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AN/PolyGLYN propellant formulations – approaches to less sensitive rocket propellants

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ASNR – TMP Project (US, UK, F and GE cooperation)

Development of minimum smoke, less sensitive solid rocket propellants for tactical missile applications

Potential benefits:

☞ Rocket motors with improved camouflage, ability for active guidance, enhanced availability of weapon platforms and cheaper storage and transportation facilities

Objektives (ASNR - TMP Group)

- Specific Impulse $I_{SPEQ} \geq 240$ s (2356 Ns/kg) (1000 psi, 68.9:1) density $d \geq 1.60$ g/cm³
- sensitivity to detonation and hazard classification UN Klass. 1.3 (70 US Cards in 40mm Gap-test, corresponding pressure ca. 70 kbar)
- Exhaust signature acc. AGARD classification AA (Minimum Smoke)
- Burning rate $r \geq 8$ mm/s (7 MPa), $n \leq 0.5$
- Good processibility, akzeptable chemical stability and mechanical properties

Propellant ingredients:

Energetic solids: 64 - 70%

AN 160, 55, 20 μm	30 - 54 %

HMX 5 μm mps	16 – 18%
CL 20 5 μm mps	16 - 18 %

Burn rate modifiers:	
MOVO	2.0 - 2.4 %
GZT	5 - 6 %
TAGN	20 %

Binder: 30 - 35 %

PolyGLYN/N100, GAP/N100

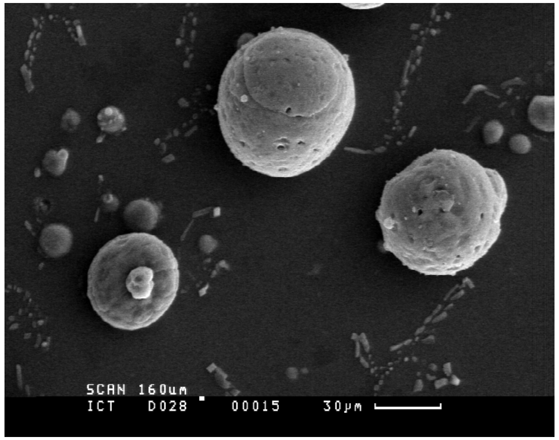
plasticizer	60 - 66% v.B.
TMETN / BTTN	

Energetic solids

Oxidizer: spherical ammonium nitrate
with 0.5 – 0.8% Aerosil
SCAN
160, 55, 20 µm

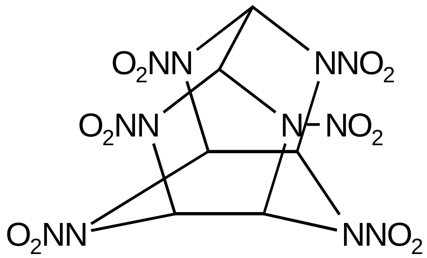
O_2:	+19.99 %
ΔH:	-4567 kJ/kg
d:	1.72 g/cm³
FP:	170 ℃
BP:	210 ℃

NH_4NO_3



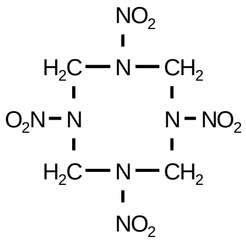
Energetic solids

CL20 3 - 5 µ



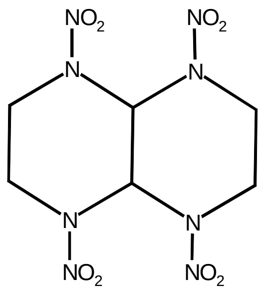
O_2: -10.95 %
ΔH: +920.5 kJ/kg
d: 2.04 g/cm³

