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Development of Energetic Additives for Propellants in China

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The development of energetic azide binders and plasticizers for solid propellants in China is described in this article. Fourteen representatives of azides synthesized mainly by the authors on a small laboratory scale are involved. The reaction routes and conditions for preparing these azides are summerized; performance of the azides, including density, melting point, enthalpy of formation, thermal decomposition temperature determined by differential scanning calorimetry or differential thermal analysis, impact sensitivity, etc, were tested and are presented. The application of these azides to solid propellants or plastic-bonded explosives is still comparatively new in this country, with very little information available at the present time. A few results are briefly mentioned in this article. We arrange the stated azides under the following six categories: 1) azide polyether: glycidyl azide polymer ($[C_3H_5N_3O]_n$, the homopolymer of 3,3-bis(azidomethyl) oxetane ($C_5H_8N_6O$) (BAMO), and the copolymer of BAMO/tetrahydrofuran (C_4H_8O); 2) Azidonitramine: 1,5-diazido-3-nitrazapentane, *N*-nitro-N-azidomethylgemdinitroethyl methylamine, and *N,N'*-bis(azidomethylgemdinitroethyl)ethylenedinitramine; 3) Azidonitro compounds: 2-nitro-2-methyl-1,3-diazidopropane, 2-nitro-2-azidomethyl-1,3-diazidopropane, and 1-azido-2-(2,4,6-trinitrophenyl)ethane; 4) aliphatic azide: 1,2,4,triazidobutane and tetraazidomethylemethane; 5) Azidonitrate: pentaerythritol diazido dinitrate; and 6) oxygen heterocyclic azide: 3-azidomethyl-3-ethyloxetane, and 2,2-dimethyl-5-azidomethyl-5-nitro-1,3-dioxane.

Nomenclature

A = pre-exponential factor
A_e = nozzle exit area
A_t = nozzle throat area
E = observed activation energy
I_{sp} = specific impulse in vacuum
I_{ss}^0 = standard theoretical specific impulse
$\bar{M}_n$ = number-averaged molecular weight
$\bar{M}_w$ = weight-averaged molecular weight
n_D^{20} = refractive index at 20°C
P_c = chamber pressure
P_e = nozzle exit pressure
Q = heat of explosion (constant volume, liquid water)
R = expansion radius of outside wall of cylinder
$R - R_0$ = diametral expansion distance
R_0 = outside radius of cylinder before expansion
T_{ch} = chamber temperature
T_d = decomposition temperature
T_g = glass transition temperature
T_m = exothermic peak temperature on differential scanning calorimetry curves
T_v = explosion temperature
ΔH_f^0 = standard enthalpy of formation
ΔI_{ss}^0 = gain in standard theoretical specific impulse
ε_b = elongation at breaking
η = viscosity
ρ = density
ρ_t = crosslink density
σ_m = tensile strength

Introduction

THE use of energetic additives, mainly binders and plasticizers, is considered to be one of the practical ways to improve the energy level and other technical performances of solid propellants and gun propellants. Organic azides are attracting researchers' attention more and more in this aspect. Since the 1970s, organic azides as energetic binders or plasticizers for advanced solid propellants have been extensively studied in many countries.[1–15] Organic azides possess a number of advantages.[16,17] Replacement of binders and/or plasticizers presently in use with energetic azides, including those containing other energetic groups, cannot only make a significant energy contribution to propellants, but can also reduce or minimize the amount of flame and smoke in the exhaust gases generated during the propulsion phase of solid propellants. Therefore, azides are suitable ingredients for minimum-signature propellants. During the past two decades, a large number of organic azides that can, or might, find applications in propellants or plastic-bonded explosives (PBXs) have been synthesized and examined. They include azido polyether, azidonitramine, azidonitro compound, azidoalkane, azidoether, azidoester, etc. Some of them are discussed in Refs. 1–15. To illustrate the energy contribution of azides to the propellant system, consider glycidyl azide polymer ($[C_3H_5N_3O]_n$) (GAP) as an example. GAP, as an important binder, has been and is being extensively investigated in a number of countries, including China. Very high specific impulse propellants composed of GAP, hydrazinium nitroformate ($N_2H_5C(NO_2)_3$) (HNF), and aluminum have been proposed.[18] Calculation shows that when P_c = 10 MPa and A_e/A_t = 100, the maximum specific impulse in vacuum (I_{sp}) at equilibrium flow of 59% HNF/21% Al/20% GAP propellant was 215.5 N·s/kg higher than that of 76% AP/13%Al/11% hydroxyl-terminated polybutadiene (HTPB) propellant.[18] Feng et al.,[19] from our institute, calculated the energy contribution of azido prepolymers (binder) to the ammonium perchlorate (NH_4ClO_4)/cyclotrimethylene trinitramine ($C_3H_6N_6O_6$) (AP/RDX)/Al/binder composite propellants based on the minimum free energy method. Several results are summarized in Table 1.

The azido prepolymers can also be used in nitro ester plasticized polyether (NEPE) propellants to enhance I_{ss}^0 without causing difficulties of compatibility.[19]

As stated above, energetic ingredients (including binders and plasticizers) used in formulating solid propellants, gun propellants, or explosives increase energy levels and appear to be the emerging tendency for the next generation of high-

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Table 1 Theoretical maximum performances for selected composite propellants

Composition[a]	P_c, MPa	Expansion ratio, P_c/P_e	I^0_{ss}, N·s/kg	ΔI^0_{ss}, N·s/kg	$\Delta I^0_{ss}\cdot\rho$, N·s/dm^3
45% AP, 25% RDX, 18% Al 8.82% HTPB, 1.8% IPDI, 2% DBP[b]	6.86	70	2618.6	0	0
20% AP, 50% RDX, 18% Al 8.82% GAP, 1.18% IPDI, 2% DBP	6.86	70	2675.6	57	256.9
20% AP, 50% RDX, 18% Al 8.82% BAMO, 1.18% IPDI, 2% DBP	6.86	70	2673.9	55.3	253.9
30% AP, 40% RDX, 18% Al 8.82% AMMO, 1.18% IPDI, 2% DBP	6.86	70	2657.3	38.7	108.8

[a] With this composition, the maximum I^0_{ss} is achieved for each type of binder.
[b] Dibutyl phthalate ($C_{16}H_{22}O_4$).

Table 2 Main properties of PECH and GAP

Property	PECH	GAP	Test method
$\bar{M}_n$	2628 (VPO)	2600 (VPO)	Vapor pressure osmometer (VPO)[a] and gel permeation chromatography (GPC)[b]
$\bar{M}_w$	2220 (GPC) 2884 (GPC)		
$\bar{M}_w/\bar{M}_n$	1.30 (GPC)		Rotating cylinder viscometer
η(30°C), Pa·s	11.0	2.5	Differential scanning calorimeter (DSC)[c]
T_g, °C		−41.0	
T_d, °C			
Onset	170 (DTA) 221 (DSC)		Differential thermal analysis (DTA)[d] and DSC[e]
End	179 (DTA) 224 (DSC)		
Impact sensitivity, %		0	4-kg drop hammer, 50-cm drop height, 25-mg sample, and 25 runs
Friction sensitivity, %		0 0	80 deg, 2.05 MPa, 32-mg sample, and 25 runs, 66 deg, 4 MPa, 26-mg sample, 25 runs

[a] Parameters for VPO: solvent $CHCl_3$, standard dibenzoyl, temperature 35 ± 0.1°C.
[b] Parameters for GPC: solvent tetrahydrofuran (THF), standard polystyrene (PS), flow rate 1 ml/min, chart speed 5 mm/min.
[c] Parameters for DSC: rate of heating 10°C/min, 27.80-mg sample.
[d] Parameters for DTA: rate of heating 10°C/min, chart speed 5 mm/min, 12.85-mg sample.
[e] Parameters for DSC: rate of heating 10°C/min, 16.80-mg sample.

energy/density materials (HEDMs). The main purposes of our synthetic research are 1) to find novel families of organic azides and methods of preparing them, 2) to provide an improved technology for producing the organic azides that have appeared in literature, 3) to test and examine the newly synthesized azides in order to select the most promising ones, and 4) to provide a certain amount of samples for the application investigations carried out at another laboratory in our institute.

