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MODERN TECHNOLOGY OF PROPELLANTS FOR MISSILE

(Volume Two)

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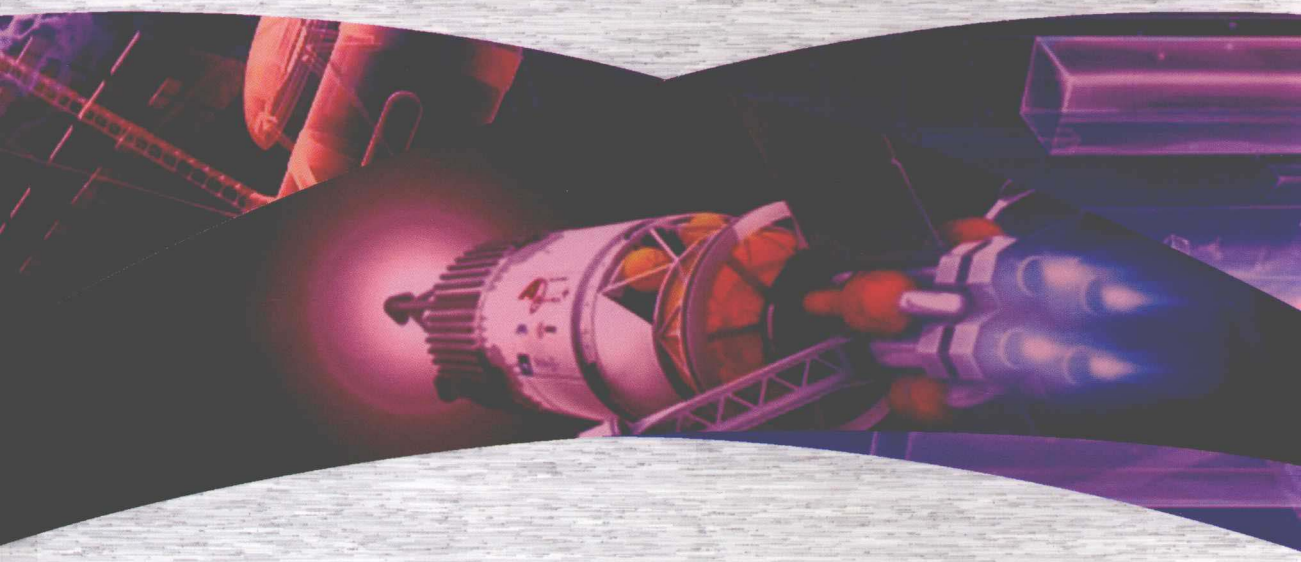

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Modern Technology of Propellants for Missile

（Volume Two）

黄智勇　窦文辉　编著

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【内容简介】 本书分上、下两册。上册分四个部分，共13章。第一部分介绍了液体推进剂仪器分析方法，包含仪器分析概述、气相色谱法、色质联用分析方法、近红外分析方法和自动颗粒计数分析方法；第二部分介绍了偏二甲肼分析，包含推进剂概述、偏二甲肼的使用与管理、偏二甲肼分析方法；第三部分介绍了硝酸-27S分析，包含硝酸-27S的使用与管理、硝酸-27S分析方法；第四部分介绍了DT-3分析方法。下册分四个部分，共17章。第一部分介绍了固体火箭推进剂，包括固体推进剂的性能及复合固体推进剂的制造概述；第二部分介绍了液体推进剂污染监测与治理，包括液体推进剂污染来源及特点、污染监测与环境评价、废气治理技术和废水处理技术；第三部分介绍了推进剂现代安全技术，包括安全基本原理、液体推进剂安全技术、固体推进剂安全技术和推进剂突发事故与应急处置；第四部分介绍了液体推进剂个体防护装备与检测方法，包括液体推进剂呼吸防护装备、躯体防护装备、手足部防护装备和个体防护装备检测方法等内容。

本书可供学习“导弹推进剂理论与技术”专业课程的本科生和研究生作为双语教材，也可供从事导弹推进剂研究的技术人员参考使用。

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前　言

双语教学是我国高等教育国际化趋势的发展需要，教育部先后于2001年、2004年、2005年和2007年出台了关于高等学校本科双语教学的文件，明确提出要提高双语教学课程的质量，扩大双语教学课程的数量，推动双语教学课程建设，探索有效的教学方法和模式，提高大学生的专业英语水平和直接应用英语从事科学研究的能力。

