Development of Propellants Containing Ammonium Nitrate

W. Engel & K. Menke

Fraunhoferinstitut für Chemische Technologie (ICT)
D 76327 Pfinztal-Berghausen, Germany

ABSTRACT

The phase properties of ammonium nitrate (AN) were investigated using thermal analysis by means of X-ray diffraction for unambiguous results. A series of X-ray diffraction patterns were measured while the samples were heated and cooled and the phases and their transitions occurring on heating and cooling were identified. Rietveld refinement was used to extract structural data from the diffraction patterns. Attempts were made to improve the phase behaviour of AN by incorporating amine complexes into the lattice. The resulting products as well as pure AN were produced in necessary quantities in a pilot plant, as spherical particles for propellant development. Propellant development was carried out with AN, GAP and energetic plasticizers as main ingredients. Thermodynamic calculations revealed that specific impulses of about 235 s could be expected, which was confirmed in the experimental work. The prepared propellants showed acceptable stabilities in the Dutch and the vacuum stability test, when stabilizers selected from the phenylamine family were used. The propellants yielded burning rates up to 8 mm/s and pressure exponents $n < 0.6$. With the 50 mm gap test using PMMA material, results were obtained which meet the insensitive ammunition requirements according to MIL Standard.

NOMENCLATURE

AP	Ammonium perchlorate
AN	Ammonium nitrate
SCAN	Spray crystallized ammonium nitrate
PSAN	Phase stabilized ammonium nitrate
*Ni*PSAN,	Ammonium nitrate stabilized with the
*Cu*PSAN,	*Ni, Cu*
*Zn*PSAN	and Zn complexes
GAP	Glycidyl azido polymer
BTTN	1,2,4-Butanetriol trinitrate
TMETN	Trimethylolethane trinitrate
RDX	Cyclo-1,3,5-trimethylene-2,4,6 trinitramine
DPA	Diphenyl amine
NDPA	Nitrodiphenyl amine
MNA	Methylnitroaniline
PMMA	Polymethyl methacrylate

1. INTRODUCTION

Ammonium perchlorate containing propellants fulfil the present day requirements nearly perfectly. A high specific impulse, high burning rates, good stability, controlled processing with conventional binders, good processability and good mechanical properties are achieved. The search for new propellants is engendered by the demand for smokeless and less sensitive propellants and by ecological requirements calling for *HCl*-free burning. The solution of these problems requires replacing AP by a different oxidiser. Leaving aside substances like ammonium dinitramide, which are not available in the necessary quantities, suitable candidates are found amongst nitrates and nitramines. As using nitramines in large rocket motors means replacing expensive equipment to prevent hazards, nitrates and especially ammonium nitrate are attractive candidates for the near future.

Ammonium nitrate is cheap and available in large quantities. AN-propellants burn without producing *HCl* or other harmful exhaust gases. Besides, they are less sensitive to friction and impact. However, there are drawbacks like its phase transitions under storage conditions, its hygroscopicity, the low burning rates of

AN-propellants and especially the loss of performance compared to AP-propellants. For the solution of these problems, efforts were necessary to reach a better phase behaviour. Catalysts had to be found to improve the burning rates. For improving the' specific impulse, the use of an energetic binder like GAP is generally accepted.

In ICT, special equipment for thermal analysis by means of X-ray diffraction were built up for investigating and improving the phase behaviour of ammonium nitrate. A pilot plant produced the necessary quantities that are used for propellant development. This paper reports the results obtained in the investigation.

2. AMMONIUM NITRATE & ITS PHASE STABILIZATION

2.1 Phase Transitions

AN crystallizes in 5 phases (Table 1). The structurally related phases I, II, IV and V appear on cooling dry AN from the melt after passing through order/disorder transitions. The structurally not related phase III appears only in the presence of water, which helps to nucleate the phase[1,2].

Table 1. Phases of ammonium nitrate

Phase	V^3	IV^4	III^5	II^6	I^7
Crystal System	ortho rhombic	ortho rhombic	ortho rhombic	tetra- gonal	cubic
Stability humid (°C)	<-18	-18/+32	32/84	84/125	125/melt
dry	<-18	-18/+55	-	55/125	125/melt

On heating and cooling, different transition paths are observed depending on water content and maximum temperature[8-11]. Cycling dry AN to 20/150/-50 °C beyond the transition II/I at 125 °C, the expected transition path IV/II/I/II/IV/V is found. With a water content > 0.1per cent, phase III appears at least partially on heating, but not on cooling: IV/III/II/I/II/IV/V. When a maximum temperature below 125 °C is chosen, humid AN shows the transitions IV/III/II/III/IV/V, while with dry AN the transitions IV/II/IV/V are reported.