More than 50 organic azides have been synthesized in our laboratory since 1980. We describe here 14 representative azides for the purpose of discussion and the opinions and suggestions of experts.

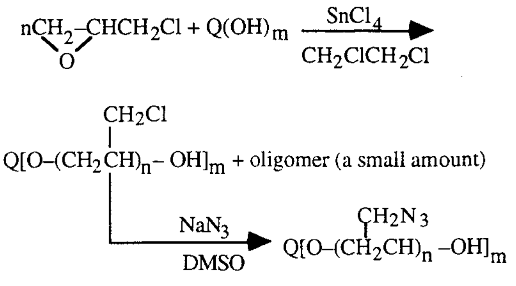
Azido Polymer

GAP (I_1)

GAP has been one of the most attractive energetic binders used for solid propellants, gun propellants, and explosives,[20] because it offers a number of advantages.[16,21] In 1981, Frankel et al.[22] successfully prepared GAP with a molecular weight of about 3000 and functionality of about 2. GAP was first reported at the 1982 ICT conference.[23] Since then, it has been extensively investigated as an energetic ingredient of solid propellants and gun propellants.[12,24–35] Recently, Ahad[36] reported that a branched hydroxyl-terminated GAP can be prepared by degradation of epichlorohydrin (C_3H_5OCl) (ECH) rubber with a molecular weight of about 10^6, followed by reaction of the degraded polymer with sodium azide in an appropriate solvent. Compared with GAP prepared by the conventional procedure, GAP obtained in this manner has a narrower molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.220), a higher functionality of 6.9–11.0, a lower glass-transition temperature (−65°C), and a lower viscosity.

The preparation, characteristics, and applications of GAP to solid propellants and plastic PBXs have been the subject of a study in China for several years.[37–39]

Hydroxyl-terminated GAP was prepared at one laboratory via a two-step procedure[39] [see Eq. (1)]. The first step is the cationic ring-opening polymerization of ECH that yields epichlorohydrin polymer ($[C_3H_5OCl]_n$) (PECH). The polymerization was carried out at 30°C in 1,2-dichloroethane using 1,3-propanediol as the initiator and anhydrous stannic chloride as the catalyst. The second step is the nucleophilic substitution reaction of PECH with sodium azide in dimethyl sulfoxide (C_2H_6OS) (DMSO). This reaction procedure was performed at 95°C for 72 h. The effects of initiators, catalysts, solvents, reaction time, and reaction temperature on PECH's quality are discussed in detail in Ref. 39:



(I_1)

where Q = $—CH_2CH_2CH_2—$ (1)

The prepared PECH and GAP were identified by infrared (IR), ^{13}C nuclear magnetic resonance spectroscopy (NMR), mass spectroscopy (MS), and elemental analysis, and some of the properties determined are shown in Table 2.

The GAP obtained was used as a binder to form polyurethane (PUR) film that was cured by tolylene diisocyanate ($C_9H_6N_2O_2$) (TDI) or isophorone diisocyanate ($C_{12}H_{18}N_2O_2$) (IPDI). The formulations and mechanical properties of two films are presented in Table 3.

At another laboratory, GAP was also prepared and tested.[37,38] It is an amber liquid with a density of 1.30 g/cm^3, number average molecular weight of about 2000, and a solidification point of below -45°C. Having been crosslinked with TDI (GAP/TDI = 8/2) at 50–55°C, GAP was turned into a elastomer with ε_b of 500%, and T_g lower than -35°C. The GAP/TDI elastomer was tested with differential thermal analysis (DTA) at a heating rate of 5°C/min and weight loss method. The observed onset and exothermic peak temperatures were 218.1 and 245.3°C, respectively, conforming to the data provided in Refs. 34 and 40. The weight loss at 74°C was 1.13% (24 h) or 1.57% (48 h), while the corresponding figures were 3.50 and 6.80% for bis(2-fluro-2,2-dinitroethyl) formal ($C_5H_6N_4O_{10}F_2$) (FEFO). That is to say that the GAP weight loss in the application temperature range of weapons was three times less than that of FEFO. For the novel energetic binders and plasticizers, the thermal stability proposed by Lawrence Livermore National Laboratory (LLNL) and Defence Advanced Research Projects Agency (DARPA)[41] should be superior to FEFO. Experimental results at this laboratory also indicated that GAP/TDI could lower the impact sensitivity of HMX. The percentage of explosion was 26% for HMX/GAP-TDI(88/12) (not cured completely) and 100% for HMX under the conditions of 10-kg drop hammer and 25-cm drop height. In order to explore the GAP's energy contribution, the HMX/GAP-TDI(88/12) sample was subjected to the cylinder test. Data in Table 4 comprise a comparison of the results between HMX/GAP-TDI and several conventional explosives. Table 4 indicates that the specific kinetic energy of HMX/GAP-TDI amounted to 89.3% of that of HMX, only 1.33% lower than that of PBX 9501, but 8.9% higher than that of PBX 9011. This demonstrated that the azido group in GAP could release its energy synchronously with the explosive detonation, resulting in a sizable energy contribution.

Table 3 Formulations and mechanical properties of PUR films

Film	1	2
Formulation, g		
GAP	10.51	10.51
IPDI	0.84	0.95
N-100[a]	1.78	1.00
TPB[b]	0.10	0.10
T-12[c]	0.01	0.01
ρ_t	0.60	0.53
Mechanical property		
σ_m,[d] MPa	0.485	0.190
ε_b,[d] %	164	220

[a] Cross-linking agent.
[b] Triphenylbismuth ($C_{18}H_{15}Bi$).
[c] Dibutyltin dilaurate ($C_{32}H_{64}O_4Sn$).
[d] Measured by Instron universal testing machine at speed of 1000 mm/min.

Table 4 Cylinder test results

Explosive	ρ_0,[a] g/cm^3	D,[b] km/s	E,[c] kJ/g ($R - R_0$ = 19 mm)
HMX/GAP-TDI (88/12)	1.761	8.480	1.556
HMX	1.891	9.110	1.743
PBX9501[d]	1.834	8.792	1.557
PBX9011[e]	1.777	8.500	1.428

[a] Density. [b] Detonation velocity. [c] Specific kinetic energy.
[d] Contains 95% HMX, 2.5% thermoplastic polyurethane elastomer (Estane), and 2.5% bis(2,2-dinitropropyl) formal ($C_7H_{12}N_4O_{10}$) (BDNPF).
[e] Contains 90% HMX and 10% Estane.

