Full Paper

KDNP – A Lead Free Replacement for Lead Styphnate

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Abstract

Efforts directed towards creating new environmentally friendly replacements for existing primary explosives have resulted in development of potassium 5,7-dinitro-[2,1,3]-benzoxadiazol-4-olate 3-oxide (KDNP). The chemical and physical properties of this material have been investigated and it appears that KDNP is a suitable drop-in replacement for lead styphnate in a variety of ordnance applications. KDNP is easily prepared, has excellent thermal stability and has safety and performance properties, which are equivalent to or exceed those for lead styphnate. KDNP has been qualified for military use per NAVSEAINST 8020.5C.

Keywords: KDNP, Basic Lead Styphnate, Normal Lead Styphnate, Primary Explosives

1 Introduction

Lead styphnates (LS), both normal and basic, are primary explosives widely used in ordnance systems as components of initiation trains. These applications include percussion primers, stab initiated devices, bridgewire initiated compositions and detonators. LS is a reliable explosive material and, due to extensive study, its chemical, physical and performance properties are well defined. Despite its utility as an energetic material, LS contains lead which is released into the environment during production and use. Environmental, health and safety regulations on materials containing toxic heavy metals including lead are quite extensive and are likely to increase in severity in the future, along with associated compliance costs. The manufacture, use, demilitarization and disposal of LS and related ordnance are impacted by these regulations and lead free alternatives have been sought for a number of years.

Executive order 12856 was issued in 1993 to reduce or eliminate procurement of hazardous substances by federal facilities. As a result, the CAD/PAD group at the Naval Surface Warfare Center – Indian Head established a study to find replacements for LS which do not contain objectionable elements such as mercury or lead. Pacific Scientific Energetic Materials Co. (PSEMC) in Chandler, AZ, in conjunction with chemists at NSWC-IH and elsewhere have been involved in a program to develop existing or new materials which would serve as a drop in replacement for LS and which would incorporate no toxic or environmentally undesirable elements. Preparation, characterization and investigation of over twenty chemically unique materials identified a number of materials which may be suitable as potential targets for investigation.

One material that has found use in primers and igniters is potassium dinitrobenzofuroxan, KDNBF [1] (**2**, Figure 1). This compound exists as the Jackson-Meisenheimer adduct formed via reaction of 4,6-dinitrobenzofuroxan with KOH and has relatively low thermal stability (DSC exotherm approx. 488 K) as may be expected from a charge transfer complex. A phenoxide salt of similar structure should afford a higher temperature response and was one compound targeted in the PSEMC program. KDNP (potassium 5,7-dinitro-[2,1,3]-benzoxadiazol-4-olate 3-oxide, **1**, Figure 1) displays substantially higher thermal stability (DSC exotherm approx. 558 K) compared to KDNBF as expected and has properties suitable for use as a replacement of LS. This has been confirmed by subsequent performance studies in a variety of applications. Based on results of these tests [2], Naval Sea Systems Command has qualified KDNP as a primary explosive in accordance with the requirements of NAVSEAINST 8020.5C and has identified it a safe and suita-
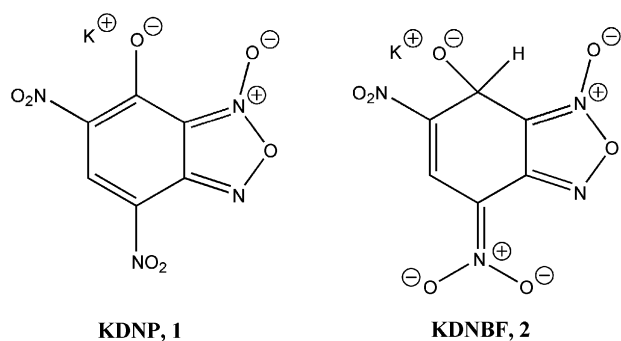
**Figure 1.** Chemical structures of KDNP and KDNBF.

ble for service use and qualified for weapons development.

Preliminary results from evaluation of KDNP samples have been presented elsewhere [3] and include information on synthesis techniques/product morphology, safety testing and closed bomb pressure-time data. The volume of chemical and performance data on KDNP has increased substantially and is presented here.

2 Experimental Section

A variety of methods are available for preparation of KDNP, including the original 1983 Norris preparation [4] from nitration and Boulton–Katritzky type [5] rearrangement of 5-chlorobenzofuroxan. Unfortunately, KDNP prepared via this approach retains water, which is used as solvent, and results in very friction/impact sensitive needles. Recrystallization may be done in a variety of solvents to give less sensitive and better handling crystalline products however an alternate synthetic method (shown in Figure 2) has been devised which precludes the use of water. In addition to the procedure shown in Figure 2, PSEMC and NSWC-IH are currently pursuing alternate methods of preparation [6].

The procedure used to prepare KDNP may be broken down into three distinct areas: nitration, azide substitution and closure, and purity/particle size control. The method starts with commercially available 3-bromoanisole (**3**), which is nitrated via a mixed acid technique [7] to give 3-bromo-2,4,6-trinitroanisole (**4**). This material is also a precursor to DIPAM (dipicramide) [7,8], and as such, this well known nitration reaction was used in the
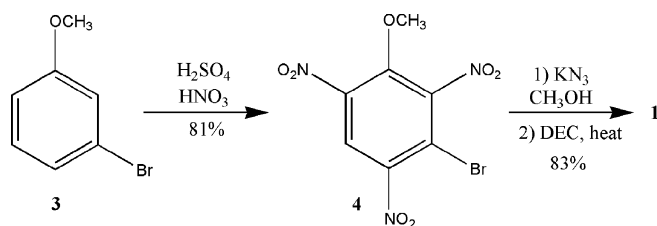
Figure 2. Synthesis of KDNP (**1**).

1960's to make DIPAM on a large scale. Compound **4** is then treated with potassium azide in methanol at reflux to furnish a brown solid wherein the bromine has been displaced by an azido moiety. The solvent is removed under reduced pressure and replaced with acetone in which the product is soluble but excess inorganic potassium salts are not. The reaction is filtered to remove the inorganic salts and the acetone solution containing **4** is concentrated to dryness. The solid **4** is then heated to reflux as a solution in diethylcarbonate at 408 K to close the furoxan ring and afford crude KDNP (**1**).

