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CALCULATION OF SAFE DIAMETAR OF PROPELLANTS USING HEAT FLOW MEASUREMENTS

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Abstract*: By using experimental and theorethical work, it has been made procedure in order to use microcalorimetar heat flow data to calculate safe diametar. For calculation of safe diametar two equations have been used. Calculated results were compared. If calculated value of safe diametar is comparated with diametar of ammunition loading charge, one can make assessment whether ammunition storage is safe or not. This propellant testing has great importance for chemical stability evaluation of propellants. Microcalorimetric system, whether „TAM III“ or „TAM IV“ is used, gives heat flow data in terms of released heat quantityat elevated temperaturesr. Calculation of safe diameter is important in preventing accidents due to selfignition of propellants.*

Keywords*: chemical stability, safe diametar of propellants, microcalorimetry*

1. INTRODUCTION

With the decrease of consumption of stock ammunition, and the increase of stock time, the safety problem of the ammunition in long stock becomes increasingly important. Gun powders and rocket propellants in long-term stock ammunition undergoes slow decomposition reaction and exothermic processes. If the heat can not be conducted away in time, its accumulation will lead to spontaneous combustion of propellants, which is a great threat to the safety of the stock and its surroundings. Specially, if the activation energy of the aging processes is low, degradation is fast. This will accelerate the degradation process, finally resulting in self-ignition or explosion [1]. This process is often called chemical aging.

The rate of spontaneous decomposition during storage the processes influencing property changes of the energetic materials during storage depends namely on:

a) the external factors as geometry, storage temperature, thermal insulation and
b) the intrinsic properties of the materials such as e.g. kinetic parameters of the decomposition processes, their specific heat, thermal conductivity.

In this paper the heat generation is measured for a non ground and grounded (cutted into appropriate size) propellant samples tempered during predetermined time at elevated temperatures [2]. Then, the maximum heat flow results are used to calculate the safe diameter of the propellants, using two different equations. Then, two results are compared and esstimated more accurate one.

1.1. The theory of thermal explosion. Critical conditions.

The explosive regime is characterized by a rapid conversion of the initial reactant into the end products. The term “explosion” is often used alongside that of “self-ignition” due to thermal runaway reactions with serious consequences. Nikolay Semenov (sometimes Semyonov, Semionov or Semenoff, Soviet physicist and chemist, awarded 1956 Nobel prize in Chemistry) was the first to mathematically analyse the heat balance equation and to lay foundation of the thermal explosion theory.

Semenov developed a model for thermal explosions, which demonstrated the principles of the thermal ignition phenomenon in a quantitative way.

Semenov diagram, in Figure 1, presents the relationship between heat and temperature, where the generated heat varies exponentionally with process temperature, while the removed heat varies linearly with it.

The critical condition for thermal explosion is tangency between the heat generation curve and heat loss straight line. The rates q_{rel} and q_{rem} and their derivatives are equal in the tangency point T_*.

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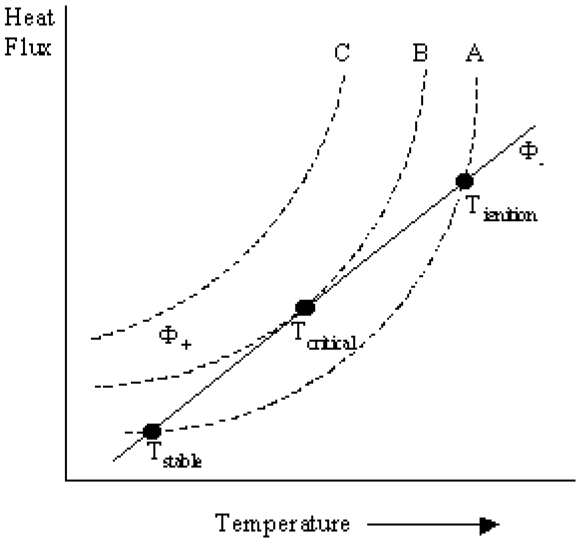

Figure 1 - Plot of the thermal fluxes against temperature

Table 1 Conductivity coefficients

Nº	Material	Heat conductivity coefficient [$Wm^{-1}K^{-1}$],
1.	diamant	1000-2600
2.	silver	406
3.	copper	385
4.	brass	109
5.	glass	0,8
6.	**propellant***	**0,1**
7.	wood	0,04-0,12
8.	air(300 K, 100kPa)	0,026
9.	styrofoam	0,038

*

Aaccording to Barendregt R.B.

To find this critical condition is the most important practical problem of thermal explosion theory.

Propellants has small heat conductivity coefficient due to good isolation properties, unfortunatelly. With the respects to the heat gained during decomposition processes inside the propellent, it is obviously that it could be dangerous due to posible heat accumulation which can lead to critical values ($T_{critical}$) and selfignition at the end.