Table 5 Calculated values[a] of some detonation parameters

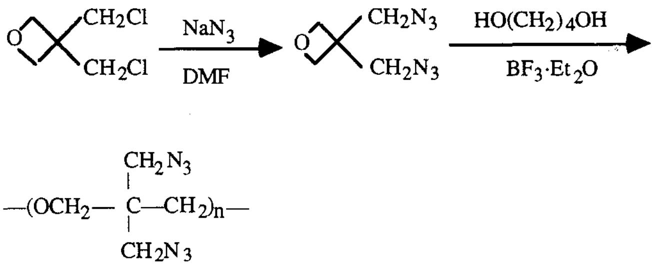
Explosives	k	Q, kJ/g	P_{cj}, GPa	$\rho_0 Q$, kJ/cm^3
HMX/GAP-TDI (88/12)	2.96	4.64	32.00	8.17
PBX9501	3.09	4.51	34.62	8.26
PBX9011	3.09	4.27	31.35	7.48

[a] Based on ρ_0 and D in Table 4.

The calculated values of polytropic exponent k, detonation pressure P_{cj}, detonation heat Q, and energy density $\rho_0 Q$ for explosives are shown in Table 5.

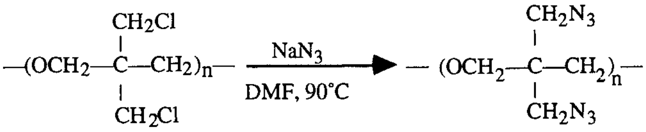
Homopolymer (II$_1$) and Copolymers (III$_1$) of 3,3-Bis(Azidomethyl) Oxetane ($C_5H_8N_6O$) (BAMO)

Polymerization of substituted four-member oxetane can produce polymers with higher molecular weight and higher elongation than GAP, and it is easier to control molecular weight and functionality during polymerization of oxetane then is the case with oxacyclopropane. In addition, synthesis of oxetane monomer bearing different energetic groups is accessible. Therefore, polymers and copolymers of oxetanes containing azido groups, such as BAMO and 3-methyl-3-azidomethyloxetane ($C_5H_9N_3O$) (AMMO), have been given more attention.[42–44] The polymerization of BAMO was investigated by Frankel et al.,[45] Manser et al.,[46] and Sperling.[47] The synthesis of BAMO consisted of treating 3,3-bis(chloromethyl) oxetane ($C_5H_8OCl_2$) (BCMO) with sodium azide in dimethyl formamide (C_3H_7NO) (DMF) at 85°C for 2 h. The polymerization of BAMO was carried out using 1,4-butanediol as the initiator and boron fluoride as the catalyst [see Eq. (2)]:



(II$_1$) (2)

The homopolymer of BAMO was prepared via the following reaction route at our laboratory[48] [see Eq. (3)]. The polymeric BCMO, a commercially available product, was degraded during azidation:

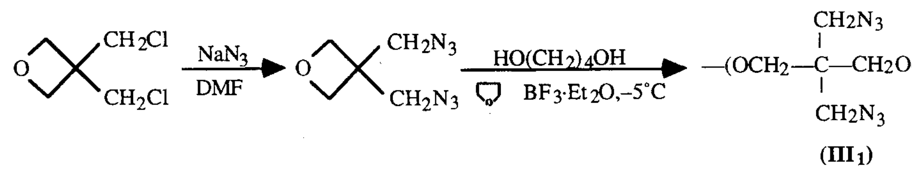


$$-(OCH_2-\underset{CH_2Cl}{\overset{CH_2Cl}{C}}-CH_2)_n- \xrightarrow[DMF,\ 90°C]{NaN_3} -(OCH_2-\underset{CH_2N_3}{\overset{CH_2N_3}{C}}-CH_2)_n-$$

(II$_1$) (3)

For the homopolymer obtained, differential scanning calorimetry (heating rate 20°C/min) showed its glass transition temperature was -28°C, melting point 76–80°C, exotherm onset 200°C, and exothermic peak 250°C.

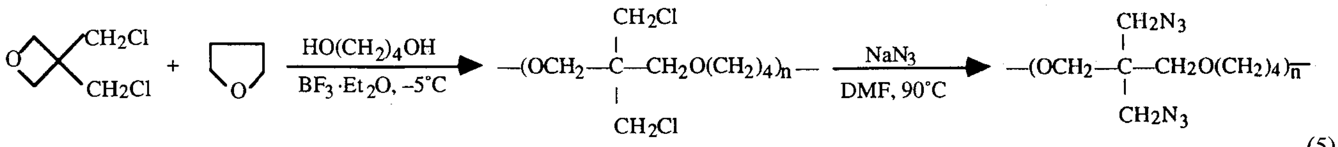
We applied two procedures, Eqs. (4) and (5), to the preparation of copolymers of BAMO/THF[48]:



(III₁)

(4)

The obtained BAMO was purified by distillation and column chromatography before copolymerization:



(III₁)

(5)

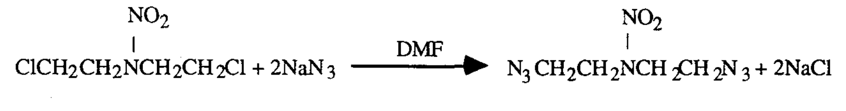
The copolymer of BAMO/THF was an oligomer that had a range of molecular weight from 2000 to 4000. Its glass-transition temperature was below −60°C, and its melting point below that of BAMO homopolymer. The 50/50 (molar ratio) copolymer was a mobile oil with relatively low viscosity at ambient temperature, and its DSC curve showed a single exotherm that began at 210°C and reached a maximum at 250°C. The higher the content of BAMO in the copolymer, the higher the viscosity of the copolymer.

Azido Nitramine

1,5-Diazido-3-Nitrazapentane ($C_4H_8N_8O_2$) (DANPE) (I_2)

DANPE could be used in liquid monopropellants as an energetic azido fuel to replace hydrazine and aqueous hydrazine that have been utilized for monopropellant applications for many years; this might make it possible to improve chemical stability and reduce the toxicity of propellants.[4] The use of DANPE as a plasticizer of solid propellants and gun propellants could lower both gas molecular weight and flame temperature without causing a decrease in burning rate.[49]

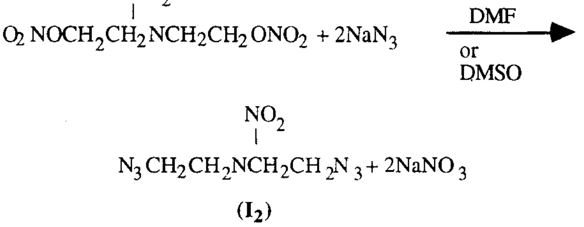
The synthesis of azidonitramines is delineated in Refs. 49–51 Rosher[50] reported the preparation of DANPE via the reaction of 1,5-dichloro-3-nitrazapentane ($C_4H_8N_8O_2$) (DCNPE) with sodium azide in DMF [see Eq. (6)]:



$$ClCH_2CH_2\overset{NO_2}{N}CH_2CH_2Cl + 2NaN_3 \xrightarrow{\text{DMF}} N_3CH_2CH_2\overset{NO_2}{N}CH_2CH_2N_3 + 2NaCl \qquad (6)$$

(I_2)

DANPE was synthesized in the authors' laboratory from 1,3-dinitroxy-3-nitrazapentane ($C_4H_8N_4O_8$) (DINA), instead of DCNPE[52] [see Eq. (7)]:



$$O_2NOCH_2CH_2\overset{NO_2}{N}CH_2CH_2ONO_2 + 2NaN_3 \xrightarrow[\text{or DMSO}]{\text{DMF}} N_3CH_2CH_2\overset{NO_2}{N}CH_2CH_2N_3 + 2NaNO_3 \qquad (7)$$

(I_2)

7.2 g of DINA and 7.8 g of NaN_3 (molar ratio 1:2) were added to 25 ml of DMF, and the reaction mixture was heated at 85–90°C for 12 h. After cooling, the reaction mixture was poured into water. The crude product obtained was dissolved in dichloroethane treated with active carbon to give 4.0 g of a colorless liquid (yield 67%, based on DINA).

