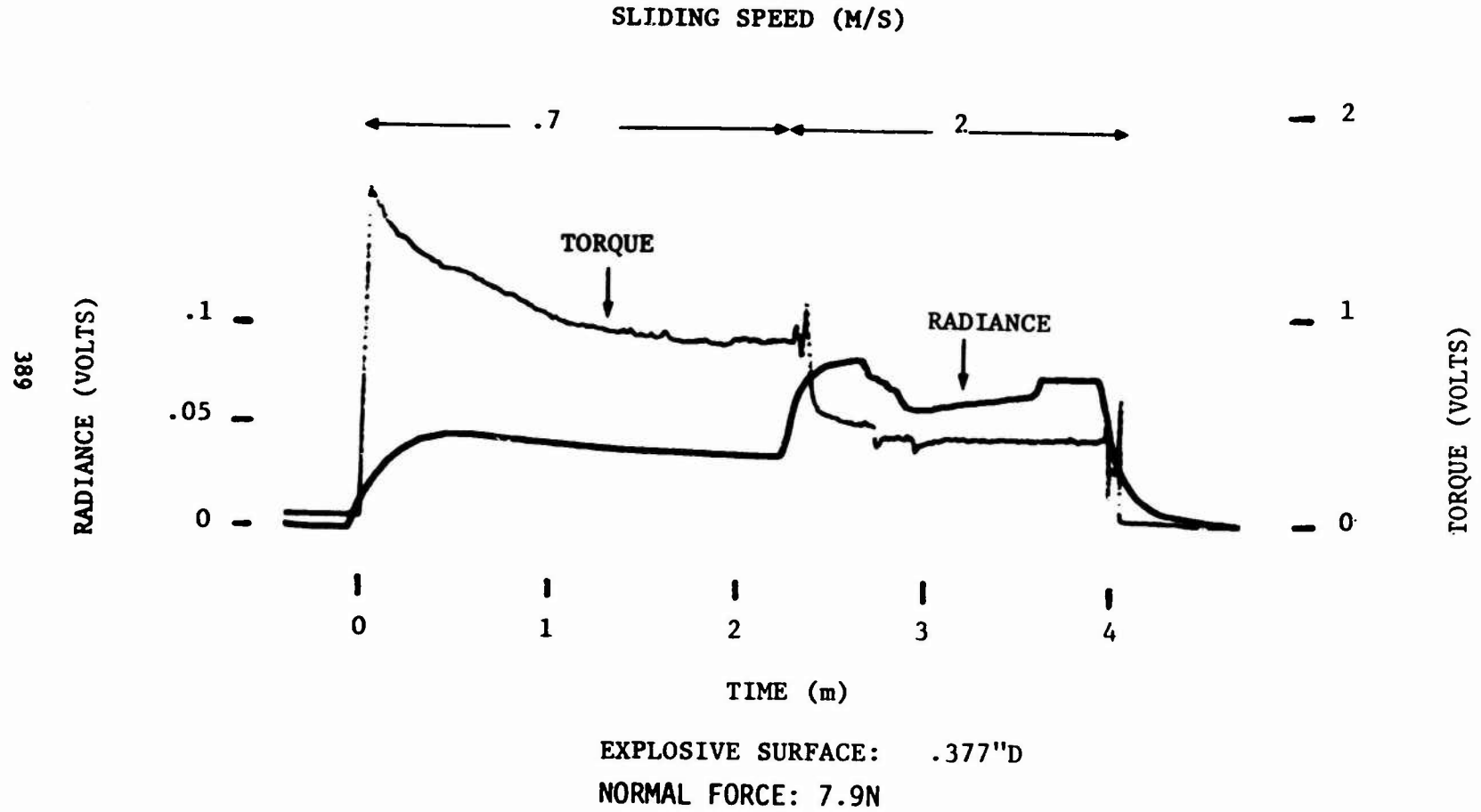


Fig 6 Radiance and torque versus time for comp B on sapphire at two sliding speeds

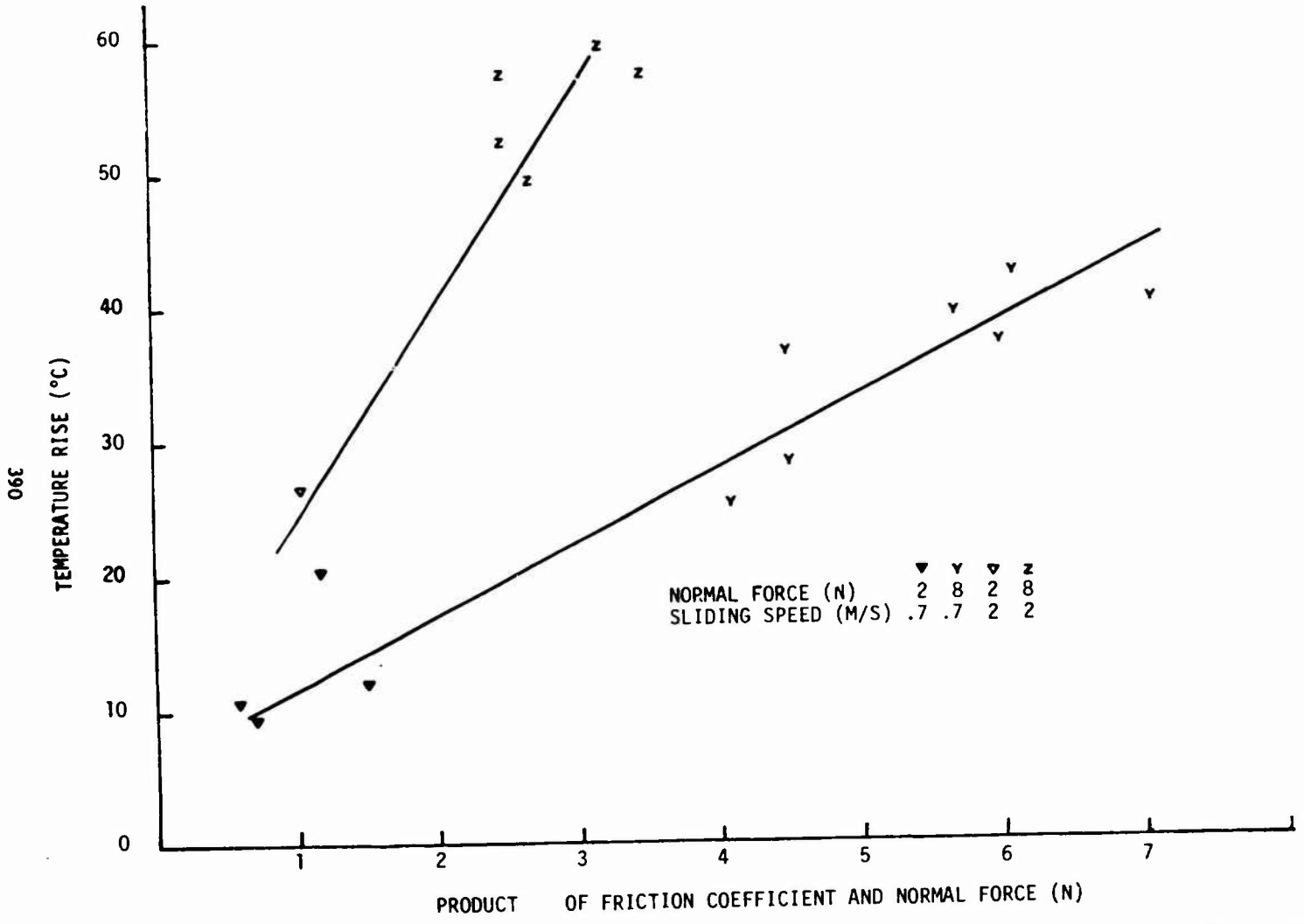


Fig 7 Temperature rise versus product of friction coefficient and normal force for comp B on sapphire

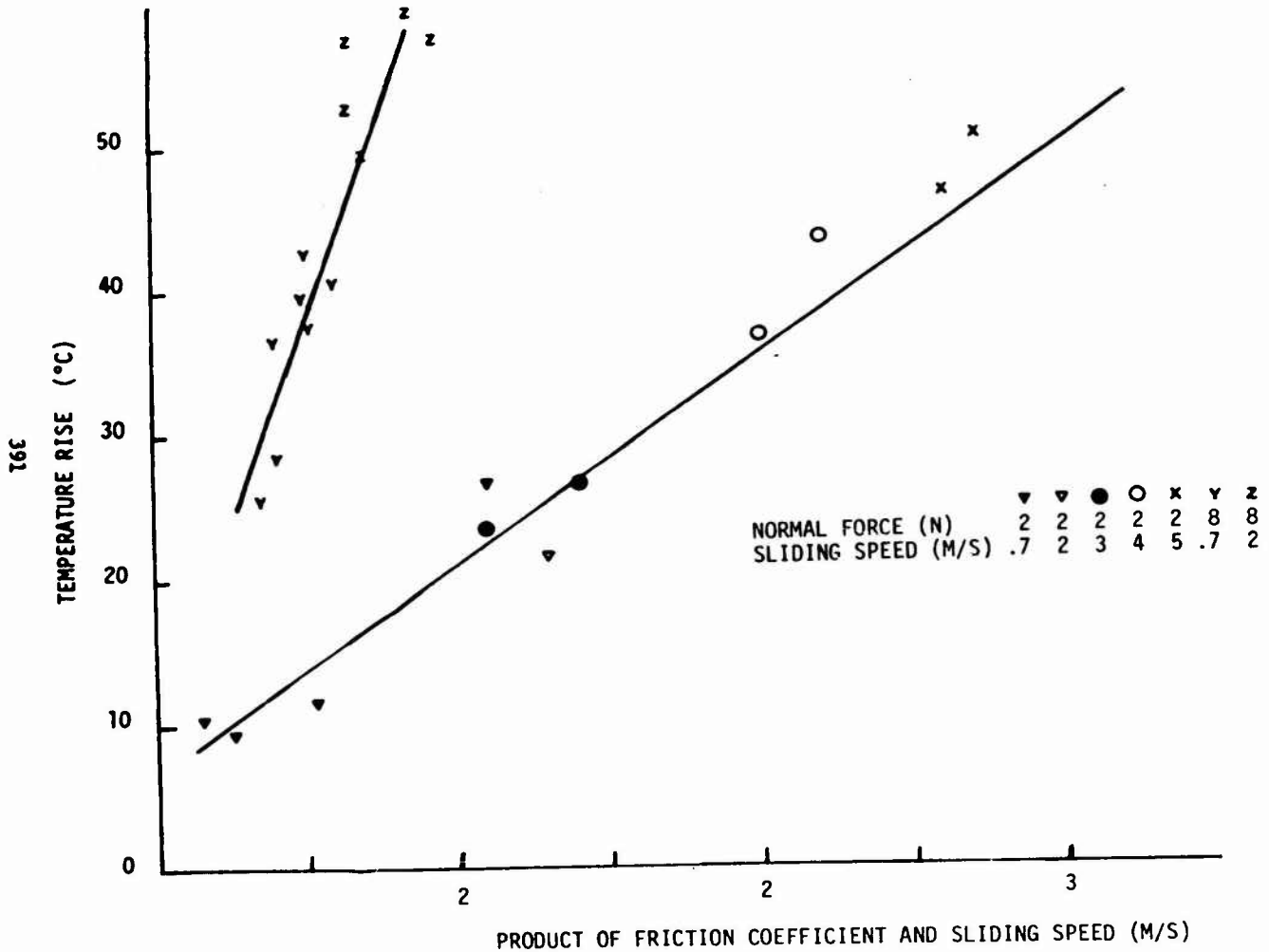


Fig 8 Temperature rise versus product of friction coefficient and sliding speed for comp B on sapphire

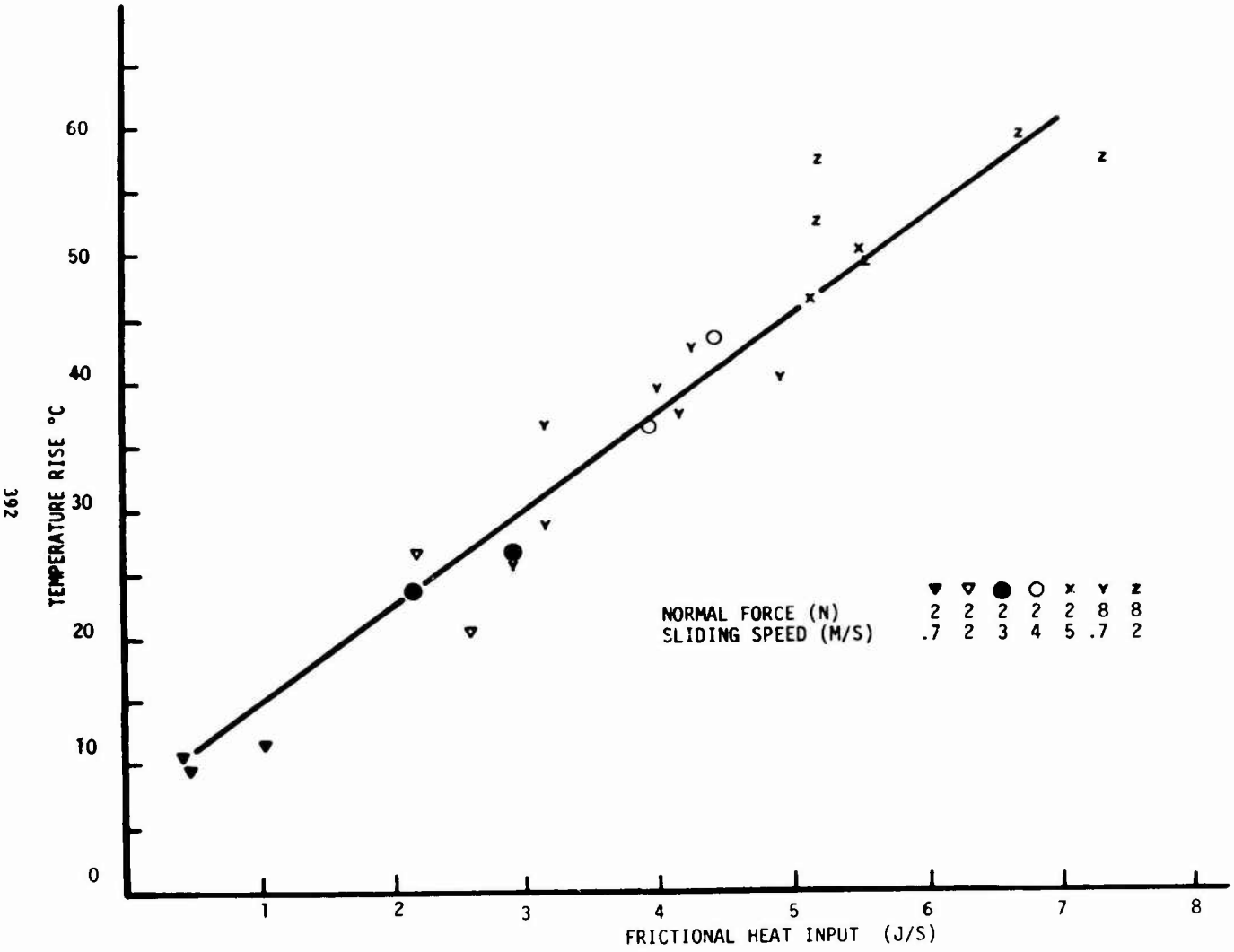


Fig 9 Temperature rise versus frictional heat input for comp B on sapphire

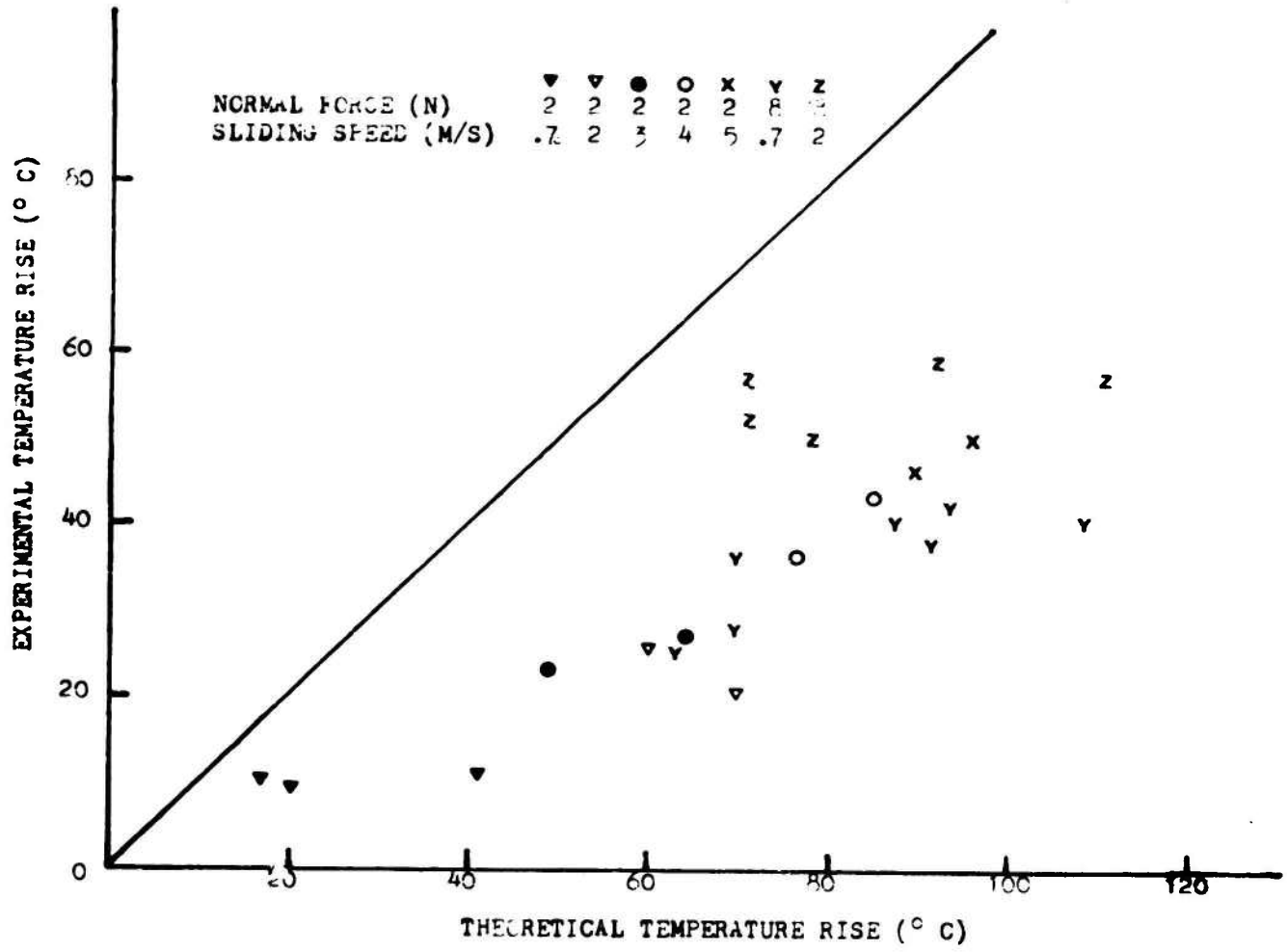


Fig 10 Experimental vs theoretical temperature rise using the elastic contact area for comp B on sapphire

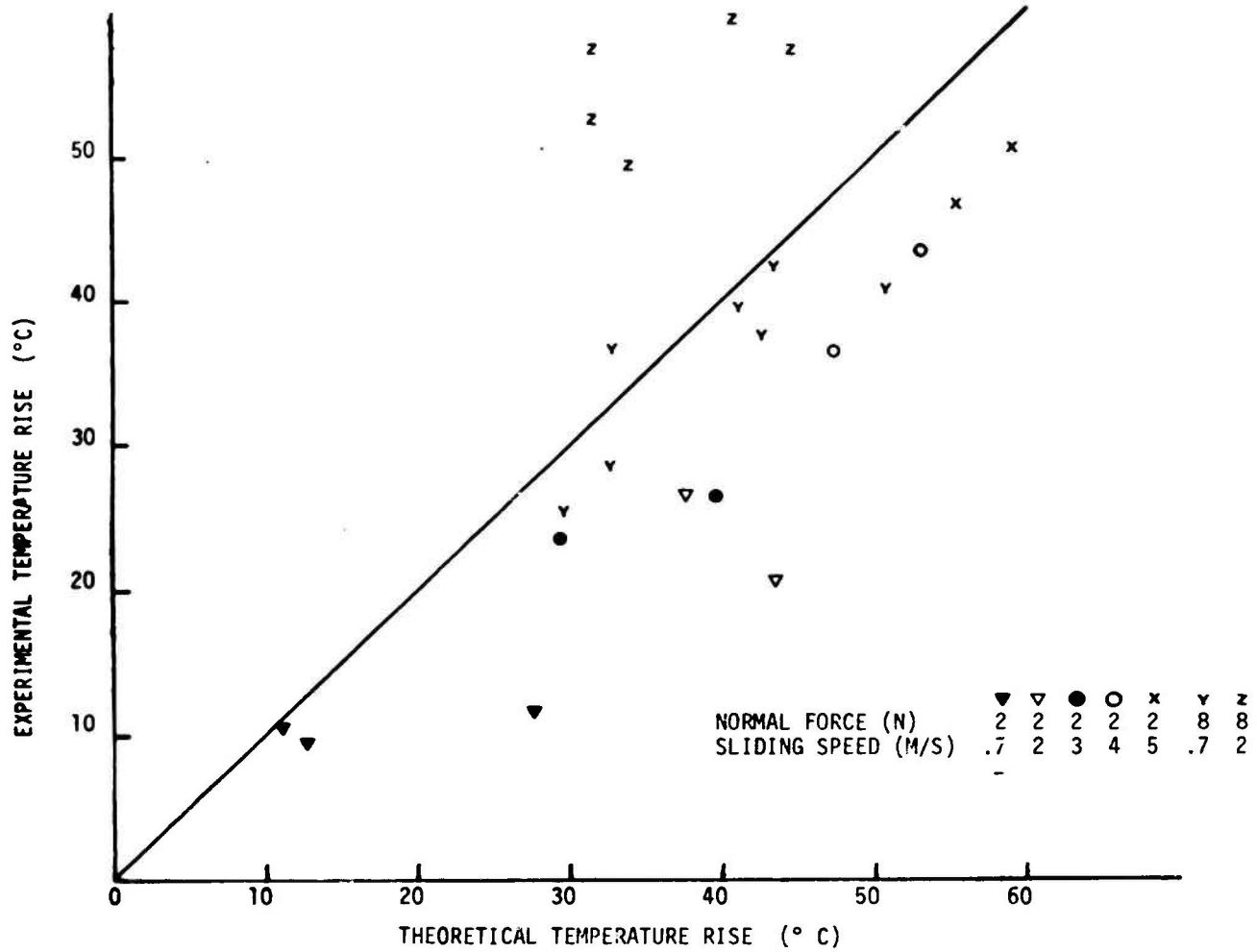


Fig 11 Experimental vs theoretical temperature rise using the plastic contact area for comp B on sapphire

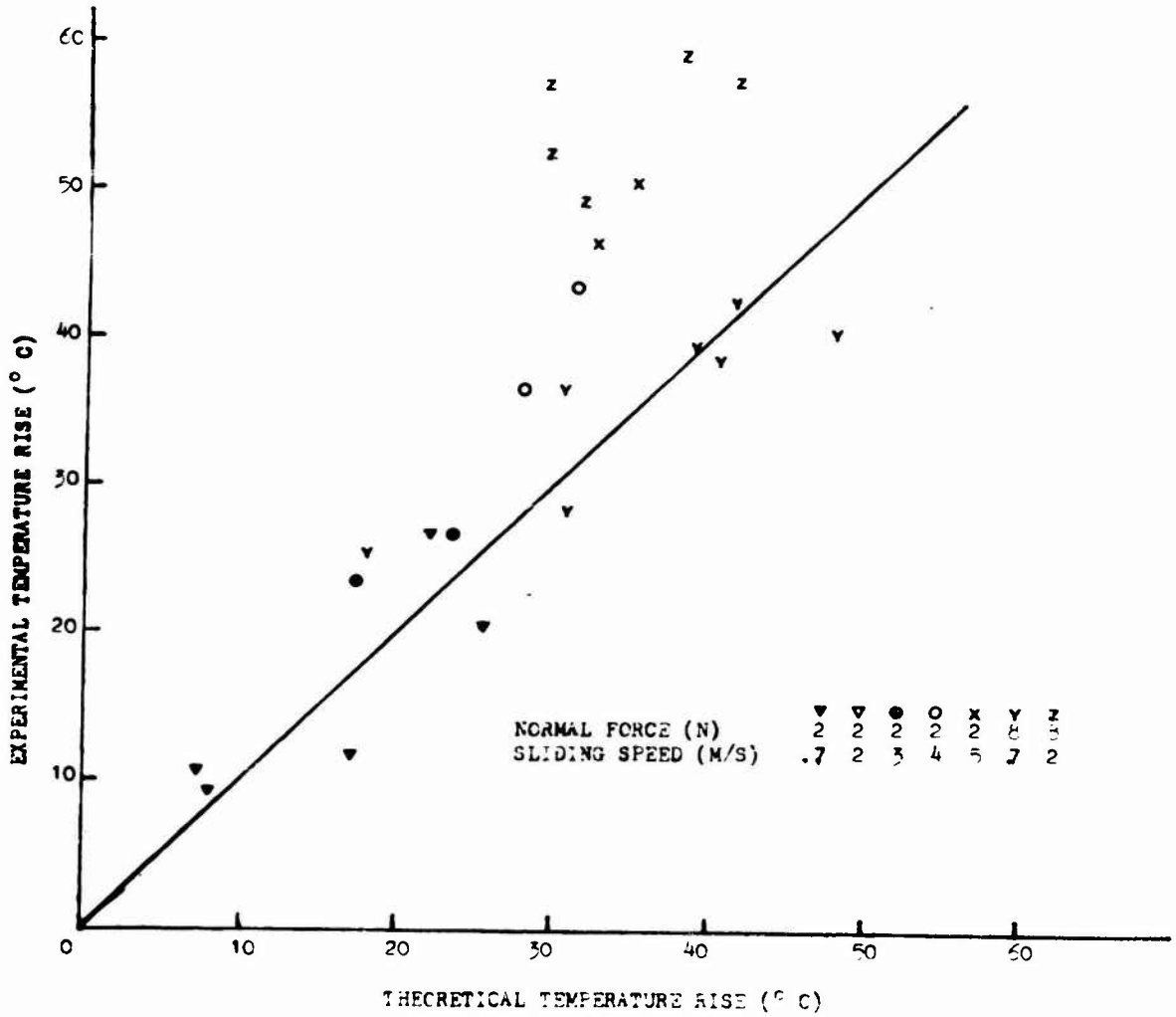


Fig 12 Experimental vs theoretical temperature rise using the apparent optical contact area for comp B on sapphire

ON THE PROBLEM OF EVALUATING THE SAFETY OF AN EXPLOSIVE

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ABSTRACT

Some general considerations on the problem of evaluating the safety of an explosive lead to the reasons why the much-criticized drop-weight impact machine remains an important tool in most explosives research and development laboratories. Problems related to the design, calibration, and use of such machines, and certain misconceptions concerning the interpretation of the test data, are discussed. The results of an unsuccessful attempt to construct a more comprehensive hazards scale also are described.

Any laboratory engaged in the development of explosives for military applications must devote some fraction of its efforts to the problem of devising reliable methods of assessing the sensitivity of an explosive under the various conditions of interest. Not only is it of local importance that those working with a new or modified explosive should have some method of gauging the relative degree of hazard involved, but further, in recommending any new material for use in a particular application, it is absolutely essential that it have been demonstrated as clearly as possible that the new material has a level of sensitivity compatible with that application, and with the production and loading techniques incidental to getting it into the weapon.

Unfortunately, the problem of measuring the sensitivity of an explosive is an exceedingly complex one. The reasons for its complexity can be stated in various ways, but fundamentally the situation seems to be as follows: The sensitivity of an explosive is not a property defined solely by the chemical composition of the material, but, on the contrary, depends more or less importantly on a variety of physical and mechanical details of the particular sample being studied, and of the particular sensitivity test being used. To anyone attempting to measure the sensitivity of an explosive, or attempting to determine the relative sensitivities of a series of explosives, the most annoying consequences of this state of affairs are, first, that many sensitivity test exhibit nontrivial irreproducibilities, and second, that different sensitivity tests will not, in general, arrange a given series of explosives in the same order of sensitiveness.

Explosives chemists struggled with these difficulties for many years before the elemental nature of their origin became generally recognized. As a result, considerable effort was devoted to the search for <u>the</u> sensitivity test, which would reproducibly place all explosives in their <u>correct</u> order of sensitiveness. This search we now recognize as hopeless, although the work was not without profit and, indeed, continues today, but with somewhat altered objectives. In any event, we now realize that when we speak of the sensitivity of an explosive, we are not talking about a single, well-defined property of the material, but about a complex pattern of its behavior. The last statement of the preceding paragraph implies that the sensitivity pattern of one explosive is not simply related to that of another.

Thus far we have discussed the problem mainly from the point of view of trying to measure sensitivity, but the same difficulties encountered there plague us from yet another, equally important direction, as follows: A primary objective of most practical work on sensitivity (and the ultimate justification for almost all work on sensitivity) is that of avoiding accidental explosions in the production, loading, and use of explosives. In a few cases, such as initiation by a static discharge, the nature of the hazard and the conditions under which it is likely to arise can be specified in sufficient detail that pertinent tests can be devised, and safe/unsafe criteria can be adopted on some basis or other. Unfortunately, after these relatively simple cases have been subtracted from the problem, we are still left with the bulk of it -- the miscellany of blows, scrapings, crushings, etc, to which an explosive is subjected, deliberately and accidentally, singly and in combination, in the course of its travels through the various operations. We include perforce in this class those causes of accidents that are inherently isolable, but whose importance is not foreseen. The stimuli that contribute to this source of hazard are so varied in nature and so unpredictable in violence (particularly under those circumstances that are truly called "accidents"), and, finally, are applied to the explosive under such a wide variety of local conditions, that we cannot even define what it is we are trying to measure except in the broadest terms. Quite aside from the much debated statistical aspects of the problem, the sensitivity scale of interest here is one that represents some kind of a weighted average response of the explosive to a variety of stimuli, under a variety of conditions. The relevance of the difficulties, irreproducibility of response and nonconstancy of order, to the problem of defining the scale are obvious.

In one sense we have a method of ordering explosives on this sensitivity scale, for it is precisely this which an impact machine, properly designed, calibrated, and used, is intended to accomplish. The test has the further virtue that it can be carried out quickly by untrained personnel with only a few grams of sample. Thus while the test is the subject of widespread criticism, sometimes even for the right reasons, it continues to occupy a unique and essential place in most explosives research and development laboratories.

The key phrase in the preceding paragraph is "properly designed, calibrated, and used". The implications of those words seem to have escaped many people, and much of what follows will be devoted to a discussion of them.

First of all, what's so hard about designing an impact machine? Nothing! Anyone can, and many people have. The trouble is, when the machine is put into use, the results it produces are quite likely to be sheer nonsense. Having constructed this monster, however, the designer may continue to use it even though he knows it is producing unbelievable data. He uses it, he swears at it, and therein lies the cause of one of the unjustified criticisms of drop-weight impact machines.

The source of the problem is not hard to find, and it can be stated very simply: The sensitivity ordering of a series of explosives can be affected drastically by minor changes in the design of the critical parts of the machine. I once had the dubious distinction of designing a machine - a minor modification of the one we still use - that nearly inverted the commonly accepted order of sensitivity of a series of test explosives.

Let us look at a few other examples. In Figure 1 I have plotted Figure of Insensitiveness data obtained with the ARD/Woolwich machine (picric acid = 100) vs the corresponding 50% points determined on the ERL Type 12 machine at Bruceton. The two sets of data were obtained on supposedly identical samples. The eye tells it all, but for those who like numbers the value of r^2 (r = coefficient of correlation) for this plot is 0.19.

Figure 2 is another example; data obtained from what was then the Naval Powder Factory at Indian Head are plotted against the ERL Type 12 data. The value of r^2 in this case is 0.12.

But, you say, the trouble might be in the ERL machine. What happens if we plot the ARD data against the NPF data? The answer to that, of course, is shown in Figure 3. I must admit that this does look a little better, and the r^2 value is 0.43 - which still leaves much to be desired, especially in view of the fact that the critical parts of these two machines do have certain similarities.

Similar examples are the rule rather than the exception. During World War II, at the Explosives Research Laboratory at Bruceton, PA, Eyster and Davis discarded eleven different tool designs before they finally came up with the model many of us now use, the ERL Type 12 machine. As an example of the difficulties they encountered along the way, the Type 9 tools gave a 50% point of 131 cm for Comp A-3 and 143 cm for lead azide. I believe the NPF machine also gives a relatively high value for lead azide.

How, then, do we know when we have the right machine? Or, to put it another way, how do we calibrate the scale? I know of only one way. That is to test a series of explosives whose relative sensitivities (safety) we think we know and see if the design puts them in what we believe should be their approximate relative positions on the scale. If it does not, we discard the design and try again. If it does, we accept the design and proceed on faith that, having ordered the ones we know about in the "right" way, it will also order the ones we don't know about in the right way. That represents an important extrapolation, and one must ever be alert for the possible exception - a point I will return to later. Note, however, that if we use a machine that does not put the familiar explosives in the right order, we cannot have much confidence in its evaluation of new ones.

At this point I would like to digress a little to comment on the significance of the disagreements between machines of differing designs.

IMPACT MACHINES DON'T LIE!!!

What I mean by that is simply this: For the particular stimulus applied by a given machine, that machine will place all explosives in their correct order of sensitiveness! The trouble is, that stimulus may be almost totally irrelevant to the problem of evaluating the safety of an explosive. A corollary of this is that one cannot rely on any single test or even on the results of a single drop-weight impact test. At LASL we routinely run the test both with and without grit present - what we call the Type 12 and Type 12B tests, respectively.

We have now considered "designed" and "calibrated", and I now want to discuss "used". I will confine my remarks to just one part of the problem, a part that has been the subject of a great deal of confusion. The confusion typically arises in the form of the following statement: The trouble with impact machines is that we use them to determine 50% points or 10% points, whereas what we are really interested in are the very low percentage points - one in a million, say. The situation is illustrated in Figure 4 for a normal distribution of mean (μ) zero and standard deviation (σ) one. Probabilities are given on the ordinate, σ units on the abscissa. The circles denote μ and $\mu \pm \sigma$, the + the 10% point determined by one of the commonly used staircase methods - the approximate lower end of the experimentally useful range. The bracket marks off the "accident" region on the probability scale - some four to five σ units from the mean. Obviously, then, if our machine is used to determine 50% points, what we should do is extrapolate the results to $-5\ \sigma$ and compare the relative sensitivities of our explosives at that point.

WRONG!!

AN INTEGRAL PART OF THE DESIGN AND CALIBRATION OF ANY IMPACT MACHINE IS THE STATISTIC DETERMINED AND THE PROCEDURE USED TO DETERMINE IT.

I will illustrate what I mean using some Type 12 data obtained for me at NOL while I was working there some years ago.

As most of you know, we use the Bruceton up-and-down method to estimate the 50% point and the standard deviation on the assumption that the underlying distribution is log-normal; it is one of the few staircase methods that gives an estimate of σ, perhaps the only one. Thus the machine is calibrated and used, and explosives are compared, in terms of 50% points. What happens if we try to use our results to compare explosives at very low percentage points?

The data I will use consist of 1000-shot runs on six different explosives, generated to study various statistical aspects of the test. The estimates of the 50% points and standard deviations are as follows:

	h(cm)	s(log units)
PETN	12.4	0.1343
RDX	23.9	0.1123
Comp B	60.4	0.1306
Comp B, D-2	110.8	0.1324
HBX	95.7	0.1894
Comp A-3	58.8	0.0870

In Figure 5 I have plotted the log of the drop height against log h_{50} - xs. What we find is that the lines cross. The ordering (decreasing sensitivity) at the 50% point is

PETN > RDX > (Comp A-3, Comp B) > (HBX, Comp B, D-2).

For $P = 10^{-6}$ we get

PETN > RDX > HBX > Comp B > (Comp A-3, Comp B, D-2).

I remind you that these are large runs on reasonably familiar materials. The situation can only get worse as I add the results of routine tests on experimental materials to the graph.

Let me put it another way. There are two possibilities:

a) The σ's are really all the same, in which case it doesn't matter at what percentage point I compare explosives, since the lines are parallel.

b) The σ's are not all the same, in which case if I have designed a machine to give the correct scale when it is used to determine 50% points, it must give an incorrect scale when operated at some other percentage point.

That is very fortunate, of course, since the 50% point is the one that's easiest to determine. Note also that estimates of σ are quite imprecise under the usual test conditions.

While we have a reasonable amount of confidence in the Type 12 machine, we are also certain that it may seriously misjudge some materials. It is for that reason that we routinely run both 12 and 12B tests on new materials. We are especially wary of explosives that appear moderately sensitive in the Type 12 test and even more sensitive in the Type 12B test; most explosives give the higher 50% points in the Type 12B machine.

Enough about impact machines! I would now like to discuss, very briefly, a different aspect of hazards analysis.

In many sensitivity tests (and in many situations of practical interest), the response of an explosive ranges more or less continuously over the scale completely inert, small partial, large partial, high-order detonation. In some tests, such as the drop-weight impact machine, the sensitivity of an explosive is determined on the basis of the ease with which a relatively mild, incomplete reaction of the sample is obtained. In other tests, such as the gap test the comparison is made on the basis of the ease with which high-order detonations are obtained. With still other tests, such as the bullet impact test, it is sometimes possible to compare the sensitivities of various explosives in two ways -- ease of initiation to an observable reaction of any sort, and ease of initiation to a relatively violent reaction.

Both levels of response are of importance in evaluating the hazards involved in handling an explosive, for a relatively mild partial explosion can be a source of personal injury in itself, and also may, under favorable conditions (such as a high degree of local confinement), grow into a violent reaction or even a high-order detonation. Accidental high-order detonations, obviously, are hazardous in the extreme.

This suggests that in evaluating the safety of an explosive we must consider both its "ease of initiation" and its "ease of detonation". Qualitatively, an explosive may exhibit these properties, in combination, in the following four ways, listed in order of decreasing hazard:

a) Easy to initiate and easy to detonate.
b) Difficult to initiate, but easy to detonate.
c) Easy to initiate, but difficult to detonate.
d) Difficult to initiate and difficult to detonate.

We could, therefore, attempt to place an explosive in one of these classes on the basis of the results of our tests.

At first sight it might appear that combination b) should be excluded from consideration on the grounds that it is not a self-consistent classification. However, if we do attempt to omit it, we soon find ourselves in difficulty, as we will demonstrate by an example. The ease of initiation of TNT, as determined by our drop-weight test, is largely independent of the physical form of the sample. On the other hand, its ease of detonation, as determined by the LASL gap test, is strongly dependent on both the density of the charge and on whether it was made by casting or pressing. This is evident from the following data:

	50% Gap, mm (density, g/cm^3)	
	High Density	Bulk Density
Flake TNT		37.1 (0.87)
Cast TNT	28.3 (1.615)	
Granular TNT	49.4 (1.626)	60.1 (0.73)

Certainly TNT deserves to be classed as difficult to initiate, and cast TNT as difficult to detonate, but where do we put pressed (granular) TNT?

Simply admitting b) as a possible combination to be used in our classification scheme does not, of course, solve the problem. So long as we are comparing only two explosives, the idea of doing so on the basis of their relative ease of initiation and relative ease of detonation seems to be a useful one, but when we attempt to expand the comparison to include more and more explosives, we soon run into trouble. The difficulty is that the scales for ease of initiation and ease of detonation are continuous scales, and the possible combinations cannot be adequately represented, even in a qualitative way, by as few as four subclasses. The logical extension, then, is to look for a continuous scale that will represent a suitably weighted combination of these two

properties (assuming we have some way of determining them in the first place).

A crude attempt at constructing such a scale is shown in Fig. 6, which is in the form of a nomograph*. For ease of initiation I have simply used the log of the 50% point, in centimeters, from the drop-weight impact machine. For ease of detonation I have used the log of the weight of 80/20 - PETN/silicone rubber required to detonate the explosive in our version of the minimum priming charge test; the test measures the ease of initiating a detonation from a highly divergent, hemispherical wave. Here we see a striking example of how different sensitivity tests produce different sensitivity orderings.

The question is, Can we construct a scale somewhere between the two outer ones that would provide us with some "index of potential destructiveness"? If, for example, we construct the scale at the point marked by the arrow, using the scale at the right, we obtain the following indexes:

9404	45
Pentolite	68
Comp A-3	95
Octol	128
Cyclotol	185
Comp B	243
DATB	560
TNT	1170
Exp D	1500

Is this a useful scale? I don't know. In a sense the impact machine is supposed to do this whole job for us - but the impact machine does not respond to the physical form of the explosive, and we know that, in shock-sensitivity tests, pressed explosives are much more easily detonated than cast ones are. To me that means that a pressed cyclotol charge is potentially much more hazardous than a cast one, and the combined scale will reflect that fact. Nonetheless, my personal opinion is that we cannot express the safety of an explosive by a

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* An earlier version of this scale appears in a paper by A. Popolato, Proceedings of the International Conference on Sensitivity and Hazards of Explosives, Session 6; London, 1963. This paper also contains descriptions of the LASL versions of the drop-weight impact and gap tests.

single number, so I do not suggest this as a major breakthrough in the solution of the problem.

What, then, is our situation? To do an adequate job of determining the safety of an explosive, we must compare it with familiar materials in a variety of relevant, properly designed sensitivity tests. Inevitably, those tests will produce inconsistent data. There is no magic formula for resolving those inconsistencies. The final decision must still represent the subjective judgement of an experienced individual who carefully examines the data. I see no prospect that this situation will change fundamentally in the foreseeable future.

