Insensitivity aspects of NC bonded and DNDA plasticizer containing gun propellants

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Abstract

New type of semi nitramine gun propellants containing crystalline energetics as RDX or FOX 7 and DNDA as plasticizer bonded by nitrocellulose (NC) show improved performance with regard to thermal sensitivity, shaped charge jet impact, force and barrel erosion. Further they show a low temperature coefficient in gun firing. The thermal sensitivity is assessed by measurements of heat generation rate and heat generation between 60°C and 90°C with microcalorimeter and mass loss between 70°C and 90°C, autoignition temperature and adiabatic self heating determined by an ARC^{TM} (accelerating rate calorimeter). The data of six propellants of new type are compared and discussed with two conventional ones: the double base gun propellant L5460 (= JA2) and the triple base GP Q5560 (MRCA). The data of mass loss and heat generation rate are modelled and Arrhenius parameters have been obtained. The often found strong increase in mass loss after the consumption of active stabilizers is not shown by the new type propellants. The autoignition temperature of the new type propellants is with 185 to 220°C at 5°C/min heat rate higher than the typical values of common NC-propellants with 170 to 175°C. Results of a shaped charge jet impact are presented as well as data for adiabatic flame temperature and barrel erosion.

1. Introduction

Conventional gun propellants show insufficient insensitivity against fuel fire, shaped charge and bullet impact. A further disadvantage is that the high dependence of combustion gas pressure on charge temperature restricts the amount of charge mass in the gun chamber in order not to exceed the maximum allowed operational pressure at temperatures above ambient, Fig. 1. The typical pressure curve of the LTC GP is the lower one. But one can

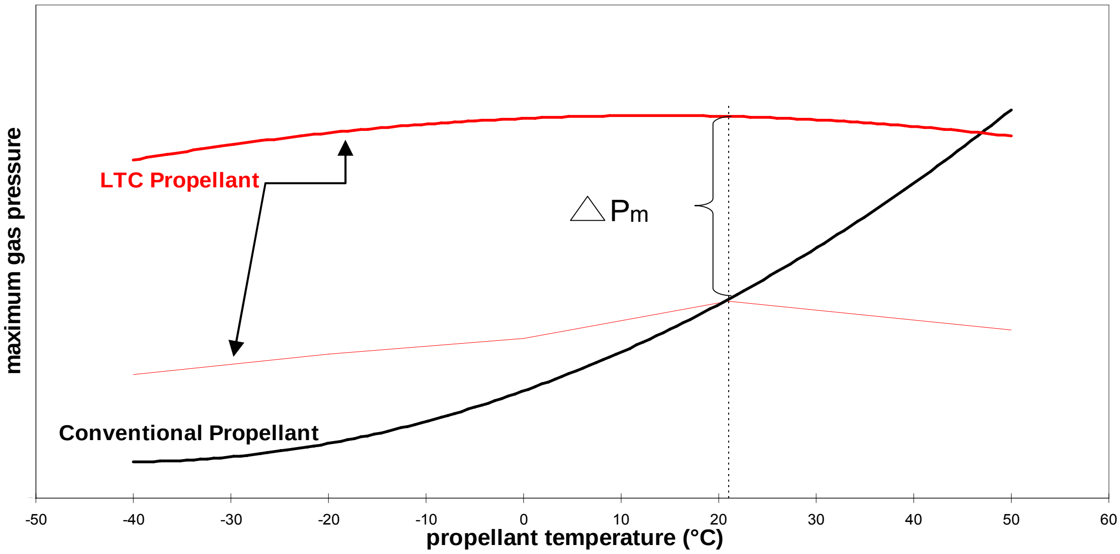


Fig. 1: Comparison of typical gas pressure curves of conventional and LTC propellants.