KDNP prepared by this method is routinely recrystallized from acetone/toluene to afford a flowable crystalline product however for some applications larger or smaller particle sizes may be useful. In those cases, the crude KDNP may be dissolved in 2-methoxyethanol and precipitated out of solution with 2-propanol to give particle sizes in the 20 to 100 + μm range. Particle size is easily controlled by varying the temperature and addition rate of the 2-propanol.

All solvents and reagents were used as received unless otherwise indicated. 3-bromoanisole (98 %), fuming nitric acid (90 %), diethylcarbonate (99 %), methanol, acetone and toluene were purchased from Sigma–Aldrich. Sulfuric acid (96 %) was purchased from Fisher Scientific. Potassium azide (99 %) was purchased from Fine Chemicals Inc. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity Inova 400 instrument. Chemical shifts are quoted in ppm relative to residual solvent (DMSO) or TMS. IR spectra were recorded on a Nicolet Magna-IR 550 FT-IR instrument. DSC spectra were recorded on a TA Instruments DSC 2910 instrument.

2.1 KDNP (1)

3-bromo-2,4,6-trinitroanisole (6.00 g, 18.63 mmol) was dissolved in methanol (100 mL) in a 250 mL round-bottomed flask. Potassium azide (2.10 equiv., 3.17 g) was added to give an orange solution which contained potassium azide solids. The flask was fitted with a reflux condenser and the solution was heated to 368 K (reflux) for 1 hour. During reflux all of the remaining solids dissolved to give a yellow/orange solution. The mixture was cooled slightly and the methanol was removed on a rotary evaporator to leave a yellow/orange solid. The solid was taken up in minimum acetone and filtered through Whatman #1 filter paper. The white/yellow precipitate (excess KN_3 and salts) was washed with acetone to give a yellow filtrate which was taken to dryness on the rotary evaporator. The resulting yellow gum was taken up in diethyl carbonate (100 mL) and heated to reflux (408 K). After 5–10 minutes all of the yellow solids had dissolved and a fine brown precipitate formed. The solution was maintained at reflux for 2 hours and afterwards cooled slowly to room temperature. The brown solution was cooled in an ice bath for 30 minutes and the brown precipitate was filtered through Whatman #1. The precipitate was washed repeatedly with 2-propanol and afterwards dried at ambi-

ent temperature to give 4.28 g (83 %) of the desired material as a light brown solid. The KDNP was recrystallized by addition to acetone (250 mL) in an 800 mL beaker. The suspension was heated to 327 K with magnetic stirring at a rate of 500 RPM. Toluene (300 mL) was preheated to 323 K in a separate beaker and quickly added to the dark brown, clear KDNP solution. The mixture became cloudy on addition of the toluene and was mixed on an ambient stirrer until it had cooled to room temperature (approx. 296 K, approx. 40 minutes). The suspension was afterwards placed in an ice bath and stirred until the temperature was 275–277 K. The resulting solids were filtered through Whatman #1 filter paper. The light brown material was washed three times with 2-propanol and dried at 338 K to give 3.17 g (75 %) of a free flowing brown product.

Alternate recrystallization: KDNP (3.35 g, 11.88 mmol) was dissolved in 2-methoxyethanol (56 mL) in a 400 mL beaker and the material was heated to 373 K to give a dark brown, clear solution. At ambient temperature, 2-propanol (223 mL) was added quickly to the brown solution. The mixture remained clear for approx. 2 seconds and afterwards a fine particle light brown precipitate formed. The mixture was slowly cooled to room temperature and the solids were filtered through Whatman #1 filter paper. The light brown material was washed three times with 2-propanol and dried at 338 K to give 2.80 g (86 %) of a free flowing brown product with approximate average particle size of 30 μm.

1: 558 K (dec.) (DSC, T_{peak}, 20 K min^{-1}). IR (KBr, cm^{-1}) $\nu = $ 1644(vs), 1575(vs), 1527(s), 1460(s), 1374(m), 1342(s), 1299(m), 1217(s), 1125(w), 1020(w), 994(w), 914(vw), 828(vw), 809(w), 784(w), 751(w), 728(w), 696(w). ^{1}H NMR ([D$_6$]DMSO, 298.15 K): $\delta = 9.02(s)$. ^{13}C NMR ([D$_6$]DMSO, 298.15 K): $\delta = 161.35$ (C8), 147.94 (C5), 134.81 (C7), 127.13 (C4), 114.88 (C6), 111.04 (C9). KDNP has been assigned CAS Registry Number 957133-99-2.

Caution! KDNP is a primary explosive with increased sensitivity to a variety of stimuli. Proper protective measures (safety glasses, face shield, Nomex lab coat, leather or Kevlar gloves and grounded equipment and shoes) should be used when working with this material, particularly when working on a gram scale.

3 Results and Discussion

3.1 Single Crystal X-ray Diffraction Analysis of KDNP

C$_6$HKN$_4$O$_7$, FW = 280.21, Monoclinic, $P2_1/c$, $a = $ 0.74789(7) nm, $b = $ 0.98999(9) nm, $c = $ 1.28390(11) nm, $\alpha = $ 90°, $\beta = $ 98.945(2)°, $\gamma = $ 90°, $V = $ 0.93904(15) nm^3, $Z = 4$, $\rho_{calc} = $ 1.982 Mg m^{-3}, $\mu = $ 0.607 mm^{-1}, $F(000) = 560$, $R_1 = $ 0.0281 for 1980 observed ($I > 2\sigma I$) reflections and 0.0361 for all 2328 reflections, Goodness-of-fit = 1.026, 163 parameters.

An irregular crystal of dimensions $0.12 \times 0.09 \times 0.05$ mm^3 was mounted on a MiteGen MicroMesh using a

Table 1. Crystal data and structure refinement parameters for KDNP (**1**).

