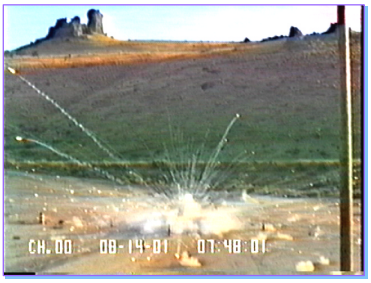
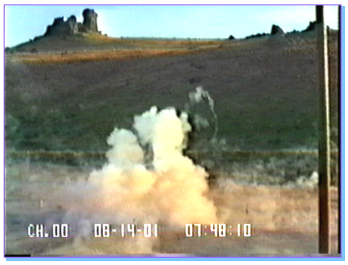
# *Castable, Solvent-Free, Red Phosphorus Smokes for Target Markers*
# *SERDP Program PP-1180*

***Final Technical Report***
***Data Item Number A006***
***June 30, 2003***




***Prepared by:***
***ATK Thiokol Propulsion***
***P.O Box 707***
***Brigham City, UT 84302-0707***

DoD EPA DOE SERDP
Strategic Environmental Research and Development Program

ATK ALLIANT TECHSYSTEMS
THIOKOL PROPULSION

## Introduction

Red phosphorous (RP) is a material that has been used historically for the production of certain types of target and location markers. Binders are necessary in the production of RP smoke grains because they provide structural integrity to the grain, whether in explosively disseminated markers such as the MK67 or in long duration markers such as the MK25/MK58. Without a binder, RP will disseminate in a fine granular form, burn rapidly, and fail to sustain a white cloud for a sufficient amount of time to adequately mark a target. In addition, a major benefit of a binder is that it coats the RP particles and desensitizes them to electrostatic energy relative to uncoated or "dry" RP. Two methods can be used to produce pyrotechnic smoke compositions containing red phosphorous. One method is to pre-blend RP with a binder (linseed oil, polyester, others) in a standard mixer, and press the resulting composition. This is the process for the MK25/MK58 and the M264. While the current MK25/MK58 process does not use solvents, the M264 process can require up to 100% by weight of solvent. These applications both require multiple pressing steps, and post-press reaming in the case of MK25/MK58. The second method is to dissolve a butyl-rubber binder in a solvent, disperse RP in the solvent/ binder, then extrude the desired RP smoke grain geometry, such as in the MK67. This method provides potential for recycling solvents, but does still require their use.

Volatile organic compounds (VOCs) such as acetone, and Hazardous Air Pollutants (HAPs) such as hexane are commonly used. The Miscellaneous Organic National Emission Standard for Hazardous Air Pollutant (NESHAP) law requires controls on VOC and HAP emissions with the clear intent to minimize these emissions and protect the environment. These solvents are typically quite flammable, ESD sensitive, and are generally harmful and/or toxic if inhaled or ingested.

Pressed compositions can utilize less binder because they are consolidated under very high static loads. However, less binder equates to greater friction, impact, and ESD sensitivity and a much greater safety hazard during use. Table 1 shows ESD sensitivities of "dry" RP compared to RP coated with various amounts of oil. This shows that even when low levels of the hydrocarbon coating are employed, such as in pressed compositions, the ESD sensitivity remains extreme. In addition, the pressed grains have been known to exhibit erratic performance.

**Table 1. Sensitivity to Electrostatic Discharge**
*The amount of electrostatic energy, in joules, required to ignite 50% of the test samples

| Material | ESD (J)* |
|---|---|
| RP (class 3) | <0.05 |
| RP (94%)<br>Oil (6%) | <0.05 |
| RP (87.5%)<br>Oil (12.5%) | 0.18 |
| RP (75%)<br>Oil (25%) | 7.28 |

Elimination of VOCs and HAPs from this process is greatly desired to diminish the attendant safety and environmental hazards. One way to accomplish this is to use a low-viscosity polymer

as the binder in these compounds. The polymer must be added at levels high enough that solvents can be avoided. This high binder content would also allow the RP composition to be remotely batch-mixed and cast or poured into the required geometry. The hazards and waste streams associated with pressing and post-pressing grain machining are eliminated. A comparison of the process for a cast composition versus a pressed or extruded composition is shown in Table 2. The performance of the cast grains, however, must match the performance of the conventional grains.

**Table 2. Process Comparison of Cast versus Pressed RP Compositions such as MK25/58 or Hydra 70**

| | **Castable** | **Pressed or Extruded** |
|---|---|---|
| **Binder** | Energetic castable | Linseed oil, polyester, or butyl rubber |
| **Process Solvent** | None | 0-100% by weight |
| **Solvent ID** | N/A | Acetone or hexanes |
| **ESD Sensitivity, J** | >8 | <1 @12.5% oil to ~7 at 25% oil; after solvent removal |
| **Process Steps** | 1. Blend ingredients<br>2. Cast to desired grain dimension<br>3. Thermal cure | 1. Dissolve binder in solvent<br>2. Blend ingredients<br>3. Remove solvent or extrude<br>4. Granulation if necessary, or cutting<br>5. Incremental pressing,<br>a. 6-8 increments, OR<br>b. ~72 pellets per unit<br>6. Ream grain<br>7. Cure |

## Summary

The solvent-free, castable RP technology developed under SERDP sponsorship (DACA72-01-C-0010, SERDP Program Designator PP-1180) was advanced to the point that it was ready to be evaluated in a preliminary prototype marker. The original proposal had selected the explosively disseminated MK67 target marker. Efforts to locate MK67 hardware were not successful as the marker is not currently in active production. Preliminary testing of the castable RP formulation was completed in prototype hardware developed on the program to match the wall thickness and strength of the MK67. Various explosive charges were evaluated with the formulation to simulate the explosive charge in the MK67.