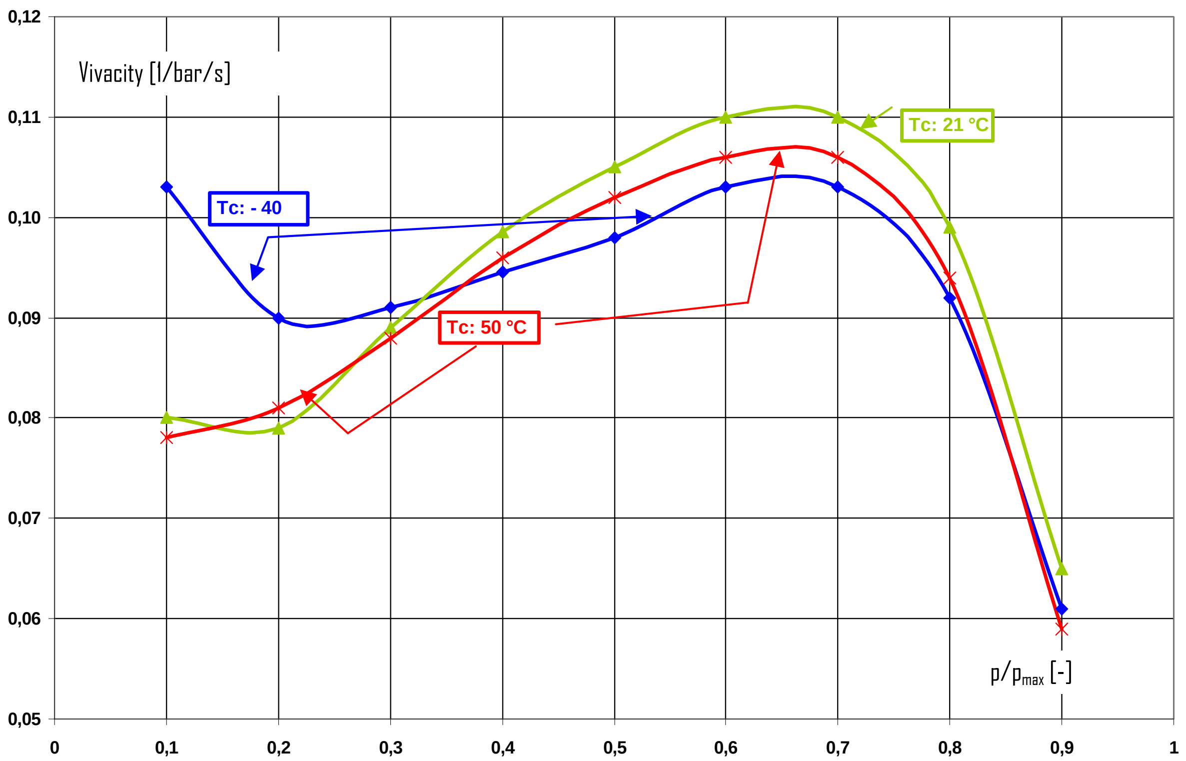


Fig. 2: Characteristics of a LTC GP. Dynamic vivacity determined in a 200ml pressure vessel at loading density of 0.3 g/ml and at three charge temperatures Tc /1/.

increase the charge amount of the LTC GP to realize the upper curve and to achieve higher muzzle velocities. To characterize the so named low temperature coefficient effect the Fig. 2 shows measured vivacity of a LTC propellant at three charge temperatures Tc. The vivacity curve is at -40°C below the ones at 21°C and 50°C. The curve at 50°C or at the high end temperature must be below the one at 21°C. This is not the case with conventional GP. The typical course of the gas pressure as function of temperature is with LTC propellants such that at high temperatures it is lower than at medium temperatures. Further to this the typical course must be independent of loading density, which can be seen in Fig. 3.

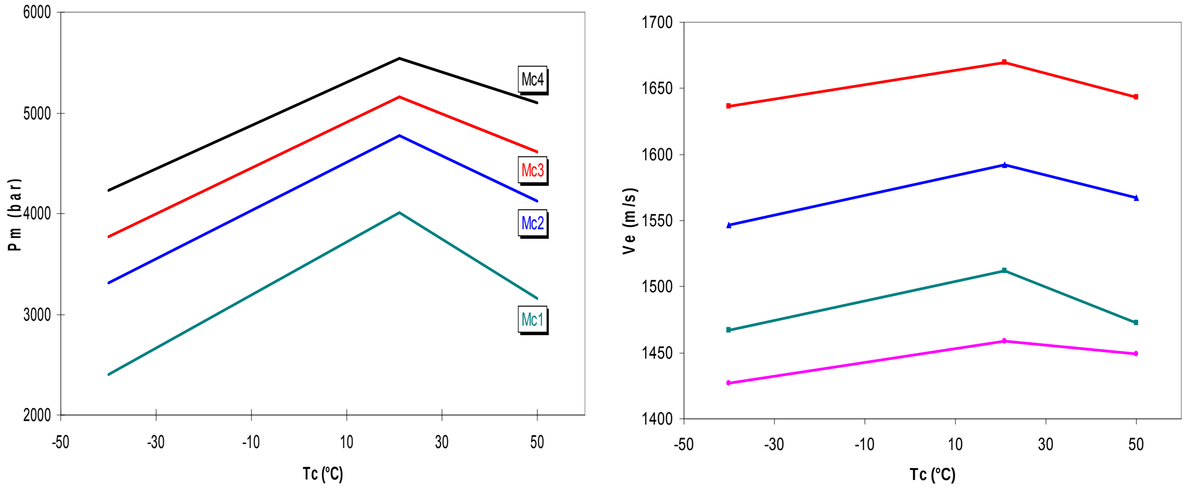


Fig. 3: Example of chamber gas pressure courses and resulting muzzle velocities as function of charge temperature Tc with charge mass Mc as parameter /2/.

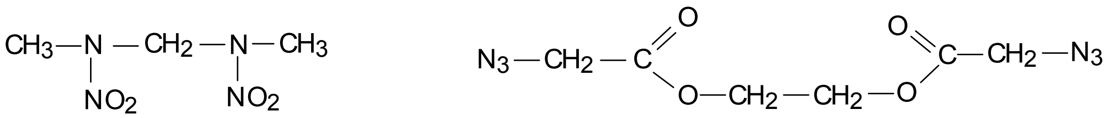
By using special new formulations this temperature coefficient could be reduced very significantly /1, 2/. One important part to achieve such a behaviour is the use of special plasticizer DNDA, which is mixed into the propellant dough. Further to this the autoignition temperatures have been raised and the adiabatic flame temperatures reduced at comparable force values resulting in less barrel erosion.

