Energetic Materials

DOI: 10.1002/anie.201202589

Periodate Salts as Pyrotechnic Oxidizers: Development of Barium- and Perchlorate-Free Incendiary Formulations**

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In light of recent environmental and public health concerns for groundwater contamination, there has been a growing appreciation for environmentally benign pyrotechnics which do not contain toxic chemicals or heavy metals.[1] In particular, potassium perchlorate ($KClO_4$) has been scrutinized by the US Environmental Protection Agency (EPA) because it promotes thyroid dysfunction and is teratogenic.[2] Similarly, barium nitrate [$Ba(NO_3)_2$] is a noxious chemical cited for cardiotoxic and bronchoconstrictor effects.[3] Because of these attendant public health risks, both $KClO_4$ and $Ba(NO_3)_2$ have been targeted for elimination from many pyrotechnic formulations. To date, the perchlorate-free formulations developed include red,[4] green,[5] and yellow[6] signal flares, flash bang grenades, and a host of training simulators.[7] In an effort to "green" pyrotechnics further, barium-free formulations for green-light emission were recently disclosed,[8] and work continues in this area to scale-up this environmentally friendly technology to manufacturing standards.

Among the classes of pyrotechnics that typically contain significant amounts of $KClO_4$ and $Ba(NO_3)_2$, many incendiary munitions combine both of these oxidizers with a metal reducing agent (a fuel). One particular incendiary formulation of interest to the Armament Research, Development, and Engineering Center (ARDEC) is IM-28, which is present in the .50'' caliber M8 armor-piercing incendiary (API) bullet. Upon impact with a hard target (e.g. armored vehicles and aircraft) and penetration of the M8 API, the kinetic energy is lost to friction, causing the incendiary formulation (IM-28) to ignite. This ignition results in an incandescent flash useful for marking an impact point and igniting fuel vapors.

Despite the emergence of new environmental standards, an environmentally benign alternative to IM-28 remains a challenge to the pyrotechnic chemist. Recently, Griffiths developed incendiary formulations having impressive performances by using only sodium nitrate ($NaNO_3$) as the sole oxidizer.[9] The hygroscopic nature of $NaNO_3$, however, poses long-term ageing risks when implemented in pyrotechnic formulations, and a more practical oxidizer replacement was sought. Accordingly, a program was initiated at ARDEC to develop a practical barium- and perchlorate-free formulation having a brighter visible-light output for use in a US Army incendiary projectile.

According to the relevant military specification document (Mil-Spec), the IM-28 control formulation is summarized in Table 1. Here, $Ba(NO_3)_2$ and $KClO_4$ serve as the oxidizers and a 50/50 magnesium-aluminum alloy (magnalium) as the fuel. To address the environmental concerns with the control, three sets of binary formulations were prepared and tested. As shown in Table 2, each set contains a single oxidizer—strontium nitrate [$Sr(NO_3)_2$], potassium periodate (KIO_4), or sodium periodate ($NaIO_4$)—the content of which co-varies with magnalium (fuel) content.

Table 1: IM-28 control formulation.

Components	Wt.%
$Ba(NO_3)_2$	40
$KClO_4$	10
50/50 magnalium	50

Table 2: General make-up of barium- and perchlorate-free formulations.

Component	Wt.%
oxidizer[a,b,c]	30–70
50/50 magnalium	70–30

[a] $Sr(NO_3)_2$. [b] KIO_4. [c] $NaIO_4$.

The main parameters for oxidizer selection in these formulation studies were commercial availability, relative non-hygroscopicity to $NaNO_3$, and high oxygen balance. In addition, the periodate salts offer a logical alternative to the chemically analogous perchlorates and were expected to avoid the toxicity issues associated with the latter.[10] Although periodates have seen only limited application in propellant formulations,[11] their use as oxidizers in pyrotechnic formulations has not been reported. Furthermore, the brightness exhibited by formulations containing $NaIO_4$ would be enhanced by the dominant spectral emission corresponding to atomic sodium.[12]

Table 3 compares the performance criteria of five $Sr(NO_3)_2$-based formulations (**A**–**E**) with that of the control. Because no performance requirements exist in the Mil-Spec for the IM-28 control, this formulation was tested in parallel with all three formulation sets. In addition to burn time, the key performance criterion was luminous efficiency, defined here as the integrated luminous intensity per unit mass. The highest luminous efficiency in this series was exhibited by the formulation with the lowest oxidizer content (**A**). This result

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[**] The authors thank the Environmental Security Technology Certification Program (ESTCP) and the US Army (Picatinny Arsenal, NJ) for funding of this work.