2.2 Thermal Analysis by means of X-ray Diffraction

The existence of several phases in a relatively narrow temperature range together with the complications caused by the presence of water makes it difficult to get unambiguous results with the normal
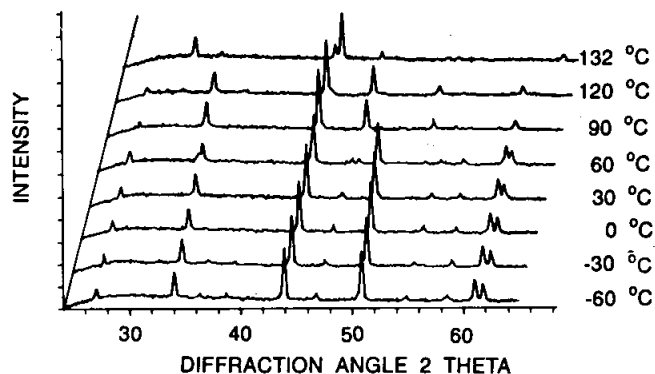

Figure 1. Selected X-ray diffraction patterns of NiPSAN-samples measured with copper radiation from -70 to 150 °C.

methods of thermal analysis like DSC and DTA, as these methods report thermal effects without identifying the occurring phases. For obtaining unambiguous results, a measuring system was built up combining Siemens X-ray diffractometers D500 and D5000 with heating/cooling devices allowing automated time and temperature-resolved X-ray diffraction measurements that can be used for thermal analysis by means of X-ray diffraction. The system is described in detail elsewhere[12,13]. The series of diffraction patterns measured during temperature programs of 20/150/-70/150 and 20/100/-70/100 °C identify the phases occurring during the transitions at determined temperatures. Fig. 1 presents selected patterns of such a series.
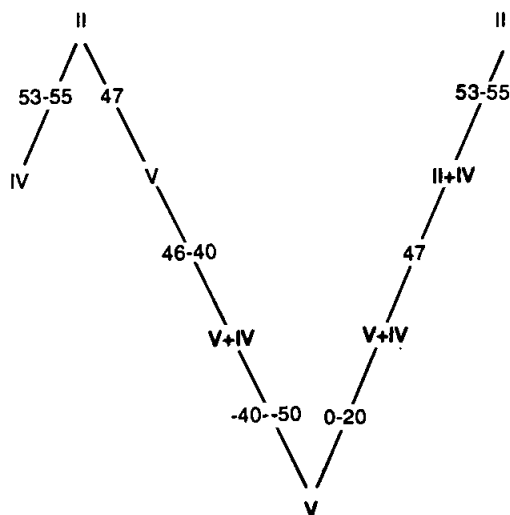

Figure 2. Transitions of AN cycled from 20/100/-70/100 °C.

The results confirmed the earlier findings reported in the literature, when a dry sample was heated to 150 °C and cooled to -50 °C. The transition path included the transitions IV/II/I/II/IV/V (Fig. 2). Heating the sample to 100 °C, the transitions IV/II/V+IV/V/V+ IV/II+IV/II were observed. The hitherto unknown sequence means that on cooling, phase II changes into V followed by a partial transition into IV at about 47 °C. The complete transition into phase V occurs below -40 °C. On reheating, a part of it changes into phase IV at about 0 °C. Phase V in the resulting mixture V/IV changes into II at 47 °C, whereas the part of phase IV shows the known transition into phase II at 55 °C[14]

Humid ammonium nitrate, on heating, follows the transition path IV/III/II/I known from literature. On cooling, the phase sequence depends on the rate of cooling. With a rate above 1-2 °C/min, the sample reaches a temperature below 45 °C and changes into phase IV, before phase III nucleates, whereas, on keeping the temperature between 75 and 50 °C for about 30-60 min, the appearance of phase III was realised.