2. Materials and formulations

The Table 1 shows the principal ingredients of the GP used in this work. DNDA57 is a dinitro-diaza plasticizer. One of its three components, DNDA5, DNDA6 and DNDA7 is shown in Fig. 4. In one formulation FOX 7 was used and in another one a further plasticizer named A17, an azido based substance, see Fig. 4. A17 is a product of ICT. It has the ability to lower significantly the glass transition temperature.

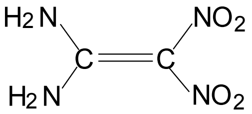
Table 1: Principal components in some new type GP and two conventional GP

GP	Web	Components
TLP 1N	7	NC, RDX, DNDA57; EC, AkII
TLP 2N	7	NC, RDX, DNDA57; EC, AkII
TLP 3N	7	NC, RDX, DNDA57; EC, AkII
TLP 4G	7	NC, RDX, FOX7, DNDA57; EC, AkII
TLP 5W	19	NC, RDX, DNDA57; with A17; EC, AkII
TLP 6	19	NC, RDX, DNDA57; without A17; EC, AkII
JA2	7	NC, Ngl, DGDN; AkII, MgO
MRCA	19	NC, NQ, K_2SO_4, DGDN, DOP; AkII



2,4-dinitro-2,4-diaza pentane, DNDA 5

A17, ethylene glycol-bis-(2-azidoacetate)



FOX 7, 1,1-diamino-2,2-dinitro-ethylene

Fig. 4: Some of the ingredients used in the GP formulations.

3. Results and Discussion

All six new type GP show the LTC effect as defined above. Table 2 lists some data of the GP formulations. The autoignition temperature determined at 5°C/min heat rate is with the new formulations significantly above the ones of the conventional GP JA2 (120mm tank gun) and the so-named MRCA GP, here type Q5560 (27mm aircraft machine gun). Different cook-off behaviour can be expected. This is also documented by the adiabatic self heating, shown in Fig. 5, determined with an ARC^{TM} (Accelerated Rate Calorimeter). The curves show the apparatus controlled adiabatic self heating of the samples. At their end points the residual sample amounts autoignited and deflagrated. The temperature is one the samples achieved by the adiabatic self heating. Fig. 5 shows also the data for a typical triple base GP of type M30 (KN 6540), of a double base propellant type JA2. For comparison the US XM39 GP is shown. All conventional GP have a low lying transition temperature from controlled self heating to deflagration in the range 148°C to 158°C. Because of the RDX and DNDA content this transition is shifted to higher temperatures with the new type GP caused by more endothermal decomposition reactions in the propellants. The GP can be compared usefully in the following way: JA2 with 1N, 2N, 3N and/or 4G, the MRCA with 5W and/or 6.

Table 2: Some characteristic data of GP formulations. adiabatic flame temperature T_{ad}, Force, heat of explosion Q_{EX} and gas volume V_{EX} have been calculated by ICT Thermodynamic Code using the data of the ICT Thermochemical Data Base /3/.

GP	LTC effect	autoignition temp. [°C]	adiab. flame temp. T_{ad} [K]	Force [J/g]	Q_{EX} [J/g]	V_{EX} at 25°C [ml/g
TLP 1N	yes	185	2905	1170	3768	961
TLP 2N	yes	220	2906	1178	4198	939
TLP 3N	yes	193	2910	1180	4201	939
TLP 4G	yes	198	2908	1185	4071	938
TLP 5W	yes	189	2510	1060	4124	931
TLP 6	yes	199	2540	1080	4177	929
JA2	no	168	3390	1139	4610	753
MRCA	no	172	3078	1040	3758	857

