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AD-A238 923

NWSC/CR/RDTR-595

SURVEY OF MILITARY PYROTECHNICS

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A-1

24 MAY 1991

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PREPARED FOR:

COMMANDER
NAVAL AIR SYSTEMS COMMAND
WASHINGTON, DC 20361-5404

91-06001

REPORT DOCUMENTATION PAGE

Form Approved
OMB No 0704-0188

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE
24 MAY 91

3. REPORT TYPE AND DATES COVERED
FINAL

4. TITLE AND SUBTITLE
SURVEY OF MILITARY PYROTECHNICS

5. FUNDING NUMBERS

6. AUTHOR(S)
DR. BERNARD E. DOUDA

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
NAVAL WEAPONS SUPPORT CENTER
ORDNANCE ENGINEERING DEPARTMENT
CRANE, IN 47522-5050

8. PERFORMING ORGANIZATION REPORT NUMBER
NWSC/CR/RDTR-595

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
COMMANDER
NAVAL AIR SYSTEMS COMMAND
WASHINGTON, DC 20361-5404

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
PREPARED FOR PRESENTATION AT THE 16TH INTERNATIONAL PYROTECHNICS SEMINAR, JONKOPING, SWEDEN, 24-28 JULY 1991. I0511/07A

12a. DISTRIBUTION/AVAILABILITY STATEMENT
APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

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14. SUBJECT TERMS
PYROTECHNICS

15. NUMBER OF PAGES
41

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

SURVEY OF MILITARY PYROTECHNICS

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ABSTRACT

About twenty-five activities from fourteen different countries contributed information about ongoing pyrotechnic projects and concerns. This information is summarized to provide an idea of the type and scope of the work underway. Although the survey is not exhaustive, an overall impression can be formed to indicate the focus and thrust of the pyrotechnic efforts.

A major concern expressed by the contributors is the environment, health, and safety associated with pyrotechnics. Governmental regulations have emphasized the ecological, toxicological, and safety aspects of pyrotechnics. This encouraged many of the countries to become involved in development of insensitive pyrotechnics to increase the margin of safety associated with these devices. With respect to health, the toxicology of heavy metals, hexavalent elements, and battlefield smoke and aerosols is being evaluated. Efforts are being directed to replace chromates in delays and to find replacements for hexachloroethane smokes to reduce human exposure to these health threatening materials. Environmental conditions related to the production of pyrotechnics as well as their eventual disposal through the demilitarization process are also addressed. Major projects are reported which deal with ecologically acceptable processes for demilitarization and disposal of all categories of pyrotechnics.

New equipment for preparing pyrotechnic compositions is reported. The focus of these efforts is not only to achieve homogeneous mixtures but also to improve the safety of the process. For example, a fluid-bed machine for blending, granulating, and drying is described in which a large number of different pyrotechnic mixtures have been processed. A twin-screw extruder is being evaluated for infrared composition processing. A disc granulator is under evaluation for processing compositions such as boron-potassium nitrate.

To a large degree, reliability and safety are the motivation for considerable effort in the study of laser ignition of pyrotechnics. Both diode and gas lasers are being evaluated to initiate combustion of compositions such as zirconium-potassium perchlorate, boron-potassium nitrate, and titanium subhydride-potassium perchlorate. A number of ignition research projects emphasize ignition theory in general as well as the determination of mechanisms directly related to laser ignition.

Several projects are reported which deal with infrared decoy flares. Research on and simulation of the combustion process is being conducted. An air-gun is described which is used to ground test the performance of flares in flight in order to simulate some of the dynamic parameters associated with the launch of a decoy from an aircraft. A number of agencies report development of improved decoy devices designed to deal with advanced infrared threats. A decoy simulator for training use is reported.

There are a substantial number of projects which address a special or peculiar problem. Some examples are work to understand and improve whistle compositions, development of riot control and explosive ordnance disposal devices, degradation and stability studies, training device and simulator development, evaluation of coatings for ingredients, development of a hydrogen burn-off igniter, and development of a non-toxic training smoke/obscurant.

INTRODUCTION

Dr. Jan Hansson suggested the preparation of this paper as an Overview or Survey of Military Pyrotechnics. To meet the objectives of such an effort, it was immediately apparent that the scope would need to be limited. First, there would be a presentation time and publication space limitation. Secondly, there would be sensitivity constraints related to some projects which could not be reported in this forum. Thirdly, the scope of this paper would need to be limited to information about energetic materials projects which were neither primarily explosive nor propellant in nature, consistent with the limited definition of pyrotechnics. And finally, in the preparation time available, it would not be possible to contact all pyrotechnicians worldwide in order to obtain contributions. Nevertheless, it was decided to compile as much information as could be made available within the stated constraints. The result is that projects could not be described in detail. All information was summarized. To compensate, references to published data were included quite liberally.

About twenty-five activities from fourteen different countries contributed information about ongoing pyrotechnic projects and concerns. These are presented herein by country in alphabetical order.

MILITARY VS CIVILIAN PYROTECHNICS

Except for one digression, no great effort will be made to show the strong relationship and similarity between the military and civilian pyrotechnics. However, it is worthy to recall that pyrotechnics is not a recent art or science. The Chinese, as Dr. Ding reminded us at the Fifteenth International Pyrotechnics Seminar, purified saltpeter about 300 AD, reported gunpowder not later than 850 AD and fireworks about 900 AD. Ever since that time, civilian pyrotechnics (fireworks) were used for personal pleasure and celebration.

One such event took place in Antwerp on 17 April 1635. A spectacular fireworks display was presented from the belfry of the Notre Dame Cathedral to celebrate the joyous entry of Prince-Cardinal Ferdinand of Austria, Governor of the Southern Netherlands. Figure 1 shows the event as recorded by Theodoor Van Thulden; painter, engraver and pupil of Peter Paul Rubens.[1] Without prior knowledge that this was a joyous occasion, one might imagine that the cathedral was on fire from a military action. Fortunately, this was not the case. The cathedral still stands in the center of Antwerp.

Figure 1: Fireworks from the belfry of Notre-Dame Cathedral in Antwerp, Belgium in 1635. Built around 1400. A copy of this engraving was graciously made available by Dr. Guy Hendrickx.

AUSTRALIA

CONTRIBUTOR: Mr. Leo DeYong, Materials Research Laboratory

Pyrotechnics work at the Materials Research Laboratory (MRL) may be broadly broken into three areas; namely materials, initiation systems, and device development. Descriptions of work in these areas follows.

MATERIALS

Delay Systems - The development of gasless delays opened up a new area of delay chemistry. But, although gasless delays are frequently used for many reasons they generally suffer from one major drawback - the oxidants are usually highly toxic. For example a common delay system comprises boron and barium chromate. Barium chromate is virtually insoluble in water and chromates, as a general class of chemical, cause severe health problems (it is a documented human carcinogen).

Several years ago MRL developed a low toxicity (no chemical is non toxic) delay composition based on boron and red iron oxide. This work has been further extended to look at a series of delays based on this fuel/oxidant combination (and variations with additives) with a reciprocal burn rate ranging from 0.4 to 4.0 seconds per centimeter. An added feature of those compositions is that they have excellent priming characteristics i.e., they are easily ignited without the use of a priming system.

Illuminating Flares - Illuminating flare compositions have been developed for two naval signal systems. Both compositions are designed to function under heavy sea conditions (up to sea state 6) and be visible at distances of up to 9km in daylight for up to 80 seconds. Flares have been developed based on the standard magnesium/sodium nitrate/binder formulation which achieved those requirements.

Smokes - Conventional white smokes contain zinc and hexachloroethane which form chlorides and oxides of zinc as reaction products; both of these are highly toxic. White smokes are used for fire fighting training in enclosed spaces which exacerbates the health problem. We have been looking at the development of new white smoke compositions based on terephthalic acid and cinnamic acid.

Smokes as obscurants may also be generated by fibres rather than as a chemical particulate. We have undertaken to participate in a collaborative program of work with laboratories in USA, UK and Canada to study the obscuration effect of fibres with particular emphasis in the millimetre waveband. This work includes not only the choice of the fibre, but also the dissemination of the fibres.

Primers - A gasless percussion primer developed at MRL several years ago based on boron, lead oxide and tetracene has caused problems in production due to poor flowability. This has entailed hand-filling of primer cups with resultant increased cost and reduced operator safety. A programme of work has been undertaken to improve the flowability of this composition whilst still retaining its performance and sensitivity. This involved granulation with a range of solvents, addition of binders and/or addition of flow modifier agents.

We also have a strong work program on the development of conducting composition caps for rapid fire weapon systems. Conducting composition caps have the advantage of enhanced electrical characteristics which enable them to pass stringent RADHAZ requirements. Currently conducting composition caps are being developed for the N43 primer.

Photoflash Compositions - Photoflash compositions based on magnesium or aluminum and potassium perchlorate (and a flow modifier) have often been used as a sound producing composition for battle effect simulators and for grenades for special forces. They also have application as a spotting charge for mortar rounds but this requires a higher filling density for efficiency reasons. Current work involves modification of the composition for application to 81mm mortar rounds. Solvent granulation and binder plus granulation modifications are being conducted to fulfill this requirement.

The use of this composition for special forces is less than ideal as the smoke signature produced is considered excessive. Work is ongoing to examine the effect of additives and changes in the oxidant and/or fuel to reduce the smoke signature to an acceptable level.

Magnesium Powder - Magnesium is one of the most common fuels used in pyrotechnic compositions. Although it has a high combustion temperature and large heat of combustion, it suffers from degradation on storage. Moisture readily attacks magnesium powder, generating hydrogen gas which presents a serious problem in sealed stores. The reaction decreases the amount of available magnesium thus reducing the efficiency and performance of the pyrotechnic composition. These effects are somewhat reduced by coating the magnesium powder with various organic binders but problems are still known to occur.

A program of work has been undertaken and recently completed in which the coating efficiency of several binder systems have been evaluated for magnesium powder. The success or otherwise of the coating was examined and evaluated using Scanning Electron Microscopy, Gas Evolution, Weight Changes, Surface Energy Analysis, FTIR and performance measurements of flares based on magnesium and sodium nitrate.

Thermites - Extensive evaluation of the MRL developed plastic thermite is being undertaken to determine its potential use for Explosive Ordnance Disposal (EOD) applications, particularly evaluation against both thick and thin cased munitions. At the same time, we are looking at new formulations for thermites based on the traditional Goldschmidt reaction and also novel intermetallic systems.

Insensitive Compositions - A program of work has been completed to examine the implications of the US Insensitive Munitions (IM) policy (and possible adoption of IM guidelines by the Australian defence forces) for pyrotechnic formulations. This has involved thermal analysis of a range of compositions (DSC, DTA, TGA) and assessment of the response of compositions to both fast and slow heating rates. This has concentrated on the use of the SSCB (Super Small Scale Cookoff Bomb) and the RARDE cookoff bomb, both of which were developed for assessing the response of explosives to thermal stimuli.

IGNITION STUDIES

Laser Initiation - Work is underway to use high power lasers to initiate pyrotechnic compositions and to study the characteristics of both the laser and the pyrotechnic that are required for reliable and sustainable ignition. Work has initially focussed on the use of a 1kW carbon dioxide laser but further developments using laser diodes and fibre optics are planned.

Slapper Initiation - Many pyrotechnic and related explosive devices use direct initiation from electro-explosive devices. Most of these require protection from induced RF energy and electrostatic discharge. Slapper detonators are increasingly being seen as a means of achieving these requirements for high explosives. Slapper initiation of pyrotechnics could be a suitable initiation system for higher hazard pyrotechnics. Initial studies using 0.25mm flyer plates succeeded in initiating several low gas pyrotechnic compositions. Microscopic examination of the pellets of the pyrotechnics which failed to ignite showed evidence of ignition but failure of the reaction to propagate.

Infrared Compositions - This work involves the development of improved infrared decoy flare compositions and systems to protect both aircraft and naval vessels from advanced infrared guided missiles. The specific work involves enhancing the performance of flares operating in the 3μm - 5μm region by the production of specific molecular emitters. Similar work is being undertaken in the 8μm - 14μm region. Included in this work is an extensive computer simulation exercise of the thermochemistry of flare combustion.

