



Cent. Eur. J. Energ. Mater. 2018, 15(3): 485-500; DOI: 10.22211/cejem/93638
Research paper

BuNENA-DNDA57 Combined Energetic Plasticizer for Modified Cast Double Base Propellants

**Ahmed M. A. Maraden^{1*}, Petr Stojan², Jan Zigmund³,
Robert Matyáš¹**

¹ *Institute of Energetic Materials,
Faculty of Chemical Technology, University of Pardubice,
532 10 Pardubice, Czech Republic*

² *OZM Research, s.r.o.,
Bliznovice 32, 538 62 Hrochuv Tynec, Czech Republic*

³ *Explosia, a.s., Semtin 107, 530 02 Pardubice, Czech Republic*

**E-mail: st50389@student.upce.cz*

Abstract: Modification of cast double base propellants is somewhat of an art form. Obtaining a final propellant grain that has the right balance between energetic liquids and solid ingredients with the desired properties requires great effort. Four formulations of a modified cast double base propellant with different RDX contents have been prepared. A combination of BuNENA and DNDA57 energetic plasticizers has been used to overcome the problems that occur with a high nitroglycerin content. The effect of the RDX content on the burning behaviour, activation energies, and sensitivity to impact has been studied. Burning rate measurements have been performed using a closed bomb SV-2 to investigate the burning behaviour under a wide range of operating pressures. DTA and DSC thermal analysis were conducted to evaluate the thermal behaviour of the prepared modified double base propellants. The results showed that the formulation with only the combined plasticizer has the highest burning rate and activation energy and the lowest sensitivity to impact.

Nomenclature:

AK II *N'*-Methyl-*N,N*-diphenylurea; Akardite II
BuNENA Butyl(2-nitroxyethyl)nitramine
DNDA-5 2,4-Dinitro-2,4-diazapentane
DNDA-6 2,4-Dinitro-2,4-diazaheptane
DNDA-7 3,5-Dinitro-3,5-diazaheptane

DNDA57	liquid mixture of DNDA-5, DNDA-6 and DNDA-7
MCDB	Modified cast double base
NG	Nitroglycerin
TA	Triacetin

Keywords: Modified cast double base propellant, burning rate, thermal analysis, BuNENA, DNDA57

1 Introduction

Preparation of propellant grains by casting techniques depends largely on the ability of nitrocellulose powder to swell and coalesce into a coherent mass when treated with a suitable solvent. Propellants manufactured by the casting process provide a wide range of energies and burning rates. The inclusion of liquid nitroglycerin as a major energetic ingredient presents both stability and performance problems. Like all nitrate esters, NG is capable of autocatalytic decomposition and has a tendency to migrate from the propellant grain during storage [1-3]. Replacement of NG with other energetic plasticizers to reduce the possibility of exudation becomes an essential priority. Modified double base (MDB) propellants are evolved from double base (DB) propellants by integrating energetic fillers such as energetic nitramines (*i.e.* HMX or RDX) [4-6]. The use of energetic additives, mainly binders and plasticizers containing groups such as nitro, nitrate, fluorodinitro, *etc.* is considered to be one of the practical ways to improve the energy level, physical integrity and other technical performances of solid propellants [7-9].

Various types of active binders, based on nitrocellulose, or an inert binder and nitroglycerin, or less energetic liquid nitrates, can be used (see [10]). The *n*-butyl nitroxyethylnitramine (BuNENA) has excellent plasticizing characteristics that impart good physicochemical properties to a propellant [11-16]. Several linear nitramines such as DNDA57 show favourable effects towards temperature independent propellants, propellants which exhibit combustion behaviour almost independent of ambient temperature [17]. Their plasticization ability is strong, their sensitivity and chemical stability are superior to those of nitrate esters, and may be used as raw material for gun propellants [18]. Wide attention has been given to BuNENA by researchers in applications to gun-propellants and rocket propellants, and its systematic study has been carried out [19]. In gun-propellants, BuNENA possesses the advantages of high plasticizing ability, good process performance, low sensitivity, high energy and further improvement

of the mechanical properties of the formulation, therefore it has wide application prospects. A literature survey revealed that a significant amount of work has been reported on the performance of NENA-based gun propellants, but there is still a paucity of information on cast double base propellants based on NENA plasticizers [13-16]. Upon heating in a nitrogen stream up to 120 °C, DNDA57 and BuNENA exhibit lower volatility than nitroglycerin due to their lower vapour pressure. Table 1 lists the characteristics of BuNENA and DNDA57 compared to NG [20].