2.3 Improvement of the Phase Properties

With the tools available for an unambiguous identification of phases and its transitions, attempts were made for improving the phase properties of AN. Literature contained information on the stabilization of phase III by KNO_3[5,16] and of phase II by $CsNO_3$[7]. The data were used for elaborating a working hypothesis, concluding that smaller cations stabilize phase III, whereas with larger cations, phase II is favoured. Instead
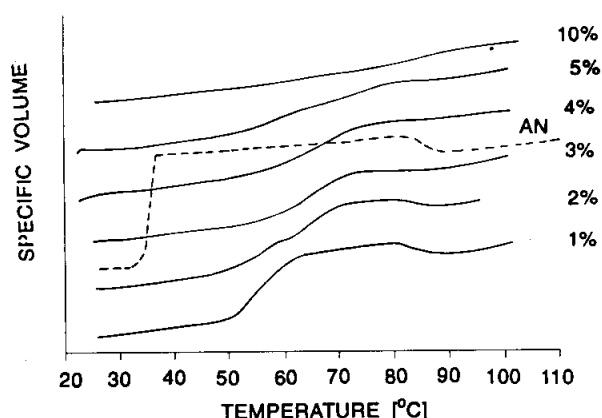
Figure 3. Thermal expansion curves of NiPSAN (1-10% Ni-oxide) compared to humid AN.

of the cesium ion, which was not available in larger quantities, diamine complexes of nickel, copper and zinc were incorporated into the ammonium nitrate lattice. The results showed that the nickel complex extends the stability of phase IV, whereas the phases II/V are favoured with the copper and zinc complexes[14]. Expansion curves of NiPSAN samples are shown in Fig. 3.

Investigations are being carried out to extract more structural details on the lattice dynamics from the measured X-ray diffraction series by Rietveld refinement. Fig. 4 shows the curves of the volumetric expansion of the various phases obtained in this way.

2.4 Production of Ammonium Nitrate for Propellant Development

Along with the investigation and the improvement of the phase properties, attempts were made to produce ammonium nitrate in sufficient quantities for propellant development. For a good processability, spherical particles are favoured for incorporating AN into propellants. A suitable way was found for atomizing AN from the melt. The procedure for producing Spray Crystallized Ammonium Nitrate (SCAN) was established so that particles from 300 to 20 μm size can be produced. With this range, bimodal mixtures can be formed for incorporation into the binder.

The procedure was modified so that materials phase stabilized with the diamine complexes (PSAN) mentioned above can also be produced in the necessary quantities. The following materials are available:

AN pure	SCAN
NiPSAN	AN containing 1-7 % Ni_2O_3
CuPSAN	AN containing 1-7 % CuO
ZnPSAN	AN containing 1-7 % ZnO
AN/KNO_3	AN containing 1-7 % KNO_3
AN/$CsNO_3$	AN containing 1-12 % CsNO3

3. PROPELLANT DEVELOPMENT

3.1 Objectives

The objectives of the development were: a) high performance: $I_{sp} \geq 240$ s at 7 MPa b) low sensitivity to
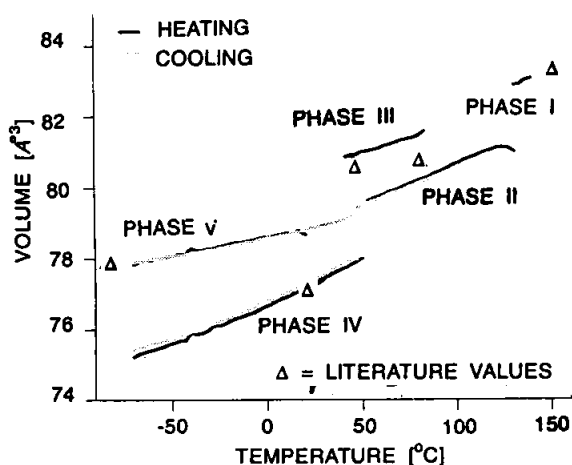
Figure 4. Thermal expansion curves of AN measured by X-ray diffraction and evaluated by Rietveld refinement.
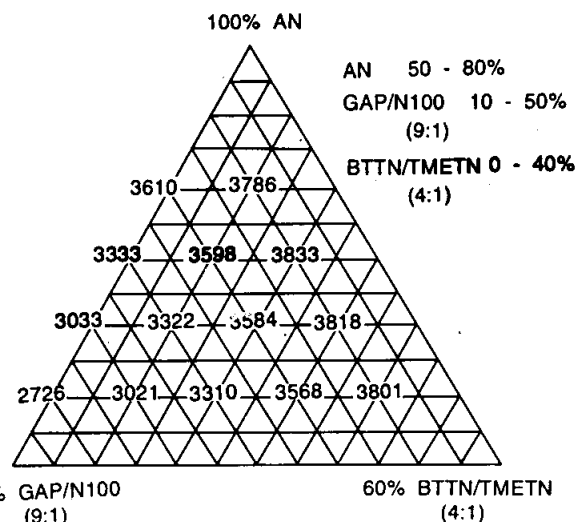

Figure 6. Calculated volumetric specific impulse of AN/GAP/BTTN/TMETN-formulations (70:1).

detonation c) smokeless combustion without polluting exhaust d) acceptable burning properties and (e) good stability, processability and good mechanical properties.