Identification code	PSC04, CAS RN 957133-99-2
Empirical formula	C$_6$HKN$_4$O$_7$
Formula weight	280.21
Temperature	103(2) K
Wavelength	0.071073 nm
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = $ 0.74789(7) nm
	$b = $ 0.98999(9) nm
	$c = $ 1.28390(11) nm
	$\alpha = $ 90°
	$\beta = $ 98.945(2)°
	$\gamma = $ 90°
Volume	0.93904(15) nm^3
Z	4
Density (103.15 K)	1.982 Mg·m^{-3}
Density (293.15 K)	1.945 Mg·m^{-3}
Absorption coefficient	0.607 mm^{-1}
$F(000)$	560
Crystal size	$0.12 \times 0.09 \times 0.05$ mm^3
Theta range for data collection	2.61 to 28.29°.
Index ranges	$-9 \leq h \leq 9$
	$-13 \leq k \leq 13$
	$-17 \leq l \leq 16$
Reflections collected	9611
Independent reflections	2328 [$R_{int} = 0.0259$]
Completeness to $\theta = 28.29°$	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9703 and 0.9307
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2328/0/163
Goodness-of-fit on F^2	1.026
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0281$, $wR_2 = 0.0700$
R indices (all data)	$R_1 = 0.0361$, $wR_2 = 0.0742$
Largest diff. peak and hole	417 and -217 e nm^{-3}
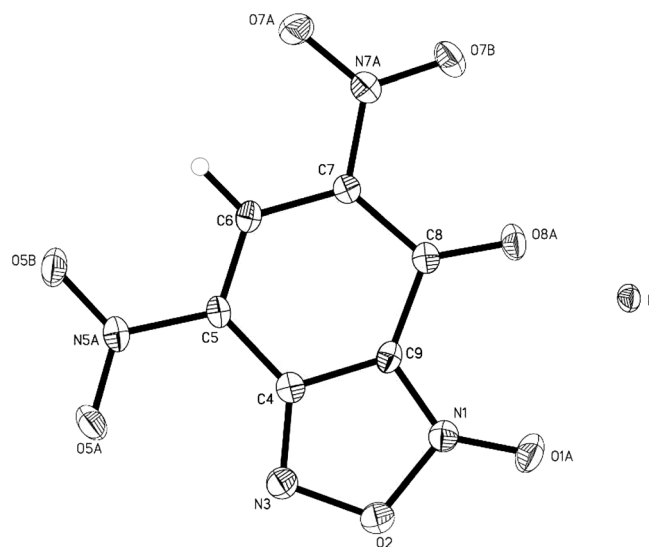
Figure 3. Molecular unit of KDNP (**1**). Thermal ellipsoids represent 50 % probability.
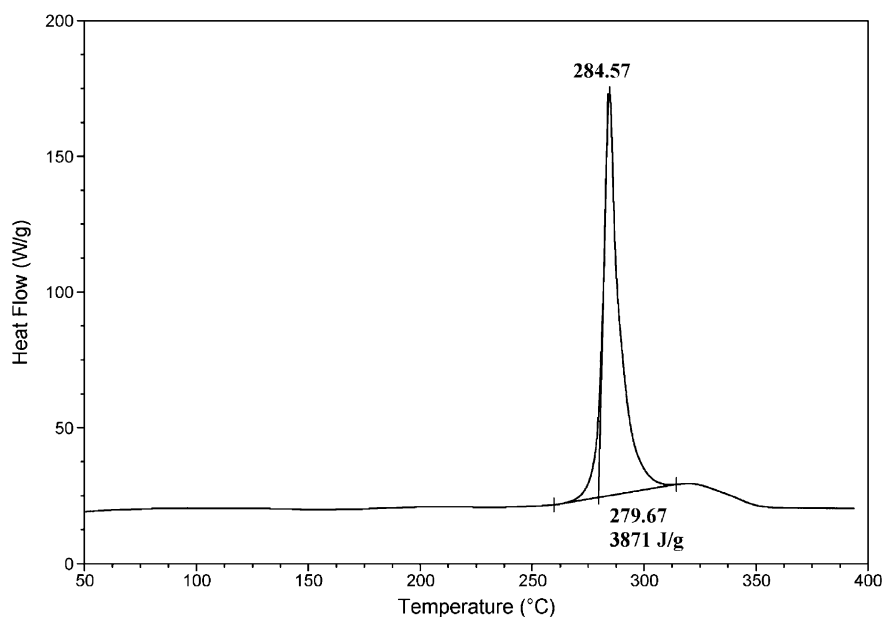
Figure 4. DSC plot of KDNP at 20 K min^{-1}.

small amount of Cargille Immersion Oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated Mo-K_α radiation ($\lambda = 0.071073$ nm). An Oxford Cobra low temperature device was used to keep the crystals at a constant 103(2) K during data collection.

Data collection was performed and the unit cell was initially refined using *SMART* v5.631 [9]. Data reduction was performed using *SAINT* v6.45 [10] and *XPREP* v6.14 [11]. Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* v2.10 [12]. The structure was solved and refined with the aid of the programs in the *SHELXTL* v6.14 system of programs [13]. The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were included using a riding model. Other relevant data and parameters of the X-ray measurements are shown in Table 1 and the molecular unit showing the atom-labeling scheme is shown in Figure 3. Additional information on the crystal structure determination including atomic coordinates, bond lengths and angles and torsion angles is available from the authors or may be obtained free of charge from the Cambridge Crystallographic Data Center [14] as supplementary publication CCDC-795787. The density of KDNP as measured by helium pycnometry (Micromeritics AccuPyc 1330) was 1.90 g mL^{-1}, in agreement with the value of 1.945 g mL^{-1} determined by X-ray at 293 K.

3.2 Thermal Analysis

DSC measurements for determining the thermal behavior of KDNP were performed in sealed aluminum cups with an argon flow of 50 mL min^{-1} on a TA Instruments DSC

2910 instrument. The DSC plot in Figure 4 demonstrates typical thermal behavior of approx. 1 mg of KDNP in the temperature range 323 to 673 K with a heating rate of 20 K min^{-1}.

TGA analysis of a variety of KDNP samples were run isothermally at 393 K in alumina pans on a TA Instruments 2950 thermogravimetric analyzer. Samples were heated at the rate of 5 K min^{-1} to 393 K and remained at that temperature for approx. 90 hours in an argon atmosphere. Analysis of collected data indicates that at this temperature KDNP samples lose $\leq 1\%$ of the initial weight with the majority of weight loss occurring during the heating ramp due to loss of surface moisture. KDNP samples which are prepared and/or recrystallized from water do incorporate water into the crystal and TGA analyses demonstrate that, in those cases, nearly 6% of the sample weight is lost rapidly during heating.