Table 1. NG characteristics compared to BuNENA and DNDA57 plasticizers [20]

Plasticizer	TGA midpoint [°C]	Mass loss [wt.%]	Glass transition temperature [°C]	Impact sensitivity [Nm]	Heat of expl. [J/g]	Oxygen balance [%]
NG	149	30	+131 ^[a]	0.2	6675	+3.5
BuNENA	152	23	-48	6.0	3573	-104.3
DNDA57	159	12	-52	3.0	3848	-72.3

^[a] Melting point

The scope of the present research was to study the impact of adding a combined energetic plasticizer, composed of BuNENA and DNDA57, at the expense of NG for a MCDB propellant.

2 Experimental

2.1 Preparation of MCDB propellant

The first step in the preparation of MCDB propellant grains is to produce a casting powder [21, 22]. The manufacturing process may be conveniently divided into four steps; mixing, granulating, drying and then finalizing the product. Nitrocellulose (provided by Explosia Company NC; 4-8% in ethanol/diethyl ether, 13.2-13.3% nitrogen, viscosity 30-50 mPa·s) was introduced into the process in a lumpy condition. All other solid ingredients (Table 2) were added and the resulting premix served as the feed for the mixer (a heavy duty, horizontal, sigma-blade Brabender mixer). The optimum capacity for the mixer was 200 g of dough. The mixer was jacketed to provide circulation of hot or cold water during various stages in the mixing operation, maintaining a mixing temperature of 20 °C. Table 2 shows the formulations of the casting powders used to manufacture the MCDB grains. A mixture of volatile solvents (acetone:ethanol 70:30

by volume) was poured onto the premixed solid ingredients and the nitrocellulose was gelatinized for 90 min at 20 r.p.m. The shaping or granulating operation proceeded by loading the dough into a cylinder and subjecting it to a pressure of 2 MPa for extrusion. Extrusion rates were normally controlled by the orifices in the hydraulic supply line and the velocity of the piston head (73 mm/min). After extrusion, strands of diameter 1 mm were cut using standard small arms. Precise control of the L/D is complex since it depends on the shrinkage characteristics during drying. Thus, the cutting operation must be conducted with full awareness of the dimensional changes to be expected in the extrusion operation preceding it and the subsequent drying operation.

Table 2. Formulations of the prepared nitrocellulose-based casting powders

Sample	Content of substances in propellant [wt.%]						
	NC	RDX	BuNENA	DNDA57	CaCO ₃	PbO	AK II
(DB0) _{Powder}	70	0	12.5	12.5	1.3	1.7	2
(DB1) _{Powder}	42	28	12.5	12.5	1.3	1.7	2
(DB2) _{Powder}	35	35	12.5	12.5	1.3	1.7	2
(DB3) _{Powder}	30	40	12.5	12.5	1.3	1.7	2

A considerable amount of volatile solvent is removed by evaporation during the latter stages of mixing. The remainder must be removed in the drying operation. Therefore, it is passed through a water dry operation. After complete drying, the average grain length was 0.81 mm with an average diameter of 0.79 mm. Several further operations are required, such as glazing, which reduces the electrostatic charge and promotes easy flow. A small amount (0.05%) of graphite was added to the propellant granules and distributed over the surface. Finally, screening was done to remove clusters, dust, and foreign material.