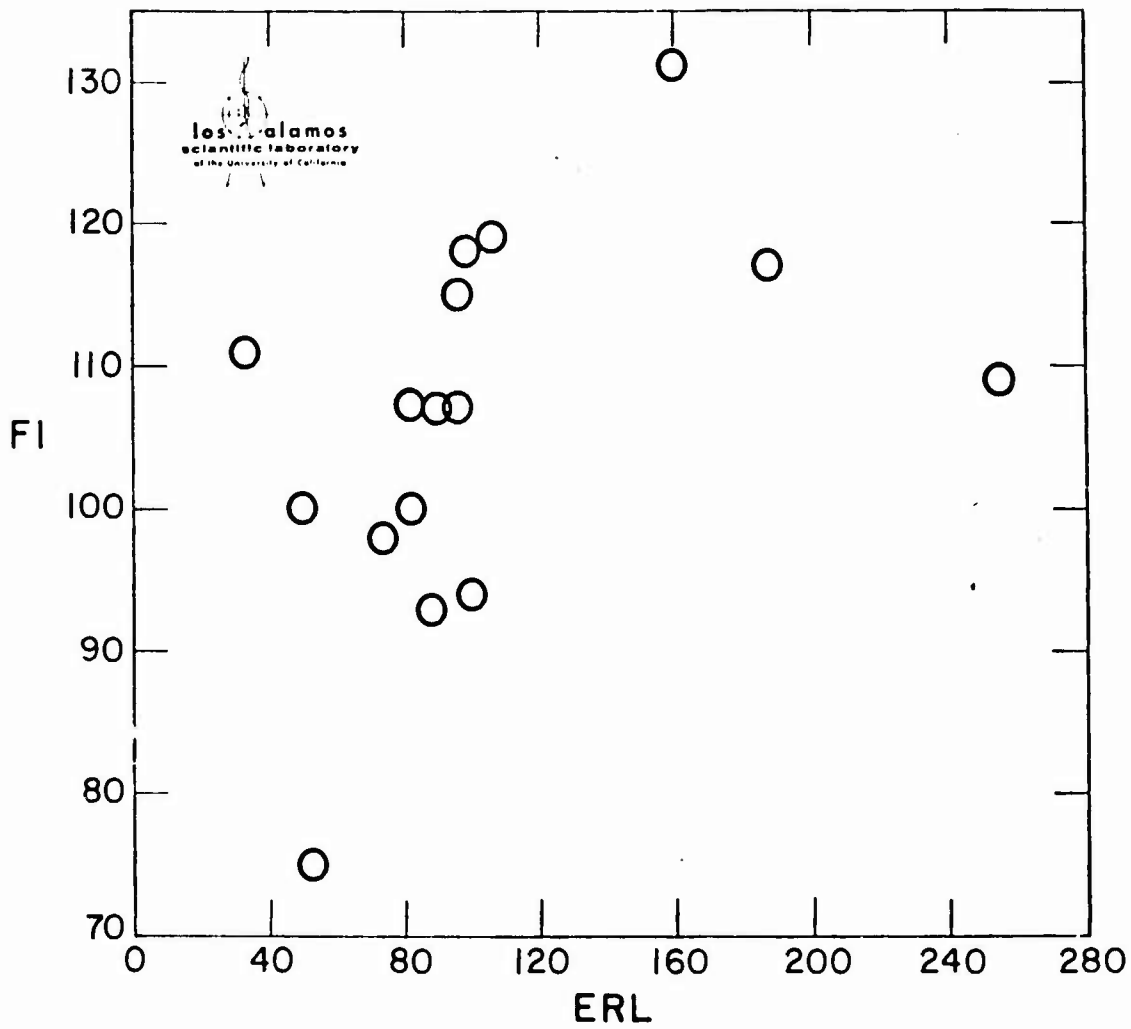

130
120
110
100
90
80
70
F1
0
40
80
120
160
200
240
280
ERL
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FIGURE 1

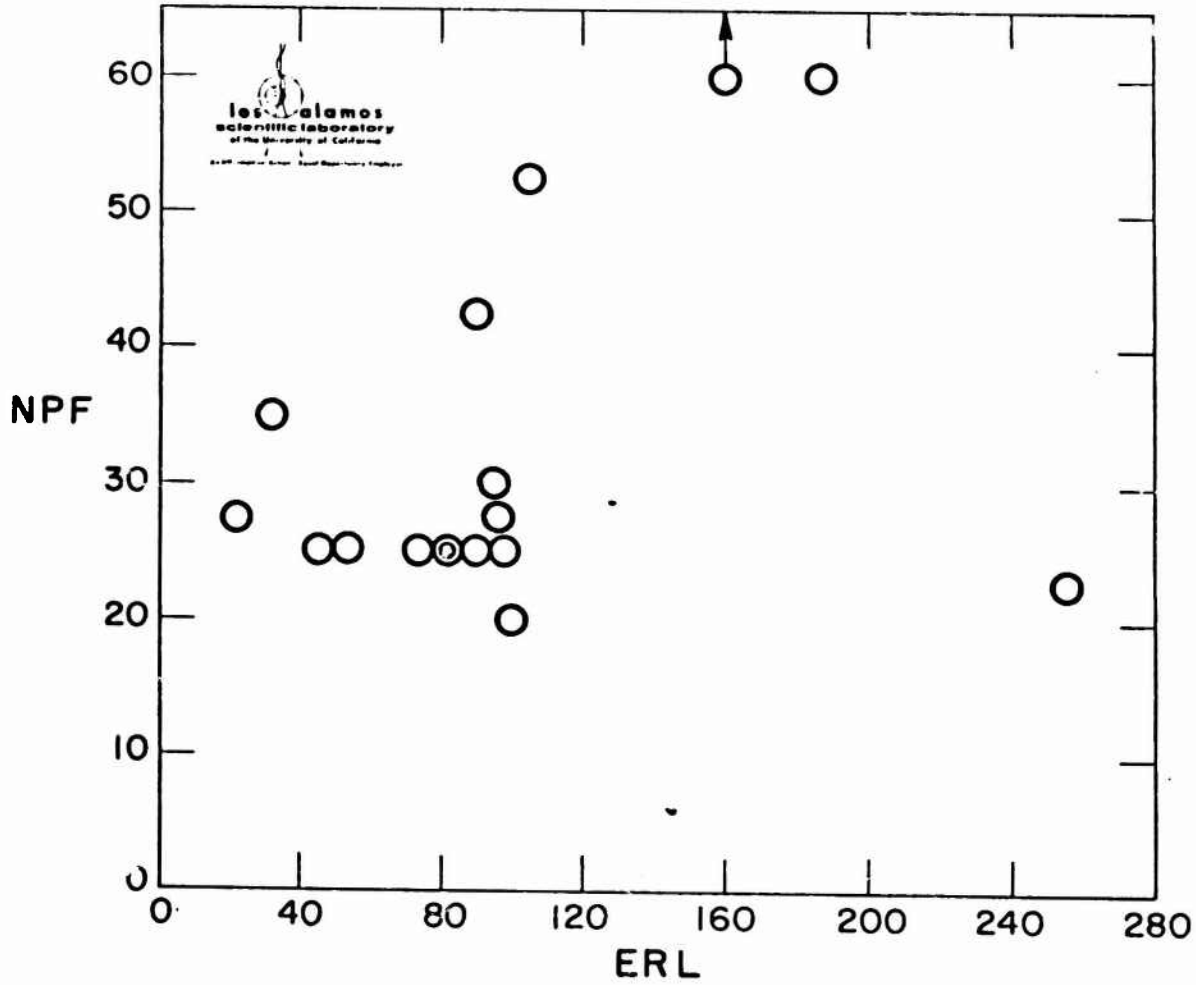


FIGURE 2

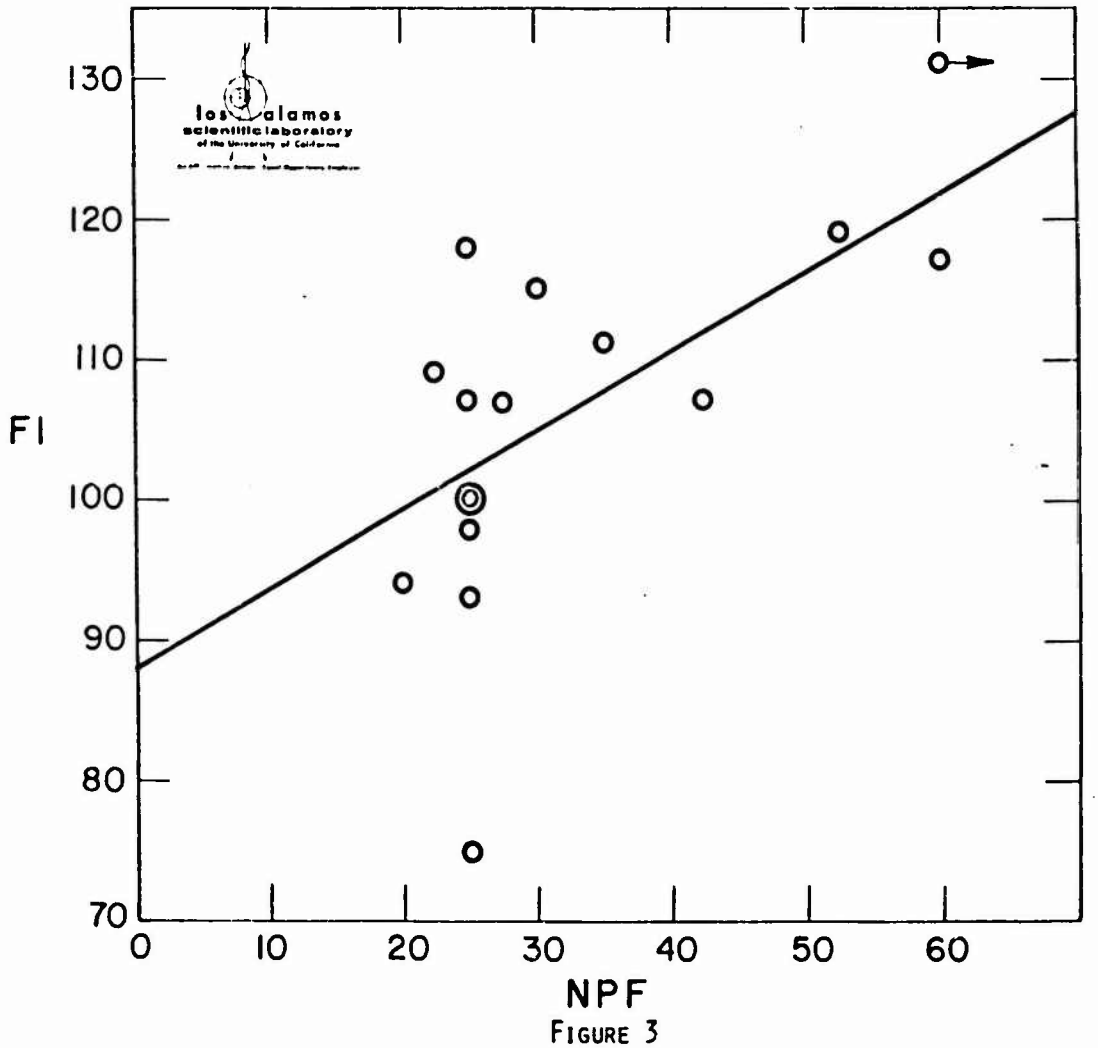


FIGURE 3

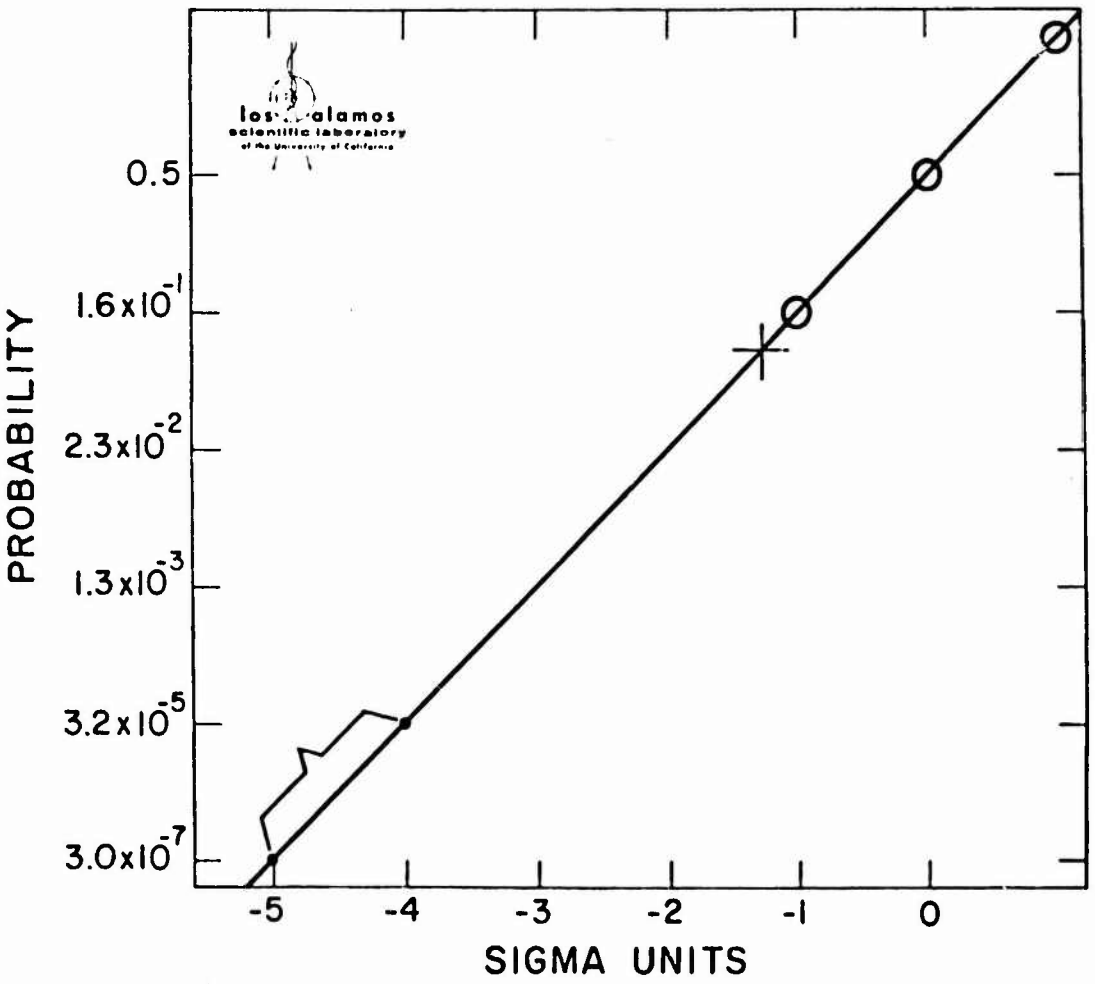

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PROBABILITY
0.5
1.6x10^-1
2.3x10^-2
1.3x10^-3
3.2x10^-5
3.0x10^-7
-5
-4
-3
-2
-1
0
SIGMA UNITS

FIGURE 4

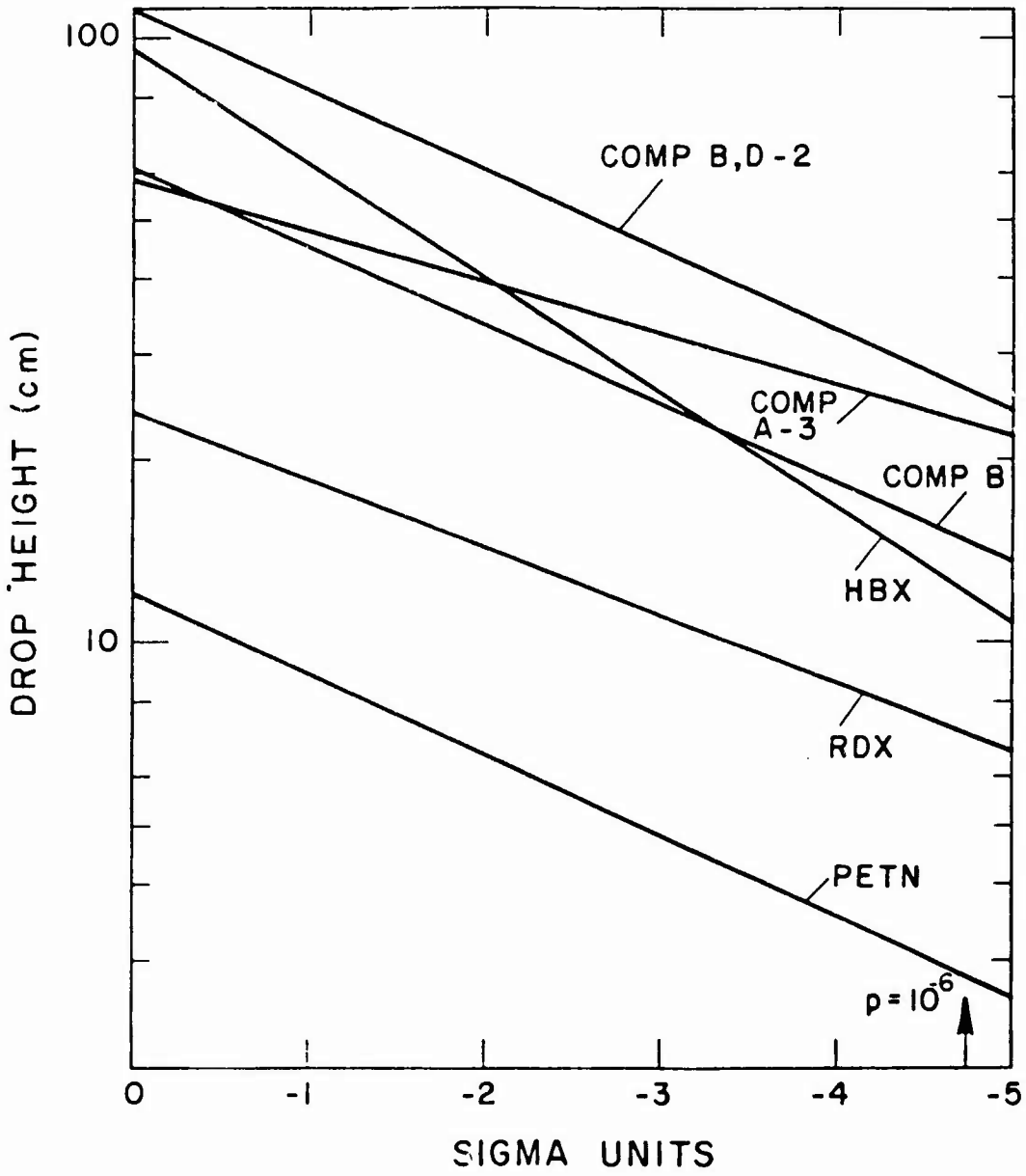

100
10
DROP HEIGHT (cm)
COMP B,D-2
COMP A-3
COMP B
HBX
RDX
PETN
p = 10^-6
0
-1
-2
-3
-4
-5
SIGMA UNITS

FIGURE 5

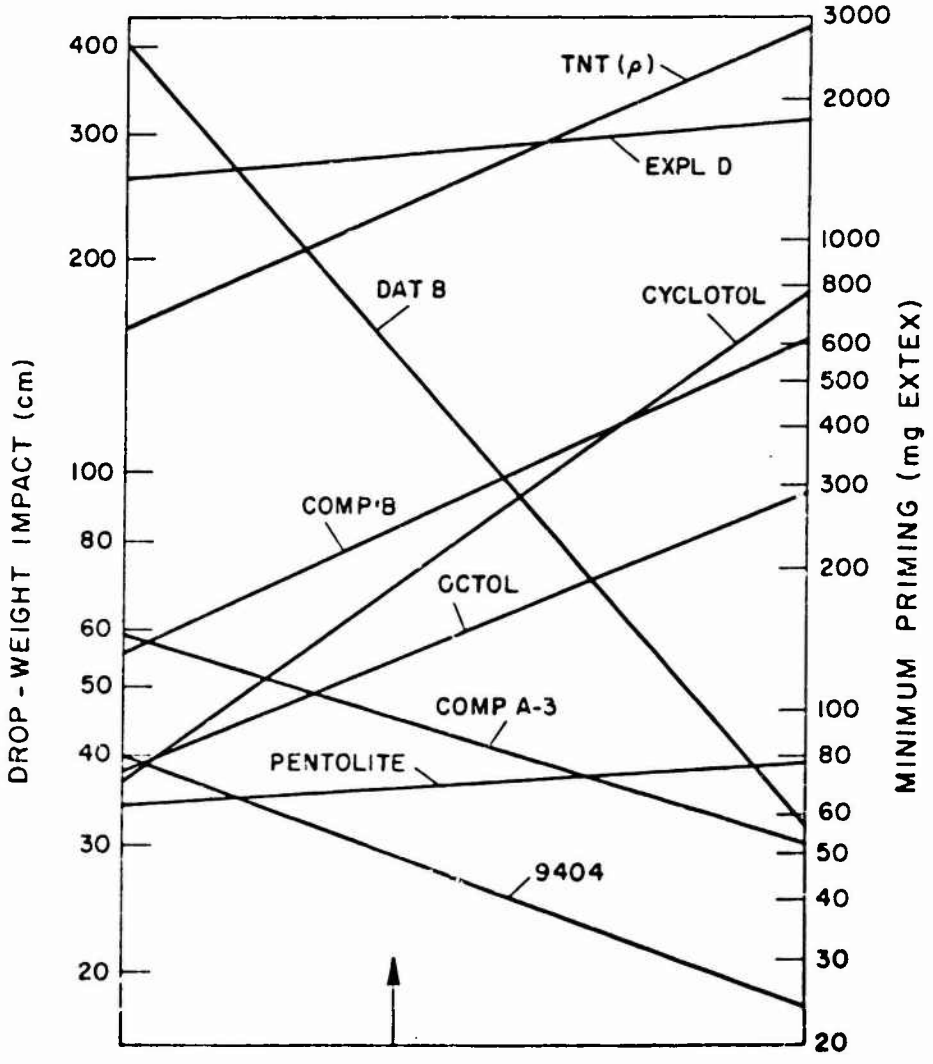

DROP-WEIGHT IMPACT (cm)
MINIMUM PRIMING (mg EXTEX)
400
300
200
100
80
60
50
40
30
20
3000
2000
1000
800
600
500
400
300
200
100
80
60
50
40
30
20
TNT (ρ)
EXPL D
DAT B
CYCLOTOL
COMP'B
OCTOL
COMP A-3
PENTOLITE
9404

FIGURE 6

A CRITIQUE FOR DROP WEIGHT IMPACT TESTING

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A CRITIQUE FOR DROP WEIGHT IMPACT TESTING

ABSTRACT

Studies are presented that provide useful insight on the mechanics of impacts and that demonstrate the variations in stimuli that a test sample is subjected to depending on the tool as well as sample parameters; the effect of a mass mismatch between the drop and intermediate weights is shown to cause oscillatory inputs to the sample. The effects of tool mass on energy transfer are also discussed.

A proposal for a method of test that has been submitted to the E-27 committee of the ASTM for approval is briefly outlined; some test parameters and test conditions are standardized without a rigid overall standardization of the apparatus, and an overcomplication of test procedures through instrumentation is avoided.

Finally, a simple normalization method is given: $(M/A)\ H_{50}$ = constant (for a given test material), where M is the mass of the drop weight, A is the area of the tool striking surface, and H_{50} is a drop height corresponding to the 50-pct probability of a reaction. Data are presented that substantiate the normalizing method.

INTRODUCTION

For many years, the drop weight impact tester has been a standard tool for determining the sensitivity of hazardous materials. Besides having advantages of simplicity and ease of operation, it utilizes a very small sample size and consequently requires minimal protection against an unwanted explosion. A well-constructed instrument is very useful in providing an index of sensitivity for a variety of materials, but the agreement between the results from different testers in terms of drop height, impact energy, or some other basis has never been satisfactory. This lack of agreement stems primarily from the inability to quantify the stimulus that test samples actually see, the response of the test sample to a given level of stimulus, and inadequate control over the physical characteristics of the test sample which are important in determining its sensitivity to drop weight impact.

An interesting approach for better defining the stimulus applied to the test sample using force gage instrumentation was developed by Smith and Richardson.[1] This technique was applied at the Bureau and led to basic improvements in the Bureau's drop weight tester.[2] This, coupled with improved control over the test specimen, has led to recommendations for a standard method for drop weight impact testing that is under consideration for adoption by the ASTM.

MECHANICS OF IMPACTS

In brief, impact apparatus (figure 1) usually consists of a sample holder (anvil) mounted on a massive steel plate and concrete foundation. Extending upward is a guide system to guide the weight in its fall; this may be rails (illustrated), wires, a shaft, etc. Some means, such as an electromagnetic lift and winch, are provided to raise the drop weight to a desired height level. The drop weight does not generally strike the test sample directly; rather, it strikes an intermediate stationary weight that is steadied in a bushing and is in contact with the test sample. Depending on its mass relative to that of the drop weight (m_1), the intermediate weight (m_2) can have a marked effect on the nature of the force applied to the test sample.[2] This is illustrated in figure 2, which shows oscillogram traces of force-time (F-t) profiles for different mass ratios of intermediate to drop weight mass obtained with the aid of a piezoelectric transducer attached to the sample holder. In each case three repetitive drops from the same height were made to observe reproducibility. Figures 2a and 2b show F-t profiles for tools having essentially the same mass ratio (m_1 = 5.0 kg; m_2 = 0.73 kg) with the exception that the stationary weight used for figure 2a utilized an expendable striking pin that was not rigidly attached, causing similar, but not exactly reproducible, F-t profiles. For figure 2b the striking pin was rigidly attached to the intermediate weight, and better reproducibility was obtained. However, the important point to be made here is that the F-t profiles are oscillatory in nature--a result of the fact that in the initial contact, the drop weight did not transfer all of its kinetic energy to the intermediate weight and hence did completely decouple from the intermediate weight, retaining sufficient energy for further interactions. Thus, figures 2a and 2b show an initial force peak of about 4.4×10^4 N (10^4 lb F) occurring at about 100 μsec, followed by a second, more dominant peak at 250 μsec, followed by two additional lesser force peaks. An undesirable feature of oscillatory input is that the test sample may be subjected to one or more compression cycles and possibly sensitized or desensitized before finally reacting. This makes it extremely difficult to interpret the impact test results in terms more fundamental than the drop height of a given weight.

In figure 2c, where R = 0.38 (m_1 = 5.0 kg; m_2 = 1.92 kg), the first force peak is now dominant but significant energy is still delivered on the second and third oscillation of m_2. Lastly, in figure 2d, where R = 0.77 (m_1 = 2.5 kg; m_2 = 1.92 kg), essentially all the energy was delivered in a single force pulse. The energy transferred to m_2 can be determined with the aid of the equation[1]

$$KE_2 = \frac{4m_1^2 m_2 gh(e)^2}{(m_1 + m_2)^2} , \qquad (1)$$

where KE_2 is the kinetic energy of m_2 after its initial interaction with the drop weight (m_1), h is the drop height, and e is the coefficient of restitution--a measure of the inelasticity of the impact having a range of values from zero (perfectly inelastic) to unity (perfectly elastic). Assuming e = 1, the equation reduces to the simpler and familiar form $E = m_1gh$ when $m_1 = m_2$. Figure 3 is a plot of KE_2/m_1gh as a function of mass ratio for e = 1 and shows that energy transfer efficiency is maximized when the masses of the two tools are the same. For the impact in figure 2d the energy transfer efficiency was about 95%, assuming e = 1. In practice, e is somewhat less than 1; however, the energy transfer efficiency is still highest when the tool masses are matched.

It is interesting to note that the compression-relaxation cycle does exhibit properties of a harmonic oscillator. For example, for a simple harmonic oscillator, the time of oscillation depends only on the mass and the elastic constant ("spring" constant) and not upon the displacement. For our purposes the time to maximum force (t) would have the form

$$t = \frac{\pi}{2}\sqrt{\frac{m_2}{k}} \quad , \qquad (2)$$

where k is the combined elastic constant for the metal parts and test sample.

The maximum force equation has the form

$$F = \sqrt{2k(KE_2)} \quad , \qquad (3)$$

where all quantities have been previously identified. Both equations were derived by considering the problem of a mass subject to a linear restoring force, F = -kx.

Elastic behavior is demonstrated with the aid of F-t profiles shown in figure 4. In 4a, the sample thickness (T) was constant and the drop height (h) was varied from 25 to 50 cm; note that the time to maximum force (about 100 μsec) is independent of h and that only the maximum force increases. In 4b, h was constant and T was increased by a factor of 2 in two steps. An increase in T reduces the value of the elastic constant k. As predicted by equations (2) and (3), the effect is to decrease the maximum force and increase the time to maximum force as T is increased. Lastly, the effect of increasing the mass may be observed by referring back to figure 2. In 2c and 2d the tool mass (m_2) was 1.92

kg as opposed to 0.77 kg for 2a and 2b, and both the time to maximum force and the maximum force itself are predictably greater in 2c and 2d. Thus, the stimuli that the test sample is subjected to can be understood and controlled somewhat by considering the mechanics of impacting bodies.

STANDARDIZATION PROCEDURES

A tentative standard entitled "Tentative Method of Test for Drop Weight Impact Sensitivity of Solid Phase Hazardous Materials" has been prepared by ASTM Subcommittee E-27.03 on Condensed Phase Reactions and is currently being considered for adoption by the ASTM. The proposed method is not viewed as one that will heal all the ills in drop weight impact testing; it is one that is expected to significantly update and improve drop weight testing procedures.

In brief, the method incorporates the well-known Bruceton up-and-down method of test[3,4] for determining the drop height corresponding to the 50-pct probability of initiation (H_{50}). Some test parameters and test conditions are either standardized or restricted without a rigid overall standardization of the apparatus so that H_{50} values for a given material obtained from different apparatus that utilize the same mass and striking area (or diameter) tools will be in reasonable agreement. For cases where the tool mass and/or tool striking area are not the same, a simple method for normalizing the data is given. A complication of test procedures through the use of instrumentation (force or pressure gages, reaction detection devices) is avoided in the interest of simplicity.

Some of the more important requirements are

1. The masses of the drop and intermediate weights should be equal to avoid oscillatory-type inputs to the sample.
2. The mass of the tools for testing most materials should be between 1.0 and 3.5 kg, and the tool striking surface (bottom face of the intermediate tool that is in contact with the sample) should have a diameter between 3/8 and 3/4 in.
3. The hardness of all tooling surfaces involved in the impact should be in the range 55-59 on the Rockwell C scale so that the elastic constants of impact tools will be reasonably alike.
4. The sample thickness, which is indirectly determined by using a constant sample volume per unit area spread uniformly over that area, must be the same in all tests. The suggested standard is 31.5 mm^3/cm^2. This assures the same sample thickness no matter what the diameter of the striking surface is. The test sample diameter must, of course, be at least as large (it may be larger) as the striking surface diameter to achieve this.
5. Detection criteria, though somewhat arbitrary, must be

established; the suggestions made in the proposal were based upon the use of the human senses, though the use of some sort of simple yes-no instrument is not ruled out. In addition it is believed important that the H_{50} result be accompanied by a qualifying statement; i.e., what kind of reaction it was, and whether or not it propagated throughout the sample. This may be important in extrapolating results to hazards--a most formidable task.

6. Other test procedures relating to a measure of humidity control, sample preparation, treatment, etc., were also proposed.

NORMALIZATION OF DATA

If different agencies utilize tools having different mass and/or striking areas, a simple technique for normalizing out the effects of mass and area has been found to bring the data into reasonable agreement provided that the standardization procedures are adhered to. The normalization equation has the following form:

$$\frac{M}{A} H_{50} = \text{constant} \ , \qquad (4)$$

where M and A are the respective mass and area of the tools, and H_{50} is the experimentally determined drop height corresponding to 50-pct probability of initiation. While equation (4) was developed empirically, it implies that the drop weight energy required to initiate a unit area (or mass) of a given test sample is constant.

Results of tests in which the tool mass and tool area were varied independently are presented in tables 1 and 2, respectively. In table 1, four test materials were impacted with matched tools ($m_1 = m_2$) having masses of 2.5 and 0.96 kg. The tool area was constant (1.27 cm^2), and the observed H_{50} values were normalized on the basis of equation (4); the results are expressed in terms of energy/unit area (joules/cm^2). The results for PETN and succinic acid peroxide obtained with different mass tools may be seen to be an excellent agreement; the results for HMX and benzoyl peroxide are also in good agreement.

In table 2, the tool mass ($m_1 = m_2 = 2.5$ kg) was held constant, and the tool striking area was varied from 1.27 to 2.87 cm^2 for HMX and benzoyl peroxide and from 0.71 to 2.87 cm^2 for PETN. In this case, the H_{50} values were again multiplied by M/A and results expressed in joules/cm^2; the normalized results are in good to excellent agreement.

Lastly, table 3 shows data for three test materials obtained in a round robin with two other agencies. Here various combinations of tool mass

and striking surface areas were used. The tool masses ranged from 1.0 to 3.5 kg, and tool areas ranged from 0.79 to 1.27 cm^2. In these tests, the participants abided by standardization procedures similar to those outlined earlier as far as tool mass ratio (R = 1), sample thickness, reaction detection criteria, etc., were concerned; the results are again expressed in terms of joules/cm^2. The results obtained by Picatinny Arsenal, BuMines, and DuPont for PETN ranged from 5.5 to 7.0 j/cm^2 and are in reasonable agreement. For HMX, the Picatinny and BuMines results were in excellent agreement (6.4 and 6.5 j/cm^2); however, the DuPont result (10.8 j/cm^2) is significantly higher. For pentolite, the Picatinny apparatus had a maximum drop height capability of only 100 cm, and their tests revealed less than 50 pct initiations at this height; hence their value of >12.4 j/cm^2 is not necessarily in disagreement with the BuMines result of 18.9 j/cm^2. DuPont did not complete the test on pentolite.

Thus, while the data from the round robin are not in as good agreement as those obtained in the BuMines "in-house" tests (tables 1 and 2), they do appear to lend themselves to normalization by this method and show that different H_{50} values obtained through the use of different mass and/or striking area tools can be brought into reasonable agreement.

SUMMARY AND CONCLUSIONS

As applied to drop weight impact test apparatus, elementary concepts on the mechanics of impacts were presented to promote a better understanding of, and means for controlling, the stimulus applied to the sample. In particular it was shown that an oscillatory force pulse stimulus to the test sample and inefficient energy transfer result when the masses of the drop and intermediate weight are not equal.

Standardization procedures that do not require instrumentation or a rigid overall standardization of apparatus were set forth. It was recommended that the masses of the drop and intermediate weight be equal; restrictions were placed on the tool mass and tool striking surface areas to insure reasonably similar inputs to the test sample. In addition, other test procedures, including reaction detection criteria using the human senses, were briefly passed upon; they are described in greater detail in an ASTM proposal for a standardized test.

A simple normalization procedure was introduced that accounts for differences in the mass (M) and area (A) of tools from various establishments; it has the form $M/A\ H_{50}$ = constant. Data were presented from "in-house" experiments performed at BuMines as well as from a round robin with other agencies. While the results obtained in the round robin were not in as good agreement throughout as the "in-house" BuMines

data, they too appeared to lend themselves satisfactorily to the normalization procedure.

ACKNOWLEDGEMENTS

The authors wish to express their appreciation to Mr. J. Campesi of Picatinny Arsenal and Dr. F. C. Chromey of DuPont for their participation in the round robin tests.

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Table 1

Results for varying tool masses

Test specimen	Tool mass (kg)	H_{50} (cm)	Normalized results (M/A) (H_{50}) (j/cm^2)
PETN (M-8342)	2.5	29	5.6
	0.96	74	5.5
HMX (X-874)	2.5	24	4.6
	0.96	69	5.1
Succinic acid peroxide	2.5	34	6.6
	0.96	90	6.7
Benzoyl peroxide	2.5	18	3.5
	0.96	57	4.2

Notes: Tool area - 1.27 cm^2
Confinement - none
Sample size - 40 mm^3

Table 2

Results for varying tool striking areas

Test specimen	Striking area (cm^2)	H_{50} (cm)	Normalized results (M/A) (H_{50}) (j/cm^2)
PETN (M-8342)	0.712	20	6.9
	1.27	29	5.6
	2.87	81	6.9
HMX (X-874)	1.27	24	4.6
	2.87	65	5.5
Benzoyl peroxide	1.27	18	3.5
	2.87	40	3.4

Notes: Tool mass - 2.5 kg
Confinement - none
Sample size - 40 mm^3

Table 3

Results from several agencies for several explosives

Explosive	Agency	Tool configuration M(kg)	Tool configuration A(cm^2)	Normalized results (M/A) (H_{50}) (j/cm^2)
PETN	Picatinny	1.0	0.785	5.5
	BuMines	2.0	1.24	7.0
	DuPont	3.5	1.27	5.6
HMX	Picatinny	1.0	0.785	6.4
	BuMines	2.0	1.24	6.5
	DuPont	3.5	1.27	10.8
Pentolite	Picatinny	1.0	0.785	>12.4
	BuMines	2.0	1.24	18.9
	DuPont	3.5	1.27	-

Notes: Sample size - equal thickness
Confinement - none

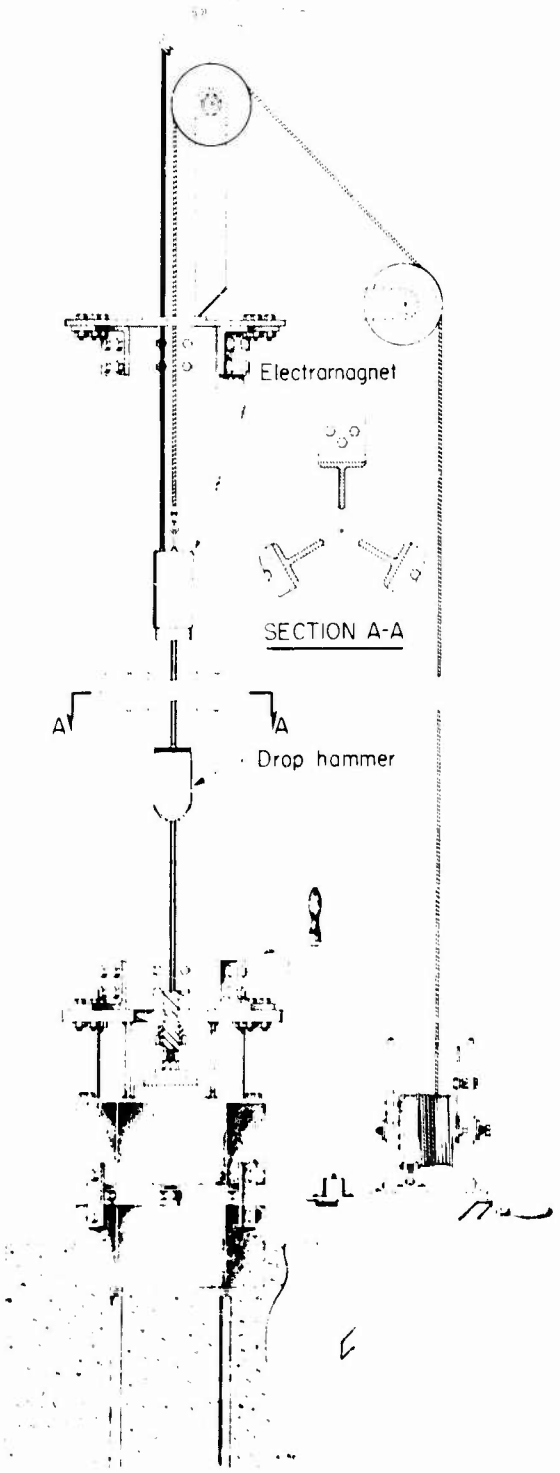


Fig 1 Impact apparatus

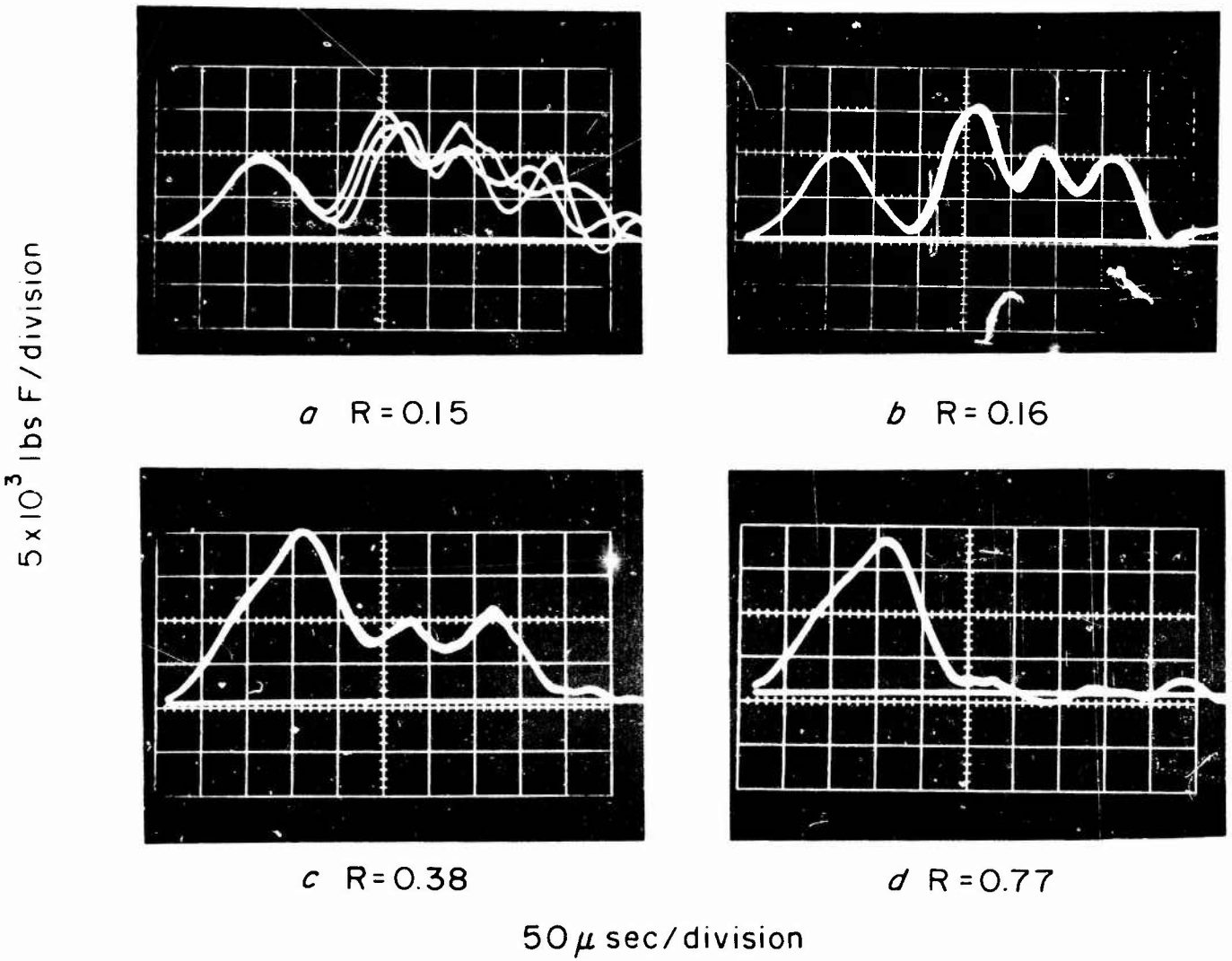


Fig 2 Effect of mass ratio (R) on force-time profiles

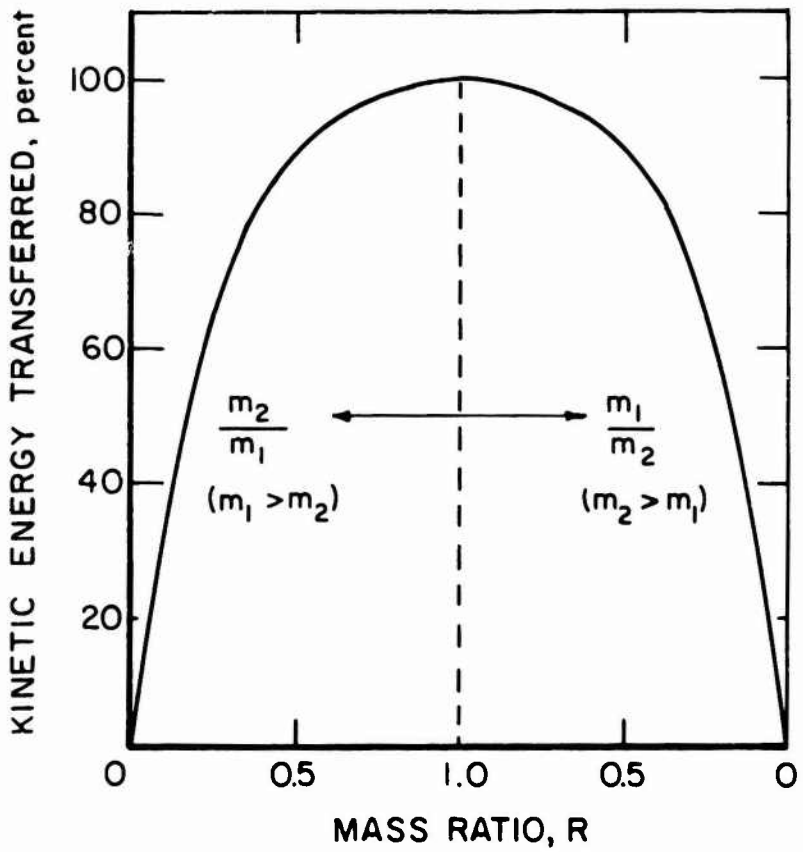


Fig 3 Kinetic energy transfer efficiency for various mass ratios of the impact tools

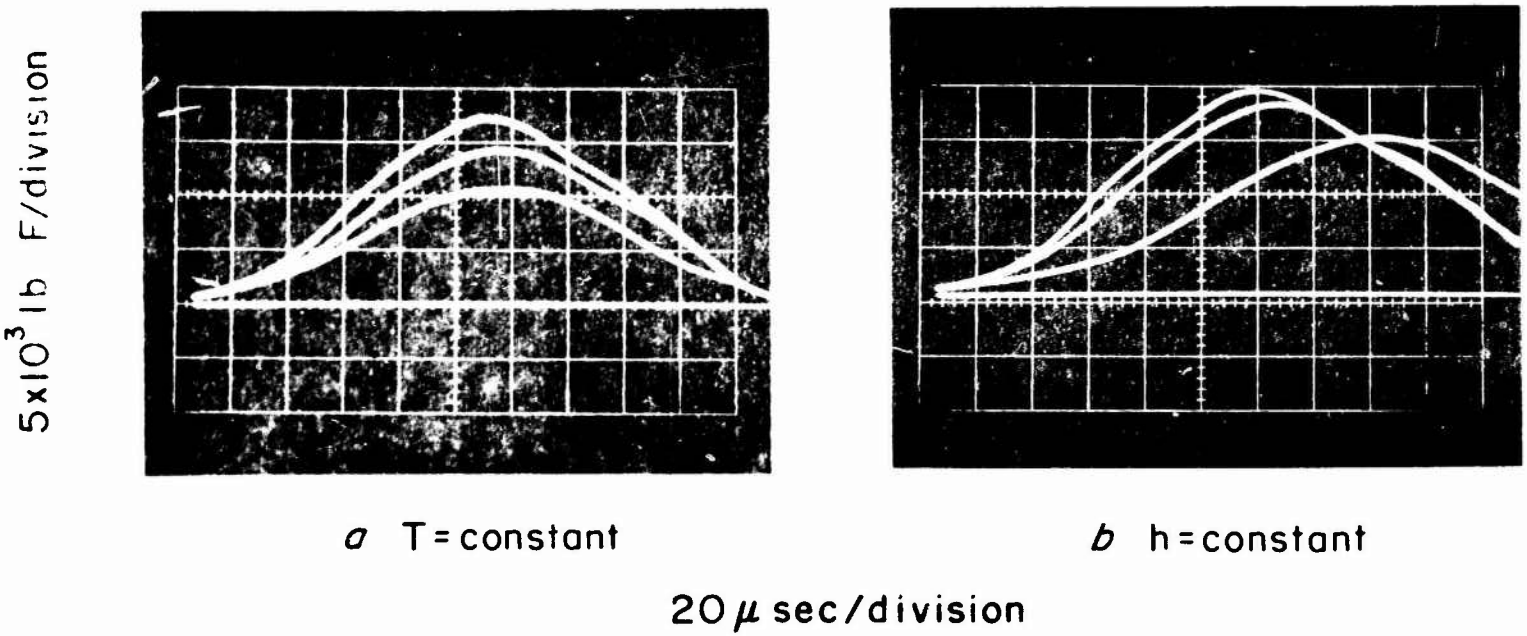


Fig 4 Effect of drop height (h) and sample thickness (T) on force-time profile

A LABORATORY SCALE EXPLOSIVENESS TEST

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ABSTRACT

A small scale test has been developed to determine quantitatively the explosiveness of confined secondary HE charges, weighing 17g, thermally ignited under conditions of impact loading. Test conditions have been chosen to simulate those in the AWRE Oblique Impact Test.

