

Burning Rate Enhancement of AN-Propellants by TAGN and GZT

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Abstract

To overcome the disillusioning combustion behavior of AN propellants, burn rate augmentations by TAGN and GZT have been investigated on a propellant system based on ammonium nitrate, GAP/PolyGLYN and nitrate ester plasticizers. Additional ingredients are HMX, CL20 and Al. When TAGN is incorporated up to 30% the specific impulse of AN/GAP/NE propellants drops only a little. With 10 and 20% Al the Isp of TAGN containing formulations is even higher than for a traditional composite based on AP/Al/HTPB with 88% solid loading. Only the volumetric specific impulse drops a little with 20 - 30% TAGN. With more than 10% GZT there is however a dramatic drop in Isp due to its more negative oxygen balance. Burn rate enhancement caused by GZT is of similar magnitude than it is caused by TAGN. The latter produces however a beneficial reduction of pressure exponents which is not seen with GZT. Additional enhancement of burn rates can be achieved by nitramines, with CL20 much more and with additional reduction of pressure exponents than by HMX and with aluminum.

Although TAGN is very favorable for thermodynamic performance and combustion, problems still exist with chemical stability in connection to nitrate esters. Lead citrate proves to be beneficial in that case and serves together with 20 to 30% TAGN not only for a good burning behaviour but for acceptable values of chemical stability in short term tests. GZT proves to be less problematic, but is not able to reduce the pressure exponents sufficiently.

If these problems can be overcome, AN/TAGN propellants may play an important role in the field of rocket propellants, AN/GZT formulations for gasgenerating propellants.

Introduction

According to thermodynamics AN propellants with Al and energetic binders like GAP, PolyGLYN or PolyNIMMO offer the perspective of environmental clean propellants which have been proposed for space application, because they are endowed with a high specific impulse and an exhaust which is essentially free of hydrogen chloride¹). Without aluminum AN propellant formulations containing energy rich nitramines, energetic binders and nitrate ester plasticizers are hot candidates for minimum smoke propellants with a specific

impulse > 240 s at 1000 psi, AA signature and a reduced hazard classification belonging to class 1.3.²⁾

Realistic AN propellants however suffer due to the predominant drawbacks of the oxidizer, its hygroscopicity, its grain destroying ability by severe crystal phase changes, its crucial behaviour towards chemical compatibility and overall its poor and disillusioning reactivity on combustion.

To overcome this general problem a lot of burn rate modifiers predominantly metal oxides or complexes have been applied to AN propellants in the past.

Sodium barbiturates, parabanates, nitriloacetates and cyanurates, iron oxide and complexes like millory blue or Prussian blue have been described in several patents in the first period of AN propellants ranging from 1956 to 1976^{3,4)}

In the second period starting in 1988, which is still going on, Copper chromite and ammonium dichromate (ADC) have been applied for AN/GAP or AN/BAMO/AMMO formulations⁵⁻⁷⁾ too, but often reveal poor compatibility with other ingredients - copper chromite and other copper complexes with azido groups, ADC with nitrate esters. Mixed molybdenum-vanadium oxides (MOVO) prove to be useful for AN/GAP propellants and do not diminish stability to much⁸⁾.

If toxic combustion products like chromium or vanadium oxides must be avoided efficient burnrate augmentation can be achieved by polynitrogen compounds like aminoguanidine nitrates, tetra-, triazolates, triazines or tetrazines. This was discovered and has been described to a large extent for airbag formulations since 1990⁹⁻¹¹⁾. TAGN was introduced plenty of years ago by Joe Flanagan et.al. for the formulation of cool burning gun propellants¹²⁾. S. Walz proposed to use it for airbag formulations after several patents coming up in this field¹³⁾. GZT and 5-ATZ have been described by Khandhadia to be useful for burn rate augmentation of comelted mixtures from AN/KN and GN⁹⁾. Two of the latest sophisticated and highly activated polynitrogen compounds in this field are BTTZ, BTATZ (3,6-bis(1H-1,2,3,4-tetrazol)-2-tetrazine, 3,6-bis(1H-1,2,3,4-tetrazol-5-amino)-2-tetrazine) and DAAT (diaminoazotetrazine) which were first synthesized and investigated by M. Hiskey at Los Alamos National Laboratory¹⁴⁾. The burning behaviour of the pure materials was described recently by A.I. Atwood from NAWC China Lake¹⁵⁾. The thermal analysis and decomposition has been investigated by S. Löbbecke¹⁶⁾. A complex synthesis however is necessary to obtain the materials. Up to now no propellant formulations with BTTZ, BTATZ and DAAT have been found in the literature.

Our contribution is going to describe the thermodynamical performance and essential features of the burning behaviour of AN propellants with energetic binders and increasing amounts of TAGN and GZT for burn rate modification. Additionally other important aspects of propellant formulations concerning chemical stability and sensitivity are discussed.

Experimental Part

Formulations have been performed with spherical AN particles, made by the spray crystallization process developed in ICT with particle fractions based on 160, 55 and 20 μm mps, coated with 0,5 to 0,8% Aerosil as anticaking agent. TAGN was crystallized to a high bulk density ($> 0,8 \text{ g/cm}^3$) and when wet ground in ethanol to 22 – 24 μm mps. GZT was used as received from its synthesis with 16-20 μm mps. Al, HMX and CL20 were applied each with 5 μm mps. GAP diol and PolyGLYN were cured with N100.

Thermodynamical performance calculations were carried out with the ICT code and data base developed by Volk and Bathelt¹⁷⁾. Standard values for specific impulse, volumetric specific impulse, combustion temperature T_c and molar output of gases n are given for a standard expansion ratio of 70:1 (1016 psi).

The burning behaviour was determined by Crawford measurements on strands of 150 mm length and 5x5 mm square cross section which were covered with an inhibiting coating. Burning times and rates were determined for 5 and 10 cm measuring distance by disruption of 0,1 mm iron wires drawn through the strands. Burning was performed top down at 7 pressures under N_2 atmosphere, in a 500 ml bomb connected to a 250 l expansion vessel.

For chemical stability Dutch test values have been obtained by determining the weight loss of a 2g propellant sample by heating for 8 – 72 h at 105°C. Vacuum stability measurements were taken after 40 h heating of a 2,5 g sample at 100°C, flash points usually by heating in a Wood's metal bath with 20°/min. As borderline for the Dutch test a 2% (3%) weight loss is generally accepted. For vacuum stability 1,2 at least 2 ml/g gas evolution should be the maximum acceptable value.

Impact and friction sensitivity were determined with the German BAM hammer and the large friction apparatus using porcelain plates and pins. The given values represent the minimum weights and energies to obtain a positive reaction of at least one from 6 trials.

