MILITARY TECHNICAL COLLEGE

CAIRO - EGYPT

CHARACTERISTICS AND PERFORMANCE OF ENERGETIC BINDERS BASED ON HETEROCYCLIC COMPOUNDS

M.A.SADEK*, M.A.RADWAN*, M.SH.FAYED*

ABSTRACT:

Energetic polymers are useful as binders in rocket propellants and plastic bonded explosives to enhance the performance and to reduce the vulnerability of the system. In this paper the performance characteristics were calculated for two polymers based on heterocyclic monomers. The first polymer, glycidyl azide polymer (GAP), was prepared from polyepichlorohydrin (PECH), previously prepared from epichlorohydrin monomer, and sodium azide. The second one which is bis-azido-methyl oxetane polymer (BAMO) was prepared from 3,3-bis-(chloromethyl) oxetane monomer, with sodium azide. The performance characteristics of these polymers in mixtures with aluminium and ammonium perchlorate were calculated through a computer program. The specific impulse, adiabatic flame temperature were also calculated and discussed.

INTRODUCTION:

Energetic polymer binders have been considered as the most interesting topic in the modern propellant chemistry. Many trials have been done to introduce some energetic groups such as $-NO_2$, $-ONO_2$, $-N{=}N-$, and $-NF_2$ into polymer molecules to increase the energetic performance of the propellant [1].

Energetic polymers containing azide groups are useful as binders in rocket propellants and plastic bonded explosives to enhance the performance and stability, to reduce the vulnerability and to improve the physico-chemical properties of the system.

Glycidyl azide polymer (GAP) has been spotlight because of its high density compared to hydroxy-terminated polybutadiene, positive heat of formation, and the capability of stop-start and thrust control [2]. Bis-azido-methyl oxetane (BAMO) homopolymer or its copolymer with tetrahydrofuran are considered as useful binders due to their chemical stability, processability and compatibility with existing formulation ingredients [3].

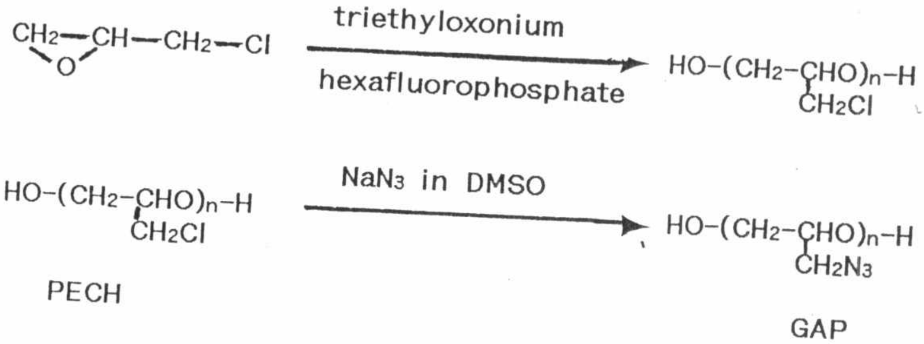
* Chemical engineering branch, M.T.C., Cairo, EGYPT

This paper describes synthesis, characterization and computation of performance of GAP and BAMO as binders for propellants containing ammonium perchlorate as oxidizer and aluminium powder as metallic fuel.

SYNTHESIS:

1. GAP:

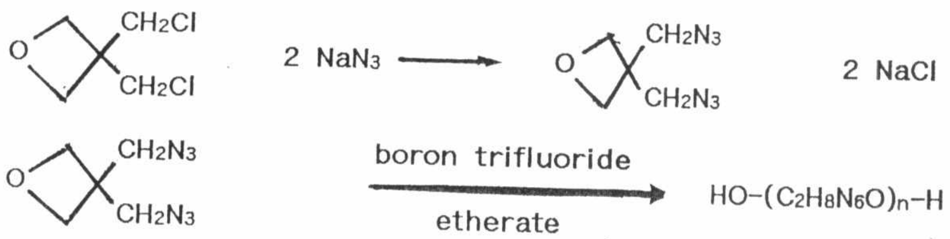
GAP was prepared from epichlorohydrin according to the following scheme :