The influence of confinement variables on the growth of reaction has been investigated and both the strength and the inertia of the confinement have been shown to be important parameters which determine the rate of product gas venting.

Experiments to assess the relationship between explosiveness and charge size, shape and mechanical properties are described.

INTRODUCTION

The Oblique Impact Test (1) is used at AWRE to assess the hazards of handling HE charges during processing and assembly, and also in a variety of other situations. In the test 14 in diameter, hemispherical billets of HE are struck obliquely onto hard gritted surfaces, with impact velocities up to 25 ft sec^{-1}. Sensitiveness is measured in terms of the minimum drop height for which explosive events are observed, and explosiveness is qualitatively assessed from the fraction of HE consumed in the event, and the damage to the surroundings. Ignition in this test is due to frictional heating at the surface of the charge (2,3), and the dynamic strength and moduli of the billets have been shown to be important parameters. The factors which control the growth of reaction and which determine the explosiveness are not well understood.

The Oblique Impact Test provides a realistic simulation of a handling accident, but has several disadvantages which include the high costs, limiting the number of charges tested, the qualitative assessment of explosiveness and the inconvenience which arises from the need to use remote test sites.

The objectives of the work reported now were (a) to develop a quantitative laboratory scale explosiveness test, having none of the limitations of the large scale test, which would rank the explosiveness of HE compositions in the same way as the Oblique Impact test, and (b) to use the test to identify and study the physical conditions and HE properties, which limit the growth of reaction in HE systems. A laboratory scale explosiveness test is described together with a series of preliminary experiments to assess the contributions of confinement, charge size and charge mechanical properties to explosiveness.

It must be emphasised that a small scale test has value as an economic explosiveness screening test for use by HE Formulators, but cannot replace the Oblique Impact Test in characterisation programmes. Hazard assessment must ultimately be based on the response of compositions in tests designed to simulate a wide range of real accident situations.

THE DEVELOPMENT OF A LABORATORY SCALE EXPLOSIVENESS TEST

Apparatus

HE charges were confined in metal cups and impacted in a drop weight apparatus.

At a predetermined point in the loading cycle the charges were ignited by a hot wire in contact with the bare face of the charge. The impact conditions were chosen to simulate the Oblique Impact Test where pressures up to 0.2 GPa and impact times of 1.0 - 2.0 msec can occur depending on the drop height and the mechanical properties of the explosive. The violence of the explosive event was assessed from the output of strain gauges fitted to a load cell mounted beneath the explosive charge.

The explosive charge assembly is shown schematically in figure 1. Explosive discs (H), weighing approximately 17g and measuring 28.6 mm diameter x 14.3 mm thick, were assembled into metal cups (c), with the bare face of the charge protruding 1.5 mm. Different strengths and inertias of confinement were obtained by using steel or aluminium alloy for the cup material, and by varying the cup wall thickness. The heights of the cups and the thicknesses of the bases were kept constant at 31.8 mm and 19.0 mm respectively.

The drop weight apparatus is shown schematically in figure 2. The explosive charge assembly (A) was impacted by a 22.7 kg drop weight (B), falling through 305 mm in a guide tube (C). A felt pulse shaper (D), 12.7 mm thick x 75 mm diameter, mounted on a tufnol (resin bonded fabric) load spreading plate (T) served to smooth the loading pulse by damping stress wave reverberations. A constantan resistance wire (F) 0.152 mm diameter x 38.1 mm long was positioned along a diameter between the bare face of the explosive charge and a tufnol spigot (G). The wire was heated for 80 µsec during the loading cycle, by the rapid discharge of a 25 uF capacitor bank charged to 600V, achieving a wire temperature 700°C. A simple switch (H), activated by the falling weight, was used in conjunction with a 15V battery to provide a reference signal to trigger both the time base of an oscilloscope, recording the output from the load cell (E), and after a delay the hot wire power pack. A schematic diagram of a typical load/time record is shown in figure 3. The drop weight has made contact with the impact switch at point (a), and the load increases smoothly to (b) as the drop weight decelerates compressing the pulse shaper. Electrical pick-up at (b) from the discharge of the heater power pack serves to indicate the loading conditions at the time of ignition. The peak load impressed on the load cell by the reaction product gases is indicated at (c). The parameter $(F - F_I)$ has been taken to be the measure of explosiveness, where F is the peak force impressed on the load cell, and F_I is the load on the explosive assembly at the time of ignition. At (d) the load/time record terminates in mechanical ringing. The curve indicated at (e) represents the load/time record in the absence of an explosive event.

A QUANTITATIVE DETERMINATION OF EXPLOSIVENESS USING LABORATORY SCALE HE CHARGES

Four HE Compositions were selected for study. These were HW4 (HMX/Wax 95/5 w/o), Octol-A (HMX/TNT/Wax 79/20/1 w/o), Octol-R (HMX/RDX/TNT/Wax 75/4/20/1 w/o) and PBX 9404 (HMX/NC/TCEP 94/3/3 w/o) These were chosen since they were known to encompass the complete range of explosiveness, in the Oblique Impact Test, from small partial to high order explosions.

Peak forces were determined for a range of cup wall thicknesses when each of the compositions was confined in mild steel and in aluminium alloy cups, and ignited in the drop weight apparatus.

The dependence of peak force on confinement wall thickness is shown for each of the compositions in figures 4, 5, 6 and 7. Peak force increased with increasing wall thickness and asymptotically approached a maximum value for each combination of explosive and cup material investigated. In addition, for a given size of confinement larger peak forces were recorded with steel than with aluminium alloy cups, for each explosive composition. Explosiveness was measured quantitatively from the force/time record. The quantity of explosive reacted and the damage to the metal confinements which are qualitative measures of explosiveness, were in good agreement with the peak force measurements. In all of the HW4 experiments most of the HE was recovered unreacted and the metal cups were always recovered undamaged. With Octol-A the damage to the confinement and the quantity of HE reacted varied with wall thickness. Some unreacted explosive was always recovered, but the fraction reacted increased with increasing wall thickness. Steel and aluminium cups with wall thicknesses not exceeding 18mm and 11mm respectively were undamaged, but significant deformation occurred for confinements with wall thicknesses exceeding these values. The quantity of Octol-R reacted showed a similar dependance on confinement to that observed for Octol-A, however damage to the confinement occurred in every experiment. Every metal cup in the PBX 9404 experiments was damaged and very little HE was recovered. In some cases complete reaction may have occurred.

Ignition in all of the experiments occurred under conditions of transient loading which simulated the impact conditions in the Oblique Impact Test. For any given confinement, the experimental results in figures 4, 5, 6 and 7 show that the ranking of explosiveness for the compositions investigated was

HW4 < Octol-A ≤ Octol-R << PBX 9404

and this ranking is also confirmed qualitatively by an assessment based on damage to the metal cups and the fraction of HE consumed in the reaction. Differences between compositions were least pronounced when the charges were confined in thin walled aluminium alloy vessels, and most pronounced for thick walled steel confinements. The explosiveness values determined for HW4, Octol-A, Octol-R and PBX 9404 confined in steel cups with walls 36.5mm thick are shown in TABLE 1, together with the response of 50 lb hemispherical charges in the Oblique Impact Test, for comparison. Care had been taken to ensure that the F_I values were similar in each experiment. The ranking of the four test compositions was in good qualitative agreement with the full scale test.

THE ROLE OF CONFINEMENT IN THE LABORATORY SCALE TEST

Following Macek's model for the deflagration -to-detonation transition (4), the build up to detonation is determined by (a) the relationship between burning rate and pressure, (b) the shock properties of the unreacted explosive and (c) the shock sensitivity of the explosive in an appropriate geometry. When venting of the product gases occurs during the build-up then the relative rates of product gas formation and venting must also be taken into account, and venting may lead to the extinction of reaction. In the small scale experiments described above the reaction was extinguished before the HE was completely consumed, except possibly for a few experiments with PBX 9404 when complete reaction may have occurred. The metal confining cups used in these experiments were either recovered undamaged or with their walls deformed. This evidence suggests two main venting modes may be operating to limit the event size, an inertial mode and a strength mode. These are illustrated schematically in figure 8. The original positions of the metal confining cup (C), the explosive charge (E) and the Tufnol base plate (B) are shown in figure 8.1. In the inertial mode illustrated in 8.2 the force exerted on the charge assembly by the product gases causes the assembly to move away from the base plate, and the product gases vent as indicated (V). The strength mode is illustrated in figure 8.3. The force exerted on the metal confinement by the product gases causes the walls to deform plastically thus allowing the product gases to vent as indicated. Figures 4-7 show that for any of the HE compositions investigated the peak impressed force measured with a steel confinement of any given size was greater than that measured with an aluminium alloy confinement of the same size. The steel and aluminium alloy used in the experiments had similar yield strengths, but confining cups of the same size differed in mass. The peak force measurements for Octol-A from figure 5 were replotted as a function of the mass of the explosive assembly as shown in figure 9. In region (I) the peak force can be seen to depend only on the mass and not the material and dimensions of the confinements.

All confinements from experiments corresponding to region (I) were recovered undamaged. This would be expected for an inertial venting mechanism since, provided the explosive assembly and the drop weight are decoupled by the felt pulse shaper, the mass of the explosive assembly will determine the acceleration of the round away from the ignition plane, and hence determine the rate of venting. Neglecting the mass of the drop weight is justified by the data shown in figure 10. This shows a static load/displacement curve for the felt pulse shaper used in the experiments. Peak load has been plotted as a function of the additional compression of the felt from some initial compressed state. The point P indicates a compression state appropriate to the ignition conditions in the small scale experiments. The data demonstrates that further compression of the felt from the state P may be readily achieved, thus allowing relative movement between the charge assembly and the drop weight which are therefore effectively decoupled.

If the inertial mode was the sole venting mode then by increasing the cup wall thickness the explosiveness could be increased until a complete explosive yield was obtained. However, the peak impressed force tends to a maximum value, which corresponds to a partial explosion, with increasing wall thickness (figures 4-7). This can be readily explained by the strength mode for venting. Failure of the walls of the metal cups, leading to product gas venting, will occur when the maximum hoop stress in the wall equals the yield stress for the material. When the cup wall thickness is increased the maximum internal stress in the cup which can be supported without failure increases, until a wall thickness is reached for which the internal stress approaches the yield stress for the material. At this stage further increases in wall thicknesses have very little effect on the maximum internal stress which can be supported. Confinements from region II figure 9 were all damaged and the peak impressed force in this region is relatively independant of further increases in confinement mass and wall thickness. The steel confinement results in region (II) lie above those fo. aluminium alloy. This may be explained since for a given mass the aluminium alloy cups have a greater wall thickness than steel cups, and the critical wall thickness therefore corresponds to a lower mass.

In general both the inertial and strength modes of venting are important in varying degrees depending on the HE and the material and dimensions of the confinement.

THE EFFECTS OF CHARGE SIZE AND MASS IN THE LABORATORY SCALE EXPLOSIVENESS TEST

The variation of explosiveness with charge mass was studied by comparing, in the standard experiment, the responses of two types of Octol-A and HW4 charges, weighing approximately 30g, with the response of 17g charges. Type A charges were cylinders measuring 28.6 mm diameter x 25.9mm thick and type B charges were discs measuring 50.8mm diameter x 8.1mm thick. The standard 17g charges measure 28.6mm diameter x 14.2mm thick. All charges were confined in thick walled aluminium cups. The impact loading conditions in the experiments were adjusted so that the impact pressures at the time of hot wire ignition were the same for each type of charge. The experimental results are summarised in Table 2. Increasing the charge mass increased the peak forces measured both for HW4 and Octol-A, compared with the small scale experiments, and the increases were greatest for HW4. The experiments have demonstrated the importance of charge shape. Larger peak forces were measured for Type A charges than for type B even though the charge masses were identical. The effects due to charge shape may be explained qualitatively by reference to figure 11, which shows three hypothetical positions of the reaction front in type A and in type B charges. At position a-a the same mass of HE will have been consumed in both types of charge. However, after this point eg. position b-b, less HE will have been consumed in type B charges compared with the type A charges, and for this reason the pressure may be higher in the type A charges. This must produce a lower rate of propagation and a lower explosiveness in type B charges because of the dependance of burning rate on pressure.

PRELIMINARY EXPERIMENTS TO INVESTIGATE THE RELATIONSHIP BETWEEN CHARGE MECHANICAL PROPERTIES AND EXPLOSIVENESS

Although a link between charge mechanical properties and sensitiveness in the Oblique Impact Test has long been recognised, the importance of charge mechanical properties in any predictive modelling of the explosiveness of charges in this test has not been established. It is probable that explosiveness is influenced by the magnitude of the stress in the ignition zone at the time of ignition and by the frangibility of the HE. Consequently the dynamic elastic moduli, the dynamic compressive and tensile strengths, the fracture properties and the HE/Binder adhesion will all be important parameters.

Laboratory scalc explosiveness experiments have been carried out for a range of compositions each of which contained 96^{W}/o HMX in a polyurethane binder. The compositions differed in the type of HMX used (fine or a bimodal mixture of coarse and fine), and in their mechanical properties, which were dependant on the degree of cross-linking in the polyurethane binder. Compositions F-1, F-2, F-3 and F-4 contained the fine HMX (top size 125 μm with 35^{W}/o in the size range 45-125 μm and the remainder in the range 0-45μm), and compositions C-1 and C-2 contained the bimodal HMX. The coarse powder used had top and bottom sizes of ~1 mm and ~100 μm respectively. Except for the differenccs mentioned the compositions were virtually identical.

Six charges of each of the compositions were assembled into mild steel cups 101mm OD, and the explosiveness was determined for each composition. The results of the experiments are shown in Table 3. The ignition load (F_I) required to achieve a propagating reaction varied with the composition. For C-1, C-2 and F-1 an F_I in the range 10-20kN was required, whereas for F-2, F-3 and F-4 much higher loads (F_I) in the range 35-50 kN were required. Explosiveness was found to vary significantly with composition in spite of their similarities. In order of increasing explosivcness the experiments ranked the compositions as follows:

$$(F\text{-}2,\ F\text{-}3,\ F\text{-}4) < HW4 < (F\text{-}1,\ C\text{-}2) < (C\text{-}1) \simeq \text{Octol-A}$$

No one mechanical property has so far been found which correlates with the observed differences in explosiveness. In general the compositions which contained coarse HMX ie C-1 and C-2, were more explosive and able to be ignited with less force (F_I) applied to the charge assembly, than the compositions which contained fine HMX (F-2, F-3 and F-4). However, Composition F-1 which contained fine HMX behaved similarly to C-1 and C-2.

These experiments have confirmed that both the HMX type and the charge mechanical properties are important parameters which must be taken into account in any predictive modelling of the hazard potential of an HE composition.

CONCLUSIONS

1. A Laboratory Scale Explosiveness Test has been developed, which has ranked four test compositions in the same order as the Oblique Impact Test. This small scale test has applications in Formulations Research and Development.

2. Explosiveness is a property of an HE system and has been shown to depend on the size and shape of the charge, and on confinement. The importance of both the strength and the inertial components of confinement has been demonstrated.

3. Explosiveness has been found to vary significantly between compositions, each of which contain 96W/o HMX and the same polyurethane binder material. Charge mechanical properties and the particle size distribution of the HMX in the composition have been identified as important parameters, but the variations in explosiveness could not be correlated with the known differences in mechanical properties.

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Table 1

A comparison between results obtained in the laboratory scale explosiveness test and the oblique impact test

Compositions	Explosiveness		
	Small Scale Test *		Oblique Impact Test
	$(F-F_I)$ kN	F_I kN	
HW4	59 ± 11	37 ± 2	Small Partial
Octol-A	371 ± 18	28 ± 4	Large Partial
Octol-R	476 ± 21	26 ± 11	Large Partial
PBX 9404	900 ± 27	30 ± 3	High Order

* Steel confinement - wall thickness 36.5mm

Table 2

The variation of explosiveness ($F - F_I$) with charge mass and shape in the small scale test

Composition	Explosiveness ($F - F_I$) kN		
	Type A 30g charges 28.6mm dia x 25.9 mm thick	Type B 30g charges 50.8mm dia x 8.1 mm thick	17g charges Standard Size
Octol-A	483 ± 9	380 ± 8	255 ± 12
HW-4	167 ± 52	128 ± 24	14 ± 7

Table 3

Laboratory scale explosiveness test results from a series of compositions containing 96 w/o HMX in a polyurethane binder

Composition	HMX type	Dynamic Modulus $Ex10^{-6}$ kNm^{-2}	DCS kNm^{-2}	(F_I) kN	$(F - F_I)$ kN
C1	Bimodal	1.79	19125	11.12	340
C-2	Bimodal	1.31	12539	19.57	96
				37.14	143
F-1	Fine	2.28	14229	19.13	30
				29.80	125
F-2	Fine	1.45	19774	17.79	Zero
				48.50	29
F-3	Fine	1.86	23133	37.40	47
F-4	Fine	1.93	24857	16.01	Zero
				49.00	25

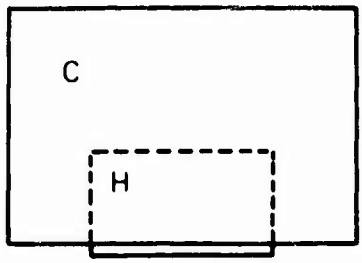


Fig 1 Explosive charge assembly (H) explosive disc 28.6 mm diameter x 14.3 mm thick. (C) metal cup, either steel or aluminum alloy

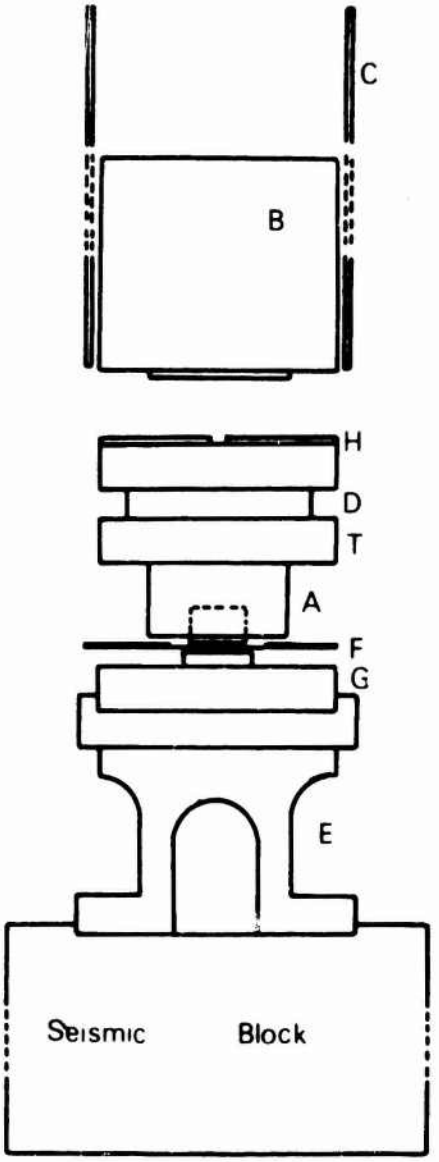


Fig 2 Drop weight apparatus (A) explosive charge assembly (B) drop weight (C) guide tube (D) felt pulse shaper (T) load spreading plate (F) heater wire (G) base plate (H) switch (E) load cell

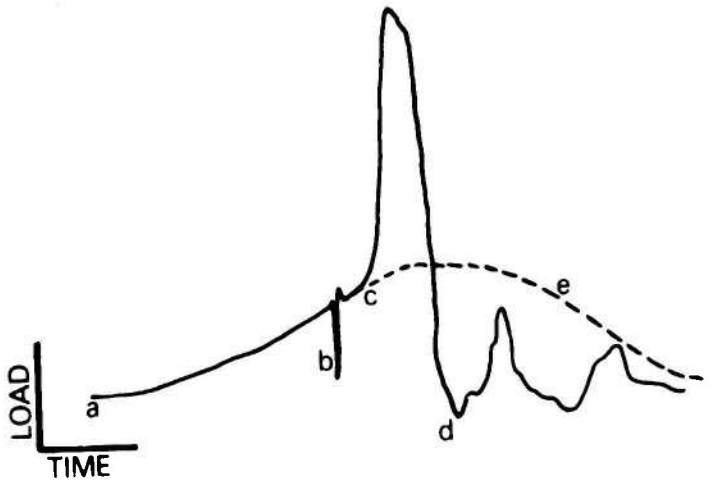


Fig 3 A typical load/time record (a) impact of drop weight (b) electrical pick-up from heater power pack (c) force impressed on load cell by reacting HE (d) mechanical ringing (e) load/time signal in the absence of an explosive event

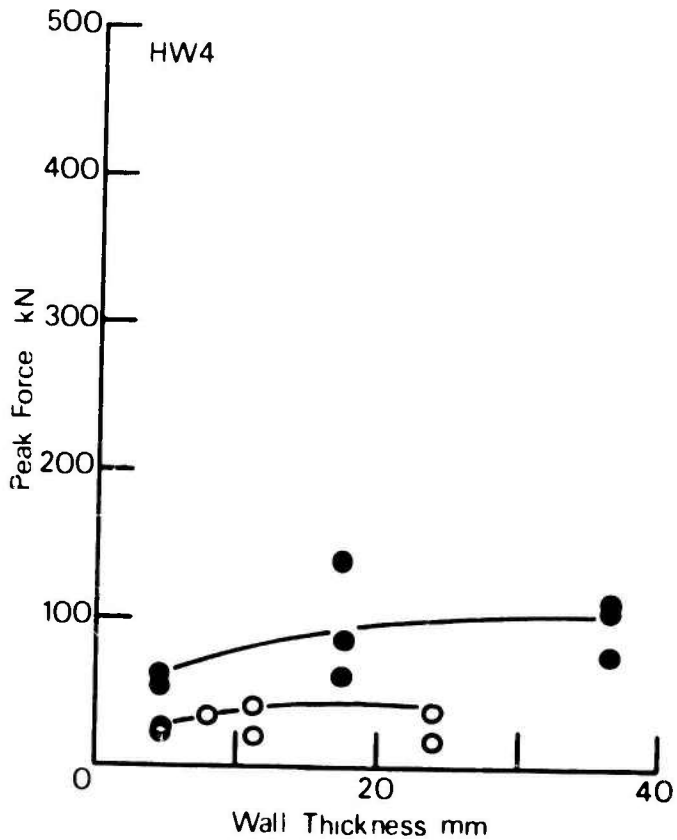


Fig 4 Dependance of peak force on confinement wall thickness in the laboratory scale explosiveness test
Explosive: HW4 (HMX/Wax 95/5)
● Steel Confinement ○ Aluminum Alloy Confinement

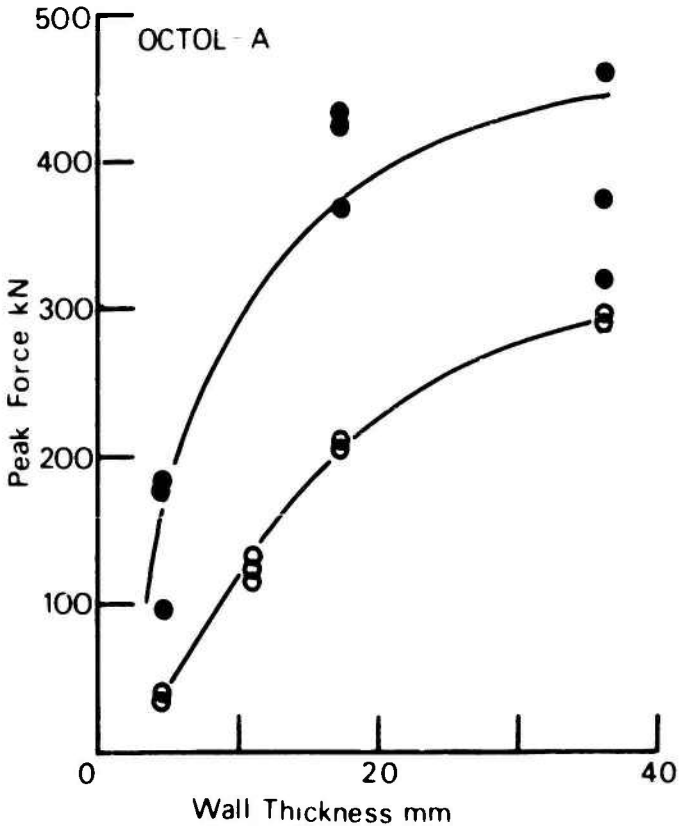


Fig 5 Dependance of peak force on confinement wall thickness in the laboratory scale explosiveness test
Explosive: Octol-A (HMX/TNT/Wax 79/20/1)
● Steel Confinement o Aluminum Alloy Confinement

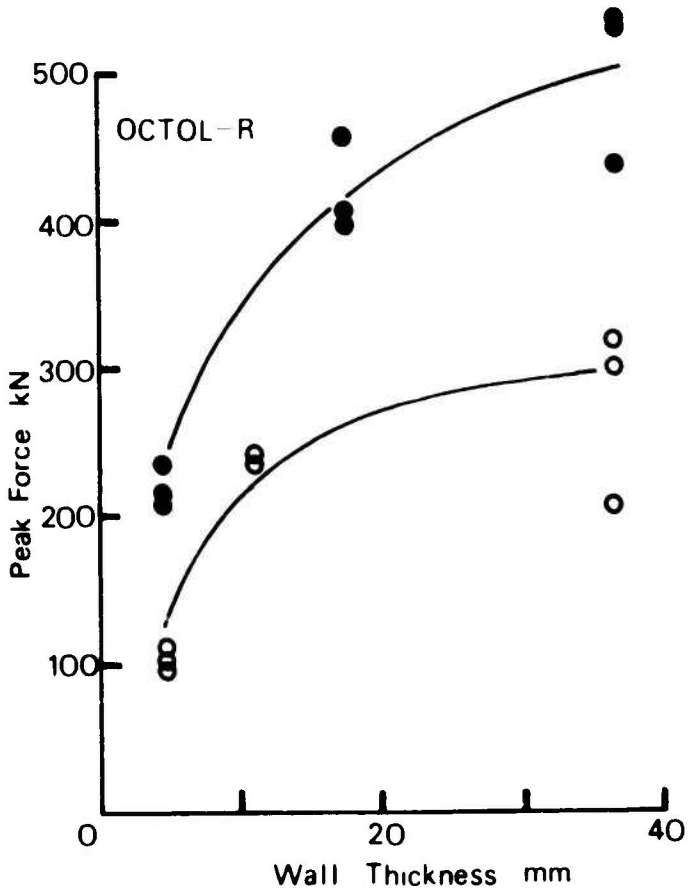


Fig 6 Dependance of peak force on confinement wall thickness in the laboratory scale explosiveness test
Explosive: Octol-R (HMX/RDX/TNT/Wax 75/4/20/1)
● Steel Confinement o Aluminum Alloy Confinement

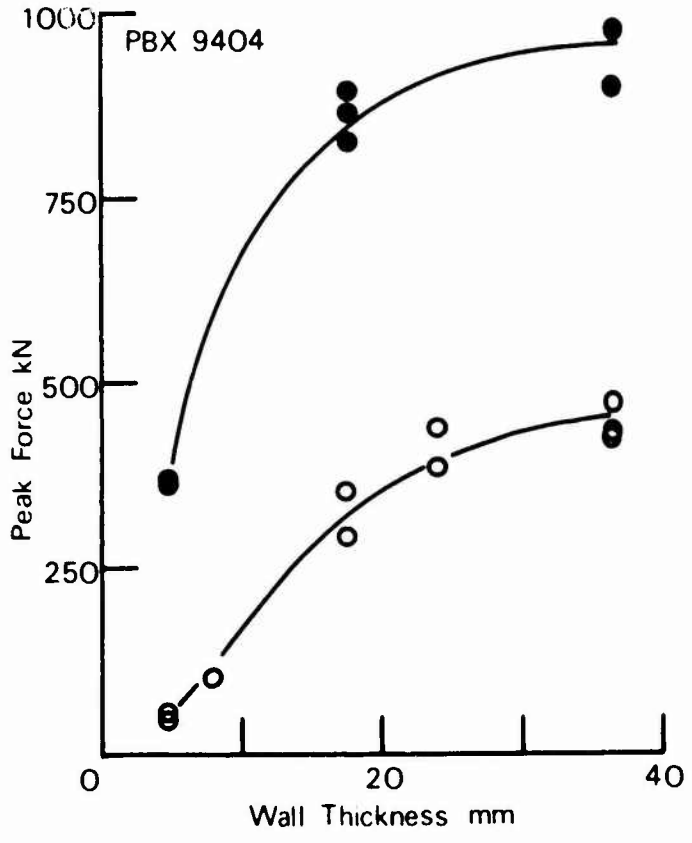


Fig 7 Dependance of peak force on confinement wall thickness in the laboratory scale explosiveness test
Explosive: PBX 9404 (HMX/NC/TCEP 94/3/3)
● Steel confinement ○ Aluminum alloy confinement

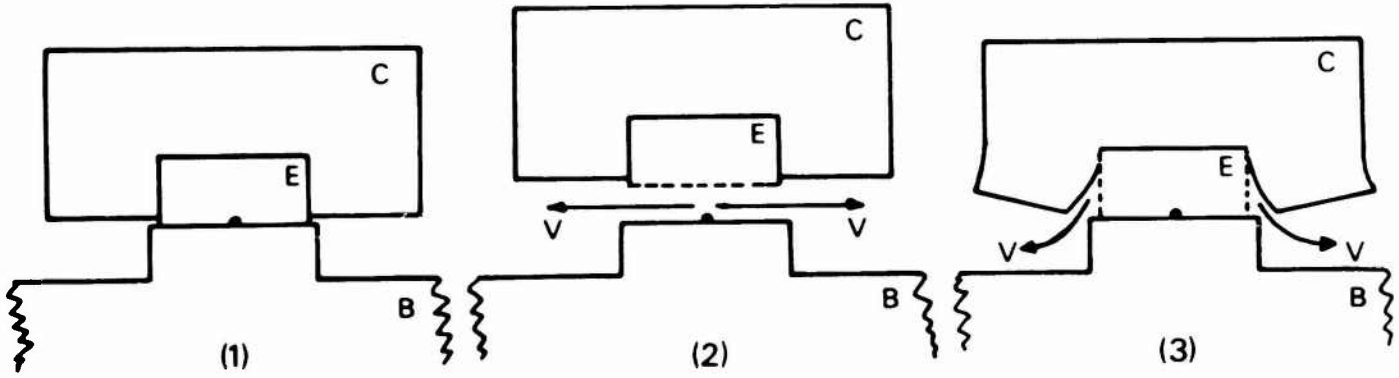


Fig 8 Venting modes in the laboratory scale explosiveness test
(C) metal cup (E) HE charge (B) base plate (V) venting
(1) original position of the charge assembly
(2) the inertial venting mode
(3) the strength venting mode

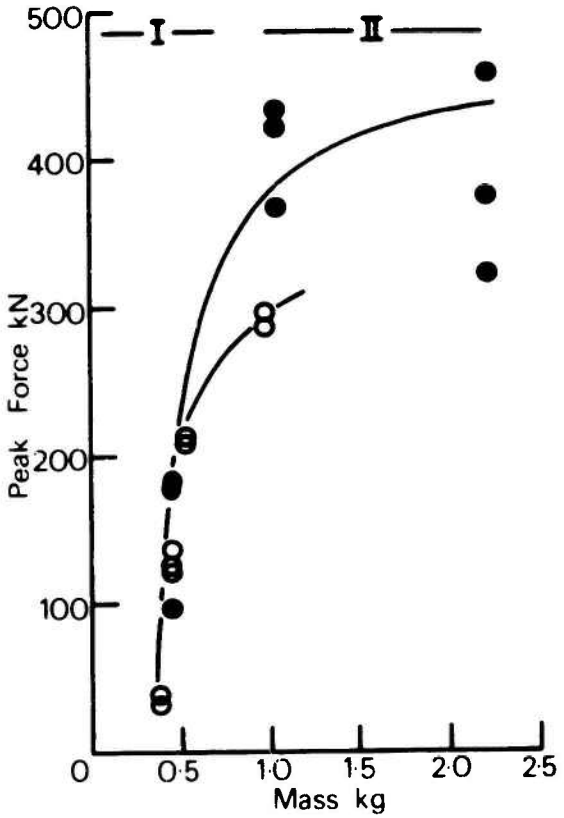


Fig 9 Peak force measurements for Octol-A plotted as a function of charge assembly mass

● Steel confinement ○ Aluminum alloy confinement

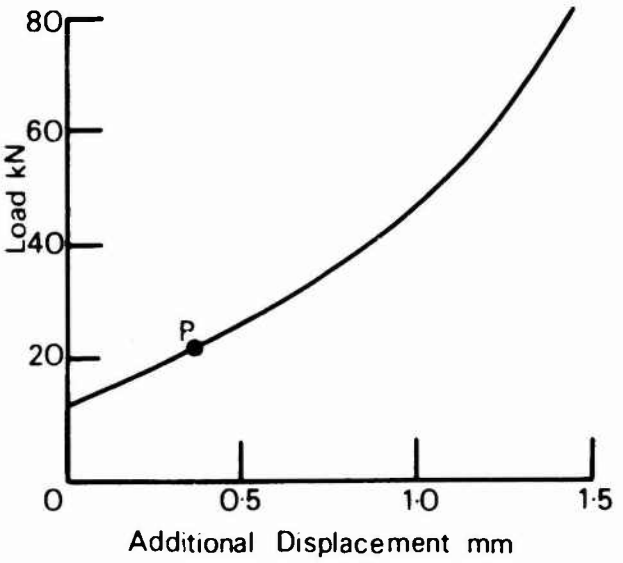


Fig 10 A static load-displacement curve for the felt pulse shaper used in the laboratory scale explosiveness test. (P) a compression state corresponding to the ignition conditions in the small scale test

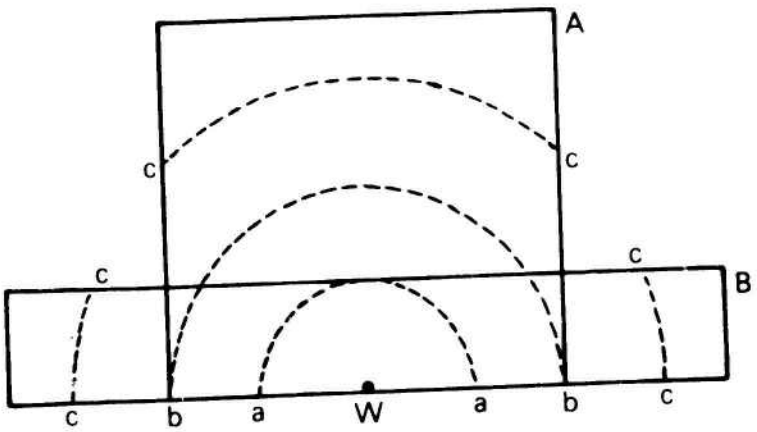


Fig 11 Equivalent positions of hypothetical reaction fronts a-a, b-b and c-c in the type A and type B charges used in the experiments to evaluate the effects of charge size and mass in the laboratory scale explosiveness test. (W) heater wire position (A) HW4 or Octol-A charge 28.6 diameter x 25.0 mm thick (B) HW4 or Octol-A charge 50.8 mm diameter x 8.1 mm thick

THE EFFECT OF GRIT ON THE POWDER IMPACT SENSITIVITY OF EXPLOSIVES

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SUMMARY

The effect of the addition of kieselguhr on the impact sensitivity, as measured by the Rotter Impact Machine, of a number of explosives and compositions has been determined and the results treated analytically. The ability of some phlegmatisers to counteract the effect of the kieselguhr and the unexpected sensitising effect of silicone oil is discussed.

INTRODUCTION

The sensitisation of explosives to impact by the addition of various inert materials has been investigated on numerous occasions, but usually in relation to some specific practical problem. It was thought that useful information could be obtained by a more systematic approach where the effect of the addition of different percentages of one inert material to a range of explosives was examined, using the Rotter Impact Machine.[1]

Kieselguhr is composed of the skeletons of minute marine organisms known as diatoms, and although it may appear to be a soft powder it is, in fact, composed almost entirely of silica and consequently its constituent particles may be extremely hard. It is well known in explosive technology, being one of the constituents of dynamite. It was used recently at AWRE as a filter medium in the preparation of one type of PETN and it was found that enough remained in the final product seriously to reduce the Figure of Insensitiveness (F of I)*. As a result of this discovery, some further tests on PETN with kieselguhr were clearly necessary and it was decided to extend the programme to include a selection of other explosives.

It was also decided to examine the ability of a selection of phlegmatisers to counteract the sensitising effect of the grit as it was known that the ability of different materials to desensitise explosives varies greatly. PETN was the only explosive used in this work.

$$* \text{ F of I} = \frac{80 \times \text{Median Drop Height of Sample}}{\text{Median Drop Height of Standard}}$$

EXPERIMENTAL

10 g of explosive was used for each test sample and the kieselguhr added and well mixed. This was not always easy because (a) the kieselguhr was the same colour as most of the explosives used, and (b) handling the explosive quickly built up a static charge. However, internal standard deviations in Rotter test data and, where performed, results of duplicate testing, suggest a reasonably homogeneous mixture.

For the first series of tests, the percentage of kieselguhr added was on a log scale, 1.0, 0.1, 0.01 with intermediate percentages added later as required. For the second series of tests, 20g of a 1% mixture was made up, 10g taken out for testing and the remainder progressively diluted with explosive to give grit percentages of 1/2, 1/4, 1/8, 1/16, 1/32, 1/64. It was thought that this method would result in a more homogeneous mixture.

For the work on phlegmatisers, the mixtures were made by dissolving the phlegmatiser in a suitable solvent, mixing the solution with the explosive and allowing the solvent to evaporate. Some experiments were done initially to compare the effect of adding the kieselguhr before and after the phlegmatiser. As the results indicated that there was no appreciable difference, the kieselguhr was added after the phlegmatiser in all subsequent experiments.

All F of I results quoted were determined using the AWRE version of the Rotter Impact Test, ie a 50 cap Bruceton run for the sample, with a running mean for the RDX standard based on a weekly 50 cap run.

RESULTS

Tables 1 and 2 show all the F of I figures obtained and these are also expressed graphically in Figures 1 and 2. Where more than one determination has been made the figures have been meaned.

Table 3 gives the percentage sensitisation which is the difference between the control F of I and that obtained at the 0.01% grit level, expressed as a percentage of the control figure.

Table 4 orders the explosives from least to most sensitive at the 0.05% grit level. This is considered to be the highest grit level which could occur through contamination during manufacture. Also included in this table for comparison are the Grit Insensitiveness

Figures (GIF) (See Analysis of Results).

Table 5 shows the effect of a selection of phlegmatisers, with and without grit, on PETN.

ANALYSIS OF RESULTS*

If a plot is made of the relationship between the percentage of grit (abscissa) against F of I (ordinate) a falling curve resembling a hyperbola is obtained, and the curve appears to run asymptotically to some minimum F of I value as the amount of grit is increased. It was found that such data could be fitted to the simple hyperbola $(F - A)(g - B) = C$ where A, B and C are constants, F is the F of I and g is the percentage by weight of grit present.

The principles underlying this regression method are described in Appendix I and it was used throughout the present work to reduce the observations to an analytical form.

From the regression constants A, B and C can be derived a number of parameters of practical value in assessing the safety properties of the explosives on the assumption that in everyday usage one will seldom be handling a pure explosive, but rather one which, in spite of the usual precaution, will almost inevitably be contaminated to some extent with adventitious grit.

The parameters which seem to be of greatest potential usefulness are the following:

1. The minimum value (M) of the F of I which is likely to arise as a result of gross contamination with grit.

2. The slope (S) of the curve at the zero grit level taken as a measure of the responsiveness of the particular explosive to very small grit concentrations.

3. A general parameter, to be called the Grit Insensitivity Figure (GIF) equal to the average F of I from zero grit up to some arbitrary level conveniently fixed at 1% grit. M, the minimum

* This method of analysis was devised by Dr C M Bean. Another treatment has been proposed by Mr H J Scullion. Ref 2

sensitivity, may be taken as the value of the constant A, ie it is the asymptotic value of the F of I as g increases indefinitely.

S is given by the following expression:

$$S = \frac{C}{B^2}$$

GIF is the area lying under the regression curve from $g = 0$ to $g = 1$ and has the value:

$$GIF = A + C \ln\left(\frac{B - 1}{B}\right)$$

Table 6 gives, for 12 explosives, the values of these parameters together with the regression constants A, B and C and a root mean square estimate of the goodness of fit (See Appendix I).

DISCUSSION

1. THE EFFECT OF GRIT

The curves plotted in Figures 1 and 2 are all approaching very closely to an asympototic F of I by the time that 1% of grit has been added. It is not easy, especially in view of the complexity of the impact process in the Rotter machine, to form anything like a quantitative physical picture of the processes taking place during impact in the presence of grit. The observations do, however, suggest that a 'saturation' process is taking place as more and more grit is added, perhaps that special locations in the explosive particle matrix capable of producing sensitisation are being progressively occupied by grit particles as the proportion of grit increases. The limit condition would be the point where two or more grit particles (assumed to be no more effective than a single one at a given site) are candidate occupants for the same site.