The DANPE prepared was identified by IR, ^1H NMR, MS, and elemental analysis. Some of its properties determined are given in Table 6.

The authors[52] have applied DANPE to prepare PBX with the following formulation: RDX 94.5%, DANPE 3.0%, polyvinyl acetate ($[C_4H_6O_2]_n$) (PVA) 2.0%, stearic acid 0.5% and, colla taurina 0.1%. This PBX had a detonation velocity of 8300 m/s when its charge density was 1.707 g/cm³. If 3.0% of DANPE was replaced by dinitrotoluene ($C_7H_6N_2O_4$) (DNT), detonation velocity and charge density were 8100 m/s and 1.643 g/cm³, respectively, under the same charge conditions (charge pressure 200 MPa, charge diameter 10 mm, charge height 11 mm).

In order to produce high-energy and low-ablation triple-base gun propellants containing azidonitramine (DA propellant), the compatibility of DANPE with other ingredients of gun propellants, such as nitrocellulose ($[C_6H_{10-m}O_{5-m}(ONO_2)_m]_n$) (NC) and RDX, was measured[54] using the method described in Chinese National Military Standard.[55] The results are collected in Table 7 and Fig 1.

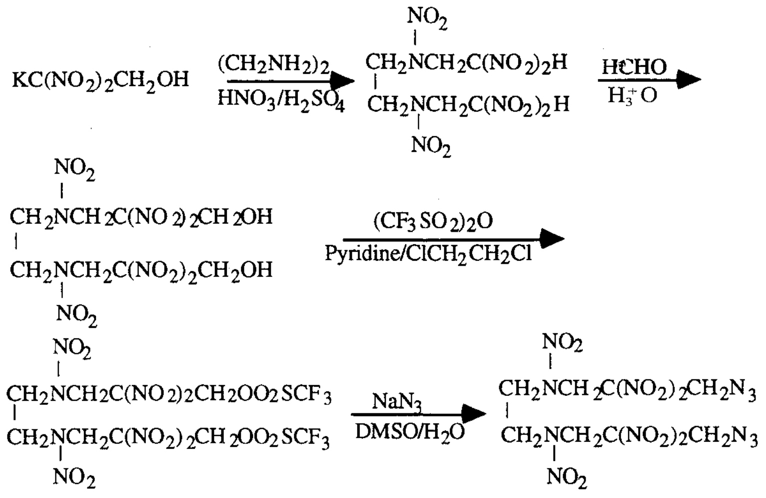
The characteristics of DA gun propellants composed of NC, RDX, and DANPE have been tested or calculated, and compared with those of M-30 propellants composed of NC, nitroglycerine ($C_3H_5N_3O_9$) (NG), and nitroguanidine ($CH_4N_4O_2$) (NQ). Details can be found in Ref. 54. The main points are given in Table 8.

N,N'-Bis(Azidomethylgemdinitroethyl)ethylenedinitramine (II_2) and N-nitro-N-Azidomethylgemdinitroethyl Methylamine (III_2)

Azido-gemdinitro compounds possess higher energy; some possess lower impact sensitivity. Their thermal stability can meet application requirements.[56] They have been used as high energetic fuel[57] and energetic diluent[58] of liquid propellants.

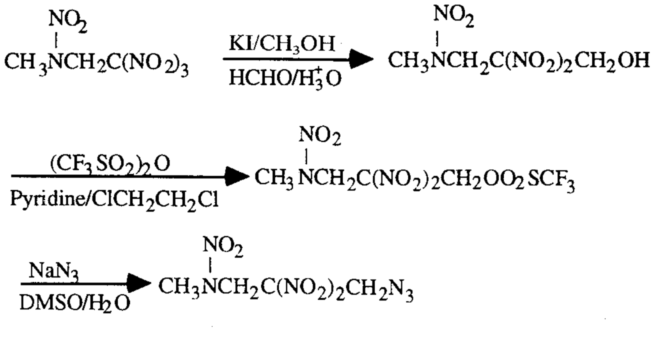
As an energetic group, gemdinitro is very attractive[59] and is considered a good selection.[60] Ethers bearing azidomethyl and gemdinitro have been reported in the literature.[61]

We synthesized *N*,*N*′-bis(azidomethylgemdinitroethyl)ethylenedinitramine and *N*-nitro-N-azidomethylgemdinitroethyl methylamine via reactions (8) and (9):[62]



(II$_2$)

(8)



(III$_2$)

(9)

Table 6 Some DANPE properties

Property	DANPE	DINA
Freezing point, °C	3.5–4.2	51.3 (Ref. 53)
Maximum thermal decomposition temperature,[a] °C	227	202
75°C vacuum stability, ml/g·24 h	0.442	0.107
Impact sensitivity,[b] %	80	100
Heat of combustion, kJ/g	16.32 (Ref. 49)	——
Standard enthalpy of formation, kJ/mol	+540.2 (Ref. 49)	−316.3 (Ref. 53)

[a] DSC method, heating rate 10°C/min.

[b] Percentage of explosion, 10-kg drop hammer, drop height 25 cm, 50-mg sample, 25 runs.

Table 7 Compatibility between ingredients of DA gun propellant

Ingredient	T_m,[a] °C	ΔT_m,[b] °C	E,[c] kJ/mol	ΔE,[d] kJ/mol	$\lvert\Delta E/E\rvert$, %	Compatibility
NC	196.00		142.6			
DANPE	233.50		115.3			
NC + DANPE	182.75	3.25	129.5	−13.1	9.2	Fair
NC	196.00		142.6			
RDX	230.50		181.9			
NC + RDX	203.25	−7.25	170.4	27.8	19.5	Excellent
RDX	230.50		181.9			
DANPE	233.50		115.3			
RDX + DANPE	232.75	−2.25	139.5	−42.4	30.4	Good

[a] Still air, heating rate 2, 5, 10, or 20°C/min, 0.7-mg sample.

[b] Difference between single ingredients and their mixtures as to exothermic peak temperatures.

[c] Calculated by Ozewa method.

[d] Difference between single ingredients and their mixtures as to observed activation energy.

Table 8 Performance data of both DA propellant and M-30 propellant[a]

Propellant	T_{m1},[b] °C	T_{m2},[c] °C	E, kJ/mol	log A, l/s	Q, kJ/mol	$f \times 10^{-4}$, kgdm/kg	T_v, K
DA[d]	202.25	226.50	184.3	18.5	3670	120.0	2998
M-30	196.00	230.00	232.2	23.4	4078	110.8	3040

[a] Calculated values except T_{m1} and T_{m2}.
[b] First thermal decomposition peak on DSC curve.
[c] Second thermal decomposition peak on DSC curve.
[d] Content of DANPE, 25%.

The properties and kinetic parameters of these two azides are collected in Table 9.

Azidonitro Compound

A number of azidonitro compounds have been studied at our laboratory during the past decade. Three representatives: 2-nitro-2-azidomethyl-1,3-diazidopropane (I_3), 2-nitro-2-azidomethyl-1,3-diazidopropane (II_3), and 1-azido-2-(2,4,6-trinitrophenyl)ethane (III_3) are described later.[63] These three azides were synthesized via condensation and nucleophilic substitution reactions, while corresponding nitro compounds were used as starting materials [see Eqs. (10–12)]. The properties of the azidonitro compounds obtained are listed in Table 10. Heat of combustion for azide (I_3) was 17.86 kJ/g. We have applied azide (I_3) as plasticizer to make a film with a copolymer of BAMO/THF at a ratio of azide/copolymer = 2.8. The azide did not separate out after the cured film had been stored at ambient temperature for half a year. When NG/1,2,4-butanetriol trinitrate ($C_4H_7N_3O_9$) (BTTN) (ratio 1/1) was used as the plasticizer instead of azide (I_3), separation was observed under the same conditions. Calculation (based on White's minimum-free-energy process) showed that the use of azide (I_3) as the plasticizer of solid propellants composed of Al, HNF, and copolymer of BAMO/THF could increase I_{ss}^0 (at expansion ratio P_c/P_e = 70/1 or 6.86 MPa/0.09507 MPa), T_{ch}, and ρ of propellant (see Table 11).