Polyephichlorohydrin (PECH) can be prepared in the molecular weight range from 500 to 3000 by cationic polymerization. The initiation is done by ethylene glycol and triethyloxonium hexafluorophosphate [4]. The prepared PECH is agitated at 100 C for 8-10 hours with sodium azide and dimethyl sulphoxide (DMSO). The precipitated sodium chloride was filtered, most of the solvent (DMSO) was distilled off in vacuum, and GAP diol was obtained by repeating the removal operation of sodium chloride precipitated by cooling down the residue [2].

2. BAMO:

BAMO is prepared according to the procedure described in reference [5] from 3,3-bis-(chloromethyl) oxetane (BCMO) by reaction with sodium azide:



The solution of 1 mole BCMO with 2 moles sodium azide in dimethyl formamide is heated at 80 C for 18 hours. After cooling, the precipitated sodium chloride is removed by filteration and the filterate is vacuum distilled to give BAMO.

The BAMO is polymerized in the presence of borontrifluoride etherate and 1,4 butanediol, where they are stirred at-5 C for 48 hours. The reaction mixture is quenched with saturated sodium chloride. The crude polymer is separated, dissolved in a minimum volume of methylene chloride and reprecipitated by addition of a ten fold volume of methanol. The precipitated polymer was isolated by decanting the methanol and drying in vacuum.

3. BAMO/THF COPOLYMER:

Since the melting point of poly-BAMO could not be lowered by molecular weight control, the research is shifted to the copolymerization of BAMO with tetrahydrofuran (THF). This copolymer is characterized by low melting point [6].

CHARACTERIZATION OF GAP AND BAMO:

The physicochemical properties of GAP, BAMO and BAMO/THF copolymer are shown in Table 1, Table 2 and Table 3 respectively [7,8].

The infrared spectrum of both GAP and BAMO polymers are shown in Fig.1 and Fig.2. The formation of azide group can be assigned by the sharp absorbance at 2100 cm^{-1} [3,9].

The Differential Scanning Calorimetric measurements (DSC) presented in Fig.3 show that there are two weight loss stages for pure GAP polymer. The first stage corresponds to an exothermic reaction. At the second stage, slow weight loss reaction occurred without heat production [10].

The Differential Thermal Analysis (DTA) and Thermo-Gravimetric Analysis (TGA) results for BAMO polymer are shown in Fig.4 These results show that there is a single weight loss stage corresponding to an exothermic reaction [3].

RESULTS AND DISCUSSION:

The thermochemical characteristics of propellants containing GAP, BAMO and BAMO/THF copolymer as binders, ammonium perchlorate as oxidizer and aluminium metal as mettalic fuel are determined using a computer program. The program determines the equilibrium composition of the combustion products and their thermodynamic properties in the chamber, at the throat, and at the exit. The fundamental equations and a brief description of the program used are presented in reference [11].

Various rocket performance parameters including specific heat ratio (γ), adiabatic flame temperature (T), exhaust velocity (We) , average molecular weight of gaseous products (M) and specific impulse (Is) were calculated at pressure equals 70 bars and pressure ratio 1/70.

In practice we meet many problems if the solid contents are higher than 80% especially the mechanical and rheological properties. For that reason, in this study the binder is varied from 25 to 40%. In the formulations containing aluminium; the ratio of binder/ammonium perchlorate is kept at 0.3/0.7 and the aluminium content is varied from 0 to 20%.

