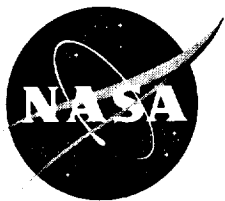


NASA/TP—2000—210186



Propellant for the NASA Standard Initiator

*Carl Hohmann
Bill Tipton, Jr.
Maureen Dutton
Lyndon B. Johnson Space Center
Houston, Texas 77058*

October 2000

The NASA STI Program Office ... in Profile

Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) Program Office plays a key part in helping NASA maintain this important role.

The NASA STI Program Office is operated by Langley Research Center, the lead center for NASA's scientific and technical information. The NASA STI Program Office provides access to the NASA STI Database, the largest collection of aeronautical and space science STI in the world. The Program Office is also NASA's institutional mechanism for disseminating the results of its research and development activities. These results are published by NASA in the NASA STI Report Series, which includes the following report types:

* **TECHNICAL PUBLICATION.** Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA counterpart of peer-reviewed formal professional papers, but having less stringent limitations on manuscript length and extent of graphic presentations.

* **TECHNICAL MEMORANDUM.** Scientific and technical findings that are preliminary or of specialized interest, e.g., quick release reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.

* **CONTRACTOR REPORT.** Scientific and technical findings by NASA-sponsored contractors and grantees.

* **CONFERENCE PUBLICATION.** Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or co-sponsored by NASA.

* **SPECIAL PUBLICATION.** Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.

* **TECHNICAL TRANSLATION.** English-language translations of foreign scientific and technical material pertinent to NASA's mission.

Specialized services that complement the STI Program Office's diverse offerings include creating custom thesauri, building customized databases, organizing and publishing research results ... even providing videos.

For more information about the NASA STI Program Office, see the following:

* Access the NASA STI Program Home Page at <http://www.sti.nasa.gov>

* E-mail your question via the Internet to help@sti.nasa.gov

* Fax your question to the NASA STI Help Desk at (301) 621-0134

* Telephone the NASA STI Help Desk at (301) 621-0390

* Write to:
NASA STI Help Desk
NASA Center for AeroSpace Information
7121 Standard Drive
Hanover, MD 21076-1320

NASA/TP—2000—210186



Propellant for the NASA Standard Initiator

*Carl Hohmann
Bill Tipton, Jr.
Maureen Dutton
Lyndon B. Johnson Space Center
Houston, Texas 77058*

National Aeronautics and
Space Administration

Lyndon B. Johnson Space Center
Houston, Texas 77058

October 2000

Available from:

NASA Center for AeroSpace Information
7121 Standard Drive
Hanover, MD 21076-1320
301-621-0390

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
703-605-6000

This report is also available in electronic form at <http://techreports.larc.nasa.gov/cgi-bin/NTRS>

Contents

	Page
Abstract	1
Background	1
Propellant Materials	2
Propellant Blending	6
Precipitation Blending	8
Graphite Addition	11
Binder Composition	13
Bridgewire Slurry	2

Acronyms

JSC	Lyndon B. Johnson Space Center
NOS	Naval Ordnance Station
NSI	NASA standard initiator
SBASI	single bridgewire Apollo standard initiator
ZPP	zirconium-potassium perchlorate

Abstract

This paper discusses processes employed in manufacturing zirconium-potassium perchlorate propellant for the NASA standard initiator. It provides both a historical background on the NSI device—detailing problem areas and their resolution—and on propellant blending techniques. Emphasis is placed on the precipitation blending method. The findings on mixing equipment, processing, and raw materials are described. Also detailed are findings on the bridgewire slurry operation, one of the critical steps in the production of the NASA standard initiator.

Background

The NASA standard initiator (NSI) is a two-pin electrically activated, hot wire, electro-explosive that was designed and qualified in 1966 as the single bridgewire Apollo standard initiator (SBASI) to meet the requirements of the Apollo lunar mission. The SBASI was subsequently adopted and standardized for use as the NSI on the Space Shuttle system, on Shuttle payloads, and on other NASA-sponsored programs as the NSI.

The NSI's function is to translate an electrical stimulus into a pyrotechnic action or train; in the pyrotechnic world, this is known as a first fire. It primarily produces a flame and hot particles that ignite or initiate other powders, but it can be used for pressure impulse in some applications. The NSI has been widely incorporated into both the pressure producers and the detonators used in pyrotechnic systems for numerous spacecraft. Owing to its well-established reliability and reputation, the NSI has been sought after by many government and commercial customers worldwide to fly on both crewed and uncrewed vehicles. Over 100,000 NSIs have been manufactured to date.

NSI uses as its propellant finely powdered zirconium metal mixed with finely powdered potassium perchlorate held together by a Viton-B rubber binder. Propellant specifics are:

Ingredient	% by weight	Specification
Zirconium	52.0	Mil-Z-399D, Type II, Class II Hafnium content: 3.0% max No ball milling to final size
Potassium Perchlorate	42.0	Mil-P-217, Grade A, Class 4 No ball milling to final size
Viton "B"	5.0	DuPont Sales specification No. 14, 1985-02-06
Graphite	1.0	Mil-G-155, Grade III. Particle size less than 1 micron
Mixed propellant	caloric content: 1340 (min) to 1450 calories per gram	

Until recently, propellant blending was considered a proprietary operation of the qualified NSI sources. Since it had worked successfully up until 1986, little government investigation was undertaken. But in 1986, Hishear experienced a failure of lot XRA to fire at -260°F . A failure investigation was launched that lasted 3 years. Many in-house tests were performed to support this investigation, and NASA gained considerable knowledge about both the blending and the bridgewire slurring processes. One result of this investigation was that NASA recognized how critical each process was to the final product, and the need to define each process better to assure NSI performance.

One of the changes imposed on the NSI as an outcome of this failure was the imposition of testing at the worst extreme of temperature. This worst extreme was analyzed to be -420°F . Consequently, a new test was originated to screen lots already manufactured and any new lots that were to be manufactured. Owing to its severe nature, the test is very sensitive to picking up changes in the processing of an initiator. The -420°F testing revealed increasing failure rates in lots manufactured by Hishear after 1982 (except for two lots) and no failures in units built by SOS. It was not until later that an explanation for the success of these two lots in the midst of other failed lots was arrived at. The surprising failure rates experienced by the Hishear units caused much concern and precipitated greater in-house effort.