Basic Properties of TAGN and GZT

Some basic chemical properties of TAGN should be mentioned for a better understanding of their influence on thermodynamical performance and combustion. They are outlined in table 1 and have been taken from ICT's database with citations from S. Walz¹³⁾ and M. Hiskey¹⁸⁾.

	formula	O ₂ -bal.	N ₂ cont.	Mol weight	density	ΔH _f	Fp Decomp	calc. gas output
		%	%	g/mol	g/cm ³	kcal/kg	°C	NI/kg
TAGN	CH ₉ N ₇ O ₃	-33,51	58,66	167,128	1,54	-68,8	215	1206,3
GZT	C ₄ H ₁₂ N ₁₆	-78,8	78,84	284,246	1,54	+344,8	240	1103,3

Table 1: Basic chemical data of TAGN and GZT

Both chemicals can be regarded as energetic fillers. They decompose exothermally slightly after their melting point. Decomposition of TAGN has been examined in detail by Brill¹⁹⁾. It follows a completely gaseous decomposition route, whereas GZT produces a lot of solid residues mainly carbon if not enough oxygen is present. GZT is equipped with a higher heat of formation together with a better thermal stability. TAGN however has a better oxygen balance which contributes more to the thermodynamic energy of a propellant.

Thermodynamical Performance Calculations

Thermodynamic calculations have been performed on a propellant system based on:

- energetic solids: AN + TAGN or GZT: 50 – 80%
- within TAGN or GZT 0 – 30%
- energetic binder: 50 – 20%
- GAP/N100 plus TMETN/BTTN ratio 1:1:1

The results are pointed out in two map like diagrams shown in fig 1 and 2. According to the baseline the maximum specific impulse for the smokeless formulation AN/GAP/TMETN/BTTN amounts to 2350 Ns/kg. If TAGN is added a slow but continuous decrease is observed down to 2315 Ns/kg (-1,5%) for a formulation with 70% solids including 40% AN and 30% TAGN. In the same way the volumetric specific impulse is decreased from 3800 to 3660 Ns/dm³ (-3,7%).

If GZT is used for burnrate modification the decrease of I_{sp} is much more significant. As it is pointed out in fig 2 the specific impulse for formulations with 70% solids drops from 2350 Ns/kg to 2030 Ns/kg (-13,6%), the volumetric specific impulse from 3800 to 3180 Ns/dm³ (-16,3%) when GZT is varied in the range from 0 to 30%.

If Al is incorporated up to 20% the specific impulse shows a different and very promising behaviour for AN/TAGN formulations. Fig. 3 is demonstrating the increase of I_{sp} from AN/TAGN/GAP formulations with increasing Al concentration based on 70% solids and a constant binder composition with 12% GAP/N100 and 18%TMETN/BTTN 1:1. Interestingly all curves pass the same I_{sp} value at 2500 – 2505 Ns/kg with 10% Al concentration. With 20% Al incorporation increasing TAGN concentration leads to a remarkable enhancement of I_{sp} from 2591 to 2641 Ns/kg at 7 MPa (264,1 to 269,2 s; + 1,9%). According to the lower density of TAGN the volumetric specific impulse pointed out in fig 4 slightly decreased with increasing TAGN concentration. The difference 4480 – 4454 Ns/dm³ from 0- 30% TAGN is however not remarkable (- 0,6%).

A further view on the other thermodynamic parameters reveal the main influence of TAGN on I_{sp} . As it is pointed out in fig. 5 a continuous decrease of the combustion temperature T_c from 2561 to 2304 K without Al and from 3390 to 3195 K with 20% Al is observed for increasing TAGN concentration. Contrary to T_c the gas output n especially of light weight gases like H₂ is continuously increased. This is demonstrated in fig. 6. For formulations with 10% Al the decrease of T_c is just compensated by the increase of n , for formulations with 20% Al it leads to an enhancement of I_{sp} .

A similar behaviour but accompanied by a more dramatic drop of I_{sp} is observed for AN/GAP formulations with 5 to 30% GZT. The I_{sp} curves for formulations with 70% solids are shown in fig. 7, the volumetric specific impulse in fig. 8. For concentrations of 20% and 30% GZT together with 20% Al carbon formation is observed. It leads to a significant drop in T_c and n , thus to a significantly lower I_{sp} (2464 Ns/kg compared to 2641 Ns/kg for the corresponding TAGN formulation. Formulations with 20% or 30% GZT without Al exhibit low combustion temperatures ($T_c = 2023$ and 1740 K) and corresponding low temperatures of the exhaust after expansion ($T_e = 807$ and 640 K). This might be of interest for low temperature cool burning gasgenerators.

Burning Behaviour

Augmentation of burnrates caused by TAGN and GZT is illustrated for formulations with 66% energetic solids including AN with 3 different fractions of 160, 55 and 20 μm mps and 16% HMX. The formulations are outlined in table 1. In this case a binder was applied based on 11% GAP/PolyGLYN with 1:1 ratio and 22% TMETN/BTTN as energetic plasticizer with a 3:2 ratio. For comparison formulation ASN 15 is shown which has a slightly reduced content of solids – 64%, including 14% HMX and a similar binder based on GAP/PolyGLYN 1:1 and 20,7% TMETN. The burning rates measured at 2,4,7,10,13,18 and 25 MPa are plotted in two diagrams shown in fig. 9 and 10. The relative increase of burnrates is given in table 2 for 2,7 and 18 MPa. The augmentation of burn rates goes roughly linear with increasing concentration of the modifier. A continuous decrease however is seen for one TAGN concentration with increasing pressure leading to the observed reduction of pressure exponents from 0,78 for ASN 15 to 0,63 for ASN 26. Up to 20% GZT the pressure exponent is not very much influenced for this type of formulation. Within error bars the burnrate augmentation appeared to be the same at high and low pressures for 5 and 10% GZT. Only for 20% GZT a small decrease appears to occur at higher pressures. This behaviour is illustrated by plotting the burnrate pressure curves of ASN 27 with 20% TAGN and ASN 31 with 20% GZT in one diagram shown in fig. 11. The burn rates are not so much different, but the TAGN formulation exhibits a more convenient pressure exponent.

Further enhancement of burnrates connected with a significant reduction in pressure exponents is achieved by replacing 16% HMX by 16% CL20, which is endowed with a better oxygen balance and higher thermodynamic energy. The diagram in fig. 12 compares the plot of the CL20 formulation ASN 46 with that of the corresponding ASN 27 with HMX. Both contain 30% AN, 20% TAGN 11% GAP/PolyGLYN and 22% energetic plasticizer based on TMETN/BTTN with a ratio of 3:2. The burn rates at 7 MPa are increased by more than 26% - from 8,6 to 10,9 mm/s. The overall pressure exponent decreased from $n = 0,65$ to $n = 0,57$ (2-25 MPa). As it is pointed out in table 2 the specific impulse for this formulation is slightly better (239,8 s = +1,1%), the data for chemical stability are of similar magnitude.

Different relations exist if an AN/TAGN formulation is equipped with Al to enhance the specific impulse. The burning behaviour which resulted from AN/TAGN GAP formulations with 65% solids including AN 160 and 555 μm mps (2:3 ratio) and 5 to 20% TAGN

formulated with a binder based on GAP/TMETN 1:1 is shown in fig 13. Again there is a continuous increase in burnrates and a decrease of pressure exponents observed.

