



Unravelling the Effect of Anthraquinone Metal Salts as Wide-range Plateau Catalysts to Enhance the Combustion Properties of Solid Propellants

**Yinglei Wang,^{1*} Qi-Long Yan,² Ting An,¹ Bin Chen,¹
Yue-Ping Ji,¹ Wei Wang,¹ Fengqi Zhao¹**

*¹Xi'an Modern Chemistry Research Institute,
Zhangba East Road 168, Xi'an Shaanxi 710065, China*

*²Science and Technology on Combustion, Thermal Structure,
and Internal Flow Laboratory, Northwestern Polytechnical
University, Xi'an, 710072, China*

**E-mail: wangyl204@163.com*

Abstract: Novel lead and copper salts based on anthraquinone, including 1,8-dihydroxyanthraquinone, 1,4,5,8-tetrahydroxyanthraquinone and 1,8-dihydroxy-4,5-dinitroanthraquinone, were prepared and characterized by Fourier transform infrared spectroscopy (FTIR), elemental analysis (EA), and X-ray fluorescence (XRF). The catalytic effects of these compounds on the decomposition of nitrocellulose (NC) and on the combustion properties of double-base (DB) and composite modified double-base (CMDB) propellants were comprehensively investigated. The results demonstrated that the burning rate is significantly increased (by 200%) in the lower pressure range (2-6 MPa) as compared to the control systems without added anthraquinone-based salts. Concurrently, the pressure exponents (n) were obviously lower, exhibiting a "wide-range plateau" combustion phenomenon in the middle-pressure region. Specifically, for the DB propellants such a plateau region extended from 10 MPa to 16 MPa for n equal to 0.10, from 10 MPa to 18 MPa for n equal to 0.11 and from 8 MPa to 18 MPa when n is 0.05. In the case of RDX-CMDB propellants, the plateau was found to be in the range 6-18 MPa, with n in the range 0.16-0.27, depending on the type of catalyst, in contrast to the reference CMDB sample, which was characterized by n equal to 0.7 for the same pressure range.

Keywords: solid propellants, burning rate catalysts, anthraquinone metal salts, wide-range plateau combustion

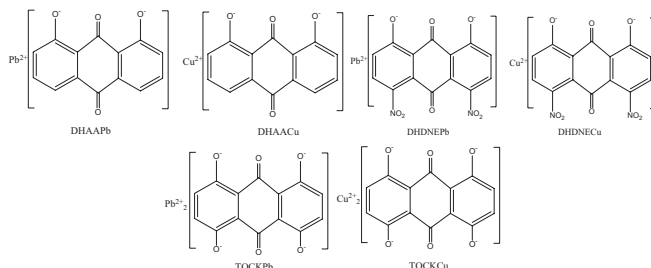
1 Introduction

Solid rocket propellants are extensively used in almost all operational rockets, missiles, satellites and space shuttle launch vehicles [1-3]. Efforts have been mainly devoted to the development of novel propellants with high performance and a wide-range plateau in order to fulfill the ever-growing and challenging requirements, *i.e.* carrying heavier payloads for longer distances [4-7]. The plateau combustion range of a solid rocket propellant determines its ballistic performance, flying speed and stability. So the control and tailoring of this combustion property is the key factor for further improving the performance of rockets and similar devices.

A combustion catalyst as a ballistic modifier is one of the most important functional additives in the formulation of solid propellant compositions [8-12]. The main function of a combustion catalyst is to tailor the burning rate and reduce the pressure exponent (n) of a solid propellant. In this context, lead(II) and copper(II) salts, including inorganic and organic compounds, have been widely investigated and are considered to be the most popular and efficient combustion catalysts for double-base (DB) and composite modified double-base (CMDB) propellants [13-19]. Specifically, some inorganic metal oxides and organic carboxylic acid metal salts are the preferred choices in DB and CMDB propellants, and include lead oxide (PbO) [20], copper oxide (CuO) [21], lead carbonate (PbCO₃), phthalic acid lead salt (ϕ -Pb) and adipic acid copper salt (β -Cu) [22, 23]. However, these catalysts are able to modify the combustion performances of solid propellants only in low pressure regimes (6-10 MPa), and cannot fulfil the requirements for the formulation of solid propellants with middle to high pressure range plateau combustion behaviour. In comparison, some energetic catalysts such as 3-nitro-1,2,4-triazol-5-one (NTO) [24-26], 4-(2,4,6-trinitroanilino)benzoic acid (TABA) [27] and 4-amino-3,5-dinitropyrazole (DNP) [28-30] metal salts, do not show a significant reduction in the pressure exponent of solid propellants, and some of them are very dangerous and require a high standard of precautions/protocols for their manufacture. Many research groups have also focused on the preparation of nano-sized catalysts, including nano-Fe₂O₃ [31], CuO [32], Bi₂WO₆ [33], and copper β -resorcyate [34]. Moreover, despite these compounds exhibiting great efficacy in enhancing the thermal decomposition rates of energetic materials, they are still unable to modify the combustion properties of solid propellants above 10 MPa because of the difficulties in maintaining a high degree of dispersion by limiting aggregation. Furthermore, high cost is also one of the most important reasons which significantly restricts their application. The design and facile

preparation of cost-effective new compounds, which have great catalytic effects on the combustion of solid propellants under a wider pressure range, especially middle to high pressures, remains a difficult and challenging task.