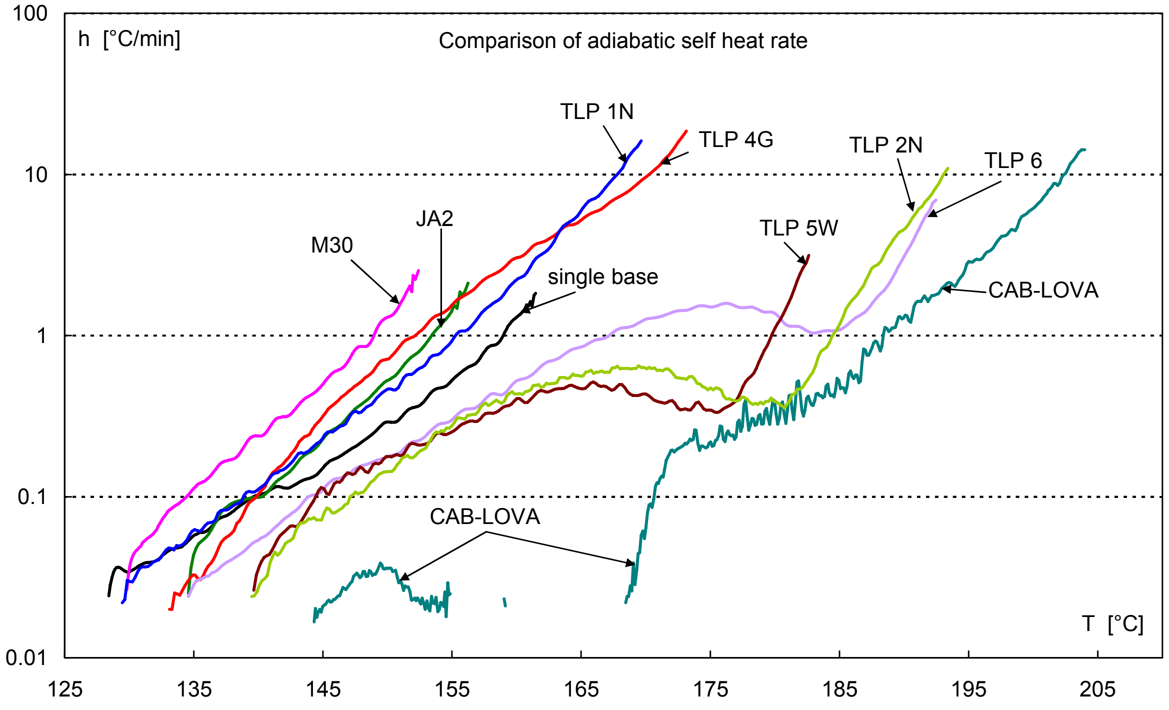


Fig. 5: Adiabatic self heating determined by an ARC^{TM} for typical conventional and of new type GP, including the XM39 GP with a binder based on CAB.

To assess stability and ageing behaviour of the new formulations compared with the conventional GP, special measurements have been made: (i) mass loss (ML) at 70°C, 80°C and 90°C with 2g of propellant in glass vials inserted in PID controlled aluminium block ovens; (ii) heat generation rate (HGR) at 90°C with about 2.5g in closed glass ampoules, determined with a microcalorimeter of type TAM^{TM} (Thermal Activity Monitor), manufactured by Thermometric AB, Sweden. Then the propellants have been measured in iso-conversion mode at 60, 70 and 80°C /4/. In Fig. 6 the mass losses at 90°C for the eight GP can be seen. JA2 as double base GP shows after about 21 days the typical strong mass loss increase. This is not the case with the new type GP. They reach the limit value of 3 % mass loss at much longer times than JA2. Mass loss is a conversion quantity and therefore directly usable for stability assessment. After 18 days at 90°C the mass loss may not exceed 3% with NC-based propellants. In Table 3 the evaluation results are compiled obtained from mass loss measurements. The Arrhenius parameters, namely activation energy Ea_{ML} and pre-exponential factor Z_{ML}, have been determined from the reverse times to 3% mass loss at the three measurement temperatures. Times ty_{ML} to reach 3% ML at three temperatures are given. With temperature dependent measurements predictions for any temperature-time profile can be made, which is important for the assessment of fielded ammunition.

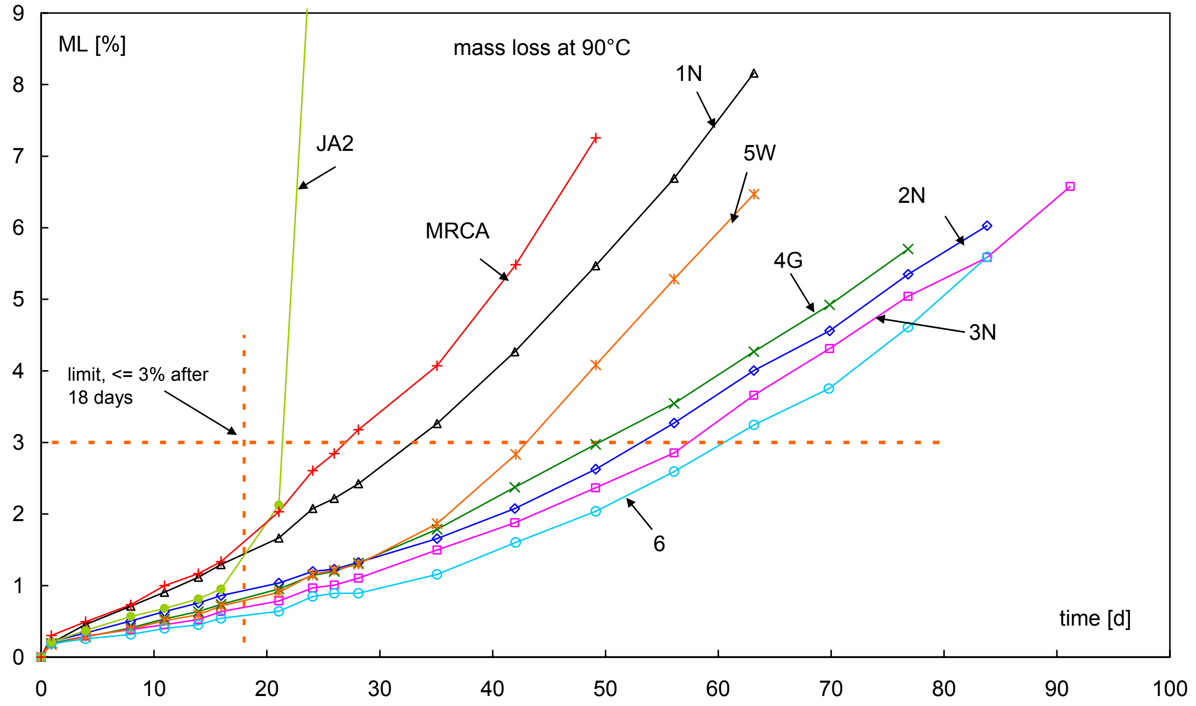


Fig. 6: Assessment of ageing and stability with mass loss. Limit value is ≤ 3% after 18 days at 90°C.