The second stage in the manufacture of MCDB is the casting process. The rate and uniformity with which casting powder granules are plasticized by the casting solvent are critical in determining the proper cure conditions and the properties of the final propellant. In this work, the process of *in situ* casting, also called granular casting, has been used. The first basic step is to fill a mold or the motor case with casting powder. Ideally, the technique selected to fill the mold is one which results in maximum reproducibility of the loading density. Simple dumping and pouring yields a low packing density. In well-loaded units, the packing density is such that 68 vol.% of the container is occupied by the casting powder. Simple dumping might lead to only 57% occupation. In combination with the above techniques, vibration has also been

used to achieve maximum bulk density in the mold. The powder bed is usually vibrated by externally mounted, pneumatic vibrators. After the mold is filled with casting powder, it is subjected to a vacuum. The casting step consists of filling the interstitial space in the powder bed with casting solvent. A mixture of nitroglycerin with triacetin mass % (7:3) was used as an energetic plasticizer, with triacetin to facilitate the diffusion of nitroglycerin into the nitrocellulose. The ratio of casting liquid to casting powder in the mold was 1:1.4 by weight. Table 3 lists the mass % for casting powder and casting liquid used for the MCDB propellant grains. The casting solvent may be introduced to the bed from the top of the mold or from the bottom. The curing process is carried out during two distinct periods: an ambient rest period, in which the unit is simply stored for one or more days at 25 °C, and a second period in a cure bay at 50-60 °C for a longer period. After several days to 2 weeks at the elevated cure temperature, the propellant has been converted to a macroscopically homogeneous mass by mutual diffusion of nitrocellulose and plasticizers. The propellant charge is then allowed to cool to room temperature.

Table 3. Components [wt.%] used for MCDB propellant grains

Component	Sample [wt.%]			
	DB0	DB1	DB2	DB3
Casting powder [from Table 2]	41.6	41.6	41.6	41.6
Casting liquid [NG + TA]	58.4	58.4	58.4	58.4

2.2 Burning rate measurement

In general, burning rates obtained by different techniques are not the same; even using identical specimens and the same technique at different facilities, the measured burning rates are different due to a variety of details not fully controllable or controlled. Closed vessel evaluation of propellants is a well-established technique by which experimental determination of a propellant performance under laboratory conditions can be conducted [23-25]. Several closed vessel configurations are currently available to obtain the burning rate of the propellant from experimental pressure records vs. time. A Stojan vessel SV-2 closed bomb, built up by OZM Research Company, was used to measure the dependency of the burning rate of the solid rocket propellants on the operating pressure. A single shot was sufficient for plotting the burning rates for the whole pressure range. Confirmation of the reproducibility of the results was achieved by one or two more shots.

2.3 Thermal analysis

A DTA 550 Ex apparatus (OZM Research) was used for differential thermal analysis [26]. The measurements were carried out at atmospheric pressure, with the tested sample in direct contact with air. The sample (10 mg) was placed in a test tube made of Simax glass, 5 mm in diameter and 50 mm long. The reference standard was 0.05 g aluminium oxide. Linear heating rates of 5, 10, 15 and 20 °C/min were used. The results were treated with the Kissinger model to evaluate the activation energies for the double base propellant compositions [27-30]. DSC experiments were carried out using a DSC instrument model 200 F3 (Netzsch) at atmospheric pressure and laboratory temperature of 20 °C. The conditions for DSC were: reference standard was an empty crucible, sample mass about 2.00 mg, heating rates 2, 5, 10, 15 and 20 °C/min, flow rate of nitrogen 45 mL/min. Thermal analysis tests were performed for a temperature range 20-400 °C. The activation energies were studied and calculated from the DSC curves by the Friedman method [31-33].

2.4 Sensitivity to impact

The Kast fall hammer apparatus [34] (produced by Reichel and Partner) was applied for determination of the impact sensitivity with 1 kg and 2 kg heavy hammers. Both piston (BFH-SR) and cylinders (BFH-SC) were produced by OZM Research. The amount of tested substance was 50 mm³. The probit analysis was used for measuring and for calculation of the final value of E50. Five levels of impact energy and 15 trials at each level were measured for each sample.