Anthraquinone-based compounds contain many carbon atoms and carbonyl groups, which can improve propellant combustion and absorb ultraviolet light, which consequently improves the burn rate during combustion. In our previous work both the barium [35] and manganese [36] salts of 1,8-dihydroxy-4,5-dinitroanthraquinone were prepared and investigated in terms of their thermal behaviour. It was found that the key components which catalyze the decomposition and combustion of propellants were the metal oxide and carbon atoms. In order to systematically study the effects of anthraquinone metal salts (AMSs) on the combustion properties of DB and CMDB propellants, we investigated in the present work the effects of several AMSs based on lead and copper, including 1,8-dihydroxyanthraquinone, 1,8-dihydroxy-4,5-dinitroanthraquinone and 1,4,5,8-tetrahydroxyanthraquinone (their molecular structures are shown in Scheme 1) as combustion catalysts of DB and CMDB propellants.



Scheme 1. Molecular structures of the anthraquinone metal salts (AMSs)

2 Experimental

2.1 Material preparation

Raw materials

The purity of all raw materials, 1,8-dihydroxyanthraquinone, 1,8-dihydroxy-4,5-dinitroanthraquinone, 1,4,5,8-tetrahydroxyanthraquinone, NaOH, $\text{Pb}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, was higher than 98%, and they were purchased from J & K Chemical Technology.

The preparative methods for 1,8-dihydroxyanthraquinone lead salt (DHAAPb), 1,8-dihydroxyanthraquinone copper salt (DHAACu), 1,8-dihydroxy-4,5-dinitroanthraquinone lead salt (DHDNEPb) and 1,8-dihydroxy-4,5-

dinitroanthraquinone copper salt (DHDNECu) were similar to those reported in the literature [35]. As an example, the preparative procedure for DHAAPb is described. 1,8-Dihydroxyanthraquinone (2.40 g, 0.01 mol) and NaOH (0.84 g, 0.021 mol) were dissolved in H₂O (100 mL; the pH was about 8). The reaction mixture was stirred for 1 h at 60 °C, and then Pb(NO₃)₂ (3.31 g, 0.01 mol) dissolved in H₂O (20 mL) was added to the reaction solution. The resulting solid was filtered off and dried in air. The product obtained (4.21 g, yield 94.6%), was 98.9% pure.

IR (KBr, ν , cm⁻¹), 3455, 1640, 1584, 1520, 1190, 981, 821, 749, 636.

Anal. Found: C 37.73, H 1.349; Calcd.: C 37.75, H 1.348.

XRF Found: Pb 46.49, Calcd.: Pb 46.52.

1,8-Dihydroxyanthraquinone copper (DHAACu): red powder; yield 5.90 g (97.8%), purity 98.7%; IR (KBr, ν , cm⁻¹), 3450, 1658, 1579, 1530, 1196, 978, 823, 746, 633; Anal. Found: C 49.76, H 2.965; Calcd.: C 49.78, H 2.963; XRF Found: Cu 20.98, Calcd.: Cu 21.06.

1,8-Dihydroxy-4,5-dinitroanthraquinone lead (DHDNEPb): brown powder; yield 5.10 g (95.3%) purity 98.8%. IR (KBr, ν , cm⁻¹): 3062, 1704, 1608, 1520, 1431, 1335, 1214, 990, 837, 693. Anal. Found: C 31.38, H 0.750, N 5.21; Calcd.: C 31.40, H 0.748, N 5.23; XRF Found: Pb 38.68, Calcd.: Pb 38.70.

1,8-Dihydroxy-4,5-dinitroanthraquinone copper (DHDNECu): red powder; yield 3.71 g (94.5%), purity 99.1%; IR (KBr, ν , cm⁻¹), 3055, 1678, 1598, 1504, 1428, 1331, 1289, 1210, 987, 840, 685; Anal. Found: C 42.90, H 1.024, N 7.14; Calcd.: C 42.91, H 1.022, N 7.15; XRF Found: Cu 16.20, Calcd.: Cu 16.22.

As an example of the preparative procedures for 1,4,5,8-tetrahydroxyanthraquinone lead salt (TOCKPb) and 1,4,5,8-tetrahydroxyanthraquinone copper salt (TOCKCu), the preparation procedure for TOCKPb is described. 1,4,5,8-Dihydroxyanthraquinone (2.73 g, 0.01 mol) and NaOH (1.68 g, 0.042 mol) were dissolved in H₂O (100 mL; the pH was about 8). The reaction mixture was stirred for 1 h at 60 °C, and then Pb(NO₃)₂ (6.62 g, 0.02 mol) dissolved in H₂O (40 mL) was added to this solution. The resulting solid was filtered off and air dried. The product obtained (6.72 g, yield 97.4%) was 98.5% pure.

IR (KBr, ν , cm⁻¹), 3044, 1561, 1509, 1176, 968, 802, 734, 628.

Anal. Found: C 23.98, H 0.858; Calcd.: C 24.00, H 0.857.

XRF Found: Pb 59.66, Calcd.: Pb 60.70.

2.2 FTIR and EA test conditions

The FTIR spectra were determined on EQUINX55 as KBr discs. Elemental analyses (EA) were obtained on PE-2400 equipment.

2.3 Catalytic thermal decomposition performance measurements

To test the catalytic effects of DHAAPb, DHAACu, DHDNEPb, DHDNECu, TOCKPb and TOCKCu on the decomposition of nitrocellulose (NC), these metal salts were homogeneously mixed with NC with a mass ratio of 1:9. The resulting mixtures were then subjected to DSC measurement. The catalytic thermal decomposition performance was carried out on a Q-200 TA instrument (made in USA) at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ at ambient pressure in a N_2 atmosphere (sample mass 0.5-1.0 mg).