If 10% Al is added a further increase in burnrates from 10,3 to 12,4 mm/s (about 20,4%) is observed at 10 MPa. It is accompanied by a small decrease of the average pressure exponent from $n = 0,71$ to $n = 0,64$ in the range of 2-25 MPa. As it is pointed out before incorporation of 10% Al will significantly increase the combustion temperature. This is usually accompanied by a parallel shift of the burn rate pressure curve to higher values. The reason for the additional reduction of pressure exponent may be a 5% enhanced solid loading for formulation AN 45 (from 65 to 70%). Further improvements of the burning behaviour are possible if lead citrate / carbon black are allowed to act as an additional modifying system. Lead citrate is known to have a positive influence on the combustion behaviour of RDX/TAGN propellants²⁰. For AN/TAGN systems it is described in a short note by Mundada²¹. In this study it has been found that lead citrate exercises not only a positive influence on the combustion behaviour but also on the chemical stability of AN/GAP/TMETN propellants. To demonstrate this the data of thermodynamic specific impulse, burning rates, pressure exponents and short term stability tests of AN 1101, 102 and 105 with 220, 25 and 30% TAGN, 10% Al and 3% lead citrate/carbon black (3:1) are outlined in table 3. The burning behaviour of these formulations is exhibited in fig. 14a and 14b, showing burn rates and variation of pressure exponents from 2 – 25 MPa. For the first time a pressure exponent $n < 0,5$ has been achieved for AN 102 and AN 105.

Chemical Stability

Together with the thermodynamic specific impulse, burn rates and pressure exponents, some of the results from short term stability tests are given in table 1b and table 3. According to the limits of Dutch test and vacuum stability most of the values indicate borderline or insufficient chemical stability for the TAGN containing formulations except those of AN 101, 102 and 105. Additionally the values for formulations with AN, HMX, GZT, GAP, NE are within the limits of the applied tests. For AN 101, 102 and 105 lead citrate was applied in connection with DPA. According to similar experimental results on other AN/TAGN formulations it may contribute to the good stability values.

As it is shown in table 3 the applied stabilizer 2NDPA appeared to be less effective than DPA. Due to sterical and electronic discrimination 2NDPA is less reactive towards nitration or nitrosation at the amine function and will be a more persistent stabilizer than MNA or DPA. White pointed out that DPA and MNA in formulations with NE and nitrate esters undergo a rapid stabilizer depletion thus feigning better chemical stability in short term tests than it is really true²²⁾. As it was stated by Michinori and Yuji^{23,24)} TAGN might act as NOx scavenger itself and will be consumed at higher temperatures. For this reason the acceptable values for formulations AN 101, 102 and 105 and even those of AN 29 – 31 with GZT might be regarded more critically.

Discussion and Summary

According to its positive influence on thermodynamic performance and augmentation of burn rates TAGN is able to act as an efficient burn rate modifier for AN propellants. The specific impulse for AN/TAGN/GAP propellants with 20% Al and 20% TAGN is even higher as for traditional AP/Al/HTPB composite propellants with 88% solids (2628 to 2592 Ns/kg). The volumetric one is however 3% lower than that of traditional composites based on 68% AP, 20% Al and 12% HTPB (4469 to 4610 Ns/dm³). For smokeless AN/TAGN/GAP propellants a slow decrease is observed even for the specific impulse of formulations with increasing TAGN concentration (2332 to 2285 Ns/kg from 0 – 30% TAGN). Strong enhancement of burn rates together with good reduction of pressure exponents are achieved if 20 to 30% TAGN are applied for AN/GAP as well as for AN/GAP/PolyGLYN formulations. Incorporation of GZT causes similar enhancement of burn rates, but a dramatic decrease of the specific impulse if it is applied in higher concentrations above 5 to 6%. Its bad influence on thermodynamic performance is mainly due to its negative oxygen balance which will be a strong disadvantage in connection with a poor oxidizer like ammonium nitrate. On the other hand the decrease of combustion temperature leads to a significant low temperature of the exhaust gases after expansion. These effect will be favorable for gas generators which are used for safety applications. They often require higher burning rates together with a low temperature of the exhaust.

Additional solutions have to be found for AN/GZT formulations to reduce the pressure exponents. This will be case if CL20 is applied for the formulations instead of HMX. The

effect on a formulation with 20% TAGN has been seen for ASN 46 in comparison to ASN 27 and can be observed for AN/CL20/GZT formulations too. The reduction of pressure exponents cannot simply be explained with a higher combustion temperature as it is the case for the Al containing formulations. Chemical complexation between suitable placed nitramine functions of CL20 and hydrazine groups of TAGN may play a role for this strong difference in combustion in comparison to AN/TAGN/HMX propellants.

If the open questions of chemical stability can be solved AN/TAGN formulations with energetic binders may play an important role in the field of applicable rocket propellants – in the smokeless version as well as in the fully aluminized form.

References

- (1) P. Doll, G. Lund; "High Performance, Low Cost Solid Propellant Compositions Producing Halogen Free Exhaust", US Patent 5,076868 (1991)
- (2) Goals of the 4 Power ASNR – TMP coordinated development
- (3) Morello, Edwin F.; "Stabilized ammonium nitrate propellants"; Standard Oil Co. Indiana, US 3020180 1962, US 19571217
- (4) Harris, Samuel W.; "Combustion catalyst for solid ammonium nitrate propellant grain"; Standard Oil Co. (Indiana), US 3498856 A 1970, US 1967-655328 1967
- (5) Oyumi, Yoshio; Inokami, Kiyotaka; Yamazaki, Kazuhiro; Matsumoto, Koki; "Burning rate augmentation of BAMO based propellants"; Propellants, Explos., Pyrotech. (1994), 19(4), 180-6
- (6) Kimura, Eishu; Oyumi, Yoshio; "Insensitive munitions and combustion characteristics of BAMO/NMMO propellants"; J. Energ. Mater. (1996), 14(3 & 4), 201-215
- (7) Nakajima, Chikako; Saito, Takeo; Yamaya, Toshio; Shimoda, Masataka; "The effects of chromium compounds on PVA-coated AN and GAP binder pyrolysis, and PVA-coated AN/GAP propellant combustion"; Fuel (1998), 77(4), 321-326
- (8) Menke, Klaus; Boehnlein-Mauss, Jutta; Schubert, Hiltmar; "Characteristic properties of AN/GAP-propellants" Propellants, Explos., Pyrotech. (1996), 21(3), 139-145
- (9) Khandhadia, Paresh S.; Burns, Sean P.; "Thermally stable gas-generating nonazide-based compositions for inflation of vehicle airbags"; Automotive Systems Laboratory, Inc., USA, US 6306232 B1 2001, PRI US 1996-681662 B2 1996
- (10) Canterberry, J. B.; Schlueter, Samuel Steven; Adams, John Herman; Walsh, Robert Keith; "High-conversion non-azide gas generating compns. contg. phase-stabilized ammonium nitrate and aminotetrazole"; Breed Automotive Technology, Inc., USA, US 6019861 A 2000
- (11) Lundstrom, Norman H.; Scheffee, Robert S.; Luke, Daniel S.; "Nonazide-containing ammonium nitrate based gas generators and propellants for inflation of automobile restraint devices"; Atlantic Research Corp., USA, US 6017404 A 2000, PRAI US 1998-220015 A3
- (12) Flanagan, Joseph E.; Haury, Vernon E.; "Gun propellant containing nonenergetic plasticizer, nitrocellulose and triaminoguanidine nitrate"; US 3732130 A 1973, PRI US 1971-192717 19711014