DEVICE DEVELOPMENT

Visual Mine Firing Indicator (VISEM) - Concepts for a visual mine indicator have been proposed for an exercise mine. VISEM is a device connected to a submerged mine which releases a pyrotechnic payload to provide an indication on the ocean surface that the mine has been "triggered" during an exercise. The visual output comprises both a colored smoke and a colored flare.

Thermite Torch - A thermite torch is being developed for use in Explosive Ordnance Disposal (EOD) applications. The torch has been engineered to provide an enhancing effect to the thermal output of the pyrotechnic payload which results in a better cutting action.

Marine Marker - A submarine launched marine marker has been developed at MRL over the last few years. The marker is launched to the surface from a submerged submarine and deploys either a parachute flare or a surface payload comprising a flare, a smoke and a dye marker.

BELGIUM

CONTRIBUTOR: Dr. Guy Hendrickx, EUG. HENDRICKX, S.A.

PHOTOMETRIC TUNNEL VERSATILITY

All producers of military and/or commercial pyrotechnic devices require a test capability such as a photometric tunnel if light measurement is to be performed. A photometric tunnel, built primarily for measurement of the photometric output of pyrotechnic illuminating devices, is equipped with radiation measurement instruments. The structure, as well as its instrumentation, can be put to a variety of uses in addition to its primary function. This versatility and capability is an important asset for the producer. It allows static testing of various devices such as flares, signals, tracers, incendiaries, delays and igniters. These static tests are useful to simulate the much more expensive dynamic performance tests. In this way, complete round destructive testing can be minimized. Production variation can be monitored. As will be shown, while the data produced in the tunnel can be quite useful, careful analysis is always necessary before taking any conclusions.

Light measurement: Testing in a photometric tunnel is a widespread method to measure the output of a pyrotechnic flare, signal, tracer, etc. Unfortunately, no two photometric tunnels conform to the same standard. They differ in structural size, shape and materials and are equipped with differing measurement instruments. All presumably are calibrated to an absolute standard. Nevertheless, the measured output data from different tunnels do not always compare. To overcome this condition, correlation factors between tunnels are established to allow tunnel-to-tunnel comparisons. Sometimes, this also needs to be done for equipment-to-equipment comparison.

An example of tunnel-to-tunnel variation follows. The same Minolta photometer containing a silicon cell was used to measure the luminous intensity, in candela (cd), of 81mm HI mortar flares in three different tunnels. The following data, based on a limited sample size, show the RARDE, UK and MEPPEN, Germany tunnels to be comparable but that data from the Eugene Hendrickx Deurne (EHD), Belgium tunnel are somewhat less.

EHD Belgium	RARDE Fort Halstead, UK	BWB MEPPEN, Germany
816,052 cd	902,838 cd	865,873 cd
756,269	852,996	863,953
804,833	884,703	867,639

To show equipment-to-equipment comparability, the output from a 40mm illuminating flare was simultaneously measured in the Naval Weapons Support Center Crane (NWSCC) tunnel using NWSCC instruments and the Minolta photometer described previously. For a sample size of 10 units, the mean with the NWSCC instruments was 134,710 cd and with the Minolta was 126,650 cd, about a six percent difference.

A second experiment was conducted similar to the above but with a different flare, the MK 1 MOD 2 illuminating hand grenade, and a 15 unit sample size. The mean with the NWSCC instruments was 134,900 cd and with the Minolta was 123,890 cd, about an eight percent difference.

The MEPPEN equipment was compared to the Minolta in the BWB MEPPEN tunnel. The flares were 81mm mortar round units. Comparable data were observed as follows:

MEPPEN equipment	MINOLTA
818,000 cd	865,000 cd
833,000	863,000
832,000	867,000

When the same experiment was conducted at RARDE Fort Halstead, UK, the data observed were:

RARDE equipment	MINOLTA
762,000 cd	902,838 cd
734,000	852,996
750,000	884,803

The data from the RARDE equipment are about fifteen percent lower than those from the MINOLTA.

The above experiments and data serve to support the caution to interpret the data carefully. There are instrumental as well as tunnel differences which remain unexplained.

Other Tunnel Uses:

A. An example of other uses of the facility and the instrumentation is the testing of a base bleed igniter. When only the output curve shape is important, but not the light intensity, the igniter reaction time and burning time can be determined during static test using a photometer. Figures 2 and 3 are examples of the measured data of a base bleed igniter lit with a squib but not in the closed vessel bomb.

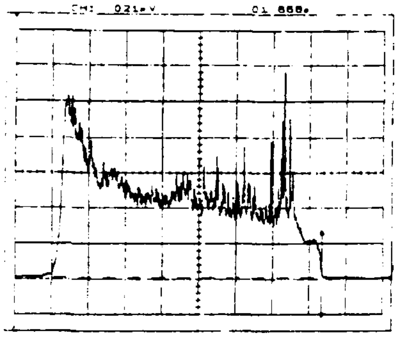

Figure 2: Igniter Output

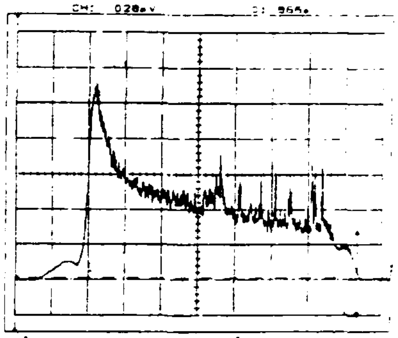

Figure 3: Igniter Output

The information can be submitted to additional statistical analysis to provide a better description of the igniter behavior and the production process. The base bleed igniter ingredients are barium peroxide, magnesium powder, aluminum powder, graphite, calcium resinate, and shellac. The latter three aid the granulation and pressing processes. Similar procedures are applied to determine performance of pyrotechnics such as tracers and rocket motor igniters.

B. To simulate dynamic firing and functioning of the base bleed igniter, the igniter is static fired in a closed vessel bomb as shown in Figure 4. A propellant powder, ignited inside the bomb, generates the pressure which simulates conditions inside the gun barrel. A rupture disc allows the internal pressure to develop to the desired value (≈2300 b). The igniter leads of a squib are fed through a small hole in the rupture disc. The squib and black powder ignite the propellant powder (≈175 g) which in turn ignites the base bleed igniter. A piezo-electric gage measures the pressure. Once again burning time is determined with the photometer. Figures 5 and 6 are examples of pressure-time curves of base bleed igniters.

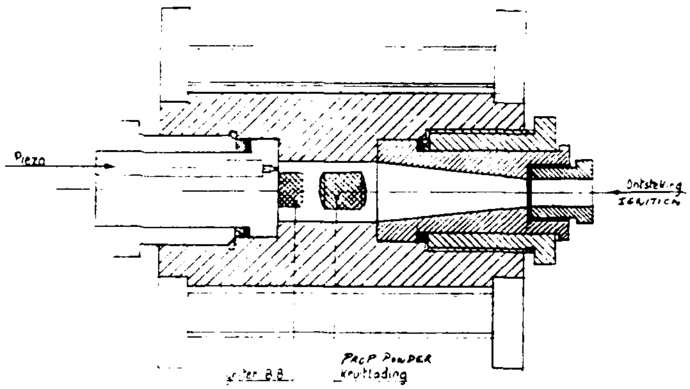

Figure 4: Closed vessel bomb.

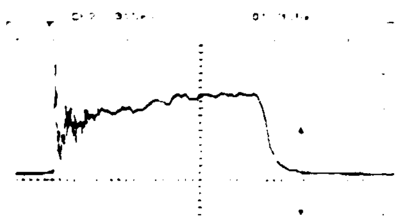

Figure 5: Pressure vs Time.

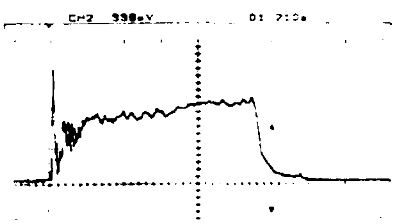

Figure 6: Pressure vs Time.

The pressure, combined with reaction time and burning time data, taken together, provide valuable information about the igniter performance. After analysis of the static data, these data are correlated with dynamic firing data. A good correlation provides assurance that the static tests are suitable for assessing the regularity in production and in functioning.

C. The same general procedures, facilities and equipment can be used to evaluate performance of rocket igniters, squibs, delays and related materials.

CANADA

CONTRIBUTOR: Mr. Guy Couture, Defence Research Establishment, Valcartier

SOME PYROTECHNICS AT DREV

MARINE LOCATION MARKER (Mr. D. Sanschagrin, principal investigator): Capable of producing both smoke and flame outputs, the marine location marker is a day and night device specially designed for marine operations including search and rescue, and anti-submarine warfare. This project was initiated at the Defence Research Establishment, Valcartier (DREV) to modify the current marker in the following four aspects to enhance its versatility and improve its performance. A fresh water battery was required to allow the marker to function in fresh water as well as sea water; a scuttling feature was required to prevent the markers from washing ashore; a new optimized smoke and flame formulation was introduced in the new marker; and finally the arming mechanism of the new marker had to be redesigned.

Fresh Water Battery: The original salt-water-activated battery was replaced by a new one, able to function also in fresh water. However, this new battery incorporated a cellulose separator which deteriorated after four years of storage. The electrolyte appears to attack the separator which turns brown and crumbles easily. For this reason, a new battery incorporating a polypropylene separator was introduced.

Smoke and Flame Formulation: The new marker contains a new patented C-55 smoke and flame formulation, containing Taktene, a polybutadiene binder. The new formulation is more rubbery and provides a better performance. It has a higher red phosphorus loading of 71 percent, compared to 51.5 percent for the current formulation. The formula is 71 percent red phosphorus, 15 percent sodium nitrate, 8 percent aluminum flakes, 1 percent calcium carbonate, 1 percent titanium isoproxide and 4 percent polybutadiene.

Arming Mechanism: Another major improvement over the current marker is the new reversible arming mechanism. It is based on the movement of a piston which, when rotated, is pushed out by a spring. Actual arming is obtained by further rotating the piston to establish the contact between the water activated battery and the squib. The battery is then fully exposed and the mechanism is locked in its armed position. Manually rotating the mechanism counterclockwise, returns the marker to the original safe.

Scuttling Feature: The scuttling capability was achieved by removing a fraction of the rigid foam, providing a ballast compartment that is filled by water through small openings of 0.5 mm in diameter made in the outside casing. These holes are permanently open and initiate the scuttling process as soon as the marker is immersed. This allows the marker sufficient time to function completely but also ensures scuttling of those that fail to ignite.

HIGH PERFORMANCE TRACER COMPOSITIONS (Mr. P. Brière, principal investigator) Over the years, DREV has acquired expertise in tracers and has built a tracer evaluation facility that allows the quantitative characterization of tracer compositions using high speed air turbines capable of spinning 7.62 mm and 5.56 mm bullets at 100,000 rpm and 300,000 rpm respectively. This computerized facility is equipped with a radiometer and a photometer to provide instant data reduction of the luminous intensity and energy of each round.

Major improvement to the luminous output of tracers has been obtained by various means. Laboratory measurements also confirmed the influence of factors such as the rotational speed and the orifice diameter of a bullet. The rotational speed has a significant effect on the burn rate and on the luminous efficiency of a tracer composition. In the case of 7.62 mm and 5.56 mm tracers, the luminous efficiency was observed to increase substantially above a certain speed and tend towards a maximum at the rifle-firing rotational speed.

The orifice diameter of a bullet is also a factor. A larger orifice gives a higher luminous efficiency. In the case of the 5.56 mm tracer, substantial trace intensity improvements were obtained by lessening the boat tail angle at the rear of the projectile. The required ballistic match of the tracer round with the ball round however limits the extent of this modification.

Formulation Improvements: With the acceptance of 5.56 mm ammunition as the NATO standard for small-arms ammunition, most tracer bullets are barely able to meet all user requirements. The physical size of the bullet, along with its high muzzle velocity, led to a relatively low brightness of the tracer bullet during flight. The development of improved tracer compositions, therefore, was initiated.