2.4 Catalytic effects on the combustion of DB and RDX-CMDB propellants

The control formulation of DB propellant was composed of nitrocellulose and nitroglycerin (NC+NG) (89 wt.%), centralite II (C2) (2 wt.%), and other additives (9 wt.%). The basic formulation of RDX-CMDB propellant contained NC+NG (66 wt.%), RDX (26 wt.%), and other additives (8 wt.%). The strand samples, composed of 500 g of the above ingredients and the prepared burning rate catalysts as ballistic modifiers, were prepared by a solvent-free extrusion technique, which involved slurry mixing, rolling and extruding. The control DB (Control 1) and RDX-CMDB (Control 2) propellants, without ballistic modifiers, were also prepared for comparison. All of the tested samples are listed in Table 1, with their identification labels and an indication of the amount of burning rate catalyst. The burning rates of the samples were measured in a strand burner filled with nitrogen at different pressures. The strands were cut into small cylinders with dimensions $5\text{ mm} \times 10\text{ mm}$ (diameter \times height) and coated with polyvinyl formal.

Table 1. Amounts of the burning rate catalysts in the DB and RDX-CMDB propellants

No.	Catalyst name and content [wt.%]	No.	Catalyst name and content [wt.%]
Control 1	0	Control 2	0
DB01	DHAAPb 2.5	CMDB01	DHAAPb 3.0
DB02	DHAACu 2.5	CMDB02	DHAAPb 2.5+DHAACu 0.5
DB03	DHDNEPb 2.5	CMDB03	DHDNEPb 3.0
DB04	DHDNECu 2.5	CMDB04	DHDNEPb 2.5+DHDNECu 0.5
DB05	TOCKPb 2.5	CMDB05	TOCKPb 3.0
		CMDB06	TOCKPb 2.5+TOCKCu 0.5

3 Results and Discussion

3.1 Effects of Anthraquinone Combustion Catalysts on the thermal decomposition of NC

In order to monitor these features, the catalytic performances of the various AMSs on the thermal decomposition of NC were determined by DSC measurement. Figure 1 shows the DSC curves for NC and its admixtures with 10 wt.% of DHAAPb, DHAACu, DHDNEPb, DHDNECu, TOCKPb and TOCKCu, in the temperature range of 40–400 °C.

The results indicated that the AMSs exerted a significant catalytic action on the thermal decomposition of NC [37]. The decomposition peak temperature and heat released for pure NC were 209.3 °C and 1463 J/g, respectively. The decomposition peak temperature of NC admixed with an AMS decreased by ~1–4.1 °C, whereas the apparent decomposition heats were significantly increased by 100–840 J/g with respect to pristine NC. These results confirmed that these compounds are better than many other reported nano-combustion catalysts in the catalyzing the decomposition of NC. Previously it was shown that the nano-Fe₂O₃ was not able to decrease reduce the decomposition temperature of NC [38]. However, of the several compounds studied here, DHDNEPb decreased the thermal degradation peak temperature of the NC to the greatest extent (around 4.1 °C), while TOCKPb increased the decomposition heat of NC at the highest level (around 840 J/g higher than the decomposition heat of NC). The structure of DHDNEPb contains Pb and energetic –NO₂ groups; the synergistic effect of the Pb element and the –NO₂ groups can well catalyze the decomposition of NC.

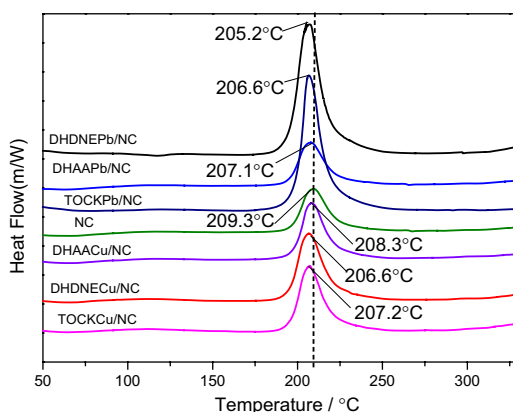


Figure 1. DSC curves of NC and its admixtures with AMSs at 10 °C/min

3.2 Effect of AMSs on the combustion of DB propellants

Burning rate (u), catalytic efficiency (η) and pressure exponent (n) are the three important factors which characterize the combustion catalytic performance of solid propellants. The relationships between u , n , and η are shown in Equations (1) and (2).

$$u = cP_i^n, \quad i = 1-9 \quad (1)$$

$$\eta_i = u_i / u_{o,i} \quad (2)$$

where c is the proportionality factor, $\text{mm}\cdot\text{s}^{-1}\cdot\text{MPa}^{-1}$, P is the pressure of the burning rate measurement, and the index i identifies the pressure measurement point.