One of the early tests performed to understand the propellant was the unbound blend propellant test. This test examined the effect Viton binder had on the propellant mix. Prevailing theories put forward were that the Viton was incorporated for electrostatic sensitivity protection and/or age life considerations, but it was unknown what effect the Viton played in the cold temperature problem. To answer this, a blend of propellant was made by Hishear without binder but with the same raw ingredients that had always been used. This blend was loaded into NSIs without any other changes. At this time, the Hishear design had no slurry on the bridgewire. All of the units were put through a simulated qualification test and were fired at -420°F . They functioned and functioned faster than had been seen before. The mean bridgewire burnout was $183\ \mu\text{s}$ and the mean function time was $384\ \mu\text{s}$. From this test it was concluded that, by not allowing bridgewire to heat the mix to ignition, the binder was part of the problem. Prior to bridgewire burnout, too much energy was being lost burning through the rubber to elevate the perchlorate particle temperature to decomposition. Although removing the binder appeared to solve the cold temperature problem, it was deemed an unacceptable solution because of potential age life reduction and other unknown effects on the propellant.

It is important to note that when binder is eliminated, the propellant reacts significantly faster. This provided an important clue toward adopting a slurry for the bridgewire and the technique for its application. Propellant grains must be laid next to the wire without binder.

Propellant Materials

The failure investigation eventually traced NSI failures to several causes: materials and processing changes as well as design differences between suppliers. Part of the problem was an unrecognized change in the processing of raw zirconium. According to literature, fine zirconium powder is pyrophoric in air; i.e., its ignition temperature is 20°C (68°F). This was known to be the case for the original Foote Mineral Co., Philadelphia, Pennsylvania, processed zirconium. Experience by persons responsible for blending this material was that sparkling could be seen

if the powder was brushed from the mixing table onto the ground. With other powders, this was not the case. Only recently has a truly pyrophoric grade of zirconium become available from CM Chemical Products, Inc. Propellant made from this material shows excellent results.

A study of the production of zirconium reveals several items of interest. According to the ASTM manual, the powder is produced by any of three methods. Its reactivity is dependent on its mode of manufacture. The different modes are:

1. **Calcium reduced powder** – Various zirconium compounds are reduced to zirconium with calcium. The powder is relatively impure.
2. **Leached powder** – Various zirconium compounds are produced by leaching the Kroll process reduction mass. The powder is fine and forms tiny spheres.
3. **Alloy powder** – Various zirconium compounds are made by a hydride-dehydride process. The material is first heated in a hydrogen atmosphere to form a hydride which is then crushed and ground to the desired size. (Hydriding makes the material brittle and reduces its sensitivity to ignition.) The hydride is then heated to about 600°C under vacuum to remove the hydrogen (dehydriding). All grinding and packaging processes are performed in an inert argon atmosphere in order to protect the fresh reactive surfaces generated during sizing from moisture, oxygen, and nitrogen.

Zirconium almost always contains hydrogen because hydrogen has an affinity for it. It also freely forms hydrides. The rule is: the less hydrogen present, the lower the ignition temperature of zirconium. Indeed, the hydrides of zirconium are much safer to handle than zirconium itself. Their “inertness,” however, shows itself as less sensitive to ignition and as producing a slower burning rate. Removal of hydrogen by heat and vacuum increases the burning rate and restores sensitivity to ignition. Prolonged storage under water may influence burning characteristics. Zirconium may slowly catalyze the breakup of the water to form hydrides. Again, heat and vacuum exposure appear to be remedial.

Handling pyrophoric zirconium can be hazardous. Zirconium fires, which are difficult to extinguish, are a constant threat. Spraying them with water only exacerbates them. Because of these difficulties, the Foote Mineral Co. lost a manufacturing facility. It appears that the powder manufacturing industry recognized the hazard and decided that processing zirconium to such a pure state was not worth the risk. Instead, hafnium and hydrogen may have been left as hazard moderators.

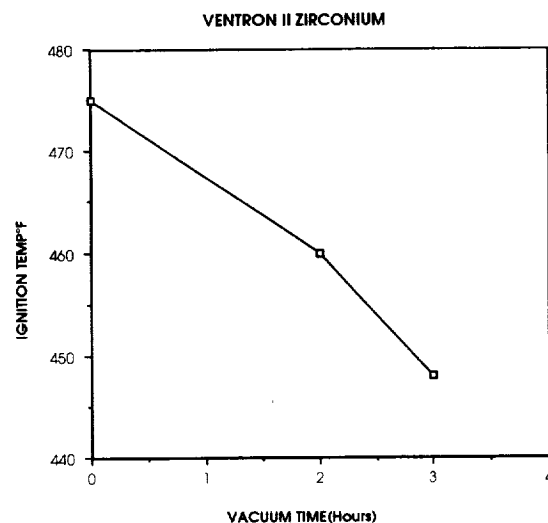
Hafnium, a metal normally found in the same ore as zirconium, is difficult to separate and may act as an ignition suppressant by elevating the autoignition temperature. Literature records a commercial grade of zirconium hydride of 2 to 6 micron particle size containing 1.8% hydrogen and 2.5% hafnium with an ignition temperature of 270°C. This closely matches the ignition temperatures of the commercially available powdered zirconium measured by the Johnson Space Center (JSC) in 1987. The Mil-Z399D spec by which zirconium is procured treats the hafnium content as zirconium in the chemical assay; hence, the quantity of hafnium in the zirconium is uncontrolled by the Mil spec.

To study the autoignition temperature of commercially available grades of zirconium, JSC originated the zirconium autoignition test in 1987 and analyzed the hafnium content

within each zirconium powder tested. This test heated the metal to increasing temperatures and exposed it to air at the same temperature as the metal. When the temperature was at or above the autoignition temperature of zirconium, a flash would occur. When this happened, the temperature would be lowered and the test would be repeated until no flash occurred. By proper iteration of temperatures, it was found that the autoignition temperature could be defined within a narrow band. The test was run with various types of zirconium that had been used by both supplies. Test results are listed below.