3.3 Physical/Chemical Properties

3.3.1 Bomb Calorimetry

Calorimetric measurements were made utilizing a Parr 6200 bomb calorimeter equipped with either a Parr 1104 or 1108 oxygen bomb. A nitrate correction was accomplished by quantitative precipitation of the nitrate using nitron (3,5,6-triphenyl-2,3,5,6-tetraazabicyclo[2.1.1]hex-1-ene). Normally, the correction for nitric acid is determined by base titration however this is not practical when a potassium salt is involved.
Heat of Formation: -197.07 kJ mol^{-1}
Heat of Explosion: 3.28 kJ g^{-1}

3.3.2 Critical Temperature and Activation Energy

The critical temperature of KDNP [15] was estimated using MIL-STD-1751A Method 1074. The thermal diffusivity of KDNP was not measured but was estimated over a range based upon known energetic materials of similar type.

$T_c = 483 - 503$ K, 1 cm diameter sphere at 80% TMD.

$E_A = 248.95$ kJ mol^{-1}

The thermal conductivity of KDNP at 303 K is 0.09 W m^{-1} K^{-1} for the free flowing powder.

3.3.3 Hygroscopicity

The hygroscopicity of KDNP was measured by drying a sample (approx. 0.0811 g, in a glass petri) in a convection oven at 348 K, cooling it to ambient temperature in a desiccator and then quickly transferring it to a humidity chamber where it was allowed to come to equilibrium. After exposure for a time period specified below the sample was removed from the humidity chamber and the weight gain was recorded. KDNP was assessed at two different humidities for times that were both convenient and realistic. It was determined that KDNP is relatively non-hygroscopic, gaining 1–2% surface water over time. This was easily reversed by drying overnight in an oven at 348 K.

92% relative humidity/293 K for 24 hours;

weight gain +1.11%

92% relative humidity/293 K for 48 hours;

weight gain +1.60%

55% relative humidity/293 K for 35 days;

weight gain +1.40%

3.3.4 Solubility

A sample UV/Vis spectrum of KDNP is shown in Figure 5. The solubility of KDNP was determined by preparing a saturated solution and filtering (over 0.45 µm Millipore) off residual solids. This solution was taken to 25 mL and diluted 200X. The absorbance of the diluted solution at 439 nm was compared to an absorbance vs.
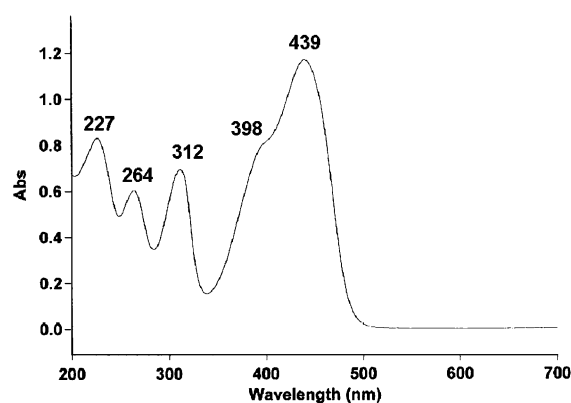
Figure 5. UV/Vis spectrum of KDNP.

concentration curve compiled for a variety of known KDNP dilutions. The molar absorptivity of KDNP was determined to be approx. 18865 L mol^{-1} cm^{-1} at 439 nm and the solubility at 293 K was 3.45 g L^{-1}.

The solubility of KDNP was confirmed by taking 10 mL of the filtered saturated solution and drying it for an extended period in a convection oven to determine the solid weight. This gravimetic method afforded a value for KDNP solubility of 3.56 g L^{-1}, in agreement with the previous method.

3.3.5 Vacuum Stability

The vacuum stability of KDNP was determined based on the method of MIL-STD-1751, Test Method #1. KDNP was dried in an oven at 338 K for 2 hours and cooled in a desiccator prior to analysis. Samples of 0.20 ± 0.05 g were analyzed in triplicate for 48 hours at 373 K. The vacuum stability of KDNP was determined to be 0.352 mL gas g^{-1} (48 h^{-1}), well within the acceptable maximum level of 2.0 mL gas g^{-1} (48 h^{-1}).

3.3.6 Hot Stage Ignition Temperature

The ignition temperature of KDNP was estimated using a hot stage apparatus and measuring time to deflagration. The hot stage device utilized was a Fisher-Johns melting point apparatus set to slowly heat to approx. 623 K. Small samples of KDNP (approx. 1–3 mg) were applied to the heated stage and the time from application to deflagration was determined. A plot of temperature vs. time was prepared to afford the following values:

Table 2. Safety data for KDNP.

Sample	Friction Level (N)		Impact (J)	ESD Sensitivity			
	No-Fire	Low-Fire		Confined		Unconfined	
				No-fire	Low-Fire	No-fire	Low-Fire
KDNP	9.81	10.79	0.047 ± 0.004	< 675 µJ	> 675 µJ	> 1.88 mJ	–
NLS	0.39	0.49	0.025 ± 0.001	–	–	approx. 75 µJ	approx. 196 µJ
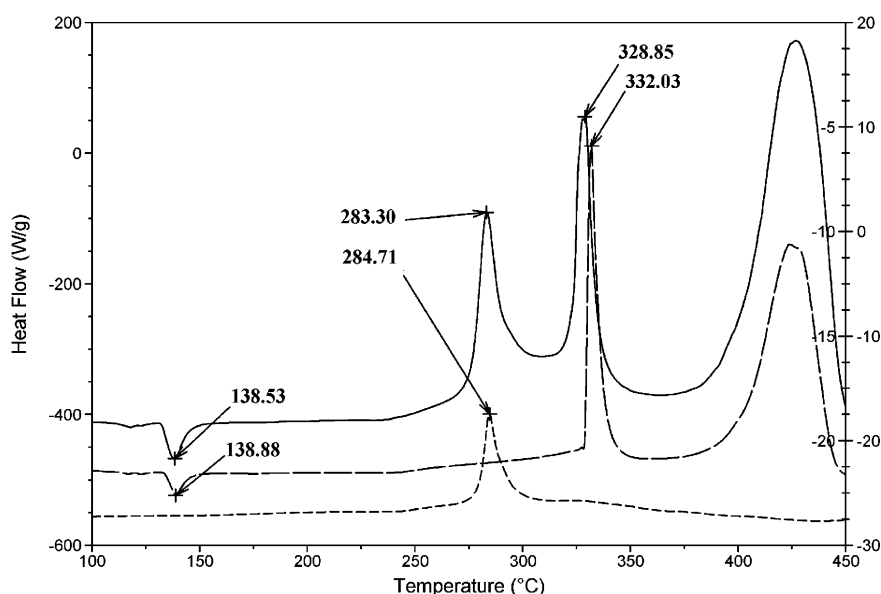
Figure 6. Compatibility of KDNP and black powder by DSC.

