Pyrotechnic Countermeasures: V. Performance of Spectral Flare Compositions Based on Aromatic Compounds

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Abstract: The radiometric performance and burn rate of four spectral flare compositions (R-X) based on 1,4-dicyanobenzene (**1**), 3,5-dinitrobenzonitrile (**2**), *E*-stilbene (**3**) and 9,10-dihydroanthracene (**4**), potassium perchlorate and polyacrylate binder are described. The burn rates, spectral efficiencies, E_λ, in both α- and β-band have been determined. The composition **R-4** displays the highest efficiency in both α- and β-band as well as lowest color ratio, $\theta_{B/A}$. **R-1** yields the highest color ratio and second highest spectral efficiency in β-band. For part IV see Ref. [1].

Keywords: spectral flare, aromatic compounds, decoy flare, pyrotechnic countermeasures

Introduction

Aerial platforms face a steadily increasing threat by infrared guided missiles such as surface-to-air (SAM) as well as air-to-air missiles (AAM). Among the SAMs especially the man-portable shoulder-fired systems (MANPADS) with two-colour counter-countermeasure capability such as e.g. the Russian SA-18 (GROUSE) pose the major threat to low flying crafts.

Recently the author has discussed the available technology to counter infrared guided missiles [2-4] with advanced pyrotechnic decoy flares. Spectral flare compositions either contain a carbon or boron based fuel in order to give the highly selective emitters CO_2 and/or X-B = O [3]. Carbon based payloads now may comprise virtually any type of carbon source [5] and oxidisers that

will readily give off oxygen such as e.g. nitrates and perchlorates. From this point of view a large number of systems should be feasible to provide a selective signature as defined in Ref. [2]. Indeed spectral characterisation of combustion flames taken from double base propellants [6, 7], sodium nitrate/magnesium/resin flare [8] and even black powder [9], display strong selective emission between 4-5 μm which is due to emission of hot CO_2.

Recently Weiser has developed an intriguing concept of a binary decoy composition consisting of a heat module with basically no emissivity at all and a source for a highly selective emitter. Experiments conducted under both static and dynamic conditions look very promising [10, 11].

Several authors have stressed the necessity of a high CO_2/H_2O ratio in order to improve the spectral ratio of the energy emitted in two bands β/α [12, 13]. In view of this it should be unwise to apply systems overloaded with hydrogen by using e.g. ammonium perchlorate as oxidizer. On the other hand Nielson showed that even Mg/HTPB/AP provides an appropriate signature [14]. A second point that weakens this argumentation is the fact that the true target fuels such as JP-5, $C_{10}H_{19}$, [15] and or the most recent JP-10 – which is *exo*-tetrahydrodicyclopentadiene, $C_{10}H_{16}$ [15] – give rise to a CO_2/H_2O ratio of ~ 1-1.25. Finally an important cause for the reduced significance of the CO_2/H_2O ratio is the ratio of the corresponding band strengths of both 1.7 μm – H_2O and 4.4 μm CO_2 band, which is as small as about 0.15. In contrary to the CO_2/H_2O ratio the C/O ratio of a composition is of concern as it determines the degree of conversion of carbon to CO_2 in the primary combustion zone which mainly accounts for the general spectral characteristic. It has been shown as early as 1974 by Ebeoglu [16] that an over-oxidized system gives rise to a large $\theta_{B/A}$ ratio. Recently the author could show the importance of the oxygen balance, Λ, of an aromatic fuel on the spectral efficiency and color ratio of standardized spectral flare compositions [5].

In the present paper the influence of CN- and NO_2 substituent effects on aromatic fuel as well as isomer effects of a C14-fuel on radiometric performance and burn rate will be discussed.