Zirconium Type	Autoignition Temperature ($\pm 10^\circ\text{F}$)	Zirconium Content	Hafnium Content
Degussa	470°F	97.8%	1.8%
Ventron II	470°F	97.7%	2.0%
Foote Grade G	470°F	97.3%	2.4%
Foote Grade 120A	490°F	97.6%	2.1%
Automergic	500°F	97.5%	2.1%

The test also demonstrated that maintaining a vacuum on zirconium can lower the autoignition temperature. Subsequent testing by one of the NSI suppliers has substantiated this conclusion. Prolonged vacuum drying (6 days) at 200°F produced a vigorous chemical with higher caloric values. Removal of hydrogen adsorbed onto the surface may be part of the explanation for this effect.



In support of this theory of the change in zirconium sensitivity, it was uncovered in 1989 that the two initiator lots which had experienced no -420°F testing failures had had a small quantity of pyrophoric zirconium added to them. Since zirconium was now less sensitive, the Hishear design manifested an intrinsic weakness: Under cryogenic conditions, the main propellant plug contracted slightly from the bridgewire, preventing good energy transfer between the wire and the propellant. At cryogenic temperatures, there is little convective and radiation heat transfer, mostly conduction. If conduction is interrupted by gaps, the small heat transfer during the time the bridgewire is intact is marginal to burn through the binder and start the main propellant slug burning. If additional energy is required owing to a loss of sensitivity, the unit will not transfer sufficient energy before the bridgewire burns out and the unit fails to fire. This failure mechanism was solved by the slurried configuration.

The slurried configuration assures good energy transfer from the wire into the main charge by using a binder to trap propellant on the wire. The slurry deposits a small quantity of propellant on the sides and behind the bridgewire. Because of heat transfer and because the propellant next to the bridgewire has been changed into a more active component (by the solvent evaporation process), the propellant is better able to be ignited. The binder in the evaporator process moves away from the active ingredients. This makes the design more forgiving to propellant variations.

In addition to other differences, the potassium perchlorate was being fluid-energy milled. The oxidizer was being rolled to a small size for pressure considerations. The particle normally has sharp broken corners that have been produced from larger particles by crushing. But once the particles are rolled for any period of time, the corners begin to round and the particle approaches a sphere. This action defeats the ignition physics by spreading the available heat over a larger surface. Ignition is essentially an aero-thermodynamic process whereby hot gas flows over and impinges against surfaces. The sharper the surface radius, the higher the resulting temperature on the surface.

To have a particle reach its autoignition temperature in the fastest time, a particle should have as sharp a radius exposed to streaming hot gas as possible. An analog to this is starting a campfire. To start a campfire in a hurry, small kindling is first ignited; i.e., material where the autoignition temperature is achieved faster and the radius is the smallest, namely twigs or grass. If a piece of paper is used, the paper is ignited on an edge rather than in the middle. Once the campfire is ignited, larger particles or logs can be placed on the fire. Because the perchlorate had been fluid-energy milled to uniformly round shapes, the ignition energy was increased and the time for conflagration to begin was lengthened. This in itself was not a problem; but in combination with other changes, it produced a unit that would not ignite in a super-cold environment where every microsecond counts. To correct this, a slurried bridgewire was adopted and the potassium perchlorate was hammer-milled to size. Hammer milling maintains edges on particles.

A summary of the lessons learned from the testing done to support this investigation follows:

1. ***Zirconium manufactured today*** has hafnium remaining within it. Hafnium content may inhibit the ignition sensitivity of zirconium.
2. ***Absorbed hydrogen or zirconium hydride*** within the powdered zirconium inhibits the ignition sensitivity of zirconium. Hydrogen can be removed from zirconium with heat and vacuum.

3. ***The caloric output of a propellant*** is strongly controlled by the powdered zirconium (the amount of oxidation and hydrogen absorbed) and by the way the test is performed. The sample should be pelletized to control the burn.
4. ***The peak pressure developed by the initiator*** is a strong function of the mean particle size of the potassium perchlorate and, to a lesser degree, the shape of the perchlorate particle, method of blending and graphite addition.
5. ***The propellant homogeneity***, particularly that of the Viton binder, is a function of the blending process and the way the solvent is allowed to evaporate from (or leave) the mix. Binder, dissolved in the solvent, moves to the evaporating surface. To achieve a uniform binder composition, the mix should be turned continuously during the drying process.
6. ***Slurry is taken from the main blend***, and its activity is highly dependent on its binder composition. Excess binder in the slurry will slow slurry speed, but insufficient binder will allow the active particles to move away from the wire.
7. ***Too small a perchlorate particle*** will weaken the slurry mix and will allow material to slough off the bridgewire.
8. ***Function time at -420°F*** is a strong function of propellant homogeneity and the slurry process. The slurry must have the proper viscosity on application and must air evaporate (2 hours recommended) to a dry consistency before being oven treated to achieve its proper speed and structure.
9. ***Final particle sizing*** on the zirconium and the perchlorate particle should be achieved by a crushing action (as opposed to a rolling action) to maintain sharp edges. Sharp edges aid the ignition process.
10. ***The -420°F cold temperature test sequence*** (bake-shake-fire) is a highly sensitive test to uncovering processing or material changes.

As part of the corrective action to this failure, NASA originated propellant batch testing to protect its suppliers from the loss of a lot due to future propellant problems. Since this test is accomplished prior to production, it allows vendors an early look at the performance of the unit without jeopardizing production hardware. It performs the same tests on just 20 units that will eventually be done in DLAT with 1000 or more units at stake.

Propellant Blending

A further outcome to this investigation is that NASA has pursued an active interest in powder blending and in the variables that affect it in order to understand and control the effect of blending on initiator performance.

As well as performing in-house testing on powder blending, NASA has sought outside help to understand blending. Early efforts include work done at EG&G Mound Laboratories in Miamisburg, Ohio, and by the Naval Ordnance Station (NOS) at Indian Head, Maryland. The Mound effort scoped a variety of propellant blending techniques and ranked each against others in a matrix. Although this work highlighted areas of interest and additional avenues to pursue, it

did not specify enough to establish a production propellant blending system. The subsequent effort with the NOS was very specific and concentrated on defining a production blending capability that used a hexane countersolvent precipitation method with specification grade ingredients. This procedure produced a propellant that was loaded into initiators and put through testing similar to flight units. The NOS effort showed excellent results.

