Energetic Materials

DOI: 10.1002/anie.201204808

2,4,6-Trinitrotoluene: A Surprisingly Insensitive Energetic Fuel and Binder in Melt-Cast Decoy Flare Compositions**

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Dedicated to Professor Dr. Cornelius G. Kreiter on the occasion of his 75th birthday

Aircraft are facing a steadily increasing threat by infrared-guided ground-to-air and air-to-air missiles working in the $\lambda =$ 1–5 μm range. To fight these threats, aerial platforms eject pyrotechnic flares, which create an intense infrared signature to distract the seeker of the incoming missile and causes it to lose track of the target.[1] Common first- and second-generation missile seekers track the hottest spot in the field of view (FOV) in the 1.9–2.6 μm range (α-band). Hence they are most advantageously countered by pyrotechnic flares that yield hot flames ($T = 2000$–2500 K) and a graybody type signature. Typical payloads of this type comprise magnesium/fluorocarbon compositions.[2] However, true aerial targets do not exhibit a graybody-type signature but radiate selectively in the range of the combustion products H_2O (1.87, 2.7 μm) and CO_2 (2.7, 4.3 μm). Thus so-called two-color seekers have been devised for advanced missiles that are able to distinguish between hot spot flares and true targets. These seekers evaluate the intensity ratio $\theta_{\beta/\alpha}$ in two spectral ranges, α-band and β-band (3.5–4.8 μm). Thus hot graybodies yield $\theta_{\beta/\alpha} < 1$, whereas aircraft yield values between $\theta_{\beta/\alpha} \approx 5$–$20$.[3] To fight these threats, pyrotechnic flares which generate predominantly CO_2 and little H_2O have been described in the literature; Table 1 shows the composition of typical formulations. These formulations often comprise potassium perchlorate ($KClO_4$) as oxidizer and oxygenated aromatic compounds, such as potassium benzoate ($C_7H_5O_2K$; **1**) or pyromellitic dianhydride (1,2,4,5-benzenetetracarboxylic anhydride, $C_{10}H_2O_6$; **2**), as fuel.[4] Mixtures of potassium benzoate and perchlorates are extremely sensitive to friction and impact and have caused disastrous explosions while mixing and handling.[5] Pyromellitic dianhydride and potassium benzoate have a large negative enthalpy of formation $\Delta_f H^\circ$ (−954 and −529 kJ mol^{-1}, respectively), and thus yield insufficient spectral efficiency E_λ (J g^{-1} sr^{-1}). In moist air, compound **2** is prone to undergo hydrolysis to give the tetracarboxylic acid, $C_{10}H_6O_8$, which does not burn well with $KClO_4$. The color ratio $\theta_{\beta/\alpha}$ increases with increasing oxygen balance Λ (wt %) of a fuel; however, the spectral efficiency E_λ decreases with the oxygen balance of the fuel.[6] Thus it was hitherto impossible to increase both E_λ and $\theta_{\beta/\alpha}$.

Table 1: Common spectral flare formulations **A**–**C**.

Composition	A	B	C
$KClO_4$ [wt %]	74	65	–
$C_{10}H_2O_6$ (**2**) [wt %]	23	–	–
$C_7H_5O_2K$ (**1**) [wt %]	–	30	–
Polyacrylate binder [wt %]	3	5	–
NC [wt %]	–	–	55
DEGN [wt %]	–	–	20
NG [wt %]	–	–	25
Theoretical Maximum-Density (TMD) [g cm^{-3}]	2.22	2.09	1.59

