FUNCTIONAL LIFETIME OF GUN PROPELLANTS

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The lifetime of conventional gun propellants is limited due to decomposition of nitrocellulose (NC). In general, research on ageing of propellants is mainly focussed on the safety aspects regarding storage of propellants. Decomposition of NC, however, not only leads to heat production that can result in run-away reactions, it also causes a decrease of the mechanical integrity of the propellant grains.

In this investigation various properties of an SB and a DB gun propellant have been determined before and after artificial ageing. Simulations based on experiments with aged propellants show that the peak pressure may increase due to enhanced grain fracture after ageing. A number of parameters is selected from which the safe use of gun propellants can be determined.

It is concluded that the lifetime of conventional gun propellants is not only determined by thermal degradation because changes of the mechanical characteristics may finally lead to unsafe employment.

INTRODUCTION

Research on ageing of propellants is in general mainly focussed on the safety aspects regarding storage of propellants. The safe storage lifetime of nitrocellulose (NC) based propellants is limited due to decomposition of NC. The decomposition is suppressed by the application of stabilisers. Many efforts have been put into the understanding of the mechanism of decomposition and behaviour of NC and stabilisers [1–6]. The stability can be predicted by measuring the stabiliser depletion by HPLC [7] or by Heat Flux Calorimetry (HFC) [8].

Decomposition of NC, however, not only leads to heat production that can finally result in run-away reactions, but the decomposition also causes a break-down of the nitrocellulose polymeric chains [9, 10]. This results in a decrease of the mechanical integrity of the propellant grains [11, 12]. In case of gun propellants the mechanical properties affect the ignition behaviour of the propellant grain bed. Embrittlement may lead to enhanced breakage of grains, which in turn leads to an increase of the burning surface area, finally resulting in an accelerated pressure rise and a diminished porosity of the propellant

bed during firing. Consequences may be an irregular pressure build-up, pressure waves or increased peak pressures [12].

The aim of this investigation is to gain more qualitative insight in the effects of ageing on the internal ballistic properties of gun propellants and to select a number of parameters that provide indications with respect to the safe use of gun propellants. For this purpose various properties of a single base (SB) and a double base (DB) gun propellant have been determined before and after artificial ageing.

EXPERIMENTAL

The gun propellants that were used for this study are a 7-hole SB propellant for Howitzer charges, and a flake DB propellant for mortar application.

The heat development of both propellants was examined by microcalorimetry at the same conditions as the artificial ageing. The ageing procedure is performed in the Isothermal Storage Test [1], in closed stainless steel vessels of 70 cm³, with a sample mass of approximately 5 grams. The advantage of this ageing procedure is that it continuously provides information about the heat generation during the measuring time. Afterwards it is possible to calculate the energy decrease by integrating the obtained heat versus time curve [2]. The calorific values of the unaged and aged propellants were determined by use of a bomb calorimeter.

The change of polymeric chain length of the propellant samples was determined by means of gel permeation chromatography (GPC). Polystyrene standard samples were used as references for the calculation of the molecular weights. Although the obtained molecular weights are therefore not absolute but relative values, the results provide a good indication of the ageing effect.

Closed vessel (CV) tests were carried out with uncompressed grains as well as grains that were quasi-statically pressed as described below. The obtained pressure-time data are used for the calculation of the dynamic and characteristic vivacity, L and L_k , and the burning rate, r. These parameters are calculated as described in STANAG 4115 [13], the burning rate is only calculated for the uncompressed samples at the pressure interval from 0.2 to $0.8\,P_{\rm max}$.

The effect of ageing on the mechanical properties was investigated by means of a quasi-static compression test, which comprises the compression of a propellant bed and subsequent firing of the fractured grains in a CV [14]. Quasi-static compression is relatively simple and provides good indications with respect to propellant bed behaviour during the first stages of ignition and combustion in a gun.