During the program, a Sources Sought Announcement (DAAA09-01-R-0106) was issued requesting information from interested producers for the MK25 Mod 3 and Mod 4 markers, and indicating the new specification will be a performance specification. A performance specification will allow replacement of the current pressed RP compositions with alternate compositions as long as the overall performance is maintained. The solvent-free, castable RP smoke technology developed for the MK67 could be readily transitioned to the MK25. ATK Thiokol Propulsion solicited the support of the Program Manager at Rock Island for NAVAIR PMA-242, the controlling design agency for the markers. They expressed a strong interest in the solvent-free, castable RP technology for the MK25 location marker. With approval from SERDP, the demonstration article was changed to the MK25 marine location marker. Two different castable RP formulations were demonstrated in the MK25 open burning configuration.

## Approach

Castable compositions eliminate the need for solvents by substituting high concentrations of liquid pre-polymer and curative along with lower RP content. This results in a syrup-like composition, which is castable and formable, without solvent. Higher liquid pre-polymer also

dramatically desensitizes the RP to ESD. The RP composition is vacuum-cast into the correct geometry and then chemically cured to the desired structural integrity. The pre-polymer/curative forms a continuous binder phase that encapsulates the RP. The binder remains in the composition, unlike the VOC solvent, which must be removed at some point in the manufacturing process. As stated previously, the RP content is lower relative to historical, pressed RP smoke compositions. This infers that the ability to generate white smoke and adequate cloud density would be deficient, however, this is mitigated by employing energetic binder systems. These binders are self-deflagrating and the compositions can be tailored for burn rate. Of greater significance is that when the energetic binders decompose, the burning RP is exposed more efficiently to air. The result is the production of copious amounts of white smoke, similar to the compositions that contain higher amounts of RP. A description of the nominal solvent-free, castable RP composition is shown in Table 3. The process method, developed under SERDP sponsorship, is illustrated in Table 4.

**Table 3. Solvent-Free Castable RP Composition**

| Material | Concentration range | Purpose |
|---|---|---|
| Energetic Polymer | 30-40% | Allow less RP to be used. Assures ignition and provides the ability to tailor burn time. The combustion of the energetic polymer produces a large yellow flame. |
| Red Phosphorus | 50- 60% | RP combusts with air to form white, smoky $P_2O_5$, which reacts with ambient moisture to form white, smoky $H_3PO_4$. |
| Gas Generant or Co-Oxidizer | 2.5-10% | The generant decomposes to produce inert $N_2$ gas, which blows off the $P_2O_5$ from the surface. The burn becomes "steady". |

**Table 4. Solvent-Free Castable RP Process Method**

| Step | Purpose | Procedure |
|---|---|---|
| **1** | Add:<br>Prepolymer<br>Curative<br>Cure Catalyst | The binder materials are added together in a heated 135 °F mix bowl. No preblend required. |
| **2** | Add:<br>RP | The RP is added incrementally and mixed into the binder components. Each incremental addition of RP is blended until "wetted" by the binder components. The RP can be added continuously with constant stirring. The RP is continually "wetted" by the binder during the continuous feed. |
| **3** | Add:<br>Gas Generant or Co-Oxidizer | The gas generant or co-oxidizer is added batch-wise or continuously just like RP. It is blended until wetted. |
| **4** | Final Mixing | All the materials have been added so the composition is mixed/stirred under vacuum until it is homogeneous and reaches 135 °F. |
| **5** | Casting | The composition is de-aerated while it is being cast. The MK25 tube is placed in a vacuum bell and the composition enters the tube under vacuum. Any entrained air or voids are removed. |

## Technical Discussion

MK67 Prototype

The item originally of interest for demonstration of the castable RP compsition was the explosively disseminated MK67. The performance requirements for the marker are:

- The smoke cloud should be greater than 50 feet wide by 50 feet high
- The smoke cloud duration should be greater than 45 sec
- The smoke cloud density may be lower than the baseline and still produce adequate performance

An explosive charge disseminates pieces of the RP composition, which burn to produce a white cloud over the target. The cloud size and duration depend on the fragment size, the fragment distribution, and the deflagration rate of the RP composition.

The deflagration rate of the RP pyrotechnic charge can be modulated by varying the energy of the binder. Table 5 shows the binders that were examined for a MK67 replacment. The deflagration rates of the constituents, in order of highest to lowest, are:

GAP>BTTN>NC>TEGDN>BuNENA>PEG>Rucoflex® polyester.

**Table 5. Energetic Binder Systems Examined**

| **Polymer Plasticizer** | GAP | Nitrocellulose | PEG | Rucoflex® |
|---|---|---|---|---|
| GAP Plasticizer | X | | | |
| BTTN | X | X | X | X |
| TEGDN | X | X | X | X |
| BuNENA | | X | | |

The safety properties of several of the new formulations were found to depend upon the nature of the binder. Nitrocellulose/nitrate ester and PEG/nitrate ester formulations were slightly more sensitive with respect to friction and impact as shown in Table 6.