HMX 3 - 5 µ



O_2: -21.61 %
ΔH: +283.7 kJ/kg
d: 1.90 g/cm³

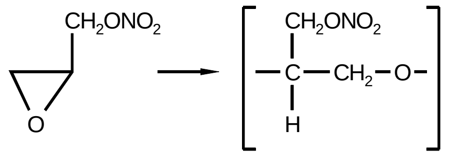
TNAD



O_2: -44.69 %
ΔH: +298.7 kJ/kg
d: 1.84 g/cm³

Energetic Binders

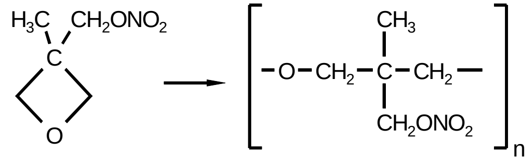
PolyGLYN



Glyn → PolyGlyn

O_2: -60.46 %
ΔH: -2586.1 kJ/kg
d: 1.47 g/cm³

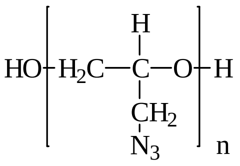
PolyNIMMO



Nimmo → PolyNimmo

O_2: -114.18 %
ΔH: -2101.5 kJ/kg
d: 1.26 g/cm³

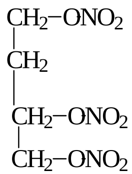
GAP
Glycidylazido - Polymer



O_2: -121.09 %
ΔH: +1150.2 kJ/kg
d: 1.27 g/cm³

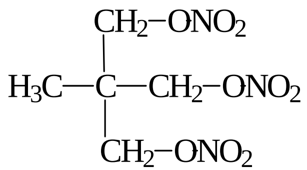
Energetic plasticizers

BTTN 1.2.4-Butantrioltrinitrat



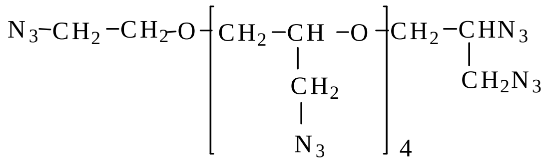
O_2: -16.59 %
ΔH: -1683.9 kJ/kg
d: 1.52 g/cm³

TMETN Trimethylolethantrinitrat



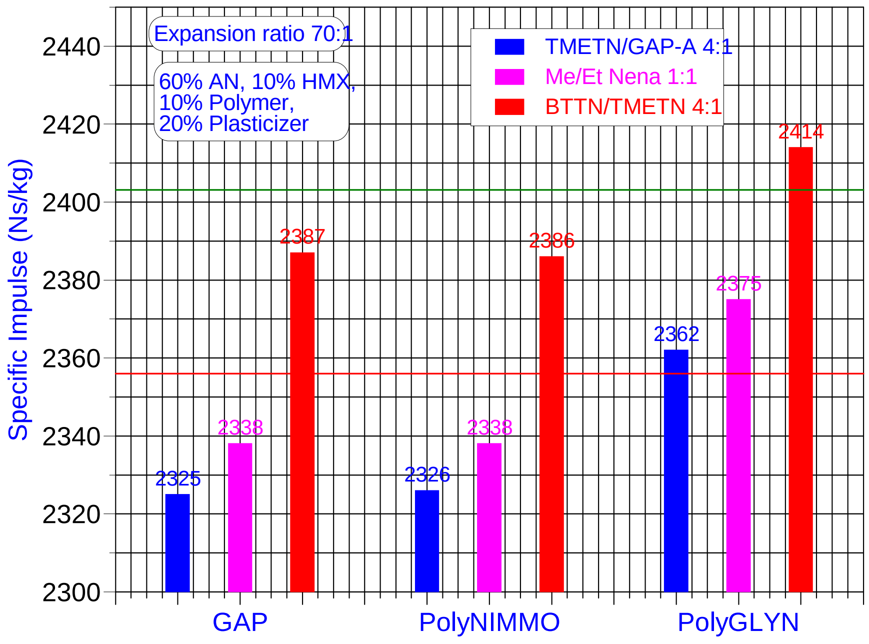
O_2: -34.49 %
ΔH: -1738.3 kJ/kg
d: 1.48 g/cm³