- (13) S. Walz; "TAGN – Eine neue Treibstoffkomponente für Gasgeneratoren" Bag & Belt 92 2. Int. Akzo Symposium Köln 1992
- (14) M.A. Hiskey et.al. "Progress in High Nitrogen Chemistry in Explosives, Propellants and Pyrotechnics" 27th Intern. Pyrot. Seminar, Grand Junction USA July 2000, pp 3-14
- (15) A.I. Atwood, et.al.; "Burning rate Studies of Energetic Materials" , 8th IWCP conference June 2002 in Pozzuoli Italy
- (16) S. Loebbecke, H. Schuppler, W. Schweikert; "Thermal Analysis of the extremely Nitrogen Rich Solids BTT and DAAT" J. of Thermal Analysis and Calorimetry Vol 72, 2003 in press
- (17) H. Bathelt, F. Volk; "The ICT-Thermodynamic Code (ICT-Code)" Proceedings 27th Intern. Annual Conference of ICT, June 25-28, 1996
- (18) M. Hiskey et.al. "High Nitrogen Energetic Materials derived from Azotetrazolate" , J. of Energ. Materials Vol. 16, 119 –127 (1998)
- (19) Y Oyumi, T. Brill; "Thermal decomposition of Energetic Materials. 6. Solid-Phase transitions and the Decomposition of 1,2,3-Triaminoguanidinium Nitrate" J.Phys.Chem. 1985, 89, 4325 – 4329
- (20) Helmy, A.M.; "Investigation of new energetic ingredients for minimum signature propellants" AIAA-84-1434, 20th Joint Prop. Conf. June 1984, Cincinnati, Ohio
- (21) Mundada, R.B.; Nazare, A.N.; Astana, S.N.; "Burn rate and thermal decomposition studies on PSAN/HMX and TAGN gas generators with DB matrix" ; Int Ann. Conf. ICT 1997, 28th Combustion and Detonation, 53.1-53.3
- (22) White, Alex; Turner, Adrian R.; Bellerby, John M.; "Stabilizers for propellants containing new energetic materials" ; Int. Annu. Conf. ICT (1993), 24th, 7-1/7-14
- (23) Takizuka, Michinori; „Combustion characteristics of GAP based composite propellants I, theoretical combustion performance and burning rate" Res. Dev. Cent., Hosoya Kako Co., Ltd., Tokyo, 197-0801, Japan; Kayaku Gakkaishi (1998), 59(4), 181-191
- (24) Ito, Yuji; Sato, Eishi; Taguchi, Michihisa; Ota, Kozo; „Gas generating agent for inflation of automobile airbags" Nippon Kayaku KK; WO 9532165 A1 1995, PRAI JP 1994 130993

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Figure Captions

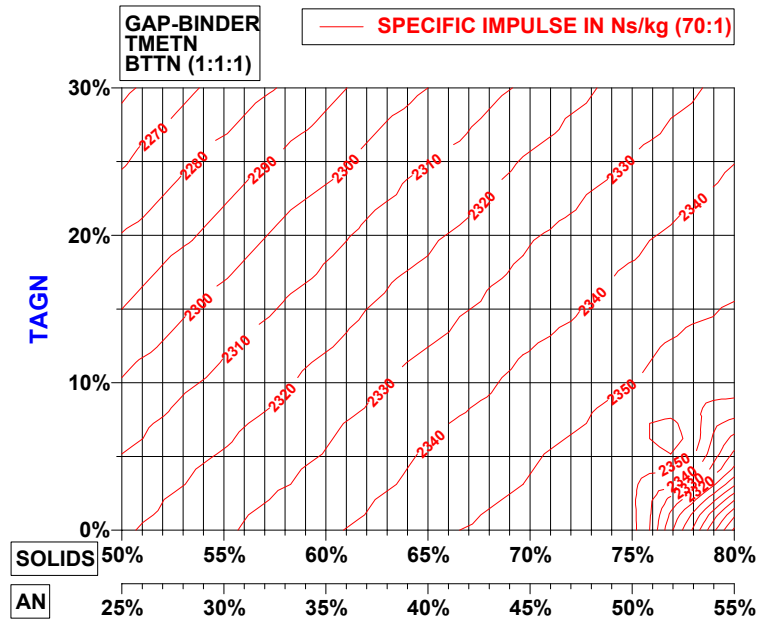


Figure 1: Thermodynamic specific impulse of the AN/TAGN/GAP/NE propellant system with increasing TAGN concentration at 70:1 expansion ratio (Sub line: ma% of AN for 25% TAGN)

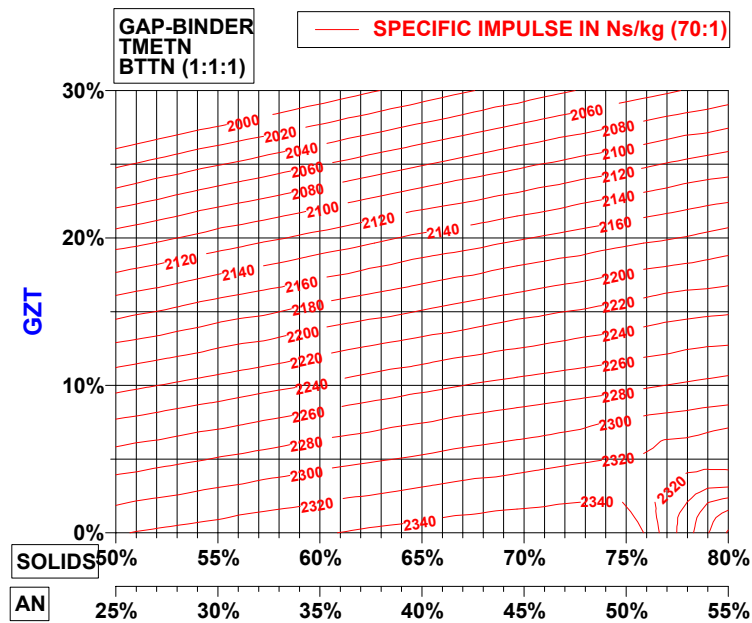


Figure 2: Thermodynamic specific impulse of the AN/GZT/GAP/NE propellant system with increasing GZT concentration at 70:1 expansion ratio (Sub line: ma% of AN for 25% GZT)