Other payload types used in spectral flares resemble double base propellants and are based on nitroglycerine, (NG, $C_3H_5N_3O_9$), diethylene glycol dinitrate, (DEGN, $C_4H_8N_2O_7$), and nitrocellulose (NC, $(C_6H_7N_3O_{11})_n$).[7] Payloads of this type are very sensitive and can detonate when struck by a bullet or nearby shock.[8] In view of the deficiencies of current payloads, there is an urgent need for spectrally matched compositions that are safer to produce and less vulnerable to accidental stimuli and that prove to be at least equally or even more powerful than prior formulations. 2,4,6-Trinitrotoluene (TNT) was probably the most widely used explosive in military stores in the 20th century. Today it still plays an important role as energetic binder in melt-cast explosives based on nitroguanidine (NQ) and guanylurea dinitramide (FOX-12).[9] TNT has been proposed as a component for detonating obscurant charges.[10] However, owing to its character as a high explosive, it has never been considered as an energetic fuel and binder in slow burning pyrotechnic compositions.

Herein, we report the findings on the use of TNT as both energetic fuel and melt-cast binder in pyrotechnic formulations. In the present study, mixtures of TNT and $KClO_4$ were considered for use in spectrally matched decoy flare compositions. Table 2 shows the compositions investigated.

The stoichiometry was varied between 35–50 wt % TNT to investigate the effect of oxygen balance of the composition, and Λ_ξ [Eq. (1)] on burn rate, color ratio, and spectral

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201204808.

Table 2: TNT-based formulations **D–G**.

Composition	D	E	F	G
$KClO_4$ [wt%]	65	60	55	50
TNT [wt%]	35	40	45	50
TMD [$g\,cm^{-3}$]	2.217	2.173	2.130	2.087
Experimental Density [$g\,cm^{-3}$]	1.865	1.854	1.737	1.712

efficiency, with n the mole number of $KClO_4$ and m_r the molecular weight for the overall composition $K_xCl_xC_aH_bN_yO_c$. The results are displayed in Table 3.

$$\Lambda_\xi = \frac{1599.94}{nm_r(\mathrm{KClO_4}) + m_r(\mathrm{TNT})}\left(2a + \frac{b}{2} - c\right) \quad (1)$$

Table 3: Performance of formulations **D–G** and the standard payloads **A** and **B**.[a]

Composition[a]	A	B	D	E	F	G
Λ_ξ [wt%]	3.2	−24.7	4.1	−1.9	−7.9	−13.9
u [$mm\,s^{-1}$]	1.3	3.6	1.4	1.3	1.2	0.9
Δ_cH [$kJ\,g^{-1}$]	4.25	4.85	6.86	7.02	7.19	7.35
$E_{3.5\text{–}4.8\,\mu m}$ [$J\,g^{-1}\,sr^{-1}$]	26.8	26.6	34.1	41.2	45.4	48.0
$\theta_{\beta/\alpha}$ (–)	5.3	6.3	8.3	7.6	5.8	4.3

[a] data for formulation **C** are unavailable. u = burn rate.

The spectral efficiency [Eq. (2); Δ_cH = enthalpy of com-

$$E_\lambda = \frac{\Delta_cH}{4\pi}F_\lambda \quad (2)$$

bustion, F_λ = fraction of energy transmitted as function of temperature and emissivity ε_λ of the combustion products] in the β-band increases steadily between 35–50 wt% TNT from $E_\beta = 34$ to $48\ J\,g^{-1}\,sr^{-1}$. This coincides well with an increase in adiabatic combustion temperature from 2760 to 2860 K (see the Supporting Information) and reflects the T^4 dependence of radiation power as known from the Stefan–Boltzmann law (see Table 4).[11] The spectral efficiency in this band is between 180–128% higher than those of the baseline formulations and shows the superiority of TNT as a fuel owing to higher enthalpy of formation $\Delta_fH°(\mathrm{TNT}) = -67\ kJ\,mol^{-1}$.

Table 4: Safety data of formulation **D** and other spectrally matched flare compositions **A–C**.[a]

Composition[a]	A	B	C	D
BAM impact energy [J]	7.5	4.5	2	15
BAM friction force [N]	80	240	120	320
ESD energy [J]	2	0.07	5	5
Shock sensitivity no-go pressure [GPa]	n.a.	n.a.	<2.6	>2.6
Ignition temperature [°C]	>300	>300	166	259

[a] BAM = Bundesanstalt für Materialprüfung. n.a. = not applicable.