Fig.5 and Fig.6 show the relation between adiabatic flame temperature, specific impulse and binder percentage for propellant formulations containing GAP, BAMO, BAMO/THF and ammonium perchlorate. From the figures; it is clear that both specific impulse and adiabatic flame temperature decrease with the increase of binder content. In general, the values of the specific impulse and adiabatic flame temperature for the propellant compositions containing BAMO as binder are higher than those containing GAP or BAMO/THF copolymer. These values are higher than those calculated for propellant containing well known hydroxy terminated polybutadiene (HTPB) binder (13%) and ammonium perchlorate (87%). The specific impulse for HTPB composition equals 244 sec while the adiabatic flame temperature equals 2950 K. These values correspond to those obtained by propellants containing 25% of GAP or BAMO or BAMO/THF binders and ammonium perchlorate oxidizer. It is well known that the increase in binder content would improve the mechanical properties and industrial processing.

The effect of addition of aluminium to the propellants containing 0.3 BAMO and 0.7 ammonium perchlorate is shown in Fig.7. The addition of aluminum increases both specific impulse and adiabatic flame temperature. Fig.8 and Fig.9 show that the addition of aluminium on both GAP and BAMO/THF copolymer has a slight effect on the specific impulse up to 10% Al, and a sharp increase in these properties up to 20%.

It is obvious that the values of specific impulse for the propellant containing 20% aluminium are very close (280 sec.) independent of the type of the energetic binder. At the same time, the adiabatic flame temperature of the propellant composition containing BAMO/THF copolymer is less than the others by about 5%. From this study , it is clear that at the same value of specific impulse, the adiabatic flame temperature is lower than those obtained for HTPB propellants, which means the decrease of thermal insulation problems. For example, the specific impulse for the propellant formulation (13% HTPB, 71% APC, 16% Al) equals 254 sec. and the adiabatic flame temperature is 3500 K. The same value of specific impulse is obtained by a formulation containing 28.5% BAMO, 66.5% APC and 5% Al with adiabatic flame temperature equals 3277 K, i.e. a formulation with low solid content, improved mechanical properties and low thermal insulation problems.

CONCLUSIONS:

Polymers containing azide groups have good mechanical, rheological, chemical and performance properties and considered as a future energetic binders in rocket propellants and plastic bonded explosives. For future work it is recommended to study the practical performance, the burning characteristics and industrial production of these polymers.

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Table 1 Physicochemical Properties of GAP.

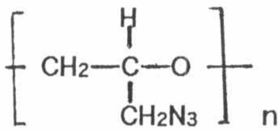
NAME	Glycidyl Azide Polymer
Chemical Formula	$C_3H_5ON_3$
Molecular Structure	
Molecular Weight	2.00 (Kg / mole)
Density	1.3 x 10^3 (kg/m^3)
Heat of Formation	957 (kj/kg)
Deflagration Point	533 (K)
Adiabatic Flame Temperature	1523 (K)

Table 2 Physicochemical Properties of BAMO.

Molecular Formula	HO-($C_2H_8N_6O$)$_n$-H
Molecular Weight	2.78 (kg/mol.) (n=16.4)
Density	1.3 x 10^3 (kg/m^3)
Melting Point Temperature	334 (K)
Glass Transition Temperature	234 (K)
Heat of Formation	2460 (kj/kg)
Adiabatic Flame Temperature	2020 (K)

Table 3 Physicochemical Properties of BAMO/THF.

Molecular Formula	HO-($C_2H_8N_6O$)$_n$-(C_4H_8O)$_n$-H
Molecular Weight	2.3 (kg/mol) (n=9.5)
Density	1.18 x 10^3 (kg/m^3)
Melting Point Temperature	273 (K)
Glass Transition Temperature	210 (K)
Heat of Formation	989 (kj/Kg)
Adiabatic Flame Temperature	1418 (K)