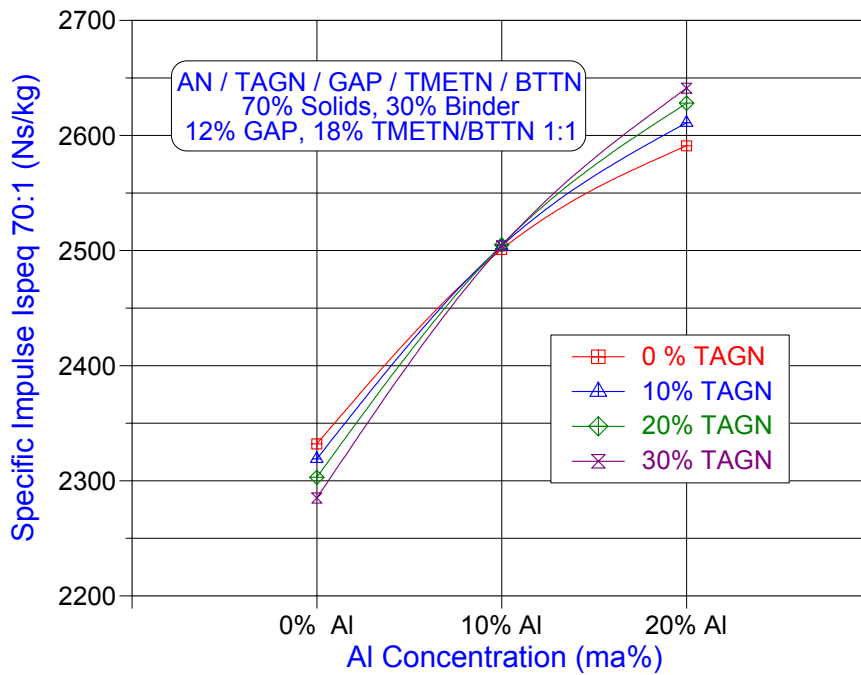


Figure 3: Thermodynamic specific impulse of AN/TAGN/GAP propellants with increasing TAGN and Al concentration at 70:1 expansion ratio

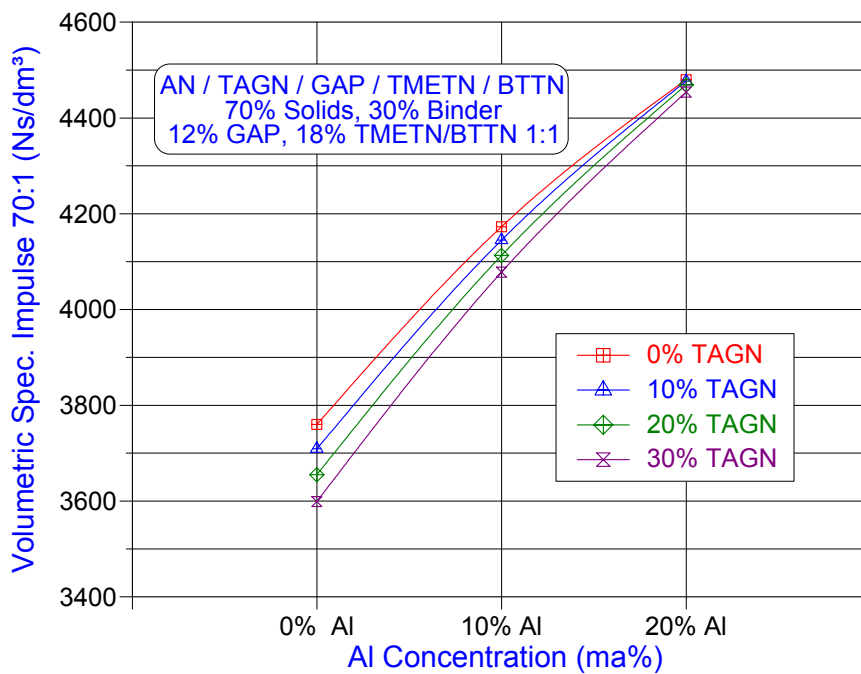


Figure 4: Volumetric thermodynamic specific impulse of AN/TAGN/GAP propellants with increasing TAGN and Al concentration at 70:1 expansion ratio

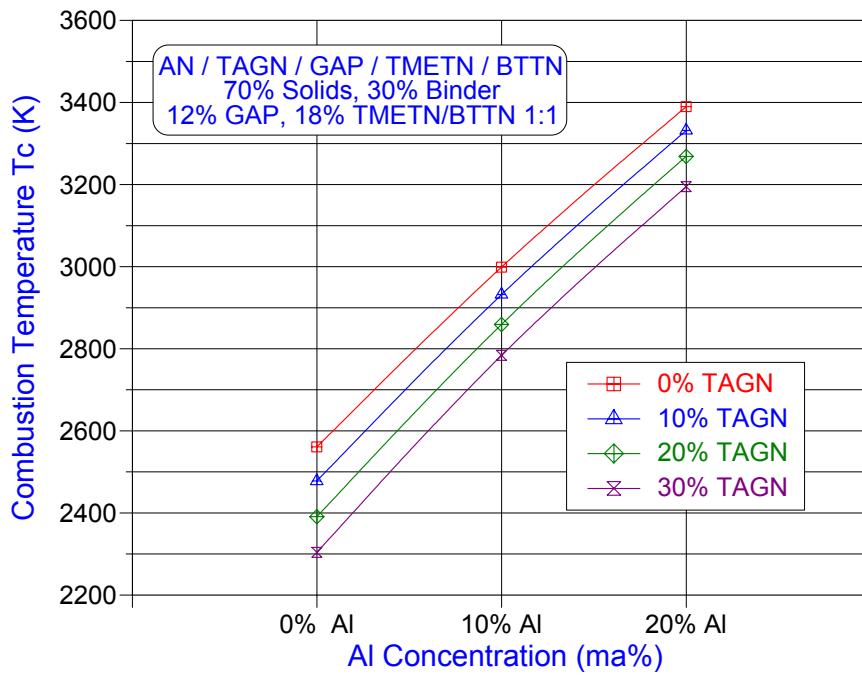


Figure 5: Combustion temperature T_c of AN/TAGN/GAP propellants with increasing TAGN and Al concentration at 70:1 expansion ratio

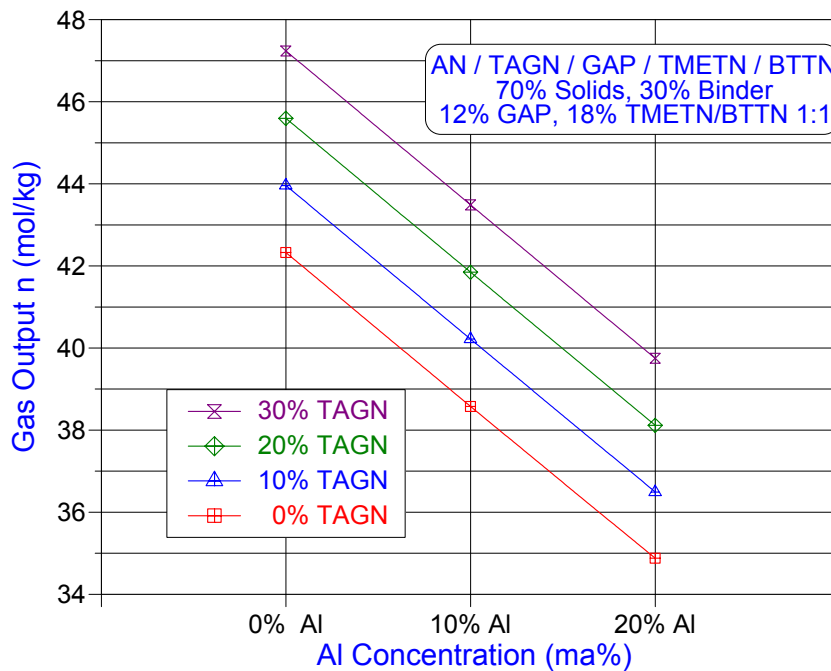


Figure 6: Molar out put of gases of AN/TAGN/GAP propellants with increasing TAGN and Al concentration at 70:1 expansion ratio