2.5 Thermal stability

The modified vacuum isothermal stability test STABIL (OZM Research) [26, 35, 36], was used for measuring the thermal stability. The amount of sample used for each measurement was 2 g and the test was performed over 40 h. A temperature of 120 °C was chosen for the isothermal measurements. Samples in evacuated glass test tubes were placed into the heating block and heated to the desired temperature. Pressure transducers continuously measured the pressure increase in the glass tubes. The results were in the form of time dependence of the gas pressure evolution per 1 g sample. Two trials were performed for each composition.

3 Results and Discussion

3.1 MCDB formulations

Four different MCDB grains were prepared by introducing the casting liquid from the bottom of the casting powder bed. The curing time was about 15 days at an elevated temperature of 60 °C. The grains were left to reach a laboratory temperature of 20 °C. The appearance of the grains was good and showed that the casting liquid had completely diffused into the casting powder forming homogenous double base grains. Disk shaped grains of height 10 mm, diameter 85 mm and weight 90 g were prepared. The calculated density of the cylindrical grains was about 1.60 g/cm³.

3.2 Ballistic testing using a Stojan Vessel

Studying the burning characteristics of the four compositions (Table 3) was carried out by three shots for each propellant at 20 °C. An advanced mathematical procedure based on the most modern computational and ballistic procedures was applied to calculate the burning rate dependency on the pressure. This dependency was calculated for pressures in the range 10-23 MPa. The resulting dependences are shown in Figure 1.

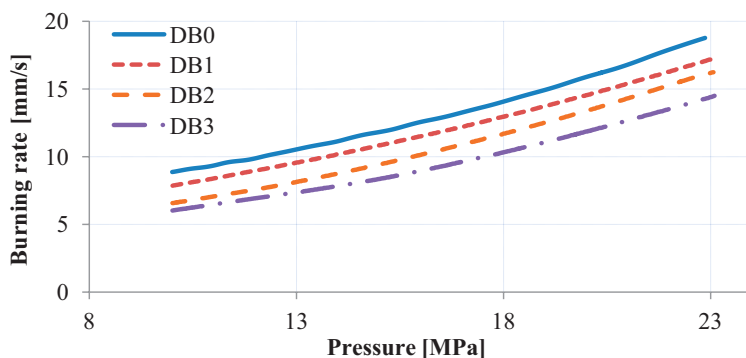


Figure 1. Burning rate dependency on the operating pressure for the prepared double base propellants

As predicted, the burning rate increased with pressure. The burning rate for composition DB0, which had BuNENA-DNDA57 combined energetic plasticizer and no RDX, exhibited the greatest rate over the whole pressure range. Crystalline RDX particles mixed with the base matrix of DBP, melts, decomposes and gasifies at the burning surface of the propellant [37-39]. The decomposed RDX gas diffuses into the decomposed gas of the base

matrix at and just above the burning surface, which produces the luminous flame at some distance above the burning surface and the burning velocity may be controlled by this diffusion step. The burning rate for the RDX-free formulation increased from 8.8 mm/s to 18.6 mm/s, an increase of 111.3%, while the burning rate for the composition DB3 increased by 137.5%, from 6.02 mm/s to 14.3 mm/s. The presence of RDX has a decelerating effect on the burning rate of the propellant at normal temperatures. The burning rate was 8.8, 7.8, 6.57 and 6.02 mm/s for the compositions DB0, DB1, DB2, and DB3, respectively, at 10 MPa. The pressure exponent was determined from the slope of the plot of logarithm of the burning rate $\log u$ against logarithm of pressure $\log p$. The results showed that the addition of RDX increases the pressure index of the propellant. Table 4 lists the maximum pressure of combustion and the pressure exponent for the prepared formulations. The maximum pressure of combustion also increased with increasing RDX content. Because the energy of RDX is higher than that of nitrocellulose, the energy of a nitramine propellant increases as the RDX content is increased. The burning rate of RDX-MDB propellant decreased with an increase of RDX content, despite an increase in the energy contained per unit mass of propellant.