Deflagration after 1 second of exposure 573 K

Deflagration after 5 seconds of exposure 562 K

Deflagration after 10 seconds of exposure 557 K

3.3.7 pH

The pH of a saturated solution of 0.45 g of KDNP in 100 mL of deionized water is 5.35.

3.4 Safety Properties

3.4.1 Sensitivities

Safety properties for KDNP are shown in Table 2 along with values for normal lead styphnate [16] (NLS) for comparison. The friction sensitivity was determined utilizing a Julius Peters small BAM tester [17] with a maximum load weight of 2075 g. The no-fire level was determined by six successive tests with no indication of ignition while the low fire level was determined by some indication of reaction in at least one of the samples at the lowest level tested above the no-fire level. Impact sensitivity testing utilized a ball drop instrument designed to meet specifications per NATO AOP-7. A chrome alloy steel ball bearing was dropped from heights varying by 2.54 cm onto a 0.33 mm thick layer of test powder (established with an aluminium template) on a polished steel block. Fire/no-fire results for at least 30 drops were determined and were analyzed by a Bruceton [18] technique to give an energy value for 50% ignition. Electrostatic sensitivity data were recorded utilizing either a LEESA [19] or an Electro-Tech Systems Model 931 firing test system utilizing methods found in MIL-STD-1751A. KDNP is less sensitive to friction, impact and ESD than is NLS.

3.4.2 Compatibility Data

Compatibility of KDNP with a variety of output powders, bridgewire materials and component metals by both metal coupon and DSC test methods [20,21] was evaluated. Metal coupon testing was done by putting a small sample of KDNP powder in contact with a coupon and placing the coupon in a humidity chamber at 93% relative humidity (saturated potassium nitrate) at ambient temperature (291–298 K). Coupon metals include 1100 aluminum, 6061-T6 aluminum, 2024-T3 aluminum, 304 stainless steel, brass and a MK107 gilding metal cup (95% copper and 5% zinc). Observations made during exposures of up to 1 year demonstrated no reaction or change in the coupons.

Compatibility testing was also done on bridgewire materials including Tophet C (Nichrome), Tophet A (StableOhm 650) and EvenOhm (StableOhm 800) via DSC. In these experiments 1.5–2 mg of the bridgewire alloy was placed in an aluminum DSC pan in intimate contact with an equal amount of KDNP and sealed. The samples were heated at 10 K min^{-1} and the resulting spectra were compared to a spectrum of 2 mg of KDNP run under identical conditions. Analyses of the various spectra indicated no shift or change in the thermal profile for KDNP and demonstrated compatibility of KDNP with these materials.

Additional compatibility tests with KDNP and a variety of output powders including BKNO$_3$, FFg black powder, Red Dot and Hi-Temp (80% RDX, 20% nitrocellulose) were also done by blending equal (by weight) amounts of KDNP and output powder and utilizing approx. 1–5 mg of the blend in DSC experiments. The blends were run in a hermetic aluminum pan with a heating rate of 20 K min^{-1} and the results were compared to

DSC spectra of the individual components run under identical conditions. As an example, Figure 6 shows a stacked DSC plot of KDNP (bottom spectrum, short dash), FFg black powder (middle spectrum, long dash) and a homogenized blend of the two materials (top spectrum, solid line). According to criteria established by STANAG 4147 [22], a temperature variation of 4 K or more would be indicative of an incompatibility and therefore KDNP is compatible with this black powder. KDNP is compatible with all materials that have been tested thus far.

3.5 Performance

A variety of performance testing including strong confinement (dent block), closed bomb (pressure-time) and hot wire tests were performed on KDNP and materials suitable for comparison. The results of these tests are shown below.

3.5.1 Strong Confinement Testing

Strong confinement tests were done on KDNP to demonstrate that it does not detonate. Lead azide (RD1333) was run for comparison and, as expected, demonstrates a tendency to detonate under identical conditions. Lead styphnate (NLS) will deflagrate under these conditions leading to no evidence of an explosive output. The strong confinement tests were run by pressing 24 mg of zirconium/potassium perchlorate (ZPP) into a PSEMC 2-300062 header having a 1 Ω 0.056 mm StableOhm 650 bridgewire at 68.95 MPa. KDNP or RD1333 was loaded into a stainless steel can (PSEMC 2-300002-1) having a 0.178 mm wall thickness and pressed at 68.95 MPa. The headers were pressed into intimate contact with the can/output charges and sealed with epoxy. The units were loaded into confining steel fixtures and fired (with a 4 μF capacitor charged to 300 V) directly into 25.4 mm aluminum blocks. The data below represent an average of 5 tests and show that KDNP, like NLS, does not transition from a deflagration to detonation (DDT).

RD1333 : Function Time, 28.4 ms;

Charge Density, 3.09 g cm^{-3}; Dent, 0.98 mm

KDNP : Function Time, 34.3 ms;

Charge Density, 1.52 g cm^{-3}; Dent, 0 mm

3.5.2 Closed Bomb Testing

Closed bomb testing on KDNP and, for comparison, NLS were performed in a standard hot-wire initiator (PSEMC 103377-32) that was bridged with a 0.051 mm 304 stainless bridgewire (3.61 ± 0.66 Ω m^{-1}). KDNP (approx. 0.15 g) or NLS was added to the unit and consolidated directly on the bridgewire at 103.4 MPa with a dwell time of 20 seconds. The units were fired (5 A, 10 ms pulse) into a 10 cm^3 closed bomb fixed with two transducers situated perpendicular to the output of the unit. During firing one transducer channel was recorded without any filtering and timing information was determined from this output. The second channel was filtered with a 2k low-pass Butterworth filter to give pressure information. In some cases the peak pressures were calculated utilizing an additional 3k low-pass Butterworth processing (software) filter to remove any stray ringing often seen in closed bomb data. Results are shown in Table 3; mean values from five tests are shown with standard deviations below.