Of the parameters M, S and GIF, the last, since it represents the average behaviour of the sample over a reasonable range of grit concentrations, is perhaps the best general indicator and moreover is a very stable figure in the sense that it is not as easily perturbed as are S and M by experimental errors. Although the number of explosives so far investigated is small, already it is possible to sketch in tentatively a division of the explosives into classes according to the GIF values. (Table 4) In the class GIF < 15 we have Barium

Styphnate and PETN. To this classone can assign primary explosives and those which although not true primaries nevertheless partake of some primary-like properties. The class ($15 < GIF < 35$) can be described as sensitive secondary explosives. Tentatively, one would put the insensitive secondary explosives in the class ($GIF > 35$).

It must, however, be emphasised not only that this is a tentative division but also that the present results have relevance only to powder impact situations where, as will probably be true in most practical instances, absolute freedom from adventitious grit cannot be guaranteed. No claim whatever can be made that the classification is any guide by itself to the sensitiveness of charges, ie to the likelihood of an event ensuing from their rough usage.

From a practical point of view, an important consideration is the F of I of an explosive at a grit level which might be expected to arise in adverse processing conditions. It is difficult to imagine that under the close control normally applied to manufacturing processes that such a grit level could exceed 0.05% without being evident in quality assurance. If, at this level, the explosives are ordered from least to most sensitive (Table 4) it will be seen that they could have been ordered in almost and exactly the same way by using the GIF and fall into the same three groups as noted above.

2. THE EFFECT OF BINDERS

The usually explosively inert binder used in HE formulation fulfils three roles:

(a) To endow the final charge with desirable mechanical properties

(b) To control the explosiveness of the charge, namely the magnitude of the event to which the charge might give rise in certain hazard situations.

(c) To act as a general phlegmatiser, that is to produce a generalised desensitisation of the explosive particularly when it is handled in powder form.

It is necessary to distinguish (b) which refers to the likely consequences of a seminal event occuring in or near the surface of the

charge, from (c) which refers to the ease of producing such an event. Experiments of the type dealt with in this report are directly relevant only to (c), although this does not preclude the possibility that some indirect conclusion as to (b) might stem from (c).

It is clear that in a formal sense at least grit can be regarded as an anti-phlegmatising agent and that therefore there is the possibility that a standard grit might be used as a yard-stick to measure the effectiveness (in the sense of (c) above) of various phlegmatisers and that this might be a useful guide to designing HE formulations.

The present results enable a start to be made on these lines. Indeed, there are results which indicate, contrary to expectation, that some binders (viton in HV 1 and silicone oil) instead of being phlegmatisers are in fact acting as sensitising agents.

Looking at the curves in Figures 1 and 2 some observations may be made. HW 4 with a polythene binder and HW5 with polythene/ liquid paraffin are the least affected by grit and only slightly worse is HT2 containing some TNT which may have some phlegmatising action, and a small quantity of wax. HT1, with a similar composition, fares significantly worse; this could possible be due to its having a higher HMX content.

The viton in HV1 has no desensitising action at all. In fact, as noted above, it has a slight sensitising effect.

A much more striking example of this effect emerged during work on the phlegmatising power of certain binders on PETN (Table 5). It is clear from these results that polythene and some mineral oils are powerful phlegmatisers for PETN and that 5% of them almost exactly neutralises the effect of 0.01% kieselguhr. Lanolin added by a wet process also appears to be similar, but the lanolin is in a hydrated form and this has probably affected the result; lanolin added by a solvent process has little phlegmatising effect.

It is suprising, especially since in general oils are very good phlegmatisers, that the silicone oil, far from being a phlegmatiser, acts almost as if it were another kind of grit, sensitising the mixture in the absence of grit and then acting synergistically with added grit to produce even greater sensitisation.

This effect persists with other samples of MS 200 with different viscosities and other silicone oils of different composition. The phenomenon is one for which there appears to be no ready explanation and it clearly needs more study.

The ultimate aim of work of this kind will be to show, for various explosives, what is the relationship between the amounts of different binders present and the amounts of standard grit required to offset the protective effect of those amounts of binder and thus to arrive at a measure of the phlegmatising effect of different binders. We can, however, derive algebraically point estimates of the phlegmatising effectiveness of the binders present in HV1, HT1, HW4, HW5 and Comp B from the appropriate regression equations. If Ao, Bo and Co are the regression constants for the pure base explosives (here RDX and HMX) and A, B, and C are those for the formulation, then the grit percentage (gn) required to neutralise the protective effect of the binder present is given by:

$$gn = B + \frac{C}{(Ao - A) - (Co/Bo)}$$

The results of this calculation are given in Table 7. As measured by this scale the superiority of the polythene/liquid paraffin binder is clear especially since HW5 is richer in HMX than is HW4. The sensitivity of TNT is low even with much grit (GIF = 72.1) (See also Figure 1) so it is perhaps fair to count TNT/WAX as a phlegmatising binder. However, the percentage, nature and perhaps also the particle size distribution of the base explosive are factors which need to be taken into account in interpreting gn values of binders; point estimates such as are given in Table 7 are insufficient, and need to be extended at least to include a range of percentage of the base explosive with the binder under investigation. The pair HT1 and HT2 may form an illustration of this effect since the gn values for the latter is about $2\frac{1}{2}$ times that of the former. It is not possible to say at this stage whether the difference is due to the different proportions of HMX in the two mixtures, whether it is due to the presence of terylene fibres in HT2 but not in HT1 or whether some other factor is responsible.

CONCLUSIONS

Useful data on the sensitising effect of one type of grit on a range of explosives and explosive competitions has been obtained and a method for the analytical treatment of this data has been devised.

It has been shown that the ability of different binders both to desensitise an explosive and to inhibit the effect of added grit varies greatly, indeed, some silicone compounds actually have a sensitising effect on their own and enhance the effect of added grit. An explanation of this curious behaviour will be sought in future work.

REFERENCES

1. SCC No 3 Explosives Hazard Assessment Manual of Tests, ERDE, September 1968.

2. H J Scullion J Appl Chem 20 (6) p 194 (June 1970).

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Table 1

F of I determinations for explosives + kieselguhr, 1st series

%K / HE	Control	0.005	0.01	0.02	0.05	0.1	0.2	1.0
Potassium Picrate	103	-	90	71	68	63	52	24
HW4	78	-	73	65	67	52	55	36
HMX	53	-	50	44	44	39	36	30
RDX	76	-	68	59	47	36	35	20
PETN	83	-	55	35	31	21	19	9
Barium Styphnate	39	28	15	15	15	14	18	17
HW5	69	-	66	-	-	57	-	37
HV1	51	-	49	-	-	34	-	28

Table 2

F of I determinations for explosives + kieselguhr, 2nd series

%K / HE	Control	1/64	1/32	1/16	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{2}$	1
HT1	91	80	72	58	42	35	34	31
Comp B	105	101	85	83	74	50	41	32
TNT	ca 170	ca 145	ca 145	131	100	89	59	49
HT2	100	82	79	64	58	47	39	35

Table 3

Percentage sensitisation at the 0.01% grit level

Explosive	% Sensitisation
Comp B	1.9
HMX	3.8
HV1	3.9
HW5	4.3
TNT	5.9
HW4	6.4
HT1	9.9
RDX	10.5
HT2	11.0
Pot Picrate	12.6
PETN	33.7
Barium Styphnate	61.5

Table 4

F of I at 0.05% grit level and GIF

Explosive	F of I	GIF
TNT	135	72.1
Comp B	87	46.9
HT2	71	43.9
HW4	68	43.8
Pot Picrate	68	36.9
HW5	60	44.8
HT1	56	36.5
RDX	47	27.2
HMX	44	33.1
HV1	41	30.3
PETN	31	14.2
Barium Styphnate	15	13.9

Table 5

F of I of PETN + various phlegmatisers

Binder	PETN + 5% Binder	PETN + 5% Binder + K
Lanolin (Solvent Mix)	85	56
Lanolin (Wet Mix)	98	74
Polythene	99	82
MS 200 + Benzoyl Peroxide (Uncured)	68	24
MS 200 (30,000cs) No Benzoyl Peroxide	77	30
MS 200 (50cs)	70	29
Si Fluid F110/300	56	19
MS 710	63	25
Cedarwood Oil	73	40
Apiezon Oil C	112	70
Edward High Vacuum Oil	109	72
Dibutylphthalate	98	63
Nujol	98	70

PETN Control F of I = 83
PETN + K Control = 55
K = 0.01% Kieselguhr

Table 6

Derived parameters and regression constants

Explosive	F of I•	F of I ex regression	M	S	GIF	Regression Parameters			
						A	B	C	RMSD
Ba Styphnate	39.3Ø	(80.3)	13.7	1.34×10^5	13.9	13.671	-0.000496	0.03306	0.205
HV1	51.4+	53.0	27.1	705	30.3	27.075	-0.03685	0.9578	0.066
HMX	53	52.5	28.4	330	33.1	28.364	-0.0733	1.773	0.102
HW5	68.6[b]	68.1	29.4	158	44.8	29.400	-0.2443	9.4602	0.0453
PDX	76	74.1	16.5	669	27.2	16.496	-0.06673	3.871	0.221
HW4	78	78.7	31.4	416	43.7	31.435	-0.1139	5.391	0.358
PETN	83	76.8	7.3	2477	14.2	7.2888	-0.02771	1.9018	0.271
HT1	91.4[a]	96.6	29.1	2130	36.5	29.285	-0.03168	2.138	0.207
HT2	100.0	97.0	30.1	858	43.9	[illegible]	-0.07877	5.272	0.117
Pot Picrate	103.0[c]	101.2	16.8	850	36.9	16.7516	-0.09941	8.4018	0.341
Comp B	105.0	108.1	21.6	625	46.9	21.615	-0.1385	11.99	0.225
TNT	170	169.2	32.1	990	72.1	32.1073	-0.1385	18.995	0.298

Notes: • This is the normal, zero grit, F of I as observed
+ Mean of 18 determinations σ (mean) = 0.75
Ø Mean of 17 determinations σ (mean) = 1.04
a Mean of 7 determinations σ (mean) = 3.7
b Mean of 15 determinations σ (mean) = 0.73
c Mean of 3 determinations σ (mean) = 5.1

A, M and GIF are expressed as F of I units. S is expressed as - (F of I units)(% grit)$^{-1}$
The units of B are (% grit)
The units of C are (F of I units)(% grit)

The units of RMSD are $[(\text{F of I units})(\%\ \text{grit})/2]^{\frac{1}{2}}$

Table 7

Values of gn for some explosive compositions

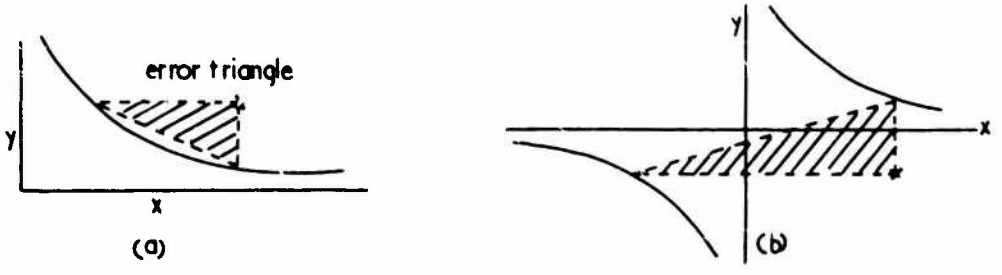
Explosive	Base Explosive	Binder	gn
HW5	HMX	Polythene/liquid paraffin	0.16
HT2	HMX	TNT/Wax	0.16
HW4	HMX	Polythene	0.14
Comp B	RDX	TNT/Wax	0.088
HT1	HMX	TNT/Wax	0.059
HV1	HMX	Viton	0.0007

APPENDIX I

HYBERBOLIC REGRESSION

1. Hyperbolae are particularly apt curves to fit to many kinds of physical data, particularly such as arise in explosives work.

There are, however, difficulties in devising a least squares regression algorithm for $(y - A)(x - B) = C$. The tactic of the present method is as follows:- Let x_i and y_i represent a pair of observations; it is then possible by standard methods to calculated the values of the constants A and B which minimise $\Sigma (C_i - \overline{C})^2 = \frac{\Sigma (C_i)}{n}$. If the fit is perfect all the values of C_i will be identical and if not it is assumed that $\overline{C}$ is the best estimate of C. It is to be noted that the dimensions of C itself are square so the minimisation is of the sums of biquadrates rather than of squares. Furthermore, as will be seen later, the algebra of the calculation of A, B and C is completely symmetrical with respect to x and y, ie the system is invariant under the substitutions $(x = y)$, $(y = x)$, $(B = A)$, $(A = B)$. Thus the error sum of squares is attributed to x and y equally and is conveniently represented by an error sum of triangle areas as is illustrated in diagram (a) below. Difficulties can arise, as is shown in sketch (b) below if an observed point is so divergent that it falls in the 'wrong' quadrant of the asymptote axis frame of reference.



The computer programme used detects and announces such occurrences and excludes the abnormal error triangle areas from the calculation of goodness of fit, which is taken as RMSD $= \sqrt{\frac{\Sigma (T)}{(n - 3)}}$ where $\Sigma(T)$ is the sum of the area of the non-excluded error triangles.

The calculation of A and B is as follows:-

$$\sum \left[C_i - \bar{C} \right]^2 = \sum (C_i^2) - \frac{\left(\sum C_i\right)^2}{N}$$

$$C_i = (y_i - A)(x_i - B)$$

By substitution of the last expression into the right hand side of the first, expressing the result in summed form, then partially differentiating it with respect to A and B, then equating each expression to zero and solving the two resultant simultaneous equations the following, after much tedious algebra is obtained:-

$$A = (mk - pq)/(mj - p^2)$$

$$B = (jq - pk)/(mj - p^2)$$

where:-

$$j = \Sigma (x^2) - \frac{\Sigma^2(x)}{n}$$

$$k = \Sigma (x^2 y) - \frac{\Sigma(x) \cdot \Sigma(xy)}{n}$$

$$p = \Sigma (xy) - \frac{\Sigma(x) \cdot \Sigma(y)}{n}$$

$$q = \Sigma (y^2 x) - \frac{\Sigma(y) \cdot \Sigma(xy)}{n}$$

$$m = \Sigma (y^2) - \frac{\Sigma^2(y)}{n}$$

Substitution of each pair of x, y observations into the basic equation $(y - A)(x - B)$ using the calculated A and B values leads to the array of (C)'s the mean of which is the value of C.

2. To fit a general rectangular hyperbola with assignment of the error to the ordinate only is somewhat more difficult. It can, however, be done on a trial and error basis by substituting tentative values of

the constant B into the following expressions for A and C and calculating the data Error Sum of Squares $\Sigma (Y - y)^2$ directly.

$$A = \frac{\sum\left[\frac{1}{(x-B)^2}\right] \cdot \sum(y) - \sum\left[\frac{1}{(x-B)}\right] \cdot \sum\left[\frac{y}{(x-B)}\right]}{D}$$

$$C = \frac{N \cdot \sum\left[\frac{y}{(x-B)}\right] - \sum\left[\frac{1}{(x-B)}\right] \cdot \sum(y)}{D}$$

where $$D = N \cdot \sum\left[\frac{1}{(x-B)^2}\right] - \sum^2\left[\frac{1}{(x-B)}\right]$$

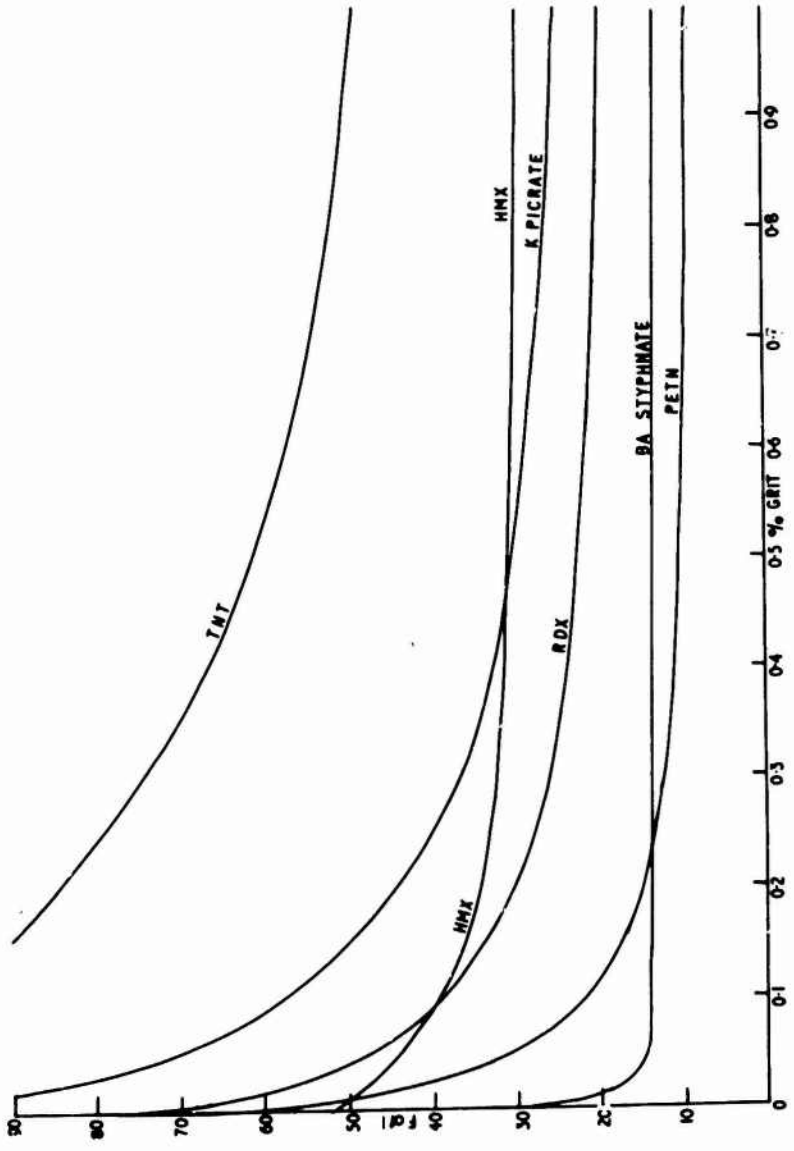


Fig 1 Effect of grit on the F of I of some single explosives

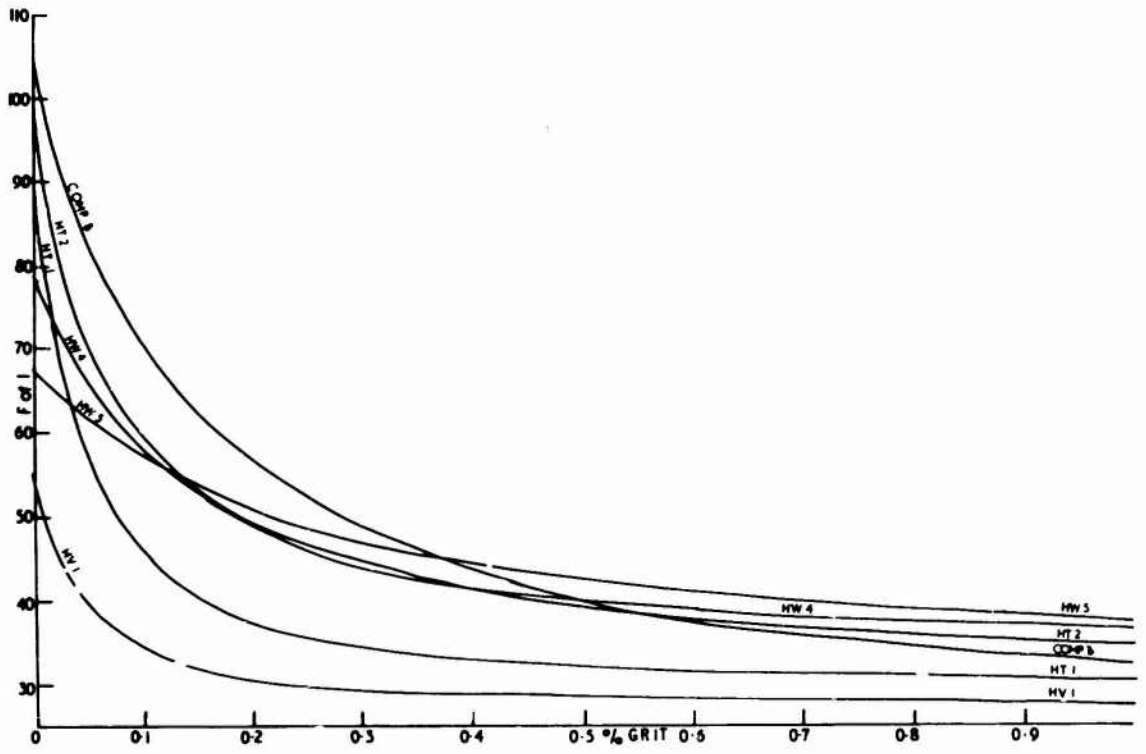


Fig 2 Effect of grit on the F of I of some explosive compositions

MODE OF IGNITION IN THE PICATINNY ARSENAL ACTIVATOR (ARTILLERY SETBACK SIMULATOR)

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ABSTRACT

Experiments at the Ballistic Research Laboratory designed to determine the mode of ignition of explosive in the PA activator as it has been used in the past have shown that the ignition is not due to adiabatic compression of the residual gas but rather that the ignition probably is caused by friction within the machine. Thus, in the past, the activator was not modeling conditions that exist within the shell during launch, and the explosive ignition in the activator was only an artifact of the activator itself. It has also been shown that when the source of frictional ignition is eliminated that the explosive is resistant to adiabatic ignition in the activator to at least three times the level previously accepted. Experiments are being continued in order to investigate conditions which will produce sufficient adiabatic heating of the explosive to ignite it. If the changes suggested are adopted, then the activator will be an acceptable test device to obtain adiabatic ignition sensitivity.

There are two other general classes of stimuli that can lead to ignition of the shell filler, namely high pressures acting directly on the explosive, and frictional phenomena. The activator is a convenient, relatively low-cost tool for investigating and characterizing all three areas, and BRL currently is using it as such.

BACKGROUND

Since 1971 BRL has been interested in the results of activator tests on explosives. At that time the activator tests on Comp B for various base gap spacings as a function of pressure indicated that it was considerably more sensitive than seemed possible. A joint effort between Picatinny Arsenal and BRL at that time lead to inconclusive results because of fund limitation. Since that time, BRL has built up a capability for activator testing. The present study has been funded by the Energetic Materials Division of the Large Caliber Weapons Systems Laboratory as a component of the Energetic Materials Research Program.

P.A. ACTIVATOR

The small scale laboratory test device which was developed by Picatinny Arsenal to simulate the setback pressure loading generated by firing an artillery shell was named the P.A. Activator. A schematic drawing of the apparatus is shown in Figure 1 (taken from Ref 1). The explosive sample is placed in the center of the hollow steel cylinder (D) between two steel pistons (C). The rear piston is normally stationary and is in contact with the adjustable rear support screw (B). The front piston is driven by the large piston (E). This large piston in turn is driven by burning propellant in the closed chamber (J) with a pressure gage to measure this pressure. When adiabatic ignition is to be tested an air gap is established between the front surface of the explosive and the front piston as shown in Figure 2. This gap is termed the base gap since it is meant to simulate the base gap region of a high explosive filled shell.

INITIAL EXPERIMENTS

The initial experiments at BRL with the activator led in a clear and direct manner to an understanding of the mode of ignition of explosive samples in the device as it has been used in the past and also as it presently is being used at BRL. These experiments are listed in Table 1. Initial experiments started with Comp B at 60°C (140°F) with a 1.6 mm (1/16 in.) base gap in an attempt to reproduce the data obtained by PA several years earlier shown in Figure 3. The shots started at 410 MPa (60,000 psi) and the pressure was repeatedly increased in an attempt to obtain the first ignition with the apparatus so as to assess the violence of it and determine if the BRL activator was properly constructed to withstand the explosion. The first shot at 410 MPa (60,000 psi) had only a 5%

probability of ignition so that lack of ignition wasn't too surprising. One shot was then fired at 480 MPa (70,000 psi) where the probability was 16% and again the lack of ignition was not a surprise. Next, two shots at 620 MPa (90,000 psi) where the probability was 70% each proved some surprise when neither ignited. Then another shot was fired at what was set as the top pressure for the apparatus, 830 MPa (120,000 psi) where the probability was 99.9%. Lack of ignition here was cause for concern. After verifying that the test samples were indeed high explosives, another test was made again at 830 MPa (120,000 psi), this time with a 3.2 mm (1/8 in.) base gap where, on an extrapolated basis, the probability should have been 99.99%. Again no ignition occurred. Finally, on the next test at 830 MPa (120,000 psi) with a 6.4 mm (1/4 in.) base gap ignition occurred. A later series of tests performed at 830 MPa (120,000 psi) with a 3.2 mm (1/8 in.) base gap gave one ignition in twenty-eight shots.

This left two questions to answer: What was responsible for the ignition that PA reported at appreciably lower pressures and lesser base gaps, and what was responsible for the BRL ignition at 630 MPa (120,000 psi) and a 6.4 mm (1/4 in.) base gap?

MODE OF IGNITION IN BRL TESTS

To determine what was responsible for the BRL ignition, it would have been desirable to have evacuated the air from the 1/4" base gap to prevent adiabatic heating of an appreciable mass of air and thus directly test the adiabatic heating hypothesis. Unfortunately, no vacuum hardware was available at that time, so an equivalent experiment was performed. For five shots, precompressed Comp B was used to render it insensitive to shock ignition and conditions were arranged so that there was 6.4 mm (1/4 in.) free run between the 12.7 mm (1/2 in.) dia. piston and the 76.2 mm (3 in.) dia. driver piston. This experiment would subject the Comp B to the same stimulus as if there were a 1/4" gap between the Comp B and the small piston. However there would be no air to be adiabatically heated adjacent to the Comp B. When these five shots were made none ignited, Table 2. When eleven more precompressed samples of Comp B were tested, this time with a 6.4 mm (1/4 in.) air gap between the Comp B and the small piston and with no free run gap between the 12.7 mm (1/2 in.) dia. piston and the 76.2 mm (3 in.) dia. piston, ten of the samples ignited. Since the difference between the two tests was the presence or absence of air adjacent to the Comp B, this was taken as proof that adiabatic compression of air with a 6.4 mm (1/4 in.) gap could ignite Comp B and was responsible for our ignition in these tests. This just recently has been verified in a

more direct manner. Using cylinders and pistons modified so that a vacuum pump could exhaust most of the air in the 6.4 mm (1/4 in.) base gap, five shots were made on precompressed explosive with a vacuum of 133 PA (1000 millitorrs) or less, and none ignited.

POSSIBLE MODE OF IGNITION IN PA TESTS

If it is accepted that adiabatic heating is responsible for the BRL ignition at 830 MPa (120,000 psi) with a 6.4 mm (1/4 in.) base gap, then this same adiabatic heating cannot be responsible for the ignitions obtained by PA shown in Figure 3. This is due to the fact that the PA ignitions occurred at much less pressure and smaller base gap spacings than did those of BRL. The pistons and cylinders used by PA had an appreciably looser fit. Dimensions of pistons, cylinders, and explosive pellets as used or reported by BRL and PA are shown in Table 3. There are two major differences between the BRL and the PA dimensions. The clearance between the confinement cylinder and the piston is approximately five times greater for PA than for BRL, and the diameter of the explosive sample is smaller for PA. The experimental set-up used in activator testing is so simple that these dimensions represent the only significant differences that could be found between the BRL and PA experiments. Tests were then made concerning these differences.

When the BRL pistons were machined down to 12.573 mm (0.495 in.) diameter and tested with Comp B at 830 MPa (120,000 psi) and a base gap of 3.2 mm (1/8 in.), three ignitions were obtained in three tests as tabulated in Table 4. This compares to one ignition obtained in twenty eight tests with the normal full size BRL pistons cited earlier.

The next step was to determine if this increased sensitivity was sufficient to account for the results obtained by PA, shown in Figure 3, where with a base gap of 1.6 mm (1/16 in.) there is a 50% probability of ignition at about 620 MPa (80,000 psi). Table 5 gives the results using a base gap of 1.6 mm (1/16 in.) and undersize pistons of 12.573 mm (0.495 in.) diameter and also undersize Comp B pellets. Here ignition was obtained at 690 MPa (100,000 psi) and at 648 MPa (94,000 psi) with one shot at each pressure level, and no ignition was obtained with one shot at 400 MPa (50,000 psi). The amount of data is minimal, but it does indicate that using undersize pistons and Comp B pellets increases the sensitivity to ignition with a base gap of 1.6 mm (1/16 in.) so as to satisfactorily explain the results obtained by PA shown in Figure 3.

Of course, with the larger clearance of 0.102 mm (0.004 in.) that occurs with the PA hardware compared to the 0.020 mm (0.0008 in.) with the BRL hardware, Table 3, there is the question of whether the ignition is due to steel-on-steel hot spots or is due to viscous heating of the Comp B as it is extruded into the gap between piston and cylinder. To test these two possibilities, rear (stationary) pistons used that were cut down to 12.573 mm (0.495 in.) diameter for a length of 25.4 mm (1.00 in.) with the remainder of the piston being the full 12.725^{+} mm (0.501^{+} in.) diameter. The front (moveable) pistons were full size (12.725^{+} mm/0.501^{+} in. diameter). Two shots were made with pistons selected so that the full diameter part (12.725^{+} mm/0.501^{+} in.) of the rear piston supported this piston in the cylinder so that the tip portion (12.573 mm/0.495 in. diameter) was centered within the cylinder. When these were tested at 690 MPa (100,000 psi) with a base gap of 1.6 mm (1/16 in.), neither sample ignited. Two more shots were made where the rear (stationary) pistons were located so that the full diameter (12.725^{+} mm/0.501^{+} in.) portion was outside the cylinder so that the cut down portion (0.495 in. diameter) was in contact with the cylinder wall. When these two samples were tested at 690 MPa (100,000 psi) with a base gap of 1.6 mm (1/16 in.), both ignited. These results are tabulated in Table 6. This indicated that the main ignition component was steel-on-steel friction and not viscous shear heating of the Comp B.

If one accepts that the mode of ignition in the PA case is due to hot spots caused by steel-on-steel friction between the piston and the confining cylinder, then a further interesting observation can be made. Obviously, in the BRL case hot spots caused by steel-on-steel friction also occur. The major difference between the PA and BRL designs is that the clearance in the PA case is approximately five times that in the BRL case. This means that the layer of explosive which is extruded into the clearance space is five times thicker in the PA case than in the BRL one. This suggests that the hot spots may cause ignition of the Comp B in both cases, but perhaps the layer is too thin to propagate in the BRL case and thus does not ignite the main body of the explosive sample.

CONCLUSIONS

Experiments at BRL to determine the mode of ignition of the explosive in the activator as it has been used in the past have shown that the ignition is not due to adiabatic compression of the residual gas, but rather that the ignition is probably caused by friction within the machine. There is a fortunate side to this since it also has been shown that when frictional ignition in the activator

is eliminated, that the Comp B explosive is resistant to adiabatic ignition to at least three times the pressure and twice the cavity size previously accepted.

Thus, in the past the activator was not modeling conditions that exist within the shell during launch, and the explosive ignition obtained in the activator was only a machine effect. If the changes suggested by BRL are adopted, then the activator will be an acceptable test device to obtain adiabatic ignition sensitivity. There are three general classes of setback stimuli that can lead to ignition of the shell filler, namely adiabatic compression of the residual gases, the high pressure impulse acting on the explosive, and frictional phenomena. The activator is a convenient, relatively low cost tool for investigating and characterizing all three areas, and BRL currently is using it as such.

REFERENCES

1. Robert T. Schimmel, "Setback Sensitivity of Composition B Under Conditions Simulating Base Separation in Artillery Projectiles," PA Technical Report 3857, ARRADCOM, Dover, New Jersey, February 1969 (AD 848-944)

Table 1

Initial BRL activator tests

Pressure MPa / (psi)	Base gap mm / (inch)	Probability of ignition per shot based on PA data (percent)	Number of shots	Results
410 (60,000)	1.6 (1/16)	5%	1	No ignition
480 (70,000)	1.6 (1/16)	16%	1	No ignition
620 (90,000)	1.6 (1/16)	70%	2	No ignition
830 (120,000)	1.6 (1/16)	99.9%	1	No ignition
830 (120,000)	3.2 (1/8)	99.99%	1	No ignition
830 (120,000)	6.4 (1/4)	99.99%	1	Ignition
830 (120,000)	3.2 (1/8)	99.99%	28	27 No ignition 1 Ignition

Table 2

Test of adiabatic compression hypothesis

No Air Gap at Explosive But Piston has 6.4mm (1/4 in.)

Free Run:

5 Tests - 0 Ignitions

Air Gap (6.4mm/1/4 in.) at Explosive:

11 Tests - 10 Ignitions

Vacuum Gap (6.4mm/1/4 in.) at Explosive:

5 Tests - 0 Ignitions

Table 3
Dimensions

	PA		BRL	
	(mm)	(in.)	(mm)	(in.)
Piston O. D.	12.675	$0.499^{+0}_{-0.001}$	12.736	0.5014 (Actual)
Cylinder I.D.	12.751	0.502 Max	12.756	0.5022 (Actual)
Clearance (Max)	0.102	~0.004	0.020	0.0008
Explosive O.D.	12.573	0.495	12.675	0.499^{+}

Table 4

Test of effect of undersize piston

Piston Dia. 12.573mm (0.495 in.) vs 12,725mm (0.501+ in.) Normal Size

3.2mm (1/8 in.) Air Gap - 830 MPa (120,000 psi)

3 Tests - 3 Ignition

vs

28 Tests - 1 Ignition

For Full Size Piston

Table 5

Further test of effect of undersize piston and undersize explosive

1.6mm (1/16 in.) Air Gap - 690 MPa (100,000 psi): Ignition

1.6mm (1/16 in.) Air Gap - 648 MPa (94,000 psi) : Ignition

1.6mm (1/16 in.) Air Gap - 400 MPa (58,000 psi) : No Ignition

Table 6

Test of effect of friction with undersize piston

1.6mm (1/16 in.) Air Gap - 690 MPa (100,000 psi)

Piston Centered in Cylinder:

2 Tests - 0 Ignitions

Piston Touching Cylinder:

2 Tests - 2 Ignitions

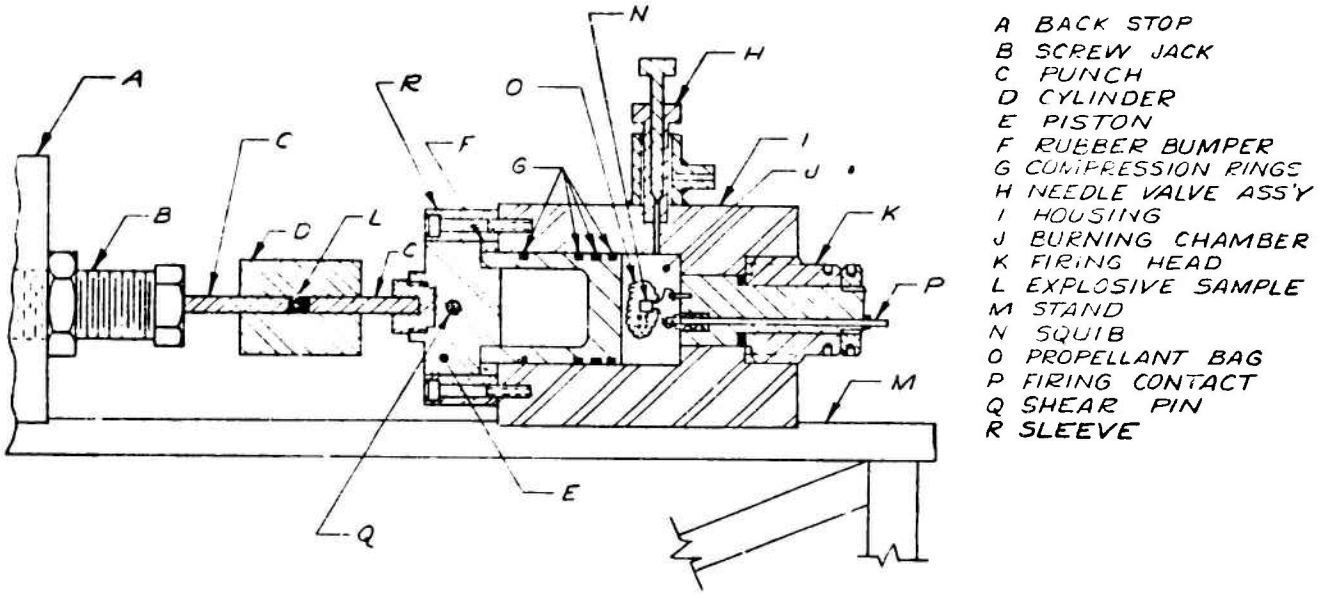


Fig 1 Schematic Diagram of PA Activator

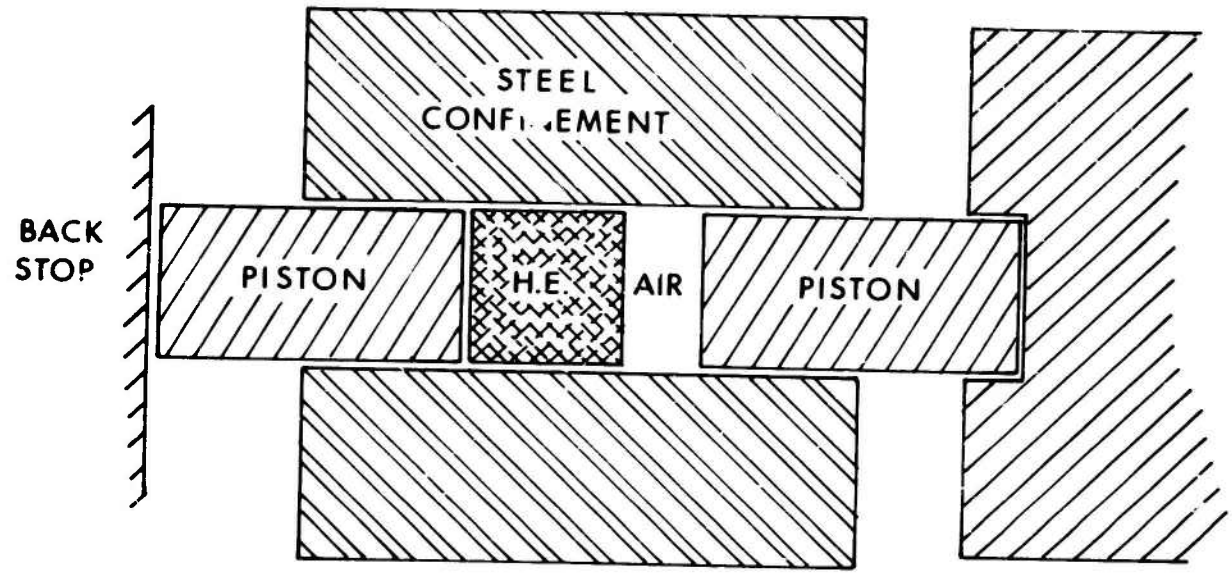


Fig 2 Activator Test Chamber

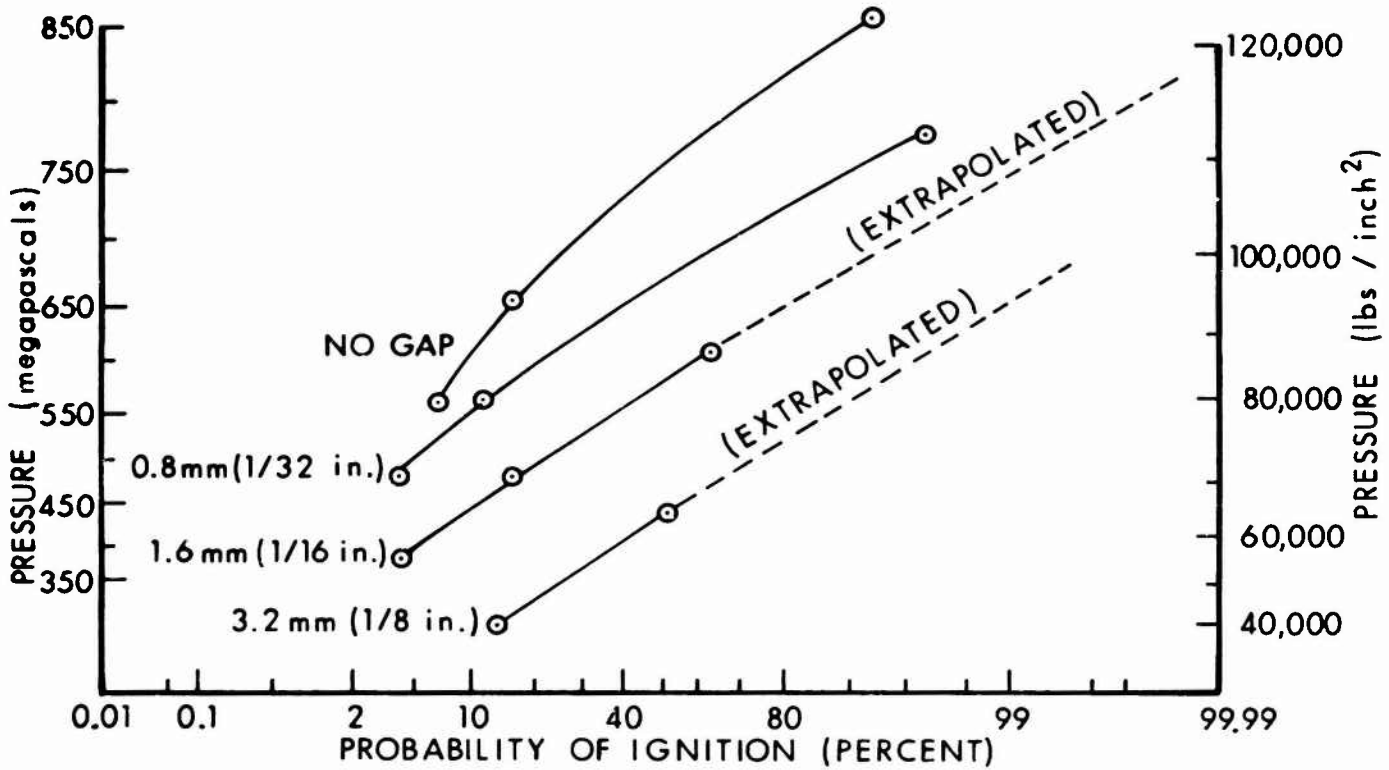


Fig 3 PA Activator Data

THE SENSITIVENESS OF HIGH EXPLOSIVES TO IMPULSIVE LOADS

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SUMMARY

This paper describes a charge sensitiveness test using a "Vertical Activator" which simulates gun launch conditions. The design of the activator permits the inclusion of air cavities and/or particles of grit such as are found in shell filling defects.

The compressive stress in this test is produced by means of a falling weight. The median drop heights for a 50% probability of ignition for various explosive compositions have been determined.

INTRODUCTION

The premature explosion of a shell in a gun barrel can give rise to a devastating event which, apart from the physical damage it may cause, can have a profound effect on the morale of gun crews. Prior to about 1964 all such premature events were assumed to be brought about by fuze malfunction or by direct enemy action. It has since been established that most prematures are caused by the deflagration of the explosive filling initiated by the set-back stresses on firing. However, before the development of the Picatinny Arsenal "Set-Back Simulator" and the UK (Fig 1) and Australian copies no test existed for the assessment of the relative set-back sensitiveness of high explosive shell fillings.