Table 4. Constant volume combustion characteristic parameters of the propellants

Sample	Max pressure [MPa]	Pressure exponent n
DB0	281.14	0.90
DB1	301.46	0.94
DB2	312.70	1.04
DB3	319.58	1.09

3.3 Thermal analysis

DTA curves for the prepared MCDBs at heating rates 5, 10, 15 and 20 °C/min were used to estimate the apparent activation energies using the model proposed by Kissinger, which takes the form [27-30]:

$$\ln\left(\frac{\phi}{T^2}\right) = -\left(\frac{E_a}{R}\right) \cdot \frac{1}{T} + \ln\left(\frac{A \cdot R}{E_a}\right) \quad (1)$$

where ϕ is the heating rate [°C/min], E_a is the activation energy [kJ/mol], R is the gas constant, A is the frequency factor for thermal decomposition and T is the exothermic peak temperature [K]. The dependency of $\ln(\phi/T^2)$ on $1/T$ for all four compositions is presented in Figure 2.

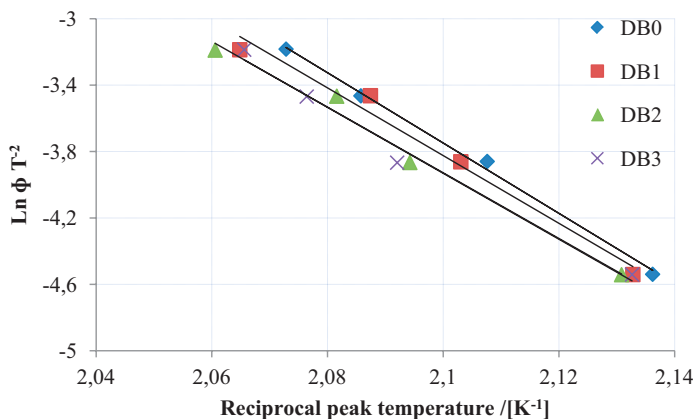


Figure 2. Kissinger plots to evaluate the activation energy E_a

The plots for all measured samples form straight lines, which indicated that the mechanism of thermal decomposition of the propellants is first order [40-41]. Preliminary estimation for the activation energies can be done from the slopes of the regression lines. The slope is equal to $-E_a/R$. Therefore, the activation energy (E_a) was obtained from the slope of the graph. Values of the activation energy and logarithm of the frequency factor for the samples are tabulated in Table 5.

Table 5. Calculated activation energies using the Kissinger model

Sample	Kissinger E_a [kJ/mol]	Log A [s ⁻¹]	Linear regression coefficient r
DB0	175.9	19.00	0.9966
DB1	169.5	18.26	0.9806
DB2	166.3	17.44	0.9879
DB3	164.9	15.88	0.9864

The DSC data were treated with the most common differential isoconversional method of Friedman [31-33] to calculate the activation energies (E_a). This method is based on Equation 2, which takes the form:

$$\text{Ln} \left[\beta_i \left(\frac{d\alpha}{dT} \right)_{\alpha,i} \right] = \text{Ln} [f(\alpha) A_{\alpha}] - \frac{E_{\alpha}}{RT_{\alpha,i}} \quad (2)$$

where β is the heating rate (°C/min), E_a is the activation energy (kJ/mol), R is the gas constant, α is the extent of conversion. In this method the degree of conversion can be computed from the DSC curves. The activation energy

can be determined by the Friedman method without a precise knowledge of the reaction mechanism from plots of the logarithm of the heat flux *versus* the inverse of the temperature. The regression correlation coefficients R^2 were all greater than 0.982. The calculated activation energies and the dependency of the activation energy on the conversion rate are illustrated in Table 6. The value of the activation energy can be determined by an isoconversional method without assuming the kinetic model function [42, 43]. A single-step rate equation cannot generally be adequate for a multi-step mechanism. However, it can provide an adequate kinetic representation of a multi-step process that has a single rate-limiting step. The occurrence of a multi-step process does not immediately invalidate the application of the isoconversional principle, although the latter holds strictly for a single-step process. The principle continues to work as a reasonable approximation because isoconversional methods describe the process kinetics by using multiple single step kinetic equations [44]. In the case of a mechanism of two consecutive reactions when the first reaction is significantly slower than the second, the first process would determine the overall kinetics that would obey a single-step, whereas the mechanism involves two steps.