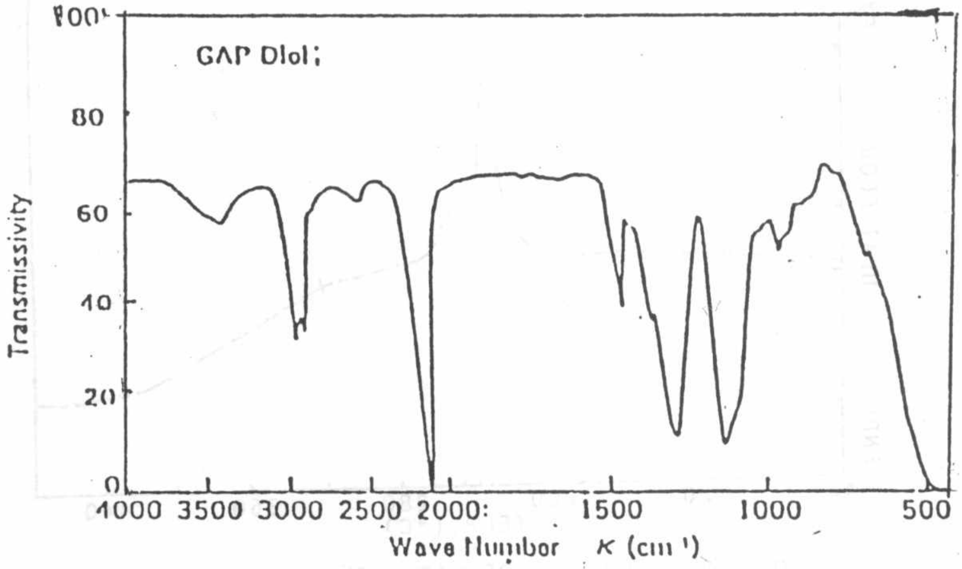


Fig.1.Infrared Spectrum of GAP diol.