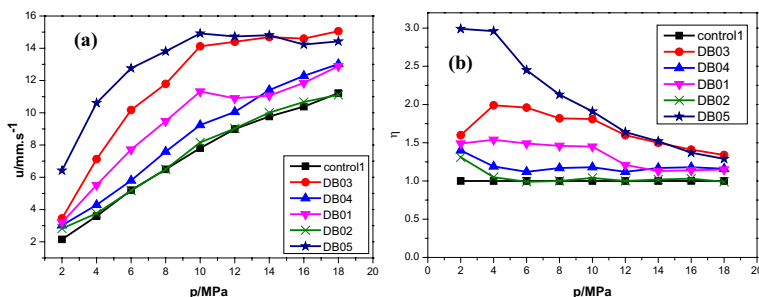


Figure 2. Burning rate (a) and catalytic efficiency (b) curves of different DB propellants

Figure 2 shows the burning rates and catalytic efficiencies for the anthraquinone salt-based DB propellants, together with the related data for the Control 1 sample, for comparison. The u value of the anthraquinone lead-based DB propellants increased rapidly with pressure in the range 2-10 MPa, and then became slower or in some cases became reduced. DHAAPb was able to enhance the burning rate of a DB propellant by about 45% in the pressure range of 2-10 MPa, with an η value greater than 1.45. Furthermore, the burning rate of DHAAPb-DB shows an approximate “plateau” in the middle to high pressure range (10-16 MPa) with an n of 0.1, whereas the “mesa” burning appeared between 10-14 MPa ($n = -0.07$). The burning rate of the DB propellant prepared with DHDNEPb catalyst was increased by more than 80% compared to the Control 1 system, with η greater than 1.8 in the pressure range 4-10 MPa (the catalytic efficiency was ~ 2.0 at 6 MPa). The u value of DHDNEPb-DB showed a “wide-range plateau” in the high pressure range (10-18 MPa) with a low pressure exponent ($n = 0.10$). The burning rate increased about twofold with

TOCKPb as the catalyst in the pressure range 2-8 MPa (η greater than 2.1). The catalytic efficiency was surprisingly high ($\eta=3.0$), especially in the pressure range 2-4 MPa. Moreover TOCKPb-DB also demonstrated a “wide-range plateau” combustion in the pressure range 6-18 MPa, with $n=0.11$. Finally, the use of DHAACu and DHDNECu as degradation catalysts did not bring any significant advantages in terms of increased u and decreased n .

The plateau combustion region of the DB propellants was found to be 6-10 MPa when PbO was used, which is an ordinary inorganic combustion catalyst. Lead 2,4-dihydroxybenzoate (PbDHB), lead *o*-aminobenzoate (PbAB) and lead phthalate (PbP) are the most popular organic metal salt combustion catalysts in DB propellants, and efficiently decrease the value of n in the pressure range 4-8 MPa. It is also well known that by using nano-PbDHB, nano-PbAB and nano-PbP, the plateau region is extended to 4-12 MPa [39, 40], while it is difficult to decrease the n value above 12 MPa. K. Z. Xu *et al.* [33] found that the use of nano-Bi₂WO₆, can improve n in the high pressure region, but the catalytic efficiency was only up to 1.5. Some energetic combustion catalysts, including 4-amino-3,5-dinitropyrazole lead [28] and 3-nitrophthalate lead [40], also generate plateau combustion below 10 MPa. All of the above mentioned combustion catalysts do not facilitate the achievement of “wide-range plateau” combustion, in contrast to that obtained by using the catalysts developed in this work. Furthermore the catalytic efficiency of the already investigated catalysts is always much lower than that exhibited by the lead-based anthraquinone salt catalysts.

The present work has demonstrated that the anthraquinone lead compounds significantly improve DB propellant combustion performance by extending the pressure regime for the “plateau” combustion towards higher pressures (range 12-16 MPa). Comparing the structures of these three compounds, they all contain conjugated benzene and carbonyl groups, the bond between the hydroxyl groups and the lead ion is easily broken to generate new, highly dispersed lead radicals or PbO [28], and carbon is also produced during propellant burning, which can permeate the gaps left by lead, because they are from the same main element and form a homogenous complex. However TOCKPb has the highest burning rate at 10 MPa of all three DB propellants, with the widest “plateau” combustion region. There are four hydroxyl groups in the structure of 1,4,5,8-tetrahydroxyanthraquinone, which can combine with two Pb ions and can decompose to more lead radicals or PbO during combustion, and the p- π conjugative effect from the lone pair electrons and the benzene ring improves the electron fluidity, and increases the catalytic efficiency. There are two hydroxyl groups (-OH) and two nitro groups (-NO₂) in the structure of 1,8-dihydroxy-4,5-dinitroanthraquinone; the hydroxyl groups could react with lead ions, whilst

the nitro groups supply energy during decomposition to improve the combustion of these propellants. In summary, the overall catalytic efficiency on combustion of DB propellants is as follows: TOCKPb>DHDNEPb>DHAAPb.

3.3 Effect of AMSs on the combustion of RDX-CMDB propellants

In order to evaluate the possible utilization of the various AMSs in the preparation of RDX-CMDB propellants, the burning rates of the RDX-CMDB propellants containing the different combustion catalysts (as shown in Table 1) were measured. Figures 3a and 3b report the burning rates of the RDX-CMDB propellants and the corresponding catalytic efficiencies under different pressures, respectively. The parameters relating to the various combustions, in terms of the plateau region, plateau width, plateau burning rate, and plateau pressure exponent, were calculated and are listed in Table 2.