Previous work showed that a fluoroelastomeric binder produced tracer bullets with higher luminous output than those containing the standard carnuba wax. A further investigation of various polymers demonstrated that rubbers with a high fluorine content provided tracer compositions with the highest luminous output. This study also indicated the importance of the processing techniques used in the preparation of the compositions. Various processing methods were studied including dry processing, wet processing and a combination of both depending on the solubility of the binders. Kynar 9301, Viton A and Kynar 461 were used as they contain more than 60 percent by weight of fluorine; the Kynar 461 was used only in dry processes because it is not easily dissolved in common solvents. The best two methods were as follows. The first involves a dry process in which the magnesium is mixed with the binder in one step and the strontium nitrate is mixed with the magnesium carbonate as a separate premix; then both premixes are blended together. The second is a wet process in which only the magnesium powder is coated by the binder via a co-precipitation process. The polymer is dissolved in a solvent (acetone), adding the magnesium while stirring, then adding a nonsolvent (hexane) to cause precipitation of the polymer onto the magnesium. However, the best results are obtained when about half of the nonsolvent is added followed by the addition of the other ingredients while the binder is in a gel state. The precipitation is completed by adding the remaining nonsolvent. This technique allows complete coating of the magnesium powder and adhesion of the other solids to the gel surface.

Luminous intensities exceeding 3 times that of the standard Canadian 5.56 mm bullet were obtained with the new compositions. However, because of the high heat generated, a fairly large number of rounds became unstable at 550 m as a result of the deformation of the thin wall of the 5.56 mm bullet. Such compositions however should function properly in larger projectiles or bullets, offering thicker walls and lower rotational speeds. Further development led to optimized formulations containing a chlorinated rubber (Alloprene) as a cooling agent. The following BT-L252 formula is typical of the new compositions that are especially adapted for the 5.56 mm ammunition. It is 38.1 percent magnesium, 45.6 percent strontium nitrate, 4.7 percent magnesium carbonate, 1.9 percent shellac, 6.0 percent chlorinated rubber and 3.7 percent Viton A binder. Some tracer characteristics are:

Attribute	BT-L-252	Canadian Standard
Specific Luminous Efficiency ($cd \bullet s \bullet g^{-1}$ at 270,000 rpm)	2526	915
Impact sensitivity (J)	10	15
Friction sensitivity (N)	160	160
Heat of combustion (cal/g)	2331	179
Temp. of ignition (°C)	618	568

CASTABLE WHITE SMOKE POTS (Mr. Guy Couture, principal investigator) The objective of this project was to design and develop a family of castable white smoke pots of various durations, incorporating as much as possible available hardware from current devices and producing a reduced toxicity white screening smoke. Three- and five-minute durations were selected for the first phase of that program as it was thought that minor modifications could turn a three minute smoke pot into a five minute one and vice versa, both being of the same dimension and using the same ignition train.

Design: The prototype design of a five-minute smoke pot contains 1.2 kg of a castable composition. It uses a firing mechanism and ignition train whose efficiency has been demonstrated in current stores such as colored hand smoke grenades.

Characterization of combustion products: To identify predominant reaction products and to assess the health effects of the compounds, five-minute smoke pots were submitted to a contractor for an environmental evaluation. The following optimized smoke compositions were selected for the evaluations.

Ingredients	Main Comp. % of Weight	Ignition Comp. % of Weight
Cinnamic acid	50	34
Potassium Chlorate	23	35
Sucrose	6	9
Iron Oxide	1	2
Binder (HTPB-IDP-DDI)	20	20

A smoke sampling technique was adapted from standard methods used to measure the pollutant emission rates from flue gas and involves continuous analysis of combustion gases (CO, CO_2, O_2, SO_2, NO_x) and total hydrocarbons.

The following table shows the components released from a five minute smoke pot.

Component	Total Amount Released (g)
Particulate Material	143
Sulfuric Acid	8.79
Hydrogen Bromide	ND
Hydrogen Chloride	6.15
Hydrogen Fluoride	0.01
Nitric Acid	2.04
Nitrous Acid	ND
Phosphoric Acid	0.01
Styrene	4.87
Benzaldehyde	1.97
Phenols and Cresols	1.05
Chloroethenyl Benzenes	1.13
Aliphatic Hydrocarbons	26.96

PAH's	8.90
Cinnamic Acid	30.11
Other Oxygenated Hydrocarbons	14.32
Hydrogen Cyanide	0.07
Ammonia	0.20
Potassium	6.71
Iron	0.60
Calcium	0.19
Zinc	0.14
Silicon	0.11
Tin	0.05

At first sight, the components of most concern are potassium, hydrogen chloride, sulfuric acid, ammonia, tin, calcium, nickel and nitric acid. It should be noted, however, that sulfuric acid seems abnormally high and this is being re-examined during additional evaluations. Chlorinated aromatic compounds, such as dioxins and furans will be considered since these components are found during relatively low temperature combustion processes involving organic components and chlorine. Finally the health effect of the compounds will be assessed. A field dispersion model will be developed to predict smoke concentrations at various distances from the source and to assess the risks for the users.

FRANCE

COMPOSITION DEGRADATION

CONTRIBUTOR: ICA J.-C. DEPEIGNE, GERPy

The main subject of recent activities at Group d'Etudes et Reserches de Pyrotechnie (GERPy) has concerned the degradation of munitions due to their ageing. For a number of years, extensive studies have been performed on the behavior in time of nitrocellulose based gun propellants. Results of these studies have permitted development of new tests to allow a better classification of the powders (calorimetry, chemiluminescence). On the other hand, the effects of moisture on munition degradation mechanisms are now being taken into account, especially by the elaboration of a code based on a mathematical model.[2,3] It is expected that after correlation with experimental results, this code will allow an improvement of life duration determination for pyrotechnics devices under moisture attack.

SOME PYROTECHNIC PROJECTS AT SNPE

CONTRIBUTORS: M. J.-P. BRIGNOLLE and M^{me} E. SOULETIS, SNPE

In the area of ordnance pyrotechnics, there is an effort to examine laser initiation to obtain functioning (ignition) times of less than 50 ns. SNPE is using its knowledge and formulation capabilities to establish a new secondary explosive which meets not only the safety but also the low-level laser initiation requirements which are consistent with accepted transmission train concepts. SNPE is developing a short functioning time combustion to detonation transition booster, loaded with a secondary explosive, which is adaptable to different inputs such as from a laser/optical fiber, shock tubes, etc. A wide range of delays can be incorporated into the device.

SNPE is also developing submunition ejection systems based mainly on propellant gas generator and air-bag technologies. These projects take advantage of the solid propellant grain expertise at SNPE.

A third pyrotechnic project area is infrared countermeasures. In order to improve low detectability, increasing stealth, decreasing probability of reaching fighting platforms after detection, reducing damage due to war hazard, and survivability, SNPE uses its knowledge and its formulation capabilities to study, develop and manufacture conventional and advanced infrared countermeasure concepts such as: adapted trajectory decoys, infrared adapted signature decoys and infrared/electromagnetic coupled products.

GERMANY

CONTRIBUTOR: Dr. Uwe Krone, NICO-PYROTECHNIK

GERMAN PYROTECHNICS INDUSTRY

General: In Germany, the expression "Pyrotechnik" includes only pure pyrotechnic applications. These are fireworks (toy and display), pyro-ammunition (signalling, simulating and training devices operating mainly with pyrotechnic compositions), smoke ammunition [hexachloroethane (HC); NICO-TRITTAU/smoke (NT); potassium nitrate/magnesium (KM); red phosphorous (RP) and related mixtures] and technical devices such as air-bags, tracers, delays and a variety of smoke and smoulder devices for different purposes. "Pyrotechnik" does not include priming caps, propellants, primary or secondary explosives.

In Germany, old traditional fireworks factories are still in operation but are decreasing from decade to decade. Plants with a well known name and with only fireworks production (mainly display but toy also) are WECO, PIEPENBROCK PYROTECHNIK GmbH (formerly MOOG-NICO), OSKAR LUNIG, ZINK and SAUER. Plants having both, military/technical and fireworks production are today of course NICO, PIEPENBROCK PYROTECHNIK GmbH (formerly FEISTEL), COMET, and BUCK, the latter only in the military/technical field. From the former GDR, 2 or 3 rearranged plants, with so far unclear relationships to the above-mentioned factories, are moving in. These are SIBERHUTTE, RIESA, and SACHSENFEUERWERK.

The main fields of research, development and production of the second group of pyrotechnic plants in Germany are the following:

NICO: 1. Smoke devices for screening and signalling, e.g., the first training smoke (KM) having passed the tests (OECD-guidelines)[4] for environmental compatibility; HC-, NT- and infrared (IR) smokes for screening. 2. Subcalibre training ammunition for all anti-tank weapons and for mortars for all calibers (introduced in the US-Army). 3. Signalling and illuminating 26.5 and 40mm cartridges and tracers for tank ammunition. 4. Fireworks.

PIEPENBROCK PYROTECHNIK GmbH (formerly FEISTEL): 1. Signalling and illuminating 26.5 and 40mm cartridges. 2. Training and simulating devices. 3. Fireworks.

COMET: 1. Training and simulating devices. 2. Signalling and illuminating 26.5 and 40mm cartridges. 3. Fireworks.

BUCK: 1. Smokes for screening (RP, HC). 2. IR-decoys. 3. Incendiary devices. 4. Demilitarization of pyro-ammunition.

There are also some pyrotechnic activities in plants like MBB, DYNAMIT NOBEL, DIEHL and BAYERN CHEMIE which are however mainly engaged in explosives and the like.

ENVIRONMENTAL AND HEALTH CONSIDERATIONS

The main field of research in Germany these days, as regards to our industry, is to find pyrotechnic compositions or reactions which are able to replace toxic and environmentally no longer acceptable pyrotechnic ammunitions like e.g., hexachloroethane (HC) or phosphorous smokes, heavy metals containing compositions or devices which contain halogenated hydrocarbons or deliver aerosols with dyes or organic compounds with a proven or estimated health risk. Since February 1990, there is a federal law in Germany which forces every new chemical or chemical mixture before being allowed on the market to undergo environmental compatibility evaluations following the relevant OECD[4] guidelines. This obligatory testing procedure is a mix of toxicity tests regarding the aquatic, soil and aerial life of our environment. Due to this, new developments of pyro-ammunition for our armed forces will be adopted at least only if the life cycle is known and methods are tested (and offered with the tender) to recycle and/or dispose of the materials properly and in accordance with the law.

This effort must be seen especially with regards to the 300,000 tons of ammunition of all kinds of the former GDR-Army and the additional 400,000 - 600,000 tons (!) of ammunition the Soviets are going to leave here. It is obvious, that for the next two or three decades the German military industry will be more engaged in destroying and demilitarizing ammunition rather than producing it. You may imagine how these tasks now are taking over our development technology centers.

NONTOXIC SMOKE SCREEN

An example of a pyrotechnic mixture for producing a nontoxic smoke for screening which was developed by NICO is made from 15% magnesium, 30% potassium nitrate, 15% calcium carbonate, 32% potassium chloride and 8% azodicarbonamide.[5,6,7] This smoke producing composition provides a smoke screen which is particularly suitable for training purposes. The smoke is composed of a nontoxic aerosol which is unable to produce a toxic effect on humans and animals and is compatible with the environment. The smoke from the above formula is primarily composed of macronutrients suitable for plants.

ISRAEL

CONTRIBUTOR: Dr. Arie Peretz

PYROTECHNICS AT RAFAEL

Most pyrotechnic Research, Development and Production activities in RAFAEL-Armament Development Authority (ADA) take place in RAFAEL's Electro-Explosive Device Center, which is a part of the Weapon Systems Division. The Center offers comprehensive services ranging from research, design and development to production, testing and delivery of advanced pyrotechnic products. The activities rely on well equipped laboratories for thermochemical and thermal analysis (with emphasis on calorimetry and TGA/DTA) of pyrotechnic compositions, as well as chemical and ballistic testing facilities for pyrotechnic compositions and items. In addition, use is made of the broad infrastructure of RAFAEL. Besides high-quality-control production (99.9% reliability at 95% confidence level), development of modern nonconventional pyrotechnic items is emphasized.