Table 3: Performance of $Sr(NO_3)_2$-based formulations.

Formulation[a]	Burn Time [s]	Luminous Efficiency [$Cd\,s\,g^{-1}$]
control	0.109	11294.0
A	0.185	11803.1
B	0.090	11014.9
C	0.156	10543.6
D	0.577	5853.6
E	No ignition	–

[a] $Sr(NO_3)_2$/magnalium ratio: **A** 30:70; **B** 40:60; **C** 50:50; **D** 60:40; **E** 70:30.

was no surprise since superstoichiometric (fuel-rich) pyrotechnic mixtures typically afford brighter visible-light output, enhanced by secondary air oxidation of excess metal fuel in the plume of the flash.[13] Although formulation **A** had slightly higher luminous efficiency and burn time compared to the control, increasing oxidizer content above this level at the expense of fuel content (**B**–**D**) exhibited progressively diminished performance, with **E** failing to ignite.

Table 4 compares the performance criteria of five KIO_4-based formulations (**F**–**J**) with that of the control. Unlike what was observed in the $Sr(NO_3)_2$-based experiments, the highest luminous efficiency was exhibited by the formulation having the second-lowest oxidizer content (**G**). Increasing the KIO_4 content above the level in formulation **G** at the expense of the fuel content gave progressively diminished performance, with **J** failing to ignite. Unfortunately, no formulations from the KIO_4 series exhibited higher luminous efficiencies compared to the control. Though unsuccessful for this particular incendiary application, KIO_4 may find other applications in military pyrotechnics and commercial fireworks as a potassium perchlorate replacement.

Table 4: Performance of KIO_4-based formulations.

Formulation[a]	Burn Time [s]	Luminous Efficiency [$Cd\,s\,g^{-1}$]
control	0.109	11294.0
F	0.174	8275.2
G	0.169	8673.3
H	0.031	7744.7
I	0.153	5854.6
J	No ignition	–

[a] KIO_4/magnalium ratio: **F** 30:70; **G** 40:60; **H** 50:50; **I** 60:40; **J** 70:30.

Table 5 compares the performance criteria of five $NaIO_4$-based formulations (**K**–**O**) with that of the control. The same trend in luminous efficiency observed with the KIO_4-based formulations was also observed with this series of experiments. Formulation **L** had the highest luminous efficiency, while all formulations having a greater $NaIO_4$ content (**M**-**N**) showed progressively diminished performance, with **O** failing to ignite. Interestingly, formulation **L** had a comparable burn time but was 20% brighter than the control formulation. This reflects a general trend of $NaIO_4$-based formulations burning brighter than those containing $Sr(NO_3)_2$ or KIO_4 as the sole oxidizer. This observation is consistent with the spectral emission expected from atomic sodium.[12]

Table 6 compares the impact, friction, and electrostatic discharge sensitivities, and thermal stabilities of formulations **A** and **L** with those of the control. Indeed, the threshold sensitivities of formulations **A** and **L** meet or exceed those of the control.

Table 5: Performance of $NaIO_4$-based formulations.

Formulation[a]	Burn Time [s]	Luminous Efficiency [$Cd\,s\,g^{-1}$]
control	0.109	11294.0
K	0.185	13504.2
L	0.090	13545.8
M	0.156	9994.9
N	0.577	8205.3
O	No ignition	–

[a] $NaIO_4$/magnalium ratio: **K** 30:70; **L** 40:60; **M** 50:50; **N** 60:40; **O** 70:30.

Table 6: Sensitivity of formulations to various ignition stimuli.

Formulation	Impact [J]	Friction [N]	ESD[a] [J]	Thermal Onset [°C]
control	2.94	160	>0.25	460
A	6.86	360	>0.25	590
L	9.80	160	>0.25	478

[a] ESD = Electrostatic Discharge.

Particularly noteworthy about this study is the use of periodate salts as pyrotechnic oxidizers, which have many potential, wide-ranging applications in military pyrotechnics and commercial fireworks. These uses would include replacement of $KClO_4$ with KIO_4 in red- and green-light-illuminating formulations.[4,5] Also, the visible-light enhancement conferred by the sodium atom[12] in $NaIO_4$ may lend this compound as a replacement for $NaNO_3$ in a host of yellow-[6] and white-light-illuminating formulations. An added benefit of periodate salts is their reduced sensitivity to moisture, as reflected by the water solubility data[14] shown in Table 7. Compared to $KClO_4$ and $NaNO_3$, the corresponding alkali-metal periodates have drastically reduced hygroscopicities. This characteristic is essential to the function and reliability of military and commercial fireworks, especially after prolonged storage.