For the quasi-static compression test, 300 grams of propellant is quasi-statically pressed for 4 seconds at 300 Bars. The compression is performed at -40° C. After acclimatisation CV tests are performed with a loading density of 0.214. Extrapolation of the change in linear vivacity between 0.2 and 0.7 P_{max} to $P/P_{\text{max}} = 0$ results in a value that is a measure of the destruction of the propellant grains. This value corresponds to the relative surface area at the beginning of combustion due to the fractured grains [14], and is sometimes called 'relative surface area'. For various applications one can use specific criteria for the 'relative surface area'.

RESULTS AND DISCUSSION

Chain length NC

The results of the GPC measurements are given in Fig. 1a/b. Important data with respect to the polymeric chain length of NC are the (weight average) molecular weight (M_w) as well as the molecular weight distribution. The latter can be determined from the ratio between weight average and number average molecular weight (M_w/M_n) . These results of the GPC-measurements are given in table 1.

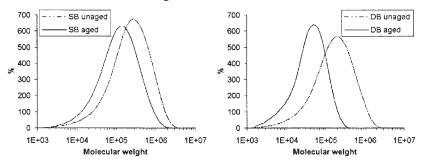


Figure 1 a/b: Results of GPC-measurements: molecular weight distributions of unaged and aged SB propellant (lett) and DB propellant (right).

The results show that the chain lengths of propellant grains, which were aged for a period that is equivalent to 20–30 years, is shortened by 50% (SB) to even 80% (DB). Further the width of the mole weight distributions is decreased as well, by 15% and 40% respectively. It is reasonable to assume that both factors affect the mechanical properties of the propellant grains.

Table 1.	Reculte	of GPC	:-measurements
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Sample $M_{\rm w}$	Molec	Molecular weight		Width of weight distribution	
	$M_{\rm w}$ (dupl.)	ratio aged/unaged	$M_{\rm w}/M_{\rm n}$ (dupl.)	ratio aged/unaged	
CD was and	331000		4.3		
SB unaged	328000		4.1		
	176000	0.53	3.6	0.85	
SB aged	173000		3.6		
DD	237000		4.1		
DB unaged 245000		4.0			
DD	54200	0.23	2.4	0.58	
DB aged	55600		2.3		

Burning properties

The characteristic vivacity, L_k , and the parameters in Vieille's burning law $r = \alpha \times P^{\beta}$ that were calculated from the CV test results are given in table 2. For reasons of comparison the burning rate at the arbitrarily chosen pressure of 150 MPa is given too.

	L _k [MPa ⁻¹ s ⁻¹]	α [mm s ⁻¹]	β [-]	r(150 MPa) [mm s ⁻¹]
SB unaged	1.24	1.96	0.76	86.4
SB aged	1.27	2.35	0.72	85.7

2.06

1.97

0.87

0.88

161.1

162.0

Table 2: Burning properties of unaged and aged propellants

1.71 1.70

The results show that the burning properties have hardly changed. The change of the pressure exponent, β , is compensated by the change of α , which is reflected in the calculated burning rate. This means that the burning rate curves of aged and unaged propellants overlap. This applies for both propellant types.

As mentioned above the samples were aged under confined conditions. In another (unpublished) study we have aged the same type of SB propellant in open trays. In that case, L_k showed an increase of 16% while the burning rate increased 10 to 20% as a result of significant changes in both α and β . Simulations indicated that in that case peak pressures in a gun increase by 30%.

Mechanical properties

DB unaged

DB aged

As an example the results of CV tests that were performed after quasi-static compression of SB propellant at -40° C are plotted in fig. 2.

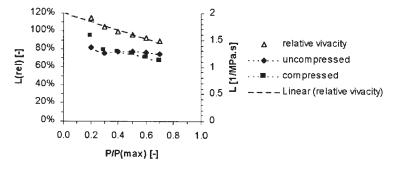


Figure 2: Vivacity curves of unaged (left) and aged (right) SB gun propellant.