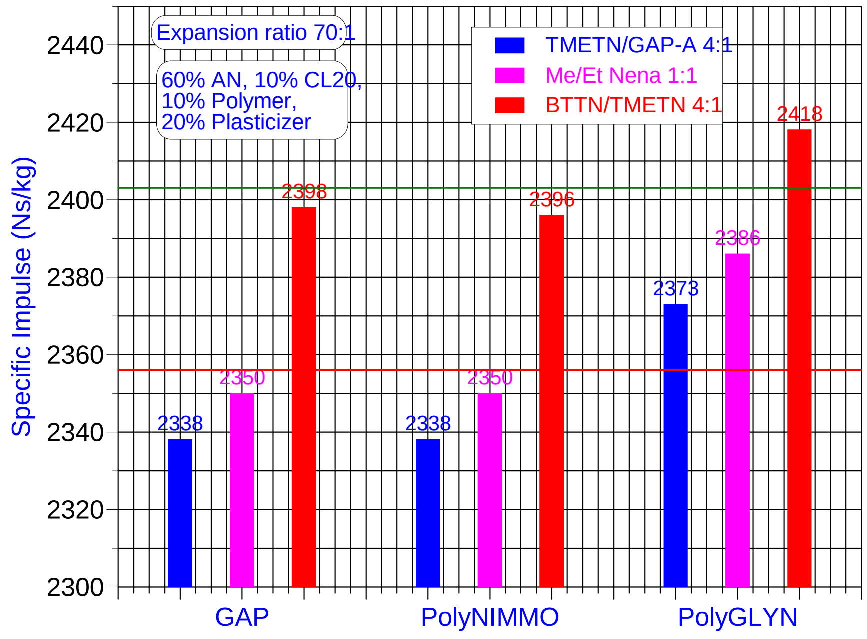
GAP-A Glycidylazidopolymerazid



O_2: -113.28 %
ΔH: +2246.4 kJ/kg
d: 1.27 g/cm³

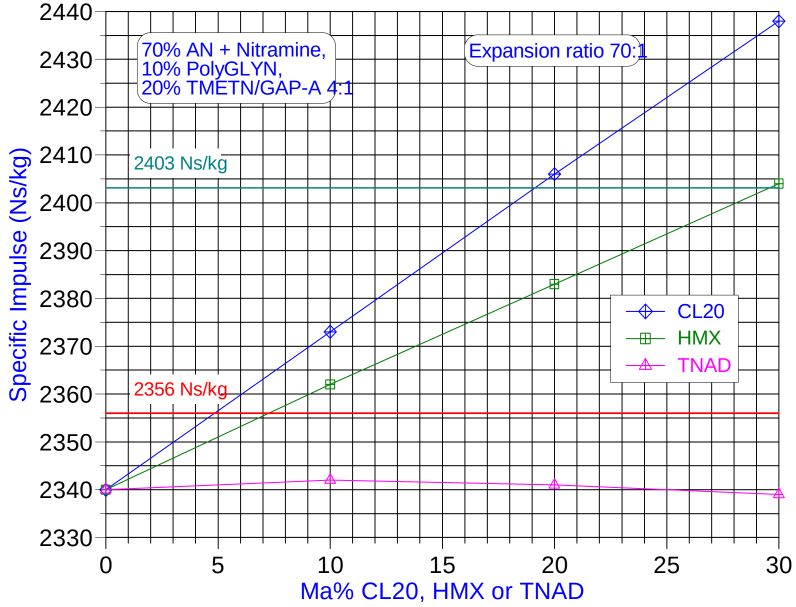
Specific Impulse of AN formulations with energetic binders