Studies using these simulators clearly demonstrated that deflagrations could be initiated in explosive samples by the compression of small air cavities purposely introduced into the systems. However, certain difficulties were experienced during the operation of the apparatus among which were:

(a) The problem of consistently sealing the explosive under test into the system. Owing to the variation in the tolerances of the cartridge bore and the punch diameter, the degree of explosive confinement varied from shot to shot. Additionally, the explosive sample was often extruded out of the system between the punches and the cartridge and appeared to ignite some time after emergence. Thus the test conditions were not sufficiently representative of those to be found in a shell undergoing set-back on being fired. As a result it was found that the peak pressure levels necessary to cause ignition of RDX/TNT 60/40 Type A were of the order of three times greater than the peak pressure levels typically found in modern guns.

(b) It was a relatively skilled and lengthy process to set up the apparatus before firing. The air gaps between explosive and punches had to be set with a micrometer and a given propellant charge had to be weighed and loaded into the firing chamber. Errors in these operations coupled with variability of the tolerances and the slowness of the operations made it a tedious process to obtain sufficient results for a satisfactory statistical treatment.

The simulator developed by the US Naval Ordnance Laboratory goes a long way towards overcoming the objections of (a) above but it is a relatively expensive device calculated on a per shot basis.

Thus, the basic requirements for any new test equipment are that it should be simple, versatile and capable of producing a large number of results per day. At the same time the explosive test

samples should be subjected to stresses similar to those experienced by shell fillings on firing, but with some overtest facility which would enable statistical comparisions to be made between different explosive compositions.

EXPERIMENTAL

The test section of the Picatinny Arsenal "Set-Back Simulator" was retained as the central feature of the new test equipment but it was turned vertically so that the moveable punch could be driven by the impact of a falling weight rather than by a propellant driven piston.

The problems of sealing the air cavities in contact with the explosive and the accurate reproduction of the cavity dimensions were solved by the use of dished polythene discs as shown in Figure 2. On impact, the discs seal radially against the bore of the cartridge and the end-faces of the explosive pellet. Using these discs no extrusion of explosive has been observed in more than 2000 firings. The polythene discs are made by precision moulding and have a concavity reproducible to ±1.5% in the case of concavities of 0.8 mm and 1.6 mm depth and 1% for concavities of 2.4 mm and greater depth. The combination of vertical test section and dished plastic discs made it a simple affair to introduce various grits into the assembly.

The explosive compositions tested in this apparatus were in the form of cylindrical pellets 12.7 mm long by 12.7 mm in diameter and they are cast, machined or pressed as required. The explosive compositions so far tested are listed in Table 1 together with some of their composition details.

The stress is applied to the moveable punch by means of a 10 kg weight which can be dropped from heights between 0.7 and 5 m onto the assembly.

The experimental procedure adopted was as follows. The components are assembled as in Figure 2 and placed vertically in a holder which supports the bottom punch on a hardened steel anvil, the weight is then raised to the required height and dropped remotely. A positive event is recorded when all the explosive in the test sample is consumed in an explosive reaction. A partial event is recorded when there are signs of an ignition but some sample remains after testing. In the analysis of the results partial events are counted as positive events.

Two types of experimental technique have been employed, dependent upon the method of subsequent statistical treatment of the

results. These are the Run-Down and Bruceton Staircase methods. For the Run-Down experiments twenty successive impacts were conducted at each of about 5 different heights over a range giving zero to more than 50% positive events. Since it would be too time consuming to conduct Run-Down experiments on all samples to be tested, a simple Bruceton Staircase technique was applied using a linear scale of drop-heights 0.1 m apart. At least 50 experiments were conducted in each Bruceton run and the median height with its standard deviation is quoted.

In order to make the results of the experiments more meaningful it was necessary to adopt some reference standard. The standard chosen was RDX/TNT 60/40 Type A pellets using two polythene discs of 1.6 mm concavity. This assemblage was taken as a standard because the explosive is widely used in shell fillings and is, in fact, used in UK Abbot shell some 40,000 of which have been fired at Proof without incident. The implication is that explosives less sensitive to initiation in the Vertical Activator would be safer than RDX/TNT 60/40 Type A to initiation on setback. Explosives more sensitive to initiation in the Vertical Activator are likely to be less safe than RDX/TNT 60/40 and are thus less likely to be considered as contenders for the fillings of ballistically launched projectiles.

RESULTS

A variety of in-service and potential candidate shell filling explosives have been studied in the Vertical Activator. The explosives tested and some of their composition details are listed in Table 1. Table 2 lists the median heights necessary for a 50% probability of an ignition which have been obtained, together with the Figures of Insensitiveness from the UK Rotter Impact Test and the velocities of detonation. It can immediately be seen from Table 2 that the explosives tested cover almost the full range of the apparatus, with median heights from 0.74 m for RDX/Wax/Al 68/12/20 to well over 4 m for RDX/Wax 8 88/12.

The effect on the 50% drop height of changing the concavity of the polythene sealing discs has also been studied. The drop heights were measured for pellets of standard RDX/TNT 60/40 Type A using polythene discs of 0.8 mm, 1.6 mm and 2.4 mm concavity. The results are shown in Table 3. It can be seen from Table 3 that the size of the air cavities has a marked effect on the 50% drop height obtained.

In addition, the effect on the 50% drop height of the inclusion of quantities of grit into the air cavities has been examined. The drop heights were determined again for pellets of standard RDX/TNT 60/40 Type A using discs of 0.8 mm concavity and including 25 mg of

cast iron or corundum grit. The results of this study and the profound effect of grits can be seen in Table 4.

DISCUSSION

The choice of explosive filling for a shell is a fine balance between lethality requirement, represented in Table 2 by the detonation velocities, and safety criteria, represented by the set-back sensitiveness of the charge and the powder impact sensitiveness. Thus, although tetryl apparently has a low sensitiveness to set-back and a high velocity of detonation, its powder sensitiveness makes it relatively unsafe for large-scale production filling compared with some of the other compositions studied.

Again, it appears that TNT is as sensitive to set-back stresses as RDX/TNT despite its lower powder sensitiveness. This is an important consideration in shell filling design since there appears to be little or no extra margin of safety to be gained in firing relatively low performance TNT-filled shell as opposed to similar RDX/TNT-filled shell. However, recent RARDE work examining the phenomenon of explosiveness has shown that, under conditions of moderate confinement, TNT burns at only about one-half the velocity of RDX/TNT. This means that it is probable that TNT filled shell would be expected to be involved in more in-flight rather than in-bore premat'res whereas the opposite would be true for RDX/TNT-filled shell.

Table 2 confirms the suspected low set-back sensitiveness of RDX/Wax and HMX/Wax compositions, even 95/5 Explosive/Wax compositions being significantly less sensitive than RDX/TNT. This forms the basis for the view that pre-pressed charges of these compositions are worthy of consideration for HEAT shell especially since those with explosive contents in excess of about 90% perform better than RDX/TNT 60/40 in shaped charges.

Table 4 shows that the grit sensitisation of RDX/TNT is very marked over the entire range of particle sizes for both cast iron and corundum. Moreover, this sensitisation is over and above that due to what would be regarded as a gross defect in a shell, namely a 0.8 mm deep sealable cavity. The mechanism of grit sensitisation in the presence of a compressible cavity is probably a combination of intrusion and adiabatic heating. The largest particles will be heated the least but intrude to the greatest extent, whereas the smallest particles would be heated most but intrude the least. The middle fraction of both types of grit has the greatest sensitising effect, probably as a result of the combination of these two effects.

CONCLUSIONS

The Vertical Activator has shown itself to be a versatile tool in the study of the sensitiveness of explosives to stimuli similar to those experienced by munitions subjected to gun launch conditions. The instrument is simple, rapid and cheap to use and relatively straight-forward to instrument, although little instrumentation work has been carried out to date.

The Activator has been extremely useful in the study of premature initiations and has demonstrated the extreme hazard of gritty inclusions in shell cavities. This conclusion has led to an improvement in the inspection techniques for shell. It has been very useful in the assessment of potential new shell fillings.

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Table 1

Explosive compositions

Explosive Compositions	RDX	TNT	HMX	Al	Beeswax	Wax 6	Wax 8	Polyurethane	Terylene fibre	Tetryl
RDX/TNT 60/40 Type A	60	40			+1					
TNT		100								
Torpex 4D	20	55		25						
RDX/Pu 88/12	88							12		
RDX/Wax/Al	68			20		12				
RDX/Wax/Al + Terylene fibre	68			20		12			+1	
EDC 1A	4	29	66		1					
RDX/Wax 8 88/12	88						12			
RDX/Wax 8 91/9	91						9			
RDX/Wax 8 93/7	93						7			
RDX/Wax 8 95/5 (smeared)	95						5			
HMX/Wax 95/5 (smeared)	95						5			
Tetryl										100

Table 2

Comparison of the set-back sensitiveness of different explosives (2 X 1.6 mm concavity discs)

Explosive	Loading Method	Median height (m)	F of I (RDX = 80)	Velocity of Dtonation (ms^{-1})
RDX/TNT 60/40 Type A	Melt pour	2.16	130	7700
TNT	Melt pour	2.50	160	6930
Torpex 4D	Melt pour	3.50	130	6800
RDX/Pu 88/12	Pressed	3.73	90	8100
RDX/Wax/Al 68/12/20	Hand stemmed	0.74	140	6800
RDX/Wax/Al 68/12/20 +5% Terylene fibre	Hand stemmed	1.34	140	6800
EDC1A	Melt pour	2.12	80	8400
RDX/Wax 8 88/12	Pressed	4.61	140	7700
RDX/Wax 8 91/9	Pressed	3.51	130	7700
RDX/Wax 8 93/7	Pressed	3.14	120	8200
RDX/Wax 8 95/5 (smeared)	Pressed	2.91	110	8300
HMX/Wax 8 95/5 (smeared)	Pressed	3.04	95	8700
Tetryl	Pressed	4.20	90	7850

Table 3

Effect of the concavity of the polythene discs

Explosive	Disc concavity (mm)	Median height (m)	Standard deviation (m)
RDX/TNT 60/40 Type A	0.8	2.45	0.25
	1.6	2.16	0.22
	2.4	1.70	0.23

Table 4

The effect of grit on set-back sensitiveness

Explosive	Grit Type	Particle size mm	Median height (m)	Standard deviation (m)
RDX/TNT 60/40 Type A	None	-	2.45	0.25
	Cast iron	1-0.75	1.45	0.24
		1-0.625	1.26	0.10
		0.75-0.5	1.01	0.14
		0.625-0.375	1.14	0.05
		0.5-0.25	1.01	0.17
		0.375-0.25	1.63	0.27
	Corundum	1-0.625	1.05	0.19
		0.625-0.375	0.93	0.10
		0.375-0.25	1.66	0.13

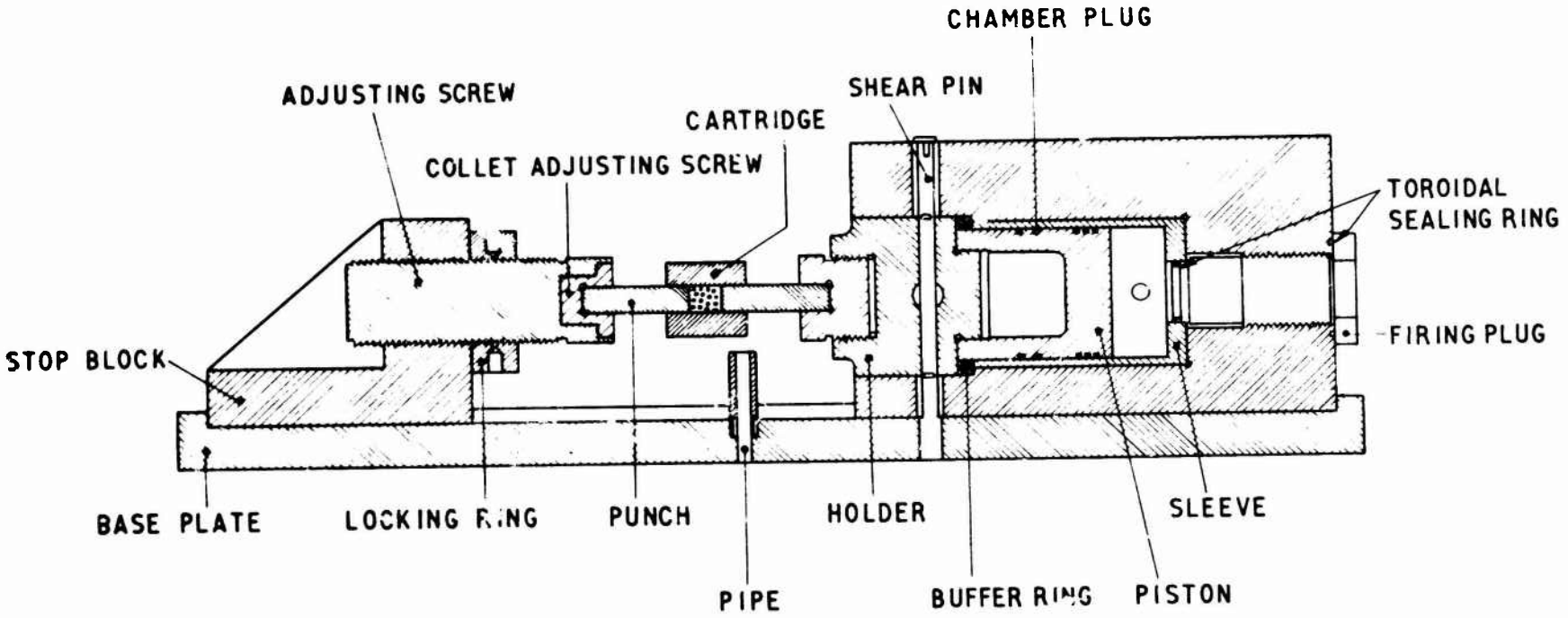


Fig 1 UK modification to Picatinny Arsenal activator

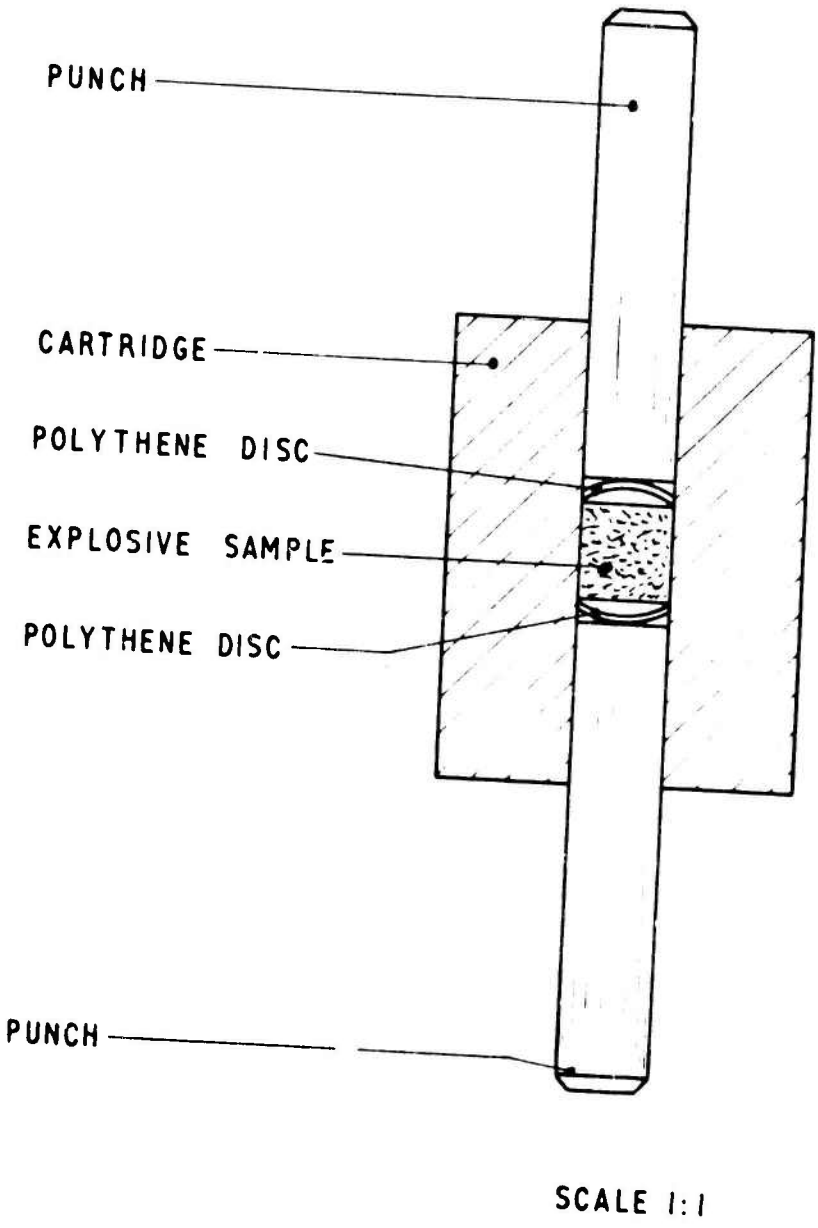


Fig 2 RARDE vertical activator test

METHOD USED TO ASSESS SENSITIVITY TO DDT OF SHELL FILLS

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ABSTRACT

The purpose of this paper is to describe a method of quantitatively evaluating the tendency of explosives and propellants to undergo a deflagration to detonation transition (DDT). The method uses burning 94/6 RDX/wax as an auxiliary gas loader to produce DDT in materials which are too slow burning to show transition under self gas loading. No attempt has yet been made to develop this method into a standardized test. Instead we used the apparatus and instrumentation from a continuing long range study of DDT[1,2] to obtain data needed for sensitivity ratings.

Earlier studies have shown that the first necessary condition for DDT is a rapid pressure buildup, generally in the ignition area of our setup. The RDX/wax mixture, with its rapid burning production of gases, satisfies this condition. It can be used at a fixed density to determine the critical length ($\ell_g{}^c$) just necessary to cause transition in each material. In other cases, it can be used at a fixed density and a fixed length. Then the predetonation column length (ℓ') or a relative time to detonation is used as a sensitivity index. This application, however, is valid only for comparisons at the same charge permeability whereas ($\ell_g{}^c$), more tedious to measure, has validity as a general index.

INTRODUCTION

It is generally recognized that secondary explosives as well as primaries can undergo a deflagration to detonation transition (DDT). Such a transition from the burning to the detonating mode, when it occurs in the high explosive (HE) used as a shell fill, can cause an in-bore premature during gun firing. Because DDT under such conditions can cause a great deal of damage, we were asked to devise a method of assessing the tendency of HE to undergo such a transition.

It is far from a simple problem to obtain any sensitivity rating. That for DDT is particularly complex since the phenomena involved range from simple combustion all the way to a shock to detonation transition (SDT) which must terminate any successful DDT. Moreover, any quantitative rating requires a positive result; failures cannot be placed on a rating scale. Finally, all results will inevitably be tied to the conditions of the experiment; those conditions may or (more generally) may not approximate the conditions of use.

There are many reasonable ways in which to attempt to find the desired sensitivity rating. Because we were already studying the mechanism of DDT, we incorporated the sensitivity problem into our studies. In other words, we used the same apparatus, and applied information available from previous work as the most expeditious way to obtain a method of rating sensitivity. To obtain positive results from insensitive materials, an auxiliary gas loader (94/6 RDX/wax) in a rapid burning but nondetonating column is inserted between the igniter and the test explosive. The rapid pressure buildup that results, coupled with ignition and subsequent burning of the explosive, is sufficient to induce DDT[1] in explosives such as porous TNT, Explosive D, and cast Composition B which do not show the transition in our apparatus under self-loading. It is the purpose of this paper to report sensitivity ratings obtained in this way, i.e. by varying the ignition system with an auxiliary gas loader.

EXPERIMENTAL ARRANGEMENT AND PROCEDURE

The experimental setup and procedures have been described in detail elsewhere[2]. In brief, a seamless steel tube (16.3 mm ID, 50.9 mm OD) with heavy end closures was used. The length of the B/KNO_3 ignitor column was 6.3 mm; the length of the explosive column was 295.4 mm. In the present work, the gas loader is inserted between the ignitor and the test explosive; the explosive column length is decreased accordingly. See Figure 1.

Explosives were taken from commercial lots and satisfy the relevant military specifications. The same lots as those of the previous work were used; the weight mean particle sizes were ammonium picrate (285μ), TNT (325μ), RDX (200μ) and Tetryl (470 & 160μ). The carnauba wax (125μ) and the blending procedures were also those used previously.

The auxiliary gas loader used throughout is a mechanical mix of 94/6 RDX/wax. It will be referred to as the loader.

The DDT tube is instrumented with ionization probes and strain gages to monitor ionization fronts and internal pressure, respectively.

EXPERIMENTAL RESULTS AND DISCUSSION

Gas Loader

The basic concept of these experiments is that the gas loader chosen reacts only in the burning mode, i.e., does not itself build up to either a shock or a full scale detonation capable of initiating the

test material. For this reason the loader has been examined for its behavior under self-loading. Over the range of 70 to 97% TMD, the predetonation column length ℓ varied from a minimum of 92 mm to a maximum of 135 mm[3]. In general, the loader length used ℓ_g was 55% ℓ or less.

Most of our experiments have been designed for an approximate permeability match between loader and test material. In general this also means an approximate match of loading densities and impedance as well.

Experiments at 70% TMD

Each of the shots reported were fully instrumented. Hence for each there is the usual set of space-time and strain-time records. However, a third of these records have been reported[2], and the rest will be reported shortly in a WOLTR. Since the main interest here is not on mechanism, only one space-time record will be given; it will be used to illustrate the parameters that can be measured in each shot. (Previous work[1] has already indicated that the mechanism of DDT is the same whether a loader is used or not.)

Figure 2 is the space-time plot for Shot 409: 70% TMD Explosive D with 19.6 mm 70% TMD loader. It shows the convective flame front (0.39 mm/μs), the postconvective (PC) compression front (1.1 mm/μs), and the detonation front (5.7 mm/μs). The parameters that can be measured, in addition to front positions and velocities, are predetonation column length, $\ell' = \ell - \ell_g$ where ℓ and ℓ_g are both measured from the igniter/loader interface, and various time intervals. Thus, Δt_D is relative time to detonation from ionization pin response at pin 1 or 2. Similarly Δt_P is relative time to formation of the PC wave at the same pin location. Finally

$$\Delta t_E = \Delta t_D - \Delta t_P$$

would represent the relative time to detonation after the PC wave had formed at the particular pin location chosen.

Table 1 contains the data collected from four different explosives at 70% TMD subjected to the same length of auxiliary gas loader ($\ell_g \sim 20$ mm, 70% TMD). It is quite evident from the tabulation that the predetonation column length (ℓ') varies in the opposite direction

from the relative times Δt_D and Δt_p. On the other hand, the correlation between ℓ' and Δt_E (time to detonation relative to the formation of the PC wave at the first pin) appears good. From Figure 3 either ℓ' or Δt_E will give the same rating for these 70% TMD charges.

Experiments at 88% TMD

Table 2 contains the data collected from five different explosives at 88% TMD subjected to the same length of auxiliary gas loader (ℓ_g = 19.1 mm, 88% TMD). In contrast to the more porous charges, ℓ' and Δt_D exhibit the same trend. This occurs because the compacted charges show either no convective front or one that is rapidly replaced by a compressive front. (See, for example, Figure 7 of reference 1). Thus $\Delta t_D \sim \Delta t_E$ here. Nevertheless, Δt_E still shows a better correlation with ℓ'; the latter is illustrated in Figure 4. As in the previous section, either ℓ' or Δt_E will give the same rating for these 88% TMD charges. Both sets of results confirm that, of the porous HE tested, Explosive D is the least sensitive to DDT and TNT is the next best shell fill candidate in this respect. Nevertheless we have ratings for sensitivity to DDT at two compactions on two different scales. Of course the loader length and density must be specified with the rating number, just as the P-t profile must be specified with the corresponding run length or time interval in SDT.

We could have avoided using either ℓ' or Δt_E by determining the critical loader length, ℓ_g^{cl} for each charge. The rating would then be given by the critical values, each of which would require two or more shots for a determination. However, this would not suffice to compare charges of two different compactions. To do this we must abandon the experimental design of the same compaction of loader and test explosive. Instead, the higher compaction loader is used for both charges. (This is based on the assumption that sensitivity to DDT decreases with decreasing permeability and active surface area as it does for Explosive D[1]). Then the critical ℓ_g values should serve to rate charges of various compactions as long as the range in sensitivity is not too great.

Cast Explosives

The U.S. Navy still uses pressed shell fills, but other U.S. services and other countries prefer cast fills. With the more general availability of plastic bonded materials, the Navy too is considering castable fills. Hence the present procedure was modified to examine cast charges.

Since loader and test material cannot both be cast into the tube to form known compositions on either side of a planar interface, it was decided to use high density (ca 95% TMD) pressed 94/6 RDX/wax as the loader. The test explosive is cast into the tube with a metal spacer in the gas loader position. When the test material has hardened and the tube has been conditioned at 25°, the loader can be inserted into the cavity provided by the spacer. The isostatically pressed loader is machined into a cylinder of the desired size (0.636 in. dia.). The curved surface of the cylinder is then covered with a thin layer of an uncured polyurethane (PU) mixture. The loader cylinder is then "slip-fit" into the metal tube (ID 0.641 in.) with care to avoid trapping any PU at the loader/explosive interface; PU at the ignitor end of the cylinder is avoided by glueing the gas loader and ignitor together before applying the PU. Cure time at room temperature for this PU is 24 hours. After that interval, the annular space between the gas loader and the metal tube is filled with solid; this eliminates any possible "flash-down" from the ignitor toward the test explosive.

Preliminary tests showed that our usual column length of 295 mm (loader plus test HE) was inadequate to produce a transition in cast Comp B (60/40/1, RDX/TNT/wax). Consequently, a column length of 410 mm has been used for most of the shots on cast HE. Even so, Comp B is the least sensitive cast HE on this sensitivity scale.

The positive results we have obtained are listed in Table 3 and sketched in Figure 5. It is quite evident that in order of decreasing sensitivity the castings are pentolite, cyclotol, and Comp B. A quantitative ordering can be obtained by using a 50 or a 60 mm loader length and measuring ℓ', or by determining ℓ_g^c in each case. Negative results were obtained with a 60 mm loader on cast TNT. Evidently the experiment must be further modified to obtain a scale covering more of the less sensitive castings.

However, the present results make it very clear that good castings will be far less sensitive to DDT than pressed charges. Thus pressed TNT (88% TMD) showed a transition when loaded with 19.1 mm 88% TMD loader whereas cast TNT failed to show a transition with 60 mm 95% TMD loader (i.e., 3.4 times the mass of the 88% TMD loader). Moreover, cast pentolite (50/50 PETN/TNT), a relatively shock sensitive HE, required 40 mm 95% TMD loader to produce a transition at the same predetonation column length exhibited by 88% TMD 91/9 RDX/Wax loaded by 19.1 mm 88% TMD loader (i.e., only 44% of the mass of the 95% TMD loader). Since cast pentolite is more shock sensitive than 88% TMD 91/9 RDX/Wax, there must be another factor that makes it less sensitive to DDT. An obvious factor differentiating cast and pressed HE is the available reactive

surface area. Hence with all other factors the same, pressed charges would be expected to exhibit DDT more easily than cast because they have more internal burning surface and thus produce more gas products and greater pressure buildup in less time.

These results do not guarantee that a shell filled with any cast HE will be less sensitive than a press filled charge. The sensitivity to DDT will be determined in large part by the surface available for burning; that can be minimized in a casting only by avoiding cracks and annular spacings resulting from large volume changes during cooling or setting of the charge. From the present results we recommend that the ideal shell loading (ideal in that it is most resistant to DDT) is a cast material of negligible volume change on solidification and sufficiently rubbery to avoid cracking under rough handling; its explosive components should, of course, be relatively insensitive.

General Control Problems

The transitional portions of the DDT process are neither equilibrium nor steady-state behaviors; they are therefore difficult to reproduce. Moreover, the physical factors (e.g. initial particle size, permeability, etc.) have a very large effect on the results. Consequently, we X-ray each charge before instrumenting it. To be sure, this is not an extremely sensitive test, but we can be sure that if it detects cracks, density gradients or other heterogeneities, the charge should not be fired.

From past experience with pressed charges, we estimate the scatter of the data in any given investigation of trends to be of the order of magnitude of $\pm$10%. This is also the size suggested by the apparent reversals in sensitivity of 88% TMD tetryl vs 88% TMD Comp A, according to whether ℓ' or Δt_E is used for rating. The difference between these two HE at 88% TMD is considered experimentally insignificant.

We have not yet run enough tests on cast HE to estimate the scatter, but the large role played by the physical form of the charge is still very evident. Thus in an attempt to increase the range to include less sensitive materials, we tried increasing the charge diameter (ID/OD was kept constant). But this increased the solidification time of the charge which, of course, affected its crystal size. We believe this is why ℓ' for cyclotol and Comp B increased with larger tube diameter and the same ℓ_g.

It should be emphasized again that the present results are reflecting the present experiment. It is carried out under very high confinement and charge support. Many uses of both explosives and propellants are under little or no confinement and with little physical support. In fact, some damaging effects result from a charge breakup which is largely avoided in the present experiment. Hence the present results offer guidance to sensitivity to DDT, but their rating is not necessarily that which will be found in the application.

Finally, any test development of this method should explore the effect of varying test conditions: length, diameter, finish, and confinement (ID/OD) of tube. In addition, an investigation should be made of variation in charge preparation: (1) pressing by increments into the tube vs isostatic pressing, machining and potting of the charge and (2) change in rate of cooling of cast charges with tube diameter.

SUMMARY AND CONCLUSIONS

Sensitivity of HE to DDT can be rated in the present apparatus by use of an auxiliary gas loader. Several ways of obtaining a quantitative rating are pointed out, and such ratings are presented for pressed charges at 70% and 88% TMD. Work on evaluating cast charges is still preliminary, but results are sufficient to indicate that castings are, in general, less sensitive to DDT than pressed charges.

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Table 1
Experimental Results at 70% TMD with 20 mm Loader

	Test Material[a]			Gas Loader				Relative Times, μs[b]		
Shot No.	Mat.	ρ_o g/cc	%TMD	ρ_o g/cc	%TMD	ℓ_g(mm)	ℓ'(mm)	Δt_D	Δt_p	Δt_E
1011	RDX	1.244	68.9	1.214	70.6	19.8	80	201	148	53
1009	Tet.	1.215	70.0	1.215	70.6	20.1	110	209	120	89
410	TNT	1.214	73.4	1.208	70.2	19.7	127	176	81	95
409	D	1.210	70.3	1.212	70.5	19.6	153	167	48	119

a Tet. is tetryl with nominal average particle size of 160μ. It is the production tetryl (470μ) which has been ball milled for one hour. D is Explosive D or ammonium picrate.

b Δt_D is relative time to detonation from discharge of first probe. That probe was at x = 28.7 mm except for Shot 1011 where it was at 28.4 mm.
Δt_p is relative time of formation of PC front at first probe.
$\Delta t_E = \Delta t_D - \Delta t_p$ = time interval, formation of PC front at first probe to onset of detonation.

Table 2
Experimental Results at 88% TMD with 19 mm Loader

	Test Material[a]			Gas Loader				Relative Times (μs)[b]	
Shot No.	Mat.	ρ_o g/cc	%TMD	ρ_o g/cc	%TMD	ℓ_g (mm)	ℓ' (mm)	Δt_D	Δt_E
714	Tet.	1.543	87.6	1.515	88.1	19.1	66	52.5	46
701	A	1.477	87.9	1.515	88.1	19.1	76	54.0	40
510	TNT	1.467	88.7	1.516	88.1	19.1	101	61.0	59.0
716	95/5	1.398	87.5	1.515	88.1	19.1	116	87.5	73.0[c]
608	D	1.513	88.0	1.513	88.0	19.1	226	111.5	119

a Tet. is production tetryl (470μ); A is a mechanical mix of 91/9 RDX/wax; 95/5 is a mechanical mix of TNT/wax; and D is Explosive D.

b Δt_D is relative time to detonation from discharge of first probe at x ≃ 29 mm in Shots 510 and 608; x ≃ 23.6-23.7 in remainder. Δt_E is the time interval, formation of PC front at the loader/explosive interface to onset of detonation. This requires a small extrapolation.

c In this shot, the SG records were lost. The steeper part of the IP curve intersects the interface at 68μs from onset of detonation. This interval has been increased by 5μs to allow for the leading compressive front in charges at this compaction.

Table 3
Rating of Cast HE by Gas Loading With 95% TMD 94/6 RDX/Wax*

Shot No.	Explosive (Cast)	ℓ_g (mm)	ℓ' (mm)
908	Pentolite 50/50**	40	79
1003	Cyclotol 75/25**	40	244
1415	Cyclotol 75/25	50	212
1409	Cyclotol 75/25	60	169
1206	Composition B	60	253
1309	Composition B	50	311

* 410 mm Charges
**295 mm Charges

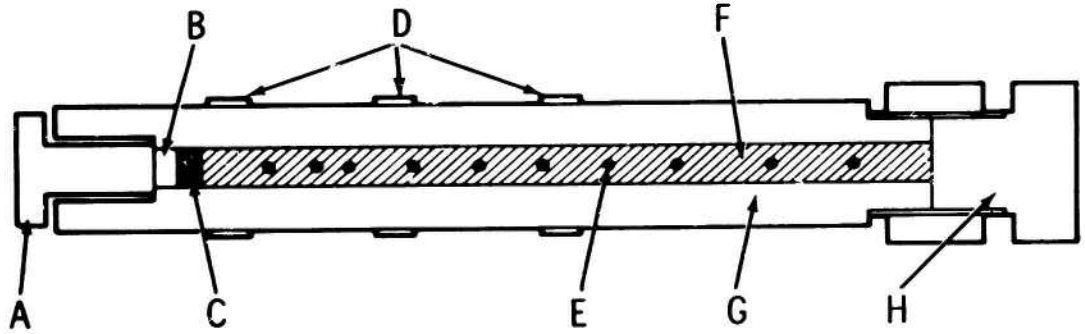


FIG. 1 CROSS SECTION OF DDT TUBE

(A - IGNITOR BOLT; B - IGNITOR; C - GAS LOADER COLUMN; D - STRAIN GAGES; E - IONIZATION PROBE LOCATION; F - EXPLOSIVE CHARGE; G - TUBE; H - BOTTOM CLOSURE. INNER DIAMETER = 16.3 mm, OUTER DIAMETER = 50.8 mm, DISTANCE FROM IGNITOR/GAS LOADER INTERFACE TO BOTTOM CLOSURE = 295.4 mm.)

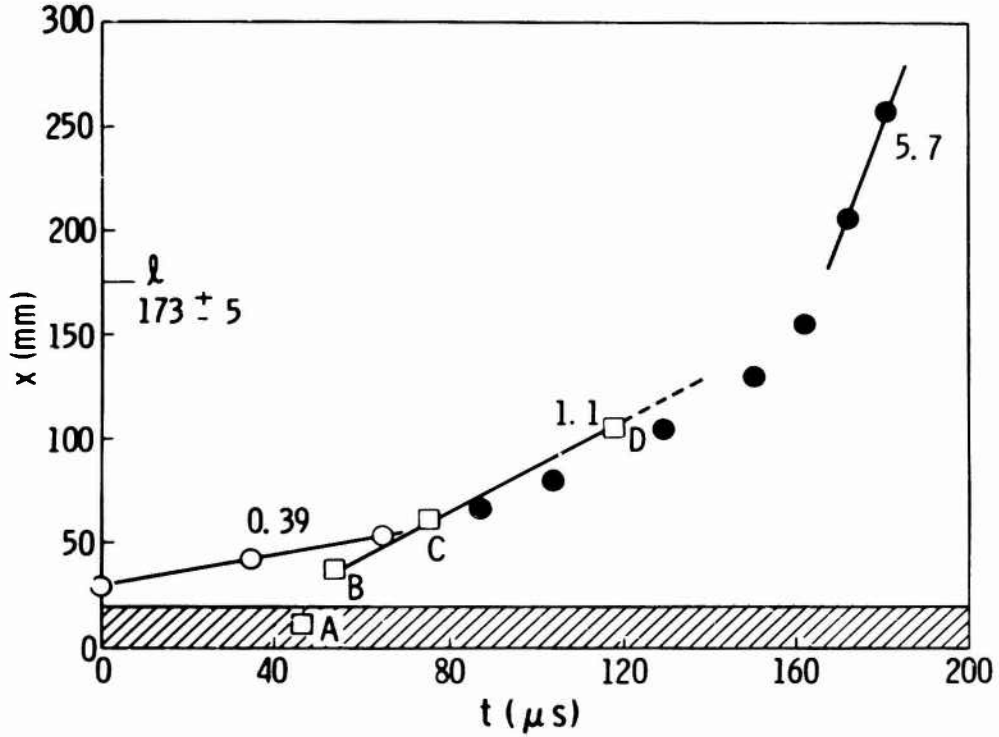


FIG. 2 EXPLOSIVE D WITH 19.6 mm LOADER, BOTH AT 70% TMD, SHOT 409.

SPACE-TIME PLOT (IONIZATION PROBES: ○ CUSTOM-MADE, ● COMMERCIAL. CROSS-HATCH SHOWS LOADER. STRAIN GAGE EXCURSION TIME: □. NUMBERS ON CURVES ARE VELOCITIES IN mm/μs)

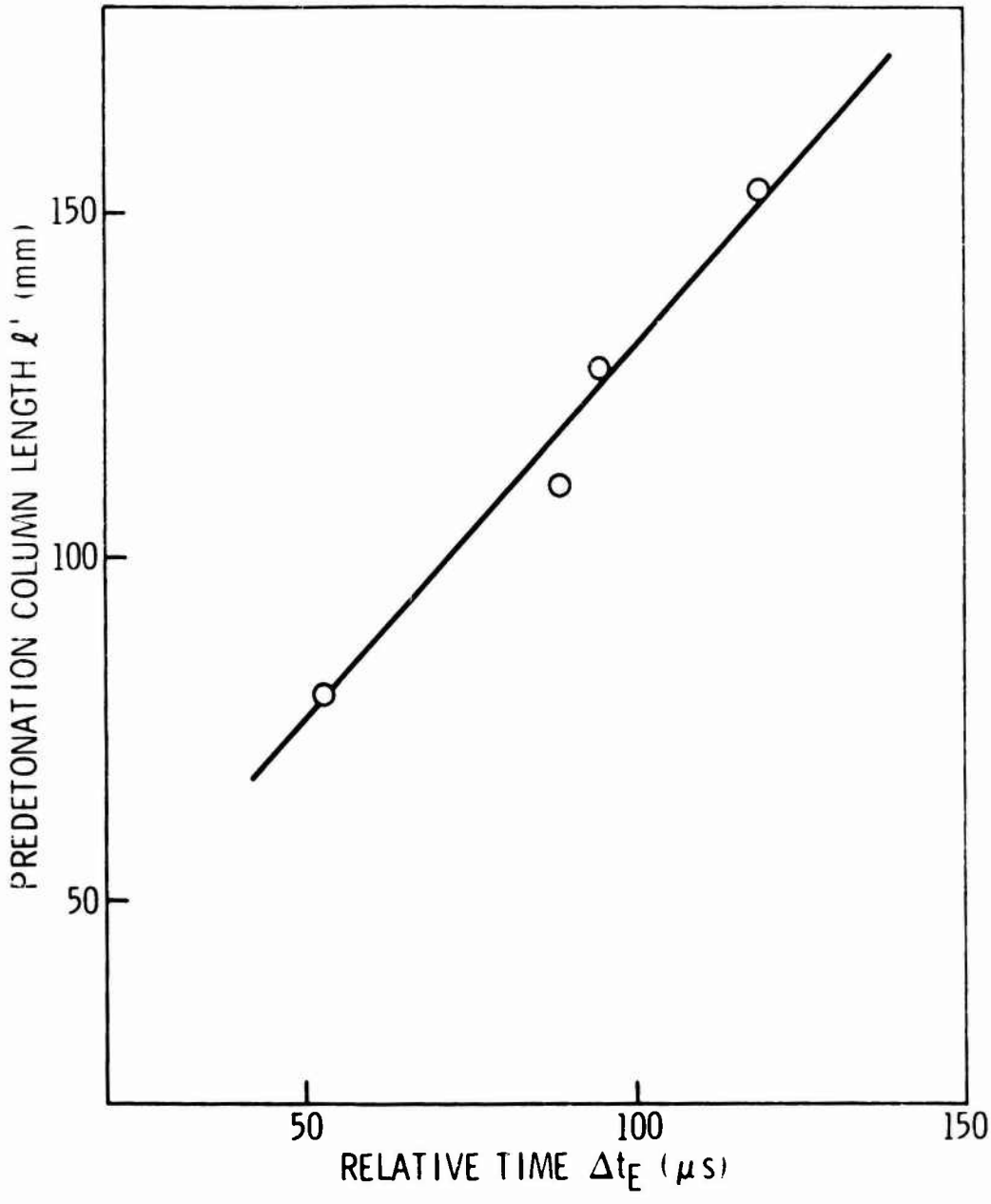


FIG. 3 PREDETONATION COLUMN LENGTH VS RELATIVE TIME Δt_E FOR 20mm LOADER AT 70% TMD

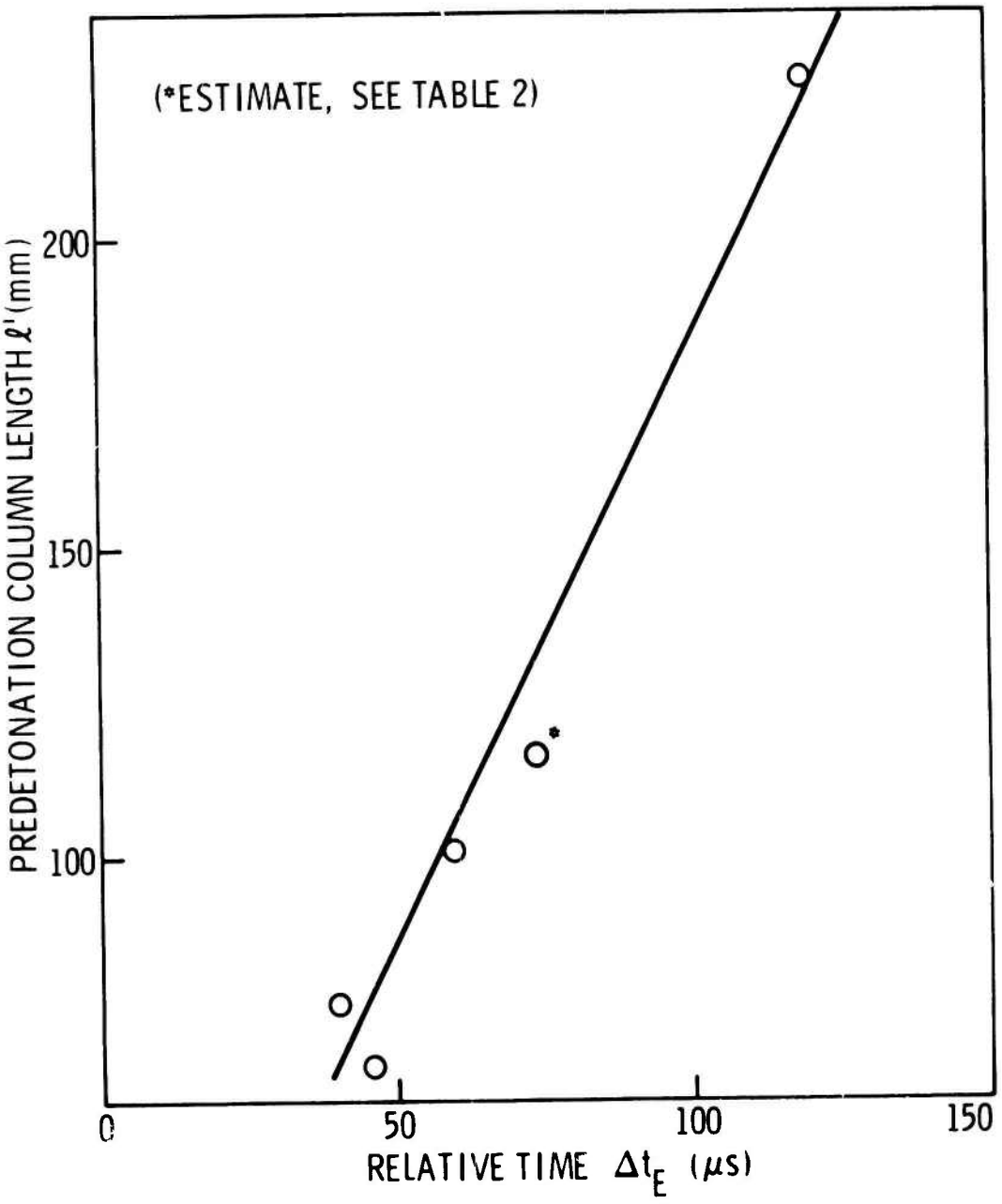


FIG. 4 PREDETONATION COLUMN LENGTH VS RELATIVE TIME Δt_E FOR 19 mm LOADER AT 88% TMD

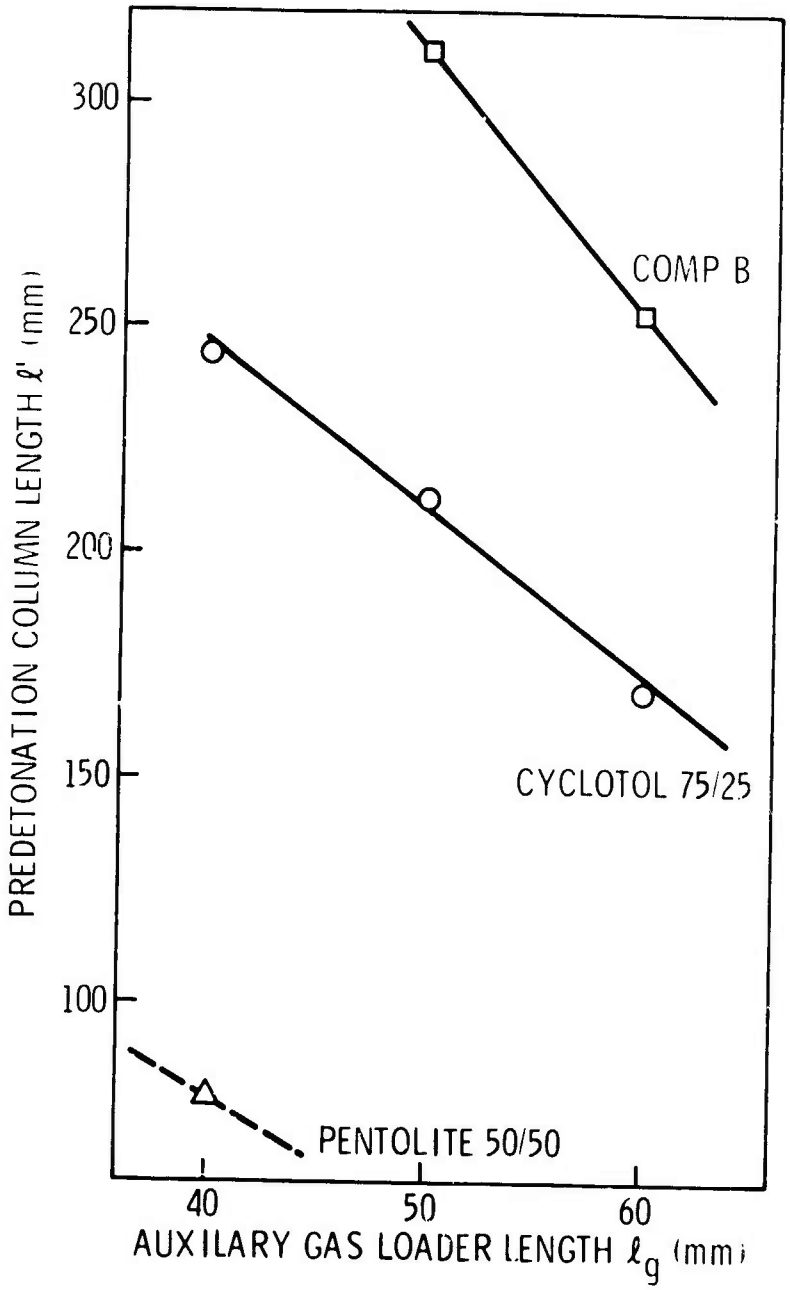


FIG. 5 RELATIVE SENSITIVITY TO DDT OF THREE CAST HE

A NEW TECHNIQUE FOR DETERMINING THE SHOCK INITIATION SENSITIVITY OF EXPLOSIVES*

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Abstract

A new technique for determining the shock initiation sensitivity of explosives is described. It involves a flyer plate impinging upon the test explosive to induce initiation of detonation. An electrically exploded foil propels the flyer plate, which is a thin disk of polyimide (Kapton) 1 mm in diameter; the charging voltage applied to the capacitor discharge fireset is used to preselect the desired velocity of the flyer plate. Its impact on the explosive introduces a rectangular pressure pulse, P, whose amplitude depends on the velocity of the flyer at impact and the shock properties of the flyer and the explosive. The duration of the pulse, τ, depends upon flyer thickness. The test objective is to establish the critical pressure at a given duration which results in a 50% probability of detonating the explosive. The data, presented in a log P-log τ plot, generate a demarcation line between detonation and nondetonation regions.