与传统的英语教学相比，双语教学更重视英语与学科专业的渗透，让学生全方位地应用英语。双语教学不仅仅让学生以英语为工具来获取知识，更重要的在于能够让学生了解国外先进的教育理念、教学模式和教学方法。同时，双语教学通过以第二语言学习学科知识为目的，塑造学生的跨文化意识，学生逐步达到双语思维，从而提高多维创新能力。

毋庸置疑，目前双语教学遇到较大困难。其中一个重要原因就是缺乏适合专业内涵及学生实际情况的教材。实践证明，解决双语教学教材问题的方法包括引进适合专业教学的原版教材、根据专业实际情况编写、翻译中文教材等。本书就是结合环境工程专业，针对液体推进剂分析和推进剂管理与使用两门课程开展双语教学而编写的。

本书是在中文讲义的基础上翻译而成的，教学讲义分别是由苟小莉编写的《液体推进剂现代分析技术》，黄智勇编写的《偏二甲肼分析》《硝酸-27S分析》及《DT-3分析》，崔虎编写的《固体火箭推进剂》，张剑编写的《液体推进剂污染监测与治理》，吕晓猛编写的《火箭推进剂现代安全技术》和韩启龙编写的《液体推进剂个人防护设备及检测方法》。本书分上、下册，上册各部分及下册第1～3部分由黄智勇翻译，下册第4部分由窦文辉翻译，全书由窦文辉统稿。对于各位老师在中文讲义编写中所付出的辛勤劳动，以及对译者在翻译过程中提供的有益帮助表示衷心感谢。本书的出版得到了第二炮兵工程大学训练部的大力支持，在此一并表示感谢。

由于水平有限，肯定会有疏漏和翻译不当之处，敬请读者和专家批评指正。

编　者

2014年9月

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PART Ⅰ SOLID PROPELLANT

CHAPTER 1 INTRODUCTION

Solid propellant is used as the energy source and working medium of solid-propellant rocket engine. As one of the chemical propellants, it takes the thermal energy from the chemical reaction as the power for propelling system. It is a kind of high-molecule-based energetic material with specific characteristics.

1.1 GENERALIZATION

Power unit is the main part in the constituent of solid rocket. The mass and volume of power unit account for 40%—60% of solid rocket. Solid propellant is widely used in large boost motor, upstage engine, attitude controlling engine and orbit-in engine. Some application examples of solid propellant in solid missiles are listed in table 1 - 1.

Table 1 - 1 Solid propellants used in strategic missiles

Missile Type	1st stage	2nd stage	3rd stage	Range/km	Country
MX	HTPB/AP/Al 12/69/19	HTPB/AP/Al (HMX)	NEPE	Intercontinental 11,000	U. S.
Dwarf	NEPE	NEPE	NEPE	Intercontinental 11,000	U. S.
S—3	PU	PU	/	Ground - ground 3,500	France
Polaris A—3	PU/FYZ—1/AP/Al 8. 2/12. 3/63. 5/16. 0	CMDB NC/NG/AP/Al	/	Submarine - ground 4,600	U. S.
Poseidon (C—3)	PBAN/AP/Al	CMDB NC/NG/AP/Al HMX	/	Submarine - ground 4,600	U. S.
Trident I(C—4)	XLDB HMX43%	XLDB HMX40. 5%	XLDB HMX54%	Submarine - ground 7,400	U. S.

cont.

Missile Type	1st stage	2nd stage	3rd stage	Range/km	Country
Trident II(D−5)	NEPE	NEPE	XLDB HMX54%	>7,400	U. S.
M−20	PU/AP/Al	CTPB/AP/Al	/	Submarine−ground 3,000	France
M−4	CTPB/AP/Al	CTPB/AP/Al	CTPB/AP/Al	4,000 to 6,000	France

According to the theoretic analysis and experience, the ideal solid propellant should meet the following requirements,

1) High specific thrust, high density, high specific heat of constant pressure, small molecule weight combustion products, big specific heat combustion products, gaseous combustion products, and small decomposition yield combustion products.

2) Good physico-chemical stability, high self-combustion temperature, good mechanical property, poisonless and harmless, no smog in the exhaust gas.