**Table 6. Safety Properties of RP and Compositions Containing RP (asterisks indicate cured samples)**

| Composition | ESD (J) | Friction (lbs.) | Impact (cm) |
|---|---|---|---|
| RP | 0.01 | 25 at 3 ft/sec | >46 |
| RP/oil (87.5/12.5) | 0.18 | <25 at 2 ft/sec | 26 |
| RP/oil (75/25) | 7.3 | <25 at 2 ft/sec | 27.2 |
| 69% RP with PEG and BTTN* | 7.5 | 25 at 3 ft/sec | 3.9 |
| 69% RP with nitrocellulose and TEGDN* | 4.8 | <25 at 2 ft/sec | 3.3 |
| 68% RP with GAP--fast burning | >8 | 25 at 8 ft/sec | >46 |
| 68% RP with GAP and PolyG®--slow burning | >8 | >800 at 8 ft/sec | >46 |
| 68% RP with Rucoflex® and TEGDN | >8 | >800 at 8 ft/sec | >46 |

The processing steps to load the prototype are shown in Figure 1.

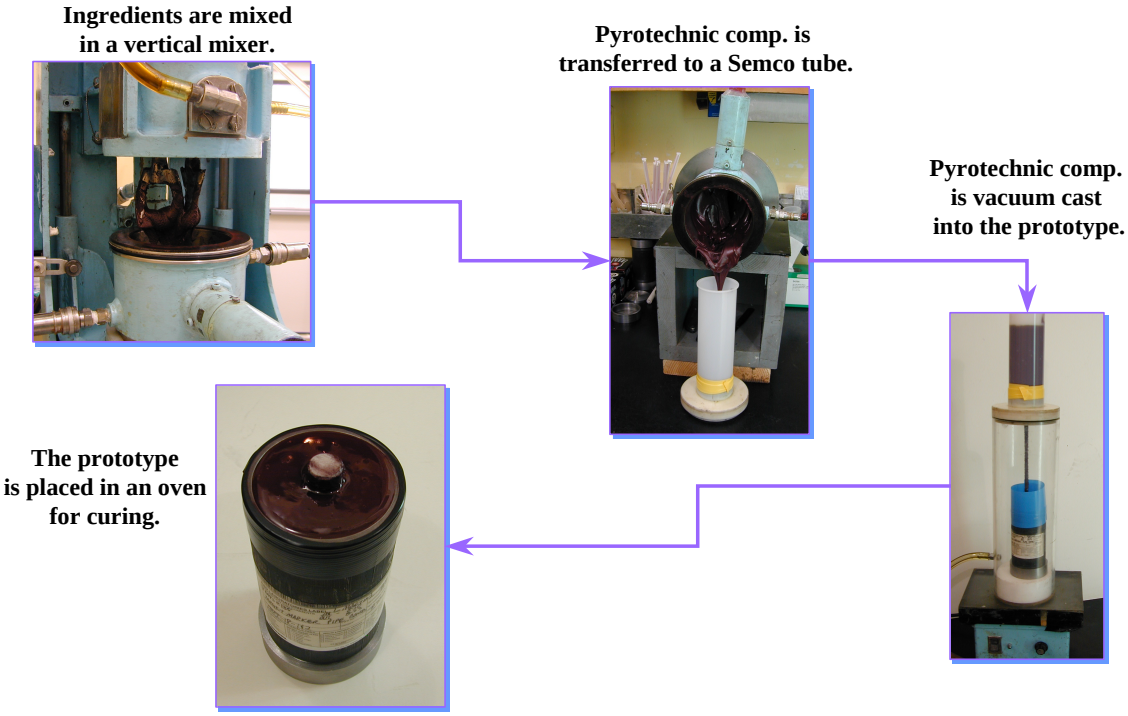



**Figure 1. Processing Steps for the Castable RP Composition in a MK67 Prototype**

The prototype test fixture is shown in comparison to the MK67 Mod1 marker in Figure 2. As mentioned previously, since actual hardware was not available, a prototype was built to match the confinement and size of the actual hardware as closely as possible.