In their landmark disclosure Posson and Baggett have proposed to use aromatic polycarboxylic anhydrides as fuels in spectral flare compositions [17]. These fuels have both high C/H and low C/O ratio, and thus yield high color ratios, $\theta_{B/A} \gg 5$. However the low exothermicity of these compositions due to the large negative enthalpy of formation of the oxo-substituted arenes causes considerably low spectral efficiency values. Being already aware of this it is hence that the inventors advise the use of nitrated aromatic polycarboxylates, so called NAPAs. But despite 3-nitro-phtalic acid anhydride, $C_8H_3NO_5$, CAS-No. [641-70-3] $(\Delta_f H° = - 353$ kJ mol^{-1} vs

$\Delta_f H^\circ (C_8H_4O_3) = -460$ kJ mol^{-1}) and its position-4-isomer [5466-84-2] these are not commercially available and still suffer easy hydrolytic decomposition to give nitrated aromatic carboxylic acids.

Results and Discussion

The author has investigated the use of cyano-compounds as non-sooting high energy fuels and advised to use them in spectral flare payloads [18, 19], hence results obtained with both 1,4-dicyanobenzene (**1**) and 3,5-dinitrobenzonitrile (DNBN) (**2**) will be presented in this study. In addition it could be shown by the author, that the structure of a fuel actually influences the color ratio of a composition [5]. Although both anthracene and phenanthrene, contain three fused benzene rings with the same general composition, $C_{14}H_{10}$, it is because of the higher resonance stabilization energy for the latter that soot formation occurs more readily with this one, hence causing a lower color ratio for a phenanthrene based composition as compared to the anthracene based formulation [5]. Now two constituent isomers, *E*-stilbene and 9,10-dihydroanthracene have been chosen to test the influence of structure on color ratio in spectral flare compositions.

The physicochemical properties of the ingredients are given in Table 1, the structures are shown in Figure 1.

The payload stoichiometry was adjusted to allow for complete oxidation of carbon and hydrogen to carbon dioxide and water. The compositions contain potassium perchlorate as oxidizer and were blended with additional 3 wt-% of a polyacrylate binder.

Table 1. Components of spectral pyrolants

Specie	Unit	$C_8H_4N_2$	$C_7H_3N_3O_4$	$C_{14}H_{12}$	$C_{14}H_{12}$	$KClO_4$	$C_5H_8O_2$
CAS-No	--	623-26-7	4110-35-4	103-30-0	613-31-0	7778-74-7	9011-14-7
C/H	1	2.0	2.33	1.17	1.17	n.a.	0.63
C/O	1	--	1.75	--	--	n.a.	2.50
Λ	wt-%	-224.76	-95.27	-301.79	-301.79	+46.19	-191.77
m_r	g·mol^{-1}	128.134	193.120	180.249	180.249	138.549	100.118
$\Delta_f H^\circ$	kJ·mol^{-1}	+268	+92	+133	+66	-432	-430
mp	°C	224	130	124	111	580(dec.)	n.a.
dp	°C	n.a.	n.a.	n.a.	n.a.	--	n.a.
density	g·cm^{-3}	1.290	1.732*	1.156	1.207	2.52	1.18
Designat.		**1**	**2**	**3**	**4**		

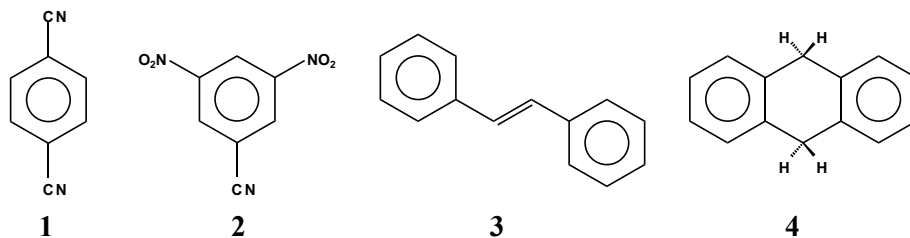*calculated according to the method described Ref. [20]

Figure 1.   Structures of fuels.