The blending of explosive powders has always been an art for which there are few masters in the pyrotechnic community. Most people only observe at a distance. (It could be said to be a dying art.) The few master blenders left usually guard their secrets jealously. For NASA to maintain its corporate asset, blending operations had to be documented in detail, particularly with zirconium-potassium perchlorate (ZPP), which historically is unforgiving of mistakes. ZPP is one of the most sensitive of propellants to stray energy discharge. Sparks undetectable to the naked eye will cause ZPP to ignite. The metal powder used in the initiator is so fine and active that it has to be handled as "pyrophoric;" i.e., it can burst into flame on exposure to air. To be able to manipulate and produce a blend with these ingredients, the utmost skill and care is required. Few persons have managed to do this reliably over a sustained period.

Blending by pyrotechnic manufacturers has principally been achieved by hand. Powders are mixed dry and/or poured into a 45-degree inclined bowl rotating with a Viton/acetone solution. Because of the blender's manipulation, a homogeneous mix is produced and the solvent is evaporated down. After this the moist solid is sieved in air through a U.S. standard screen by hand. The process is labor intensive, it requires hours to accomplish, it is hazard intensive; and it relies on subtle and frequent manipulations (secrets) of the mixture to produce a homogeneous Viton binder. Most blending is done by solvent-evaporation blending.

To produce the Viton-coated ZPP mixture, two basic methods can be used. One allows the blending solvent, which has the rubber in solution, to evaporate from the mix, leaving the rubber behind. This is the evaporation method. The other relies on the displacement of rubber from the blending solvent onto the active particles and the liquid is decanted from the solid mixture. This is the precipitation method.

The precipitation method uses two fluids for blending: a solvent for the rubber (Viton) and a countersolvent fluid to make the rubber drop from solution. The evaporation cycle uses only a single fluid for blending: a solvent for the Viton. The most frequently used solvent for Viton is acetone. Viton is readily taken into solution by acetone, where it makes a viscous rubber liquid to which active ingredients are added. Once a homogeneous mixture is attained by some mixing style, the solvent is allowed to evaporate and coat the particles with a film of Viton. This film, which acts as a binder for the propellant, can significantly affect its working response. To get consistent and rapid function times, homogeneity is required throughout the entire blend. To assure homogeneity, the binder must be uniformly distributed throughout the mix.

In an evaporation blend, where the Viton in solution is constantly moving to an evaporating surface with the solvent, care must be taken to continuously provide new surfaces while there is solvent left to evaporate. This method relies on manual and frequent movements of the mix during processing to achieve good blends; not surprisingly, it also requires several hours per blend. The bowl full of mix cake must be broken into a fine powder to be of any use. This is done by waiting until the cake has dried to a "moist" state that will still break apart but not be

too dry to cause a static hazard. The mix cake is then pushed by hand through a U.S. Standard sieve no. 20 to produce a fine powder, is spread into a thin layer, and is oven dried.

The precipitation method relies less on individual blenders and requires less manipulation. Blend homogeneity is more dependent on blending hardware, which can remain the same from blend to blend, and on fixed procedures. The process, which uses considerably more solvent than the other method, starts when a solution of Viton within acetone is created. The solution is placed in a high-speed blender where it is turbulently stirred. While the blender is running, active ingredients are added and are allowed to mix. When a second fluid or countersolvent is added to the spinning mixture, the Viton becomes saturated and begins to precipitate. It comes out of solution using a propellant particle as a nucleus on which it can coalesce. Because of the extreme turbulence, all particles are eventually coated with a uniform layer of rubber. After a short time, graphite is added into the sticky, wet mass. The particles are allowed to settle, and the liquid is decanted off. The wet mix is rinsed with a countersolvent to remove all acetone from the Viton-coated particles; this hardens the rubber surface. The mix is then poured, while in a wet state, onto a sieve submerged in a countersolvent. Here the mix normally breaks apart, usually through a finer screen (U.S. Standard sieve no. 30). It is then spread wet, air dried, and sent to the oven for final drying.

Different fluids may be used as countersolvents to precipitate Viton from acetone. These fluids include toluene, heptane, hexane, and mixtures thereof.

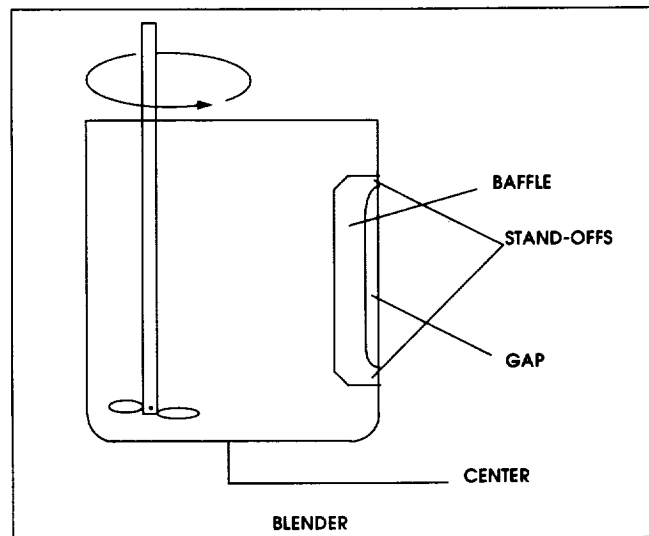
Precipitation Blending

Difficulties met in the manufacture of NSI propellant led to an in-house investigation on the manufacturing process. This in-house study focused on the precipitation process because of its inherently lower risk, high product quality, speed of manufacture, repeatability, and application to automation. It should be noted that the evaporation process can also produce an excellent end product and is still favored by some manufacturers. Each process has its fine points that, once understood, will serve the artisan well. It is our belief, however, that most manufacturers will eventually turn toward the precipitation process in an effort to reduce risk and simplify the production task.

Manufacturing any pyrotechnic composition is hazardous and makes the investigation of manufacturing processes difficult. To circumvent these obstacles, it was decided to start making blends using inert materials. The first inert material used was sieved glass powder, but this was quickly replaced by tin powder and sodium sulfate to more closely simulate the densities of zirconium and potassium perchlorate, respectively. Blending operations were carried out in a transparent glass container so that particle movement and grain growth could be observed. During the first blending observations, deficiencies of the mixing apparatus were noted and addressed by application of a baffle and a centrally offset impeller. Subsequent runs revealed interesting behavior of the binder during precipitation and eventually led to a detailed study of the polymer and its solutions. By continuing to use inert blends, important findings on the rate of solvent addition, mixing time, and impellers were made. Over 25 inert blends were produced.