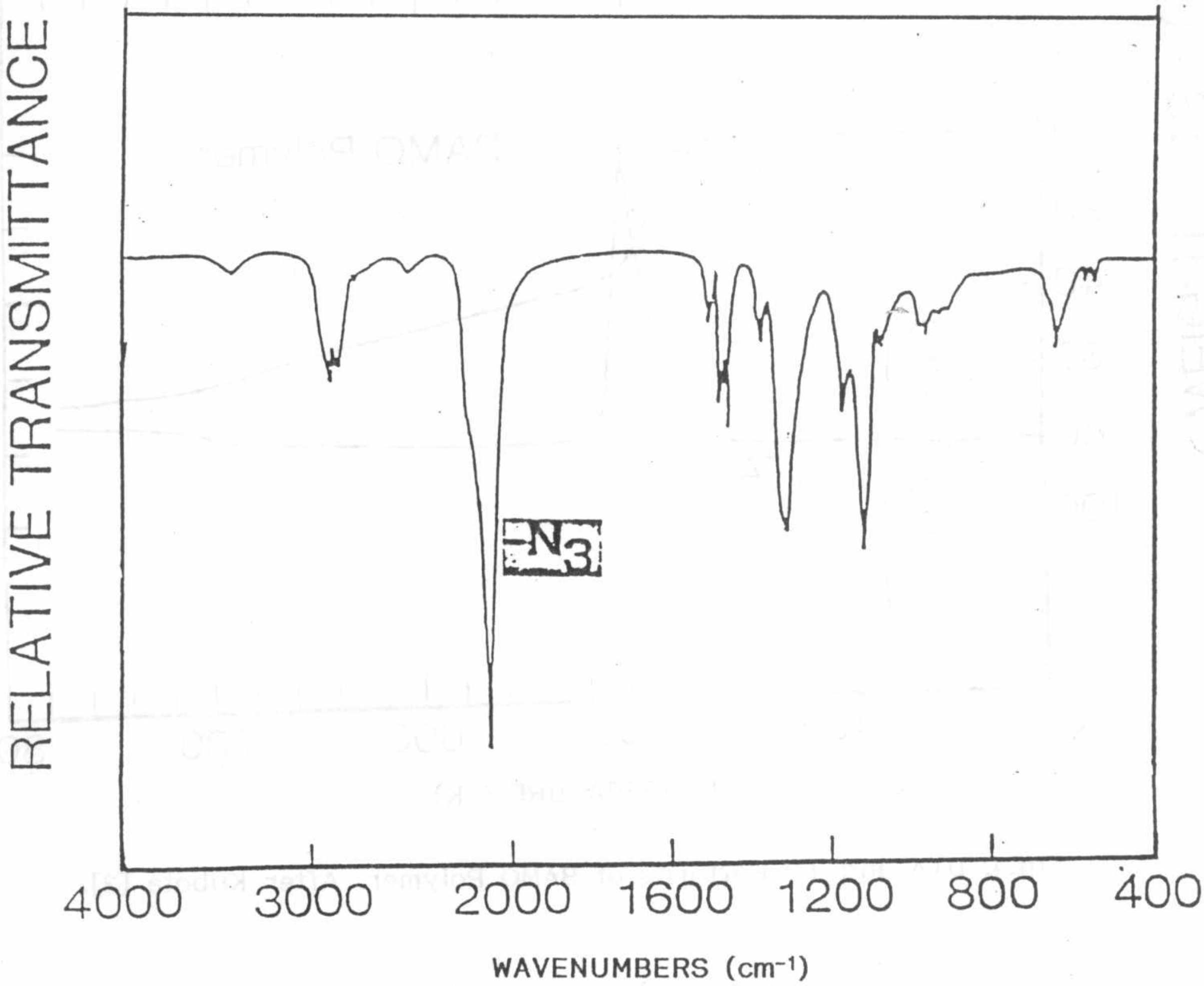


Fig.2.Infrared Spectrum of BAMO Polymer

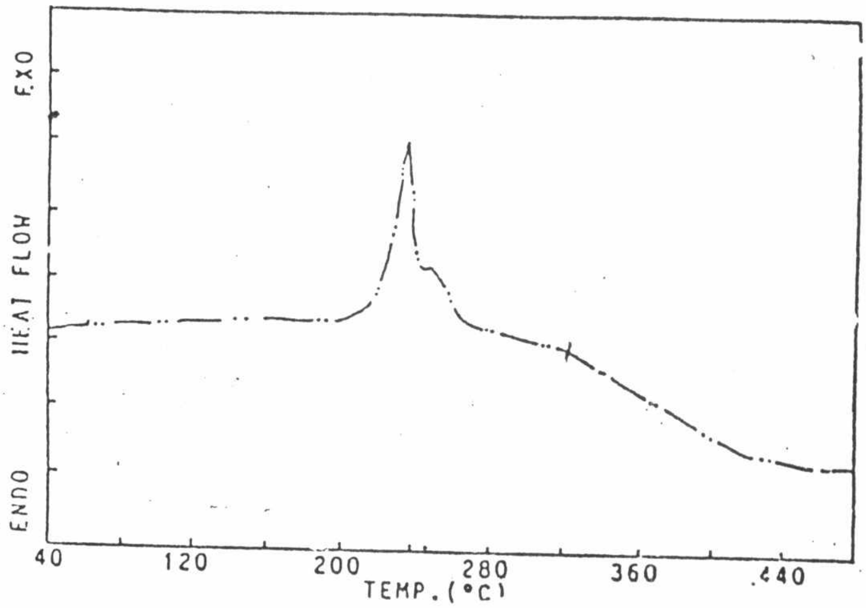


Fig.3. DSC Pattern Of GAP. After Nakashita [10].