The most important differences between both **1** and **2** are the oxygen balance, Λ and the enthalpy of formation, $\Delta_f H$. It has been shown that Λ strongly influences spectral efficiency and burn rate [5]. The enthalpy of formation in addition influences the available combustion enthalpy and hence spectral efficiency, E_B as given in Eq. 1. Whereas **1** has a pronounced negative oxygen balance, the oxygen balance of **2** is only half of that. Similarly the enthalpy of formation decreases from **1** to **2**. Expectedly the spectral efficiency in B-band decreases when changing from **1** to **2** as fuel. The high burn rate of **R-1** in comparison to **R-2** may be due to the higher adiabatic combustion temperature of first (2768 K versus 2625 K). The high color ratio obtained with **R-1** ($\theta_{B/A}$ = 6.37) may be explained by the beneficial effect of cyano groups on the combustion mechanism of the benzene ring discussed earlier [18]. In view of this the nitro groups in **2** seem to be unable to compensate for the missing CN group despite the overall increase of Λ.

$$E_{\lambda_1 - \lambda_2} = \frac{\Delta_c H}{4 \cdot \pi} \cdot F_{\lambda_1 - \lambda_2} \; [\text{J g}^{-1} \text{ sr}^{-1}] \tag{1}$$

with $F_{\lambda_1 - \lambda_2}$, the fraction of energy emitted in the band, λ_1-λ_2 of interest [-].

The results obtained with both *E*-stilbene and 9,10-dihydroanthracene show the strong influence of the structure on the combustion mode. It appears that **4** is very prone to undergo cyclodehydrogenation to soot in the primary reaction zone as is indicated by the low color ratio and the highest spectral efficiency obtained in both bands. In contrary **3** seems to be fragmented very early resulting in an overall high color ratio not obtained with anthracene type fuels of similar oxygen balance [5]. This is surprising as stilbene is known to undergo oxidative cyclicisation to phenanthrene upon pyrolysis conditions [22].

If we assume a fictive single jet engine signature in the 3.5-4.8 μm range of 500 W sr^{-1} [23], this requires some 1750 J for a burning decoy (3.5 s burn time) to be radiated in the band of interest and per steradian to imitate the target. Typical CIS 50 mm flares comprise a payload mass of ~ 500 g [24]. Thus a dynamic

spectral efficiency, $E_{\lambda,v}$ of > 3.5 J g⁻¹ sr⁻¹ is necessary to achieve the same signature at high speed, that is at 250 kts. Typically carbon type payloads degrade by factor of 10 when subjected to airspeed of ~ 250 kts [25]. Thus the minimum static spectral efficiency is > 35 J g⁻¹ sr⁻¹. In Ref. [17] it is stated that a color ratio of $\theta_{B/A} = 2.0$ at 0.83 MACH is sufficient to decoy a two-color seeker. The color ratio of carbon based compositions degrades under the influence of airspeed to 66% at 250 kts. Thus a minimum static color ratio of 3.0 is necessary to achieve an appropriate ratio under dynamic conditions.

Figure 2 now shows the $E_B/\theta_{B/A}$ graph for the above described compositions and previous described compositions taken from Ref. [5] and [19].

Table 2. Radiometric properties of pyrolants

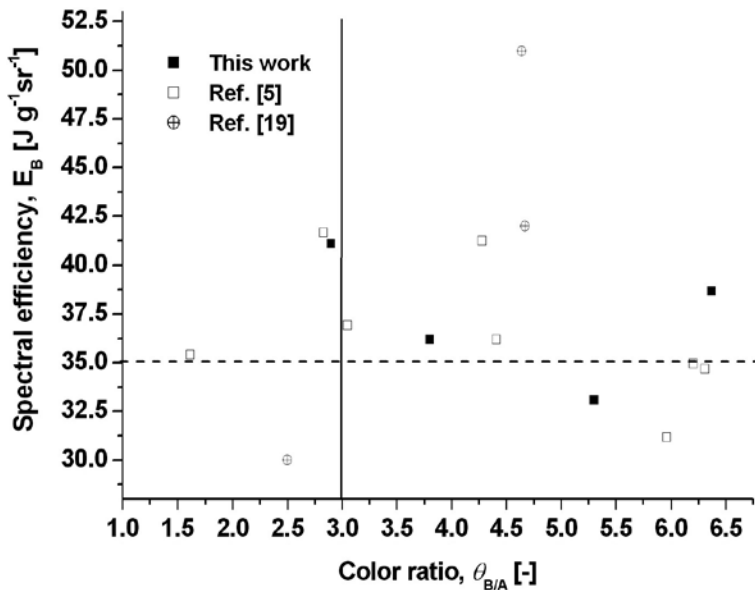|	Unit	R-1	R-2	R-3	R-4
$\Delta_c H$	kJ kg⁻¹	5.32	4.88	5.43	5.39
E_β	J g⁻¹ sr⁻¹	38.7	33.1	36.2	41.1
E_α	J g⁻¹ sr⁻¹	6.08	6.2	9.5	14.1
F_β	1	0.091	0.085	0.084	0.096
F_α	1	0.014	0.016	0.022	0.033
$\theta_{\beta/\alpha}$	1	6.37	5.3	3.8	2.9
r	mm s⁻¹	1.5	1.2	1.4	1.6