Table 3: Times ty_{ML} to reach 3% mass loss in years calculated with Arrhenius parameters obtained from mass loss measurements at 70°C, 80°C and 90°C.

	1N	**2N**	**3N**	**4G**	**5W**	**6**	**MRCA**	**JA2**	**JA2, HT**
Ea_{ML} [kJ/mol]	116.5	104.3	101.8	105.6	105.7	102.2	147.9	102.0	149.0
$\log(Z_{ML}$ [1/d])	15.235	13.286	12.865	13.457	13.56	12.888	19.837	13.282	20.102
	time ty_{ML} to reach 3% mass loss ML in years at preset temperatures								
65°C [a]	1.6	1.8	2.0	1.9	1.6	2.2	2.8	0.8	2.2
50°C [a]	10.6	10.3	10.6	11.1	9.2	11.9	31.9	4.5	26.3
35°C [a]	87.8	68.1	67.1	75.1	62.3	75.6	465.1	28.3	391.2

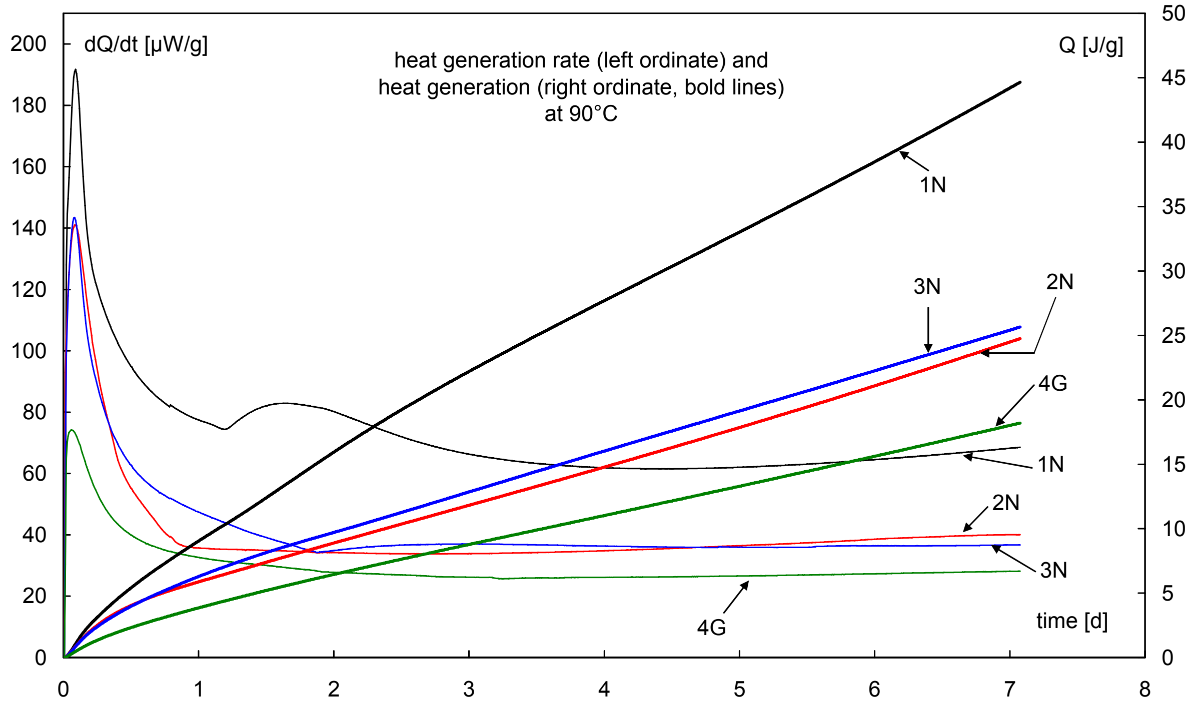


Fig. 7: Assessment of ageing and stability by heat generation rate (dQ/dt) and heat generation (Q, these curves are directed to the right upwards) at 90°C. Part 1, gun propellants 1N, 2N, 3N and 4G.