The density of KDNP is substantially less than that of NLS due to the replacement of lead with potassium so charge weights are less per volume. This produces impetus values for KDNP which are 90 % higher than those for NLS on a weight basis but only slightly higher (16 %) on a volume basis. Importantly, the ignition times of KDNP are comparable to NLS while the rise time (from first indication of pressure to peak pressure) is faster for KDNP. An additional feature that KDNP affords is high post-fire resistance which may be desirable to avoid current drain on battery sources. Other bridgewire ignition materials such as NLS and ZPP often display undesirable low post-fire resistance due to deposition of constituent metals.

3.5.3 Hot Wire Initiation Testing

Constant current and capacitor discharge hot-wire ignition tests were performed in P-12 plugs (BuOrd Drawing 1386180) as per NAVSEAINST 8020.5C (NATO AOP-7). Sixty P-12 plugs bridged with 12.7 μm Tophet C wire and sixty P-12 plugs bridged with 25.4 μm Tophet C wire were loaded with 20 mg of KDNP and pressed at 34.47 MPa with a 20 second dwell time. Sixty P-12 plugs, with each bridge size, were also loaded with NLS (20 mg) under similar conditions for comparison. The constant current test units had current applied for 10 seconds in steps of 10 mA while the capacitor discharge units were tested off

Table 3. Closed bomb data for KDNP vs. NLS.

Sample	T_0-T_{P0} (ms)	T_0-T_{PK} (ms)	T_{P0}-T_{PK} (ms)	Ignition Time (ms)	Peak Pressure (MPa)	Charge Weight (g)	Impetus (J·kg^{-1})
KDNP	0.781 0.048	0.913 0.041	0.132 0.010	0.710 0.028	10.20	0.149	53.53
NLS [16]	0.785 0.045	1.034 0.035	0.250 0.020	0.734 0.045	9.38	0.238	30.88

NOTE: t_0-application of pulse, t_{PO}-time to first indication of pressure, t_{PK}-time to peak pressure.

Table 4. Hot wire initiation testing.

Material	Bridge (μm)	Constant Current			Capacitor Discharge	
		Mean (A)	All-fire 99.9%	No-fire 0.1%	Mean (V, μF)	Stored Energy (mJ)
KDNP	25.4	0.247 ± 0.007	0.269 A	0.224 A	90.2 ± 3.8, 1.0	4.07
KDNP	12.7	0.100 ± 0.000	0.100 A	0.100 A	170.2 ± 50.3, 0.1	1.45
NLS [16]	25.4	0.270 ± 0.019	0.330 A	0.210 A	250.6 ± 18.3, 0.1	3.14
NLS [16]	12.7	0.118 ± 0.006	0.135 A	0.100 A	124.6 ± 16.3, 0.1	0.78

either a 0.1 or 1.0 μF capacitor with 0.3 log unit voltage steps. In all cases a Bruceton analysis was applied to 30 unit tests. The results of these tests are shown in Table 4.

In the capacitive test with KDNP utilizing a 25.4 μm Tophet C bridge, the power supply used was close to maximum output for firing so a 1 μF capacitor was substituted to provide variability for the Bruceton analysis. KDNP is slightly more sensitive than NLS in constant current testing and somewhat less sensitive under capacitor discharge conditions.

The preceding tests and following performance tests were run in conjunction with a program designed to qualify KDNP for military use [2] as outlined in NAVSEAINST 8020.5C. As such, a KDNP sample was subjected to aging at 343 K for 1 year and periodically tested to evaluate any change in safety or performance per the above protocols. The periods for testing included un-aged samples, samples aged (at 343 K) for three months, for six months and for twelve months. In addition, a sample was aged for twelve months in a relative humidity (31%, saturated calcium chloride/water) chamber at ambient temperature. Friction and impact sensitivities, thermal characteristics (DSC), FTIR closed bomb and hot-wire results were evaluated at each aging period (5 data sets total). KDNP did not display any aging effects over the 1 year period and results relative to un-aged NLS did not change.

3.6 Applications

In addition to safety and performance tests, KDNP has been used as a substitute for LS in a variety of applications to test suitability as a direct replacement.

3.6.1 CCU-63/B Impulse Cartridge

The CCU-63/B Impulse Cartridge provides a power source for the ejection of a variety of IR countermeasures (decoy flares) and radio frequency active countermeasures from military aircraft. CCU-63/B units are manufactured at PSEMC-Hollister using a milled NLS ignition mix which contains nitrocellulose, butanetriol trinitrate and butyl acetate and is applied as a slurry to the device bridgewire. This ignition mix (100 mg) is applied to the units in two increments with 20 minutes between applications to allow the solvent to flash. After the second increment, the units are cured at 322 K overnight. As a substitute for this ignition mix, an *un-milled* KDNP slurry of similar weight was prepared with butyl acetate only to

avoid any solubility issues and applied to the bridge in a similar fashion in a number of these units. The output charges for both the NLS and KDNP units were then added and consisted of identical $BKNO_3$ (50 mg) charges followed by 100 mg of Hercules Hi-Temp propellant and MIL-V-16399 varnish and a shield which is pressed into the units over the output. After additional curing time a crimp closure disk is pressed on to seal the units.

Both the KDNP and NLS units were tested according to a standardized test procedure by placing them in a test fixture and firing with a 75 ms 5 A DC pulse. The applied current was measured as was the ignition delay (by monitoring a break in a break lead) and slug velocity (by timing slug velocity through a pair of inductor coils). Units (approx. 10) were fired at each of three different temperatures as indicated in Table 5 and the measured velocity and timing was comparable to values determined for lead styphnate. All units passed the acceptance criterion with the exception of one of the KDNP units fired at ambient temperature and another KDNP unit fired at 347 K. These units both demonstrated low slug velocity but with only slightly lower ignition delays. This lower velocity was accredited to the difference in the ignition mixes. The NLS was milled for 24 hours before use while the KDNP used in the tests was un-milled and had an average particle size of approx. 40 μm. The particle size difference would have an effect on the ability of the ignition slurries to properly seat on the bridgewire but appropriate milling of KDNP was considered outside of the program scope for this project. A review of the data in Table 5 indicates that appropriate milling of the KDNP would undoubtedly provide a material suitable for replacement of the NLS component.