Typical products of the EED Center are: a. Squibs and initiators (conventional-size and miniaturized), b. Pressure cartridges of various sizes, c. Gas generators, d. Igniters for various rocket motors, e. Pyrotechnic delays, f. Special ignition formulations, g. Pyrotechnic smoke compositions, h. Explosive bolts and cable cutters, i. Through-bulkhead initiators (TBIs) and j. Pyrotechnic compositions and devices for simulation of various military events.

The finished products undergo simulated environmental tests in RAFAEL's most advanced testing facilities All products are tested and qualified according to the latest U.S. Mil. Standards.

JAPAN

CONTRIBUTOR: Dr. Naminosuke Kubota, Japan Defense Agency

COMBUSTION OF BORON/POTASSIUM NITRATE

Ingredients for rocket igniters and pyrotechnics are of continuing interest. Specifically, the reaction process of boron (B) with potassium nitrate (PN) is under investigation. A thermochemical analysis of the composition was conducted. The oxidation temperatures and rate of oxidation were examined as a function of particle size and weight fraction of the boron mixed within the B/PN mixture. Yano[8] observed that the oxidation of boron starts from the surface of each boron particle and forms an oxide shell around the surface. This prevents penetration of the oxidizer through the oxide shell toward the interior portion of the particle. For small particles (0.15μm), the oxidation reaction terminates when the thickness of the oxide shell is about 0.0041μm and for large particles (5.0μm), it is about 0.387μm.

Yano also observed that the reaction process consists of a three-stage gasification reaction. In the first stage, the mixture of B and liquified PN reacts to form KBO_2 and NO with significant heat evolution. In the second stage, the remaining PN decomposes to form gaseous oxidizers. In the third stage, the KBO_2 produced in the first stage starts to decompose and produces K_2O and B_2O_3.

Yano and Kubota[9] continued to study the thermochemical properties of B/PN and made burning rate measurements. The burning rate depends largely on the weight fraction of B in the mixture. At 60% and 80% boron, the burning rates are pressure insensitive below 100 kPa. At a pressure of 0.5 MPa, the burning rate reaches a maximum of about 38 mm/s for fine particle boron with weight fractions between 0.2 and 0.4 where stoichiometric is 0.25. For large sized boron, the burning rate is lower (maximum about 18 mm/s) than that of the small sized boron, but the rate characteristics appear to be the same, i.e., the weight fraction versus burning rate profiles are similar in shape.

They concluded that the burning rate is highly dependent on the weight fraction of boron and the particle size of boron at a constant pressure. In addition, the burning rate is dependent of pressure. Further extended experiments are planned in order to understand the detailed physicochemical process of the B/PN combustion.

SMOKELESS IGNITERS

In order to reduce the amount of smoke from a double base propellant when burned at low pressures below 3 MPa, one percent of metallic nickel (0.1μm in diameter) was added to the propellant grain. The nickel acts as a catalyst to promote the gas phase reaction of double base propellants at pressures below 2 MPa.[10]

The flameless burning stage becomes flame burning and the gas phase temperature increases. The catalytic action improves ignitability and reduces smoke generation due to more complete combustion. The catalyzed grains were compared directly to B/PN igniters, the latter exhibiting about four times as much smoke attenuation for a grain weight of 40 g.

CONCEPT AND THE USE OF NEGATIVE MIXTURES

CONTRIBUTOR: Dr. Takeo Shimizu, KOA Fireworks Co.

In 1986, the concept of "negative explosives" was introduced. These are mixtures of a fuel, such as magnesium, and a substance such as sulfates, oxides, carbonates, etc.[70] Whether or not a mixture is called negative or positive depends on the oxygen value. The latter is the amount of positive or negative oxygen in grams per 100 grams of mixture. When the fuel is mixed with a substance such as a nitrate, chlorate, perchlorate, etc., the mixture is generally a "positive explosive". This work showed that relatively inert substances such as oxides would act as active materials when mixed with fuels with a large reduction capacity, such as magnesium. Fifty types of negative mixtures were studied, including magnesium as the oxygen acceptor and water (H_2O) as the oxygen donor.

The concept to use water as the oxygen carrier was studied further.[71] A proposed application is a marine emergency flare. A mixture of 95% magnesium and 5% cryolite (Na_3AlF_6) is placed in a cardboard tube sealed by a 0.02mm vinyl chloride film. Ignition is with a fuse, the end of which is coated with four grams of a 92% lead oxide and 8% ferrosilicon mixture. Styrene foam 10mm cubes are mixed into the charge to make the item buoyant. The flare containing about one kilogram of the magnesium mixture is lit by the fuse and thrown into the water. The luminous intensity was 430,000 cd and the burning duration was 150 s. There is 24.7 kJ of heat produced for each gram of magnesium.

The oxygen values were studied of 59 mixtures with both positive and negative values to determine combustion effects. One purpose was to find mixtures suitable for use as a non-illuminating delay charge. The latter denotes a mixture that produces no visible flame or sparks when viewed from a distance.

It was determined that the following mixtures were best suited as non-illuminating charges for the transition layer of color-changing stars:

calcium nitrate	84%	86% (% by weight)
sulfur	8%	7%
Paulownia charcoal	8%	7%
oxygen value (g per 100 g of mixture)	+5.16	+9.47
combustion speed (mm/s)	2.8	2.2

It is not advisable to use these mixtures with paper tubes since a visible flame is formed because of the excess oxygen value. It is necessary to add some binding material such as rice starch to the transition layer. However, too much binder will result in too little oxygen to produce a visible flame.

PEOPLES REPUBLIC OF CHINA

CONTRIBUTOR: Professor DING, Jing

At the Fifteenth International Pyrotechnics Seminar,[11] Professor DING presented a paper on the discovery of "huo yao", gunpowder in China. The purification of saltpeter was reported about 300 A.D.; the gunpowder was used not later than 850 A.D., and fireworks about 900 A.D. The development of gunpowder was certainly one of medieval China's greatest achievements. Investigations of energetic materials have continued there throughout the ages.

In pyrotechnics and related technologies, current investigations include the a. study of properties of whistling compositions for use in military sound signal devices and in civilian fireworks, b. theoretical analysis of extinction efficiencies and coefficients of spherical particles for obscuration of visible and infrared radiation, and c. the development of failure rate equations for bridge wire ignition systems which take into account factors associated with degradation of performance.

HUANG and LI are continuing to study properties of whistling compositions.[12,13] They report that a combustion response function can be used as a characteristic parameter of whistling compositions. That function relates the formula and properties of the composition with the whistle frequency. While direct computation is not yet possible, they provide an experimental method to determine the function for mixtures of potassium hydrogen phthalate and potassium perchlorate (35:65) and for potassium benzoate and potassium perchlorate (30:70). Also see Öztap.[60]

LI and LAO are conducting theoretical analyses of spherical particles for the purpose of understanding their relationship to the maximum extinction coefficient and extinction efficiencies, K.[14] In terms of the extinction efficiency from Mie theory, they proposed a relative function K/x for practical analysis where x is the size parameter which is directly proportional to the radius and is inversely proportional to the incident wavelength. From their calculations, they report for a given material that there is an optimal particle size corresponding to the maximum extinction coefficient and that optimal particle size is always smaller than the size related to the peak value of the extinction efficiency. Their initial studies treated spherical particles formed from water droplets, carbon and iron powders. Their plans are to extend the studies to particles of other shapes.

For a bridge wire electric ignition system, SHEN and DAI reported static failure rate equations which relate the hygroscopicity of the composition, chemical compatibility and chemical corrosion.[15] They relate each of these to a failure rate for the system. The parameters of the static failure rate equations relate to manufacturing technology and the system structure. The equations have been compared to experimental results. Moisture absorbed in the ignition composition is the principal factor which causes the system to fail. The relative humidity of the composition is inversely proportional to the ignition temperature and ignition temperature rate of change. These data can be related to deterioration of the device during storage under varying conditions of temperature and humidity. It will be necessary to introduce other factors into the equations to treat ignition systems other than those with a bridge wire.

SOUTH AFRICA

CONTRIBUTOR: Mr. John Crewe, Swartklip Products (PTY) LTD

Military pyrotechnics in South Africa really began in 1971 when the Armaments Corporation of South Africa (Armscor) took over the Ronden Manufacturing Company, situated near Cape Town in what was then open country. This company had previously made some military products in addition to display fireworks and other commercial items but the facilities were very limited although the actual site was extensive. The new company was called Swartklip Products and the capital available enabled full utilization of the site, which now occupies 700 acres and provides employment for 1,000 people.

New buildings were erected in brick or reinforced concrete and plant and equipment were provided so that a wide range of products could be manufactured and tested, both in test houses and on a proving ground. Since the objective of the company is to provide pyrotechnics products to meet requirements by all three services the variety has been immense, especially as pyrotechnic sub-systems, such as tracers, are manufactured for other members of the Armscor group.

Meeting the requirements for new products has meant a high Research and Development effort with the emphasis very much on development. With South African forces being involved in combat duties it was often important that new items were available at short notice, but at least this also gave the opportunity for field evaluation. In order to use our research and development resources most usefully, work has been directed toward a. Enhancement of existing products, b. Technology transfer, c. Reproduction or modification of designs being used elsewhere, and d. Original designs where nothing suitable was known.

Since the opportunities for technology transfer have been very limited, we have been very involved in copying or adapting items already in use. However, because of unique environmental conditions and particular requirements dictated by the type of operation, we have been involved with a number of original designs - probably the most publicized South African military product is the 155mm gun system for which Swartklip Products manufactures a variety of carrier rounds. These are only superficially similar to rounds in use elsewhere and are the result of a major development effort especially as field-fitted base-bleed is a standard feature.

One area in which we have done a considerable amount of original work is in the formulation and manufacture of compositions containing red phosphorus. Previously white phosphorus had been used in a number of items for both smoke and incendiary use and we were anxious that it should be discontinued. The formulations developed fall into two categories:

a. Compositions which are rubbery in nature, such that they could be extruded and granulated. These can be made into discrete particles of controlled size and burning characteristics, which would normally be dispersed by detonation. Grenades and mortar bombs are being manufactured and, besides the uses already mentioned, we have found that they are being used as position markers.

b. Compositions which can be formed into precise geometric shapes but take on good mechanical properties such that they could be used in bombs and shells. Much attention was given good combustion properties but also to the problems of ensuring safety both in manufacture and use.

Swartklip has also been closely involved in manufacturing equipment for riot control. This has involved not only the development of non-lethal weaponry but also in techniques for disseminating lacrimatory agents. This is an area where there is considerable opportunity to apply new techniques to cope with civil unrest wherever it may occur. Currently efforts are being directed more towards commercial applications for pyrotechnics, ranging from conventional distress signals to new techniques for controlled blasting in quarries.

SWEDEN

CONTRIBUTOR: Dr. D. Loyd, Linkoping University and Institute of Technology; Linkoping

A method to analyze the burning rate of a slow-burning pyrotechnic delay composition is being developed. This composition is used to delay the ignition of, for example, an illuminating composition. Generally the delay of ignition is short and the burning rate of these delay compositions is very high. For such compositions (fast burning rate), the delay is mainly determined by the properties of the pyrotechnic compositions and by the geometry of the case. In this case, the heat transfer to the surrounding structure and fluid is of minor importance. On the other hand, for slow burning rate delay compositions, which are the subject of this research, the heat transfer from the compositions has great influence on the burning rate. The reaction products are mainly solids. The initial temperature, the heat flux transfer to the case and to the surrounding structure and fluid are of great importance for the burning rate of such compositions. It is thus necessary to include heat transfer in the calculation of the burning rate. The hardware design, containing the delay composition is complex. For these reasons, both experiment and numerical calculations are needed.[16]

Some of the properties of this slow-burning delay composition and its case are as follows. The heat of combustion of the pyrotechnical composition used in the test example is 2.15 MJ/kg and the ignition temperature 200°C. The density of the composition is 1600 kg/m^3, the specific heat 1600 J/kg•K, and the thermal conductivity 0.30 W/m•K. The heat of combustion corresponds to an energy of 72.9 J. The composition studied here does not melt before ignition and the composition gives mainly solid reaction products. The case and the housing are made of steel; density 7800 kg/m^3, specific heat 460 W•s/kg•K, and thermal conductivity 48 W/m•K.