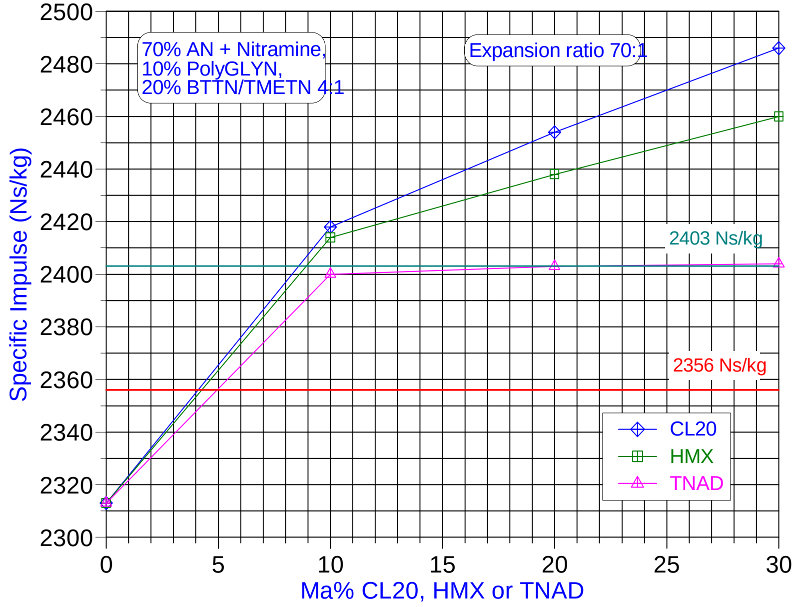


Specific Impulse of AN/PolyGLYN formulations

plasticizer: TMETN/GAP-A 4:1

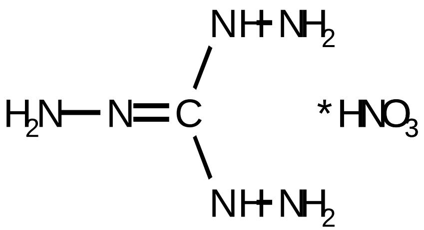


plasticizer: BTTN/TMETN 1:1

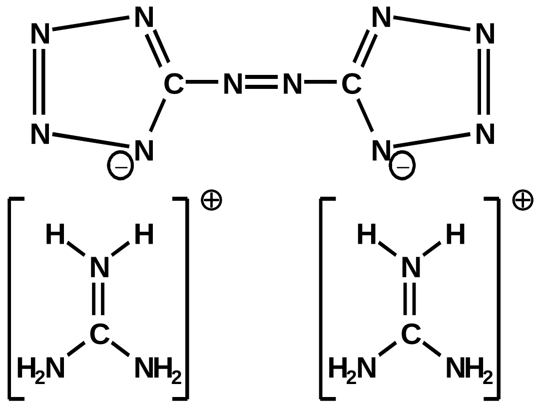


TAGN and GZT - Energetic solids for burn rate modification

Triaminoguanidine nitrate

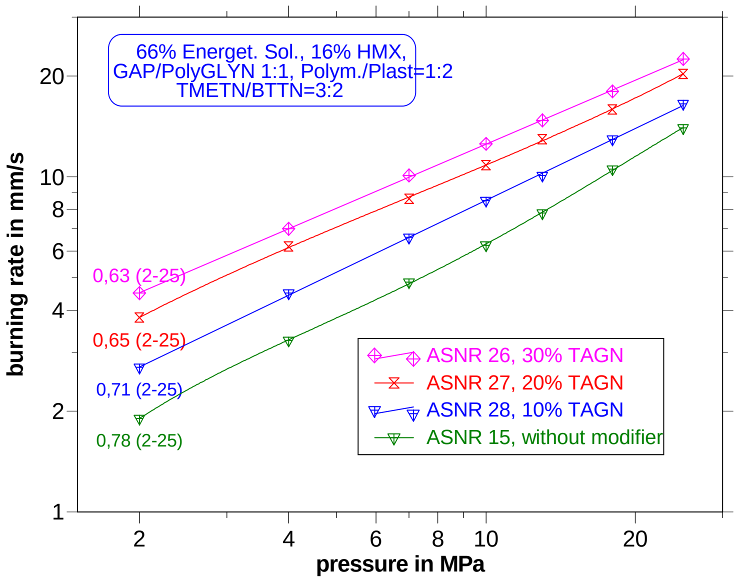


Guanidine -5.5'-azotetrazolate

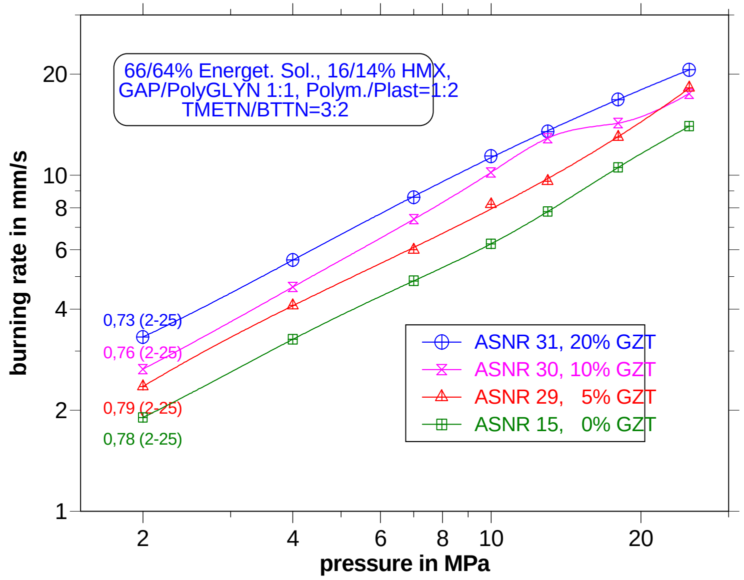


	formula	O_2-bal.	N_2 cont.	Mol weight	density	ΔH_F	Fp Dec.	calc. gas output
		%	%	g/mol	g/cm³	kJ/kg	°C	Nl/kg
TAGN	$CH_9N_7O_3$	-33.51	58.66	167.128	1.58	-287.9	215	1206.3
GZT	$C_4H_{12}N_{16}$	-78.8	78.84	284.246	1.54	+1442.5	240	1103.3