Figure 2. Performance graph.

The equilibrium combustion for all compositions was calculated at 0.1 MPa and is displayed in Table 3. It is remarkable that nearly equivalent compositions (CO, CO_2, H_2 and O_2) are obtained for **R-1**, **R-3** and **R-4** applying NASA CEA code but very differing values obtained experimentally calling for treatment of such data with reserve when trying to make signature predictions.

Table 3. Equilibrium composition of experimental spectral flare compositions [21]

		R-1	**R-2**	**R-3**	**R-4**
Fuel content	Wt-%	17.05	23.00	13.27	13.27
Oxidizer content	Wt-%	82.95	77.00	86.73	86.73
Combustion temperature	K	2768	2625	2738	2728
Specie	Mol-%				
CO		0.154	0.057	0.138	0.135
CO_2		0.304	0.336	0.302	0.306
HCl		0.016	0.010	0.020	0.020
H_2		0.006	0.002	0.009	0.010
H_2O		0.082	0.064	0.145	0.147
KCl		0.231	0.221	0.238	0.239
N_2		0.054	0.080	--	--
O_2		0.068	0.169	0.065	0.060

Experimental

1,4-Dicyanobenzene (**1**) # D 76722, 98%, 3,4-dinitrobenzonitril (**2**), # D195006, 97%, *E*-stilbene (**3**) # 139939, 96%, 9,10-dihydroanthracene (**4**) # 126179, 97% were all purchased from Sigma-Aldrich Chemie GmbH, D-82018 Taufkirchen/Germany. Potassium perchlorate was purchased as reagent grade material from Tropag Oscar H. Ritter Nachf. GmbH, D-20146 Hamburg and milled in a RETZSCH pin mill down to achieve a particle size < 40 μm. Polyacrylate binder, Hytemp 4454 was purchased from Zeon Europe GmbH, D-40547 Düsseldorf/Germany.

2 kg of the composition each were mixed in a 5-liter blender equipped with a planetary mixing blade. The composition was dried for 12 h at 60 °C and 10 mbar. The granulated composition was pressed to give cylindrical strands of 19 mm diameter of ~ 98% of each TMD.

Strands of about twofold diameter height were equipped with electrical

igniter wrapped with tape match and fixed between steel splint pins having square geometry on a blackened brass cylinder. The lateral surfaces of the pellet were coated with polyurethane laquer (thickness ~ 250 μm). The combustion of the pellet was recorded with a two channel IR radiometric system (RM 6600, Laserprobe USA; uncooled pyroelectric detector RkP575). The radiometer was calibrated with a blackbody of temperature T = 1000 K (SR-32-SR, CI Electro-Optics Systems, Haifa, Israel).

Conclusion

The composition based on 9,10-dihydroanthracene displays the highest efficiency in both α- and β-band due to high level of particulate carbon in the flame. Hence this composition also yields the lowest color ratio, $\theta_{B/A}$. The highest color ratio ($\theta_{B/A}$ = 6.37) in turn is obtained with 1,4-dicyanobenzene as fuel and second highest spectral efficiency in β-band (41 J g^{-1} sr^{-1}). *E*-stilbene upon combustion yields less soot thus improving the color ratio.

Symbols and Abbreviations
  α Alpha-Band 1.8 – 2.5 [μm]
  β Beta Band 3.5 – 4.8 [μm]
  λ wavelength [μm]
  Λ Oxygen balance [wt-%]
  $\theta_{B/A}$ Color ratio [-]

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Note
This work has been performed by the author in his previous industrial occupation in 2006, before joining MSIAC.

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