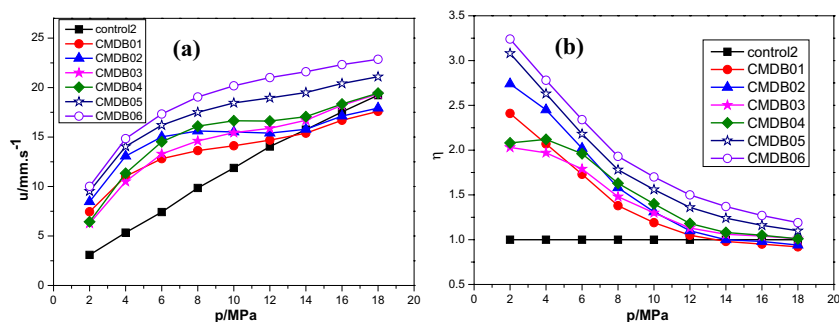


Figure 3. Burning rate (a) and catalytic efficiency (b) curves of the different RDX-CMDB propellants

Table 2. The burning rate characteristics for RDX-CMDB propellants containing different catalyst systems

No.	Plateau region [MPa]	Width of plateau [MPa]	Pressure exponent	Burning rate on plateau [$\text{mm}\cdot\text{s}^{-1}$]
CMDB01	6-14	8	0.22	14.13
CMDB02	6-18	12	0.16	16.06
CMDB03	6-14	8	0.27	15.19
CMDB04	6-18	12	0.16	16.96
CMDB05	6-18	12	0.24	18.87
CMDB06	6-18	12	0.25	20.62

Table 3. Comparison of the catalyst properties of previous and our advanced catalysts for RDX-CMDB propellants

Catalysts	Plateau region [MPa]	Width of plateau [MPa]	Burning rate on plateau [$\text{mm}\cdot\text{s}^{-1}$]
ϕ -Pb [22]	4-10	6	7.90
ϕ -Pb/ β -Cu [22]	6-12	6	10.2
NP/AC [39]	4-8	4	9.00
nNP/nAC [39]	6-12	6	13.73
PbGal [41]	2-8	6	7.11
LCBTATz [42]	4-12	8	9.70
DNPPb [28]	6-10	4	10.97
TOCKPb	6-18	12	18.87
TOCKPb/TOCKCu	6-18	12	20.62

It is well-known that ϕ -Pb and β -Cu [22] are the most commonly used burning catalysts, but they modify the combustion performance only in the pressure range 6-12 MPa for RDX-CMDB propellants, with an average u of $10.2 \text{ mm}\cdot\text{s}^{-1}$. The plateau regions of RDX-CMDB propellants are 4-8 MPa and 6-12 MPa when using 3-nitrophthalate lead (NP)/p-amino benzoic copper (AC) and their nano particles (nNP/nAC) as complex combustion catalysts [39]. When the nanoparticle Pb(II)-gallate complex (PbGal) is used as the combustion catalyst, the plateau regions of RDX-CMDB propellants are 2-8 MPa [41]. The plateau regions of RDX-CMDB propellant containing 3,6-bis(1*H*-1,2,3,4-tetrazol-5-yl-amino)-1,2,4,5-tetrazine lead compound (LCBTATz) [42] are 4-12 MPa, with an average u of $9.7 \text{ mm}\cdot\text{s}^{-1}$. G. F. Zhang *et al.* [43] synthesized p-nitrocalix[n]arene lead or copper compounds, which could slightly increase the u of RDX-CMDB propellants, but without the formation of “plateau” combustion. We prepared the 4-amino-3,5-dinitropyrazole lead (DNPPb) [28], which increased the burning rate of RDX-CMDB propellants, but the plateau combustion region was only 6-10 MPa. Most of the reviewed compounds are inferior to ϕ -Pb, especially in decreasing the pressure exponent.

As shown in Figure 3 and Table 2, the u of AMS-RDX-CMDB propellants increased rapidly with increase in pressure in the range 2-8 MPa, then improved slowly at higher pressure ranges. DHAAPb was able to enhance the burning rate by over 100% in the pressure range 2-4 MPa with $\eta > 2.07$, compared to the Control 2 system; the burning rate of DHAAPb-RDX-CMDB exhibited a “plateau” with $n = 0.22$ in the pressure range 6-14 MPa, and an average u of $14.13 \text{ mm}\cdot\text{s}^{-1}$. The burning rates were increased by more than 80% for the system with DHDNEPb as catalyst, in the pressure range 2-6 MPa (η greater than 1.8).

In this case the “plateau” combustion region was in the range 6-14 MPa, with n equal to 0.27 and an average u of $15.19 \text{ mm}\cdot\text{s}^{-1}$. The burning rates were increased by about three fold with TOCKPb as catalyst in the pressure range 2-6 MPa, with η greater than 2.2, whereas the catalytic efficiency was up to 3.0. The u of TOCKPb-RDX-CMDB exhibited a “wide plateau” in the pressure range 6-18 MPa, with n equal to 0.24 and an average u equal to $18.87 \text{ mm}\cdot\text{s}^{-1}$. According to the combustion parameters exhibited by the various salts, it appears that TOCKPb is the best combustion catalyst of the three anthraquinone lead compounds; the combustion flame structures of RDX-CMDB propellants with the different catalysts also showed an increase in u (see Figure 1S-5S in Supporting Information). All three anthraquinone lead salts were much better than the traditional ϕ -Pb and can be proposed for potential applications in future propellants.