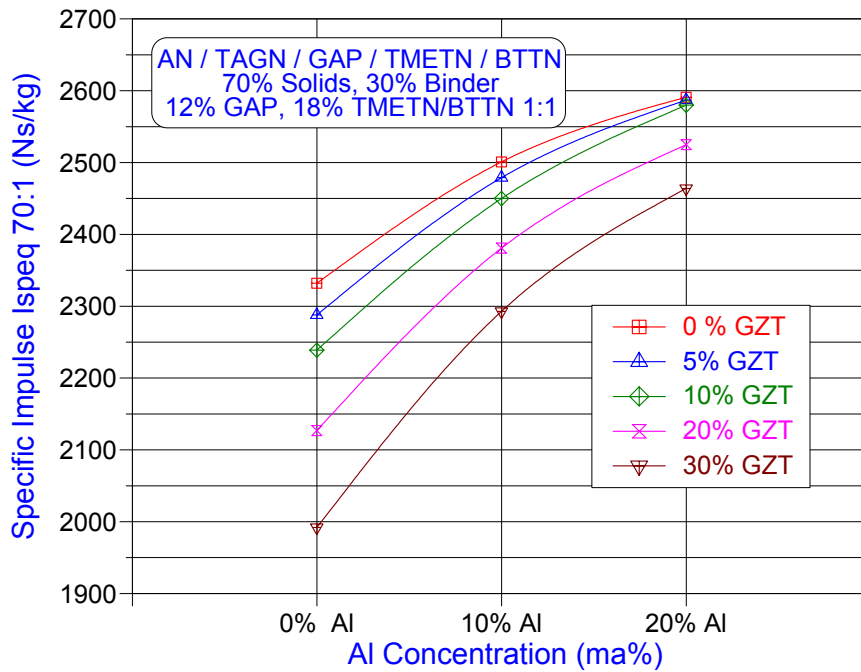


Figure 7: Thermodynamic specific impulse of AN/GZT/GAP propellants with increasing GZT and Al concentration at 70:1 expansion ratio

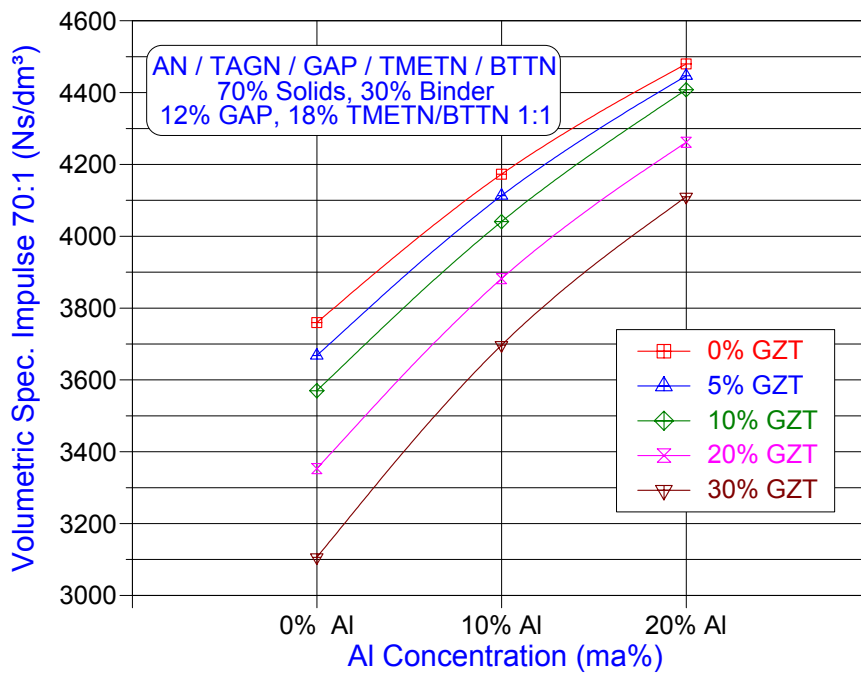


Figure 8: Volumetric thermodynamic specific impulse of AN/GZT/GAP propellants with increasing GZT and Al concentration at 70:1 expansion ratio

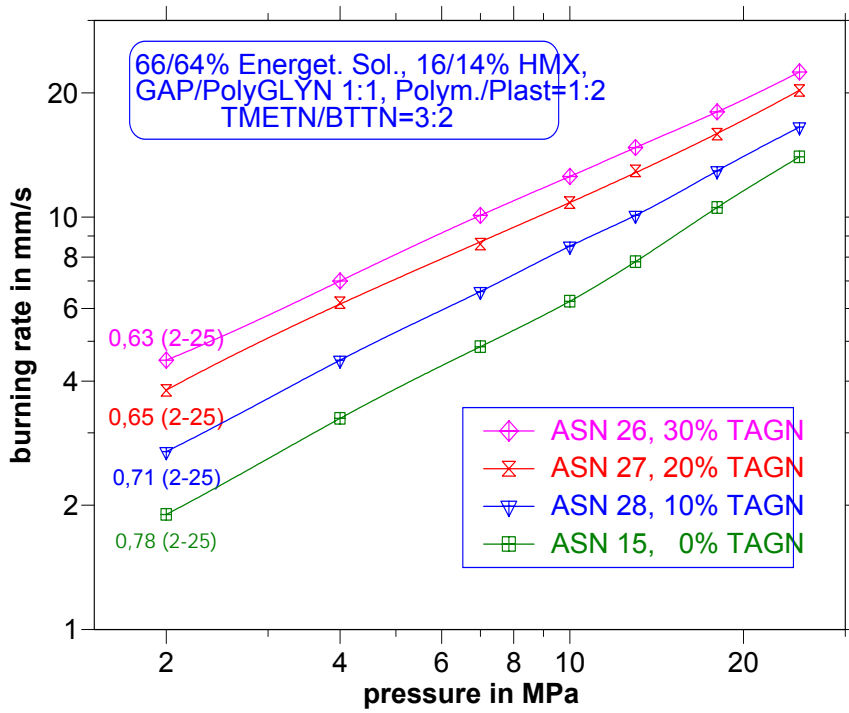


Figure 9: Plot of burnrates for AN/HMX/TAGN/GAP/PolyGLYN formulations with increasing TAGN concentration