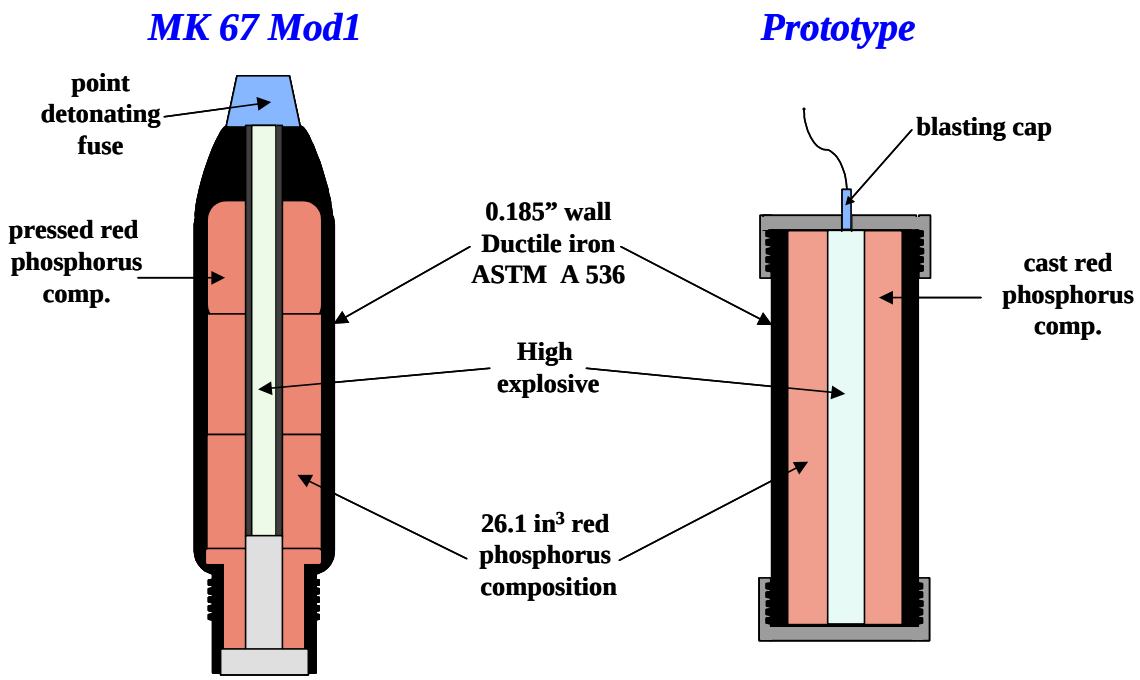



**Figure 2. Drawing of the MK67 Mod1 and the Prototype Test Unit**

The prototype was used with serveral combinations of formulation and explosive charge. Dispersion of the particles can be modulated by brisance of the explosive charge and the weight of the explosive. The explosives evaluated included Comp C-4, Comp B, and TNT, in order of descending brisance. The test results are shown in Table 7 and Figure 3.

**Table 7. MK67 Prototype Test Results**

| Test # | Composition of pyrotechnic | Explosive used | Result |
|---|---|---|---|
| 1 | GAP/GAP-P/RP (68 % RP) | Comp C-4 (0.58" dia.) | Large fraction of particles dispersed > 50' RP composition burned too rapidly |
| 2 | GAP/GAP-P/RP (68 % RP) | Comp B (0.58" dia.) | Large fraction of particles dispersed > 50' RP composition burned too rapidly |
| 3 | GAP/GAP-P/PolyG®/RP (68 % RP) | Comp B (0.58" dia.) | Large fraction of particles dispersed > 50' RP composition burned too rapidly |
| 4 | GAP/GAP-P/RP (68 % RP) | TNT (0.58" dia.) | Very little particle dispersion RP composition burned too rapidly |
| 5 | Rucoflex®/TEGDN/RP (70% RP) | Comp B (0.45" dia.) | Good particle dispersion RP composition did not produce adequate smoke |

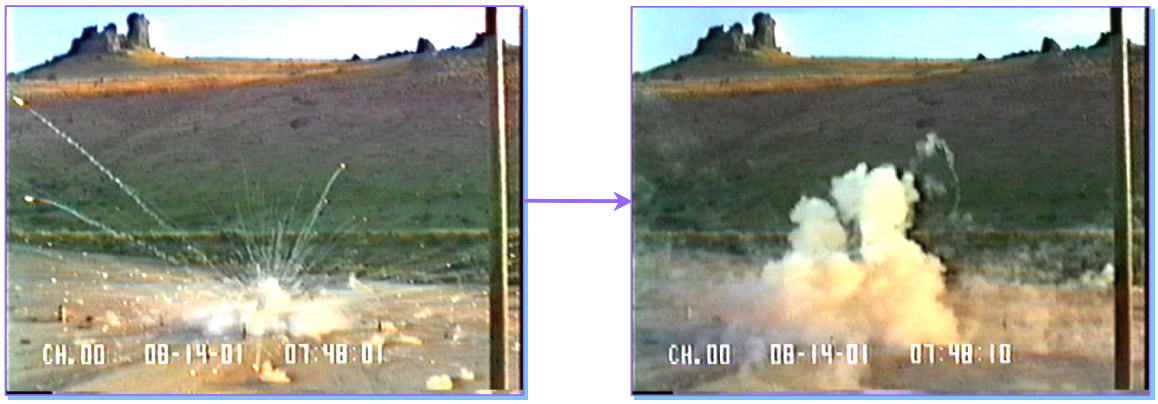



**Figure 3. Prototype Test Number 1, GAP/GAP-P/RP (68%).** Smoke cloud properties are close to meeting requirements, although further optimization in actual hardware would be required.

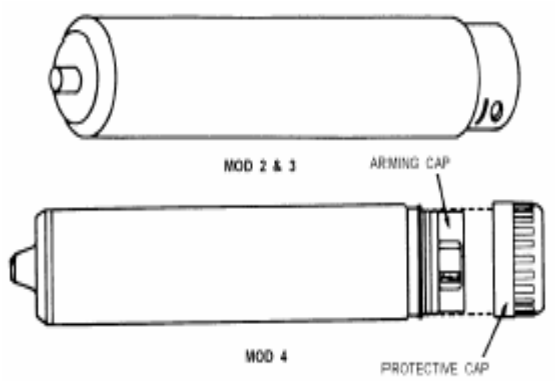
The feasibility of the castable RP compositions in an explosively disseminated marker has been shown, although further optimization of the compositions in combination with the bursting charge would be required to meet cloud size and duration requirements. The optimization testing would be best accomplished in the actual MK67 hardware.

MK25 Prototype

The US Army Operations Support Command, Rock Island Arsenal, has published the need for smoke technology (DAAA09-01-R-01060) for the MK25. The MK25 marker consists of a cylindrical outer tube approximately 18.5 inches long and 2.9 inches in diameter. Smoke and flame are emitted from the marker's nose end, while the heavy end causes the marker to float with the marker nose out of the water. A photo showing the MK25 in field operation is shown in Figure 4.