Also provided in Table 7 are the standard Gibbs free energies[14] and oxygen balances for the relevant pyrotechnic oxidizers in this study. Clearly, the periodate salts are powerful oxidizers while maintaining comparable stability to $KClO_4$. While it is not surprising that $Sr(NO_3)_2$ and $NaNO_3$ are the most thermodynamically stable of these oxidizers, it is noteworthy that both KIO_4 and $NaIO_4$ are more thermodynamically stable than $KClO_4$, as described by Cotton et al.[16]

In summary, periodate salts have been introduced as versatile alternatives to common ingredients which are now under scrutiny because of regulatory and moisture sensitivity issues. The use of periodate salts in military and civilian

Table 7: Properties of periodate and other oxidizers.

Ingredient	Water solubility[a] [g per 100 g H_2O]	ΔG°_f[a] [$kJ\,mol^{-1}$]	Oxygen balance [%]
$KClO_4$	2.08	−303.1	46.2
KIO_4	0.51	−361.4	27.8
$NaNO_3$	91.2	−367.0	47.0[15]
$NaIO_4$	14.4	−323.0	29.9
$Sr(NO_3)_2$	80.2	−780.0	37.8[15]

[a] Standard temperature and pressure.

pyrotechnics has wide-ranging potential, especially with $NaIO_4$ in the area of illumination. Formulations **A** and **L** above have been identified as viable, environmentally friendly alternatives to the in-service perchlorate- and barium-containing IM-28 control incendiary formulation. These formulations had equal or lower impact, friction and electrostatic discharge sensitivities, and higher thermal stabilities than the control. The new formulations will also simplify downstream manufacturing operations since they are binary instead of ternary systems. The use of periodate salts in other pyrotechnics is currently being explored in our laboratories and these results will be disclosed in forthcoming papers.

Experimental Section

Materials: 50/50 Magnalium (mean particle diameter of 18.4 μm) was purchased from Reade. $Ba(NO_3)_2$ (mean particle diameter of 74.4 μm), $KClO_4$ (mean particle diameter of 17.3 μm), and $Sr(NO_3)_2$ (mean particle diameter of 7.7 μm) were purchased from Hummel Croton. KIO4 (mean particle diameter of 42.3 μm) and $NaIO_4$ (mean particle diameter of 61.8 μm) were purchased from Alfa Aesar.

Preparation of M8 Formulations: 20-Gram formulations were prepared by screening the appropriate chemicals through a 60-mesh sieve and combining them in conductive rubber containers, according to their corresponding weight percentages shown in the above formulation tables. Each container was tumbled end-over-end for 30 min and taken to the loading operation without further blending. Formulations were weighed in aluminum cans (1.27 cm in diameter and 2.50 cm in height) and manually pressed into pellets in one increment. Between 0.773–0.783 g of energetic material was used per pellet, 4 pellets were tested per formulation, and the average performances were determined and reported. Pellets were ignited using a nickel-chromium hot-wire with an energy of two volts.

Characterization: Optical emissive properties of these formulations were characterized using both a single-element photopic light detector and a 2048-element optical spectrometer. The light detector was manufactured by International Light and is composed of a SED 033 silicon detector (33 mm^2 area silicon detector with quartz window) coupled to a photopic filter (Y-filter) and a field of view limited hood (H-hood). The current output of the detector was converted into voltage using a DL Instruments 1211 transimpediance amplifier. Voltage output was collected and analyzed from the amplifier using a NI-6115 National Instruments data card and in-house developed Labview based data acquisition and analysis software. Impact sensitivity tests were carried out according to STANAG 4489[17] using a BAM drophammer. Friction sensitivity tests were carried out according to STANAG 4487[18] using the BAM friction tester. Electrostatic discharge sensitivity tests were carried out using an electric spark tester (Albany Ballistic Laboratories). Thermal stability was determined using a PerkinElmer DTA/TGA instrument at a heating rate of 2 °C per minute. Particle size analysis was determined with a Malvern Morphologi G3 Particle Size Analyzer.

Received: April 3, 2012
Published online: May 25, 2012

Keywords: energetic materials · environmental chemistry · green chemistry · periodate · pyrotechnics

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