In Table 1 are given some examples of material conductivity coefficients.

1.2. Safe diametar

According to Serbian standard for assesment of chemical stability, safe diametar is criteria for chemical stability assesment revealing critical condition and possibility for selfignition. Also, safe diametar can be determined as the largest diametar of a cylindrical filled container with propellant for which selfignition is just excluded [3]. The definition is also valid for other sample geometry.

If a propellant has been stored, no self-ignition will occur as long as equilibrium exists between heat generation and heat transfer to the surroundings. Whether this equilibrium will establish or not, depends on the storage temperature, also. The other parameter that make influence is the resistance encountered by the heat flow on its way to the surroundings. This resistance depends on the heat conductivity of the propellant and the dimensions of the propellants mass (package size). At a certain diameter the heat transfer will lag behind and the temperature will continue to rise, resulting in self-ignition.

Also the ageing of the propellant plays a role, because the heat generation depends on rections heat released and different reactons gives different heat quantities and heat summary gives appropriate safe diammeter calculated. In other words, stage of stabilizer depletion plays significant role in heat generation issue. According to Serbian standard for monitoring of chemical stability of gun powders and rocket propellants, there is mathematical dependence safe diametar of released heat and others and it looks like:

$$\text{Dcr} = \sqrt{\frac{\lambda \cdot \delta_c \cdot R \cdot T^2}{E \cdot \rho_b \cdot q}} \qquad (1)$$

where is:
λ – the heat conductivity coefficient [$Wm^{-1}K^{-1}$],
$\boldsymbol{\delta_c}$ – constant denote critical value of thermal explosion, depends on propellant shape and for cylinder it`s equal to 2,
R – universal gas constant [$kJmol^{-1}K^{-1}$],
E_a – activation energy of reactions, depends on temperature [$Jmol^{-1}$],
$\boldsymbol{\rho_b}$ – the bulk density [kgm^{-3}],
q – heat velocity coresponding to D_{cr} and vessel with L equal to 40 mm
T – temperature for which D_{cr} is calculated, [K].

According to Merzhanov [4] and Barendregt, formula to calculate the safe diameter, at 344 K (the worst case of ammunition storage temperature conditions), is as follows in Equation 2.

$$Dcr = \frac{2.7\cdot\lambda}{2} + \sqrt{\frac{(2.7\cdot\lambda)^2}{4} + \frac{4\cdot RT_a^{\,2}\cdot\delta_c\cdot\lambda\exp\left(\frac{E_a}{R}\left(\frac{1}{T_a}-\frac{1}{T_m}\right)\right)}{\rho_b\cdot E_a\cdot Q_{max}}} \quad (2)$$

where is:
λ – the heat conductivity coefficient [$Wm^{-1}K^{-1}$],
R – universal gas constant [$kJmol^{-1}K^{-1}$],
δ_c – constant denote critical value of thermal explosion, depends on propellant shape and for cylinder it`s equal to 2,
T_a - temperature for which D_{cr} is calculated, [K],
T_m- teperature at which is measured heat flow, [K],
E_a – activation energy of reactions, depends on temperature [$kJmol^{-1}$], it is quit satisfied to take 120 $Jmol^{-1}$ for temperatures beyond 333 K, [5]
Q_{max} – maximum heat flow during measurement [Wkg^{-1}] and
ρ_b – the bulk or loading density [kgm^{-3}].

1.3. Equipment. Microcalorimeter.

To measure small heat effects microcalorimeters have been developed. For investigations of safe diameter, Heat Flow Calorimetry (HFC) results was used. The maximum heat flow results was obtained from experiments that was many years long performed. Tests were performed on TAM III and TAM IV device, made by TA Instruments Company.

HFC is very sensitive technique, with possibility to detect small quantities of heat, e.g. range of microwatts. With such a high sensitivity it is possible to investigate processes in early stages of decompositions.

Figure 2. Microcalorimeter TAM III

Data evaluation in HFC measurements consider:
- The data must be normalised to one gram of propellant.
- Determination of the maximum heat flow in the region between the time corresponding to a heat release of 5 J/g and the defined measuring time.
- Loading density 0,7-1,1 g/cm³; for the porous propellants 0,4-0,6 g/cm³.
- Positive heat flow values means exothermic reactions.

2.EXPERIMENTAL

2.1.Experimental conditions

Several types of propellants were estimated from the thermally stability point of view. In this paper, there were used single and double based propellants with different formulations. Labels SB1, SB2 and SB3 identify diverse single base propellant compositions, while DB1, DB2, DB3 identify double base propellants. DB4S1, DB4S2, DB5S1, DB5S2 and LOVEX denotes samples of various types of double base propellants used for small caliber ammunition.