**Figure 4. Field Test of the MK25 Mod3 Marine Location Marker Burning in Pensacola Showing Smoke and Flame (Photo courtesy of NSWC Crane)**

The MK25 marker and specifications are shown in Figure 5. Inside the marker is a cardboard tube, which contains the pyrotechnic. The cardboard tube is 11.75 inches in length, has an outside diameter of 1.96 inches, and an inside diameter of 1.75 inches.



| Parameter | Current Specification |
|---|---|
| Length | 18.5 in. |
| Diameter | 3 in. |
| Weight | 3.74 lbs. |
| Pyrotechnic weight | 28 oz. |
| Ignition | Within 20 seconds |
| Burn time | 13 minute minimum |

**Figure 5. The MK 25 Marine Location Marker with Current Specifications**

Figure 6 is a photograph of the solvent-free RP composition that was produced in the vertical mixer and vacuum cast into the actual MK25 cardboard tubes. Photographs of the solvent-free, castable RP composition burning in the MK25 tube were used to evaluate the smoke production over the burn time. Each photograph, shown in Figure 7, was taken in minute intervals from start of ignition. For perspective, in this test the candle was placed on top of a road construction barrel (the orange striped object in the photographs), which is the approximate size of a 55-gallon drum. The smoke generation appears promising over the whole burn time of 15 minutes. The photograph in Figure 8 provides a sense of the flame height, which approximates the height of the cardboard tube (11”). A closer view was acquired during a separate test and is shown in Figure 9.

**Figures 6. Castable RP Composition. a. Nose end of tube where burning is initiated; b. Lateral view of the pyrotechnic charge which is inserted into the MK25 marine location marker hardware.**

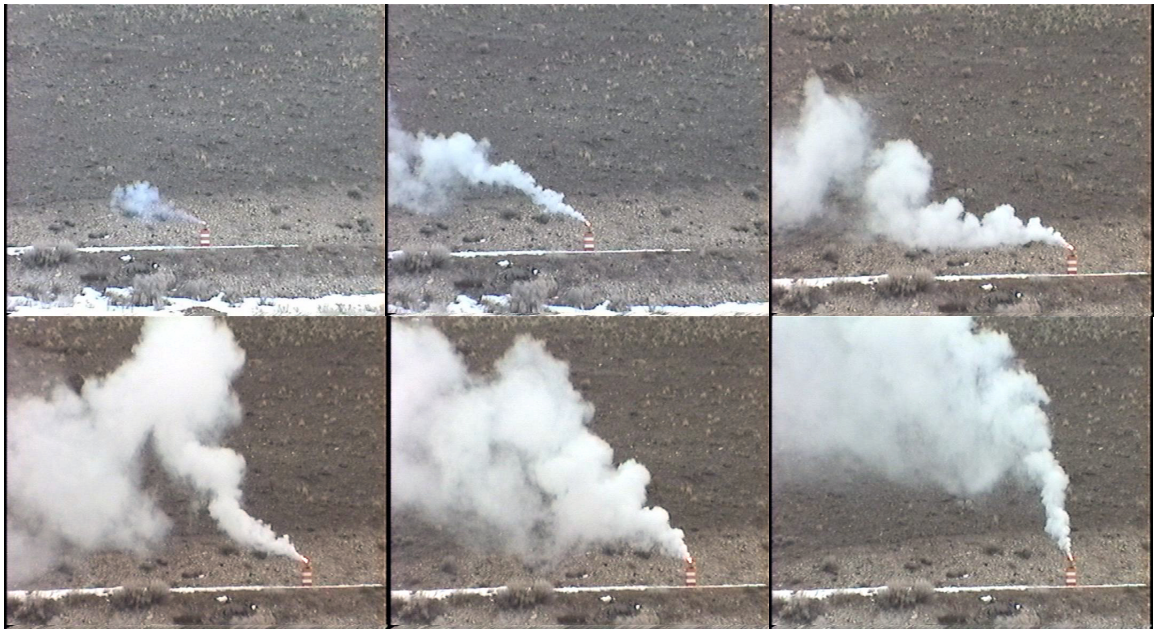


**Figure 7. Solvent-Free, Castable RP Composition Burning in the MK25 Form Factor. Each frame is one minute after the previous frame; not all data are shown.**

**Figure 8. A Distant View of the Yellow Flame from the Solvent-Free, Castable RP Composition Burning in the MK25 Cardboard Tube Insert**

**Figure 9. A Close View of the Yellow Flame Generated During the Burn of the Solvent-Free, Castable RP Composition**

Night-time location relies primarily on the ability to locate the yellow flame. Figure 10 shows the flame at three distances during a night-time burn. The photographic documentation of the smoke and flame generation appears very promising for the solvent-free, castable technology for MK25.