In our experiments the impact pressure was in the range of 1 to 10 GPa and the duration from 0.039 to 0.070 μs. We evaluated pentaerythritol tetranitrate (PETN) and three forms of hexanitrostilbene (HNS). For both materials the variation of the threshold stimulus with initial compaction density was measured. Since a single flyer thickness was used in all but one of the experiments, the data for each explosive give only a single value (P, τ) on the demarcation line which separates detonation from nondetonation. Additional tests with other flyer thicknesses are needed to define this line over a broad range of τ.

This new technique employs conventional laboratory equipment and a simple, inexpensive test device. The initiation stimulus may be expressed in a clearly defined form which is directly applicable to safety or performance computations.

Introduction

The initiation sensitivity of explosives has been measured by many methods. Some of the more common ones are included in Table 1. These and similar tests provide useful information to the experimenter and permit the ranking of explosives according to their relative sensitivity values. One serious limitation of these tests is that the input stimulus delivered to the explosive has not been quantified. Rank-order lists generated by one method are often different from rank-order lists generated by another method. A more complete characterization of the input stimulus might explain some of these anomalies or sensitivity reversals. Two such cases have been analyzed (1) which confirm this need for an accurate definition of the input stimulus.

The impact of a thin flyer plate on an explosive provides a reproducible means for applying a pressure whose intensity, P, and duration, τ, are independently controlled. Walker and Wasley (2) have shown that an independent assessment of P and τ is essential to define the threshold initiation sensitivity based on the critical energy concept for explosives such as PBX-9404 and TNT. DeLongueville showed that some explosives do not follow the cirtical energy concept but can be characterized by a critical curve in the pressure-time plane (1).

It is the intent of this report to describe a test method which utilizes a simple, flyer-plate impact system to provide a fully characterized input stimulus for initiation sensitivity testing. This device can be used to map out the critical lines or curves which describe sensitivity to shock for explosive materials.

Experimental Technique

Test Device

A small test device, identified as the TC-817, was used to provide the input shock stimulus. This device, which was originally conceived by Stroud (3), is shown in Fig. 1 along with the acceptor pellet. The firing set was a capacitor discharge unit which, when discharged, applied a current pulse through the metal bridge-foil; this vaporized the foil, propelling the Kapton flyer to the desired impact velocity. The velocity determined the impact pressure intensity and the flyer thickness determined the pressure duration. Since the shock impedance

of the flyer was less than that of the explosive, a well-controlled, single-step, rectangular pulse was introduced into the test explosive.

Two methods were used to calibrate the flyer velocity as a function of electrical input. The streak camera method is illustrated in Fig. 2. The camera was a Beckman and Whitely Model 189 which provided a timing accuracy of ± 1/4% and a total measurement accuracy over short flight distances of approximately ± 5%.

During a test on the TC-817, light is produced when the copper foil bursts. Since Kapton is transparent, light can travel through the flyer during the free-flight period. Hence, light is transmitted through the lucite window and is observed with the camera. When the flyer impacts the lucite, the stress produces changes in the optical properties of the lucite indicating the time of impact of the flyer on the window. Using onset of light from the foil as the start time, total flight time can be determined over a preselected interval. Therefore, average flyer velocity can be computed. The streak camera records showed that the center of the flyer impacted the target first (by as much as 0.05 μs).

A second and more precise method, VISAR,* was used to measure the entire velocity history. Different histories were measured as a function of charging voltage. From these data velocity versus displacement was computed, and it was determined that a flight distance of 0.38 mm was an appropriate standoff distance for the flyer to reach 90% or more of terminal velocity.

Figure 3 shows the flyer velocity for this standoff distance versus charging voltage. The streak camera data are also given for comparison but were not used in subsequent calculations. The data in Fig. 3 apply only to a specific firing set whose lumped circuit characteristics match those given (C = 5.32 μF, L = 180 nH, R = 88 mΩ). The circuit impedance plays a significant role in establishing flyer velocity.

A more fundamental plot (5) of the data, flyer velocity versus burst-current density (burst current/cross section of foil), is given in Fig. 4. This presentation is independent of the circuit characteristics. Note that the fit is linear when the burst-current density is greater than 400 GA/m^2. The nonlinearity below 400 GA/m^2 probably results from

*Acronym for Velocity Interferometer System for Any Reflector; operational details in Ref. 4.

the influence of flyer shear properties and other edge effects. Since velocity measurements by VISAR are accurate within ± 1% and burst-current density measurements within ± 2%, system accuracy within ± 2.5% is reasonable for the data in Fig. 4.

A charging voltage of about 600 V (corresponding to a burst-current density of 180 GA/m^2) represented the minimum electrical input for which any flyer velocity was achieved; at less than 600 V the flyer was perturbed by the electrical discharge and showed some bulging, but did not shear out and achieve free flight.

Test Procedure

The following step-by-step procedure was used to conduct an initiation sensitivity test on a typical explosive.

1. The group of test devices were assembled per Fig. 5.

2. The charging voltage was preselected to provide the desired flyer velocity (e.g., 2000 volts for 2.40 mm/μs).

3. For each shot the current through the bridge-foil and the voltage across the foil were recorded on oscilloscope traces (see Fig. 6). Burst current was that value in time at which the voltage peak occurred. Explosive response, i.e., detonation or nondetonation, was noted by measuring the time from flyer impact to shock output and comparing this value with that calculated for steady detonation. Rough equivalency of timing indicated detonation. Dent block response was also noted. Lack of an audible "bang" supported by lack of powder consumption were obvious indications of nondetonation.

4. An "up-down" method, in which the charging voltage was adjusted upward after a nondetonation and downward after a detonation, was used to determine the threshold voltage. Threshold voltage is that value of charging voltage on the firing set which, when discharged, results in a flyer velocity sufficient to induce a 50% probability of initiation to detonation. In these early experiments, only five to nine samples were expended per test; a more rigorous application of the Bruceton technique (6) with a larger sample size would improve the statistical accuracy of the data.

5. The burst current density was determined at the threshold voltage and the corresponding flyer velocity, v_f, was taken from Fig. 4.

6. Shock pressure, P, at the explosive surface was determined graphically per Fig. 7 using v_f and the Hugoniot data on the unreacted explosives and Kapton (Appendix A); pressure duration, τ, was computed as illustrated.

Test Results

Shock sensitivity data for several explosive types are contained in Table II; these include three different forms of HNS and one form of PETN along with initial density variations for each of the two kinds of explosives. The data are also presented graphically in the log P-log τ plots of Figs. 8 and 9.

The demarcation line separating detonation from nondetonation for PETN is shown in Fig. 8. The slope of the line was shown as -1/2 based on some unpublished data. A sharp dependence on initial density is clearly shown. Low density PETN is relatively shock sensitive and is not much different from the single crystals of β-lead azide reported on by Chaudhri (7). That datum is included for comparison in Fig. 8. This does not imply that the present usage of PETN is hazardous, but it should encourage caution in applications where shock environments might provide sufficient stimuli. Of course shock is only one of several hazard environments, including electrostatic fields, which affect the selection of an explosive.

HNS data are given in Fig. 9. HNS-II has the largest particle size (150 μm, mean length); HNS-I and HNS-SF are fine-particle-size materials (35 and 7 μm, respectively) and HNS-SF is supposed to be purer than HNS-I. The data show that HNS-II is less sensitive than either of the other two forms; no investigation was instituted to correlate different performance with specific chemical or physical properties, although particle size probably has some effect.

The role of original density upon sensitivity is illustrated for HNS-SF; the trend toward increased sensitivity, as density was decreased, duplicated the results obtained for PETN.

An additional datum for HNS-SF at density of 1.50 Mg/m^3 was obtained with a flyer whose thickness was 0.127 mm, providing a τ of 0.070 microseconds. The demarcation line separating detonation from nondetonation was assumed to be a straight line connecting the two points; these data indicate the slope of the line to be approximately -1/4, considerably different from that for PETN. The slope of the demarcation line is believed to be a significant sensitivity parameter, but experimental verification is needed.

The "excess transit time" data of Table II indicate that all samples initiated promptly.

On each experiment where the flyer velocity was just below the threshold for initiation, post-mortem examination revealed a cavity in the explosive sample. Generally there was evidence of melting based on the glassy appearance of the HE surface.

A measure of the precision or repeatability, of this test technique is illustrated by the plot of Fig. 10. The constancy of performance is shown for a 2-year time span for HNS-SF when gaged both by burst-current density at initiation threshold and by impact pressure at initiation threshold. It is of interest that the mean pressure at threshold for the 2-year period was 6.8 ± 0.1 GPa.

Conclusions and Recommendations

A new technique, employing conventional laboratory equipment and a simple test device, has been used to provide shock initiation sensitivity data. The initiation stimulus may be quantified. The stimulus is regulated by firing-set charging voltage, on a finely adjustable basis.

It was shown that the test is capable of providing initiation sensitivity data which distinguishes differences between explosive types (PETN, HNS).

It was shown that the test is able to distinguish changes in sensitivity due to differences in initial density (PETN, HNS) and to differences in morphology (HNS).

It was shown that the test has the potential for good precision. Planned future work includes the following:

- Obtain P-τ sensitivity data for a range of pulse durations so that an accurate demarcation line may be established for each sample formulation.

- Improve the one-dimensional character of the test. This includes providing better flyer planarity at impact and assuring adequate flyer diameter, especially for explosives that exhibit long growth-to-detonation distances or large "critical" diameters.

- Extend the flyer velocity achievable in both directions.

- Expand the data bank of Hugoniot data for unreacted explosives (or other energetic materials).

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TABLE I

Some Common Initiation Sensitivity Tests

Test Method	Reference (No.)
• Small Scale Gap Test	Ayres (8)
• Rifle Bullet Impact	USAMC (9)
• Susan Test	Dobratz (10)
• Drop Hammer Impact Test	USAMC (9)
• Skid Test	Dobratz (10)

TABLE II

Summary of Initiation Sensitivity Data for PETN and HNS

Explosive	Density (Mg/m^3)	Current Density at Threshold (GA/m^2)	Flyer Velocity at Threshold ($mm/\mu s$)	Initiation Conditions		
				P (GPa)	τ (μs)	Excess Transit Time* (μs)
PETN	1.60	405	1.70	4.5	.043	-0.08
	1.40	345	1.45	3.2	.045	-0.04
	1.20	220	.75**	1.0	.047	+0.01
HNS I	1.60	755	2.42	7.2	.040	-0.01
HNS II	1.60	910	2.73	8.3	.039	+0.04
HNS-SF	1.60	710	2.37	6.9	.040	0.00
	1.50	660	2.26	6.5	.041	-
	1.50	760	2.05	5.8	.070	-
	1.30	640	2.22	6.4	.041	+0.01

*Difference in elapsed time between: (1) flyer impact on the acceptor until shock output and (2) time for steady detonation to have occurred over the same distance. Estimated accuracy ± 0.01 μs.

**Taken from Fig. 3

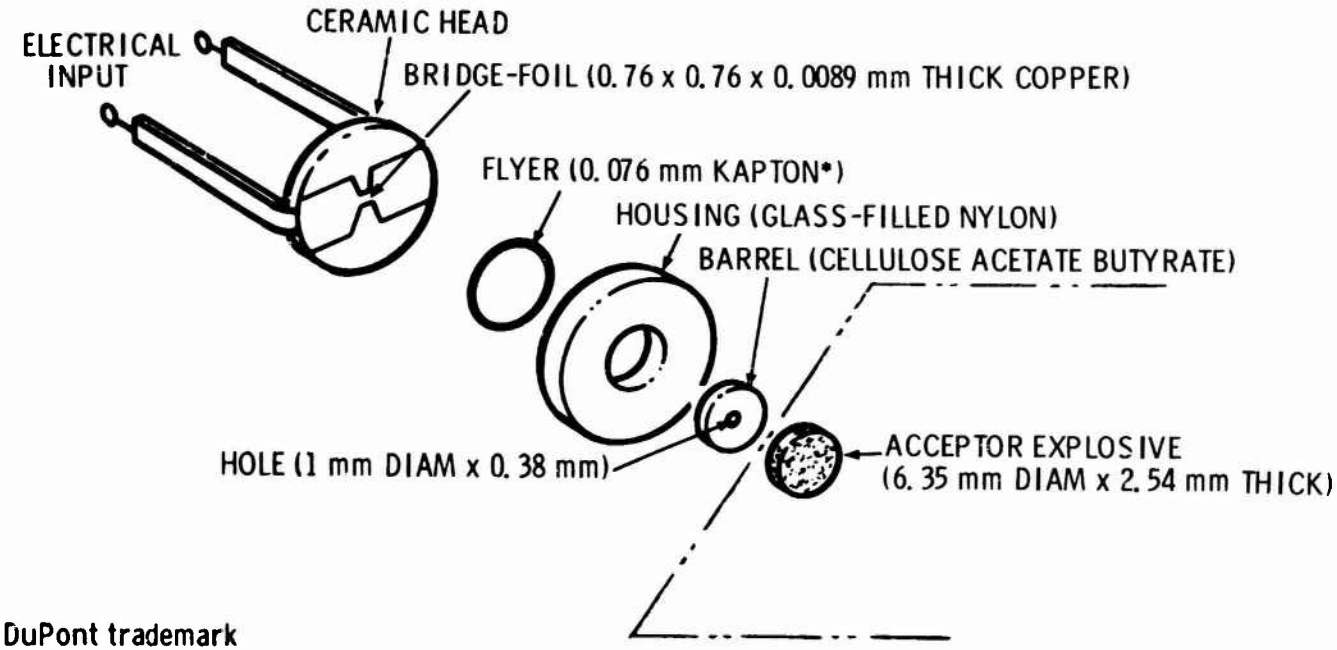
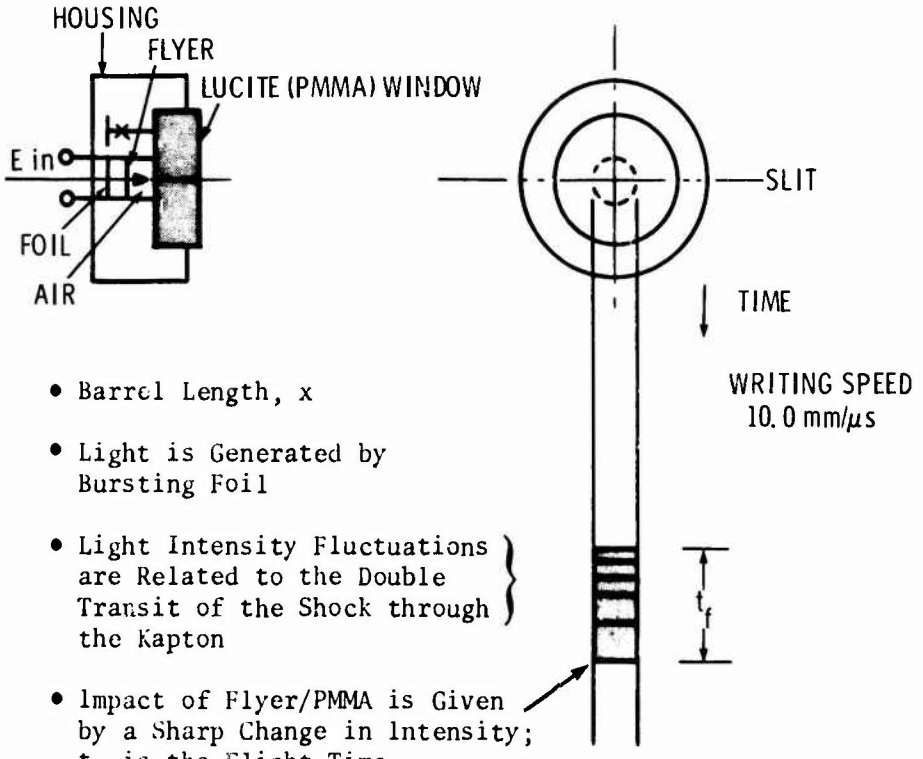


Fig 1. Exploded View of the TC-817 with Acceptor Explosive



- Barrel Length, x
- Light is Generated by Bursting Foil
- Light Intensity Fluctuations are Related to the Double Transit of the Shock through the Kapton
- Impact of Flyer/PMMA is Given by a Sharp Change in Intensity; t_f is the Flight Time.
- $v_f = \dfrac{x_2 - x_1}{t_{f_2} - t_{f_1}}$

Fig 2. Schematic Drawing for Streak Camera Measurement of Flyer Velocity

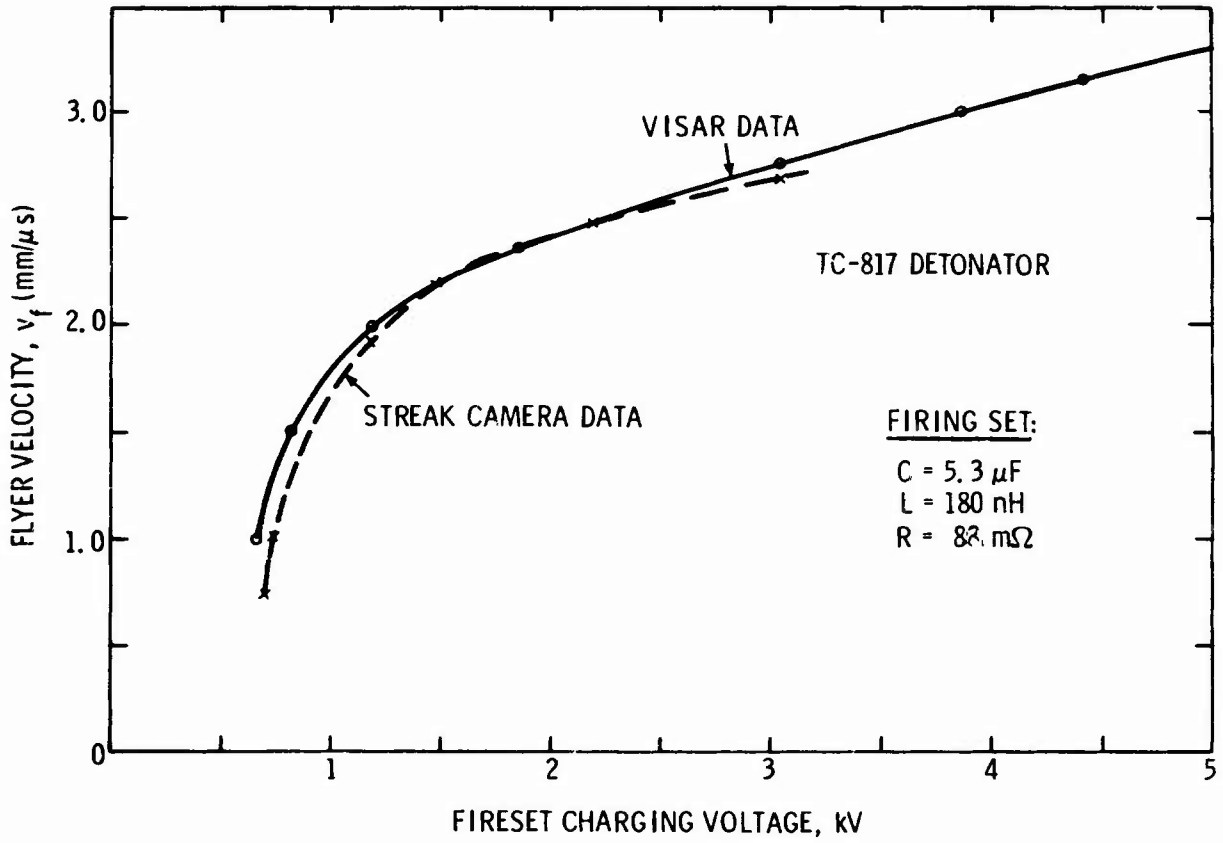


Fig 3. Flyer Velocity vs Charging Voltage

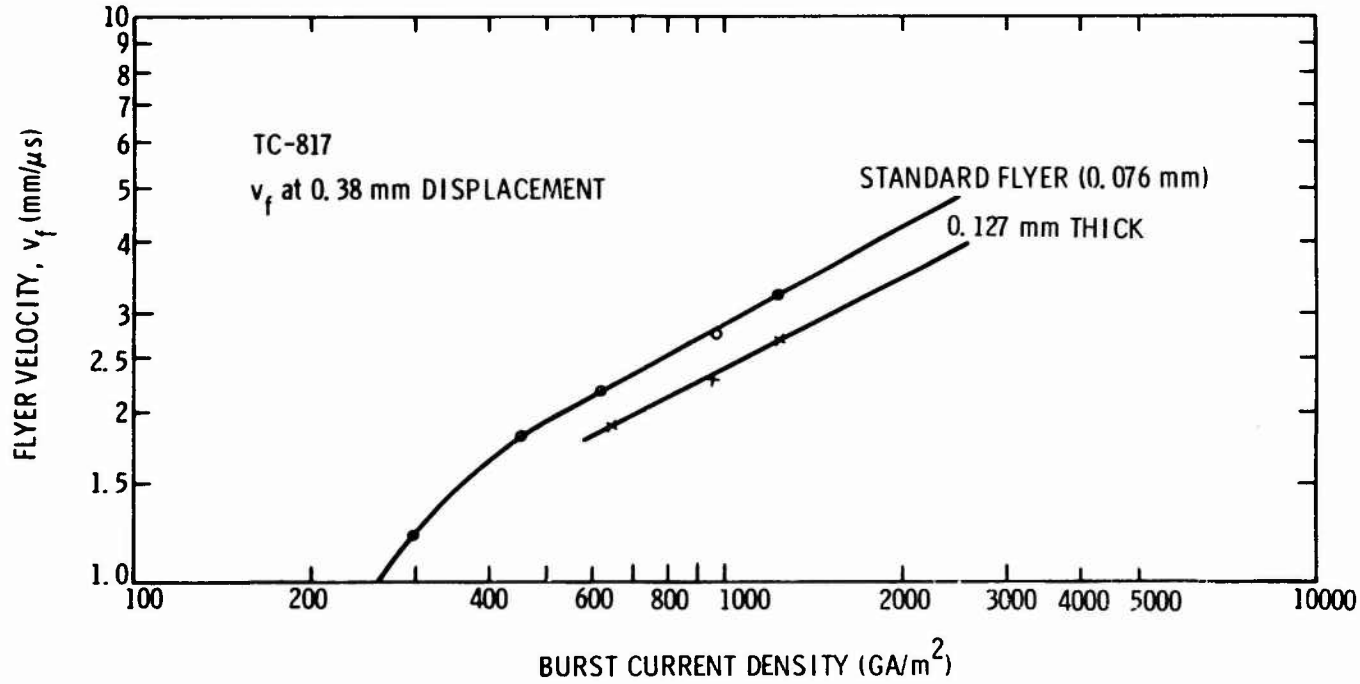


Fig 4. Flyer Velocity vs Burst Current Density

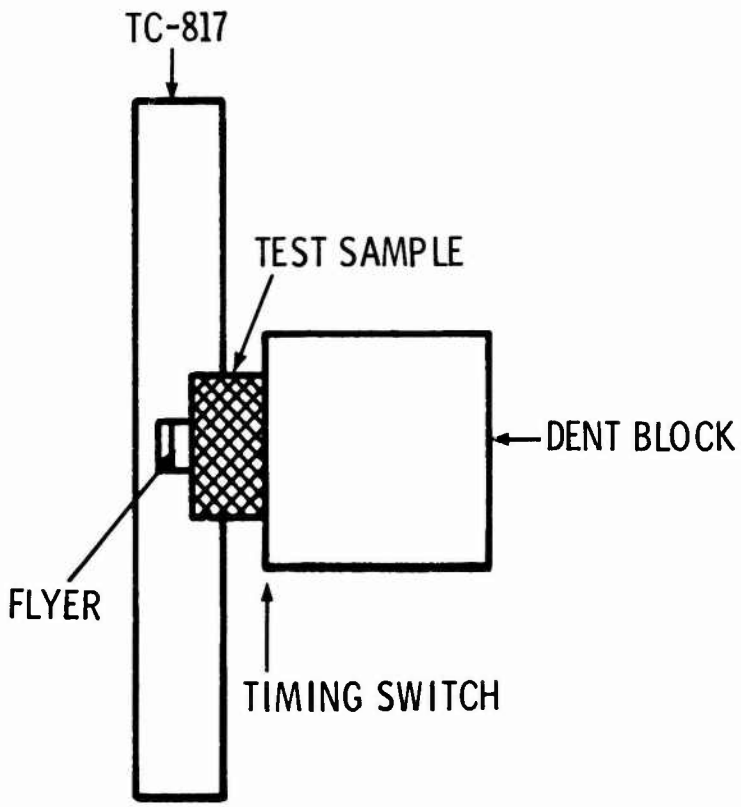


Fig 5. Schematic Drawing (Cross-Section) of Test Assembly

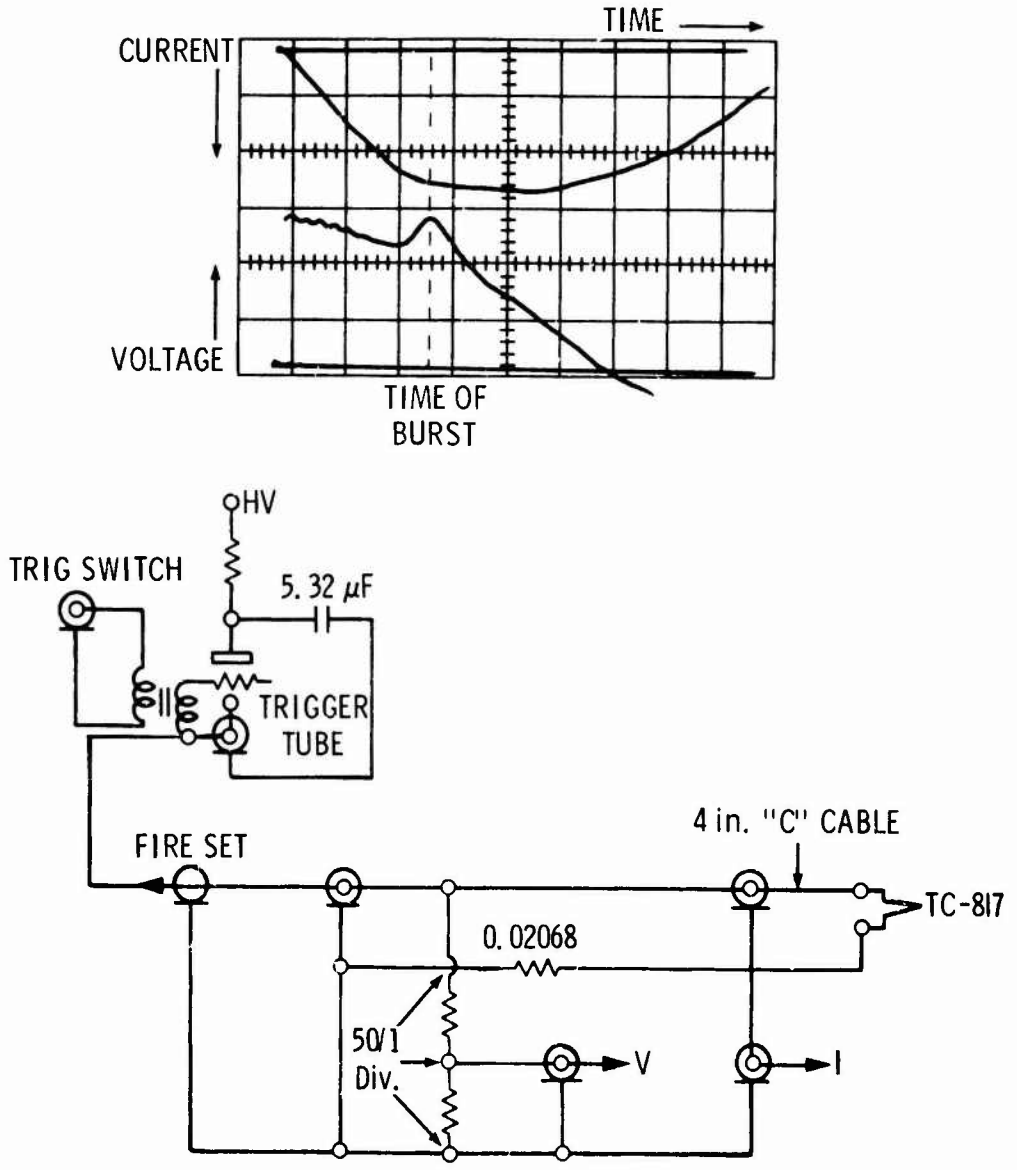
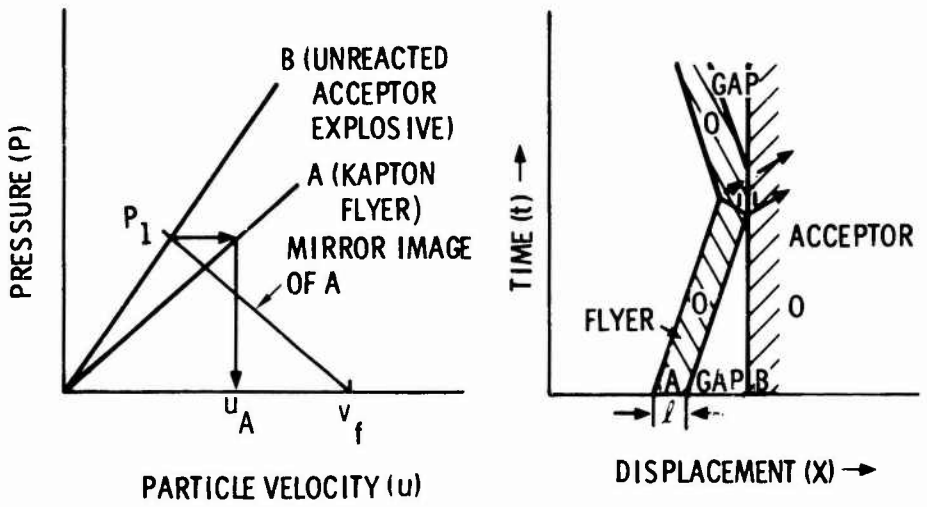


Fig 6. Typical Oscilloscope Record and Measurement Circuit



P_1 = Pressure Imparted to Acceptor When Kapton Impacts at Velocity, v_f

$$\tau = \frac{2\ell u_A \rho_A}{P_1}$$

where

τ = Pulse Duration of P_1

ℓ = Thickness of Flyer

u_A = Particle Velocity in Flyer

ρ_A = Original Density of Flyer

Fig 7. Graphical Solution to Determine P_1 and τ from P-u and x-t Diagrams

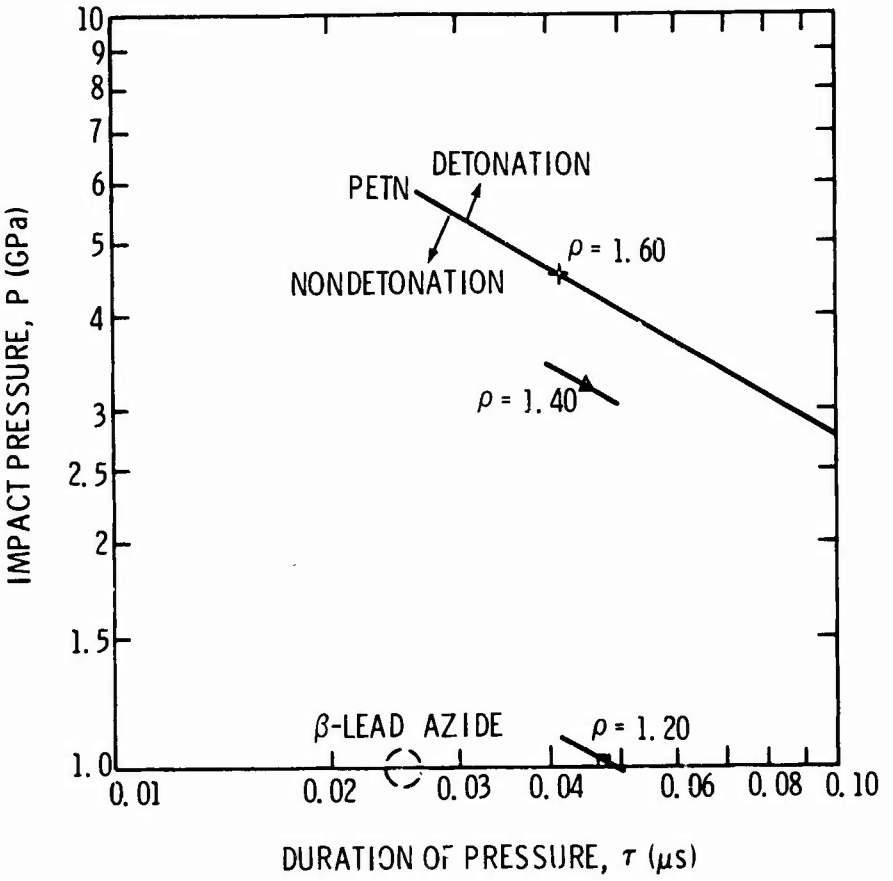


Fig 8. Initiation Sensitivity of PETN

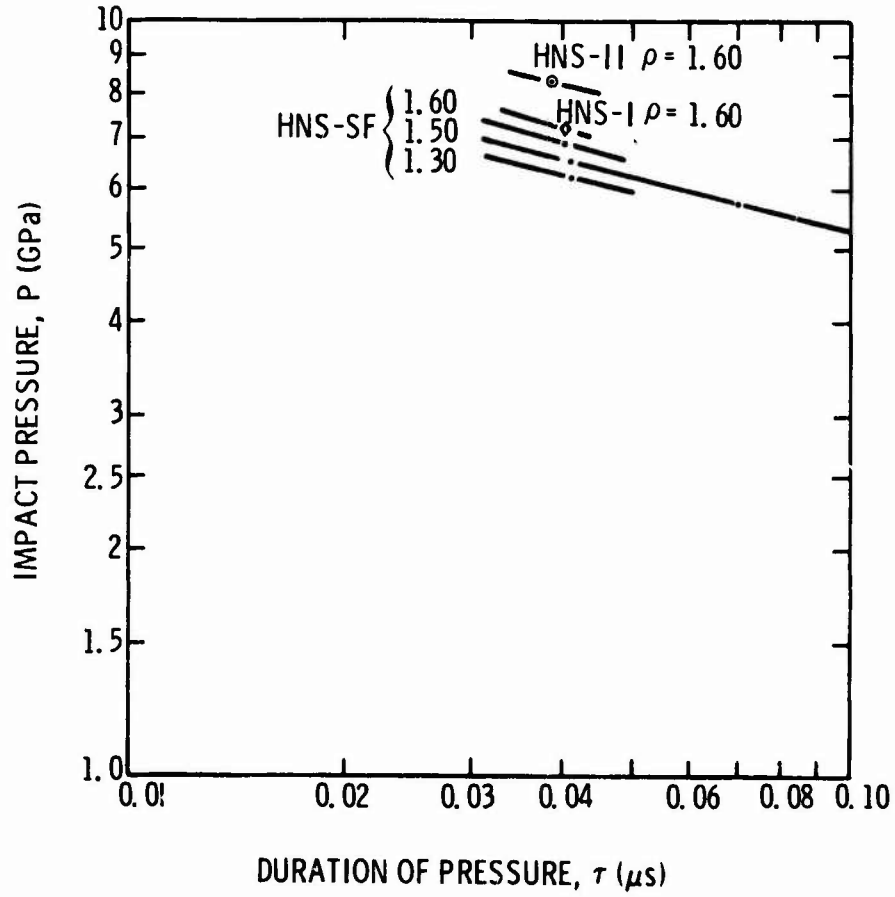


Fig 9. Initiation Sensitivity of HNS

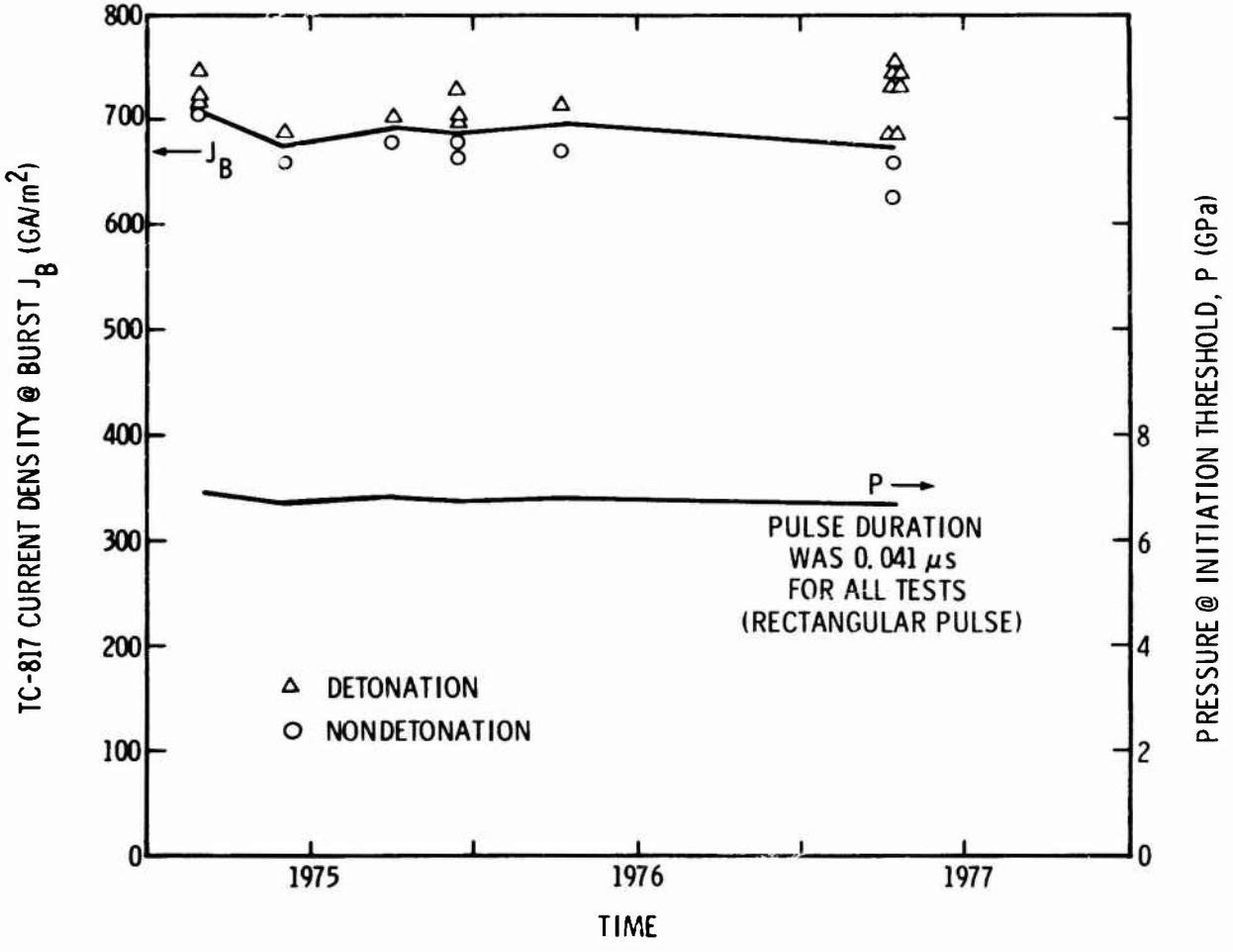
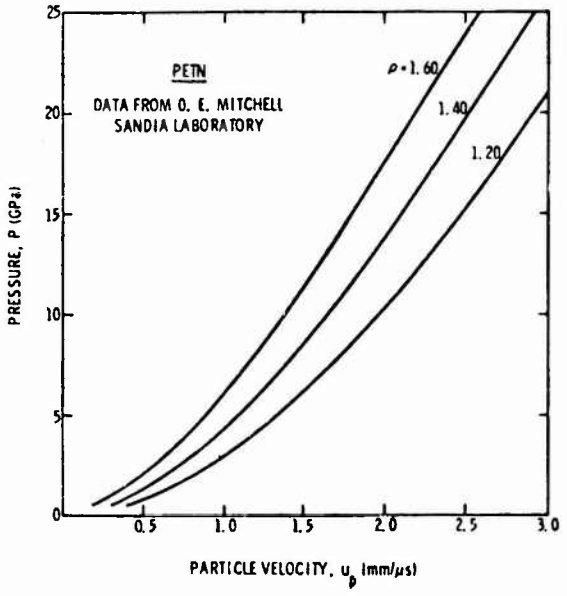
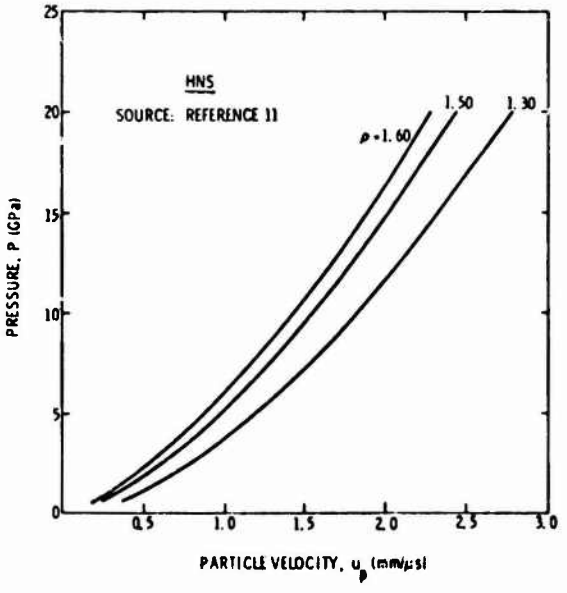


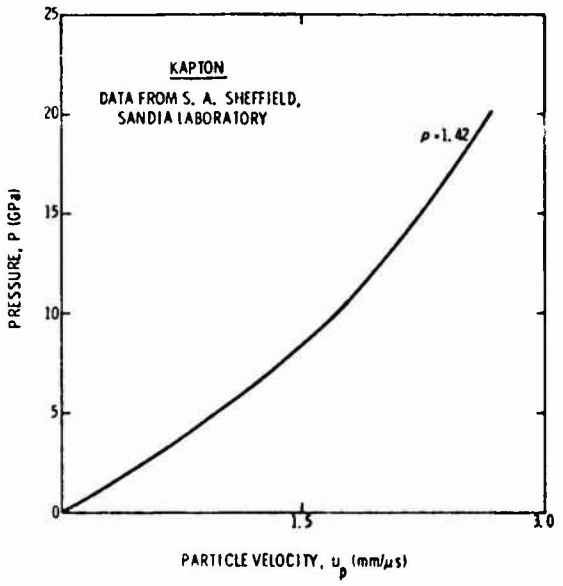
Fig 10. TC-817 Performance with HNS-SF Explosive over a 2 Year Period

APPENDIX

P-u Hugoniots






KAPTON
DATA FROM S. A. SHEFFIELD,
SANDIA LABORATORY
ρ = 1.42
PRESSURE, P (GPa)
25
20
15
10
5
0
1.5
2.0
PARTICLE VELOCITY, u_p (mm/μs)

SENSITIVITY OF HIGH EXPLOSIVES TO SHOCK STIMULATION: TESTS AND QUALIFICATION CRITERIA

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INTRODUCTION

In the production, handling, application and transportation of explosives, a knowledge of their characteristic properties is essential. To obtain this necessary information, testing methods were developed in the course of time that provided a means of determining the explosive characteristics of such substances on a laboratory scale.