The numerical calculations are based on the finite element method, FEM. The influence on the burning rate of the initial temperature, of the heat flux to the case, of the heat of combustion, and of the thermal properties of the composition is shown in a test example. See Figure 7. The example chosen is a slow-burning pyrotechnical delay composition used for delaying the ignition of illuminating compositions. The test equipment is designed to promote a large heat flux to the case and the surrounding material.

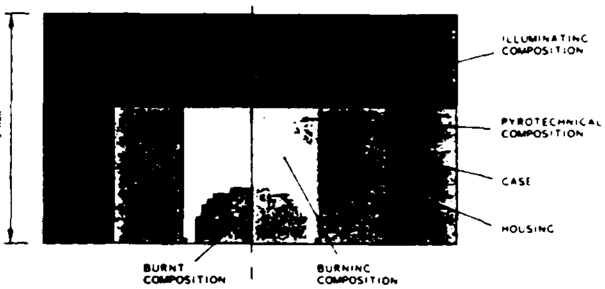

Figure 7. The extension of the reaction zone at time 8.0 seconds.

It is shown in reference 16 that the burning rate can be studied numerically with good agreement between calculation and experiment. The numerical result is also of great value for planning the laboratory experiments. A combination of computer experiments and laboratory experiments reduces the number of tests as well as the cost.

THE NETHERLANDS

CONTRIBUTOR: Dr. N. H. A. van Ham, Prins Maurits Laboratory

GRANULATION AND COATING OF PYROTECHNICS MIXTURES

Granulation: Some years ago, the Pyrotechnics section of the Prins Maurits Laboratory started a small research program in order to develop and build a disc granulator for the processing of pyrotechnic compositions. Efforts were put into the underlaying theory needed to understand and optimize the performance of the disc granulator. After this, a laboratory scale disc granulator was designed and built at the Prins Maurits Laboratory.

It was shown that pyrotechnic mixtures of solids with roughly the same particle size (although not too small, otherwise particles start to "stick" together) can be granulated with a suitable dissolved binder. It seems that boron/potassium nitrate mixtures can be granulated easily using Viton-A® (dissolved in acetone) as binder. The obtained granules showed a good homogeneity. The only disadvantage that occurred was the rather high porosity of the granules. More experiments are needed before detailed characteristics of this disc granulator can be given.

Coating: A pyrotechnical mixture is a suitable combination of reductor(s) and oxidizer(s). Quite often the reductors are reactive metals like magnesium, aluminum and boron. During storage these mixtures give rise to undesirable side reactions. The reactivity of these compositions can be decreased by coating the fuel.

The Pyrotechnics section of the Prins Maurits Laboratory has started a research program in order to gain some practical experience in coating techniques, to understand more about the mechanisms and to establish a suitable coating for especially magnesium. A coating should be: effective, firmly bonded, (relatively) environmental friendly and should not alter the burning characteristics.

The metals in pyrotechnic mixtures are mostly used as powdery materials, therefore, it is impossible to use the well known electrochemical reduction processes. The metal particles have to be coated in-situ; a so-called electroless plating process.

Satisfactory results have been obtained by using several methods. These are a. Non-catalytic displacement plating; a more noble metal (zinc) is being exchanged with magnesium at the surface of a magnesium particle, and b. Non-catalytic reduction plating; nickel ions are reduced at the magnesium surface with the aid of a suitable reduction-chemical.

The corrosion resistance and further characterization of these coatings is under examination at the moment. In addition, some efforts are directed towards finding a coating system for boron and aluminum.

UNITED KINGDOM

CONTRIBUTOR: Mr. James Queay, Royal Armament Research and Development Establishment, Fort Halstead

SOME PYROTECHNICS IN THE UK

The question is often asked of pyrotechnics "What is new in pyrotechnics, they have been around for 3000 years, there is nothing more to be learned?" The answer has to be "consider the requirements placed on the performance of pyrotechnics over the past 3000, 1000, 100 or even last 10 years". This is nowhere demonstrated better than in the defence area, for who would have thought 100 years ago that pyrotechnics would be functioning in the environs of space. The space shuttle contains some 135 applications for pyrotechnics in manual, emergency or mission abort functions. Also modern gun systems are very searching of pyrotechnic igniters. For instance considered the igniter for the extended range carrier shells.

<u>EXTENDED RANGE CARRIER SHELL</u>:[64] Artillery officers require that ammunition has an extended range and this can only be achieved by increasing the launch velocity or by reducing the drag during flight. Increases in launch velocity is unlikely. Future work on extended range shells will concentrate on reducing the retardation along the trajectory. When a shell is fired from a gun it first experiences high pressures in the breach but when it leaves the barrel, the pressure at the rear of the shell reduces to low values. It is this low pressure region which gives rise to base bleed drag. The means of overcoming base drag is to fit a base bleed unit which ejects hot gases of low molecular weight into the low pressure region thus reducing the base drag. Although the base bleed propellant can be ignited from the hot gases by the burning gun propellant, it is usually extinguished by the rapid pressure reduction at the base of the shell as it exits the barrel. A pyrotechnic igniter has been formulated capable of being ignited from the gun propellant and staying ignited through the rapid changes in pressure then finally igniting the base bleed propellant.

<u>IR COUNTERMEASURES</u>: The simplest answer to defeating a heat seeking missile is to use a flare which produced a point source of radiation greater than the target thus seducing the attacking missile. With the development of more sophisticated electronics in the missile head, a more sophisticated decoy is needed to counter the improvements. A missile head can be designed which is capable of distinguishing between the target and the decoy by considering the distance between them and if this is

increasing then it will ignore the decoy and continue towards the target. The obvious answer to this is to keep the decoy flying alongside the target until the missile is locked onto the decoy.

Two flare types are being investigated in this context, an aerodynamic flare and a propulsive flare. When a flare is deployed from an aircraft it becomes ballistically unstable, starts to tumble and rapidly loses speed. However, by weighting one end it becomes more aerodynamic and when deployed maintains target. A similar effect can be achieved by incorporating into the flare design a propellant which propels the flare in the direction of the aircraft.[65] The UK is currently trialling their own versions of propelled flares.

MODELLING OF FLARE PERFORMANCE: A model has been proposed[66] to predict the variation of radiant intensity with time for burning pyrotechnics and assumes that the radiant intensity at any time is proportional to the mass flow of composition which in turn is calculated in terms of the surface area of the pellet, the combustion rate and the efficiency of the composition radiating in any given waveband. The model has been expanded to give radiance values when the flare is subjected to different air speeds. Work has continued to refine the model as more experimental data becomes available.

SPONTANEOUS IGNITIONS OF IR FLARE COMPOSITIONS: Spontaneous ignition with magnesium/teflon/viton (MTV) compositions[67] continues despite much work to understand the problem. Studies of dielectric breakdown within small pellets has shown that breakdown occurs at relatively low field values and is a function of sample thickness. Application of a dc voltage across samples caused ignition at an energy of 20μJ, far lower than previously reported values. It has also been shown in samples of MTV compositions the formation of "trees" and that the formations of these "trees" enhances the susceptibility of materials to ignitability in electric fields. A theoretical capacitor model for dielectric breakdown with MTV compositions is under examination.

PRODUCTION OF PYROTECHNICS BY VAPOUR DEPOSITION: The manufacture of pyrotechnics systems by vapour deposition of materials onto substrates have been given at two previous seminars.[68,69] Two different manufacturing processes have been described. One is the continuous coating of magnesium onto polytetrafluoroethylene (PTFE) sheet. The second is the putting down of multi-layers of material to produce patterns in the same way as a printed circuit board. The coated magnesium/PTFE sheet is being investigated as a energy transfer medium in modular gun propellant systems to improve ignition and to replace the primed cambric. Initial results from trials are promising with improved times to reach maximum peak pressure being achieved. Most of the time since the last papers has been spent in procuring and installing new equipment which gives better control of the deposition process.

EXPLOSIVE CORDS: There are two types of explosive cord, disruptive and non-disruptive. Disruptive cards are used for cutting or breaking up munitions. One example is the use of miniature detonating cord (MDC) for disruption of an aircraft canopy when a pilot has to eject from his aircraft. Another example is the break-up unit fitted to missiles and munitions when they are test fired so that the trial can be aborted should the trial go wrong. A mitigation device has been designed based on disruptive detonating cord which can be attached to rocket motors whilst in storage. Should the motor then be involved in an accidental fire situation, at a prescribed temperature, the mitigation device is activated thus opening up the motor and reducing the risk of a catastrophic explosion.

Non-disruptive detonating cords have been used as time delays in warheads. An advantage is that explosive energy can be transferred from one explosive event to another, giving a required time delay. Another advantage is that the transfer of the explosive energy can take place within confined spaces without damage to the surrounding area which may contain sensitive components such as electronic equipment.

UNION OF SOVIET SOCIALIST REPUBLICS

CONTRIBUTOR: Professor Yu. V. Frolov

PYROTECHNICS IN THE USSR

In the USSR, anti-hail rockets have been developed ("Alazagne Crystal") which are designed to induce changes in clouds with the purpose of hail prevention. These rockets are characterized by the safety level of 0.9995, have high efficiency and use pyrotechnic compositions which ensure release of large amounts of active crystallization nuclei.

For the exploration of physical processes going on in the atmosphere of the earth, pyrotechnic systems have been worked out which permit the creation of artificial luminous and ionized clouds. The pyrotechnic devices can ensure the formation of one or several spherical clouds, of a long continuous or interrupted trace. The long continuous trace cloud consists of one reagent but gives the appearance of the other.

New systems of gaseous fire-extinguisher have been offered, these on the basis of pyrotechnic mixtures which generate technically pure nitrogen during combustion.

According to the requirements of the International Convention on People Salvation at Sea, in the Soviet Union a set of facilities has been developed and put into serial production - for sea boat equipment, which consists of firecrackers, sound and smoke rockets, luminous and luminous-smoke bobbers.

The Soviet industry has mastered the production of high-altitude night fireworks (105, 195 and 310 mm calibre) of more than 60 denominations. The fireworks broadly vary in colour, possess high characteristic colour purity, great safety and a lot of spectacle effects.

UNITED STATES OF AMERICA

CHEMICAL RESEARCH, DEVELOPMENT, AND ENGINEERING CENTER,
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CONTRIBUTOR: Mr. Joseph A. Domanico

SMOKE AND RELATED PROJECTS

A number of efforts are underway which utilize terephthalic acid as the smoke producing agent. The high interest in this material derives from its relative nontoxic property which may make it acceptable for use for both training and combat. Terephthalic acid along with a form of ammonium chloride are being evaluated as a screening agent replacement for hexachloroethane (HC) for use in combat and as a training variant.

Terephthalic acid in a special white smoke formulation is being developed for use in the Pyrotechnic Smoke Simulator, a training device. The unit produces high volume, high smoke density clouds. A terephthalic acid based smoke system is being developed to protect underground storage areas. The pyrotechnically generated smoke provides an instantaneous white cloud of long duration (hours).

Training versions of the 76mm self-protection grenades are also under development. The units are being filled with titanium dioxide and an explosive booster. These materials are expected to have a lesser environmental impact than the current load materials.

As a part of smoke materials technology base studies, an effort is currently underway to examine several candidate configurations to enhance the 2.75" rocket's screening capability. The current red phosphorous smoke warhead has been improved to prevent corrosion damage during long term storage and storage at elevated temperatures. Wafers containing a phosphine absorbing chemical are placed between the one quarter circle wedges and have been successful in preventing damage to the internal metal parts. Also, work is currently underway to improve the reliability of red phosphorous pellet ignition by means of a combination expulsion/ignition charge. However, several designs which were successful in igniting the pellets did not always meet safety requirements. Other solutions are being explored.

New materials are being investigated for use as signalling and marking smoke warheads for the 2.75" rocket. These materials must possess a unique signature on the battlefield, whether in size, shape, color, or wavelength. Screening smoke materials will provide smoke which will expand the U.S. Army's ability to screen increasing areas of the electromagnetic spectrum. Near infrared, mid-infrared, far-infrared, and beyond are some areas of interest.