3.6.2 TOW Missile Squib

The Tube-launched, Optically-tracked, Wire command data link, guided missile or TOW is one of the most widely used *anti*-tank guided missiles and number of variants are produced which contain warheads for different purposes. The TOW squib is produced at PSEMC-Chandler and utilizes milled BLS off a hot-wire for ignition followed by $BKNO_3$ and MTV as transfer and output charges. Twenty five units were prepared using standard production processes utilizing milled BLS (approx. 63 mg, approx. 0.48 mm column height) and an additional 25 units were prepared using *un-milled* KDNP (approx. 33 mg, approx. 0.48 mm column height). The column height of the BLS and KDNP were kept equivalent to

Table 5. CCU-63/B results.

| Temperature | n | KDNP | | n | NLS | |
		Ignition Delay (ms)	v (m s^{-1})		Ignition Delay (ms)	v (m s^{-1})
Ambient	9			10		
mean		17.25			16.50	
s		0.44			0.79	
σ		0.42			0.75	
219 K	10		within	10		within
mean		17.75	specified		16.48	specified
s		0.29	limits		1.18	limits
σ		0.27			1.12	
347 K	8			10		
mean		16.90			15.35	
s		0.42			0.87	
σ		0.39			0.83	

Table 6. PVU-12/A percussion primer data.

Primer Mix	Fire/No-fire Level (mJ)	No-fire Level (mJ) mean-2σ	All-fire Level (mJ) mean+5σ	Flame Length (cm)
PVU-12/A	143.116 ± 34.877	73.362	317.501	4.1 ± 3.6
PVU-12/A (2)	120.131 ± 31.353	57.425	276.898	–
NLS-5086	150.369 ± 8.396	133.576	192.350	0
KDNP-5086	136.705 ± 32.490	71.724	299.156	0.6 ± 0.6

afford comparable output pressures however, the charge weight of the BLS was nearly double the weight for KDNP due to density differences.

The units (50 total) were fired into a calibrated 13.11 ± 0.085 cm^3 bomb with an L/D = 1.02. Twin Kistler transducers monitored the output produced at ambient temperature from a firing pulse. Tests are considered successful if the peak pressure generated from the TOW units is 6.89–8.96 MPa with a function time of < 15.0 ms. Under the standard test conditions both the BLS and KDNP based TOW units passed the peak pressure and function time criteria.

BLS : Peak Pressure 7.84 ± 0.25 MPa,

Function Time 2.29 ± 0.22 ms

KDNP : Peak Pressure 7.85 ± 0.32 MPa,

Function Time 2.65 ± 0.92 ms

3.6.3 PVU-12/A Percussion Primers

A standard percussion primer composition (NLS5086) was prepared as per NavAir Drawing 851AS111 and consisted of tetrazene, NLS, barium nitrate, calcium silicide and antimony sulfide. The components were blended as a slurry in 2-propanol, dried at 333 K for 48 hours and afterwards screened three times over a No. 40 sieve. A similar primer composition (KDNP5086) was prepared using the same methods with substitution of KDNP (approx. 40 μm) for the NLS component. Percussion primers with NLS5086 composition were loaded per NavAir Dwg. 851AS400D and contained shellac solution as binder and

5086 mix followed by a paper disk and anvil. The composition height of the first 10 units was measured and this height was used to load the KDNP5086 primers. The density of KDNP is substantially less than that of NLS so the KNDP based primers contain slightly more KDNP on a per mole basis. The primer units were dried/conditioned at 322 K for 24 hours before testing. The percussion primer units (30 of each) were tested by pressing into #.38 caliber shell casings and performing a F/NF test with a ball drop primer tester. The testing was carried out with a 95.02 g ball bearing and varying the drop height from 0 to 31.8 cm according to a Neyer protocol. In addition to the NLS5086 and KDNP5086 primers, two runs (30 primers each) were made using NSWC-IH supplied PVU-12/A units. Average fire, all-fire and no-fire levels are shown in Table 6.

Also shown in Table 6 are the results from a flame length test. The primer tester hardware was positioned on a bench such that the output from the casing could be recorded with high speed video capture (2000 frames per s) and measured against a calibrated background. The drop height of the ball bearing for three tests (PVU-12/A, NLS5086, KDNP5086) corresponded to the all-fire height from Table 6 *or* the maximum height of the test apparatus. Of the 10 PVU-12/A units fired, nine resulted in a flame output (varying between 1.3 cm and 11.4 cm) and one with only a smoke output. Three of the PVU units with a flame output had hot particles (sparks) associated with the flame while the remaining six had only smoke output with the flame. Ten PSEMC produced NLS5086 units were fired, all of these produced an output with smoke only. No flame was observed associated with these units. Ten KDNP5086 units were also fired and of these

Table 7. RSCB data, un-milled KDNP and milled NLS.

Temperature/Loading Pressure	KDNP			NLS	
	n	Pressure (kPa), σ		n	Pressure (kPa), σ
Ambient					
No consolidation	0(4)	0		4(4)	5839.9 (97.4)
34.47 MPa consolidation	3(4)	6012.2 (25.9)		4(4)	5012.5 (312.6)
68.95 MPa consolidation	4(4)	6023.9 (227.25)		4(4)	5212.4 (98.5)
219 K					
No consolidation	0(3)	0		3(3)	5688.2 (76.5)
34.47 MPa consolidation	3(3)	6143.2 (362.7)		3(3)	5612.3 (31.4)
68.95 MPa consolidation	3(3)	6095.0 (105.9)		3(3)	5667.5 (69.2)
347 K					
No consolidation	0(3)	0		3(3)	6095.0 (105.9)
34.47 MPa consolidation	3(3)	6074.3 (178.8)		3(3)	5240.0 (218.1)
68.95 MPa consolidation	3(3)	5819.2 (200.6)		3(3)	5177.9 (236.4)

five had a minor (approx. 1.3 cm) flame output while all had a smoke output. No hot particles were observed with either the PSEMC produced NLS or KDNP units.