Especially the wish to guarantee safe transport by rail led in Germany at an early stage to the development of such sensitivity tests, in which the explosive is exposed to the types of stimulation thought to be most probably encountered during transport (i.e. impact, friction, heat). Among these are the BAM drop-weight and friction tests, which today are solely used in the Federal Republic of Germany for the determination of the sensitivity to impact and friction. Their exclusive position is further corroborated through national and international regulations (EVO, RID) and the German Explosives Law (Sprengstoffgesetz). Together with the Gap-Test introduced several years ago, they form the group of tests applied at the Bundesinstitut für chemisch-technische Untersuchungen (BICT) for the determination of the sensitivity of high explosives to shock stimulation.

SENS TIVITY TO IMPACT

Description of the Drop Weight Apparatus

The sensitivity of explosives to impact is tested by means of the BAM drop weight test. The apparatus is described in detail in several publications of Koenen et al (Ref 1,2) and is shown in Figure 1. It consists essentially of a cast steel block with foot mounted on a concrete base. Imbedded in the steel block is the main anvil, on which an intermediate anvil with a die device containing the explosive sample is placed. Attached to the rear of the steel block is a column to which the guide rails are connected by means of transverse bars. The guide rails, provided with a ratched to arrest the recoiling drop weight, allow for the vertical movement of the drop weight and the release mechanism. In addition to a protective box around the lower part of the apparatus, a suction device is provided for the removal of reaction gases and dust particles.

The Drop Weights

Drop weights of 1kg, 5kg and 10kg are used in testing. Each drop weight is provided with a groove on either side to enable its movement between the guide rails. A holding device and a cylindrical impact piece of hardened steel complete the weight.

For heights of 10cm to 50cm, the 1kg weight is used, giving impact energies from 1 to 5 Joule. Impact energies from 7.5 to 30 Joule are received using the 5kg weight in connection with heights from 15cm to 60cm. Finally, employing the 10kg weight for heights from 35cm to 50cm, impact energies from 35 to 50 Joule are realized.

The Die Device

The substance to be tested is sieved and only the fraction with a particle size of 0.5 to 1mm used for investigation. 40cmm of the substance are enclosed between two coaxial steel cylinders held in place by a hollow steel guide ring. This die device is positioned on the intermediate anvil with the aid of a centering ring having a ring of perforations for the escape of the reaction gases. The plane surfaces of the steel cylinders in contact with the test substance may only be used for one impact test. If an explosion occurs, the entire die device must be replaced for the next test.

Performance of the Test

After the required quantity ($40mm^3$) of the powdered, pasty or liquid substance to be tested has been measured out, it is placed in the open die device, which is standing in the centering ring on the intermediate anvil. The upper steel cylinder is carefully pressed down until it touches the substance. With liquids, a gap of 1mm must be left between upper and lower cylinder, guaranteeing that the entire fluid is located between the plane surfaces of the cylinders.

The entire arrangement is next placed on the main anvil and the drop weight and release mechanism are positioned at the desired height. After the protective box has been closed, the weight is released and the suction device actuated. The test is performed six times for each height.

Judgement of the Test Results

In judging the results of the sensitivity test to impact, it is distinguished between the effects "no reaction", "decomposition" and "explosion". Decompositions without flame or other report are recognized by smell, smoke or charring.

The sensitivity of a substance to impact is defined by the drop weight and the lowest height from which in a series of six tests one explosion is realized. These values are quoted together with the resulting impact energy. To allow for a more reliable judgement of the impact sensitivity of the substance tested, BICT data sheets generally show the entire spectrum of tested impact energies from six "none reactions" to six "explosions".

The variations in the mechanical characteristics of the drop weight apparatus lead to errors in the determination of the impact sensitivity of the explosive substances. These apparatus-bound errors can be estimated from the standard deviations of the drop and impact times. Since the measure of sensitivity is the energy, which is dependent on the square of the time, the relative deviations in the energies therefore are twice the coefficients of variation of the times. The apparatus-bound error is as a result, about 20% to 25% in the worst case (Ref 3). Errors of this order are known for other drop weight machines also. For a technical testing method such as the BAM drop weight test, it is therefore not necessary to reduce the intervals between the used heights.

SENSITIVITY TO FRICTION

Description of the Friction Apparatus

The apparatus used for the determination of the sensitivity of a substance to friction has also been developed by BAM (Ref 1,4,5). As Figure 2 shows, it consists of a base plate of steel on which the actual device is mounted. The porcelain plate, fixed on a sliding support, is moved with the aid of an electric motor, over a crankshaft and a connecting rod. Each movement, activated over a starter button, consists of a forward and backward motion of 10mm. The holder of the porcelain rod carries the load arm which is provided with six notches for the positioning of one of the nine available weights. Load arm and rod holder can be pivoted for easy replacement of the porcelain rod. With the aid of an attached counter weight, the arrangement can be balanced in the zero position. When the rod holder is positioned on the porcelain plate, its longitudinal axis is perpendicular to it. The desired loads are obtained by hanging one of the weights into the proper notch with a hook. Thus the rod load can be varied from 5 to 360 N.

Description of the Porcelain Plates and Rods

The plates are of white unglazed porcelain and measure 25x25x5mm. In order to increase friction, the two surfaces are roughened with a sponge prior to baking. The cylindrical rods are made of the same material as the plates. They are 15mm long, have a diameter of 10mm and rounded ends with a radius of curvature of 10mm.

As the natural, unblemished roughness of the plates and rods is an essential condition for the reaction of the explosives tested, each may only be used once.

Performance of the Test

In performing the test, a porcelain plate is fastened to the sliding support of the friction apparatus with its sponge mark in a transverse position to the direction of movement. After the proper amount of the substance to be tested ($10mm^3$) has been heaped on the plate, the rod is placed on the substance in such a way, that the major part of the sample is in front of the rod. This is to guarantee that substance will come under the rod as the plate is set in motion. After a weight has been placed in the desired position on the load arm, the apparatus is actuated by pressing the starter button. For each load, the test is performed six times.

Judgement of the Test

In judging the results of the test, it is distinguished between "no reaction", "decomposition", "ignition", "crackling" and "explosion". The relative degree of sensitivity of a substance to friction is defined as the lowest rod load expressed in Newton at which ignition, crackling or explosion occurs at least once in the series of six tests. It is assumed in this case, that ignition and crackling are already dangerous forms of reaction. On the data sheet, the lowest load on the rod and the type of reaction observed are registered. The sensitivity to friction of a substance increases with decreasing weight on the porcelain rod. The apparatus-bound error is about 10%.

Liquids and pasty substances are usually not tested with the friction apparatus due to their lubricating properties and the resulting low heat development, which is not sufficient to cause ignition.

SENSITIVITY TO SHOCK WAVES

Description of the Gap-Test Used at BICT

The Gap-Test used at BICT (Ref 6) determines the sensitivity of explosives to shock waves. As in all gap tests, it is a measure of the hydrodynamic shock required to initiate the detonation of a sample charge, called the acceptor, separated from a standard donor charge by an attenuating medium.

Figure 3 shows the main test components. The entire test assembly rests on a pedestal at a convenient working height. A slit in the base plate takes up the leads of the electric squib, which rests in a vertical position in a hole in the central part of the plate. The blasting cap inserted in the squib supports the actual test arrangement. Enclosed in a plexiglas cylinder with an inner diameter of

21mm, an outer diameter of 25mm and a length of approximately 100mm are the donor charge, the variable water gap, and above this, as acceptor, the substance to be tested.

The donor charge is a 10g pellet of RDX with 5% wax and approximately 0.6% graphite, measuring 21mm in diameter and 20mm in height and having a density of 1.60g/ccm. The pellet is provided with a central hole of 7mm diameter and 15mm length for the insertion of the No. 8 blasting cap.

The acceptor usually consists of a pressed or cast charge having a diameter of 21mm and a length of 40mm. However, in specific cases the explosive can also be tested in the loose state, that is, as a powder. It is then placed in a plastic receptacle inserted in the plexiglas cylinder. This mode also allows for testing of liquid explosive substances.

For indication of the test result, a lead witness plate with one end of a detonating cord attached is used. The plate is fastened to a steel pipe screwed into the base plate. The other end of the detonating cord rests snugly on the acceptor charge. A positive test result is registered on the witness plate in the form of a groove made by the detonating cord.

Test Preparation

The first step towards performing the test is that of assembling the necessary components in the plexiglas cylinder. For this purpose the RDX donor charge is glued into one end of the cylinder. After the household cement used for this purpose has hardened, the cylinder is filled with water to the desired height. Next the acceptor charge is positioned in such a way above the water, that its lower end is in contact with it. Care must be taken to avoid air pockets in the water gap. Hygroscopic substances or substances that in the pressed state absorb water due to porosity are insulated at the contact area with a thin layer of wax.

The above arrangement is then set on the blasting cap, which has prior been inserted in the electric squib positioned in the ground plate as described. After the free end of the detonating cord is placed on the acceptor charge, the test is performed.

Determination of the Detonation Limits

The location of the sensitivity values for a given explosive substance follows a fixed pattern. Starting at an arbitrary height, a test is made. If the substance fails to detonate at this value, one half of the height is used in the second test. If a detonation is

registered, the second test is performed with one half of the value added to the first height. This procedure is continued until a reversal in trend is observed, that is, a transition from failure to detonation or vice versa. The height for the following test is then fixed at the arithmetic mean of the last negative and the last positive result, or vice versa. This pattern is maintained until a reversal in trend occurs with a change in height of only 1mm. The ensuing trials are carried out by increasing the water gap by 1mm after a detonation and decreasing the gap by 1mm in the case of a negative result. The procedure is continued until for one height three detonations and for another height three non-detonations have been registered.

For the particular explosive tested, these values are quoted in the data sheet in mm water gap and also, using the following equation, in terms of shock pressure in kbar.

$$p = p_o \, e^{-\frac{x}{x_o}} \qquad (1)$$

p_o is the pressure at zero height and x_o is a parameter, that is constant for the given gap test arrangement.

$$p_o = 58 \pm 3.1\text{kbar}$$

$$x_o = 13.5 \pm 2.2\text{mm}$$

Generally a substance is considered to be more sensitive to shock waves than another, when its detonation limit, given in mm H_2O, lies above that of the other substance.

New calibration measurements show the pressure dependence to be not represented exactly by the above equation. For the pressure region below 25kbar first results show the pressure to lie about 20% above the values determined with the above equation.

DISCUSSION OF THE TEST RESULTS

Test results for several widely used military explosives are given in Figures 4 to 6. Of special interest are the results for Tetryl, as this substance is a reference explosive in many national and international regulations concerning hazard assessment and qualification for military use.

The impact test (Fig 4) gives a first reaction for Tetryl with the 1kg drop weight at a height of 40cm, which corresponds to an impact energy of 4 Joule. Repeated impact testing shows, that the sensitivity limit of Tetryl can vary to some extent, often giving an impact energy for first explosion at 3 Joule (1kg,30cm) and occasionally at 5 Joule (1kg,50cm). Under consideration of the apparatus-bound errors, setting the limit for impact sensitivity at 4 Joule (1kg,40cm) seems therefore reasonable.

With an impact energy of 3 Joule, corresponding to a drop height of 30cm and a drop weight of 1kg, PETN is somewhat more sensitive to impact than Tetryl, whereas from the test results of TNT, RDX and HMX it is evident, that their impact sensitivities lie below the reference substance Tetryl.

The friction test (Fig 5) shows Tetryl to be an explosive of low frictional sensitivity. No reaction is registered up to a load on the porcelain rod of 360 Newton, a result equalled only by TNT. On the basis of the values found, a rejection of explosives such as RDX or HMX would be necessary. Since frictional properties, especially of explosives in the powdered state, are of secondary importance in ammunition however, the qualification limit for sensitivity to friction has been arbitrarily set at 80 Newton, so that only the extremely sensitive PETN is excluded for ammunition.

Results of the gap test are compiled in Figure 6. The detonation limit is given as the lowest attenuator height at which in testing three detonations are achieved. The non-detonation limit, on the other hand, is defined as the lowest attenuator height at which three negative results are registered. For attenuator heights below the detonation limit, detonation is attained regularly, whereas detonations are not found for heights above the non-detonation limit.

Based on the test results for Tetryl pressed to a density of 1.67g/ccm, the qualification limit for shock wave sensitivity is set at 20 to 23mm water gap. This represents, according to equation (1), a shock pressure at the acceptor end of the attenuating medium of 13 to 10.5kbar respectively.

Test values for PETN, RDX and HMX show these substances to be more sensitive to shock waves than Tetryl. As a result, under the present qualification conditions, these explosives cannot be accepted for military use in the pure state, as for example in booster explosives.

CONCLUSION

The methods applied for the determination of the sensitivity of explosives to shock were described and qualification limits presented. The difficulties of judging an explosive on the basis of the results of these tests are apparent. Although the methods are adequate for hazard assessment, they are worthy of improvement if they are to be used further for qualification purposes, since, for example, none allow a determination of the explosive characteristics in the state of use of the explosive substance. Also, as in the case of the drop weight test, the performance and judgement of the test and the test results are worthy of alternation, since a total of six tests at each height does not seem adequate for the determination of the behavior of an explosive to impact. Work towards this end is at present being undertaken.

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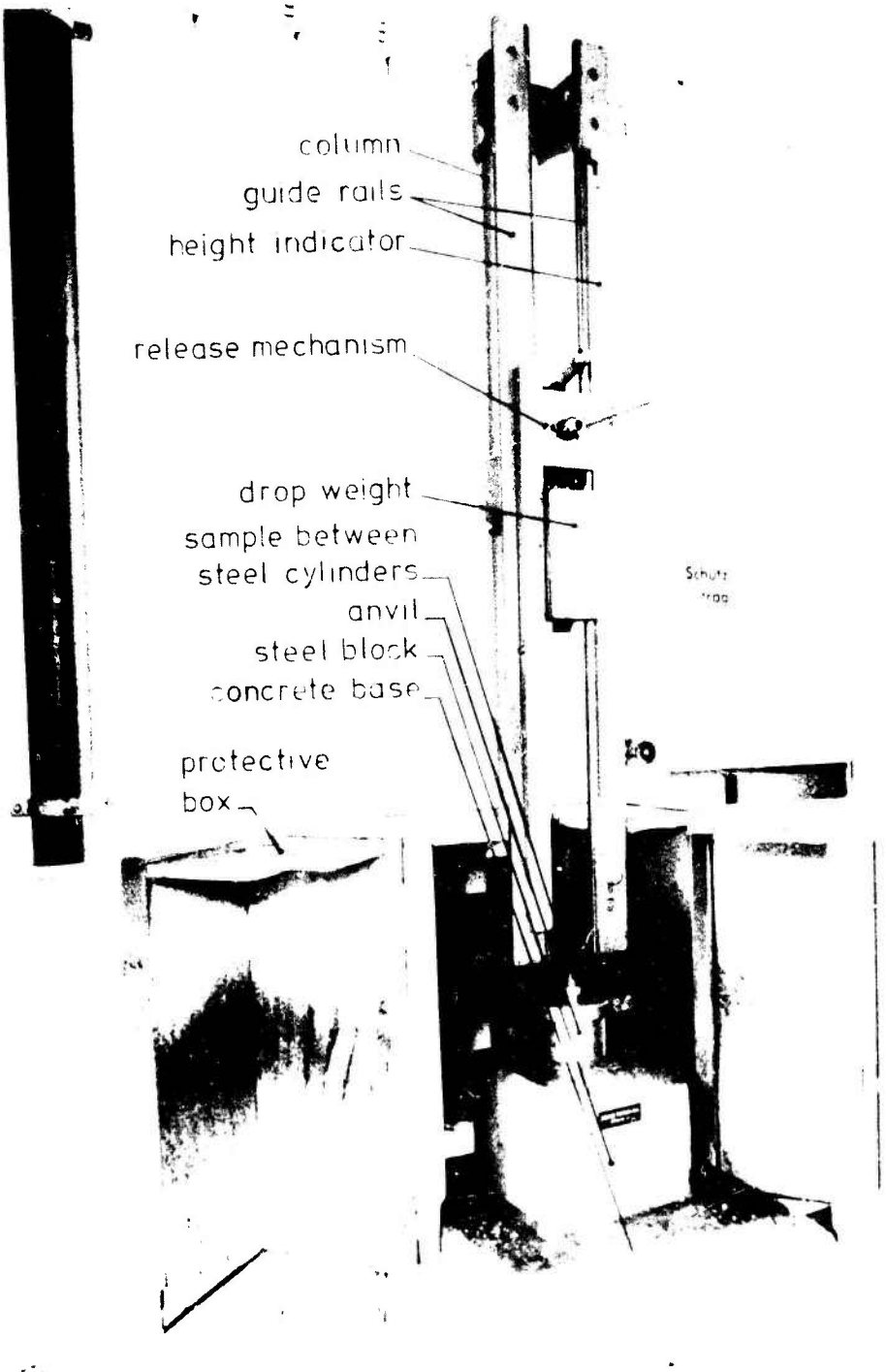


Fig 1 BAM drop weight apparatus

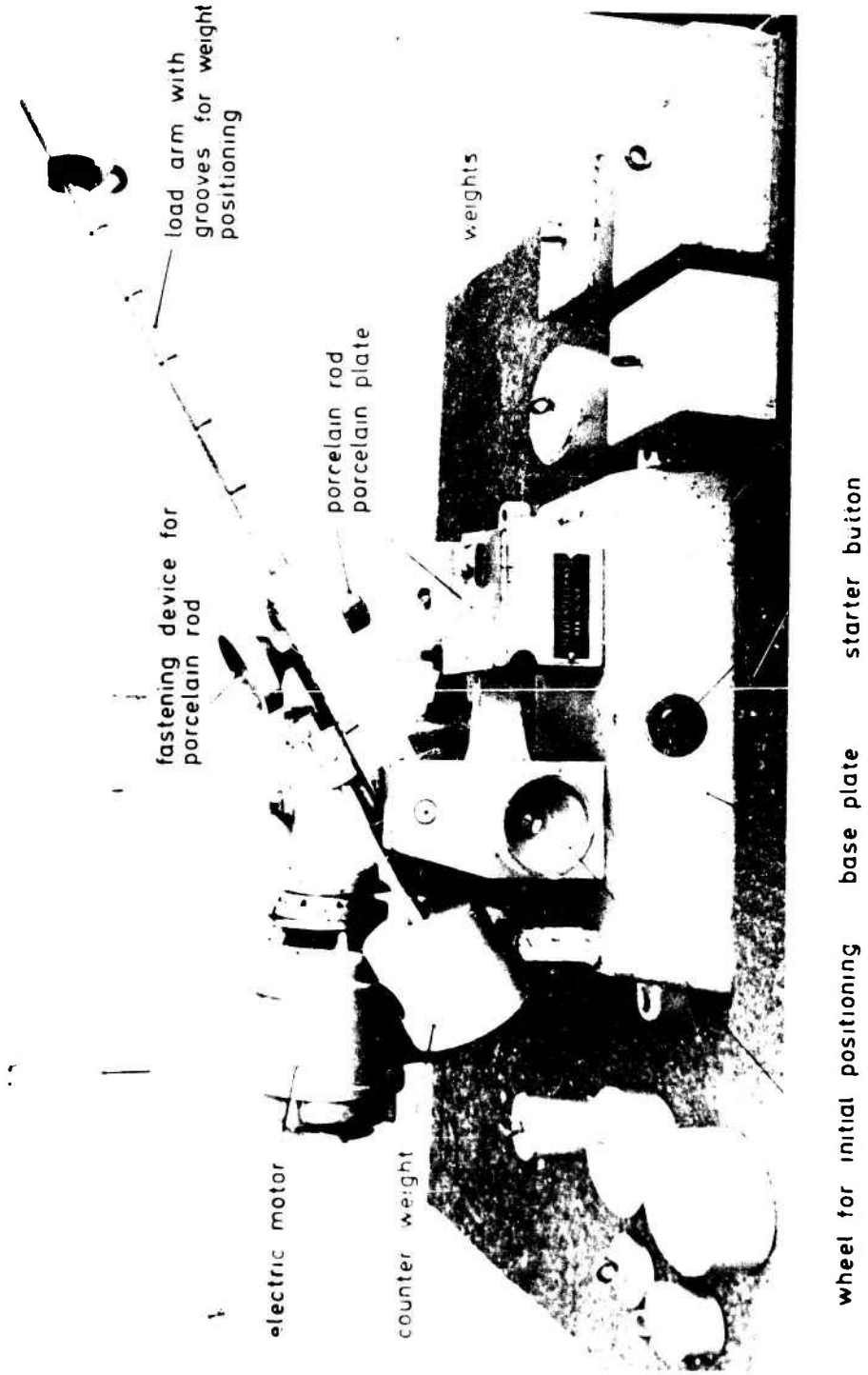


Fig 2 BAM friction apparatus

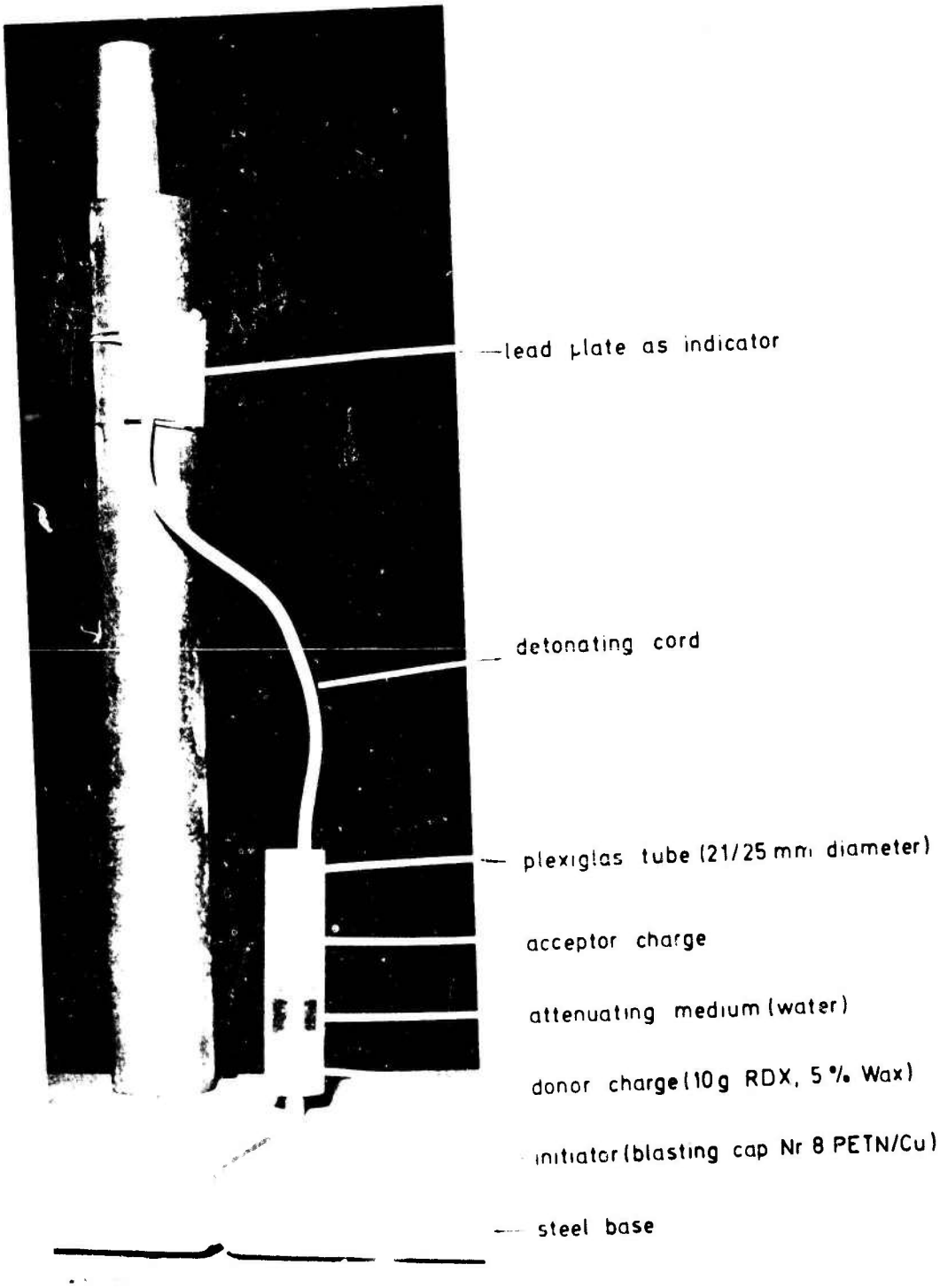


Fig 3 BICT gap-test

Substance	Reaction	1 kg weight					5 kg weight						10 kg weight			Impact energy [Joule]
		height [cm]					height [cm]						height [cm]			
		10	20	30	40	50	15	20	30	40	50	60	35	40	50	
Tetryl	none			6	5	4	5	3	2	4	-					4
	Decomposition			-	-	-	-	-	-	-	-					
	Explosion			-	1	2	1	3	4	2	6					
TNT	none							6	5	3	4	1	-			15
	Decomposition							-	-	-	-	-	-			
	Explosion							-	1	3	2	5	6			
PETN	none		6	5	3	2	-									3
	Decomposition		-	-	-	-	-									
	Explosion			1	3	4	6									
RDX	none					6	4	4	3	2	2	-				7.5
	Decomposition					-	-	-	-	-	-	-				
	Explosion						2	2	3	4	4	6				
HMX	none					6	2	1	-							7.5
	Decomposition					-	-	-	-							
	Explosion						4	5	6							

Fig 4 Sensitivity to impact: BAM drop-weight apparatus

Substance	Type of Reaction and Load on Porcelain Rod
Tetryl	no reaction up to 360 Newton
TNT	no reaction up to 360 Newton
PETN	crackling, beginning at 60 Newton
RDX	crackling, beginning at 120 Newton
HMX	crackling, beginning at 120 Newton

Fig 5 Sensitivity to friction: BAM friction apparatus

Acceptor charge	Density g/cm^3	Detonation Limit		Non-detonation Limit	
		mm H_2O	Pressure kbar	mm H_2O	Pressure kbar
Tetryl	1.67	20	13.18	23	10.56
Tetryl	0.87	25	9.10	28	7.29
TNT (cast)	1.62	3	46.44	5	40.05
TNT (pressed)	1.55	20	13.18	22	11.37
PETN	1.60	34	4.67	38	3.48
RDX	1.63	26	8.45	27	7.85
HMX	1.72	24	9.80	27	7.85

Fig 6 Sensitivity to shock waves: BICT gap-test

CONSIDERATIONS FOR QUALIFICATION OF BOOSTER EXPLOSIVES

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SUMMARY

In addition to the chemical purity, the sensitiveness of booster explosives depends upon several parameters as loading density, grain-size, grain-configuration, confinement, and so on.

Among the qualification-tests for booster explosives a gap-test is most relevant to out-of-line safety. The test also should be suitable for the investigation of lead and small booster devices. Furthermore it is desirable to supervise the lot to lot variation of detonator output and lead- respectively booster-sensitiveness by a simple and economical test.

Until today, in general during quality control, only the performance tests of explosive-train devices are routinely performed.

An example will demonstrate the necessity for such a test. Finally it is pointed out a way which should come close to this goal.

INTRODUCTION

The requirements of STANAG 3525 (1) contain the agreement, to separate the so called "primary explosive compositions" from the main filling of a warhead by a physical obstruction (shutter or interrupter).
All explosives located behind the obstruction must meet a number of requirements concerning their insensitiveness. Especially the "booster-explosives", as used in leads, relays, detonating cords, and boosters may not have a higher sensitiveness than tetryl.
riteria for the selection and acceptance of booster-explosives - as required since 1972 in the USA - are compiled in a manual for qualification of explosives (2).
In addition the NATO AC/225, panel IV,2 (chemistry) is on the way to establish a STANAG, concerning the requirements for booster-explosives.
Unfortunately the task - fixing test methods and limits of acceptance - is not fully adequate regarding safety purposes. The sensitiveness of chemical substances like tetryl is not only determined by its purity and chemical composition. In spite of this tetryl until to-day is used as a standard, it does not meet these requirements. The physical parameters (loading density, grain configuration, confinement, diameter and lenght of the charge) alter their sensitiveness considerable.
Many test-methods do not allow to take above mentioned points into consideration.
Procedures like the VARICOMP (3) or simply a special sort of gap-test (4), (details see appendix), meet these requirements, because the influence of configuration and confinement must be considered likewise and simultaneously.
Both methods employ a shock-wave-stimulus. According to Stresau and coworkers (5) the shock-wave initiation is the crucial stimulus among tests for classifying booster-explosives in the USA.
Judging the sensitiveness of leads, the gap-test is employed in Germany with good results. As guideline for acceptance presently wetake as a limit a 28 - 27 mm water gap (corresponding to about 7 - 8 kbar initiating amplitude).

SAFETY CONSIDERATIONS FOR A SPECIFIC DEVICE

An example may explain reason and success of this procedure.

Developing a new design for an impact fuze it was decided to take a detonator having a very low output and to separate the fuze-train behind the rotor by a closed wall, similar to that in the 20 mm Fuze M 505 A3 (6), see figure 1.

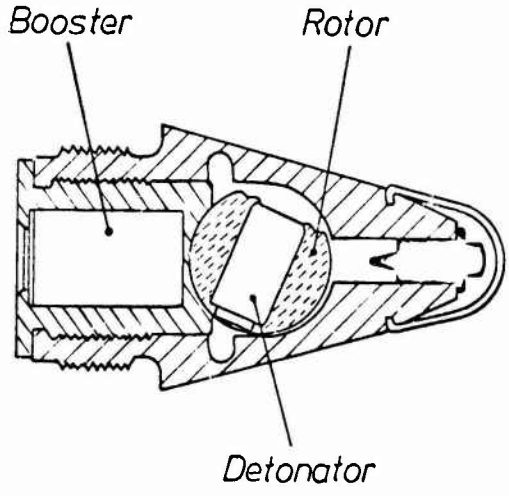


Figure 1 : 20 mm Fuze M 505 A3

The goal of this concept is to improve the results of the static detonator safety test (7).
In a later stadium of development, however, an insufficient reliability in detonation-transfer from detonator to booster was found.
The improvement of reliability with a minimum of variation in design-parameters was possible by two different ways:

Providing a hole in the fuze bottom behind the detonator. This variation would deteriorate the advantages concerning the detonator-safety test.

Changing the booster-sensitivity.

The designer decided to follow the latter way in a very unusual manner:
The first booster conception had provided a plasticbonded RDX-loading with a sensitiveness comparable to tetryl loadings currently in use. The replacement of RDX by HMX, grade B, without any additives and gently compressed (40 MPa 6000 psi) gives a better reliability but was not satisfactory.
The final procedure of booster loading by direct pressing in the case was the following (see figure 2):

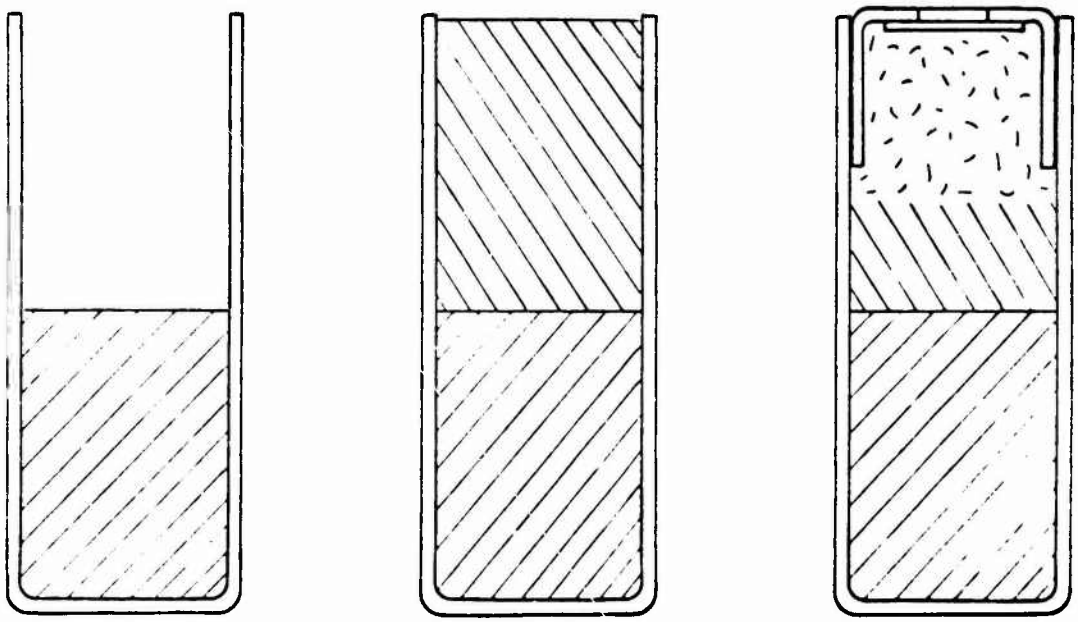


Figure 2

step 1: Consolidation of the HMX base-charge (2/3 of explosive amount) with a loading pressure of 80 MPa (12 ooo psi);
step 2: Loading the second HMX - increment with a pressure of 40 MPa (6 000 psi);
step 3: Insertion of a cup with sealing-disc and so disturbing the firmness of the upper HMX - pellet.

In the assembled booster-device, the loading behind the sealing-disc was so loose, so that the explosive was free flowing out if the disc was lifted with caution.
The poor insensitiveness of this device was detected by the gap-test (explosions by a water gap of 42 mm corresponding to about 2,5 Kbar).
For finding out the reasons of the high sensitiveness, with the following assemblies gap-tests had been performed:

a) Loaded boosters by manufacturer filled with tetryl or HMX. In each case the explosive had been pressed into the cup, and into the case. In between the explosive had been compacted by inserting and pressing the cup into the case only, see figure 3.

b) In our laboratory we reloaded the original cases from the bottom by removing it, leaving the upper part undisturbed. The filling had been performed by 3 pressure-increments, and the explosive had been tetryl in use for ordnance (8).

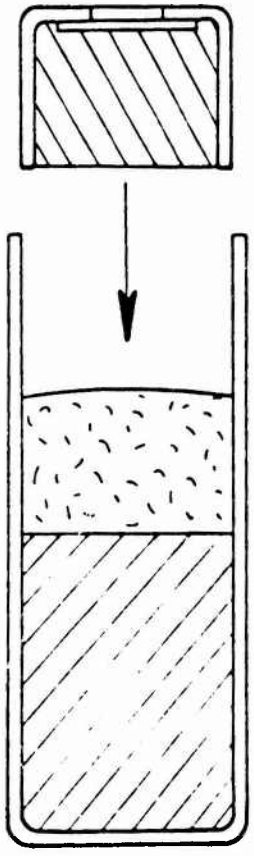


Figure 3

The gap-test results are summarized in table 1.
On may notice, that the devices of the manufacturer show an unexpected high sensitiveness. Considering the facts, that the loading pressure - shown in table 1 - had been apparently applied for filling the cup only, and besides a fine grade explosive had been used, this explains the behaviour.

FURTHER SAFETY TESTS TO BE CONSIDERED

Contrary to shock sensitiveness of the assemoly another risk exist.
With respect to reliability, a minimum donor output is required, which is tested by lead disk-, steel cent-, and similar tests (7), which are insensitive to surplus output. A surplus output, however, may possibly lead to a failure of the physical obstruction.
Up to now, no known test yields a quantitative measure of the output of an individual detonator (9). Since the donor output is a function of loading density and charge length (10), the scanning gamma ray densitometer system, developed at Picatinny Arsenal (11), may be a controlling tool.
We intend to use a barrier-test, similar to the examples in Appendix 2. By the requirement of a no-go for a maximum barrier between detonator and lead or booster an upper limitation of the output is obtained. It is projected to perform such tests from lot to lot. For getting a relevance to the actual case, the original fuze-train devices together are to be used for the test.

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Table 1

Shock-wave sensitiveness of boosters determined by gap-test.

(different explosives, loading procedures and -densities)

loading conditions	loading density (g/ml)	water gap (mm)	shock cor. (~kbar)
original design		42	2,5
PETN, fine, without additives	1,18	40	3
Tetryl* (40 MPa ≙ 6000 psi) maincharge free flowing	1,4	30	6
HMX* (40 MPa ≙ 6000 psi)	1,52	28	7
HMX* (80 MPa ≙ 12 000 psi) maincharge low compacted	1,58	27	8
Tetryl* (80 MPa ≙ 12 000 psi) maincharge low compacted	1,5	27	8
Tetryl** (7 MPa ≙ 1000 psi) granulated, ordnance quality	1,23	25	9
Tetryl** (80 MPa ≙ 12 000 psi) granulated, ordnance quality	1,56	22	11

* = loading pressure as stated by the manufacturer (loading density as determined by weight and dimensions)

** = reloading by BICT into original cases from the bottom after delaborating the HMX-charges.

APPENDIX 1

THE BICT GAP-TEST

APPENDIX 1

THE BICT GAP-TEST

The BICT gap-test evaluates sensitivity to detonation by shock-waves. The test is normally used to determine the sensitivity of high explosives. In the presented form it is modified for testing the shock-sensitiveness of fuze-train devices like leads and small boosters.
In this test a hydrodynamic shock from the standarized RDX-donor, attenuated by a definite water-gap, is transmittet to the acceptor device.

PROCEDURE

Figure 1 is a drawing of the experimental assembly. It consists of a plexiglas tube (21/25 mm diameter) into which is glued a pellet of 10 gramme RDX (5% wax, density 1,60 g/ml). The pellet contains a hole for insertion of a blasting cap.
As a "gap", water of ambient temperature is filled above the donor charge in order to attenuate its shock-wave as a function of its layer thickness.
The acceptor devices are glued to smooth aluminum rods. The rod is supported by a perforated paperboard disc allowing an easy adjustment of the "gap" between donor and acceptor.
The plexiglas tube, preferably arranged in a thick walled steel drum, retaining the fragments of rod and device, is filled above the RDX-pellet with water to the desired level. Thereupon the test specimen attached to the aluminum rod is introduced. The paperboard disc is set on the rim of the plexiglas tube and the rod is lowered until the acceptor device is contacting the water surface.
After assembling the donor with a blasting cap No.8 and a squib it is initiated remotely. Thanks to the steel drum, the rod - and in case of no explosion mostly the device or its fragments - can be recovered in a jiffy. The remainders give relevant information on the reaction (fire or no fire) of the acceptor.
Similar to Brucetons "up-down" method, the tests are continued until 3 explosions on one side and 3 non-explosions on the other side have been achieved.
For safety considerations mostly the gap is indicated where the first explosion occurred.
For more details see (1), (2), (3).