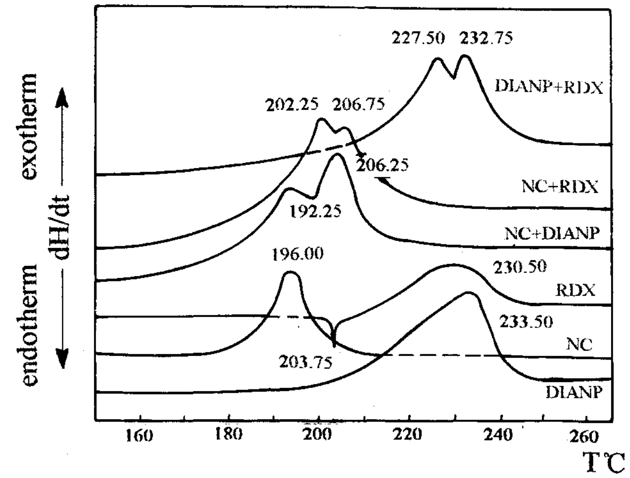


Fig. 1 DSC curves of ingredients of DA propellant and mixtures of various ingredients.

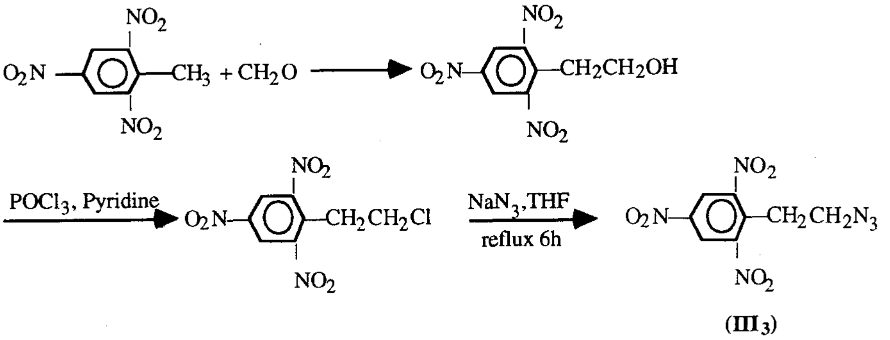
Calculation also indicated that if 4% of NG/BTTN (ratio 1/1) was replaced by azide (I_3) in NEPE propellant (AP 5–10%, Al 17–20%, HMX 45–50%, NG/BTTN 10–20%, binder 5.5–8.0%, other additives 2–4%), I_{ss}^0 could increase by about 0.7 s.

$$CH_3CH_2NO_2 + (CH_2O)_n \xrightarrow[\text{KOH or } Na_2CO_3\text{, reflux, 0.5h}]{CH_3CO_2C_2H_5 \text{ or water}} CH_3CNO_2(CH_2OH)_2$$

$$\xrightarrow[\text{0°C, 10h}]{\text{TsCl, Pyridine}} CH_3CNO_2(CH_2OTs)_2 \xrightarrow[\text{85°C, 9h}]{NaN_3\text{, DMF}} \underset{(I_3)}{CH_3CNO_2(CH_2N_3)_2} \qquad (10)$$

$$CH_3NO_2 + (CH_2O)_n \xrightarrow[\text{reflux}]{CH_3CO_2C_2H_5\text{, KOH}} CNO_2(CH_2OH)_3 \xrightarrow[\text{0°C, 24h}]{\text{TsCl, Pyridine}}$$

$$CNO_2(CH_2OTs)_3 \xrightarrow[\text{85°C, 9h}]{NaN_3\text{, DMF}} \underset{(II_3)}{CNO_2(CH_2N_3)_3} \qquad (11)$$



(12)

(III_3)

Table 9 Properties and kinetic parameters of two gemidinitro azides[a]

Azide	Melting point, °C	ρ,[b] g/cm^3	ΔH_f^0,[a] kJ/mol	E, kJ/mol	A, 1/s	$k_{100°C}$,[d] 1/s	T_m,[c] °C
II$_2$	137.4	1.722	+483.6	225.61	7.51×10^{24}	1.96×10^{-7}	203.5
III$_2$	——	——	+220.2	148.31	5.50×10^{15}	9.53×10^{-6}	216.5

[a] Kinetic parameters were obtained from DSC curves using the Ozewa method.
[b] Measured by suspending method.
[c] Calculated figure.
[d] Reaction-rate constant at 100°C.
[e] Heating rate 10°C/min.

Table 10 Properties of azidonitro compounds

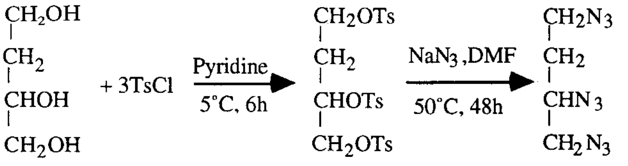
Azide	Melting point, °C	ρ, g/cm^3	ΔH_f^0,[a] kJ/mol	Impact sensitivity,[b] %
I$_3$	< -20	1.40	+590.0	——
II$_3$	< -20	1.35	+919.2	——
III$_3$	60–61	1.635	+447.2	30

[a] Calculated figure.
[b] Percentage of explosion (drop hammer 10 kg, drop height 25 cm, 25 runs).

Aliphatic Azide

1,2,4-Triazidobutane ($C_4H_7N_9$) (TAB)(**I$_4$**)[64]

TAB was synthesized via reaction (13):



(**I$_4$**) (13)

The synthesized azide was identified by IR, ^{1}H NMR, MS, and elemental analysis. Some properties of compound (*I$_4$*) were measured to be as follows: ρ 1.266 g/cm^3, m.p. < -16°C, n_D^{20} 1.4486, heat of combustion 19.84 kJ/g, ΔH_f^0 +1019.1 kJ/mol (calculated based on heat of combustion), and volatilization temperature 197.6°C on DTA curve (heating rate 10°C/min).

The thermal decomposition peaks of NC and a mixture of NC/azide (**I$_4$**) (weight ratio 1/3) were 193.9 and 200.4°C on DTA curves (heating rate 10°C/min), respectively.

Tetraazidomethylmethane ($C_5H_8N_{12}$) (TAPE) (**II$_4$**)

TAPE was reported by Anderson.[65] This azide was obtained in China via reaction routes (14 and 15)[66]:

$$\mathrm{C(CH_2OH)_4} \xrightarrow{\mathrm{SOCl_2,\ Pyridine}} \mathrm{C(CH_2Cl)_4} \xrightarrow{\mathrm{NaN_3,\ DMF}} \underset{(\mathbf{II_4})}{\mathrm{C(CH_2N_3)_4}} \qquad (14)$$

$$\mathrm{C(CH_2OH)_4} \xrightarrow{\mathrm{TsCl,\ NaN_3}} \underset{(\mathbf{II_4})}{\mathrm{C(CH_2N_3)_4}} \qquad (15)$$

TAPE is a colorless solid, with melting point 45 or 48–50°C, density 1.444 g/cm^3, standard enthalpy of formation +1260.9 kJ/mol (calculated figure), and thermal decomposition peak 250°C on the DSC curve.[66]

TAPE's crystal structure was studied at the authors' laboratory. Its single crystal belongs to the tetragonal crystal system, $a = 10.404(2)$, $b = 10.403(2)$, $c = 9.872(2)$ Å. TAPE's geometrical configuration is shown in Fig. 2.