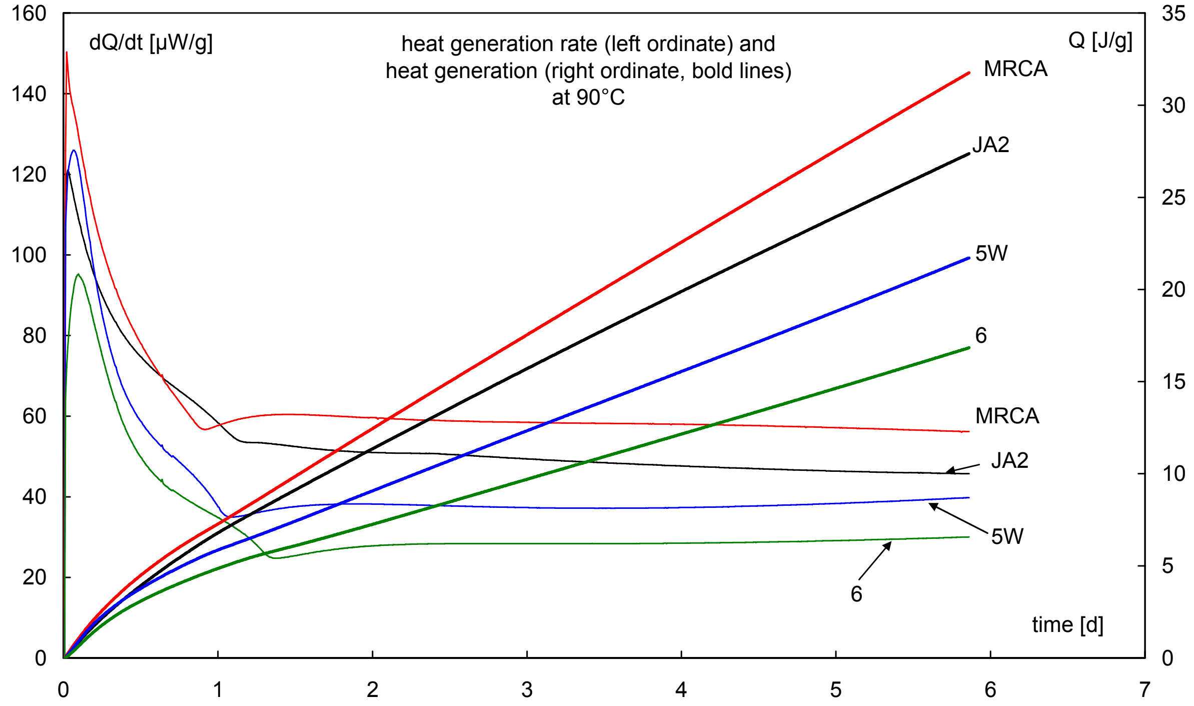


Fig. 8: Assessment of ageing and stability by heat generation rate (dQ/dt) and heat generation (Q, these curves are directed to the right upwards) at 90°C. Part 2, gun propellants JA2, MRCA, 5W and 6.

The results of the microcalorimetric measurements are shown in Fig. 7 and Fig. 8. The eight GP have been grouped for reasons of presentation in the figures. The figures show the heat generation rates dQ/dt with its ordinate on left side and the heat generation Q (HG, integrated HGR) with its ordinate on the right side. The HG curves are the ones which are directed to the right upwards. The heat generation is a comparable quantity to mass loss, but for assessment with preset conversion one needs a reference /5/, which is taken here as the heat of explosion Q_{EX}.

The Arrhenius parameters in Table 4 have been obtained from the heat generation rates at 60°C, 70°C, 80°C and 90°C in the range of the curves where they are mainly horizontal. This corresponds to a reaction of zero order. In comparing the calculated times ty_{ML} to reach 3 % mass loss (ML) and ty_{EL} to reach 3% energy loss (EL) the conclusion is, as a whole the data are good. But one recognizes some differences with the two measurement methods. GP JA2 shows from mass loss data relatively small activation energy and the times to 3% ML are comparably short, at 35°C only 28.3 years. But from the high temperature decomposition data (column JA2, HT in Table 3), this time is much longer. The reason for the difference is evaporation of blasting oil. In microcalorimetric measurements using closed measurement ampoules evaporation does not happen. GP 1N shows a higher heat generation rate compared to the other GP which shortens the times to 3% energy loss.

Table 4: Times ty_{EL} to reach 3% energy loss in years calculated with Arrhenius parameters obtained from heat generation rate measurements at 60°C, 70°C, 80°C and 90°C. Reference quantity Q_{ref} is the individual heat of explosion Q_{EX}.

	1N	**2N**	**3N**	**4G**	**5W**	**6**	**MRCA**	**JA2**
Q_{EX} [J/g]	3768	4198	4201	4071	4124	4177	3758	4610
Ea_Q [kJ/mol]	112.3	115.6	121.6	118.2	111.5	113.9	130.0	128.2
log(Z_Q [µW/g])	17.971	18.217	19.059	18.436	17.633	17.847	20.426	20.056
	time ty_{EL} to reach 3% energy loss EL in years at preset temperatures							
65°C [a]	0.85	1.74	2.12	2.57	1.53	2.22	1.62	2.45
50°C [a]	5.4	11.7	15.8	18.1	9.6	14.6	13.8	20.3
35°C [a]	42	95	142	154	73	115	146	207

In Fig. 9 the results of a (cal 44mm) shaped charge jet impact on cartridges can be seen. On the left side the cartridge was filled with GP of type XM39. In the right cartridge the GP of new type 2N was used. The main effect was a rupture of the cartridge housing in the area of the jet impact. Both propellants have not reacted. The results of erosion measurements are shown in Fig 10. The conventional GP have higher adiabatic flame temperature and cause therefore more material ablation in the barrel bore. The colder new type GP have significantly less degree of erosion at same force values. The erosion was determined with a ballistic bomb equipped with a plate of weapon steel having a die. For one determination about 30 to 40 firings have been made and then the material ablation from the die plate was determined by weighing. Mass losses ranged between 100 and 300mg. Loading density was 0.3g/ml.