Burn rate enhancement by TAGN and GZT



with 10 - 30%TAGN

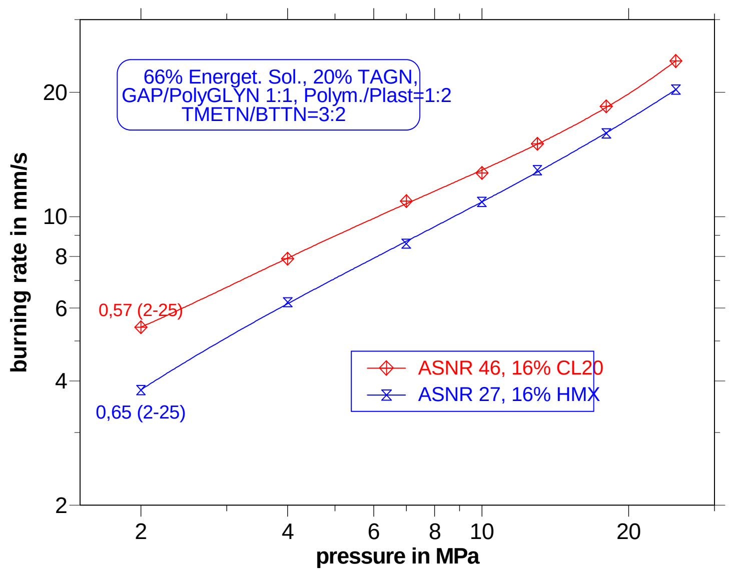


with 5 – 20% GZT

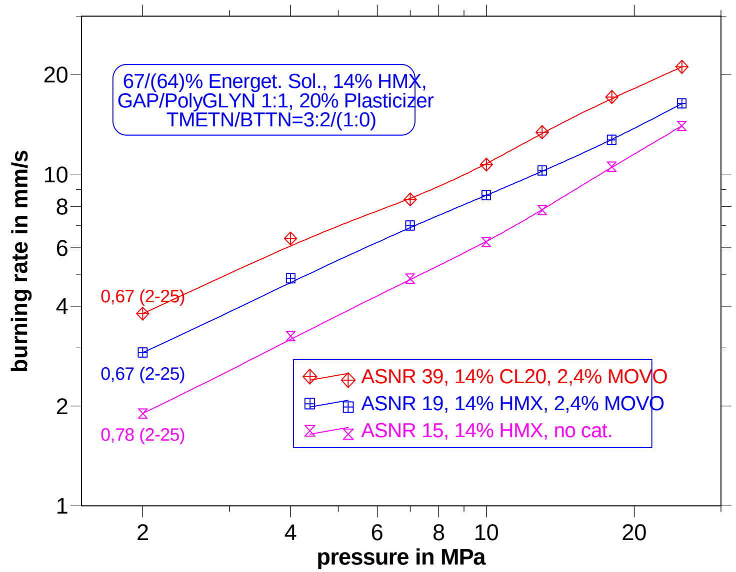
AN/PolyGLYN formulations with TAGN and GZT

ingredients	ASNR 26	ASNR 27	ASNR 28	ASNR 29	ASNR 30	ASNR 31	ASNR 46
AN 160/55/20 um	20	30	40	45	40	30	30
HMX 5 um	16	16	16	16	16	16	
CL20 8 µm							**16**
TAGN 24um	**30**	**20**	**10**				**20**
GZT 25 um				**5**	**10**	**20**	
Gap diol	4.29	4.29	4.29	4.29	4.29	4.29	4.29
PolyGLYN diol	4.56	4.56	4.56	4.56	4.56	4.56	4.56
N100 / Curing agents	2.15	2.15	2.15	2.15	2.15	2.15	2.15
TMETN/BTTN (3:2)	22	22	22	22	22	22	22
DPA	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Carbon Black	0.4	0.4	0.4	0.4	0.4	0.4	0.4
I_{SPEQ} (70:1) (s)	**235.3**	**237.2**	**238.9**	**235.9**	**230.9**	**219.3**	**240.9**
Density (g/cm³)	**1.58**	**1.59**	**1.61**	**1.61**	**1.61**	**1.59**	**1.60**
$I_{SPEQ} * \rho$ (70:1) (Ns/dm³)	3647	3700	3773	3726	3647	3421	3781
Burning rate 7 MPa	**10.1**	**8.6**	**6.8**	**6.0**	**7.4**	**8.6**	**10.9**
Press. exp. (2-25 MPa)	**0.62**	**0.65**	**0.71**	**0.79**	**0.76**	**0.73**	**0.57**