A gap tester, of Australian design, is being evaluated to determine its ability to determine the sensitivity of certain pyrotechnic mixes to various thermal influences. By using this device, the best and most efficient ignition system can be developed along with new pyrotechnic smoke formulations. This device can not only be used to determine the actual pyrotechnic mixture to use, but also can be used to enhance the current knowledge in how the ignition train functions. This should result in a much shorter development time and higher initial choice reliability for the smoke/igniter system under development.

NAVAL ORDNANCE STATION, MD

CONTRIBUTOR: Mr. Frank J. Valenta

INTERMETALLIC COMPOSITIONS FOR IGNITION/DELAY APPLICATIONS

There is currently a renewed interest in intermetallic compositions as possible replacements for conventional pyrotechnic delay and ignition compositions. Factors driving the community in this direction include the fact that, in the delay area, intermetallics are non-toxic and non-carcinogenic while most conventional delays currently in use (at least in the U.S.A.) are not. For example, the U.S. Navy's approved delays include those based on metal fuels such as tungsten, boron, manganese, and alloys of zirconium and nickel with oxidizer systems based on insoluble hexavalent chromates (e.g., lead chromate, barium chromate, calcium chromate, etc.). Historically, chromates were chosen for the applications because, when properly formulated, they form solid slags and release little gas when combusted. In recent years, though, there has been increasing concern about their use in pyrotechnic delay systems. Besides being toxic, recent studies (followed by governmental regulation) have identified the family of "insolvent hexavalent chromates" (to which all the chromates used in pyrotechnics belong) as being "suspected carcinogens". A similar problem, though not quite as pervasive, exists in the ignition composition area.

Intermetallic compositions, based on binary or ternary mixtures of metals such as zirconium, molybdenum, tungsten, titanium, graphite/carbon, boron, etc., have the advantage of not using an oxidizer. As such, they are, in general, non-toxic and non-carcinogenic. Intermetallics offer the advantage of long term chemical stability and lower delay time shift/ degradation. Intermetallics react through an exothermic alloying reaction which is only begun at very high temperatures. In comparison, conventional pyrotechnic delays react in a oxidation-reduction reaction which are often initiated at much lower temperatures and can (for some systems) slowly take place even at ambient service temperatures.

Research on intermetallics has been widely reported by scientists (such as Y. Maksimov) in the Soviet Union, but perhaps best known in the U.S.A. is the work of Dr. Alex Hardt. Intermetallics have been used in the U.S.A. for at least the last 25 years. The first widely used intermetallic material was a system based on aluminum-palladium. It was used in delay, ignition and release applications.

Approaches for formulating intermetallic materials have included coextrusion of one metal onto another, vapor deposition, cladding, and mechanically mixing fine powders of the several materials. Besides the interest in intermetallics for pyrotechnic applications, intermetallics have also been studied in the area of self-propagating high-temperature synthesis for the production of dense refractories.

The only known U.S. currently active effort, directed at pyrotechnic applications, is the evaluation of mechanically mixed intermetallic delays in pressed columns. This work is being performed locally by Mr. J. Rose.

LASER IGNITION OF PYROTECHNIC MATERIALS

Laser ignition technology is only now reaching the level of maturity required to be considered a viable candidate for new or upgraded military applications. Recent advances in materials, electronics and optics are beginning to make the size, weight, cost and reliability of laser systems compare quite favorably to conventional pyrotechnic ignition systems. Laser based ignition systems are attracting a lot of interest because of the recent emphasis on ordnance safety. Being a non-explosive and non-electrical ignition stimulus, the laser has obvious advantages in adverse electrical and thermal environments.

A laser ignition system generally consists of a laser rod or laser diode, a stored energy supply to fire the laser, a switching or distribution system to properly direct the output, a fiber optic transmission system and an optically initiated pyrotechnic device. Packaging and selecting/ interfacing the various components continue to pose occasional "engineering challenges" when developing the laser ignition system for a specific application.

In recent years, laser ignition/initiation systems have been developed for applications such as strategic ballistic missiles, aircrew escape systems for high performance military fighter aircraft, aircraft stores separation systems, and arm-fire devices (AFDs) for air launched rockets and missiles. Both discrete rod lasers and the newer high power laser diodes have been used for these similar applications. The choice of which to use is dependent on the application, interface requirements, etc.

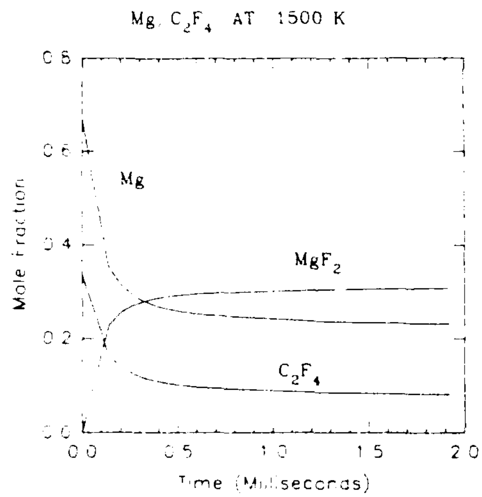
In most of these systems, the pyrotechnic component being initiated by the incident laser radiation is either zirconium-potassium perchlorate or boron-potassium nitrate. Some developers have added glass microbeads to these compositions to act as small lenses. This approach increases the radiant ignition sensitivity of the pyrotechnic materials (and therefore its reliability at a given input energy level) without lowering the autoignition temperature. Work in laser ignition of pyrotechnic materials is continuing.

NAVAL RESEARCH LABORATORY, Washington, DC

Contributor: Dr. H. D. Ladouceur

Ladouceur is developing a computer code to numerically simulate combustion of magnesium and polytetrafluoroethylene. The objectives are to identify important gas-phase combustion species, determine parameters which control the burning rate, and understanding how to increase the conversion efficiency of chemical energy to mechanical and/or radiative energy. The kinetic model utilizes a SANDIA code[17] for a perfectly stirred reaction and data concerning the chemical species involved, thermodynamic properties, kinetic mechanism and rate constants.

Figure 8 shows species predicted in the 1500K reaction between magnesium and polytetrafluoroethylene.



EQUILIBRIUM VALUES

MOLE FRACTIONS

CF2	7.9273-9
CF3	5.8180-9
CF4	1.8747-4
C2F4	4.319-12
F	3.788-10
MGF2	1.1370-8
C(S)	5.0000-1
MGF2(S)	4.9981-1

FROM NASA-LEWIS CODE

Figure 8: Thermodynamic equilibrium species predictions.

Polytetrafluoroethylene decomposes to form C_2F_4 which, in less than a millisecond, dissociates to CF_2. Contrary to previous reports,[18] the predominant reactive chemical species with magnesium is probably CF_2. Ladouceur concludes that the direct reaction of magnesium metal or vapor with free fluorine is unlikely inasmuch as predicted levels of elemental (F) and molecular (F_2) fluorine available in the present reaction mechanism are several orders of magnitude below CF_2. The predictions are limited by the lack of reliable kinetic rate constants. In addition, preliminary calculations indicate that about 80% of the heat of combustion is utilized in decomposing the polytetrafluoroethylene. One might recall its application as a heat shield. Analysis of this characteristic in the context of a Burke-Schumann[19,20] solution of the diffusion flame is in progress.

Another conclusion is that the combustion of polytetrafluoroethylene with oxygen produces a considerable amount of CF_4. This product has a high heat capacity which tends to lower the effective flame temperature and ties up the available fluorine as a nonreactive species. Oxygen may effect the ignition process in magnesium-polytetrafluoroethylene by providing a channel to produce CF_4. The latter being nonreactive, it contributes to delay of ignition.

NAVAL SEA SYSTEMS COMMAND, Washington, DC

CONTRIBUTOR: Mr. D. M. Porada

NAVY INSENSITIVE MUNITIONS PROGRAM

The U.S. Navy experienced a number of high cost and deadly ordnance accidents aboard aircraft carriers and other ships. For example: USS FORRESTAL 1967; USS ENTERPRISE 1969; USS NIMITZ 1981; USS ORISKANY 1966 and USS BADGER STATE 1969. The incident aboard the USS ORISKANY was associated with the MK 24 Aircraft Parachute Flare, a pyrotechnic illumination device. These incidents led to a major analysis on how to minimize these events.

In 1984, an insensitive munitions policy was set forth which stated that all Navy munitions will a. be designed to minimize effects of unplanned stimuli, b. incorporate least sensitive materials, c. meet or improve upon published insensitivity standards and d. meet performance standards. The goal was to have inventory transition by 1995.

Tri-Service management organizations have been established to implement service objectives The U.S. Navy objective is to develop and demonstrate technology needed to reduce vulnerability of Fleet munitions by reducing the severity of reactions from fast and slow cook-off, bullet impact, fragment impact and sympathetic detonation. Efforts are being focused on a. all new weapon developments, b. 15 designated munitions for priority forward fit and c. low-cost back fit alternatives. A military standard, MIL-STD-2105A (Draft) sets out requirements concerning the stimulus to be applied to the munition and passing criteria. Some related information is provided in references 21, 22 and 23.

All Services want less sensitive and insensitive munitions. The payoff is increased survivability and combat effectiveness, improvement in storage density and a number of shore-based benefits such as less vulnerability to terrorist attack and safer land-based munitions transportation. Not only are insensitive munitions a U.S.A. concern, but also, they are an international concern. To further exchange of information, the NATO Pilot Insensitive Munitions Information Center (Pilot NIMIC) was created in 1987 as an active means of speeding up the interchange of NATO information.[24] Pilot NIMIC was organized as an off-shoot of the Chemical Propulsion Information Agency (CPIA) at the Johns Hopkins Applied Physics Laboratory. The staff of Pilot NIMIC comes from different NATO countries. The intent is to make technical information on explosives and propellant hazards, test procedures, and test results available to all NATO nations so that uniform standards will eventually be adopted. Pilot NIMIC finished a three year trial at the end of 1990. By May 1991, the entire organization will become operational at NATO, Brussels.

NAVAL WEAPONS CENTER, China Lake, CA

CONTRIBUTOR: Dr. Russell Reed

SUMMARY OF SMOKE PROJECTS

Compositions are being developed which contain a liquid curable binder, a halogen source and a powdered metal which, when burned, give copious yields of dense metal halide smoke clouds. Various hydroxyl terminated binders were used including polybutadiene, polyether and azido polyether (GAP). GAP is a glycidyl azide polymer. The GAP binder produced smokes having higher burning rates and denser smoke clouds than were attained with the other binders. The GAP may enhance the combustion of metals by the formation of metal nitrides.

Halogen sources were organic chloro and bromo compounds. Dechlorane, Dechlorane Plus, and the diol derived by the reaction of tetrachlorophthalic acid with ethylene oxide were used to provide chlorine for the formation of metal chlorides. Bromine sources included pentabromodiphenyl (a liquid plasticizer) and decabromodiphenyl oxide (a powder). Ammonium iodate and iodine pentoxide were used as sources of iodine as well as oxygen. A number of powdered metals were used including aluminum, bismuth, magnesium, manganese, zirconium, hafnium, titanium, and zinc. The compositions exhibited a wide range of burning rates. Smoke colors attained were white, yellow, orange and orange-red.

NAVAL WEAPONS SUPPORT CENTER, Crane, IN

CONTRIBUTOR: Dr. B. R. Hubble

DEVELOPMENT OF INSENSITIVE COLORED SMOKE COMPOSITIONS

This project addressed a shortfall exhibited by conventional colored smoke pyrotechnic devices in that they fail to meet slow cook-off Insensitive Munition test requirements. In the slow cook-off test, the item is subjected to a uniform heating rate of 3.3°C/hour until a response or reaction occurs. To pass the slow cook-off test, the response of the test item in essence cannot be more severe than burning. The response of pyrotechnic devices containing colored smoke compositions, which consist of sugar, potassium chlorate, dyes and additives, was deflagration.

In this project, it was demonstrated that an acceptable colored smoke composition with respect to meeting the Insensitive Munition slow cook-off test requirements results when a commercially available flame retardant material is used as an additive to the pyrotechnic smoke compositions. The flame retardant material chemically is 2,4,6-tribromophenol. Additive concentrations between 1 and 15 weight percent have resulted in smoke compositions meeting the slow cook-off test requirements.