In order to investigate the synergistic effect of copper and lead salts, some systems were also prepared by replacing part of the lead salt with a copper based salt. The results demonstrated that when 0.5 wt.% of the lead salt was replaced by the corresponding copper salt, the combustion properties were significantly enhanced. The burning rates of propellants containing a binary catalyst composed of 2.5 wt.% DHAAPb and 0.5 wt.% DHAACu were higher than that containing only DHAAPb (3.0 wt.%), whilst the “plateau” combustion pressure range was in the range 6-18 MPa with a u value equal to $16.06 \text{ mm}\cdot\text{s}^{-1}$. The “plateau” combustion zone was expanded while the u value was further increased, and, more importantly, the n value was decreased dramatically. For the DHDNEPb/DHDNECu and TOCKPb/TOCKCu systems, the “plateau” combustion region was 6-18 MPa with a low pressure exponent. The u value of propellants containing TOCKPb/TOCKCu was much higher than the others, including the traditional, energetic and nano combustion catalysts in Table 3, and is also one of the best combustion catalyst combinations for RDX-CMDB propellants. The O-Pb bond is easily broken to form new Pb or PbO, because of the conjugative and inductive effects in the anthraquinone structure, and the carbon atoms are changed into elemental carbon during the burning process, then an alloy is formed by the elemental carbon permeating lead and copper, the synergistic effect of Pb-Cu-C modifying the combustion of the propellant. The anthraquinone copper and lead salts can synergistically decrease the pressure exponent and improve the burning rate.

4 Conclusions

Six copper(II) and lead(II) salts based on anthraquinone were prepared and exhaustively characterized. These salts are able to decrease the exothermic peak temperatures and increase the apparent decomposition heat of NC.

DHAAPb, DHDNEPb and TOCKPb can dramatically increase the u values of DB propellants from 50% to 200% in the low pressure range (2-6 MPa). The formation of specific “wide-range plateau” combustion occurs in the middle to high pressure zone, the plateau regions, with n values of 0.1, were found to be 10-16 MPa, 10-18 MPa and 8-18 MPa for DB01, DB03 and DB05, respectively.

The catalysts DHAAPb, DHAAPb/DHAACu, DHDNEPb/DHDNECu and TOCKPb/TOCKCu can increase the u values of RDX-CMDB propellants by more than 100% at 4 MPa. The pressure exponents were found to be 0.22 and 0.27 for CMDB01 and CMDB03 in the plateau regions of 6-14 MPa, respectively. The pressure exponents were calculated to be 0.16, 0.16, 0.24 and 0.25, with plateau regions of 6-18 MPa, for CMDB02, CMDB04, CMDB05 and CMDB06, respectively.

Acknowledgements

This investigation received financial assistance from the National Science Foundation of China (Grant No. 21303133).

Supporting information (SI) available at:

<http://www.wydawnictwa.ipo.waw.pl/CEJEM/contents/2018/vol-15-no-2.html>

References

- [1] Degirmenci, E. Effects of Grain Size and Temperature of Double Base Solid Propellants on Internal Ballistics Performance. *Fuel* **2015**, *146*: 95-102.
- [2] Bello, M. N.; Pantoya, M. L.; Kappagantula, K.; Wang, W. S.; Vanapalli, S. A.; Irvin, D. J.; Wood, L. M. Reaction Dynamics of Rocket Propellant with Magnesium Oxide Nanoparticles. *Energ. Fuel* **2015**, *29*: 6111-6117.
- [3] Han, X.; Wang, T. F.; Lin, Z. K.; Han, D. L.; Li, S. F.; Zhao, F. Q.; Zhang, L. Y. RDX/AP-CMDB Propellants Containing Fullerenes and Carbon Black Additives. *Defence Sci. J.* **2009**, *59*: 284-293.
- [4] Vargeese, A. A. A Kinetic Investigation on the Mechanism and Activity of Copper Oxide Nanorods on the Thermal Decomposition of Propellants. *Combust. Flame* **2016**, *165*: 354-360.
- [5] Reshmi, S.; Vijayalakshmi, K. P.; Thomas, D.; Rajeev, R.; Reghunadhan Nair, C.P.

- Polybutadiene Crosslinked by 1,3-Dipolar Cycloaddition: Pyrolysis Mechanism, DFT Studies and Propellant Burning Rate Characteristics. *Combust. Flame* **2016**, *167*: 380-391.
- [6] Isert, S.; Hedman, T. D.; Lucht, R. P.; Son, S. F. Oxidizer Coarse-to-fine Ratio Effect on Microscale Flame Structure in a Bimodal Composite Propellant. *Combust. Flame* **2016**, *163*: 406-413.
- [7] Li, X. Y.; Guerieri, P.; Zhou, W. B.; Huang, C.; Zachariah, M. R. Direct Deposit Laminate Nanocomposites with Enhanced Propellant Properties. *ACS Appl. Mater. Interfaces* **2015**, *7*: 9103-9109.
- [8] Kumar, P.; Joshi, P. C.; Kumar, R. Thermal Decomposition and Combustion Studies of Catalyzed AN/KDN Based Solid Propellants. *Combust. Flame* **2016**, *166*: 316-332.
- [9] Hu, H. X.; Feng, C. G.; Wang, J. N. The Burning Characteristics of RDX-CMDB Propellants. *Theory Pract. Energ. Mater.*, 4th [Proc. Int. Autumn Semin. Propellants, Explos. Pyrotech.] **2001**, 223-226.
- [10] Dey, A.; Athar, J.; Varma, P.; Prasant, H.; Sikder, A. K.; Chattopadhyay, S. Graphene-iron Oxide Nanocomposite (GINC): an Efficient Catalyst for Ammonium Perchlorate (AP) Decomposition and Burn Rate Enhancer for AP Based Composite Propellant. *RSC Adv.* **2015**, *5*: 1950-1960.
- [11] Demidova, L. A.; Htwe, Y. Z.; Denisjuk, A. P. Catalytic Mechanism in Combustion of Propellant with Ammonium Nitrate. *Sci. Technol. Energ. Mater.* **2015**, *76*: 87-91.
- [12] Yan, Q. L.; Gozin, M.; Zhao, F. Q.; Cohen, A.; Pang, S. P. Highly Energetic Compositions Based on Functionalized Carbon Nanomaterials. *Nanoscale* **2016**, *8*: 4799-4805.
- [13] Li, Z. M.; Zhou, M. R.; Zhang, T. L.; Zhang, J. G.; Yang, L.; Zhou, Z. N. The Facile Synthesis of Graphene Nanoplatelet-Lead Styphnate Composites and Their Depressed Electrostatic Hazards. *J. Mater. Chem. A* **2013**, *1*: 12710-12714.
- [14] Li, Y.; Zhao, W. Y.; Mi, Z. H.; Yang, L.; Zhou, Z. N.; Zhang, T. L. Graphene-modified Explosive Lead Styphnate Composites. *J. Therm. Anal. Calorim.* **2016**, *124*: 683-691.
- [15] Jiao, Q. Z.; Liu, H. B.; Zhao, Y.; Zhang, Z. Preparation and Application of Cu/Cr Hydrotalcite-like Compounds. *J. Mater. Sci.* **2009**, *44*: 4422-4428.
- [16] Sathiskumar, P. S.; Thomas, C. R.; Madras, G. Solution Combustion Synthesis of Nanosized Copper Chromite and Its Use as a Burn Rate Modifier in Solid Propellants. *Ind. Eng. Chem. Res.* **2012**, *51*: 10108-10116.
- [17] Vargeese, A. A.; Muralidharan, K. Kinetics and Mechanism of Hydrothermally Prepared Copper Oxide Nanorod Catalyzed Decomposition of Ammonium Nitrate. *Appl. Catal. a-Gen.* **2012**, *447*: 171-177.
- [18] Gao, W. J.; Liu, X. Y.; Su, Z. Y.; Zhang, S.; Yang, Q.; Wei, Q.; Chen, S. P.; Xie, G.; Yang, X. W.; Gao, S. L. High-energy-density Materials with Remarkable Thermostability and Insensitivity: Syntheses, Structures and Physicochemical Properties of Pb(II) Compounds with 3-(Tetrazol-5-yl) Triazole. *J. Mater. Chem. A* **2014**, *2*: 11958-11965.