Table 6. Calculated activation energies using the Friedman model based on DSC data

α reacted	DB0		DB1		DB2		DB3	
	E_a [kJ/mol]	R^2	E_a [kJ/mol]	R^2	E_a [kJ/mol]	R^2	E_a [kJ/mol]	R^2
0.10	156.52	0.9913	124.62	0.9923	195.46	0.9986	169.10	0.9921
0.20	161.54	0.9956	151.53	0.9964	197.75	0.9956	180.94	0.9992
0.30	164.54	0.9983	158.55	0.9978	187.77	0.9975	184.94	0.9955
0.40	166.14	0.9947	163.31	0.9985	178.24	0.9998	187.35	0.9886
0.50	168.26	0.9961	159.15	0.9935	160.72	0.9961	188.86	0.9859
0.60	172.06	0.9883	176.17	0.9925	142.95	0.9913	186.69	0.9824
0.70	175.33	0.9944	175.20	0.9921	121.30	0.9919	170.42	0.9964
0.80	184.67	0.9853	243.88	0.9971	171.88	0.9949	106.45	0.9878
0.90	198.09	0.9837	176.34	0.9825	164.29	0.9894	114.69	0.9823
Mean value	171.9	-	169.86	-	168.93	-	165.49	-

3.4 Sensitivity to impact

The sensitivity of the MCDB propellants to impact was determined with a Kast fall hammer. For comparison of our values with standard explosives (PETN, RDX) we used data from [45]. The conditions of measuring the impact sensitivity for RDX and PETN and the method used for calculating their impact sensitivity

are exactly the same as those we used for calculating the impact sensitivity for the prepared compositions. The impact energies were calculated for 50% probability of initiation and are summarised in Table 7.

Table 7. Sensitivity of MCDB propellants to impact compared with the sensitivities of PETN and RDX

Sample	E_{50} [J]	Linear regression coefficient r
DB0	4.97	0.9965
DB1	2.78	0.9991
DB2	2.27	0.9980
DB3	2.17	0.9846
PETN	3.90	-
RDX	7.00	-

The results of the impact sensitivity tests for the MCDB propellants are quite surprising. The impact sensitivity can reflect whether a propellant is easy to explode or not under the surrounding mechanical effect. All samples (DB0-DB3) differ only in their NC and RDX contents. In the order of the designations of the samples (from DB0 to DB3), the RDX content increases while the NC content decreases. One would expect that samples containing mainly NC should be the most sensitive and the samples containing less NC should be less sensitive. But the order of sensitivities is reversed. The reason for such behaviour is not completely understood. An explanation for such behaviour is that replacing nitrocellulose with RDX increases the oxygen balance of the formulation and consequently increases the impact sensitivity. Another explanation tends to relate such behaviour with the structure of the double base matrix, which is altered significantly by the addition of RDX particles. The propellant matrix becomes more sensitive with a higher percentage of fine solid particle. The addition of RDX decreased the mechanical properties of the base matrix and facilitates the initiation mechanism by providing more opportunities for the formation of hot spots. Generally, samples DB1-DB3 were quite sensitive to impact, they are more sensitive than pure PETN. The sensitivity of sample DB0 was between PETN and RDX.