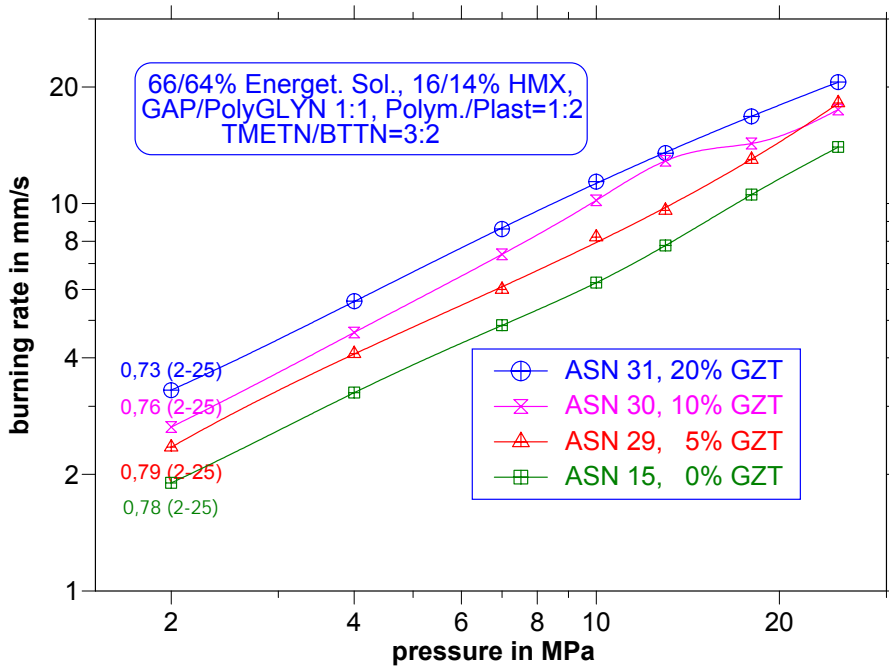


Figure 10: Plot of burnrates for AN/HMX/GZT/GAP/PolyGLYN formulations with increasing GZT concentration

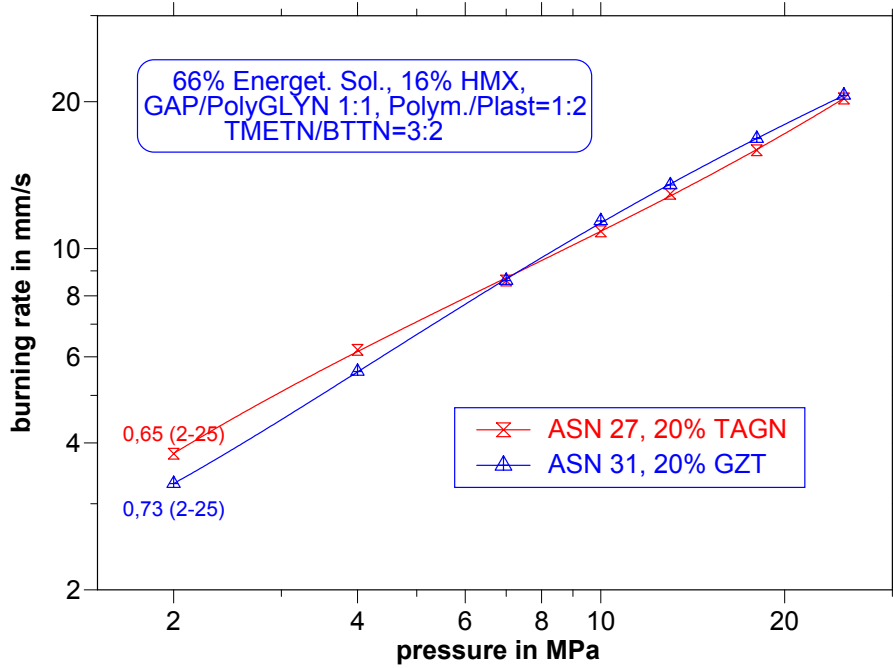


Figure 11: Comparison of burning behaviour for 20% TAGN and 20% GZT containing AN/HMX/GAP/PolyGLYN formulations

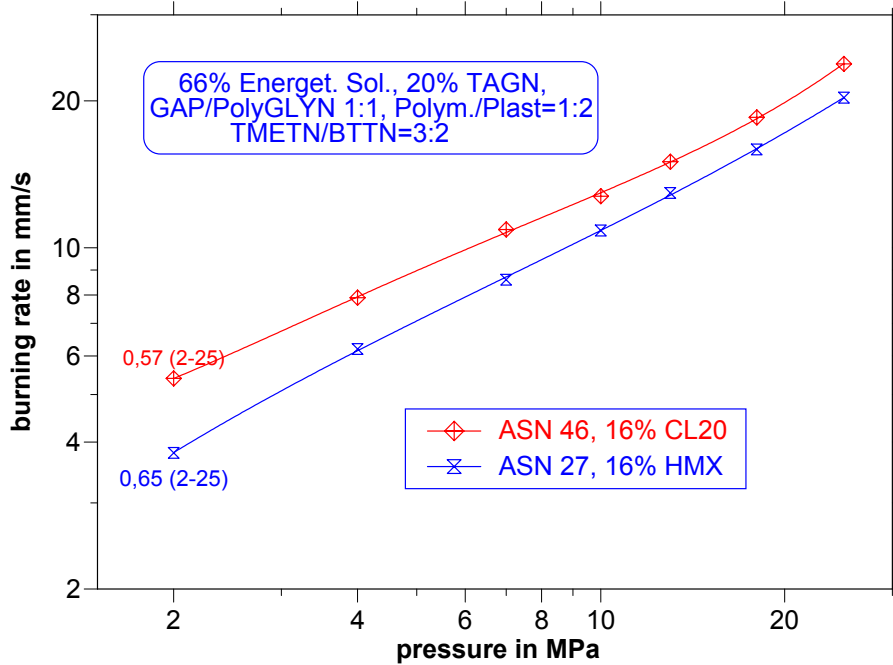


Figure 12: Comparison of burning behaviour for 16% CL20 and 16% HMX containing AN/TAGN/GAP/PolyGLYN formulations with 20% TAGN

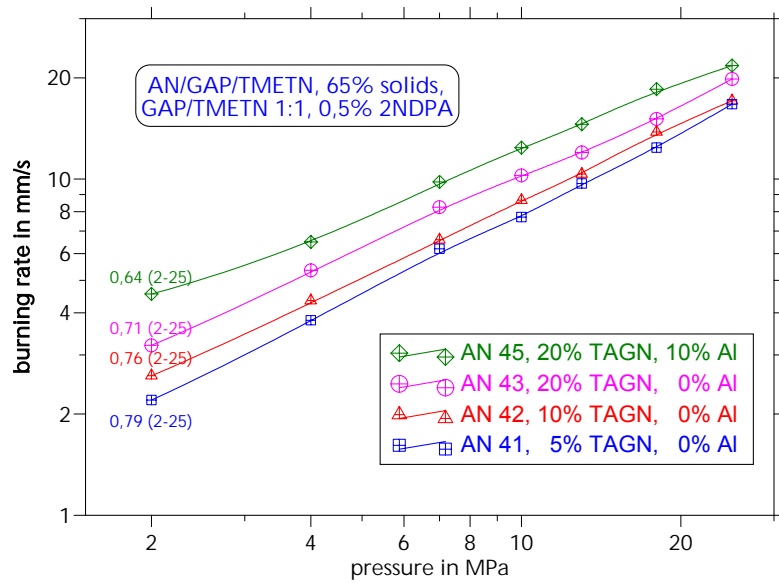


Figure 13: Plot of burnrates for AN/TAGN/GAP formulations with increasing TAGN concentration and further incorporation of 10% Al