A number of papers have appeared on ammonium nitrate propellants including those containing energetic binders and plasticizers. However, generally, low performance, insufficient stability and unacceptable burning properties are reported[18-22]. Our efforts are aimed to improve the results using SCAN and PSAN of

different particle sizes as oxidizer, GAP as an energetic binder and BTTN/TMETN as energetic plasticizers.

3.2 Thermodynamic Performance Calculations

The investigations were started with thermodynamic calculations to find out promising formulations. In literature, it is reported that high specific impulses (I_{sp}) are achieved with nitrate ester plasticizers, BTTN/TMETN being amongst those with the highest energies and compatibilities with GAP. Therefore, calculations were performed with the system AN/GAP+N100/BTTN+TMETN (4:1) with 50-80, 10-50 and 0-40 weight per cent, respectively. The results of the specific impulse and of the volumetric specific impulse with a 70 : 1 expansion ratio are presented in the Figs. 5 & 6. The corners of the triangles shown represent the following values in weight per cent:
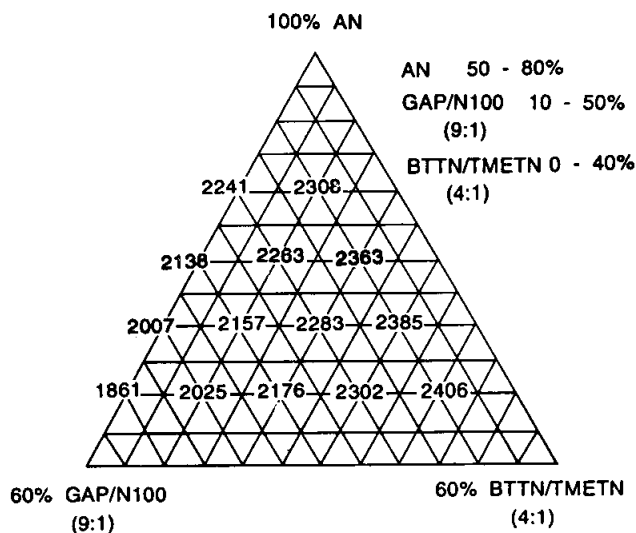
AN	GAP/N100	BTTN/TMETN
40	60	0
100	0	0
40	0	60

Figure 5. Calculated specific impulse of AN/GAP/BTTN/TMETN-formulations (70:1).