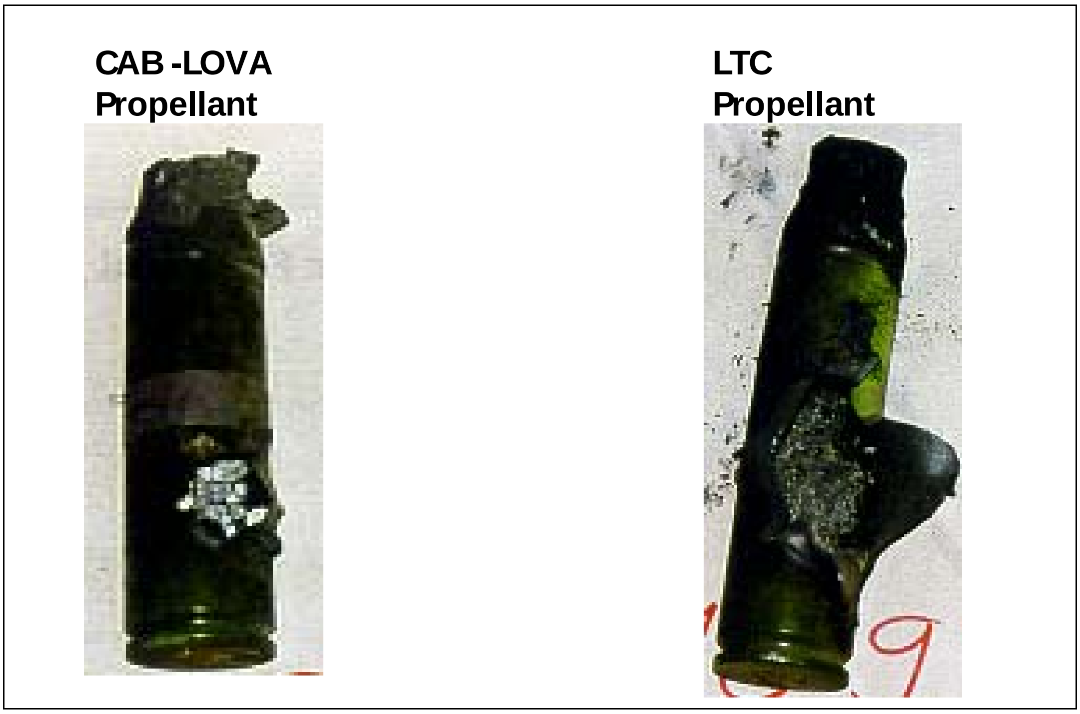


Fig. 9: Results of shaped charge jet impact (cal 44mm) on cartridges filled with US GP XM39 (left) and GP type 2N (right). The XM39 propellant reacts very mild, but also the GP type 2N does it /1, 6/.

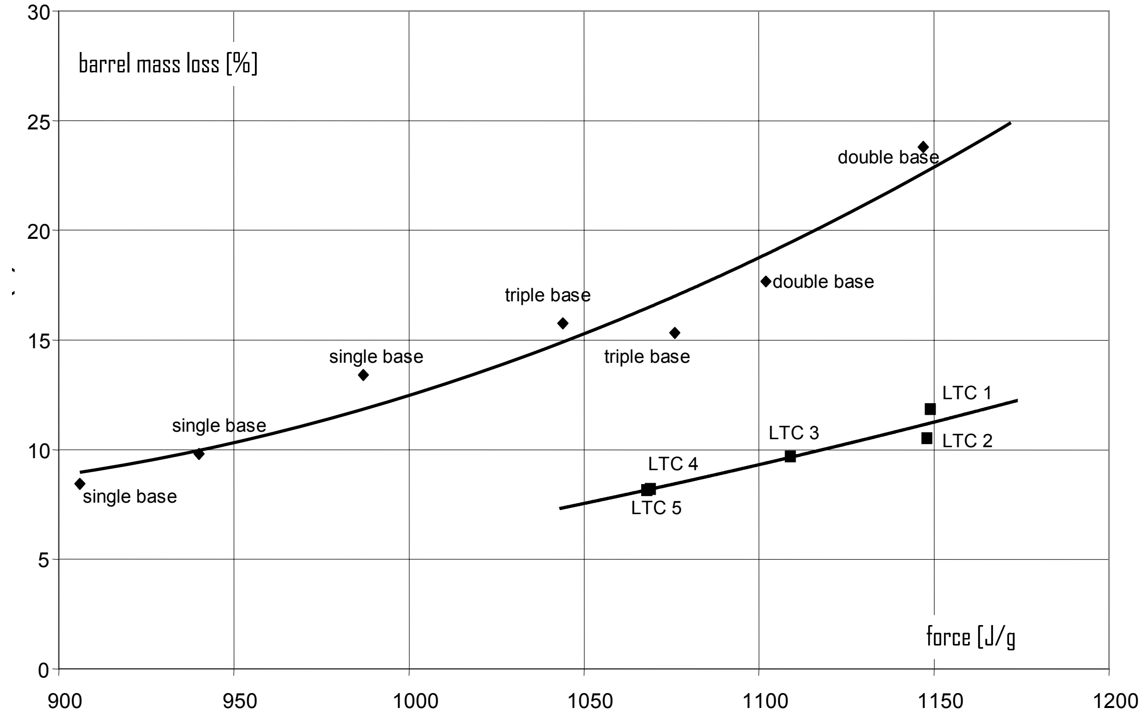


Fig. 10: Results on erosivity. Shown is the degree of erosion as function of GP force. As expected the hotter the combustion gases the higher the erosion. Conventional double base GP with high flame temperatures show the highest values /1, 2/. data determined with a ballistic bomb equipped with plate of weapon steel having a die. the mass loss of the plate quantifies the erosivity.