The color ratio $\theta_{\beta/\alpha}$ decreases with increasing TNT content from 8.3 down to 4.3. This can be explained with both the depletion of the carbon dioxide content (see Table 4) and an increase of the continuum-level radiation that is due to thermally excited soot particles, which are products of the primary combustion reaction [Eq. (3)] of TNT seen in Figure 1.[12]

$$C_7H_5N_3O_{6(s)} \rightarrow 6\,CO + 1\,C_{(soot)} + 2.5\,H_2 + 1.5\,N_2 \quad (3)$$

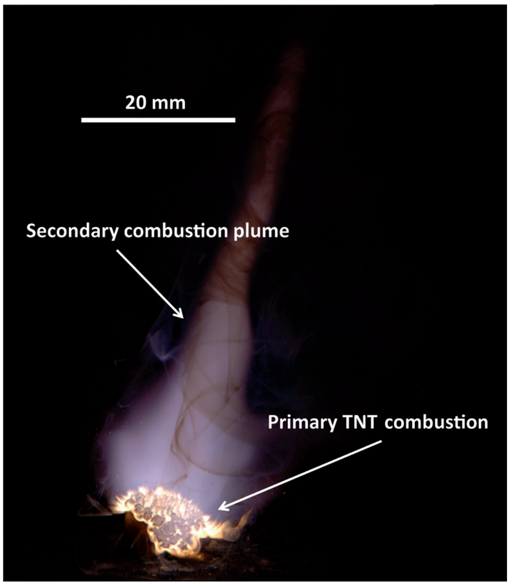

Figure 1. Close-up of a TNT/$KClO_4$ (35:65) combustion flame.

Figure 2 shows the IR spectra of the pyrolants **D** and **G**. The emission spectrum of the combustion flame of pyrolant **G** displays a significant continuum emission between 2.4–4 μm, whereas pyrolant **D** shows nearly no continuum and only a H_2O emission band at 2.7 μm, thus explaining the different color ratio. The CO_2 band at $\lambda = 4.3$ μm in turn is more intense

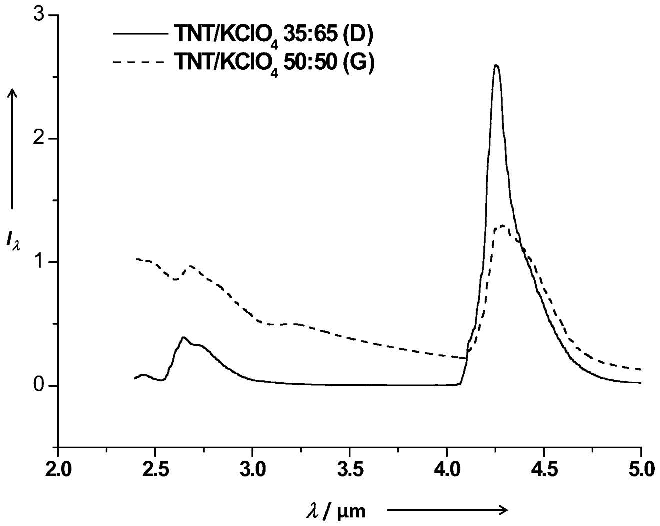

Figure 2. CVF-IR spectra of pyrolant **D** and **G**.

with the latter pyrolant **D** and much weaker with pyrolant **G**. Both formulations **D** and **E** have significantly higher color ratio than the baseline **A** and **B**, which is thought to result from higher combustion temperatures, thus favoring faster oxidation of carbon.

The burn rate for TNT/$KClO_4$ decreases with increasing TNT content, despite increasing combustion temperature. This observation is surprising, as prior findings with binary $KClO_4$/aromatic fuel pyrolants indicated a high burn rate at low oxygen balance.[6a,12a] Thus a different mechanism has to be envisaged with TNT/$KClO_4$.