3.6.4 RSCB Initiator Testing

A RSCB (Reactive semiconductor bridge) unit is a laminated reactive bridge device used for initiation in situations which require more energy than a "normal" resistive bridgewire can provide. They often take up significantly less volume and may be used in situations where space is at a premium.

The RSCB results shown in Table 7 demonstrate a marked difference between milled NLS and KDNP, particularly for the unconsolidated tests, that may be again ascribed to the difference in particle size between the powders. The milled NLS has a particle size that is ($<5\ \mu m$) much less than that of the approx. 40 μm KDNP. As a result, the NLS has a more intimate contact with the RSCB and presents a larger surface area that the RSCB plasma may interact with. On the other hand, the relatively large KDNP particles present less surface area for the (relatively small) RSCB plasma and consequently show less or no output when consolidated at pressures <34.47 MPa. As can be seen from the data, when the

Table 8. Closed bomb data with NLS/KDNP and various output charges.

Sample	Ignition Time (ms)	T_0-T_{P0} (ms)	T_0-T_{Pk} (ms)	$T_{P0}-T_{Pk}$ (ms)	Peak Pressure (kPa)	Charge Weight (g)	Impetus (J·kg^{-1})
NLS	0.840	0.964	1.62	0.656	2206.3	0.0441	39.18
BKNO$_3$ (granules)	0.059	0.118	0.18	0.169	261.3	0.0003	
KDNP	0.848	1.000	2.30	1.300	2089.1	0.0449	36.43
BKNO$_3$ (granules)	0.174	0.028	0.38	0.373	42.5	0.0003	
NLS	0.804	0.860	1.59	0.734	2227.0	0.0450	38.75
BKNO$_3$ (pellets)	0.017	0.020	0.15	0.142	109.1	0.0003	
KDNP	0.924	1.080	2.03	0.946	2185.6	0.0449	38.13
BKNO$_3$ (pellets)	0.017	0.135	0.28	0.229	67.8	0.0002	
NLS	0.792	0.844	3.07	2.222	1475.5	0.0490	23.58
2-BP	0.033	0.036	0.32	0.295	41.6	0.0005	
KDNP	0.944	1.120	2.26	1.178	1882.3	0.0592	24.90
2-BP	0.022	0.121	0.16	0.251	188.9	0.0003	
NLS	0.864	0.972	2.97	1.936	1627.2	0.0586	21.75
4-BP	0.030	0.090	0.36	0.427	70.6	0.0002	
KDNP	0.952	1.228	2.56	1.200	1771.9	0.0498	27.86
4-BP	0.030	0.170	0.42	0.455	65.2	0.0004	
NLS	0.812	0.864	4.46	3.596	2716.5	0.0405	52.53
Red Dot	0.011	0.033	0.22	0.202	122.7	0.0003	
KDNP	0.884	0.968	5.54	4.564	2578.6	0.0405	49.86
Red Dot	0.036	0.066	0.45	0.396	336.5	0.0003	
NLS	0.808	0.864	1.32	0.458	2626.9	0.0405	50.80
Hi-Temp	0.030	0.048	0.12	0.077	146.2	0.0002	
KDNP	0.916	0.952	3.59	2.642	2426.9	0.0402	47.28
Hi-Temp	0.026	0.023	0.73	0.720	102.3	0.0001	

NOTE: T_o-application of pulse, T_{po}-time to first indication of pressure, T_{pk}-time to peak pressure.

KDNP is consolidated and in intimate contact with the RSCB, the output is equivalent to or greater than (by approx. 20 %) that for NLS and is reasonably independent of temperature. In addition, previous studies using identical RSCB units along with *fine* particle (< 10 μm) KDNP demonstrated that the KDNP was equivalent to NLS even with no consolidation [23] and independent of the presence of the consolidation material.

The 20 μm RSCB units shown in Table 7 were prepared with either 30 mg of milled NLS or un-milled approx. 40 μm KDNP followed by 60 mg of diatomaceous earth for retention and 85 mg of zirconium-ammonium perchlorate as output. The units were fired into a 10 cm^3 closed bomb with an NSWC-IH delay board with a 0.44 μF ceramic capacitor and a firing voltage of 25 V.

3.6.5 Additional Closed Bomb Testing

Additional closed bomb testing with both KDNP and NLS were performed to evaluate the ability to ignite a variety of output powders including $BKNO_3$, black powder, Red Dot and Hi-Temp. These powders were included in the compatibility testing and all materials were found to be compatible with KDNP. These tests were done by pressing NLS (0.23–0.24 g) or KDNP (0.14–0.15 g, *to same volume as NLS loads*) into bridged headers with 68.95 MPa consolidation pressure and a 10 second dwell time. Thirty headers were prepared with each powder. Ten charge cups were prepared with the powders listed in Table 8 and consolidated by hand tamping to a height of 0.4 cm. The average weights of each output powder are included in the table. Five of each (with either NLS or KDNP) header were pressed flush into the output cups and the headers were welded to the charge cups. The units were fired using a 5 A constant current pulse into a closed bomb. Voltage, current and pressure were recorded for each test with the output results shown in Table 8. Each entry represents an average of five tests with the standard deviation given below.

Of primary importance is that all units fired which indicates that KDNP is equivalent to NLS in terms of ignition capability. From Table 8, KDNP appears to be superior in ability to ignite both cannon grade and FFg black powders while NLS is superior in ability to ignite $BKNO_3$, double base powders and Hi-Temp.

4 Conclusions

KDNP has been evaluated as a replacement for lead styphnate under a variety of conditions. KDNP has chemical and physical properties and safety and performance properties which demonstrate its utility as a drop-in replacement for LS and its potential for use in a wide range of explosive component applications. KDNP offers significant environmental improvements over lead styphnate during manufacture, use and disposal. Based partially on the data presented here, KDNP has been qualified by the Department of the Navy (Naval Sea Systems Command) as suitable for use as a primary explosive in weapons development. KDNP was incorporated into Technical Manual SW010-AG-ORD-010 in 2009 and a product specification for this material has been developed. An MSDS for KDNP may be obtained by contacting the authors. PSEMC currently has patents pending on a variety of synthetic methods and applications related to KDNP.

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