The 'relative surface areas' that are derived from the extrapolated relative vivacities are given in table 3.

Table 3: Results of quasi-static compression: relative surface areas

	Unaged	Aged	Relative increase
SB propellant	107%	121%	+ 13%
OB propellant	188%	229%	+ 22%
2B propellant	100%	22570	

The data in table 3 show that the mechanical integrity of both propellants decreases significantly due to ageing. The increased surface area of the propellant bed will lead to an accelerated pressure rise in a gun during firing while the increased fines fraction results in a diminished porosity. Consequences may be an irregular pressure build-up, pressure waves or increased peak pressures [12].

Criteria for the 'relative surface area' depend greatly on the weapon system for which the propellant is developed. Further, loading density and design peak pressure determine whether problems will arise due to increased 'relative surface area' caused by ageing. Simulations show that the peak pressure strongly rises at increasing 'relative surface areas' in case of at high loading densities, while the muzzle velocity is hardly affected (Fig. 3a/b).

Unsafe situations or damage to the weapon as a result of the change in burning behaviour can obviously be expected in the case of high loading densities and when ammunition operates near the maximum allowable peak pressure. In these cases gun simulator tests are recommended to rule out the danger of unsafe application of the propellant.

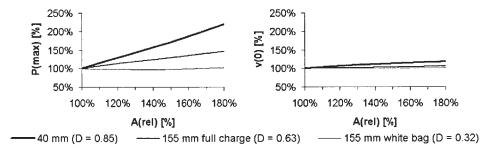


Figure 3a/b: Peak pressure and muzzle velocity plotted as a function of the 'relative surface area', A(rel), for some weapon configurations ($D = loading density \lceil kg/dm^3 \rceil$).

Heat development and energy content

The thermodynamic properties of both propellant types hardly change when aged under confined conditions as shown in Table 4.

Table 4: Change of calorific values due to ageing

	Microcalorimetry	Bomb calorimeter
SB propellant	- 3%	(change not significant)
DB propellant	– 1.9%	-1.5%

The change of calorific value is often used to determine whether an aged propellant meets the ballistic criteria. Usually the calorific decrease is very small, theoretically resulting in a minor decrease of the muzzle velocity [15]. This is, however, only true if other propellant parameters that are related to the burning behaviour, like the mechanical properties, remain unchanged.

Discussion

The results described above indicate that a number of parameters significantly change during ageing. These parameters are specifically those that are related to the mechanical properties. Their changes arise mainly from the decrease of the polymeric chain length of the main constituent, NC. Parameters like the energy content, on the contrary, hardly change.

The burning rate appears not to change during ageing under confined conditions As mentioned above, however, if propellants are aged under unconfined conditions a rather dramatic increase of vivacity and burning rate can be found, possibly caused by evaporation effects leading to (hair) cracks and hence an increased surface area.

The safe lifetime of conventional gun propellants is generally derived from propellant parameters that are closely connected to thermal properties. These might be the heat development caused by NC degradation or the content of stabilisers that prevent NC degradation and heat production. In fact, in these cases the safe *storage* lifetime is considered.

The results of this study show that the decrease of mechanical integrity as a result of ageing may lead to unsafe application of propellants. The same applies in case of diffusion of a phlegmatiser due to ageing, which causes a comparable change of vivacity. In other words, the safe *ballistic* lifetime may be limited due to ageing.

In order to be able to provide the user with complete information about the conditions of propellant with respect to its lifetime, both the safe storage lifetime and the safe ballistic lifetime should be considered.

A number of parameters that provide good indications with respect to mechanical integrity is mentioned in table 5. If proper criteria for these parameters are available, the execution of only a small number of these tests will be sufficient.