- [19] Yan, Q. L.; Cohen, A.; Petrutik, N.; Shlomovich, A.; Burstein, L.; Pang, S. P.; Gozin, M. Highly Insensitive and Thermostable Energetic Coordination Nanomaterials Based on Functionalized Graphene Oxides. *J. Mater. Chem. A* **2016**, *4*: 9941-9948.
- [20] Ren, H.; Liu, Y. Y.; Jiao, Q. J.; Fu, X. F.; Yang, T. T. Preparation of Nanocomposite PbO Center Dot CuO/CNTs via Microemulsion Process and Its Catalysis on Thermal Decomposition of RDX. *J. Phys. Chem. Solids* **2010**, *71*: 149-152.
- [21] Vargeese, A. A. Pressure Effects on Thermal Decomposition Reactions: a Thermokinetic Investigation. *RSC Adv.* **2015**, *5*: 78598-78605.
- [22] Jin, B.; Peng, R. F.; Zhao, F. Q.; Yi, J. H.; Xu, S. Y.; Wang, S. B.; Chu, S. J. Combustion Effects of Nitrofulleropyrrolidine on RDX-CMDB Propellants. *Propellants Explos. Pyrotech.* **2014**, *39*: 874-880.
- [23] Hong, W. L.; Zhao, F. Q.; Liu, J. H.; Tian, D. Y.; Luo, Z. K.; Chen, P.; Luo, Y. Synthesis and Combustion Catalytic Activity of Nanoparticle Pb(II)-Phthalate Complex. *Chinese J. Inorg. Chem.* **2004**, *20*: 996-1000.
- [24] Najafi, M.; Samangani, A. K. Non-Isothermal Kinetic Study of the Thermal Decomposition of Melamine 3-Nitro-1,2,4-triazol-5-one Salt. *Propellants Explos. Pyrotech.* **2011**, *36*: 487-492.
- [25] Yi, J. H.; Zhao, F. Q.; Hong, W. L.; Xu, S. Y.; Hu, R. Z.; Chen, Z. Q.; Zhang, L. Y. Effects of Bi-NTO Complex on Thermal Behaviors, Nonisothermal Reaction Kinetics and Burning Rates of NG/TEGDN/NC Propellant. *J. Hazard. Mater.* **2010**, *176*: 257-261.
- [26] Kulkarni, P. B.; Purandare, G. N.; Nair, J. K.; Talawar, M. B.; Mukundan, T.; Asthana, S. N. Synthesis, Characterization, Thermolysis and Performance Evaluation Studies on Alkali Metal Salts of TABA and NTO. *J. Hazard. Mater.* **2005**, *119*: 53-61.
- [27] Kulkarni, P. B.; Reddy, T. S.; Nair, J. K.; Nazare, A. N.; Talawar, M. B.; Mukundan, T.; Asthana, S. N. Studies on Salts of 3-Nitro-1,2,4-triazol-5-one (NTO) and 2,4,6-Trinitroanilino Benzoic Acid (TABA): Potential Energetic Ballistic Modifiers. *J. Hazard. Mater.* **2005**, *123*: 54-60.
- [28] Wang, Y. L.; Zhao, F. Q.; Xu, K. Z.; Ji, Y. P.; Yi, J. H.; Wang, W.; Yu, T.; An, T. Synthesis, Thermal Behavior, and Application of 4-Amino-3,5-Dinitropyrazole Lead Salt. *J. Therm. Anal. Calorim.* **2014**, *115*: 1219-1225.
- [29] Wang, Y. L.; Zhao, F. Q.; Xu, K. Z.; Ji, Y. P.; Yi, J. H.; Chen, B.; An, T. Synthesis, Crystal Structure and Thermal Behavior of 4-Amino-3,5-Dinitropyrazole Potassium Salt. *Inorg. Chim. Acta* **2013**, *405*: 505-510.
- [30] Wang, Y. L.; Zhao, F. Q.; Ji, Y. P.; Pan, Q.; Yi, J. H.; An, T.; Wang, W.; Yu, T.; Lu, X. M. Synthesis and Thermal Behaviors of 4-Amino-3,5-dinitro-1H-pyrazole. *J. Anal. Appl. Pyrolysis* **2012**, *98*: 231-235.
- [31] Patil, P. R.; Krishnamurthy, V. N.; Joshi, S. S. Differential Scanning Calorimetric Study of HTPB Based Composite Propellants in Presence of Nano Ferric Oxide. *Propellants Explos. Pyrotech.* **2006**, *31*: 442-446.
- [32] Yang, Y.; Yu, X. J.; Wang, J.; Wang, Y. X. Effect of the Dispersibility of Nano-