4. Conclusion

GP based on NC, RDX and plasticizer DNDA (new type triple base GP) have significant advantages compared to conventional NC-based GP. The autoignition temperatures are higher. The ageing behaviour is comparable to conventional triple base GP and with respect to blasting oil migration and evaporation also better than the high performance double base GP JA2. The force values are high but the flame temperatures expressed as T_{ad} are less than with conventional GP regarding the same force range by about 400 to 500 K. The sensitivity against shaped charge impact is low to very low and comparable to US XM39. A special feature of this new type GP is the low temperature coefficient of the combustion gas pressure. This allows the efficient use of a given gun construction pressure over the whole in-service temperature range from – 40°C to + 63°C. The barrel erosivity of LTC GP is much less than the one of comparable conventional double and triple base GP and is in the range of single base propellants.

5. List of abbreviations

GP	gun propellant
LTC	low temperature coefficient
Mc	mass of propellant charge
Tc	temperature of propellant charge

ARC^{TM}	**A**ccelerating **R**ate **C**alorimeter, determines adiabatic self heat rate
TAM^{TM}	**T**hermal **A**ctivity **M**onitor, microcalorimeter, determines heat generation rate
ML	mass loss
EL	energy loss
HGR	heat generation rate (dQ/dt)
HG	heat generation (Q)
Ea_{ML}	activation energy from mass loss data
Z_{ML}	pre-exponential factor from mass loss data; $k_{ML} = Z_{ML} * \exp(-Ea_{ML}/RT)$
Ea_{Q}	activation energy from heat generation or HGR data
Z_{Q}	pre-exponential factor from HG or HGR data; $k_{Q} = Z_{Q} * \exp(-Ea_{Q}/RT)$
ty_{ML}	time to reach a certain value of mass loss
ty_{EL}	time to reach a certain value of energy loss

EC	ethyl centralite, stabilizer	
Ak II	acardite II, stabilizer	
NC	nitrocellulose	
CAB	cellulose acetate butyrate	
RDX	1,3,5-trinitro-1,3,5-triaaza-cyclohexane (Hexogen, **R**esearch **D**evelopment e**X**plosive or **R**oyal **D**emolition e**X**plosive)	
FOX 7	1,1-diamino-2,2-dinitro-ethylene (DADNE)	
DADNE	= FOX 7	
NQ	nitroguanidin	
DNDA	plasticizer, mixture of DNDA5, DNDA6 and DNDA7	
	DNDA5	2,4-dinitro-2,4-diaza pentane
	DNDA6	2,4-dinitro-2,4-diaza hexane
	DNDA7	3,5-dinitro-3,5-diaza heptane
A17	azido based plasticizer, ethylene glycol-bis-(2-azidoacetate)	
DGDN	diethyleneglycol dinitrate (also DEGN)	
Ngl	nitroglycerine	
DOP	dioctyl phthalate	

6. References

/1/ D. Mueller, W. Langlotz
LTC- Propellants.
Proceed. of the Sixth International Symposium on Special Topics in Chemical Propulsion (6–ISICP). March 8 - 11, 2005, Santiago, Chile.

/2/ D. Mueller, W. Langlotz
LTC Gun Propellants for Use in Machine Gun Ammunition.
Proceed of the 36th International Annual Conference of ICT & the 32nd international Pyrotechnics Seminar, pages 48-1 to 48-7. June 28 - July 1, 2005, Karlsruhe, Germany. Fraunhofer-Institut für Chemische Technologie (ICT), D-76318 Pfinztal-Berghausen, Germany.

/3/ H. Bathelt, F. Volk, M. Weindel.
The ICT Thermochemical Data Base.
Proceed. 30th International Annual Conference of ICT, pages 56-1 to 56-12, June 29 - July 2, 1999, Karlsruhe, Germany. Fraunhofer-Institut für Chemische Technologie (ICT), Postfach 1240, D-76318 Pfinztal-Berghausen, Germany.

/4/ M.A. Bohn.
Thermal ageing of rocket propellant formulations containing ε-HNIW (ε-CL20) investigated by heat generation rate and mass loss.
Thermochim. Acta 401 (2003) 27 - 41.

/5/ M.A. Bohn.
Kinetic Description of Mass Loss Data for the Assessment of Stability, Compatibility and Aging of Energetic Components and Formulations Exemplified with ε-CL20.
Propellants Explosives Pyrotechnics 27 (2002) 125 -135.

/6/ D. Mueller
Low Temperature Coefficient (LTC) Gun Propellants.
Proceed. of the 29th International Pyrotechnics Seminar (IPS), pages 633-642. July 14 - 19, 2002, Westminster, CO, USA.