Important findings in the precipitation blending method are that it is necessary to

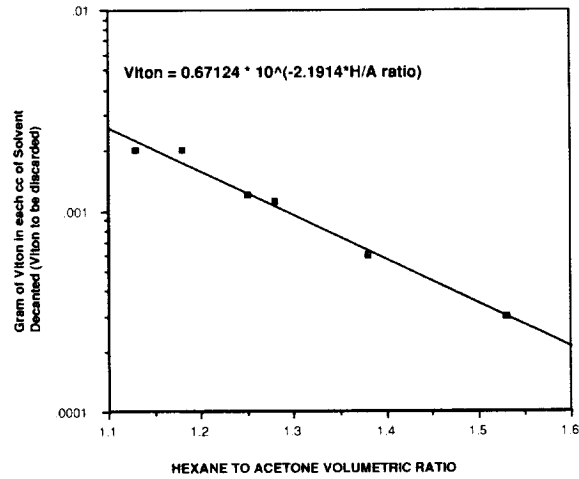
1. achieve good turbulent mixing so that particles will repeatedly pass through the mixture, particularly when precipitate is being formed. In ordinary blenders, it is important to add a baffling system (baffles and gap) to ensure turbulence by defeating the tangential velocity which forms off the blade and to prevent stagnation of solids behind the baffle, if possible, by moving the blade off center. The vortex the blade forms causes evaporation and stratification.



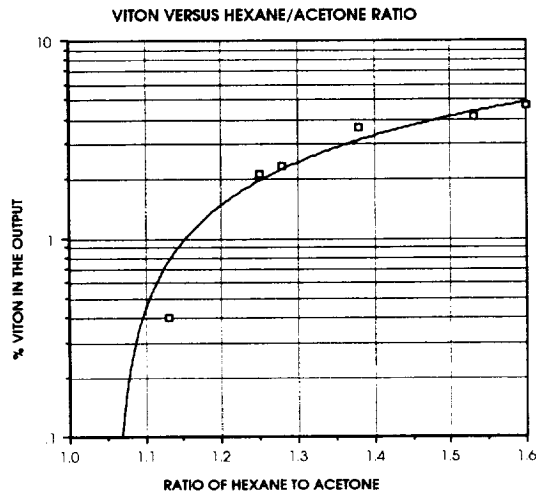
2. establish the rate and place at which a countersolvent is added (determined by each blender) so the mixer can quickly incorporate the countersolvent evenly into the entire solution without forming a local oversaturation condition that might cause a sticky rubber layer to develop and form on itself.
3. recognize that the ratio of countersolvent to solvent is very important in determining the amount and texture of rubber that precipitates. The amount and molecular weight of the rubber lost in the decant fluid depends on this ratio.
4. be aware that, if graphite is used as the partitioning agent, its uptake onto the particles is assisted by the precipitation of Viton. Graphite should be added when the countersolvent is added at a ratio where the last 0.5 to 1% rubber is left to precipitate so that the final coating of lightweight, tacky rubber may help to bind the graphite to the surface.

Testing with powder produced by the precipitation cycle technique by both JSC and its NSI vendors has shown excellent results. From these tests, a curve for the solubility of Viton in an acetone/hexane, solvent/countersolvent combination has been determined. The curve obtained is shown in the following figure.

**SOLUBILITY OF VITON IN
HEXANE/ACETONE BLEND**



When these data are used in conjunction with a blending recipe, another curve can be generated that gives the Viton content in the output mix versus countersolvent/solvent ratio. Data from a hexane countersolvent recipe used by JSC have produced the following:



Analysis of this curve shows that by using a hexane-to-acetone ratio of 1.3, more than half of the rubber available (5%) has dropped out of solution; and by increasing the amount of hexane-to-acetone from 1.3 to 1.6, nearly all of the rubber is liberated from the solution.

A simple lab test with 10 ml of a Viton/acetone solution (in a ratio of 20 g of Viton in 700 ml of acetone) in each of 8 vials when mixed with enough hexane to achieve a hexane-to-acetone ratio of 1.1, 1.2, 1.25, 1.3, 1.4, 1.5, 1.6, and 1.7 gives a clear view of what is happening in the

blending process. What this experiment shows is the texture of rubber when it is precipitated. At 1.1 and 1.2, there appears to be no precipitate. At a 1.25 ratio, due to the amount of acetone still in solution, the Viton is an emulsion—i.e., it is diaphanous and thin and flows easily—that does not stick to the container. It requires a long settling time for separation. In a quiescent solution, the separation line between the Viton layer and the remaining liquid is indistinct and the layer holding the Viton is not viscous. As the ratio is pushed toward 1.6, the Viton becomes more viscous and slower to flow; and, when agitated, the Viton readily separates and drops out of solution. The separation line of the Viton becomes more distinct. At a 1.6 ratio, the Viton has settled completely out of the liquid to the bottom of the container as a tough rubber film. It is extremely viscous and tenacious. Above a 1.6 ratio, the rubber clings to the container without moving. With these observations in mind, it becomes apparent what is happening in the mixer as precipitation occurs.

At a hexane-to-acetone ratio of 1.2 or lower, little to no precipitation takes place. At approximately 1.25, a large quantity of thin, lightly viscous rubber is liberated which flows and disperses easily. At 1.4, the rubber is much thicker but still flows and disperses when agitated sufficiently. Above 1.4, the rubber becomes very thick, settling of the Viton-coated particles occurs rapidly, and solids are starting to aggregate. The Viton precipitates as a semisolid with acetone remaining within it. The acetone is absorbed within the rubber like a sponge absorbs water. This acetone affects the texture of the rubber and the mixing process. The more acetone absorbed, the less viscous the Viton is. As the acetone is drawn out, the rubber becomes more viscous and tacky, hardening at its surface until, when dry, it becomes solid. This allows the finished material upon which the rubber is coated to be screened and worked as a powder. However, during the mixing process if the material is worked too long in a tacky stage, the particles upon which it has coated will aggregate and propellant particle size will increase. Settling and stratification will occur prematurely, bringing inhomogeneity into the mix process. Over-mixing will, therefore, ruin the output product.