- CuO Catalyst on Heat Releasing of AP/HTPB Propellant. *J. Nanomater.* **2011**, *21*: 335-338.
- [33] Wei, T. T.; Zhang, Y.; Xu, K. Z.; Ren, Z. Y.; Gao, H. X.; Zhao, F. Q. Catalytic Action of Nano Bi_2WO_6 on Thermal Decompositions of AP, RDX, HMX and Combustion of NG/NC Propellant. *RSC Adv.* **2015**, *5*: 70323-70328.
- [34] Hao, G. Z.; Liu, J.; Gao, H.; Xiao, L.; Ke, X.; Jiang, W.; Zhao, F. Q.; Gao, H. X. Preparation of Nano-Sized Copper beta-Resorcyate (beta-Cu) and Its Excellent Catalytic Activity for the Thermal Decomposition of Ammonium Perchlorate. *Propellants Explos. Pyrotech.* **2015**, *40*: 848-853.
- [35] Wang, Y. L.; Zhao, F. Q.; Ji, Y. P.; Yan, Q. L.; Yi, J. H.; Xu, S. Y.; Luo, Y.; Lu, X. M. Synthesis and Thermal Behaviors of 1,8-Dihydroxy-4,5-dinitroanthraquinone Barium Salt. *J. Anal. Appl. Pyrolysis* **2014**, *105*: 295-300.
- [36] Wang, Y. L.; Zhao, F. Q.; Ji, Y. P.; Yi, J. H.; Wang, W.; Xu, S. Y.; An, T.; Pei, Q. Synthesis and Thermal Behavior of 1,8-Dihydroxy-4,5-dinitroanthraquinone Manganese Salt. *Chem. Res. Chinese U.* **2014**, *30*: 468-471.
- [37] Shamsipur, M.; Pourmortazavi, S. M.; Hajimirsadeghi, S. S.; Atifeh, S. M. Effect of Functional Group on Thermal Stability of Cellulose Derivative Energetic Polymers. *Fuel* **2012**, *95*: 394-399.
- [38] Zhao, N. N.; Gong, H. J.; An, T.; Zhao, F. Q.; Yang, A. W.; Hu, R. Z.; Ma, H. X. Effects of Fe_2O_3 Nanoparticles on the Thermal Behavior and Non-isothermal Decomposition Kinetics of Nitrocellulose. *J. Anal. Appl. Pyrolysis* **2016**, *107*: 451-454.
- [39] Li, H.; Zhao, F. Q.; Li, X. J.; Fan, X. Z.; Wang, G. Q. Effect of Nanometer Organic Metal Salts on the Combustion Properties of RDX-CMDB Propellant. (in Chinese) *Chin. J. Explos. Propellants (Huozhayao Xuebao)* **2014**, *37*: 78-83.
- [40] Wang, H.; Zhao, F. Q.; Gao, H. X.; Li, S. W.; Hao, H. X. Preparation of Nano-size Lead Phthalate and its Catalysis for Double-base Propellant Combustion. (in Chinese) *Chin. J. Energ. Mater. (Hanneng Cailiao)* **2006**, *14*: 45-48.
- [41] Hong, W. L.; Liu, J. H.; Zhao, F. Q.; Li, Y. M.; Tian, D. Y.; Zhang, P. X. Synthesis and Combustion Catalytic Activity of Nanoparticle Pb(II)-Gallate Complex. *Acta Chim. Sinica* **2005**, *63*: 249-53.
- [42] Li, W.; Ren, Y. H.; Zhao, F. Q.; Zhang, X. B.; Ma, H. X.; Xu, K. Z.; Wang, B. Z.; Yi, J. H.; Song, J. R.; Hu, R. Z. Effects of Lead Complex-Based BTATz on Thermal Behaviors, Non-Isothermal Reaction Kinetics and Combustion Properties of DB/RDX-CMDB Propellants. *Acta Phys.-Chim. Sin.* **2013**, *29*: 2087-2094.
- [43] Zhang, G. F.; Wang, C. Y.; An, T.; Zhao, F. Q.; Fan, X. Z. Synthesis, Characterization, and Combustion Catalytic Activities of Copper(II) and Lead(II) Salts of p-Nitrocalix[n]arenes (n=4, 6, 8). *Propellants Explos. Pyrotech.* **2014**, *39*: 802-808.