The chemistry surrounding the use of 2,4,6-tribromophenol in the slow heating environment associated with the slow cook-off test has been shown to involve two contributions. The major contribution results in the sucrose undergoing a caramelization reaction and as a result removing the availability of sucrose to subsequently react with the oxidizer. A smaller contribution is the result of the 2,4,6-tribromophenol undergoing a polymerization reaction with the result that the polymer coats the surface of the potassium chlorate particles which inhibits its subsequent reaction with sucrose.[25,26,27]

USE OF SMOKE AT SEA

This project evaluates the effectiveness of using smoke screening to protect small Navy craft, for example patrol boats, in a combat environment. Tests were carried out both at sea as well as in a harbor to evaluate the effectiveness of different smoke generation technologies. The smoke generation technologies were (a) pyrotechnic smoke blocks which generated zinc chloride aerosols, (b) a pulsed jet generator (U.S. Army model M3A3E3), and (c) a turbine exhaust smoke generator. The latter two technologies are based on the use of conventional fog oil.[28]

A total of 21 at-sea tests were performed in the Atlantic Ocean. In addition, tests were performed in the harbor at Ft. Eustis in Virginia to evaluate the feasibility of using smoke generators on small craft to provide smoke protection for a harbor.

The at-sea test results indicate that small craft, when appropriately equipped with proper smoke generating devices, can quickly and efficiently produce smoke screens that effectively reduce susceptibility to small arms fire. The turbine type smoke generator was found to be especially suited for use aboard small naval craft. For example, smoke generation for only 30-60 seconds produced a smoke cloud that persisted for over five minutes.

The cloud was over 1220 meters long. In comparison, the pyrotechnic blocks produced a zinc chloride smoke cloud for a duration of three minutes. The cloud also was about 1200 meters long but had thin spots where the naval craft were not obscured. Finally, it was not possible to get the pulsed jet smoke generator to operate consistently in the ocean environment.

Equally promising results were obtained in the harbor tests. In general, the results of these tests indicate screening smoke has the potential to significantly enhance the survivability of small naval craft in a combat environment.

INFRARED DECOY FLARE SIMULATOR

Large numbers of infrared decoy flares, which are used to counter infrared missile threats, have been expended during past training exercises of Naval combat pilots. In an effort to maintain a current level of training using the most cost effective manner, a low cost training simulator was desired. The deployment of relatively low cost simulators in place of decoy flares during training exercises will be a savings of nearly 90% of the cost of the expendables used.[29]

The Simulator, Tactical Use, Flare (STUF) was developed for use as a training substitution for IR decoy flares as shown in Figure 9. The purpose of this round is complete visual simulation of an expendable decoy flare. The main composition, which produces white smoke and flame as does an infrared flare, is a mixture of magnesium, sodium nitrate, and a binder. Ignition is achieved with a red lead-silicon mixture.

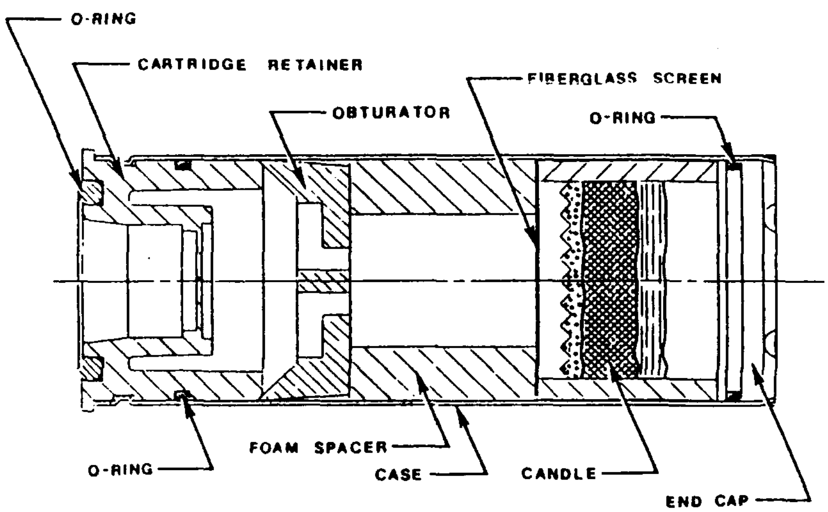


Figure 9: Simulator, Tactical Use, Flare (STUF).

The unit was designed with the intention to meet certain criteria which would make the unit more desirable for the end users. The unit must a. be safe to handle, b. be compatible with the CCU-41 and CCU-63/B impulse cartridges, c. have visible signature within 250 milliseconds after ejection, d. produce visible signature for approximately 5 seconds, e. eject at a velocity of approximately 100-200 feet/second, f. be functional out of ALE-29, ALE-39 and ALE-47 dispenser systems, and g. be constructed from components which are easily manufactured. All of these design goals were met or exceeded. STUF meets the primary requirement of an inexpensive item which can be used instead of decoy flares for training purposes. Simple components molded or cut from stock materials, a pressed candle composition made from inexpensive materials, common assembly procedures and minimal acceptance testing helped minimize development as well as production costs.

PYROTECHNIC PRODUCTION ASSURANCE ENHANCEMENT

Magnesium metal in particulate form is a fuel used in many different pyrotechnic compositions, e.g., illuminating flare formulations. This study addresses the chemistry associated with the undesired degradation reactions that the magnesium metal can undergo either while in a storage environment or while being processed on the pyrotechnic composition production line. The laboratory technique of microcalorimetry is used to characterize the reactions of magnesium with water vapor and air. In both these reactions, surface reaction product films are formed which retard the remaining magnesium from subsequent chemical reactions, i.e., degrades the performance of magnesium in a subsequent pyrotechnic reaction.

We used a LKM Model 2277 Multi-channel Microcalorimetry system. Microcalorimetry, originally developed by Professor Ingemar Wadso and Dr. Jack Suurkuusk of the Thermochemical Laboratory in Lund, Sweden,[30] has been used extensively in the energetic materials area.[31-34]

In this project it has been shown that for every 1% degradation that the powdered magnesium undergoes, there is a 10% decrease in the performance of a pyrotechnic composition which incorporates the degraded magnesium. However, the degradation reactions are relatively slow, e.g., at 70°C and 100% relative humidity, 1% degradation requires approximately 15 hours of reaction time.

In this study, the degradation of the powdered magnesium has been shown to be strongly moisture and temperature dependent. For example, at 25°C in air, the chemical rate of the degradation process is an order of magnitude higher at 25% relative humidity than at zero percent humidity and increases another order of magnitude when the relative humidity is increased to 75%. The dependence on temperature is equally strong in that the degradation chemistry rates increase exponentially with temperature.

ECOLOGICAL DISPOSAL OF PYROTECHNICS

CONTRIBUTOR: James E. Short, Jr.

Ecologically acceptable procedures have been developed for the demilitarization and disposal of pyrotechnic munitions. The thrust of this work was to dispose of or reclaim the energetic materials and chemical components of the devices. After the experimental procedures were validated one-tenth scale pilot plants were built and operated to evaluate the process further. These were built for the preponderant pyrotechnic categories; namely compositions for illumination, colored flames, photoflash, tracers, infrared decoys and those containing red phosphorus. Information about these efforts are contained in references 35 to 49. The processes are also suitable for disposal of production line waste and scrap.

PYROTECHNICS CONTROLLED-AIR INCINERATOR

CONTRIBUTOR: Mr. Curt Stephenson

Construction of a pilot scale Controlled-Air Incinerator (CAI) has been completed at Los Alamos National Laboratory. The State of New Mexico has approved a test burn. Because of cold weather (freezing weather would hamper the startup and test) the test burn has been delayed until March of 1991.

The pyrotechnics pilot plant is a specially designed incinerator for the thermal destruction of Navy colored smoke, flare and dye materials. The waste material is slurried with #2 fuel oil, water and a polymer wetting agent and pumped into the combustion zone of the incinerator. Off-gas clean-up is by wet scrubbing techniques. The pilot plant has been configured into three modules which can be transported on conventional semi-trailers and a control trailer.

The incinerator, with emission control and monitoring systems, consists of a feed module, an incinerator module, a utility module and a control trailer. The major components of the feed module are a slurry feed tank, slurry feed pump, recycle pump and associated piping and instrumentation. The major components of the incinerator module are the incinerator vessel, dual fuel slurry burner, off-gas quencher, demister, combustion air blower, venturi scrubber and scrub recycle pump. The utility module includes an air compressor, an air dryer, an electric steam generator and the electrical switch gear. The control trailer contains the monitoring/ analytical equipment, the incinerator instrument packs, etc.

The incinerator has been designed to process mixtures of waste components found in colored smoke, flare and dye compounds. These components are listed below.

<u>Major Constituents:</u>
Auramine hydrochloride
Barium chlorate
Barium nitrate
Hexachlorobenzene
Magnesium powder
Potassium chlorate
Potassium perchlorate
Sodium oxalate
Strontium nitrate
Sugar
Xylene-azo-beta-naphthol
1-methylamino-antraquinone
1,4-di-p-toluidino-anthraquinone
1,9-benz-10-anthrone
3,4,8,9-dibenzpyrene-5,10-benzoquinone

<u>Minor Constituents:</u>
Asphaltum
Castor oil
Dextrin
Diatomaceous earth
Ethyl alcohol
Graphite
Gum Arabic
Linseed oil
Orange shellac
Red gum
Sodium bicarbonate

Additional components are added to the above to permit injection of the waste components as a liquid or slurry. Other additives are used to enhance transport and combustion properties. Mixture additives can include the following:

Fuel oil - solvent for smoke/flare components, adjustment of heating value.
Water - solvent for smoke/flare components.
Surfactant - emulsifying/wetting agent for oil/water mixtures.
Aluminum stearate/aluminum oleate - gelling agent for adjustment of suspension properties.

The waste feed system includes the waste feed tank and the waste feed pump. The waste feed tank is a 379 liter (100 gal) feed mix tank which is a free-standing, hinged top, stainless steel tank fitted with an electric mixer and an internal tank mixer. The waste feed pump is a severe-duty chemical pump developed for transferring slurries which can operate at no-flow conditions without overheating the captured feed material.

The incinerator is a refractory-lined cylinder, vertically oriented and supported by adjustable clips. The interior volume of the incinerator chamber is estimated to be about 1.13 m^3 (40 ft^3). The operating range of the incinerator is 782-1205°C (1440 - 2200°F). The slurry feedrate to the incinerator is 38.6 kg/hr (85 lb/hr). The incinerator head and exit transition are lined with castable refractory secured with metal anchors.

SANDIA NATIONAL LABORATORIES, Albuquerque, NM

CONTRIBUTOR: Dr. David Anderson

TRANSIENT BURN STUDIES

SANDIA National Laboratories continues to study the burning behavior of titanium subhydride/potassium perchlorate ($TiH_{1.65}/KClO_4$). Recent research is aimed at studying the dynamic compaction of the confined cylindrical charge as the pyrotechnic burns.

Flash radiography, optical fibers and piezoelectric pressure transducers were used to study the phenomenon. Lead disks, placed between the increments of powder, serve as x-ray tracers. Fiber optics are used to monitor the location of the ignition front. The pressure transducers monitor the pressure history inside the closed test device. The data indicate that a significant amount of compaction occurs as the charge burns. References 50 and 51 provide additional information. To complement this research, a semi-analytical model was developed[52] to determine the pressure-time history based on the measured burning front velocity. Razani et al.[53] also studied the effect of equations of state on the transient burning analysis of pyrotechnic materials in a closed system. They show that defining a co-volume for use in transient burning analysis in the presence of condensed species requires careful considerations. They define a variable co-volume for use in a simplified transient burning analysis and show its effect on the pressure-time history of the pyrotechnic materials burning in a closed system.

The effect of charge mixture ratio of titanium subhydride to potassium perchlorate and the titanium subhydride particle size on the plume heat transfer characteristics was also studied.[54] The coarse (8μm) titanium subhydride produced the best performance when in a 41:59 stoichiometric ratio with the potassium perchlorate. This material produced the highest average maximum wall heat transfer rate. This mixture was compared to those containing 2μm titanium subhydride and a 33:67 oxidizer-rich ratio with potassium perchlorate.