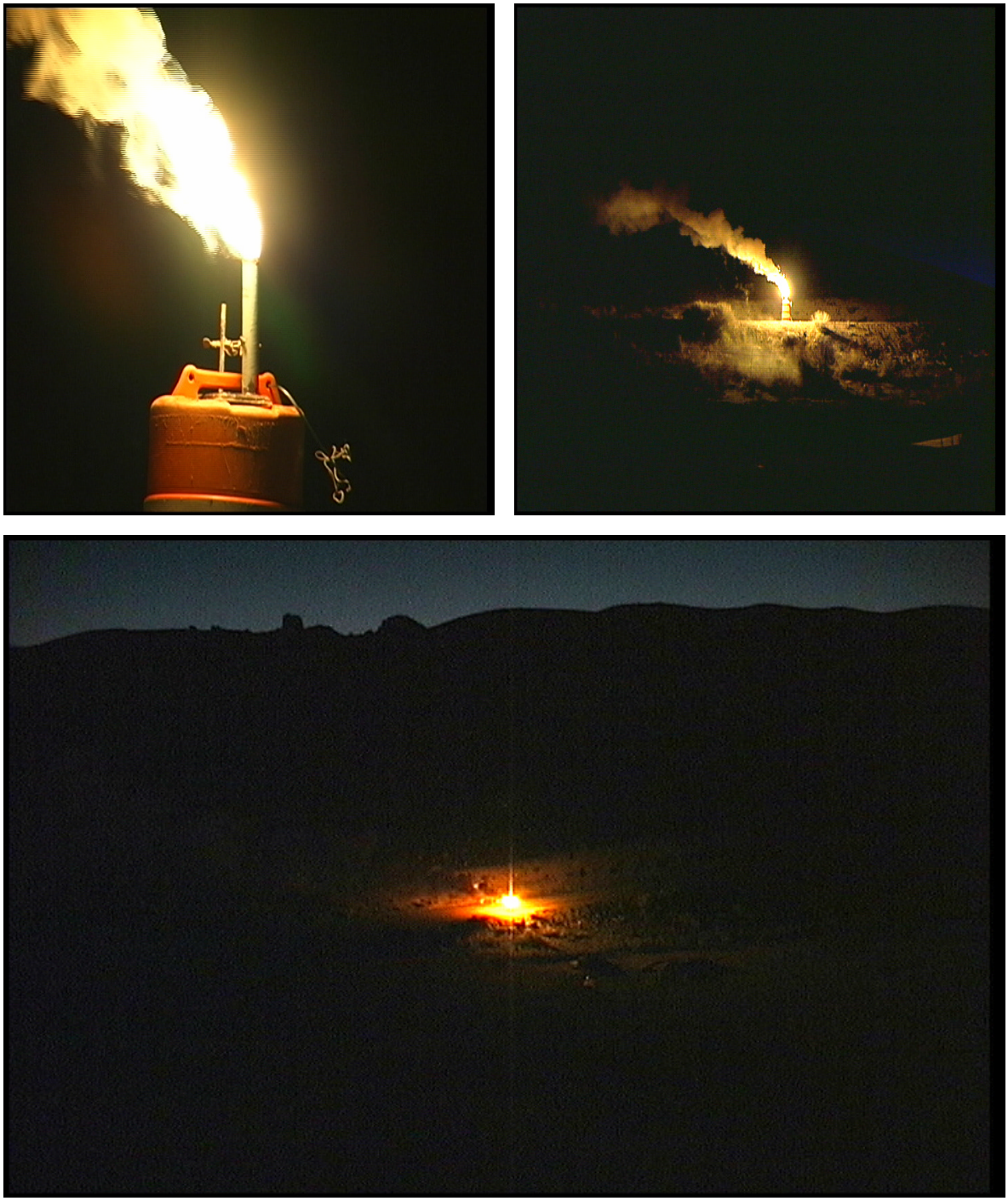


**Figure 10. The Flame of the Solvent-free, Castable RP Composition in a MK 25 Form Factor at Distances of 10 Feet, 65 Feet, and 432 Feet**

The formulation (PGN, TEGDN, RP, gas generant) demonstrated in these photographs is shown in Table 8. The viscosity of the composition was 7.7 Kp @ 135ºF, which is a typical viscosity for conventional, cast/cure composite solid rocket motor propellants.

**Table 8. The Baseline RP Composition Selected for Demonstration in the MK25**

| Material | Wt% |
|---|---|
| Polyglycerol Nitrate (PGN) Polymer | 21.11 |
| Triethylene glycol dinitrate (TEGDN) | 11.55 |
| Desmodur N-100 curative | 2.34 |
| Red Phosphorus (RP) | 62.5 |
| Gas Generant (GG) | 2.5 |

The hazard sensitivity of the baseline castable composition was evaluated and compared to RP and RP desensitized with oil (oil is typically used in the pressed composition). The sensitivity values are listed in Table 9. RP is relatively insensitive to hazardous stimuli with the exception of electrostatic discharge (ESD). RP is extremely ESD sensitive. Even when it is desensitized with oil, the ESD sensitivity is extreme. However, the baseline RP composition is two orders of magnitude "less" sensitive to ESD relative to RP and an order of magnitude less sensitive than RP/oil. The impact sensitivity of the baseline castable composition is greater (lower values = greater sensitivity) than RP, but the sensitivity is not extreme. The friction sensitivities for the baseline and RP are not extreme, however, the RP with oil is extremely friction sensitive. The exotherm onset temperature, which is indicative of decomposition, is lower for the baseline. This is due to the PGN/TEGDN binder components, which contain nitrate ester chemical moieties. This is a typical exotherm onset temperature for nitrate esters. However, this onset temperature exceeds the processing temperature by 140ºF and provides a wide margin of process safety for the baseline composition. In addition, these types of ingredients are typically used in tactical rocket propellants, and have been proven to provide adequate storage and operational service life.

*Alternate Castable RP Formulations Based on Polyether/Nitrate Ester (PE/NE)*

The formulation based on the energetic binder PGN/TEGDN is more costly than the baseline pressed formulation, with respect to ingredient costs. Much of the difference is made up by the elimination of solvent associated costs, and by simplified processing. An alternate binder system utilizing a commercially available polyether, Seegot Pluracol HP6500T (PE), was examined as a way to maintain performance and lower ingredient cost. In this case, the polymer provides oxygen, while the energetic nitrate ester plasticizer TEGDN (NE) provides increased energy. The formulations are still castable, do not use solvents, and do not require post-cure machining. The formulations, and their safety test results are shown in Tables 10 and 11, respectively. Again, the safety properties are much improved over the pressed RP formulations.