Table 11 Contribution of azide (I$_3$) to the energetic performances of solid propellants

No.	1	2	3	4
Ingredient %				
Al	18	18	18	18
HNF	62	62	62	62
BAMO/THF	20	16	12	8
Azide (I$_3$)	0	4	8	12
I_{ss}^0, s	279.8	281.7	283.8	285.7
T_{ch}, K	3689	3785	3871	3948
ρ, g/cm^3	1.794	1.801	1.807	1.814

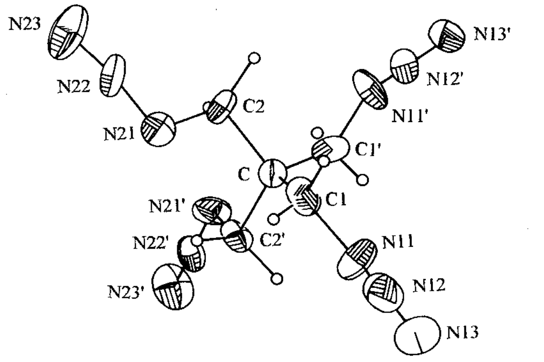


Fig. 2 TAPE's molecular geometrical configuration.

Azidonitrate pentaerythritol diazido dinitrate ($C_5H_8N_8O_6$) (PDADN) (I$_5$)

PDADN was synthesized by Frankel[67] using BCMO as the starting material. Frankel reported that the PDADN obtained was a colorless oily liquid having n_D^{20} 1.5161. Wang et al.[68] from the Institute of Chemical Materials, China Engineering Physics Institute, tried to synthesize PDADN via reaction (16):

$$\mathrm{C(CH_2OH)_4} \xrightarrow{\mathrm{2TsCl}} \mathrm{C(CH_2OTs)_2(CH_2OH)_2} \xrightarrow{\mathrm{2NaN_3}} \mathrm{C(CH_2N_3)_2(CH_2OH)_2} \xrightarrow{\mathrm{nitration}} \underset{(\mathbf{I_5})}{\mathrm{C(CH_2N_3)_2(CH_2ONO_2)_2}} \qquad (16)$$

Unfortunately, they failed to obtain diazidomethylhydroxymethylmethane instead of tetraazidomethylmethane, which has a melting point of 45°C. Even the amounts of tosylchloride or *p*-toluenesulfonyl ($C_7H_7O_2ClS$) (TsCl) or NaN_3 used in the reactions were decreased; the resulting product was still TAPE, but in a lower yield. Later, Wang prepared PDADN according to the Frankel's procedure. The difference was that Wang's product was a colorless solid with a melting point of 37–39°C, while Frankel's product was a colorless oily liquid. The IR spectrum and elemental analysis of Wang's product were in agreement with PDADN's molecular structure. All of the intermediates of pentaerythritol diazido mononitrate ($C_5H_8N_9O_4$) (PDAMN) from Wang and Frankel were pale-yellow oily liquid. Some performances of the synthesized PDADN tested were as follows[68]: impact sensitivity 100% (percentage of explosion, 10-kg hammer, 25-cm drop height); friction sensitivity 80% (percentage of explosion, friction pendulum method, 90 deg); heat of decomposition −2.32 kJ/g (average value of 5 samples); thermal decomposition temperature, onset 189.3°C (average value of 5 samples); exotherm peak 203.9°C (average value of 5 samples).

Oxygen Heterocyclic Azide Monomer[69]

2,2-Dimethyl-5-Azidomethyl-5-Nitro-1,3-Dioxane (**I_6**)

This azide has a melting point of 42–43°C, density of 1.25 g/cm³, and standard enthalpy of formation of −93.3 kJ/mol. It becomes volatile at 162°C, and its thermal decomposition temperature could not be measured by the differential scanning calorimetry (DSC) method. The synthetic reactions are shown in Eq. (17). IR, ^1H NMR, MS, and elemental analysis confirmed the molecular structure of this prepared azide. In order to understand the structural characteristics of this azide and other azido derivatives of 1,3-dioxane, the crystal structure of compound (I_6) was determined by X-ray diffraction and is shown in Fig. 3.

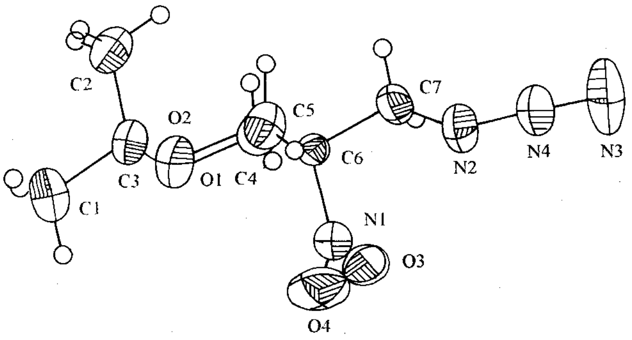
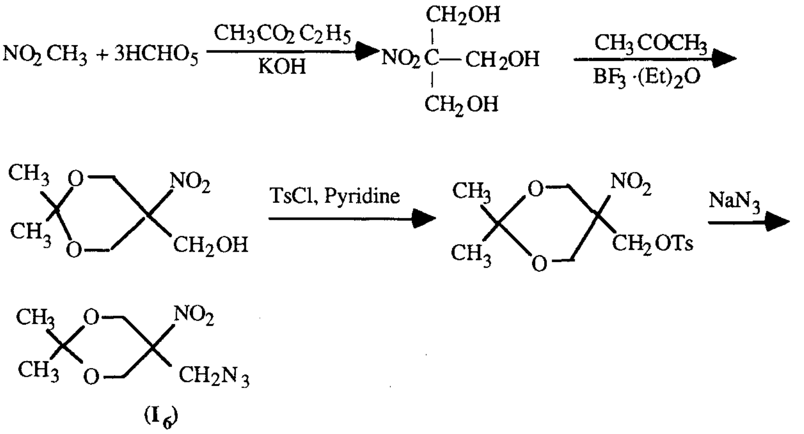


Fig. 3 Geometrical configuration of compound I_6.

The X-ray diffraction pattern indicates that the six-member ring exists in chair form. On one side of the ring sit two methyl groups, one in axial position and the other in equatorial position. On the other side of the ring sit the nitro group and the azidomethyl group, the former in axial position and the latter in equatorial position. The molecular-packing diagram reveals that there are four molecules in one crystal cell. Two molecules eclipse opposite to each other, which positions the bulk nitro group and azidomethyl group in a staggered arrangement. In turn, the intramolecular tension will be decreased, and the system will be in a stable state. The two bond lengths of the azido group are 1.226 and 1.121 Å, respectively, and the bond angle is 172.7 deg. This indicates that the three nitrogen atoms in the azido group are in a slightly bending arrangement. The parameters of the crystal cell are as follows: a = 6.1598 Å, b = 10.3078 Å, and c = 16.0819 Å, α = 89.8740 deg, β = 96.752 deg, and γ = 90.126 deg.