The calculations reveal that specific impulses of 240 s are reached only with a high plasticizer content. The maximum of the volumetric specific impulse
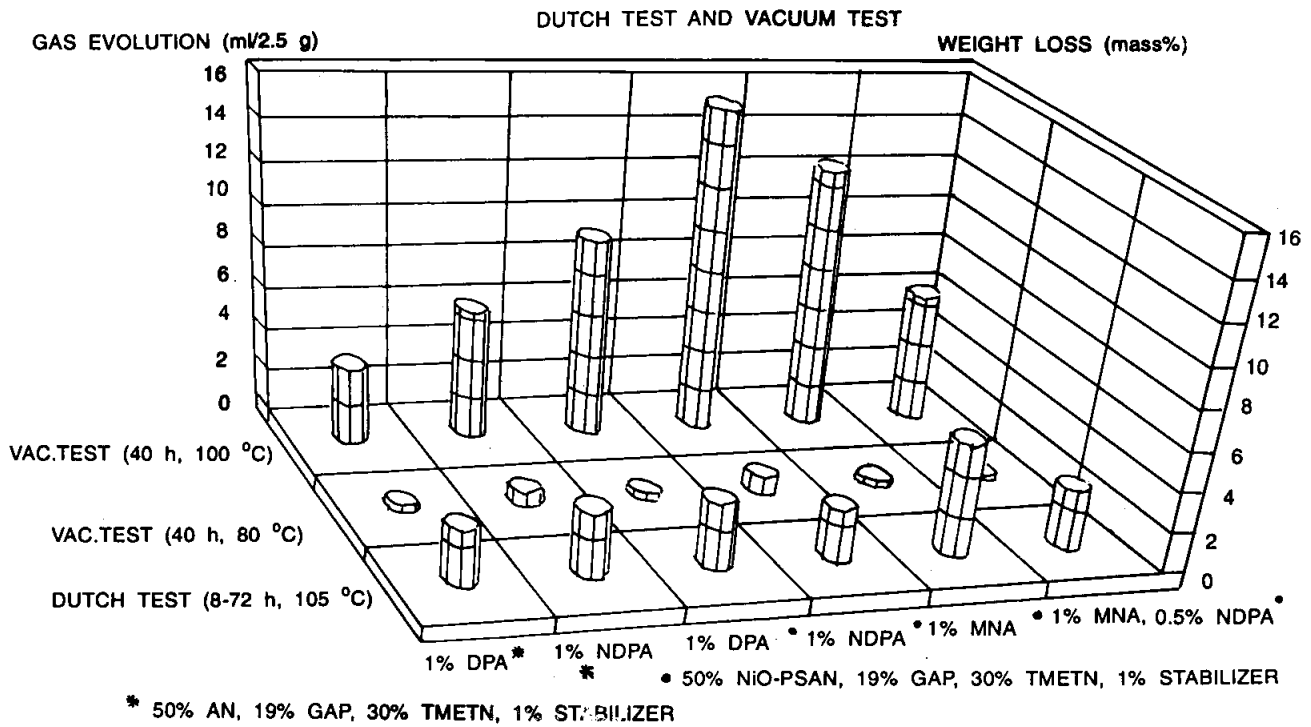
DUTCH TEST AND VACUUM TEST

GAS EVOLUTION (ml/2.5 g)   WEIGHT LOSS (mass%)

Figure 7. Dutch test and vacuum stability values of SCAN and NIPSAN/GAP formulations with different stabilizers.

DUTCH TEST AND VACUUM TEST

GAS EVOLUTION (ml/2.5 g)   WEIGHT LOSS (MASS%)

*0.5% NDPA AS STABILIZER
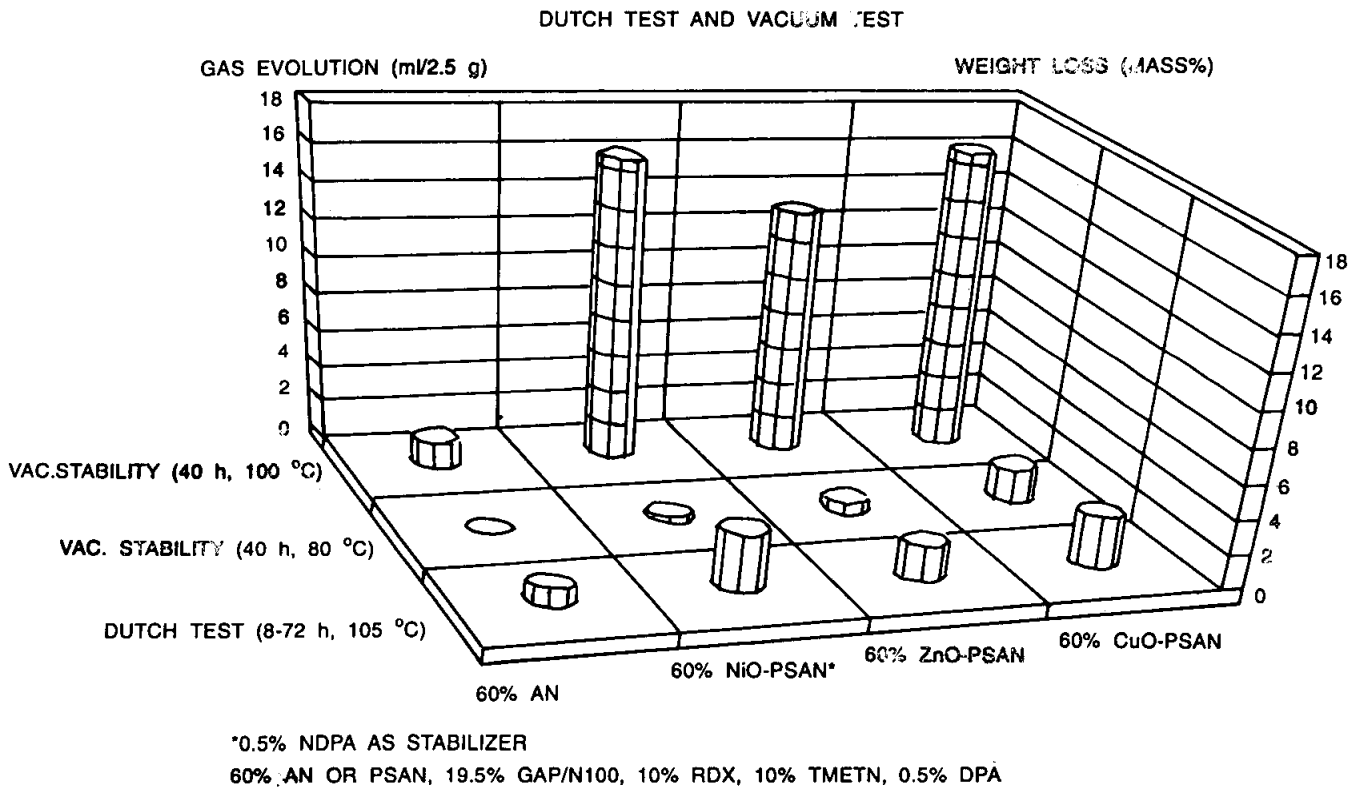60% AN OR PSAN, 19.5% GAP/N100, 10% RDX, 10% TMETN, 0.5% DPA