**Table 10. Castable RP Formulation Comparison**

| Formulation | PGN Baseline 1939-21-1 | PE/NE Baseline 1939-21-2 | PE/NE Mod 1 1939-25-1 | PE/NE Mod 2 1939-25-2 | PE /NE Mod 3 1939-25-3 |
|---|---|---|---|---|---|
| **Polymer** | PGN | HP6500T | HP6500T | HP6500T | HP6500T |
| **Plasticizer** | TEGDN | TEGDN | TEGDN | TEGDN | TEGDN |
| **Pl/Po** | 0.5 | 1.0 | 2.0 | 1.0 | 2.0 |
| **RP, %** | 60 | 60 | 60 | 60 | 60 |
| **RDX, %** | 5 | 5 | 5 | -- | -- |
| **AP, %** | -- | -- | -- | 5 | 5 |

**Table 11. Safety Test Results on Castable RP Formulations (Cured)**

| Formulation | PGN Baseline 1939-21-1 | PE/NE Baseline 1939-21-2 | PE/NE Mod 1 1939-25-1 | PE/NE Mod 2 1939-25-2 | PE /NE Mod 3 1939-25-3 |
|---|---|---|---|---|---|
| **ABL Impact, cm, TIL** | | | 11 | 6.9 | 3.5 |
| **ABL Friction, lbs @ ft/sec** | 50@4 | 800@8 | | | |
| **TC ESD, J** | >8 | >8 | >8 | >8 | >8 |
| **SBAT, F** | 274 | 286 | 290 | 280 | 240 |
| **TC Impact, in** | 40.4 | 13.67 | 6.08 | 5.86 | 4.4` |
| **TC Friction, lbs** | | | >64 | >46 | >64 |
| | | | | | |

*Bondline Testing*

Some flare compositions are known to exhibit erratic ballistic performance due to side-burning, or "chunking". Use of liners can improve performance in some cases. To determine if liners had any influence on the ballistic behavior in this application, a series of tests were completed with and without liners.

Sufficient MK25 cardboard tubes were not available, so the specification for the tubes was obtained, and tubes of similar dimension were ordered from Custom Paper Tubes. Foil-lined tubes were selected for their barrier effect to potenetial nitrate ester migration. Bondline testing consisted of lining the foil-lined tube, then casting the RP composition. The RP composition was cured and then pushed out using a punch, specially designed for this program. Normally, bondline tests are run on "flatstock", but such material was not available for the foil-lined paper tubes. Force to push the composition, and failure mode are recorded. Four potential bond systems were used in the testing for the PGN-based and PE/NE based formulations. These were:

- A direct bond of the RP composition to the foil-lined tube
- Bonding to the foil-lined tube to which A-187 primer had been applied
- Bonding to the foil-lined tube to which UF-2222 liner had been applied,
- Bonding to the foil-lined tube to which UF-2228 wet coat (WC) liner had been applied. The wet coat liner is not cured before propellant cast.

The highest bond strengths were obtained with the UF-2222 and UF-2228 WC liners. Higher bond strengths were obtained with the PGN baseline formulation than with the PE/NE baseline formulation. The results are shown in Table 12.

**TABLE 12**
**Bond Test Result to RP Composition**
Push Out Test at 0.05 ipm and ambient (75°F)

| **Bond System** | **1939-20-1 (PGN)** | | **1939-20-2 (PE)** | |
|---|---|---|---|---|
| | **Shear Stress** | **Failure Mode** | **Shear Stress** | **Failure Mode** |
| **Direct to Al** | 25.33<br>15.23<br>13.45 | A to Al<br>A to Al<br>A to Al | 18.68<br>9.22<br>7.03 | A to Al<br>A to Al<br>A to Al |
| | Avg. = 18.00<br>s.d. = 6.41 | | Avg. = 11.64<br>s.d. = 6.19 | |
| **A-187 Silane** | 12.61<br>21.87<br>27.02 | A to Al<br>A to Al<br>A to Al | 11.62<br>11.39<br>6.84 | A to Al<br>A to Al<br>A to Al |
| | Avg. = 20.50<br>s.d. = 7.30 | | Avg. = 9.95<br>s.d. = 2.70 | |
| **Silane/UF-2222 CC** | 44.33<br>41.56<br>38.36 | 30 RP,70RPFonL<br>RPFonL<br>RPFonL | 29.40<br>21.72<br>18.71 | A to Al<br>A to Al<br>A to Al |
| | Avg. = 41.42<br>s.d. = 2.98 | | Avg. = 23.28<br>s.d. = 5.51 | |
| **Silane/UF-2228 WC** | 70.49<br>59.68<br>53.76 | 15RP,85AtoAl<br>15RP,85AtoAl<br>60RP,40AtoAl | 12.37<br>12.30<br>11.51 | A to Al<br>A to Al<br>A to Al |
| | Avg. = 61.31<br>s.d. = 8.48 | | Avg. = 12.06<br>s.d. = 0.48 | |

A to Al Adhesive failure to Aluminum foil
RP Failure in RP composition
RPFonL Failure with a light film of RP composition on the liner

*Formulation Testing for Smoke and Night-time Visible Output*

The MK25 has requirements for day-time smoke, flame height, and night-time visible intensity. The requirements are shown in Table 13. In this round of testing, three cameras were used: a close-up camera and a wide-angle camera each at approximately 30 feet, and a camera at 4,027 feet from the test. This is the most distant vantage point available to view the testing. The visible radiant intensity (W/Sr) was measured over time for night-time testing. Visibility, flame height, and smoke were recorded photographically.