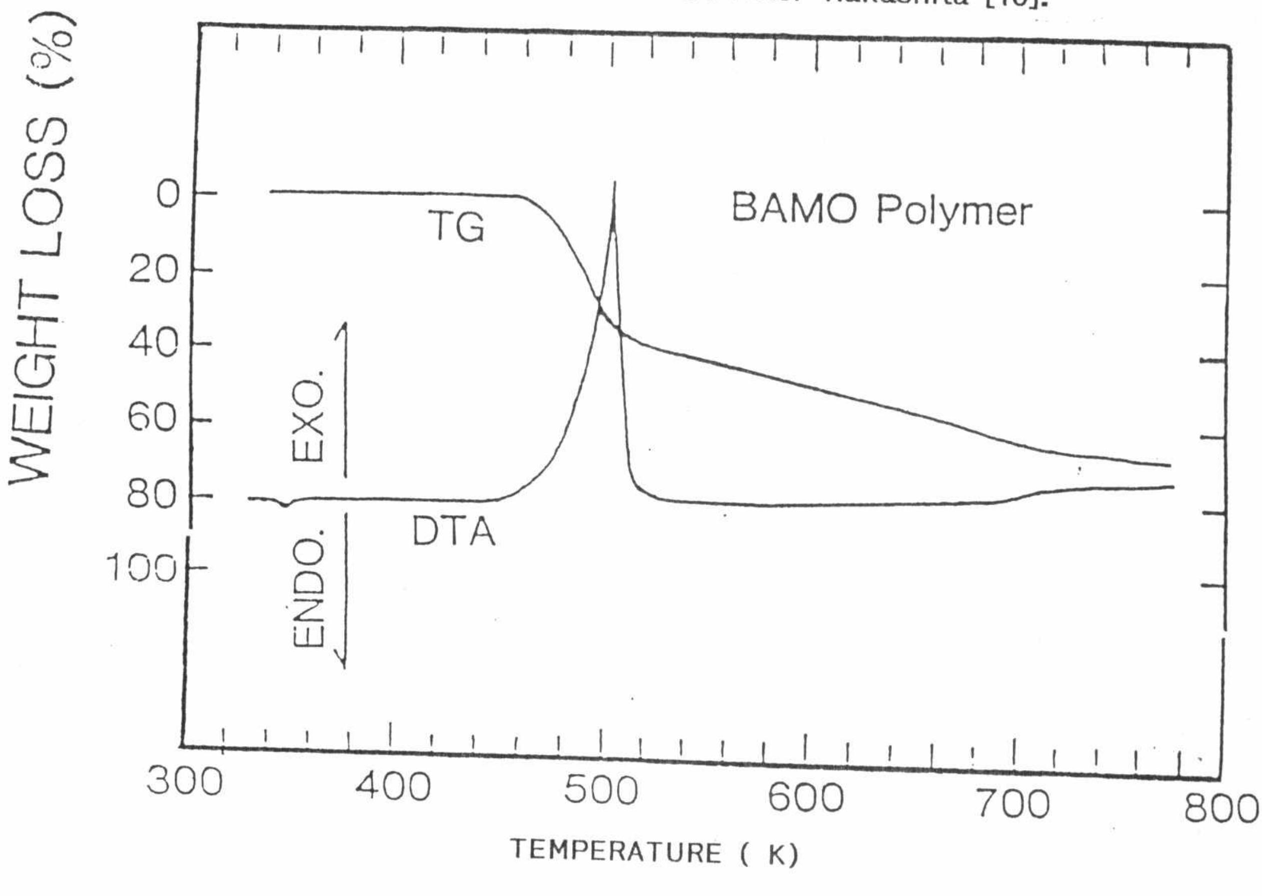


Fig.4. DTA and TG Patterns of BAMO Polymer. After Kubota [3].