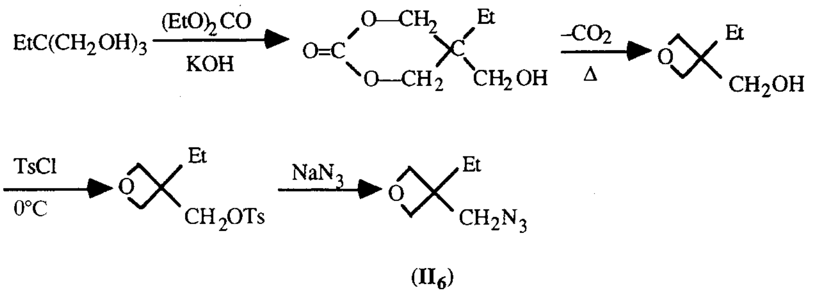
3-Azidomethyl-3-Ethyl Oxetane (**II_6**)

This azide was synthesized via reaction route (18). The compound obtained was characterized by IR, ^1H NMR, MS, and elemental analysis. It has a melting point of < −15°C, density of 1.12 g/cm³, and ΔH_f^0 of +51.5 kJ/mol (calculated figure).



(I_6)

(17)



(18)

(II_6)

Conclusions

Researchers in China believe that the use of high-energy fuels, high-energy oxidizers, and high-energy additives (binders and plasticizers) is necessary for the development of HEDMs. The azido energetic additives have spawned considerable research aimed at providing various binders and plasticizers for formulating solid propellants, which yield greater energy and possess better physical and chemical properties. In fact, there is a continuing search for such purposes at several laboratories in this country. For example, a significant number of organic azides have been synthesized and identified at the authors' laboratory during the period of 1980–1994. Fourteen representative azides are described in this article. Some are novel, and may be of interest as future propellant additives. Some azidogemdinitro compounds possess very high density (up to 1.835 g/cm^3). The main physical properties and thermal stabilities of most of the synthesized azides were examined. Little work has been devoted to their applications, and much work is yet to be done before we can identify those that are promising. The use of GAP as a binder for solid propellants and azidonitramine as plasticizers for PBX and gun propellants may now be more interesting and accessible in light of the fundamental research conducted in China. The polymer of BAMO and copolymer of BAMO/THF are promising binders being studied in China, but they are less developed than GAP, and are therefore considered to be of less interest at the present time. Regarding other novel families of synthesized azido energetic additives, examination of their potential for practical applications will continue over the next few years.

References

[1] Flanagan, J. E., Hills, W., and Frankel, M. B., "1.3-Diazido-2-Nitrazapropane," U.S. Patent 4,085,123, 1978.

[2] Witucki, E. F., Nuys, V., Flanagan, J. D., and Hills, W., "Azido Ester," U.S. Patent 4,432,814, 1984.

[3] Manser, G. E., "Energetic Copolymers and Method of Making Same," U.S. Patent 4,483,978, 1984.

[4] Flanagan, J. E., Hills, W., Wilson, E. R., and Valley, S., "Advanced Monopropellants," U.S. Patent 4,427,466, 1984.

[5] Witucki, E. F., Nuys, V., Flanagan, J. E., and Hills, W., "Azido Nitramine Ethers," U.S. Patent 4,440,687, 1984.

[6] Frankel, M. B., Wilson, E. R., and Woolery, D. O., "Energetic Azido Compounds," AD-A 083,770, 1980.

[7] Gilbert, E. E., "Propellant Compositions," U.S. Patent 4,568,399, 1986.

[8] Frankel, M. B., Witucki, E. F., and Nuys, V., "Axido Fluorodinitro Amines," U.S. Patent 4,432,815, 1984.

[9] Wilson, E. R., Valley, S., and Frankel, M. B., "Azide-Terminated Azido Compounds as Energetic Plasticizers for Propellants," U.S. Patent 4,781,861, 1988.

[10] Stacer, R. G., and Husband, D. M., "Molecular Structure of the Ideal Solid Propellant Binder," *Propellants, Explosives, Pyrotechnics*, Vol. 16, No. 4, 1991, pp. 167–176.

[11] Bazaki, H., and Kubota, N., "Energetics of AMMO," *Propellants, Explosives, Pyrotechics*, Vol. 16, No. 2, 1991, pp. 68–72.

[12] Nakashita, G., and Kubota, N., "Energetics of Nitro/Azide Propellants," *Propellants, Explosives, Pyrotechnics*, Vol. 16, No. 4, 1991, pp. 177–181.

[13] Eisele, S., Menke, K., and Schubert, H., "Solid Rocket Fuel," U.S. Patent 4,938,813, 1990.

[14] Mitarai, Y., Anan, T., Irie, A., Ohuchi, S., and Tamura, N., "Physical Properties of AMMO Polymer," *Industrial Powder*, Vol. 51, No. 4, 1990, pp. 240–245 (in Japanese).

[15] Flanagan, J. E., and Hills, W., "Azidodinitro Propellants," U.S. Patent 4,797,168, 1989.

[16] Shi, M., "A New Kind of Energetic Materials—Organic Azides," *Propellants and Explosives*, Vol. 15, No. 4, 1992, pp. 24–30 (in Chinese).

[17] Wang, Z., "Recent Development of Binders for Solid Propellants Abroad," *Chemical Propellants*, No. 41, 1989, pp. 16–25 (in Chinese).

[18] Schoyer, H. F. R., Korting, P. A. O. G., Schnorhk, A. J., Mul, J. M., Van Lit, P., Gadiot, G., and Meulenbrugge, J., "High-Performance Propellants Based on Hydrazinium Nitroformate," *Journal of Propulsion and Power*, Vol. 11, No. 4, 1995, pp. 856–869.

[19] Feng, Z., and Tan, H., "The Energetic Analysis of a New Generation of High Energy Solid Propellants," *Journal of Propulsion Technology*, Vol. 11, No. 6, 1992, pp. 66–74 (in Chinese).

[20] Helmy, A. M., "Investigation of New Energetic Ingredients for Minimum Signature Propellants," AIAA Paper 84-1434, June 1984.

[21] Sayles, D. C., "Non-Nitroglycerin-Containing Composite-Modified Double-Base Propellants," U.S. Patent 4,707,199, 1987.

[22] Frankel, M. B., and Flanagan, J. F., "Energetic Hydroxy-Terminated Azido Polymer," U.S. Patent 4,268,450, 1981.

[23] Rothstein, L. R., "Past, Present and Future of Plastic Bonded Explosives," 13th International Annual Conf. of the Inst. of Chemical Technology, Karlsruhe, Germany, June–July 1982.

[24] Nazare, A. N., Asthana, S. N., and Singh, H., "Glycidyl Azide Polymer (GAP)—An Energetic Component of Advanced Solid Rocket Propellants—A Review," *Journal of Energetic Materials*, Vol. 10, No. 1, 1992, pp. 043–063.

[25] McParland, G. G., "Integrated Stage Concept System Study Results," AIAA Paper 86-1581, June 1986.

[26] Tokui, H., Saithoh, T., Hori, K., Notono, K., and Iwama, A., "Synthesis and Physico-Chemical Properties of GAP and the Applications of GAP/AN Based Propellants to a Small Motor," 21st International Annual Conf. of the Inst. of Chemical Technology, Karlsruhe, Germany, July 1990.

[27] Earl, R., "Use of Polymeric Ethylene Oxides in the Preparation of GAP," U.S. Patent 4,486,351, 1984.

[28] Helmy, A. M., "GAP Propellants for Gas Generation Application," AIAA Paper 87-1725, June–July 1987.

[29] Reed, R., Jr., and Chom, M. L., "Propellant Binders Cure Catalysts," U.S. Patent 4,379,903, 1983.