No solid propellant can meet all the requirements mentioned above though these requirements are not so comprehensive. According to the fly mission, the solid propellant of the best properties should be selected to meet the main requirements.

1.2 COMPOSITION AND CLASSIFICATION OF SOLID PROPELLANT

1.2.1 CLASSIFICATION OF SOLID PROPELLANT

With the development of rocket technology, the varieties of solid propellant have been increased gradually. There are many classification methods for solid propellants at present, such as, in terms of energy criterion, solid propellants can be classified into the low energy solid propellant (specific thrust less than 2,156 $N \cdot s \cdot kg^{-1}$), the medium energy solid propellant (specific thrust 2,156 to 2,450 $N \cdot s \cdot kg^{-1}$) and the high energy solid propellant (specific thrust more than 2,450 $N \cdot s \cdot kg^{-1}$); in terms of mechanical property, solid propellant can be classified into the soft charge solid propellant and the solid charge solid propellant; in terms of concentration of smoke in the exhaust gas, solid propellants can be classified into the smoke solid propellant, the non-smoke solid propellant, and the kind in between.

Solid propellant can be classified into the composite solid propellant and the homogeneous solid propellant according to the criterion whether there are phase interfaces between compositions of solid propellant. The composite solid propellant can be classified into the ammonia perchlorate solid propellant (AP) and the ammonia nitrate solid propellant (AN). According to the adhesive varieties, composite propellants are classified into many

series. The classification of solid propellant. is shoun as Fig. 1 - 1.

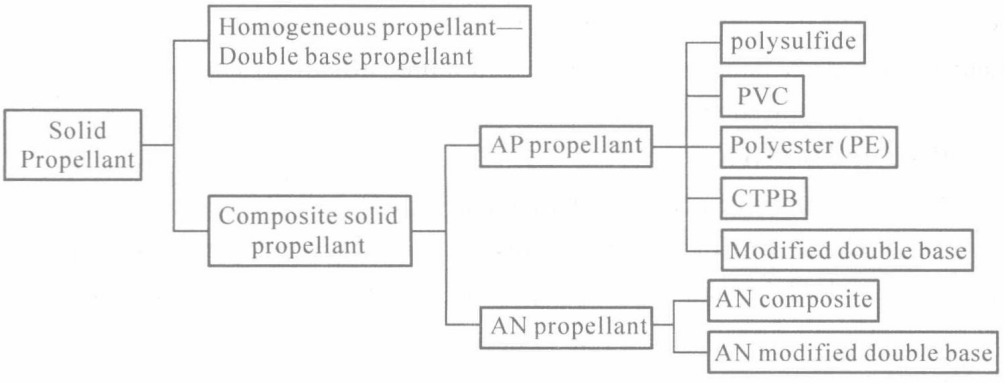

Fig. 1 - 1 Classification of solid propellant

1.2.2 COMPOSITE SOLID PROPELLANT

The composite solid propellant takes the polymer adhesive as the elastic base material and supplies the combustive elements for combustion. There filled some solid oxidant, metallic powder and a few other components in the adhesive. The composite solid propellant is a kind of multiple phase mixture, also called heterogeneous propellant because of the obvious interfaces between compositions and the uneven structure. The main components of composite solid propellant shall be classified as follows.

1. Oxidant

(1) High content of available oxygen

Available oxygen means the left oxygen in the oxidant molecule after the combustive elements combine with the oxidizing elements (O, Cl, and F) and the entire valence are satisfied. The content of available oxygen means the ratio of the mass of available oxygen (expressed with atomic mass) to the molecule mass of oxidant in the oxidant molecule.

Take the ammonia perchlorate as an example.

$$NH_4ClO_4 \rightarrow 0.5N_2 + HCl + 1.5H_2O + 1.25O_2$$

So the content of available oxygen $= (1.25 \times 32)/117.5 = 34.04\%$.

For the given amount of composite solid propellant, the higher content of available oxygen there is in the oxidant, the less the needed oxidant for the same completeness of combustion. If the content of oxidant isn't changed, the oxidant with high available oxygen can supply more oxygen and thus the combustion completeness of propellant shall be increased so as to increase the energy.