There are used heat flow measurements for propellants at several temperature profiles to calculate results for safe diametar. Temperatures used for thermal activity monitoring are 353, 356, 358 and 363 K.

Although, at elevated temperatures many processes are occured in propellants, heat flow represents the heat summary of all reactions, weather exothermic or endothermic they are. So, we use final reaction heat to determine safe diametar by both equations.

It is assumed that for all elevated temperatures, reaction mechanisms are to be the same.

Activation energy of reactions is assumed like 120 kJ/mol.

Loading density,**ρ_b**, was calculated for every sample itself, for representativness of the conditions.

Single base ropellants were not grounded, to conduct experiments with „ammunition like“ conditions. Double base propellants were grounded, because of no possibillity to test them in original shape. Double base propellants for small ammunition calibersvare tested in original shape and size. Results are in tables below.

2.2.Results

Test results reveals slightly differences in calculated safe diametars by both equations. Safe diametar calculated by Serbian standard seems to be to harsh, regarding to fact that the biggest diametar of ammunition cartridge for SB1, SB2 and SB3 propellant is about 0,12 m and for DB1, DB2 and DB3 0,09 m . Therefor, it seems Equation 2 gives more appropriate band realistic values of safe diametar.

Also,results confirms that stage of stabilizer depletion plays significant role in heat generation issue, because during time heat flow value increases and safe diammetar decreases. That is, the older propellant the greater number of exothermic reaction with lot of released heat.

Table 2. Experimental results for safe diametar obtained by two different equations for single base propellant samples

Propellant	Maximum Heat Flow μWg^{-1}	Bulk Density (kgm^{-3})	SAFE DIAMETAR (m) by Berendregt - Merzhanov	SAFE DIAMETAR (m) by Serbian standard	Testing Year	Testing Temperature (K)
SB1	67,1	0,70	0,64	0,13	2009	363
	128	0,72	0,21	0,092	2013	353
SB2	346	0.68	0.27	0.08	2012	358
	747.4	0,70	0,099	0,056	2013	353
SB3	385.3	0.71	0.35	0.077	2009	363
	350	0.71	0.17	0.081	2014	353
	374.6	0.80	0.15	0.074	2015	353

Table 3 Experimental results for safe diametar obtained by two different equations for double base propellant samples

Propellant	Maximum Heat Flow μWg^{-1}	Bulk Density (kgm^{-3})	SAFE DIAMETAR (m) by Merzhanov-Berendregt	SAFE DIAMETAR (m) by Serbian standard	Testing Year	Testing Temperature (K)
DB1	205.3	0.63	0.34	0.11	2012	356
	207.2	0.74	0.31	0.10	2013	356
	453.7	0.63	0.34	0.075	2014	363
	397.9	0.66	0.36	0.079	2015	363
	114.3	0.60	0.41	0.15	2016	353
	360.7	0.80	0.34	0.075	2021	363
	141.3	0.76	0.38	0.12	2022	356
DB2	393,7	0,70	0,35	0,077	2014	363
	377,6	0,77	0,34	0,075	2015	363
	144,5	0,81	0,36	0,12	2016	356
DB3	143.3	0.71	0.64	0.13	2014	363
	35.95	0.71	0.74	0.25	2015	353
	25.76	0.96	0.73	0.28	2020	353
DB4S1	238.6	0.89	0.25	0.088	2022	356
	166.9	0.89	0.25	0.11	2022	353
DB4S2	501.7	0.88	0.25	0.088	2021	363
DB5S1	230.4	0.95	0.24	0.086	2022	356
DB5S2	539.3	0.94	0.23	0.057	2021	363
LOVEX	567.6	1.03	0.21	0.053	2021	363

2.3.Thermograms

In Figures 3, 4 and 5 diagrams heat flows against time is presented, for several propellants, for heat flow measurements.

It is evidentially that this samples can not meet criterion for chemical stability by STANAG 4582 but if it is used maximum heat flow information to calculate safe diametar, the prediction and evaluation of chemical stability can be slightly different. According to calculations in this paper, acctually, it is possible to make conclusion as follows: propellant will remain chemicaly stable and safe if storage conditions are fullfilled, respectively, propellant is safe if diameter of ammunition charge - cartridge is less then calculated safe diameter.