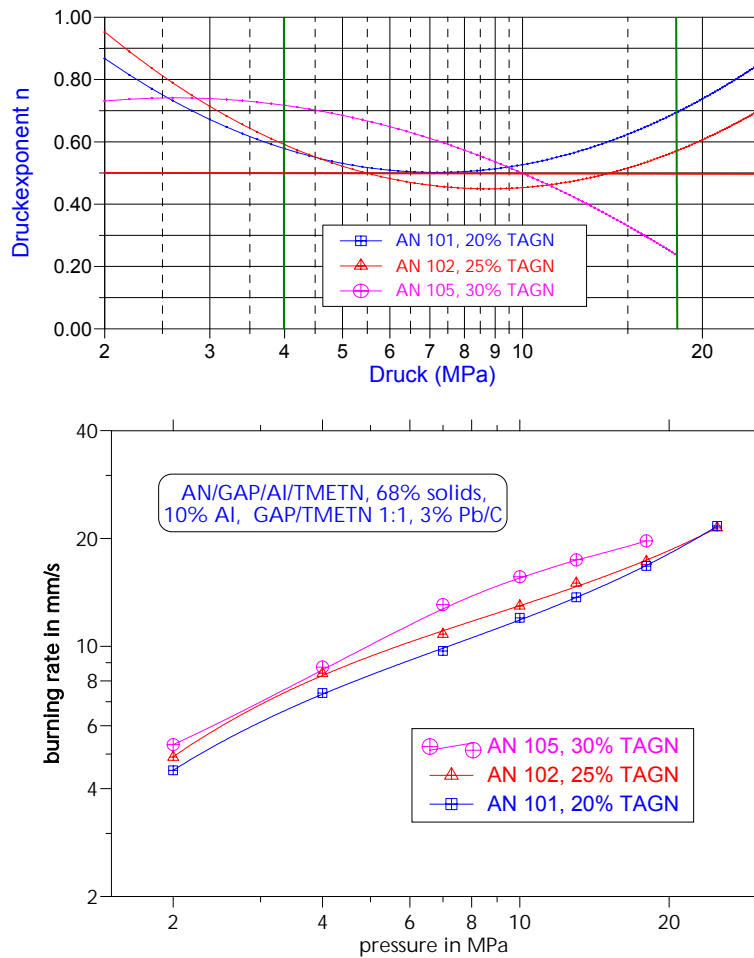


Figure 14: Plot of burnrates for AN/TAGN/GAP formulations with 20, 25 and 30% TAGN concentration, incorporation of 10% Al and 3% lead citrate burnrate modifier together with the corresponding pressure exponents

Table Captions

Table 1: Propellant composition and basic properties of ASN formulations

	ASN 15	ASN 28	ASN 27	ASN 26	ASN 29	ASN 30	ASN 31	ASN 46
energ. solids ma%	64	66	66	66	66	66	66	66
AN 160/55/20 μ (6:3:1)	50	40	30	20	45	40	30	30
TAGN 24 μ	--	10	20	30	--	--	--	20
GZT 20 μ	--	--	--	--	5	10	20	--
HMX 5 μ	14	16	16	16	16	16	16	--
CL20 5 μ	--	--	--	--	--	--	--	16
GAP/PolyGLYN binder	11	11	11	11	11	11	11	11
TMETN	20,7	13,2	13,2	13,2	13,2	13,2	13,2	13,2
BTTN	--	8,8	8,8	8,8	8,8	8,8	8,8	8,8
DPA	0,8	0,6	0,6	0,6	0,6	0,6	0,6	0,6
Carbon	0,7	0,4	0,4	0,4	0,4	0,4	0,4	0,4
I_{SPEO} 70:1 s		238,9	237,2	235,3	235,9	230,9	219,3	239,8
ρ g/cm ³	1,60	1,61	1,59	1,58	1,61	1,61	1,59	1,60
$I_{SPEO} * \rho$ Ns/dm ³		3773	3700	3647	3726	3647	3421	3764
burn rate 7 MPa mm/s	4,85	6,8	8,6	10,1	6,0	7,4	8,6	10,9
press. expo. (2-25 MPa)	0,79	0,71	0,65	0,62	0,79	0,76	0,73	0,57
Dutch T. (105°C/8-72 h) (%)	1,48	1,51	1,66	3,15	1,11	1,07	1,03	1,72
flash point (20°/min) (°C)	182	170	174	171	175	175	176	174
vac. stab. (40h/100°C) (ml/g)	0,84	5,24	2,54	5,36	1,03	1,12	1,12	4,62

Table 2: Burnrate enhancement caused by TAGN and GZT in ASN formulations

pressure	2 MPa		7 MPa		18 MPa	
	r (mm/s)	Δ (%)	r (mm/s)	Δ (%)	r (mm/s)	Δ (%)
AN plus	1,9	--	4,85	--	10,55	--
0% TAGN / GZT	1,9	--	4,85	--	10,55	--
10% TAGN	2,7	48,1	6,6	36,1	12,95	22,7
20% TAGN	3,8	100	8,6	77,3	15,9	50,7
30% TAGN	4,5	136,8	10,1	108,2	17,3	64
5% GZT	2,35	23,7	6	23,7	13	23,2
10% GZT	2,65	39,5	7,4	52,6	14,3	35,5
20% GZT	3,3	73,7	8,6	77,3	16,8	59,2

Table 3: Propellant composition and basic properties of AN/GAP formulations

	AN 41	AN 42	AN 43	AN 45	AN 101	AN 102	AN 105
energ. solids ma%	65	65	65	70	68	68	68
AN 160/55 μ (2:3)	60	55	45	40	35	30	25
TAGN 24 μ	5	10	20	20	20	25	30
Al 5 μ	--	--	--	10	10	10	10
GAP / N100	17,5	17,5	17,5	15	16	16	16
TMETN	17	17	17	14,5	15,5	15,5	15,5
DPA / 2 NDPA*	0,5*	0,5*	0,5*	0,5*	0,5	0,5	0,5
Lead citrate	--	--	--	--	2,25	2,25	2,25
Carbon	--	--	--	--	0,75	0,75	0,75
I_{SPEQ} 70:1 s					244,8	243,1	241,1
ρ g/cm ³	1,55	1,54	1,53	1,60	1,61	1,60	1,59
$I_{SPEQ} * \rho$ Ns/dm ³					3866,4	3815,7	3761
burn rate 7 MPa mm/s	6,3	6,6	8,3	9,8	9,7	10,4	13,1
burn rate 10 MPa mm/s	7,7	8,65	10,3	12,4	12,0	12,9	15,6
press. expo. (4-18), (7-18)*	--	--	--	--	0,54	0,45	0,43*
press. expo. (2-25), (2-7)*	0,79	0,76	0,71	0,64	0,61	0,58	0,72*
Dutch T. (105°C/8-72 h) (%)		2,4			1,25	1,01	0,96
flash point (20°/min) (°C)		5,0			1,48	1,35	1,36
vac. stab. (40h/100°C) (ml/g)		176			180	177	176

Pfinztal, April 30, 2003