(2) High forming enthalpy

As known from the thermal chemistry, the thermal effect of chemical reaction at constant pressure equals the enthalpy decrease of system in the standard state (298 K, 101.315 kPa), i. e.

$$Q_s = \sum_i n_i \Delta H_i^\theta - \sum_j n_j \Delta H_j^\theta \qquad (1-1)$$

If the propellant burns under the condition of thermal insulation, here Q_v is the explosion heat of constant pressure of the propellant; n_i and $\Delta H_i^\ominus$ are the molar number of component i of the propellant and its standard forming enthalpy respectively; n_j and $\Delta H_j^\ominus$ are the molar number of product j from the combustion of the propellant and its standard forming enthalpy respectively.

It can be seen from formula (1 - 1) that for high Q_v, the bigger the standard forming enthalpy of each component of the propellant, especially the oxidant of big content is, the better and the standard forming enthalpy of each combustion product should be as low as possible.

(3) High density

The higher density of the oxidant, the bigger density the produced solid propellant shall be. It can reduce the volume of combustion chamber, and also reduce the volume ratio of oxidant adhered with big density of oxidant when the content of oxidant in propellant keeps unchanged. If the volume ratio is fixed, the content of oxidant can be increased with increasing the density of oxidant so as to supply more oxygen for more complete combustion and high energy.

(4) Big gas formation

The gas formation is generally expressed with the volume produced by 1kg oxidant in the standard state. To meet this requirement, the oxidant should be composed of the elements of low atomic mass.

Some property data of oxidants are listed in table 1 - 2.

Table 1 - 2 Properties of oxidant

Name	Molecule mass	Density / $kg \cdot m^{-3}$	Content of available oxygen / (%)	Produced gas / $kg \cdot dm^{-3}$	Standard forming enthalpy / $kJ \cdot kg^{-1}$
Potassium perchlorate	$KClO_4$	2,520	46.2	323	−3,130.66
Ammonia nitrate	NH_4NO_3	1,730	20.0	980	−4,568.85
Ammonia perchlorate	NH_4ClO_4	1,950	034.0	790	−2,473.40
Lithium perchlorate	$LiClO_4$	2,430	60.2	437	−3,856.26
Nitryl perchlorate	NO_2ClO_4	2,250	66.7	616	+255.68
RDX	$C_3H_6N_6O_6$	1,818	−21.6	907	+318.0
HMX	$C_4H_8N_8O_8$	1,870	−21.6	908	+252.8

2. Adhesive

Composite propellant is a multiple phase system, taking the adhesive as the continuous phase and the solid filler (solid component such as oxidant, aluminum, etc.) as the dispersed system, so the mechanical property of solid propellant depends mainly on the adhesive. The adhesive can also supply the necessary combustible elements, such as C, H and S, etc. The properties of adhesive also take great effect on the producing process, combustible properties and storage of the solid propellant. The development of solid propellant is mainly based on the development of adhesive, so the existing propellants are named according to the varieties of adhesive. The requirements for adhesives are as follows.

- High energy
- Low viscosity
- Glass temperature T_g after solidification
- Good storability

The existing adhesive can be classified into two kinds, the thermosetting adhesive and the thermoplastic adhesive.

(1)The thermoplasticity adhesive

The solidification system of this kind of adhesive is composed of adhesive and plasticizer. Its solidification is a physical procedure. When heated, the plasticizer enters the molecules of polymer (adhesive) through diffusion to make the particles or powder polymers become even and continuous solid microscopically, thus the solidification is completed. This adhesive system is hard at room temperature and is softened as plasticity when its temperature attains to certain value, so it is called thermoplasticity. Nitrated cellulose plastisol adhesive, composed of NC and NG, is thermoplastic adhesive. This kind of adhesive has plenty of oxygen elements and produces great amounts of gas, so its energy is high and has good storability. But its glass temperature is high and has poor mechanical properties at low temperature.

(2)The thermosetting adhesive

This kind of adhesive is liquid macromolecule prepolymer of low polymerization degree. The thermosetting adhesive (liquid prepolymer) reacts with crosslinker and curing agent to make the adhesive be polymerized into a net-structured polymer of suitable crosslink. Thus the adhesive is transferred from liquid to the propellant elastic base of good mechanical property. Here the adhesive, the curing agent and the crosslinker are called adhesive system. After being solidified, the thermosetting adhesive can not be softened at higher temperature.