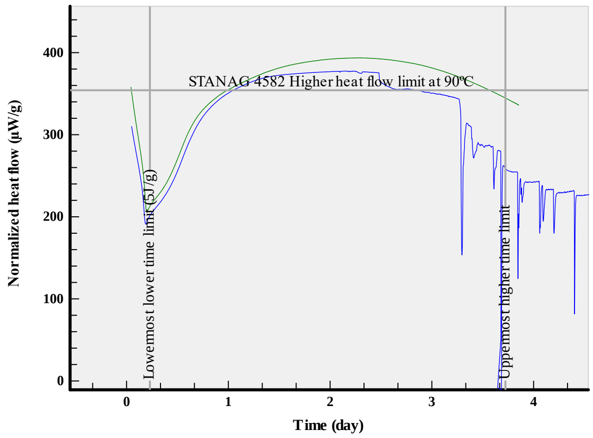

Figure 3. Heat flow against time for DB2 propellant

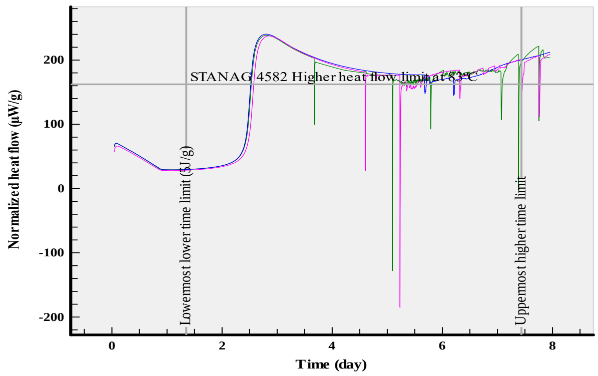

Figure 4. Heat flow against time for DB4S1 propellant

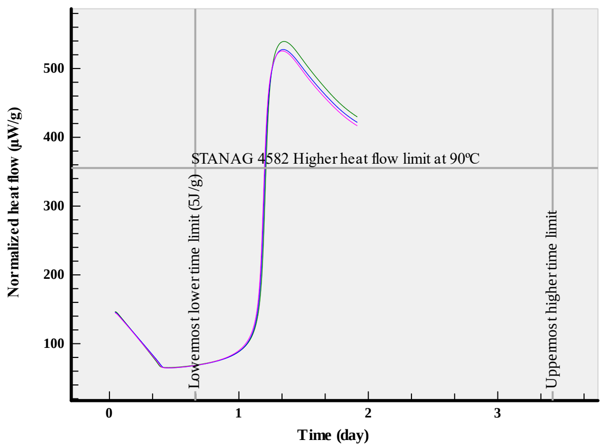

Figure 5. Heat flow against time for DB5S2 propellant

3.DISCUSSION

Calculated safe diametars by two different equations shows more appropriate seems to be equation of Berendregt-Merzhanov for their more realistic outcomes. When safe diametars are compared to diametar of ammunition cartriges the propellants service in, one more information about safety ammunition is easy to obtain.

It can be noticed that there is good reproducibility of results at different teperature regimes of heat flow measurements, and that confirms similarity of reaction mechanisms at different temperatures. Yet, it should avoid higher temperatures, like 363 K and carry out heat flow experiments at as lower temperatures as possible. Recommendation is to conduct experiments at 353 K.

Especially good illustration of the better mathematically interpretation of propellant stabillity by Berendregt-Merzhanov equation is given in Table 1. If SB kind of propellant is made for about approximatelly 0,12 m ammunition loading charges, for big span of years the propellant and ammunition would be on the border zone of stabillity criteria or even do not meet criterion at all, as showed in fifth column of the table.

For some propellants STANAG 4582 is unsuitable standard method to examine as though too strict stabillity criteria. Even brand new propellant can easily fail to meet criteria of stability. Calculating safe diametar is,in that case better and more confortable choice for testing them and assess stability. Figure 3, 4 and 5 shows evidentelly exceeding heat flow upper limits by method mentioned. Calculated safe diametar for those samples gives the condiotions in which the propelllant would be safe to store and handle in, in a manner, propellant would be safe if its diametar of ammunition cartidge charge or storage vessel is not higher than those calculated. And for that purpose Equation 2 seems to be more appropriate then Equation 1.

4.CONCLUSION

Calculations of propellants safe diametar was made by using two different equations. Calculations were perfomed by using heat flow measurements conducted at elevated temperatures.

Benefits of calculating safe diameter are:

- Determination of safe diametar, described in paper is dedicated for stability testing of nitrate ester based propellants by use of Heat Flow Calorimetry method.
- Safe diametar determination contribute to chemical stability assessment of single base, double base and triple base propellants.
- It is possible to find all necessary conditions for ammunition to stay safe and chemicaly stable and conditions are different from one type of propellant to another.
- Using Equation 2 is more realistic than Equation 1.
- The procedure is equally applicable to propellants containing different types of stabilizers and even, for those without any.

- Benefitially method for those samples which falls the criteria of stability by STANAG 4582, with exact conditions recommened to be fullfilled.

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