**Table 13. MK25 Performance Specifications**

| *Performance Criteria* | *Minimum goal* | *Maximum goal* |
|---|---|---|
| ***Burn Time*** | 13 min. | 18 min |
| ***White Smoke (Radius @ 20')*** | 5 feet | 20 feet |
| ***Yellow Flame (height)*** | 10 inches | 24 inches |
| ***Visible intensity (nighttime)*** | 50 W/Sr | 150 W/Sr |

The PGN baseline (Formulation 1939-21-1) was tested without liner, and with UF2228 liner applied to the foil-lined tube. The PE/NE baseline (Formulation 1939-21-2) was tested without liner, and with UF2222 liner. In the initial round of testing without liner, the PGN formulation was within specification for burn time (15 minutes) while the PE/NE formulation burned much longer than the specification (45 minutes). Flame height was slightly better for the PGN formulation. The PE/NE formulation exhibited slower ignition. Both were visible from the distant camera (Tests 1 and 2), although the PE/NE formulation was not as bright, especially early in the burn, Table 14, Figures 11-16. The visible output, Figure 17-18, illustrate the effect of the very long burn rate of the PE/NE. While the PGN formulation approaches 30 W/Sr, the PE/NE output was much lower at an average of 5 W/Sr. This is a function of mass flow of the combustion products, which are much lower at the low burn rate. Both formulations exhibited a relatively smooth burn.

**Table 14. Performance Tests for PGN and PE/NE Castable RP Compositions in Prototype Tubes.** Samples were cast into foil-lined prototype tubes; an adhesive liner was used where indicated. Full-length tubes are 11.75 inches in length; cut-back tubes are 8.0 inches in length with a diameter of 1.75 inches ID, 1.96 inches OD. Flame heights were all greater than 12 inches; smoke cloud radius at 20 ft were all greater than 5 ft. in diameter

| **Formulation** | **Configuration** | **Burn Time, sec** (Normalized to Full-length) | **Night Visible, W/Sr** Avg | **Comments** |
|---|---|---|---|---|
| **PGN Baseline 1939-21-1** | Unlined Full-length | 15 | 30 | Smooth Burn |
| **PE/NE Baseline 1939-21-2** | Unlined Full-length | 45 | 5 | Smooth Burn<br>Not as bright as PGN<br>More white residue |
| **PGN Baseline 1939-21-1** | UF2228 Lined Full-length | 9 | 25 | Vigorous burn<br>Some erratic burn |
| **PE/NE Baseline 1939-21-2** | UF2222 Lined Full-length | 50 | 10 | Slow ignition<br>Smooth burn<br>More white residue |
| **PGN Baseline 1939-21-1** | Unlined Full-length | 15 | N/A | Smooth burn |
| **PGN Baseline 1939-21-2** | UF2228 Lined Full-length | 9 | N/A | Some erratic burn |
| **PE/NE Mod 1 1939-25-1** | Unlined Cut-back | 37 | 7 | Smooth burn |
| **PE/NE Mod 3 1939-25-2** | Unlined Cut-back | 18 | 13 | Whiter flame<br>Smooth burn |
| **PE/NE Mod 2 1939-25-3** | Unlined Cut-back | 18 | 15 | Whiter flame<br>Smooth burn |

Lining did not improve ballistic performance for either formulation (Tests 3 and 4), in fact, lined PGN samples appeared more erratic in their burn behavior than unlined samples, exhibiting some chunking at end of burn. This is especially evident in the visible output measurements, which show spiking in the output for the lined PGN test, Figure 19. PE/NE samples were similar in both lined and unlined tests, Figure 20. Avoiding the requirement to line the tubes is a benefit in that it eliminates process steps and associated costs. Results are shown in Table 14. Smoke and flame are similar to the unlined tests, Figures 21-26. The unlined and lined PGN tubes were retested to confirm the effect of lining, and the burn times were repeatable. Visible output was not obtained because the tests were daytime tests. Photographs are shown in Figures 27-31 (Tests 5 and 6). No long distance view was obtained for the unlined PGN test (Test 6).

To increase the burn rate of the PE/NE formulation, the plasticizer-to-polymer (Pl/Po) ratio was increased (Formulation 1939-25-1, Test 7). AP was added as a co-oxidizer to the baseline PE/NE formulation (Formulation 1939-25-2, Test 9), and both were done in combination (Formulation 1939-25-3, Test 8). Results are shown in Table 14, and Figures 29-37. Both were effective at increasing the burn rate to meeting specification (18 minutes), and increasing ignitability and visibility. Additional optimization would be required to meet the visible output, however, as the average value was below specification, at 15 W/Sr. An increase in output could be accomplished by several routes. There is still latitude to increase the burn rate to approach the middle of the specification range. This could be accomplished by adding finer particle size AP, or by adding $NaNO_3$ as the co-oxidizer. The formulations are very low viscosity, so the RP content could be significantly increased, as well. All indications are the alternate PE/NE binder system would work as well as the PGN binder system.

**Conclusions**

Castable, solvent-free, RP compositions employing energetic binder systems have been demonstrated for two applications: explosively-disseminated target markers, and long-burning marine location markers. The formulations show improved safety characteristics over the traditional pressed RP compositions. RP content, energy content and burn rates of the formulations can be tailored through addition of gas generants or co-oxidizers, or through modification of the energetic binder. Such tailorability provides latitude for optimization to the specific application of interest.

**Acknowledgements**

The support of the SERDP Pollution Prevention Program is gratefully acknowledged, and specifically the guidance of Mr. Chuck Pellerin, Pollution Prevention Program Manager. Ms. Melissa May (NSWC Crane), Ms. Kathy Schenck (NAVAIR PMA-242), and Mr. Paul Ricuitti (OSC Rock Island; Logcon) provided valuable assistance in guiding the technology for the MK2 Marine Location Marker.