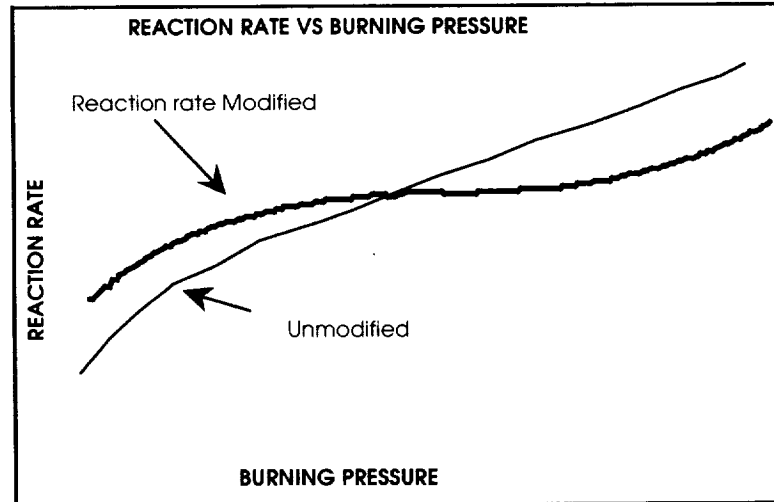
To avoid the results of over-mixing, the blend may be mixed extensively below a ratio of 1.4; but it must be worked quickly when it exceeds this ratio until it has been pushed to a high enough ratio (3.4) that will harden the outer coat and keep the particles from aggregating or clumping. If the mixture is mixed too long above 1.4 but below some ratio that will harden the outer coat, the precipitated particles will aggregate and the output will be difficult to screen. Prolonged mixing at 1.6 will cause particles to stick together and ruin the product. Hardening of the outer coat is required before over-agitation is done. This is achieved by driving the ratio of hexane-to-acetone to an excess. In practice, the processing time to reach a 1.4 ratio is not critical; but beyond this point, until an upper limit in excess of what is needed to stop the aggregation process is reached, the processing time is critical and should be accomplished in rapid order without overwhelming the blender. Particle size varies depending on the time given for aggregation. Minimum countersolvent pour times have produced powders which easily pass 100% through a U.S. Standard sieve no. 30, 90% through a no. 40 sieve, and 50% through a no. 100 sieve.

Graphite Addition

The role of graphite addition to the propellant blend has been widely discussed. Its stated purposes includes providing a partitioning agent, a lubricant for packing density, a reaction

rate modifier, and tinder for the ignition process. Its real role doubtless includes all of these. If graphite is added in the final stages of mixing, it aids the sieving process in breaking up the aggregates. It also aids the consolidation process by allowing the particles to flow together easily. Moreover, according to the literature, it can be used as a reaction rate promoter and stabilizer in solid propellants. Since its role in the reaction zone is subtle, to promote this it needs to be introduced early in the mixing process, even to the point of using dry powders to achieve intimate mixing.

Potassium perchlorate is known to decompose when heated to yield potassium chloride and oxygen. Decomposition starts at about 500°C; and the reaction is unimolecular over the temperature range from 536 to 617°C. However, more complicated processes are possible. This decomposition—when it is catalyzed by a variety of agents, ferric oxide, and manganese dioxide—can alter chemical pathways. Many solid propellants have shown increased rates of reaction when formulated with carbon black. It is known that solid potassium perchlorate and carbon black react at comparatively low temperatures (i.e., 320 to 385°C) at a rate much too fast for the normal dissociation of perchlorate into potassium chloride. The carbon, therefore, acts as starting tinder for the ignition process and catalyzes the perchlorate into a different chemical pathway with a faster response. By incorporating additives in the propellant composition, the burning rate characteristics of some propellants can be modified to yield a relatively flat portion or “plateau” over a limited pressure range. Characteristics of such propellants are shown in the following figure.



Pigmenting these propellants with carbon black can increase the burning rates in the low-pressure (ignition) region and subdue the pressure in the mid- to higher-pressure regions. This leads to more stable burning characteristics over a wide pressure and volume range.

The NSI propellant demonstrates these characteristics. When it is fired in a large volume (10cc bomb), the ash is a tan-gray color. But when it is fired in a device that drives to high pressure, the ash becomes ebony black and sooty. Burning the graphite in the first case has gone to

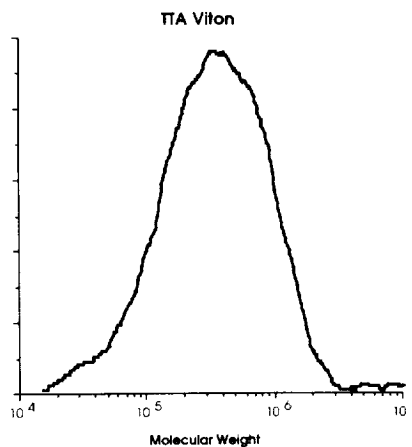
completion in the form of CO and CO₂ with good heat transfer; but, in the second case, this reaction has been interrupted and the reaction rate has been quenched by leaving unreacted solid carbon.

Combining low-concentration rate promoters has led to stabilized very high burning rates for nitrocellulose systems. Carbon black and lead compounds at low concentrations have been added to nitrocellulose to speed low-pressure (ignition) burn rates while controlling high-pressure (peak pressure) burn rates. Carbon in the range of 0.3% can double the low-pressure burning rate and maintain that rate beyond 1500 psia, while carbon concentrations in the range of 1.0% can quadruple the burning rate and hold it near that level up to 4000 psia. Above 1% carbon black, the effect disappears and burning rates fall because of the decrease in propellant energy. High concentrations of these rate promoters will usually result in decreased burning rates. The fact that small particle carbon black promotes higher burning rates suggests a simple surface area effect.