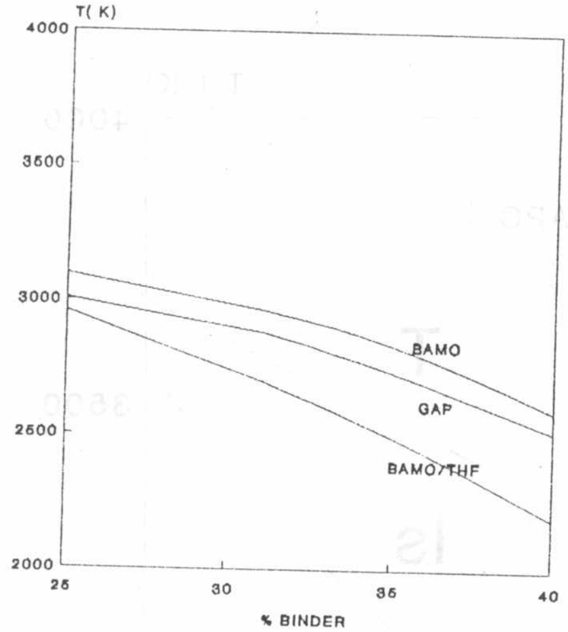


Fig.5.Relation between T and % binder

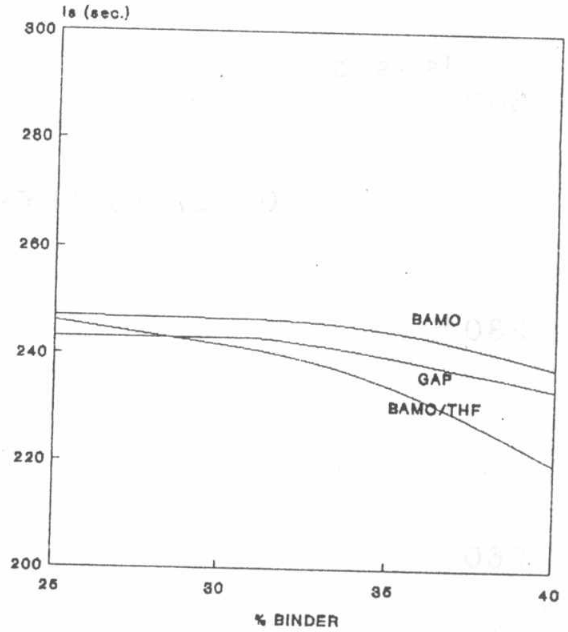


Fig.6.Relation between Is and % binder

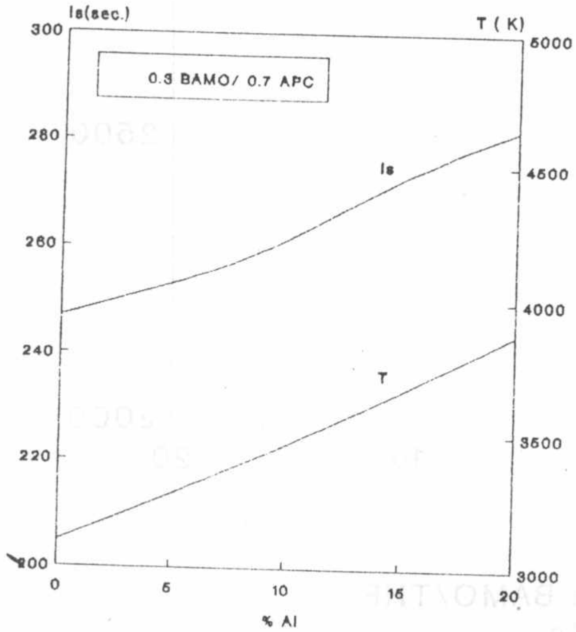