Improvement of burning behaviour by CL20



with 20%TAGN



with 2.4% MOVO

Selected AN/PolyGLYN formulations and thermo-dynamic properties:

with MOVO TAGN. GZT

ingredients	ASNR 114	ASNR 121	ASNR 115	ASNR 108	ASNR 117
SCAN 160. 55. 20 µm	50	50	48	31	44
CL20 3-5 µm	16		16	18	16
HMX ≤ 5 µm		16			
TAGN 20-24 µm				**20**	
GZT 20 µm					**5**
GAP/PolyGLYN/NCO				12	
PolyGLYN/NCO	12.4	12.4	12.4		11.4
TMETN	12	12	12	12	12
BTTN	8	8	8	6	10
MNA /2NDPA	1	1	1	0.6	1
MOVO 6 4 µm			**2.0**		
Carbon black	0.6	0.6	0.6	0.4	0.6
Energ. solids	66	66	64	69	65
Thermodynamic Performance (68.9:1. 1000 psi)					
Specific Impulse (s)	**243.5**	**241.5**	**240.9**	**240.9**	**240.4**
density (g/cm³)	**1.642**	**1.634**	**1.649**	**1.612**	**1.634**
Volum. spec. Impulse (Ns/dm³)	3923	3870	3898	3810	3853
Signature acc. To AGARD	AA	AA	AA	AA	AA

Basic Properties of AN/PolyGLYN propellants:

114: 16% CL20

121: 16% HMX

115: 2% MOVO

108: 20% TAGN

117: 5% GZT

	ASNR 114	ASNR 121	ASNR 115	ASNR 108	ASNR 117
	CL20	HMX	MOVO	TAGN	GZT
Processibility and mechanical properties					
viscosity EOM (Pas)	80	88	80	112	96
Tensile strength (N/mm²)	0.28	0.18	0.17	0.32	0.22
Elongation at break (%)	16.6	26	28	20	30
E-modul (N/mm²)	2.33	0.98	0.86	3.52	1.06
Crawford values 20°C					
Burn rate 7 MPa	7.3	5.1	8.4	11.2	7.8
Pressure exponent n (2-25MPa)	0.63	0.59	0.51	0.49	0.57
Chemical stability					
D.T.(8-72h 105°C) (%)	2.74	2.12	3.86	1.71	3.49
Vac.S. (40h/100°C) (ml/g)	4.04	0.62		6.32	
Flash P. (20°/min) (°C)	182	187	187	178	180
Sensitivity					
impact (Nm)	15	7.5	7.5	10	7.5
friction (N)	144	144	120	72	112
GAP Test (21 mm) (mm PMMA)	**7**	**9**	**9**	**7**	**7**
GAP Test (50 mm) (mm PMMA)					**29**
Correspond. Det. Press. (kbar)					**72**