Payload type **A** is very sensitive to friction, whereas type **B** and **C** are very sensitive to impact (Table 4). Type **B** is also extremely sensitive to electrostatic discharge (ESD). Payloads **A** and **B** undergo explosion when initiated, whereas payload type **C** is shock sensitive and is able to undergo detonation.[14] In contrast, the most advanced formulation **D** is only moderately sensitive to both friction and impact, and shock insensitive according to the German small-scale water gap test. Furthermore, the ignition temperature of formulation **D** is pronouncedly higher than that of composition **C**. Another surprising finding is the reduced exothermicity of the decomposition reaction of TNT at $T = 259\,°C$ in a high-pressure DSC (differential scanning calorimetry) vessel. Whereas pure TNT yields a specific enthalpy of decomposition of $-2298\,J\,g^{-1}$, the 35/65 (TNT/$KClO_4$) pyrolant **D** yields only $-925\,J\,g^{-1}$ (based on the mass of TNT). Thus $KClO_4$ appears to stabilize TNT against decomposition at this temperature.

In summary, the TNT/$KClO_4$ pyrolant system is advantageous over prior compositions in spectrally matched infrared decoy flare payloads in many ways. First, although TNT is a high explosive, its compositions with $KClO_4$ are less sensitive to friction impact and shock and possess greater thermal stability than common pyrotechnics or double base propellants. Second, it is more easily and safely processed through established melt-casting operations. Finally, TNT/$KClO_4$ is more energetic than any of the hitherto considered fuels in $KClO_4$-based formulations, thus offering both high spectral efficiency and high color ratio. Work is in progress to explore the use of TNT in other melt-cast pyrotechnic formulations.

Experimental Section

TNT (purchased from EURENCO, Sweden, Type II TNT, solidification temperature 80.4 °C) was melted in a MEISSNER 5 L experimental water-heated blending vessel at 90 °C. After TNT had melted, appropriate portions of sieved potassium perchlorate (purchased from TROPAG, Germany mean diameter 5 μm) were introduced and the mixture was blended for 1 hour. The off-yellow melt was poured into preheated (100 °C) brass tubes with 20 mm inner diameter closed by a silicone plug at one end. The tubes were cooled with a zone-heating apparatus in bottom-up direction and occasionally stirred to avoid the formation of voids. After crystallization and cooling the silicone plugs were removed and the pyrolant cylinders were pushed out. The cylinders were machined to equal length (50 mm) and laterally protected with polyurethane lacquer (Kleiberit, KLEB-CHEMIE M. G. Becker GmbH & Co. KG, Germany). The top face of the cylinder was equipped with an ignition slurry (TNT/NC/Boron/$KClO_4$ (ratio 25:5:5:65) in ethyl acetate) and an electric match.

The pellets were fixed with superglue on stainless steel plates and dried. The radiometric measurements were carried out in a radiometric testing tunnel with a two channel IR radiometric system (RM 6600, Laserprobe USA, uncooled pyroelectric detector RkP 575). The IR spectra were recorded with a circular variable filter (CVF) developed at ICT using a liquid-nitrogen-cooled InSb detector. For the temperature calibration of the radiometer and the spectrometer, a blackbody of temperature 1273 K (SR-32 CI Electro-Optic Systems Israel) was used. For the wavelength calibration of the spectrometer, the transmission spectrum of a thin polystyrene film placed between the blackbody and the spectrometer was applied.

Sensitivity determination was done with both BAM friction and impact testing machine in accordance with NATO-STANAGs.[15] The shock sensitivity test was carried out according to German TL standard.[16]

Received: June 19, 2012

Keywords: 2,4,6-trinitrotoluene · energetic materials · infrared decoy flares · metastable compounds · pyrotechnics

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