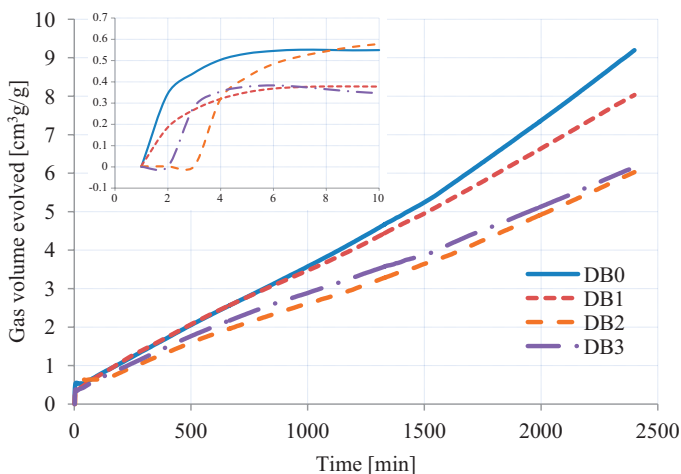
3.5 Thermal stability testing

Using the modified VST assembly, experiments were carried out at a temperature of 120 °C for a period of 40 h. Table 8 lists the volume of gas evolved by the decomposition of the propellant samples with various RDX and NC contents. The amount of evolved gas decreased with decreasing NC content.

Table 8. Volume of gas evolved over 40 h at 120 °C

Sample	NC content [%]	RDX content [%]	Gas volume at STP [cm ³ /g]
DB0	29.12	0	9.19
DB1	17.47	11.65	8.03
DB2	14.56	14.56	6.02
DB3	12.48	16.64	6.15

Such a result was expected. There was only one exception to this order; sample DB3 (containing 12.48% NC) released a slightly higher volume of gas than sample DB2 (containing 14.56% NC). However the difference between DB2 and DB3 is not significant. Figure 3 illustrates the trend of the gas evolved for the prepared compositions during the 40 h test with STABIL. The gases are evolved linearly with time during the test duration. Focusing on the first 5 min, we find that the evolution of gas has been delayed by the addition of RDX. The only important observation is that propellant DB2 was delayed longer than propellant DB3, and then started to evolve gas comparatively faster than the other compositions. Subsequently the rate of gas evolution slowed down and became the lowest volume of gas evolved during the test.

**Figure 3.** Gas evolved during the STABIL test

4 Conclusions

Modified cast double base propellant grains were successfully prepared using the combined energetic plasticizer BuNENA-DNDA57. The preparation technique showed that the energetic plasticizer can be included in the casting powder and it is not obligatory to be added to the casting liquid. The selection of the percentage between the casting powder and the casting liquid is very important to produce a totally cured, coherent and solid cast double base grain after the diffusion of the casting liquid into the casting powder, taking into consideration the optimum conditions for the curing process. Burning rate behaviour was investigated practically using the closed bomb SV-2. It was found that increasing the RDX content in MCDB decreases its burning rate over the selected pressure range, while it increases the pressure index for the propellant formulation and also increases the maximum pressure inside the closed vessel. Thermal behaviour analysis has been performed using DTA and DSC instruments. The Kissinger and Friedman models have been applied to the data obtained from DTA and DSC, respectively, to estimate the activation energies for the prepared MCDB propellants. The results from both models supported each other, with regression coefficients higher than 0.98 in spite of the complete difference between the measuring conditions for the decomposition data and the diversity of the models used for treating these data. Generally, applying the two models proved that the addition of RDX decreases the energy required for activation. Contrary to expectations, the sensitivity to impact test illustrated that the addition of RDX, at the expense of NC, highly sensitized the propellant formulations. 40% RDX in the casting powder leads to a sensitivity to impact higher than PETN. The stability of the prepared modified propellants is increased by adding RDX, as illustrated from the STABIL test results. The first 5 min in the recorded data showed that the addition of RDX postpones the evolution of gas to some extent, while formulation DB2 showed some deviations from the general trend. CMDB propellants containing the BuNENA-DNDA57 combined energetic plasticizer provides a considerable burning rate and offers good thermal properties, but attention must be paid to their impact sensitivity and their pressure exponent.

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Received: February 26, 2017

Revised: July 16, 2018

First published online: September 21, 2018