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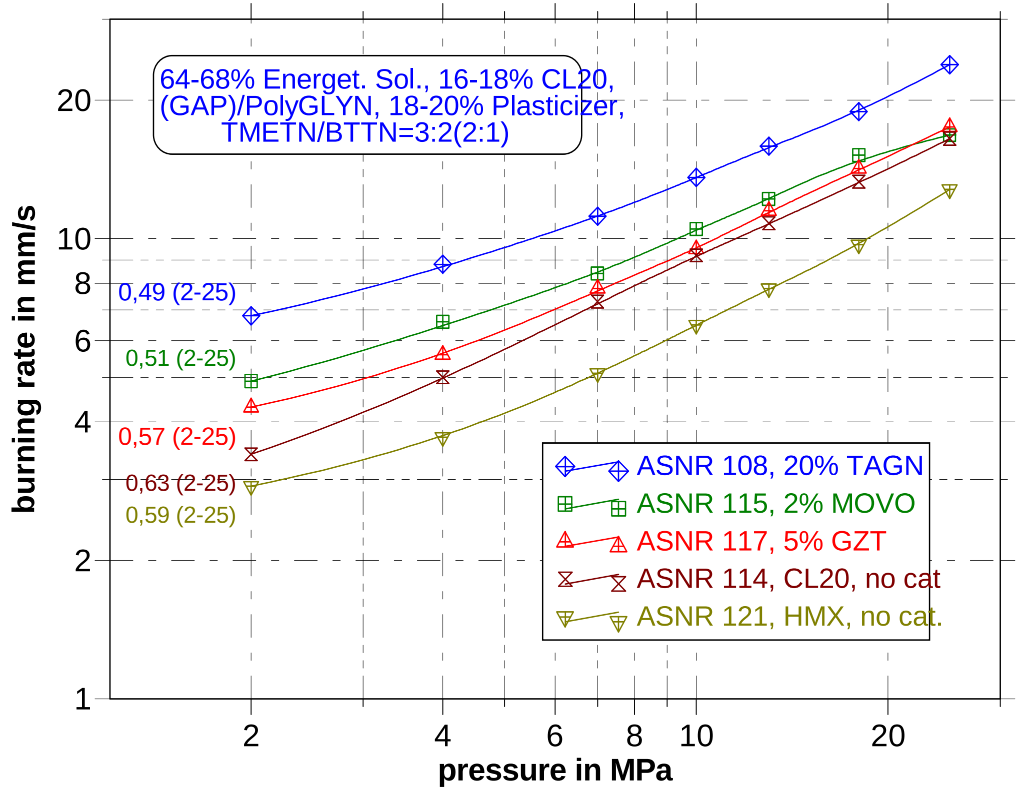
Burning behaviour of AN/HMX and AN/CL20/PolyGLYN propellants incl. :

20%	TAGN
2%	MOVO
5%	GZT
16%	CL20
16%	HMX



Conclusion

1. The AN/PolyGLYN propellants with 16% CL20 and 18-20% BTTN/TMETN fulfill the primary goals of the ASNR TMP group:
   - specific Impulse: $I_{SPEQ} \geq$ 240 s (1000 psi), density d $\geq$ 1.60 g/cm³
   - minimum smoke exhaust signature acc. AA classification
   - detonation sensitivity acc. to hazard classification 1.3, initiation pressure in 50 mm Gap test $\geq$ 70 kbar

2. Without burn rate modifier $I_{SPEQ} \geq$ 240 s at 1000 psi will be achieved by:
   - 16% HMX with PolyGLYN and BTTN/TMETN
   - 16% CL20 with GAP/PolyNIMMO and BTTN/TMETN
   - 16% CL20 with PolyGLYN together with TMETN/GAPA or Me/EtNENA

Conclusion

3. The required burning properties $r_7 \geq 8$ mm/s and $n \leq 0.5$
   - are completely fulfilled by addition of 20% TAGN or 2% MOVO,
   - are partly fulfilled by addition of 5% GZT:

   ASNR 108: 20% TAGN: r_7 = 11.2 mm/s, n = 0.49 (2-25)

   ASNR 115: 2% MOVO: r_7 = 8.4 mm/s, n = 0.51 (2-25)

   ASNR 117: 5% GZT: r_7 = 7.8 mm/s, n = 0.57 (2-25)

4. As detected by vacuum stability tests and microcalorimetrie:
   - chem. stability of formulations with TAGN and PolyGLYN/NE is not sufficient,
   - chem. stability of formulations with GZT and PolGLYN/NE is affected, but still tolerable for application

Conclusion

5. The sensitivity to detonation according to hazard classification 1.3:
   - is fulfilled by formulations with 16% CL20 and 5% GZT or 20% TAGN
   - is affected by formulations with 16% HMX
   - is affected by formulations with 2% MOVO
   - is affected by CL20 $\geq$ 18% and BTTN > 8%

6. AN/CL20/PolyGLYN propellants reflect the limit of performance for less sensitive minimum smoke propellants based on AN and energetic binders – but the property profile for burning behaviour, mechanical properties, chemical stability and service life may still be improved.

7. Minimum smoke propellants with high performance and reduced sensitivity remain a challenge for further propellant development efforts.

Acknowledgement:

Members of ASNR-TMP Group

UK	**Adam Cumming, DSTL**
USA	**John Clark, Edwards AFB**
F	**Yves Longevialle, DGA / SME**
GE	**Reiner Hühn BWB**