Figure 8. Dutch test and vacuum stability values of SCAN and PSAN/GAP formulations with DPA and NDPA as stabilizers.

315

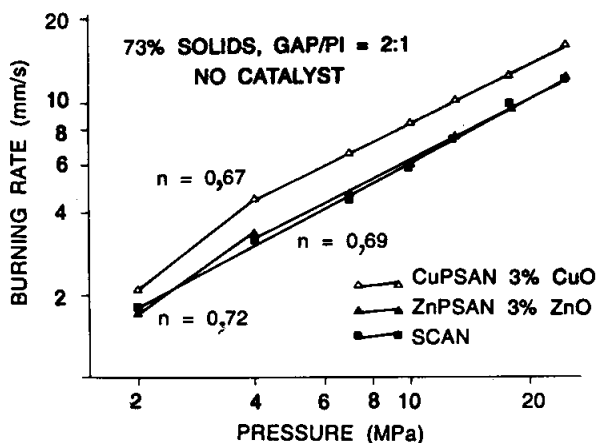Figure 9. Burn rate *vs.* pressure curves for AN and PSAN/GAP propellants without catalyst, I_{sp} = 210-214 s (70:1).

Figure 10. Burn rate *vs* pressure curves for CuPSANand ZnPSAN/GAP propellants with 10% RDX and 2.5% catalyst, I_{sp} = 224-227 s (70:1).

achieved with 70 per cent AN, 10 per cent GAP and 20 per cent BTTN/TMETN is 3810 Ns/dm^3. The corresponding weight related specific impulse amounts to 239.9 s. Taking into account stabilizers and catalysts, the specific impulse for the calculated system should not surpass 235 s with a 70:1 expansion ratio.

3.3 Chemical Stability

The chemical stability was tested with the Dutch Test, which prescribes that the weight loss should not exceed 3 per cent during storage at 105 °C between 8 and 72 hr. The vacuum stability test requires that a 2.5 g sample should not produce more than 5 cc gas at 100 °C or 0.1-1 cc gas at 80 °C. For achieving this goal, a number of stabilizers were tested in SCAN- and NiPSAN/GAP/TMETN formulations. The results are summarized in Figs. 7 & 8 which show that the formulations with SCAN are the only ones that fulfil the requirements of the vacuum stability at 100 °C. The formulations with PSAN pass the test at 80 °C with the exception of CuPSAN. Amongst the stabilizers tested, DPA shows higher efficiency compared to MNA and NDPA.