Parameter	Test method	Remarks
polymeric chain length	GPC	simple and cheap method
mechanical properties	Tensile testing	results are hard to correlate with other parameters
'relative surface area'	Quasi-static compression closed vessel tests	/simple method, clear criteria possible
regularity of pressure build during ignition / pressure waves	upgun simulator	in case of considerable loss of mechanical integrity

Table 5: Selection of parameters and test methods

CONCLUSION

The change of polymeric chain length of NC, caused by degradation of NC during ageing, results in a loss of mechanical integrity of propellant grains, while thermal properties and burning behaviour may hardly have changed. The loss of mechanical integrity leads to increased grain fracture during ignition and the first stages of combustion in the weapon. Depending on loading density and design peak pressure, this may lead to unsafe situations with respect to pressure build-up.

It is concluded that the lifetime of conventional gun propellants is no only determined by thermal stability because changes of the mechanical characteristics may finally lead to unsafe employment. Both safe storage lifetime and safe ballistic lifetime should be considered in propellant surveillance. Several test methods are recommended to examine the ballistic lifetime, like GPC, quasi-static compression followed by closed vessel tests, and gun simulator tests.

REFERENCES

- J.L.C. van Geel, "Heat generation measurements for the stability control of nitrate ester propellants", 4th Symposium on chemical problems connected with the stability of explosives, Sweden, 1976.
- 2 J.L.C. van Geel, "Self-ignition Hazard of Nitrate Ester Propellants", PhD thesis, Delfl University of Technology, 1969.
- 3. K. Kishore and G. Prasud, "Ageing studies of solid propellants: A review", in: Indian Institute of Science, 1976, p. 1–56.
- 4. L. Druet and M. Asselin, "A review of stability test methods for gun and mortar propellants 11: stability testing and surveillance", Journal of Energetic Materials, Vol. 6, 1988, p. 215–254.
- 5. T. Yoshida, "Decomposition reaction of nitrate ester", Journal of Society of Industrial Explosives, Japan, Vol. 33, 1972, p. 1–50.
- B.J. van der Meer and W.P.C. de Klerk, "Influence of environmental factors on the lifetime of gun propellants investigated with heat flow microcalorimetry", Proceedings of the TTCP workshop on the microcalorimetry of energetic materials, April 1997, Leeds, UK.
- STANAG 4117, "Explosives, stability test procedures and requirements for propellants stabilized with diphenylamine, ethyl centralite or mixtures of both".
- 8. Draft STANAG, "Explosives, Nitrocellulose based propellants stabilized with diphenylamine, stability test procedure and requirements using heat flow calorimetry", Working group Draft, september 1999.
- M.A. Bohn and F. Volk, "Bestimmung der sicheren Lagerzeit einer plastifizierten Nitrocellulose", 25th International Annual Conference of ICT, June 28–July 1, 1994, Karlsruhe, Germany.
- F. Volk and M.A. Bohn, "Ageing behaviour of propellants determined by mass loss, heat generation, stabiliser consumption, and molar mass decrease", 87th Symposium of the Propulsion and Energetics Panel of the AGARD, 1996, Athens, Greece.
- 11. F. Volk, M.A. Bohn, and G. Wunsch, "Determination of chemical and mechanical properties of double base propellants during ageing", in: Propellants, Explosives, Pyrotechnics 1987, Vol. 12, p. 81–87.
- E.A. Brönnimann, A. Sopranetti, and Ch. Stalder, "A universal test procedure to predict the shelf life of propellants", Symposium on Chemical Problems connected with the stability of explosives, part 7, Sweden, 1985.
- 13. STANAG 4115, "Definition and Determination of Ballistic Properties of Gun Propellants".
- 14. W.W. Stein and H. Jahnk, "Determination of the grain fracture behaviour of propellant beds", 4th Int. Gun propellant & propulsion symposium, 1988, p. V-363.
- H.P.J. Jongeneelen, "Ballistic Stability. The relation between the decrease in calorific value and in muzzle velocity", PML report, 1971.