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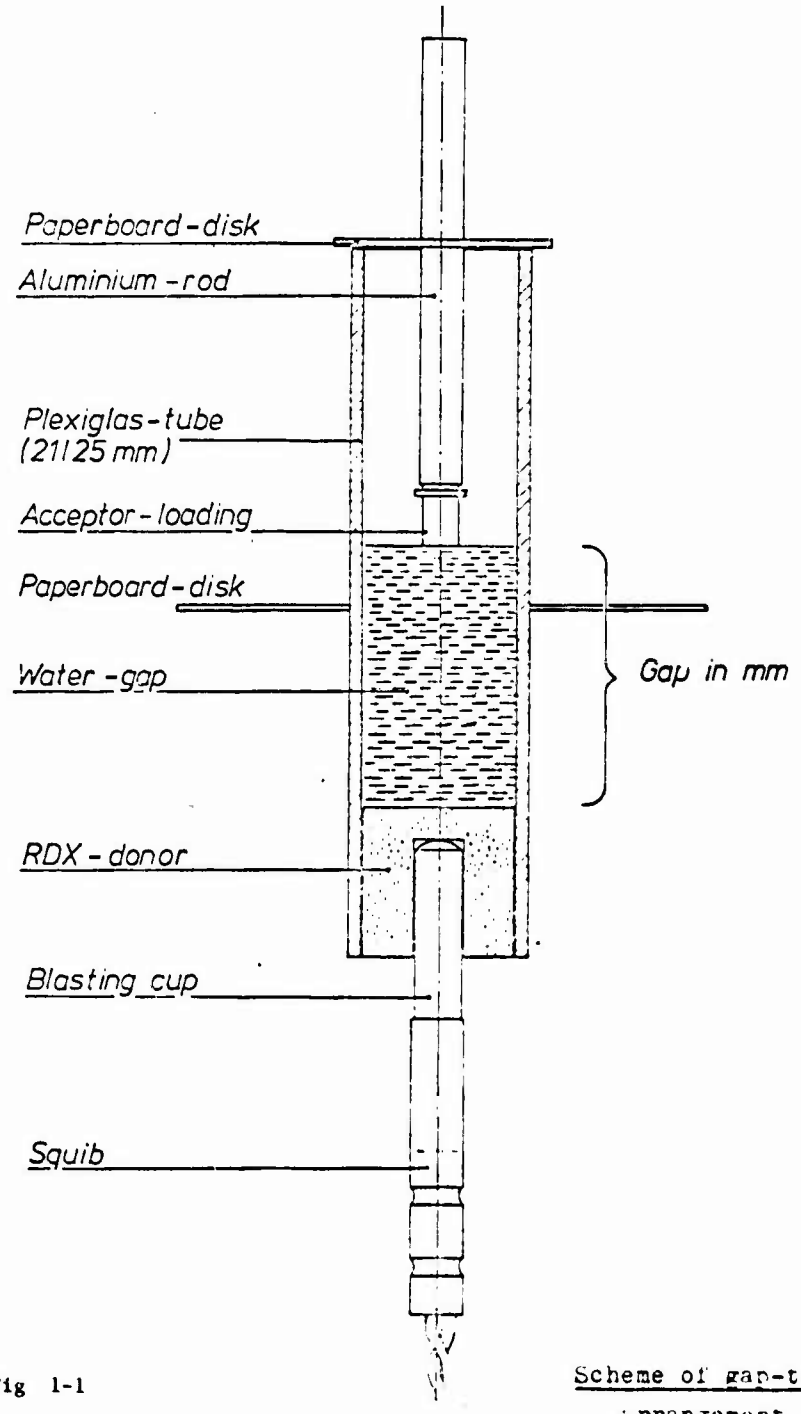


Fig 1-1 Scheme of gap-test arrangement

APPENDIX 2

EXAMPLES FOR SIMPLE BARRIER-TEST ASSEMBLIES

APPENDIX 2

Examples for simple barrier-test assemblies.

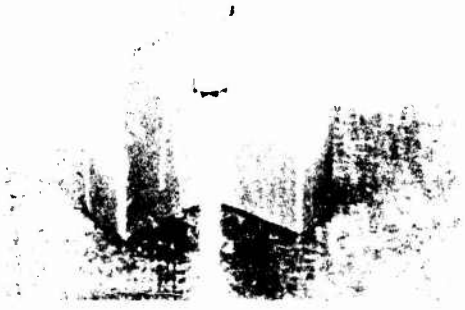


Fig 2-1 The flash-detonator is initiated by a squib. Its output is attenuated by a snuggly fitting metal-barrier. In case of explosion the witnessplate is dammaged.

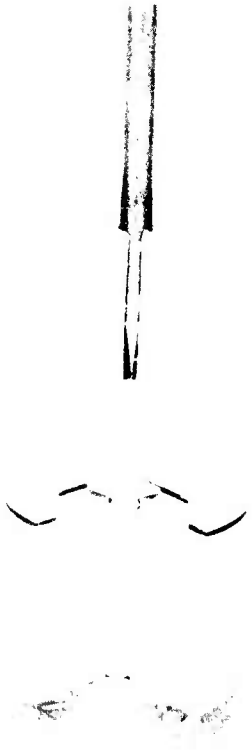


Fig 2-2 The stab-detonator is initiated by a standard firing pin. Its output is attenuated by a plastic-barrier and a perforated disk (original fuze-device). Reaction of the booster is indicated by damaging the steel-witnessplate.

DEVELOPMENT OF A FRAGMENT VELOCITY TEST OF DETONATOR OUTPUT

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ABSTRACT

In many explosive train applications, fragment impact is an important mechanism involved in detonation transfer. Although it is not the only factor involved, fragment velocities are directly related to output. Therefore, a direct measurement of fragment velocity is important for quality control and evaluation of new designs. This report describes a new test method which measures relative detonator fragment velocities over a one-inch distance with a standard deviation of < 0.02 mm/μs, part of this variation being due to the test method, and part due to sample to sample variations.

Improvements over prior test methods include: (1) Use of a 20 mil aluminum cover over the stop switch to prevent premature closing by minor fragments or shock waves. (2) Addition of a nonfragmenting flyer plate over the face of the detonator to improve precision and integrate impulse. However, measurements without added flyers are required to detect changes in closure discs. (3) Use of a 10 nanosecond digital time interval meter to permit rapid accurate data reduction.

After normalization with experimental results, one dimensional hydrodynamic calculations can be used to predict effects of variations in detonator construction. For standard M55 detonators, the open sandwich Gurney formula predicts velocities correctly.

TEST DESCRIPTION

As mentioned in the abstract most of the studies in this program were made on the M55 detonator shown in Figure 1. The detonator is initiated by a needle stabbing into the NOL-130 primer layer. The flame is built up to a detonation in the lead azide layer, and then the high output pressure and detonation velocity is produced by the RDX layer. The NOL-130 and how it is initiated has no effect on output, and beyond the minimum priming charge, the lead azide has little effect on output. However, quantity and density of RDX, its confinement, and the closure disc are major factors.

The fragment velocity test assembly developed in this program is shown in Figure 2. The assembly is held together and good electrical contact assured by use of a spring loaded clamp on the stab needle guide. The expendable components are made from a combination of inexpensive washers and lengths of tubing. The outer plastic tube is 1/2" I.D., 3/4" O.D., and 1 3/4" long. It has a 1/10" slit cut in one side to allow for variations in dimensions of the other parts, and is used to hold them in concentric alignment. The upper and lower aluminum tubes are 1/2" O.D., and 7/16" I.D. The upper tube is used, in combination with an upper steel washer which is 1/10" thick, 1/2" O.D., with a 1/8" diameter hole, to provide an electrical path from the detonator to the high voltage side of the start switch, and to transmit the clamping force to the detonator. To get accurate data, it is important that all parts be held together firmly and accurately.

The lower tube provides the desired 1" standoff and the ground return for the start and stop switches. Although fragment velocity is almost constant from 1/3" to 1 1/3", timing errors are more significant at the shorter distances, and fragment dispersion causes loss of data at longer distances.

The nylon centering washer has a thickness of 1/8" (which is slightly less than the 0.142" length of the detonator), a 1/2" O.D., and a center hole to provide a snug fit around the detonator (0.147" for a M55 detonator). It also provides the radial confinement for the explosive output charge. Nylon provides typical confinement, since most fuzes have thin die cast safe and arm sliders confining the detonator. When steel confinement was used, fragment velocity increased 5.7%.

When a flyer plate is desired, it is placed in direct contact with the output end of the detonator. The green lacquer coating over the closure disc provides some additional mass, however, tests where this was removed, where an additional 4 mil of paper were added, or where a layer of silicone grease was added, showed that the results on velocity of a 5 mil steel flyer plate were negligible. When a flyer

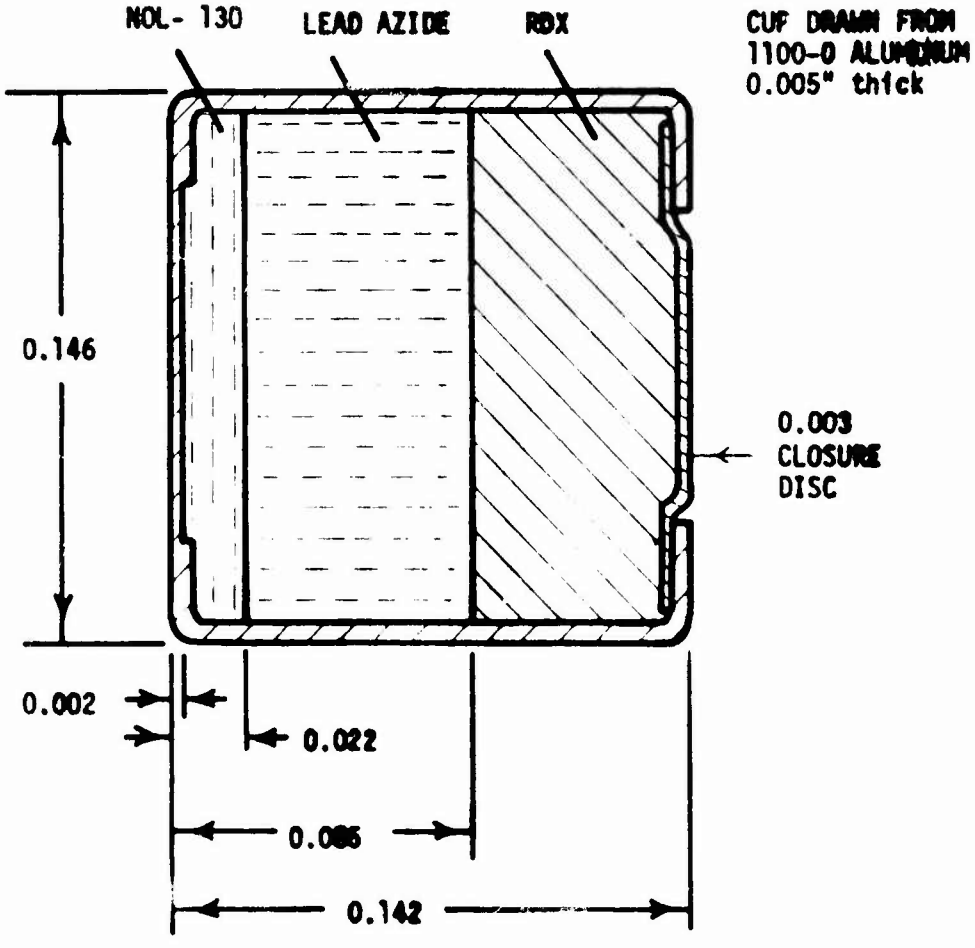


Fig 1 M55 Detonator

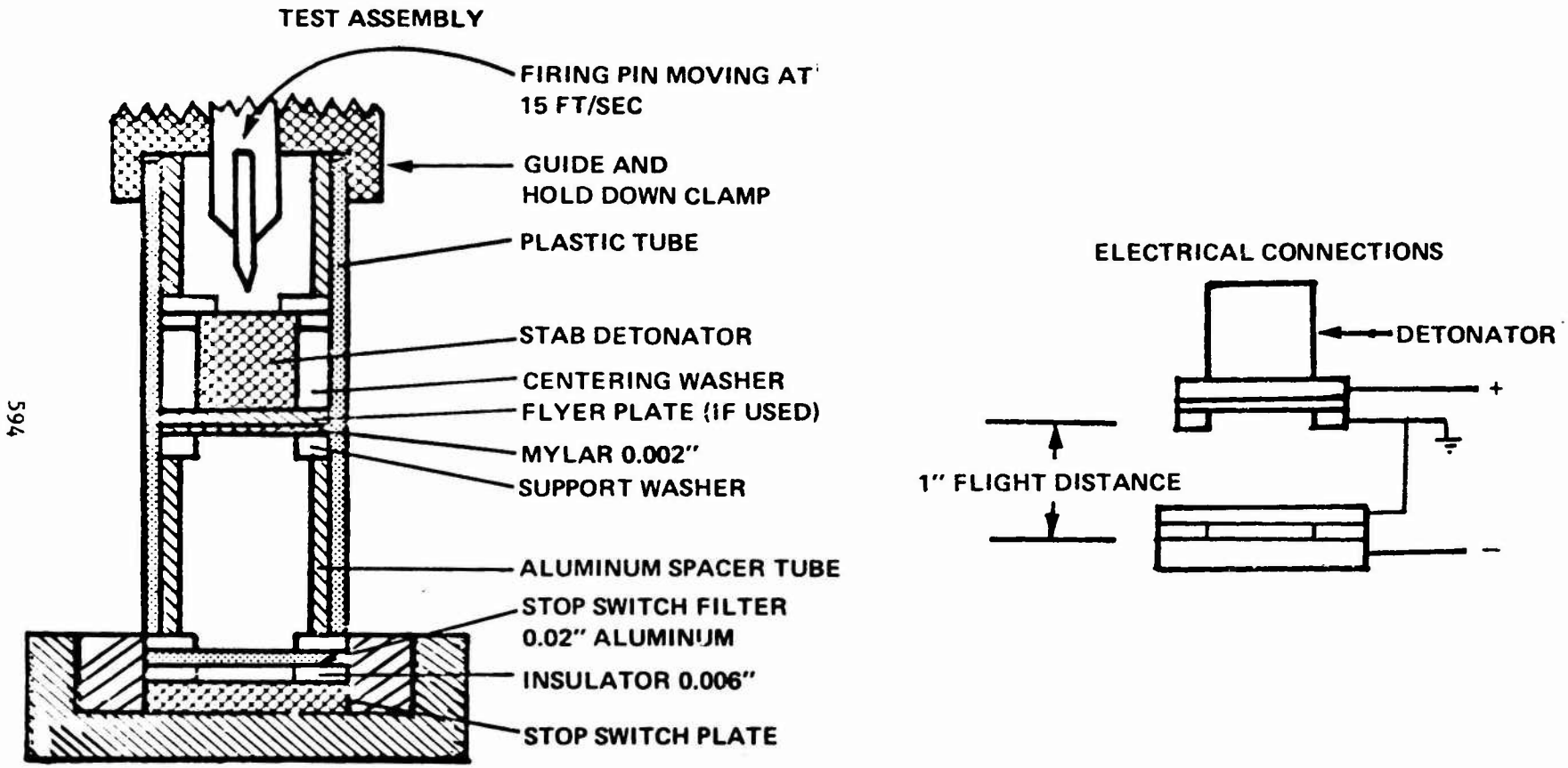


Fig 2 Detonator fragment velocity

plate was not used, addition of 2 mil of Mylar decreased the fragment velocity 5.6%. In order to get a start signal, the 2 mil of Mylar was used to insulate the detonator from its support washer. When this was shorted by the detonation, the timer started. When the fragments penetrated the 0.02" of aluminum over the stop switch, the timer stopped. Use of a timer accurate to 0.01 microseconds is needed. The switch circuit used to give single, over damped pulses is shown in Figure 3.

The stop filter thickness of 0.02" determines the size of fragment needed to stop the timer. Since smaller fragments travel faster, the observed velocity varies 0.026 mm/μs for a 0.001" change in filter thickness. (3.525 mm/μs for 30 mil, 3.75 mm/μs for 20 mil, and 3.945 mm/μs for 16 mil).

Although addition of a steel flyer plate increased the precision of the test (standard deviation was reduced by a factor of 4), its sensitivity to small changes in detonators was reduced. Therefore, for a standard output test, no added flyers are recommended.

Computer calculations of flyer plate velocity of M55 detonators were made using the SIN code (Ref 1). It was found that observed and calculated velocities agreed when the RDX length was reduced 10% (to 51 mil) to compensate for radial losses. The calculated velocity of fragments becomes constant in less than 1 mm, as shown in Figure 4 and the observed velocity was found to be essentially constant at least out to 33 mm. (Measurements were not made beyond that distance).

The fragment patterns obtained are shown in Figure 5. The pattern at short standoff in the lower view shows a central spot due to fragments from the closure disc surrounded by a ring from the thicker aluminum in the cup crimp. Flash x-ray pictures show the same effect, with the thicker ring traveling at a lower velocity. The upper left pattern is obtained at the standard test distance of 25 mm, and shows that the 3 mil flyer breaks up into pieces. The upper right pattern shows that the added steel flyer does not break up if the steel is 2 mil or thicker.

PARAMETER STUDIES

In order to prove that the fragment velocity test is better than the present steel plate dent test, as a measure of detonator output, a series of special M55 detonators were made up with known variations in closure disc thickness, RDX quantity, and with HMX vs RDX. These were then evaluated with the results shown in Table 1. As can be seen, the fragment velocity is a much more sensitive test than plate dent. In addition, the digital readout of the velocity test is more accurate,

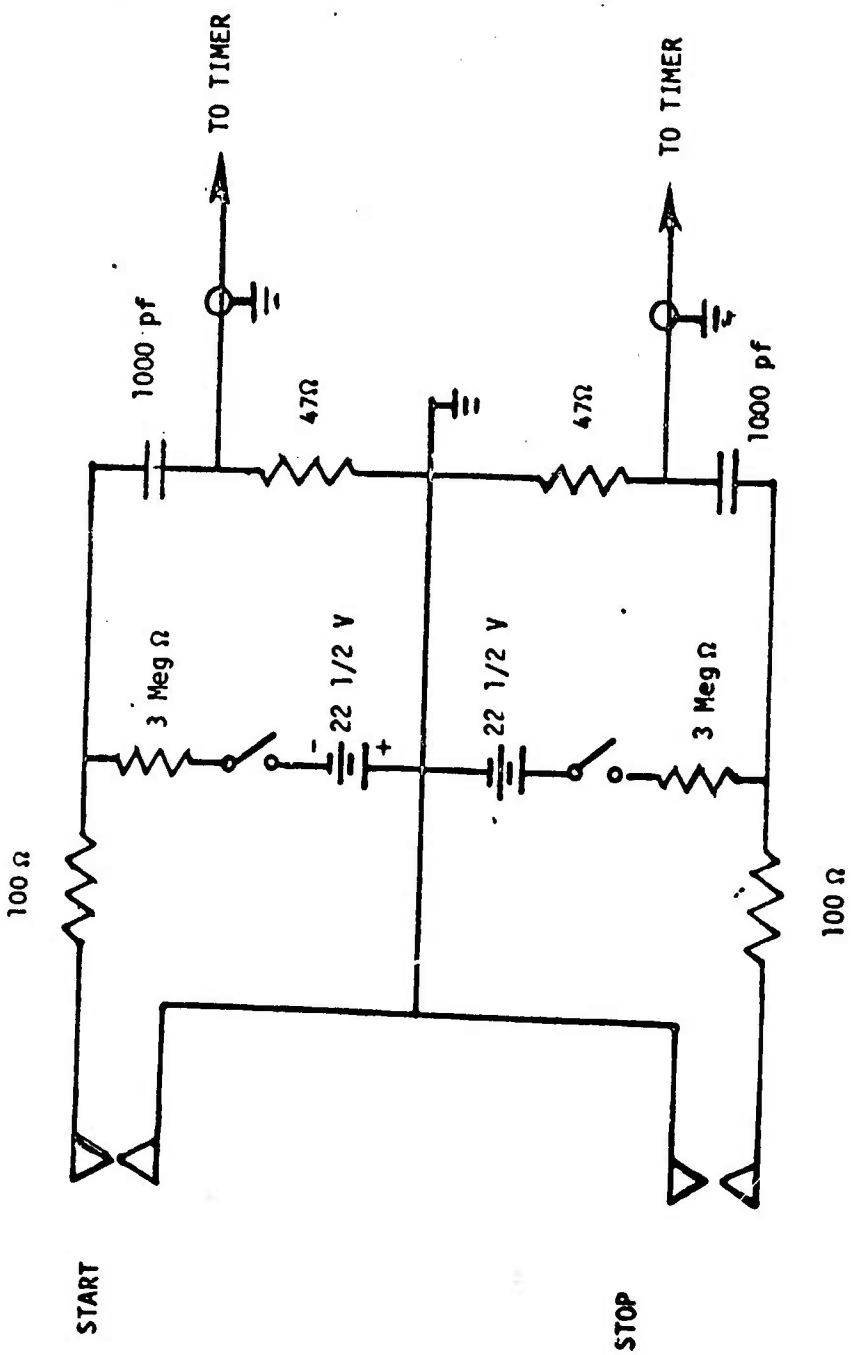


Fig 3 Start-stop pin switch circuit

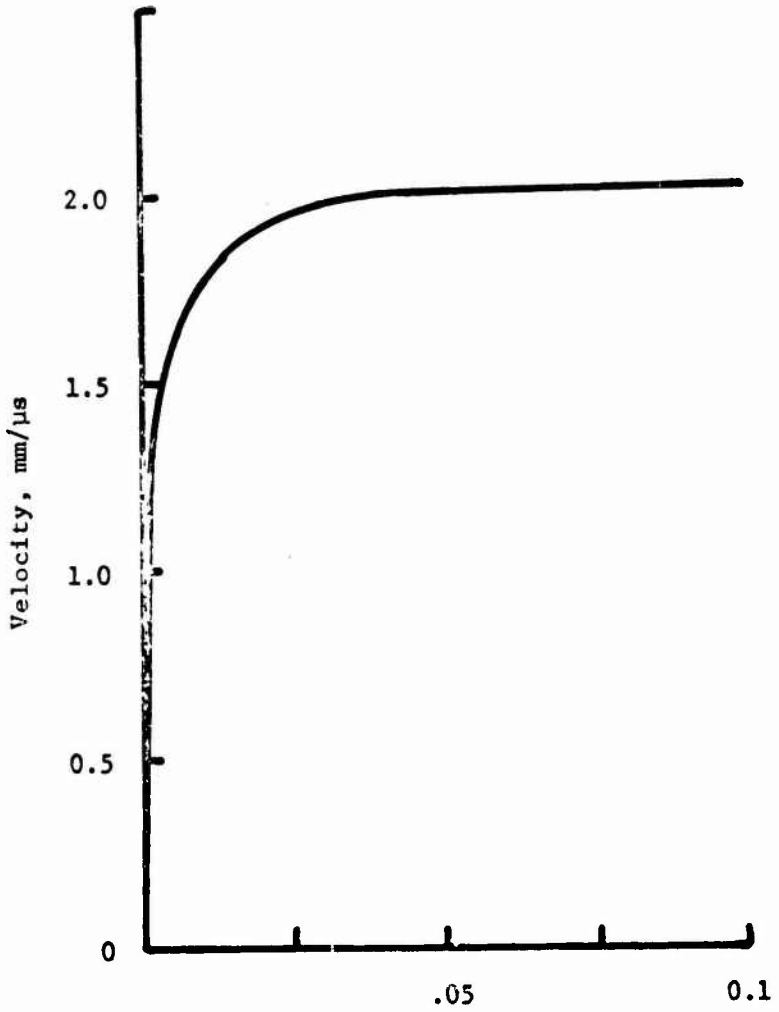


Fig 4 M55 Detonator calculated 5 mil flyer plate velocity vs distance

Distance 25mm



No Flyer



5 mil Flyer

Distance 10mm
No Flyer



Fig 5 M55 detonator fragment patterns

Table 1

Comparison of plate dent vs fragment velocity

Variable	Quantity	Plate dent fragment velocity mil N=200	Plate dent fragment velocity mm/μs n=10
Aluminum			
Foil Thickness			
(normal)	3 mil	18.1	3.76
	4 mil	17.9	3.67
	5 mil	17.7	3.48
	6 mil	17.9	3.33
	7 mil	17.9	3.23
	8 mil	17.0	3.04
	10 mil	17.1	2.69
RDX Quantity			
(normal)	19 mg	18.1	3.76
(low)	17 mg	13.2	3.34
(high)	23 mg	17.7	3.99
HMX vs. RDX	19 mg	18.3	3.74

easier to record for automatic data reduction, and more reproducible than plate dents due to their rough surface. This test method has been proposed for use in an automated measurement system for M55 detonators, but would be applicable to other detonators and leads as well.

The open sandwich form of the Gurney equation given in Table 2 correlates the observed velocities for M55 detonators quite well, and allows parameter studies to be made with less experimentation.

The thick plate form of the Stearn form of the Gurney equation gave low velocities, unless the quantity of explosive was increased by 10% to compensate for the lead azide, alternatively, $\sqrt{2E}$ could be increased. The thin plate form of the Gurney equation was closer to agreement without allowance for the azide, but velocities were still a little low. To investigate a wider range of C/M, steel flyer plates were placed over the output face of the detonators. A plot of the observed velocities for both aluminum and steel flyers vs the calculated Stearn velocity is shown in Figure 6. Fragment velocities for steel flyers could be checked by flash x-ray, and agreed well with the switch plate results, and the SIN-code calculations as shown in Figure 7.

A statistical study on a larger number of detonators was made, and the results are shown in Table 3. Again, the sensitivity of the test method was shown to be very good. A pooled standard deviation of 0.017 mm/μs for individual measurements was obtained. The standard deviation of the average of a number of tests is equal to the individual deviation quoted divided by the square root of the number of observations. Of course, some of the observed deviation is due to the detonators, in addition to the test method, so that no test method could produce a much smaller result.

The SIN-code output was then integrated to produce the total P^2t energy in the fragments, and compared to the observed kinetic energy in the aluminum flyer plates of varying thickness. Both results are shown in Figure 8, and indicate maximum energy in the fragments occurs with an 8 mil aluminum foil. However, tests where the transit time in lead cups were measured with a 0.04" to 0.1" gap between the detonator and the lead indicated that 3-4 mil flyers were optimum, because the blast hitting the booster before the fragments is more effective than the higher fragment energy, as shown in Figure 9 (Ref 2).

Fragment velocities of some other detonators were also measured and results are shown in Table 4. The apparent Gurney constants are also shown for the Stearn equation. The different value for $\sqrt{2E}$ for

Table 2

Open sandwich Gurney equation

M-55 Detonator Results

Aluminum, mil	RDX, mg	Fragment Velocity, mm/μs		
		Thick Plate Calculated	Observed	Thin Plate Calculated
3	23	3.87	3.99	
3	19	3.71	3.74	3.70
3	17	3.61	3.38	
4	19	3.58	3.67	3.49
5	19	3.40	3.48	3.31
6	19	3.25	3.33	3.14
7	19	3.21	3.23	2.93
8	19	3.04	3.04	2.86
10	19	2.75	2.69	2.64

Table 2 (continued)

EFFECT OF ADDED FLYER PLATES

Flyer, mil			Fragment Velocity, mm/μs			
Aluminum	Steel	Mylar	Observed	Calculated by Stearn (1)	Calculated by SIN (2)	Calculated by Gurney (3)
3	0	0	4.06	3.93		
3	0	2	3.74	3.69	3.96	3.70
3	1	2	3.17	3.16	3.18	3.17
3	2	2	2.89	2.77	2.82	2.78
3	3	2	2.49	2.48	2.42	2.48
3	4	2	2.37	2.24		2.24
3	5	2	2.09	2.04	2.07	2.05
3	6	2	1.95	1.88		1.89
3	12½	2	1.18	1.25	1.23	1.25

(1) Stern $V_f = \sqrt{2E}\sqrt{\frac{1+5\left(\frac{M}{C}\right)+4\left(\frac{M}{C}\right)^2}{3}}$, $\sqrt{2E}$ = 2.83 for RDX, C increased 10% (to account for azide).

(2) RDX column height reduced from 56 mil to 51 mil (to compensate for radial losses).

(3) Gurney $V_f = \sqrt{2E}\sqrt{\frac{\left(1+2\frac{M}{C}\right)^3+1}{6\left(1+\frac{M}{C}\right)}+\frac{M}{C}}$

Table 3

M55 Detonator statistical study

Variable	Average mm/μs*	Standard Deviation of Mean mm/μs	Remarks
High RDX	3.89	0.016	23 mg RDX
Low RDX	3.31	0.033	17 mg RDX
High Density	3.88	0.018	(40K PSI) 1.72 gm/cc
Normal	3.75	0.017	Lone Star 1.67 gm/cc
Normal	3.74	0.041**	Lone Star
Normal	3.74	0.010	Kansas
Normal	3.73	0.012	Kansas
Normal	3.69	0.017	Iowa

* Average of 85-95 measurements.

** Changed operators, believed due to a change in flight distance.

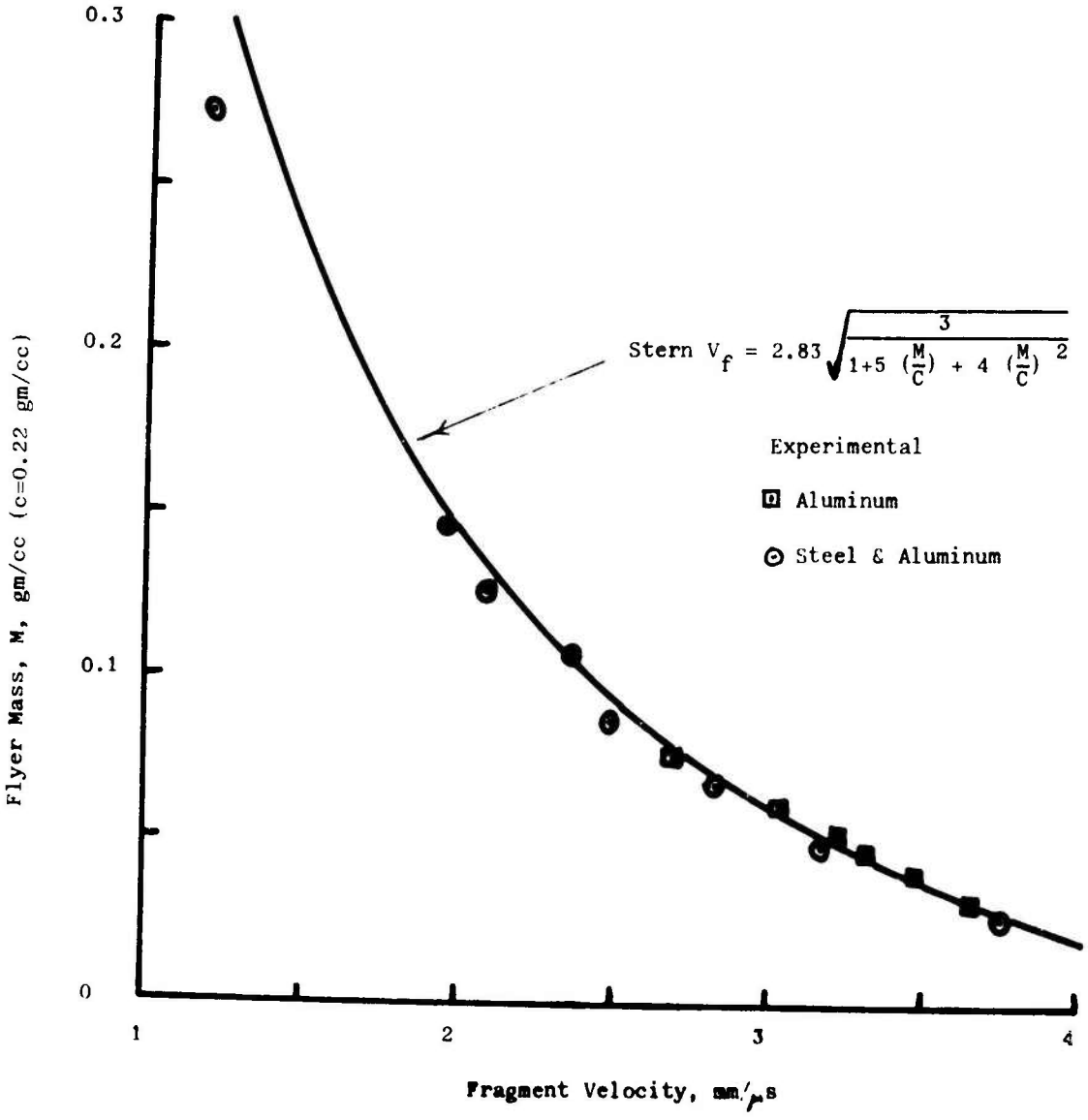


Fig 6 M55 detonator fragment velocities

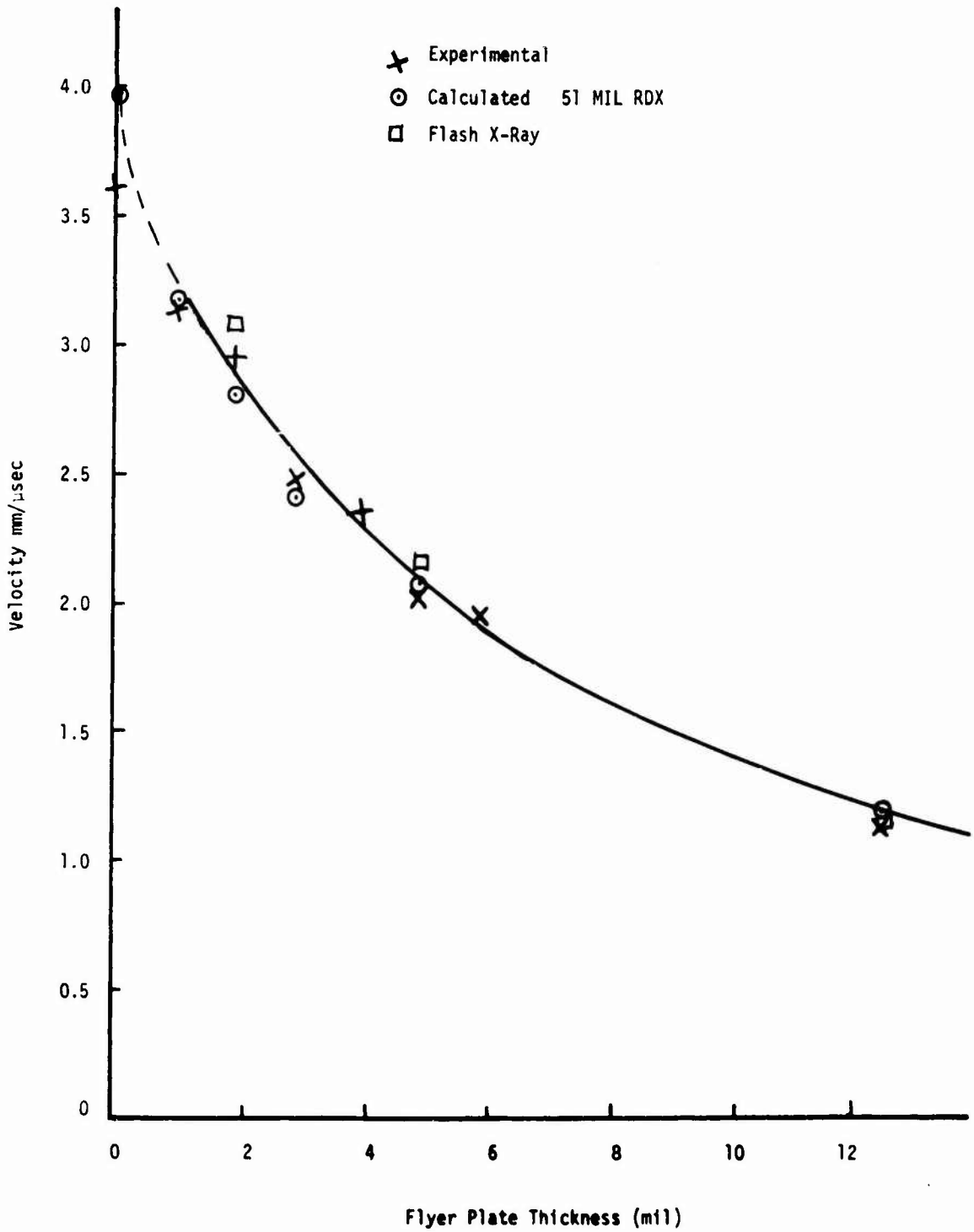


Fig 7 Effect of flyer thickness

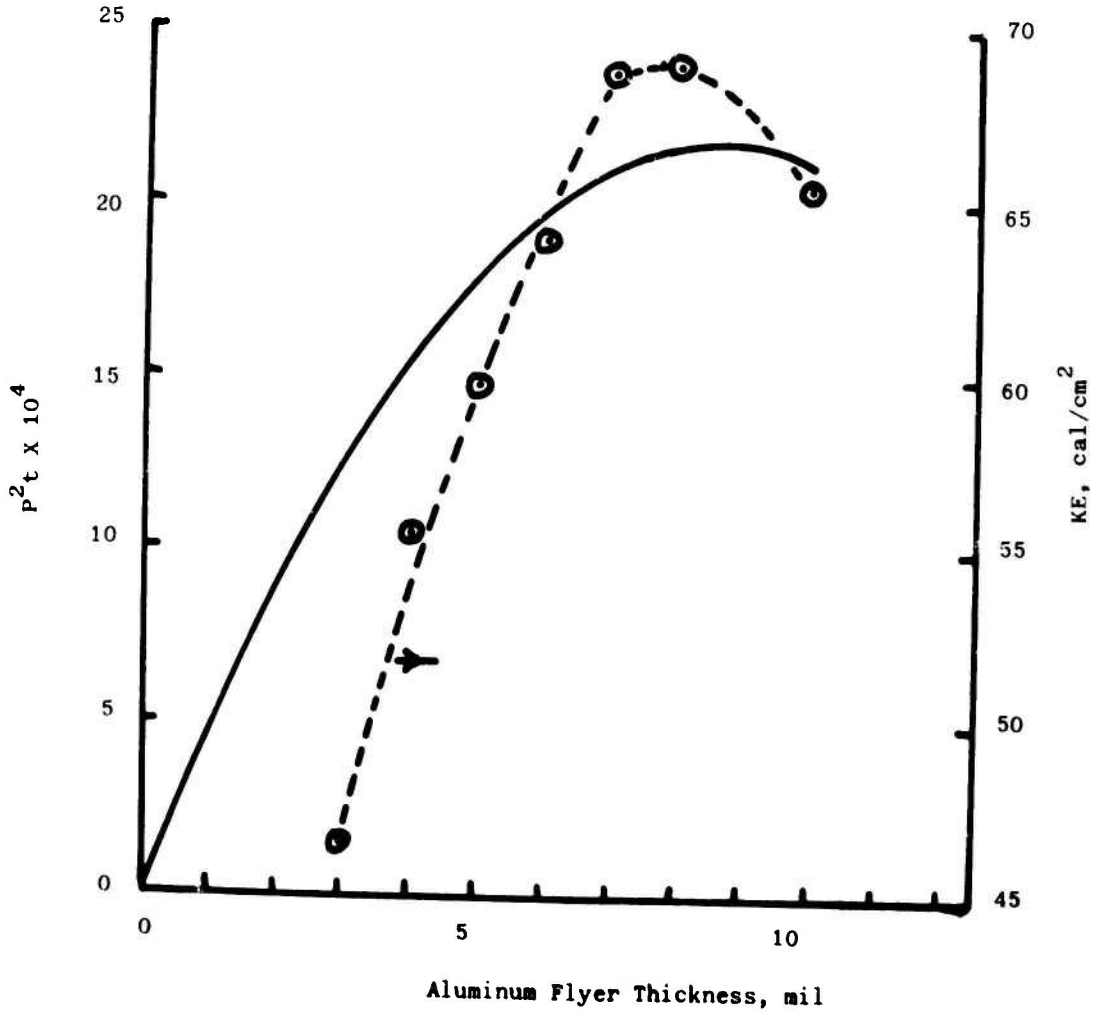


Fig 8 Peak energy into RDX with aluminum flyers

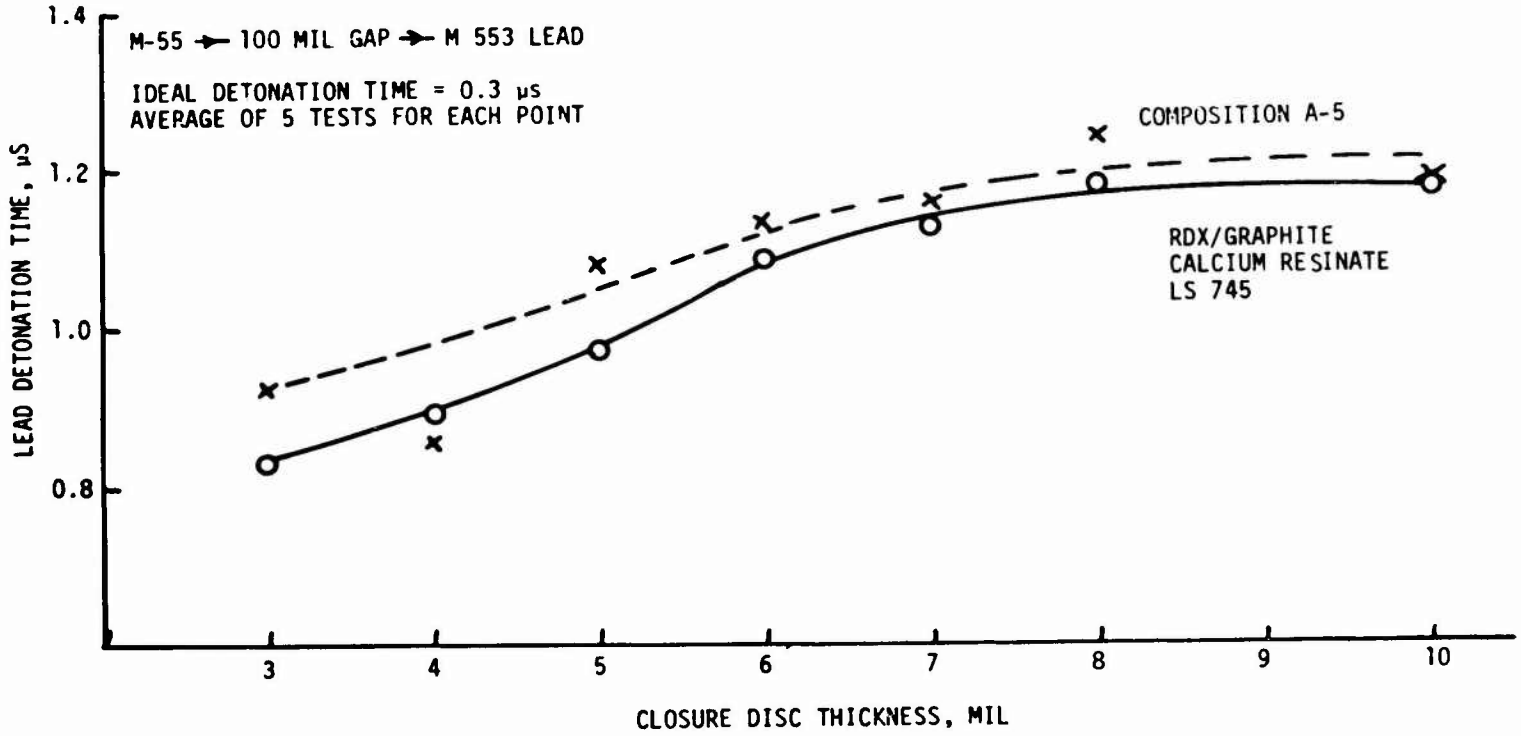


Fig 9 Effect of closure disc thickness on acceptor transit time

Table 4

Fragment velocities of other detonators

Type	Explosive Type, mg	Flyer Type	Thickness, mil	Velocity mm/μs	Standard Deviation	$\sqrt{2E}$
M-55	RDX 19	Aluminum	3	3.69	0.017	2.83
M-42	Tetryl 210	Copper	10	2.73 (2.78)*	0.175	2.55
M-63	RDX 64	Copper	10	2.33 (2.40)*	0.146	2.35
M-7	Dex. L. A. 100	Aluminum	10	1.41	0.096	1.45#

* Flash X-ray velocity.

At 3.0 gm/cc.

RDX for the M63 detonator indicates that factors such as confinement column length to diameter, and flyer materiel make it desirable to determine $\sqrt{2E}$ experimentally when possible.

CONCLUSIONS

Fragment velocity measurement is a more accurate and faster measurement method for detonator output than plate dents. It is currently being used for research and development, and should be included in future specifications for quality control. It is adaptable to high speed automatic testing, which will be needed for plant modernization.

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