DIODE LASER IGNITION

Development is continuing toward optically ignited devices using a (GaAl)As laser diode (820 nm) to replace low energy, hot-wire igniters, detonators and actuators.[55] Optical energy is transmitted from the laser diode to a pyrotechnic powder such as titanium subhydride/potassium perchlorate by way of fiber optics. The fiber is coupled to the composition through a hermetically sealed window, fiber feedthrough or a reimaging lens/window system. Some advantages are the absence of a bridgewire and electrical leads. It eliminates powder-bridgewire interface decoupling and corrosion concerns. The problems of no-fire, conductance after firing, electrostatic discharge, electromagnetic radiation and infrared concerns are either eliminated or reduced.

Design parameters of the components needed to assemble the diode laser ignition system have also been studied.[56] The effects and characterization of radiative transfer associated with a model of titanium subhydride/potassium perchlorate laser ignition has been studied from a theoretical aspect.[57] Prototype optical headers containing sealed windows or fiber segments have been fabricated, loaded with titanium subhydride/potassium perchlorate, and test fired. The principal findings of this effort are that a. High optical absorptance at the ~800 nm diode laser wavelength is the most important material factor in obtaining low ignition thresholds. Titanium subhydride/potassium perchlorate is inherently a good absorber, b. Powder density and confinement, laser spot size, and the thermal conductivity of materials at the ignition interface are other parameters which must be considered when optimizing a diode laser igniter, and

c. Ignition of titanium subhydride/potassium perchlorate has been achieved from commercially available diode lasers at energies below 2 mJ (200 mW for 10 ms).

SRI INTERNATIONAL, Palo Alto, CA

CONTRIBUTOR: Dr. Donald J. Eckstrom

FREE-FLIGHT TEST FACILITY

An important aspect of this program is the need to test the performance of flares in a turbulence-free windstream. The turbulence-free requirement precludes the use of wind tunnels or blowdown test facilities like the one at the Naval Weapons Support Center at Crane, Indiana. Therefore, we developed a free-flight test facility based on a pneumatically driven (airgun) launcher. The airgun barrel is 15 cm ID by 6.1 m long and is made of honed steel. The air tank is of 454 liter capacity and is designed to ASME specifications and pressure tested for 3.4×10^6 Pa (500 psi). The tank is fitted with welded flanges that provide O-ring seals to the barrel. Ten radial ports, each 2.5 x 7.5 cm, provide rapid air passage between the pressure tank and the barrel.

The flare model is mounted in a sabot consisting of a polyethylene bottle of approximately 4 liter (1 gallon) capacity that had been filled with polyurethane foam and allowed to expand into a form of the exact diameter as the barrel. The top of the bottle was then cut off, and a recess was formed in the urethane to provide a nest for the flare. The sabot is long enough to fill the barrel over a length that includes the radial ports and two O-rings, thus sealing the pressure tank from the barrel before the shot. A shot is initiated by opening a solenoid valve that connects the pressure tank with the breech. The resulting buildup of pressure moves the sabot forward until the radial ports are unsealed, allowing the full tank pressure to be applied to launch the sabot and flare. A heavy steel ring is placed on the support beam just beyond the end of the barrel to serve as a sabot stripper to ensure that there is no interference between the flare plume and the sabot.

The flare is ignited by an electric match fitted into the hole in the aft end of standard MJU-8/B flare grains or is taped to the surface of candidate flare compositions, fabricated locally. The match leads are brought forward to the front of the sabot and connected to leads soldered to copper conducting tape that is wrapped on the front 3 cm of the sabot in such a way that it provides two electrodes. As the sabot exits the barrel, these electrodes brush against contacts mounted at the end of the barrel. The contacts, in turn, are connected to a charged capacitor. This arrangement provides a reliable, fail-safe ignition procedure that successfully ignites the flare on every launch.

SVERDRUP TECHNOLOGY INC., NSTL, MS

CONTRIBUTOR: Mr. Fred McIntyre

VECTOR MIXER STUDY

The U.S. Army identified the need to study pyrotechnic mixing technology. Several new and safer mixing concepts were identified[58,59] for potential use in the manufacturing of pyrotechnics. The MIGRAD mixer manufactured by APV, was chosen as an alternative to current manufacturing methods (mix/muller and/or Hobart). A study was conducted on the MIGRAD (Mixer-Granulator-Dryer) by Pine Bluff Arsenal personnel. The Pine Bluff Arsenal study showed that the MIGRAD mixing concept, which takes advantage of the current state-of-the-art technology, was a safe and viable alternative to current mixing techniques. The VECTOR FLO-COATER was also evaluated in a similar manner to the MIGRAD mixer. This study was necessary because some of the candidate pyrotechnic mixtures identified by the operating plants could not be safely blended in the MIGRAD mixer.

The VECTOR FLO-COATER is a multi-purpose fluid bed granulation and/or coating machine for blending, granulating and drying. The FLO-COATER uses controlled temperature air flow introduced into the bottom of the mix container to combine raw materials. A controlled rate binder spray system, using a pump for delivery and compressed air for atomization, wets the dry powder and provides for particle growth. The mixing, granulating, drying, and discharge of the final product are accomplished remotely by either manual or automatic operation. Timers on either an analog or digital control panel are used for mixing, binder addition, drying, filter blowdown, and discharging the finished product.

Typically, once the FLO-COATER power is turned on, dry mixing is accomplished in approximately one-minute. Mixing is accomplished by fluidic air flow that lifts and folds the product material over and the rotor action which moves the mixture in a 360° movement while it is fluidized in the product bowl. Binder addition can take place either from a spray nozzle located in the expansion chamber or in the periphery of the product bowl. Average binder addition time is approximately 16 minutes. Once the binder has been added and particle growth has been achieved, drying is accomplished by adding heated air into the product bowl. Average drying time is approximately 4 minutes. Remote discharge of the finished product is accomplished in approximately 3 minutes. A typical mixing, granulation, drying, and discharging scenario then is approximately 23 minutes for a typical pyrotechnic batch.

A total of 100 live batches of 18 different pyrotechnic mixtures have been successfully blended in the FLO-COATER without incident. The FLO-COATER has been certified to mix a total of 58 different pyrotechnic mixtures.

THIOKOL CORPORATION, Marshall, TX

CONTRIBUTOR: Dr. David R. Dillehay

TWIN SCREW EXTRUDER

The initial studies at Thiokol of twin-screw extruder processing used Werner & Pfleiderer (W&P) twin-screw extruders of a modular barrel design. This modular design offered flexibility in setup since the barrel modules could be arranged to give any configuration of feed ports, process sections and vacuum ports desired. A major problem identified with this design concerned the problem of jamming of the screws due to feed problems. If the screws become jammed, the modular barrel design must be disassembled by disconnecting the screw shaft coupling and pulling the screws through the barrels with live material on the surfaces, or by unbolting each section of the barrel and pulling the barrel section over the shafts, again with live material on the surfaces. To avoid this situation, W&P designed and built a split barrel extruder that could be remotely opened in case of screw jamming and also incorporated many other design features specifically engineered for safety.[39]

The extruder has a nominal screw diameter of 58mm (2.3 inches) and a barrel length of 1440mm (56.7 inches). The length of the assembled screw elements on the shaft is 1440mm. This gives an L/D ratio of 24:1. Screw elements are available in several combinations of length and pitch. The elements are assembled on splined shafts and end caps are torqued to a minimum of 10.4 kg•m (75 ft-lb).

There are three tempered zones in the extruder barrels and a fourth tempered zone in the die head when using direct extrusion. The tempered zones are temperature controlled by pumping heated water from hot water heaters through the barrel sections. The heaters are capable of heating the water to 149°C (300°F).

The top barrel section has four openings into the bore of the extruder. The first opening is near the back of the barrel for feeding polymers or slurries to the extruder. This port is approximately 6.35mm (0.25 inches) in diameter. The second port is also near the back of the extruder and is a large (10.16 x 12.7 cm; 4x5 inches) opening for feeding solids to the extruder. This is followed closely by another liquid feed port, also 6.35mm (0.25 inches) in diameter. Near the discharge end of the extruder, there is a large opening (10.16 x 20.32cm; 4x8 inches) used for removing volatile solvents or gases from the composition. A vacuum vent is attached to this port and a water-seal vacuum pump is used to draw off volatiles.

Live infrared decoy flare composition was processed on the twin-screw extruder in the mixer mode and pressed into test pellets. The pellets were finished with normal production handling and were tested in the test tunnel. Performance was excellent. All test parameters were met. Reproducibility from pellet to pellet was excellent even though the material is in the mixer for only about 2 minutes. Additional live runs have been accomplished on the extruder facility with good replication from mix to mix. Future efforts will include developing criteria and techniques for processing in the extruder mode. Recharging of feeders and take-away of processed material are also major areas of interest. One of the main safety features is the low amount of material in process at any time. The extruder is run starve-fed with approximately 900g (2 pounds) of composition in the barrels at any one time. The solvent content of the flare composition can be reduced through the use of vacuum at the vacuum port. Test and evaluation of the twin-screw extruder is continuing.

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USE OF TITANIUM IN BRIDGEWIRE-SENSITIVE PYROTECHNICS

Fine particle size ($\leq$10 μm) titanium is widely used in applications requiring bridgewire-sensitive pyrotechnics with fast function times. Unidynamics uses this constituent in compositions for pyrotechnic igniters and ballistic actuators. Recent Independent Research and Development studies have shown that the particle morphology of this ingredient is critical to its performance in hot wire applications. Scanning electron microscope images of different grades of fine titanium have disclosed that the type of material which requires the lowest bridgewire firing currents and yields the shortest function times and fastest pressure rise rates in actuators is the product exhibiting particles with rough, highly irregular surfaces resembling cauliflower heads. Materials with smoother, more rounded particles are less sensitive and slower burning.

HYDROGEN BURNOFF IGNITER

Early in 1980 it was discovered during static firings of liquid hydrogen/liquid oxygen Space Shuttle Main Engines that excessive overpressures were encountered below some engine assemblies. These overpressures were attributed to explosive deflagration of the cloud of hydrogen gas which formed around the base of the engine just prior to ignition. Such deflagrations could cause damage in the base heatshield area and nozzles. The approach taken to resolve this problem was the use of pyrotechnic compositions to ignite the hydrogen prior to excessive buildup. Initially, compositions such as magnesium/polytetrafluoroethylene were used but were not totally satisfactory, e.g., short plume range. Unidynamics developed an ignition system based on a metalized ammonium perchlorate/hydroxyterminated polybutadiene polymer composite propellant.

The metal used was large particle (~ 550 μm) zirconium. This system has performed successfully and is still in use today for the shuttle launchings.

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INFRARED DECOY FLARES

Recognizing that advanced infrared missile technology is now able to discriminate decoy flares from aircraft targets and subsequently to reject the decoy flares, an advanced aerodynamic flare (AAF) program was started. The decoy flare simulates the infrared radiative power and aerodynamic characteristics of the aircraft. The decoy contains a pyrotechnic source to provide the desired infrared radiation and thrust to simulate the aircraft forward motion. This kinematic property to produce a trajectory more like that of the target aircraft plus infrared radiative power distributed as in that of the aircraft makes the decoy flare quite effective against advanced seekers employing kinematic discrimination.[61,62,63]

Another development being evaluated is the special infrared flare (SIRF).[63] This development is intended to be less susceptible to missile infrared counter-countermeasures and to simulate aircraft flight and spectral signature. When dispensed from the aircraft, it flies along for a short period while it seduces the missile before separating further to create the needed miss distance. Research efforts are continuing.

Another effort is to optimize decoy flares to be effective at supersonic speeds where future aircraft are expected to operate. This study will address the requirement for protection of the aircraft and identify technologies which should be pursued after wind-tunnel and rocket-sled testing.[63]

ACKNOWLEDGEMENTS

The author wishes to thank all the contributors of the information and the visual aids for this paper. The assistance provided by Ms. Janet Hooper in getting an article translated is appreciated.

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