3.4 Combustion Properties

High burning rates and low pressure exponents are not reported in literature for AN-propellants using energetic binders. Our first tests with propellants containing 73 per cent solids and GAP/TMETN in the ratio of 2:1 without catalyst also exhibited a high pressure exponent $n > 0.6$. The burning rates in Fig. 9
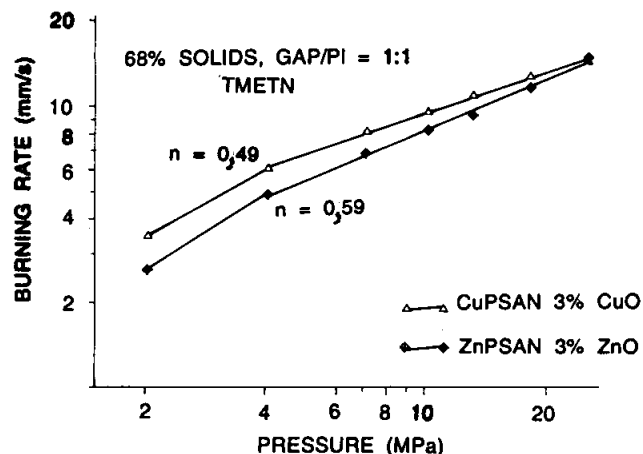
showed an enhanced effect for CuPSAN. Burning rates increased by 10-20 per cent on addition of small particle size RDX together with 3 per cent lead salt and carbon black. A significant improvement was found by using an optimized AN particle size distribution together with a transition metal catalyst, when pressure exponents $n < 0.6$ and burning rates from 7-8 mm/s at 7 MPa were obtained. Fig. 10 shows that the best results were obtained with CuPSAN, reducing the pressure exponent
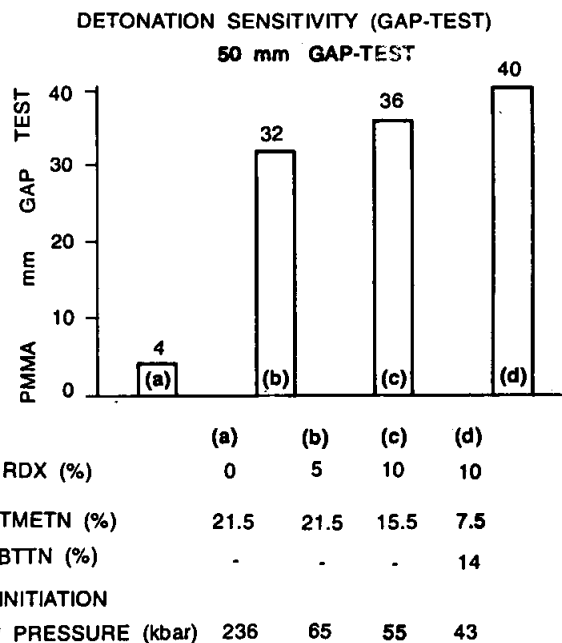

	(a)	(b)	(c)	(d)
RDX (%)	0	5	10	10
TMETN (%)	21.5	21.5	15.5	7.5
BTTN (%)	-	-	-	14
INITIATION				
• PRESSURE (kbar)	236	65	55	43

Figure 11. Results of 50 mm gap tests for AN/GAP-propellants with varying amounts of 5 μm RDX and TMETN/BTTN plasticizer.

n to 0.49 and increasing the burning rate to 8 mm/s at 7 MPa. With an increased plasticizer content and a GAP/plasticizer ratio of 1:1 together with 10 per cent RDX and 68 per cent AN, these propellants attain a specific impulse of 226-229 s.The specific impulse was further increased to 235 s with a GAP/plasticizer ratio of 1:2.15 without using RDX, when for a good stability SCAN was used, while good burning properties with rates of 7-8 mm/s at 7 MPa and pressure exponents n between 0.52 and 0.58 could only be maintained by further optimization.

3.5 Sensitivity to Detonation

One of the most promising potentials of AN/GAP propellant is its low sensitivity suggesting its use for insensitive ammunition requirements. According to MIL-STD 2105, the detonation sensitivity should be below 70 cards in the 40 mm gap test as per US and UN standards. These requirements correspond roughly to 28 mm gap thickness in the 50 mm gap tests with PMMA material, as they were performed at an early stage of the development.

The results presented in Fig. 11 demonstrate that only propellants without RDX meet the requirements for insensitive ammunition, whereas propellants with smaller amounts of RDX fail.