[30] Flanagan, J. E., Hills, W., and Gray, J. C., "Gun Propellants Containing Glycidyl Azide Polymer," U.S. Patent 4.288,262, 1981.

[31] Kubota, N., Sonobe, T., Yamamato, A., and Shimizu, H., "Burning Rate Characteristics of GAP Propellants," *Journal of Propulsion and Power*, Vol. 6, No. 6, 1990, pp. 686–689.

[32] Frankel, M. B., Grant, L., and Flanagan, J. E., "Historical Development of GAP," AIAA/ASME/SAE/ASEE 25th Joint Propulsion Conf., Monterey, CA, July 1989.

[33] Manser, G. E., "Nitrate Ester Polyether Glycol Prepolymers," AD-A 143025, Laurel, MD, 1984.

[34] Kubota, N., and Sonobe, T., "Combustion Mechanism of Azide Polymer," *Propellants, Explosives, Pyrotechnics*, Vol. 13, No. 6, 1988, pp. 172–177.

[35] Kubota, N., Sonobe, T., Yamamato, A., and Shimizu, H., "Combustion of GAP Propellants," 19th International Annual Conf. of the Inst. of Chemical Technology, Karlsruhe, Germany, June–July 1988.

[36] Ahad, E., "Branched Hydroxy-Terminated Azido Polymers," 21st International Annual Conf. of the Inst. of Chemical Technology, Karlsruhe, Germany, July 1990.

[37] Li, C., Wang, P., and Huang, Y., "Investigation of Glycidyl Azide Polymer," Vol. 1, edited by Y. Ou, Z. Feng, and B. Zhang, *Proceedings of the 17th International Pyrotechnics Seminar Combined with 2nd Beijing International Symposium on Pyrotechnics and Explosives*, Beijing, PRC, 1991, pp. 451–459.

[38] Li, C., Wang, P., and Huang, Y., "A Study on GAP," *Binggong Xuebao (Acta Armamentarii), Huohuagong Fence (A Branch of Propellants and Explosives)*, No. 1, 1991, pp. 6–9 (in Chinese).

[39] Li, Z., "Synthesis and Applications of Energetic Binder GAP,", M.S. Thesis, Beijing Inst. of Technology, Beijing, PRC, 1994 (in Chinese).

[40] Leu, A., Shen, S., and Wu, B., "Thermal Characteristics of GAP, GAP/BDNPA/BDNPF, PEG/BDNPA/BDNPF and the Energetic Composities," 21st International Annual Conf. of the Inst. of Chemical Technology, Karlsruhe, Germany, July 1990.

[41] UCRL-21042, The BDM Corp., BDM/Mty-TR-0030-87, 1987.

[42] Zhang, C., "Development and Application of Energetic Binders and Plasticizers," Technical Rept., Inst. of Scientific and Technical Information, Ministry of Machine Building Industry, Beijing, PRC, 1988 (in Chinese).

[43] Farbar, M., "Mass Spectrometric Decomposition Studies on Several Azido and Nitrate Polymers, Thermal Plasticizers and Novel Nitramines," AD-A 134636, Monrovia, CA, 1983.

[44] Manser, G. E., "High Energy Binder," AD-A 142347, Brigham City, UT, 1984.

[45] Frankel, M. B., Wilson, E. R., Woolery, D. O., and Kistner, R. L., "Energetic Azido Compounds," AD-A 110292, Canoga Park, CA, 1982.

[46] Guimont, J. M., Manser, G. E., and Ross, D. L., "Synthesis of Energetic Polymers," AD-A 089,948, Canoga Park, CA, 1980.

[47]Sperling, L. H., "Characterization of Novel Binders Based on Energetic Thermoplastic Elastomers," AD-A 148993, Bethlehem, PA, 1984.

[48]Zhou, Z., *Synthesis of Azido Substituted Polyether Prepolymer*, Preprints of Xian International Symposium on Functional and Fine Chemicals, Xian, PRC, 1988, pp. 402–404.

[49]Simmons, R. L., and Young, H. L., "Azido Nitramine," U.S. Patent 4,450,110, 1984.

[50]Rosher, R., "Organic Azides and Method of Preparation Thereof," U.S. Patent 3,873,579, 1975.

[51]Witucki, E. F., Nuys, V., and Flanagan, J. E., "Azido Nitramine Ether Containing Solid Propellants," U.S. Patent 4,482,404, 1984.

[52]Chen, B., and Zhou, Z., "Synthesis and Applications of a Multifunctional Energetic Material," *Binggong Xuebao (Acta Armamentarii), Huohuagong Fence (A Branch of Propellants and Explosives)*, No. 1, 1987, pp. 34–36 (in Chinese).

[53]Kohler, J., and Meyer, R., *Explosives*, 4th ed., VCH Publishers, New York, 1993, p. 112.

[54]Wu, S., Hu, R., Li, S., and Kang, B., "Compatibility and Thermal Characteristics of Propellant Containing Azido Nitramines," *Binggong Xuebao (Acta Armamentarii), Huohuagong Fence (A Branch of Propellants and Explosives)*, No. 2, 1993, pp. 34–38 (in Chinese).

[55]Chinese National Military Standard 772202-89, Beijing, PRC, 1989 (in Chinese).

[56]Wright, C. M., "1-Azido-1, 1-Dinitro Alkanes Useful as Propellants," U.S. Patent 3,883,377, 1975.

[57]Weber, J. F., and Frankel, M. B., *Propellants, Explosives, Pyrotechnics*, Vol. 15, No. 1, 1990, pp. 26–29.

[58]Frankel, M. B., Wilson, E. R., and Valley, S., "Method of Preparing 1.1.1-Azidodinitro Compounds," U.S. Patent 4,472,311, 1984.

[59]Frankel, M. B., "Electrolytic Preparation of Novel Azidodinitro Compounds," AD-A 127812, Lancaster, PA, 1983.

[60]Hill, M. E., "Structure Property Relationships in Propellants Ingredients," AIAA Paper 78-119, June 1978.

[61]Frankel, M. B., and Wilson, E. R., "Energetic Azido Monomers," *Journal of Chemical Engineering Data*, Vol. 26, No. 6, 1981, p. 219.

[62]Yan, H., "Synthesis of Organic Azides," Ph.D. Dissertation, Beijing Inst. of Technology, Beijing, PRC, 1994 (in Chinese).

[63]Xie, S., "Synthesis of Energetic Azido Additives," Ph.D. Dissertation, Beijing Inst. of Technology, Beijing, PRC, 1991 (in Chinese).

[64]Cui, Y., "Synthesis of Organic Azides," Ph.D. Dissertation, Beijing Inst. of Technology, Beijing, PRC, 1994 (in Chinese).

[65]Anderson, W. S., and Rlyen, H. J., "Some New Aliphatic Polyazides Derived from Pentaerythritol," AD-A 103844, 1981.

[66]Huang, Y., and Li, C., "Synthesis of Tetraazido Pentaerythritol," 3rd Conf. of Chinese Society of Propellants and Explosives, Beijing, PRC, 1991 (in Chinese).

[67]Frankel, M. B., "Azido Derivatives of Pentaerythritol," U.S. Patent 4,683,086, 1987.

[68]Wang, P., Li, S., Huang, Y., and Li, C., "Studies on Diazido Dinitrate of Pentaerythritol," *Energetic Materials*, Vol. 2, No. 3, 1994, p. 29 (in Chinese).

[69]Fu, S., "Synthesis of Energetic Oxygen Heterocyclic Azides," Ph.D. Dissertation, Beijing Inst. of Technology, Beijing, PRC, 1988.