Fig.7.Effect of Al on BAMO propellants

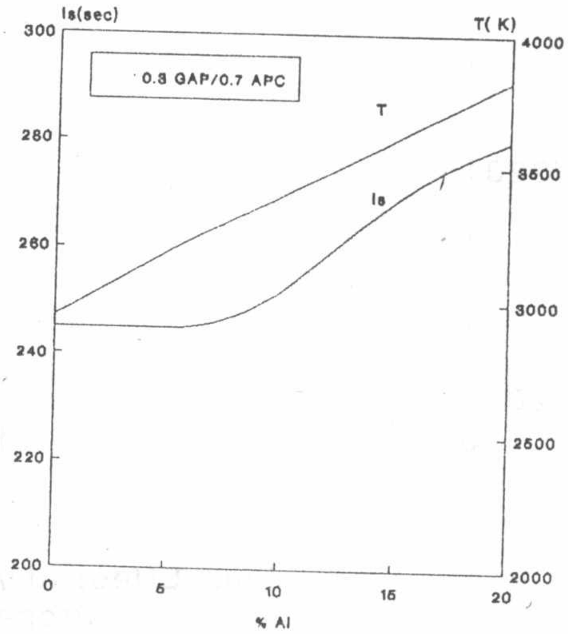


Fig.8.Effect of Al on GAP propellants

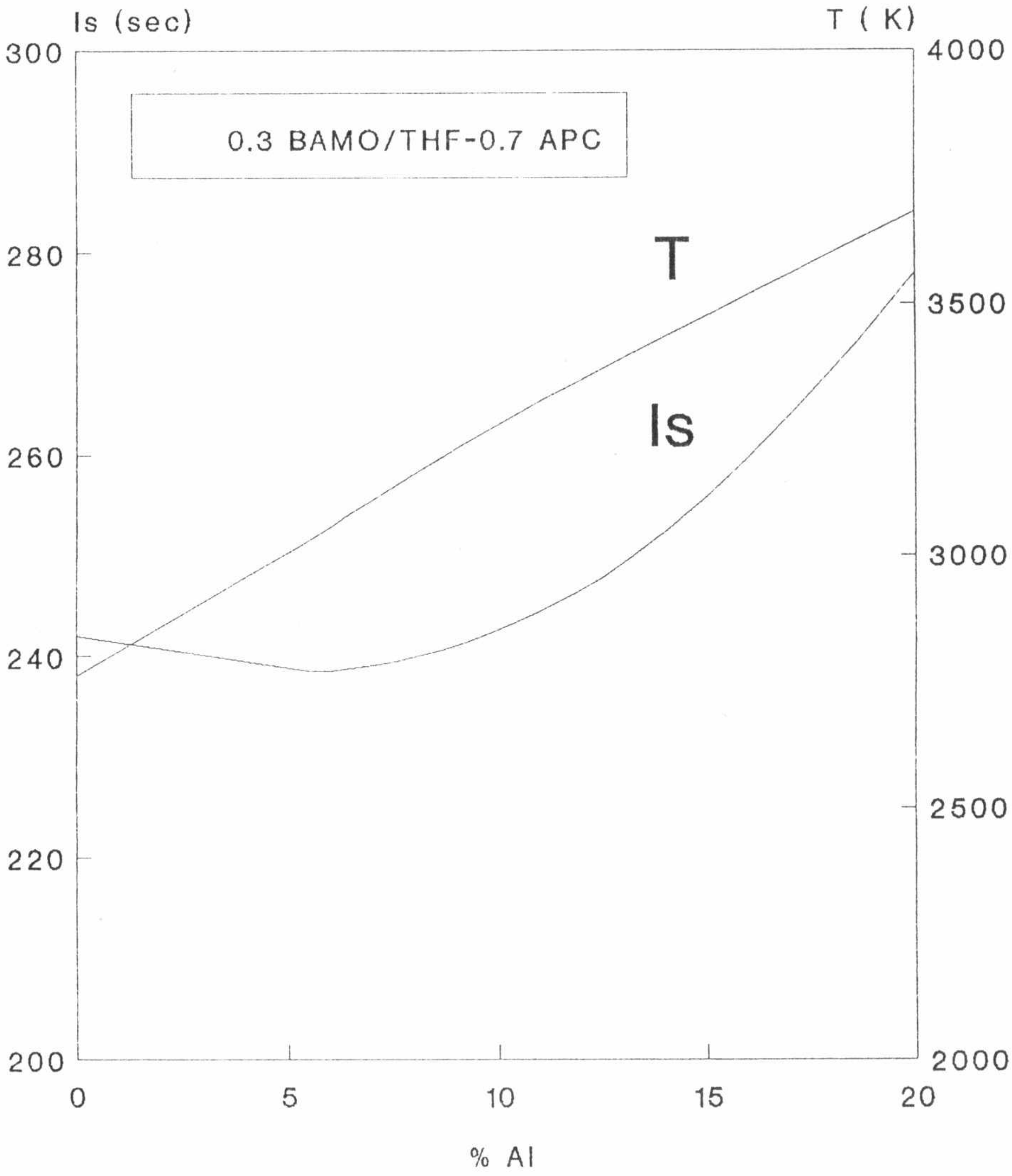


Fig.9.Effect of Al on BAMO/THF Propellants.