4. CONCLUSION

The results show that the specific impulse of 235 s estimated in the thermodynamic calculations can be reached, when a high GAP/plasticizer ratio of 1:2.15 is used. Pressure exponents $n < 0.6$ and burning rates of 7-8 mm/s can only be achieved with an efficient catalyst supported by a suitable choice of AN particle size distribution. The enhancing effect of *Cu*PSAN and *Ni*PSAN on the burning rates is accompanied by a less favourable effect on the stability of the propellants.The stability tests, however, are passed with SCAN and stabilizers DPA, NDPA and MNA. Besides, the formulations without RDX pass the requirements for insensitive ammunition. Taking into account the tested properties, a system with 65 per cent AN, 10 per cent GAP, 21.5 per cent TMETN/BTTN and an efficient burn rate catalyst offers a good base for further development.

ACKNOWLEDGEMENT

REFERENCES

1. Hendricks, S.B.; Posnjak, E. & Kracek, F.C. The variation of ammonium nitrate with temperature.*J. Amer. Chem. Soc.* (1932),54, 2766.

2. Bowen, N.L. Properties of ammonium nitrate. *J. Phys. Chem.*, 1926,30, 721.

3. Ahtee, M.& Smolander, K.J. Low temperature behaviour of ammonium nitrate by neutron diffraction. *Acta Cryst.*, 1983, B39, 685-87.

4. Choi, C.S.& Mapes, J.E. The structure of ammonium nitrate (IV). *Acta Cryst.*,1972, B28, 1357.

5. Lucas, B.W. The sructure of phase III ammonium nitrate. *Acta Cryst.*, 1980, B36, 2005-08.

6. Lucas, B.W. The crystal structure of phase II ammonium nitrate. *Acta Cryst.*, 1979, B35, 1038-41.

7. Ahtee, M.& Kurki-Suonio, K. Determination of molecular orientations in cubic ND4NO3 by multipole analysis. *Acta Cryst.*, 1979, A35, 591-97.

8. Griffith, E.J. Phase transitions of the ammonium nitrate-magnesium nitrate system. *J. Chem. and Eng. Data*, 1963, 8, 22.

9. Heide, K. Thermische untersuchungen am ammoniumnitrat. *Z. Anorg. Chem.*, 1966, 344, 241.

10. Brown, R.N.& McLaren A.C. On the mechanism of the thermal transformations in solid ammonium nitrate. *Proc. Royal Soc.*, 1962, 266A, 329.

11. Sowell, R.R; Karnowsky, M.M. Walters, L.C. The transitions in phases II-III-IV in high purity ammonium nitrate. *J. Therm. Anal.*, 1971, 3, 119-29.

12. Ingman, J.S.; Kearley G.J.& Kettle, S.F.A. Optical and thermal studies of transitions between phases II, III and IV of ammonium nitrate. *J. Chem. Soc., Faraday Trans.*, 1982, 78, 1817- 26.

13. Engel, W.& Eisenreich, N. Time resolved X-ray diffraction of ammonium nitrate during temperature cycling. *Proc. of the Annual Technical Meeting of the Institute of Environmental Sciences*, 1986, 145-47.

14. Eisenreich, N.& Engel, W. Kinetic study of the solid phase reaction of ammonium nitrate and copper oxide by the use of fast X-ray diffraction. *J. Therm. Anal.*, 1989, **35**, 577-84.

15. Engel, W. *et al.* Ammonium nitrate, a less polluting oxidizer. Proceedings of the 24th International Annual Conference, Institut fur Chemische Technologie, Karlsruhe, 1995.

16. Campbell, A.N.& Campbell, J.R. The effect of a foreign substance on the transition, AN IV/AN III. *Canad. J. Res.*, 1946, **24**,93.

17. Cady, H.H. The ammonium nitrate-potassium nitrate system. *Propellants & Explos.*, 1981, **6**, 49.

18. Morand, J. Contribution a l'Etude du Nitrate d'Ammonium. *Ann Chimie, Ser. 12*, 1955, **10**, 1018.

19. Doll, P.W.& Lund, G.K. High performance, low cost solid propellant compositions producing halogen-free exhaust. US-Patent 5, 076, 868., 1991.

20. Helmy A.M. GAP propellant for gas generator application. 23rd AIAA J. Propulsion Conf., San Diego, 1987.

21. Lessard, P. *et al.* Development of a minimum smoke propellant based on GAP and AN. 78th Special Meeting, 1991. AGARD-CP511.

22. Longevialle, *et al.* Low vulnerability minimum smoke rocket propellants. ADPA Conference on Energetic Materials Technical Meeting 680, 1995, p. 125.

23. Bivin, R.L. Development of a class 1.3 minimum smoke popellants. 28th AIAA J. Prop. Conf., Nashville, 1992.