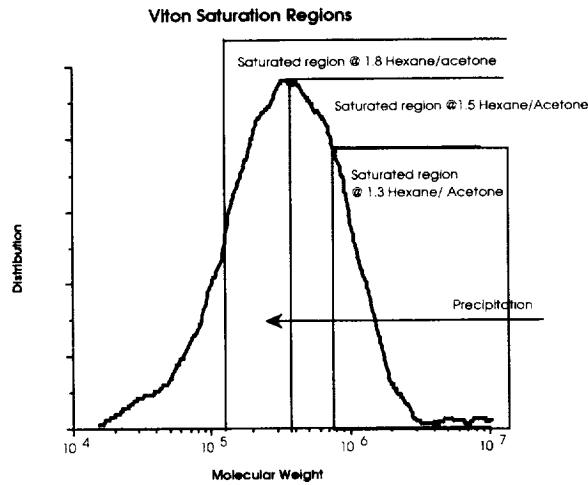
Studies of the slow decomposition of solid propellants suggest that the combustion of a propellant takes place through a surface zone decomposition that leads to the formation of a combustible gas mixture. This combustion of gas, close to the propellant surface, provides much of the energy necessary to support the primary decomposition. The combustible mixture may contain reducing gases and other more complex fragments. A knowledge of the kinetics of the various reactions would be of obvious value in attempting to understand the complete combustion process. Unfortunately, only a few of these reactions have been studied. It is highly probable that similar processes take place when burning the NSI propellant, with subtle effects on peak pressure and waveform as a result.

Binder Composition

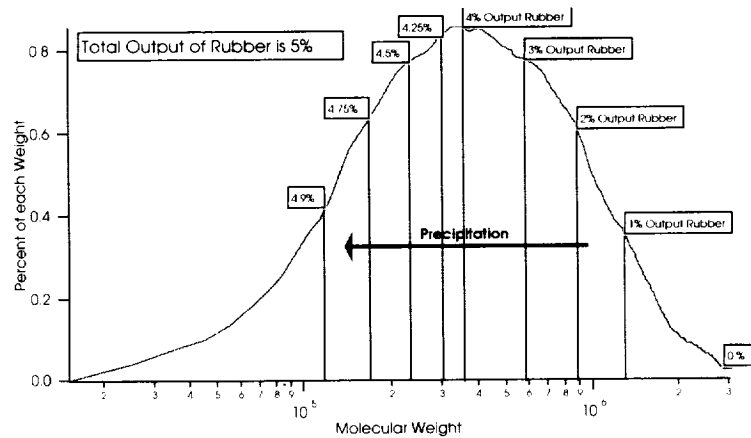
To understand what is occurring in the precipitation process, it is important to understand that Viton rubber itself is not a single molecular weight substance. It is actually composed of a mixture of different molecular weight rubbers called "mers." These mers have been blended together to produce a substance or polymer called Viton.



Each molecular weight group in the rubber has a slightly different saturation point and solubility in acetone. Therefore, the precipitation process can selectively filter out molecular weights from the rubber blend.



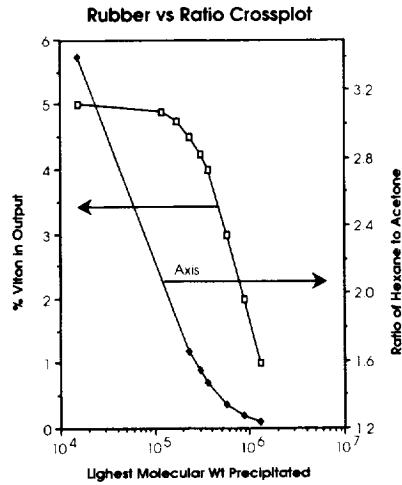
The precipitation of Viton from the solvent (acetone) by the counterosolvent (hexane) results in what is known as "fractionation" or molecular weight separation. JSC has verified, by gel permeation chromatography, the fractionation of Viton using different hexane-to-acetone ratios. Propellant mixes were produced with different hexane-to-acetone ratios, and the quantity and molecular weights of the rubber precipitated were measured. These data were used to provide the following curve:



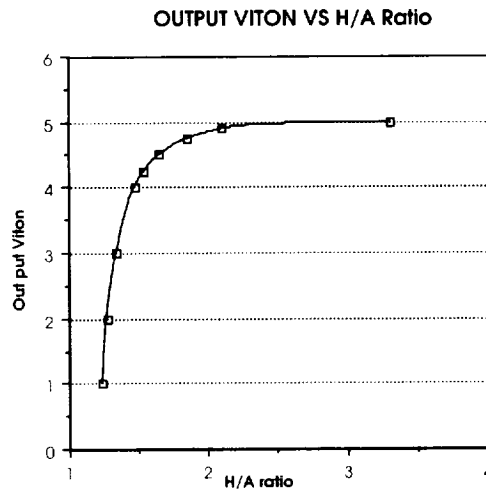
The physical properties of the Viton produced are a function of the average molecular weight precipitated. The higher molecular weight fractions are less flexible and more rigid than the lower molecular weights; the lighter fractions are more tacky and stretchable. It is, therefore,

important to maintain the rubber's properties by assuring that all the molecular weights precipitate or that the "critical countersolvent-to-solvent ratio" is reached.

The critical ratio for the hexane/acetone precipitation system to precipitate all the Viton constituents can be extrapolated from a crossplot graph of previous data. This graph gives rubber out versus molecular weight on a plot and molecular weight versus the hexane-to-acetone ratio.



By relating each ordinate axis back to the abscissa, it can be seen that the maximum rubber output has been achieved by a hexane-to-acetone ratio of 3.4, if not slightly before.



Besides fractionation, other important phenomenon occur in the precipitation cycle. When hexane is added to a Viton/acetone solution, the Viton fractions that achieve saturation precipitate first and layer onto active particles passing by. Saturation begins with the heavy weight fractions first and progresses to lighter fractions as higher hexane-to-acetone ratios are achieved. This means that the initial rubber precipitated (at a hexane-to-acetone ratio of 1.3) will be the heaviest, least soluble Viton constituent. The lighter-weight Viton molecules remain in

solution until higher countersolvent-to-solvent ratios are obtained. Since each molecular weight precipitates according to saturation, the different molecular weights are brought down in layers according to their lack of solubility. This leads to the "M&M effect," which is when the least soluble fraction is laid on the active particle first with the most soluble fractions laid on last. This has important considerations for the slurry process, where the reverse of the propellant blending process is desired. Longer soak times are required to bring all Viton constituents back into solution.

Bridgewire Slurry

Bridgewire slurry operations are key to producing NSI hardware. During this operation, a mass of propellant is placed in a solvent to dissolve the binder, and the resulting paint-like mixture is used to coat the bridgewire filament. A laboratory study was performed to better understand this process. Owing to the small size of the bridgewire unit and the lack of access within the charge cup, a mockup utilizing glass slides on a special microscope stage was used. These microscope observations, on drying, revealed the formation of crevices and pockets next to bridgewire which, in some cases, were large enough to cover the entire bridgewire filament. Such crevices severely reduce heat transfer from the filament to the slurry mass. These defects may be responsible for many "long to fire" or "fail to fire" conditions. The participation of one manufacturer in this study verified that live blends used for slurry operations produced these same types of voids. The voids are caused by stresses developed in the coating as it dries.

After the slurry mixture is applied to the bridgewire, the slurry forms an outer skin that gradually thickens. This outer "shell" must collapse upon the shrinking drop as the solvent leaves the slurry droplet. Under certain conditions, the upper shell may become so rigid that it cannot collapse owing to its increasing viscosity and solids loading. The inability of this upper shell to collapse during droplets shrinkage places the underlying structure in tension. The amount of stress developed is a function of the solvent volume still left in the droplet when the upper shell becomes rigid. Depending on the geometry (thickness) of the drop, sufficient force may develop to lift the "floor" of the drop towards the upper shell, causing voids to occur around the bridgewire. Since this situation cannot be observed from the top of the slurry droplet, it may go unnoticed. Currently it is known that the molecular weight of the Viton in propellant can influence this behavior and that certain measures can be taken to prevent void formation.

One measure that can be taken is to make the bridgewire slurry less viscous by adding extra solvent. When such slurry is added to the bridgewire, it tends to spread out more and reduce the thickness of the droplet. The first application must not attempt to provide the necessary slurry mass and should be viewed as a primer. This method works by reducing the thickness of the droplet and thus reducing the stress (top to bottom) produced in the drying film. Another way of viewing this fix is that insufficient thickness exists to form a rigid outer shell. Using this fix requires that subsequent applications be applied atop the first to achieve sufficient slurry mass. Subsequent drops need to be more viscous for mass loading and to prevent resolutionizing the first application.

A second method to reduce voids relies on the subtle effects caused by the molecular weight of the binder. In preliminary testing, this method has by far produced the most void-free slurry droplets observed. In short, this method calls for a slight reduction in the molecular weight of

the binder used in the slurry. This is done by producing a mini-blend for a slurry of the same ingredients as the main blend with fractionated Viton. Eventually this mini-blend may include the entire propellant. This method changes the molecular weight of the binder, not the percentage of binder in the propellant. An explanation of why it works follows.

The viscosity of polymer solvent solutions is strongly influenced by the molecular weight of the polymer in solution, not just its concentration. In general, the higher the molecular weight of a polymer, the more viscous the solution will be. For example, if 10 g of X molecular weight Viton are added to 200 ml of acetone and if 10 g of low molecular weight Viton are added to 200 ml of acetone, the solution made with the high molecular weight Viton will have a higher viscosity. Viscosity is very important in the bridgewire slurry operation. A slurry that is too thick does not leave the applicator, and a slurry that is too thin drips from the applicator before it can be positioned. As a consequence, most manufacturers are working within a viscosity "corridor."

The "ideal" viscosity is approached by experience. If a mixture is too thick, a little more solvent is added. If a mixture is too thin, some solvent is allowed to evaporate. What really determines how much solvent a slurry must contain is the molecular weight of the Viton in the propellant. If a high molecular weight Viton is used, more solvent is added because solutions made with high molecular weight polymers have an effectively higher viscosity. If a low molecular weight Viton is used, less solvent is added because solutions made with low molecular weight polymers have an effectively lower viscosity. The impact of these statements becomes apparent when one realizes that the stresses developed during slurry droplet drying arise from solvent loss.

Slurries made from low molecular weight Viton have less solvent in them (to achieve the right viscosity) and, therefore, have less solvent to lose. Less solvent to lose means lower stresses and dimensional changes occur during drying. Lower molecular weight Viton is less likely to form a hard shell that is incapable of movement during the drying process and should retain more of its flexibility at low temperatures. By lowering the molecular weight of the Viton, it becomes easier (wider corridor) to apply slurry to bridgewire without cracking.

Further testing will be done to determine what effects lowering of the molecular weight of Viton will have on a propellant. By applying the methods detailed here, NSI units have been prepared that function under 400 μ s with little deviation. Work continues on the impact that initial purity and preparatory treatment of starting materials have on propellant performance. Much of the propellant manufacturing process has been documented, but further work remains.

The authors gratefully acknowledge the help the NSI manufacturers have given. Their help has led to a better understanding and documentation of this product.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188		
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.					
1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE October 2000	3. REPORT TYPE AND DATES COVERED NASA Technical Paper			
4. TITLE AND SUBTITLE Propellant for the NASA Standard Initiator			5. FUNDING NUMBERS		
6. AUTHOR(S) Carl Hohmann, Bill Tipton, Jr., Maureen Dutton					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Lyndon B. Johnson Space Center Houston, Texas 77058			8. PERFORMING ORGANIZATION REPORT NUMBERS S-861		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Washington, DC 20546-0001			10. SPONSORING/MONITORING AGENCY REPORT NUMBER TP-2000-210186		
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION/AVAILABILITY STATEMENT Available from the NASA Center for AeroSpace Information (CASI) 7121 Standard Hanover, MD 21076-1320 Category: 28			12b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words) This paper discusses processes employed in manufacturing zirconium-potassium perchlorate propellant for the NASA standard initiator. It provides both a historical background on the NSI device—detailing problem areas and their resolution—and on propellant blending techniques. Emphasis is placed on the precipitation blending method. The findings on mixing equipment, processing, and raw materials are described. Also detailed are findings on the bridgewire slurry operation, one of the critical steps in the production of the NASA standard initiator.					
14. SUBJECT TERMS propellant, zirconium-potassium perchlorate; initiator, NASA standard; mixtures, blending techniques; precipitation, blending method			15. NUMBER OF PAGES 24	16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unlimited	20. LIMITATION OF ABSTRACT Unlimited		