At present, the majority of composite propellant use thermosetting adhesive. The widely used adhesives are carboxyl terminal polybutadiene (CTPB) adhesive and hydroxyl terminal polybutadiene (HTPB) adhesive. The characteristics of them are shown in the following table 1 - 3.

Table 1 - 3 Main properties of some adhesives

Name	Chemical formula	Density / kg · m^{-3}	Forming enthalpy / kJ · kg^{-1}	Viscosity / Pa · s	T_g / ℃
CTPB	$HOOC(CH_2)_3(CH_2CHCHCH_2)_n(CH_2)_3COOH$	910	−585	23	−93.0
HTPB	$HO(CH_2CHCHCH_2)_nOH$	930	−315	4—6	−84.4

1) Polysulfide rubber adhesive.

The typical polysulfide rubber adhesives are ethyl formal polysulfide compound and butyl ether polysulfide compound. This kind of adhesive has good mechanical properties and cohesiveness. Polysulfide propellants were widely used in solid engine in the 1950s. The obvious defects of polysulfide propellant are that oxygen is released in solidification reaction to form bubble inside propellant with the existence of metallic powder and the amount of produced gas is not so big with the existence of sulfur element of big atomic mass in propellant. So the energy of polysulfide propellant is hard to be increased to satisfy the need of rocket launching. Nowadays polysulfide rubber adhesive has been replaced by other adhesives of better properties gradually.

2) Polyether adhesive.

One of the typical polyether adhesive is polyether glycerin. It's rich in resources and low in viscosity, so more solid fillers can be added to produce propellant of high energy. Its solidification rate is suitable and its solidification temperature is low, so its process property is good, the thermal stress is small after solidification and its mechanical property is very good too.

3) Butadiene, acrylic and acrylonitrile polymer (PBAN) adhesive.

The glass temperature of this adhesive is low, so it can be used at lower temperature. Its price is the lowest among the composite propellants currently. The high viscosity is its defect, so the content of solid component in propellant is very high. The reproducibility of its mechanical property is not good.

4) Carboxyl terminal polybutadiene.

It is developed based on the adhesive PBAN and It avoids the effects of PBAN with poor reproducibility of mechanical property. Its viscosity is low, so it can be produced into propellant of high energy. But its aging property should be improved.

5) Hydroxyl terminal polybutadiene.

HTPB is characterized as high forming enthalpy, low viscosity, good mechanical property and long storage period. The solid propellants with this adhesive have good properties and are widely used in many kinds of rocket engines. It has been replacing the CTPB gradually at present.

3. Metallic fuel

Metallic fuel is one of the fundamental components of modern composite propellant. Metal has the high density and can release great amount of heat after being fired. Metallic fuel can increase the heat of explosion and density of solid propellant and the solid metallic oxidizer particles from burning can suppress the oscillating burning. The requirements for metallic fuel are as follows: high combustion heat, big density, no reaction with the other components under the condition of production and storage, i. e. good compatibility, low oxygen consumption. The available metallic fuels are lithium, beryllium, boron, magnesium and aluminum, etc. The main properties of them are listed in table 1 - 4.

Table 1 - 4 Properties of some metallic elements

Name	Symbol	Molecule weight	Density / $kg \cdot m^{-3}$	Combustion heat / $kJ \cdot kg^{-1}$	Combustion product	Oxygen consumption / g/g	Combustion heat with NH_4ClO_4 / $(kJ \cdot kg^{-1})$
Hydrogen	H	1.01		120,999	H_2O	7.94	5,273
Carbon	C	12.01	2,250	33,076	CO_2	2.66	4,857
Lithium	Li	6.94	530	42,988	Li_2O	1.16	10,802
Beryllium	Be	9.01	1,850	64,058	BeO	1.77	13,565
Boron	B	10.81	2,340	58,280	Be_2O_3	2.22	9,797
Magnesium	Mg	24.31	1,740	25,205	MgO	0.66	11,095
Aluminum	Al	26.98	2,700	30,480	Al_2O_3	0.88	9,509

At present, aluminum powder is mostly used as a metallic fuel. Although the aluminum powder has low combustion heat, its oxygen consumption is low and its density is high. High aluminum content in solid propellant has significant function in improving the specific thrust. It is widely used due to its rich raw material and low cost.

Magnesium powder has low oxygen consumption and releases more heat than aluminum powder combined with oxidant. But its small density makes it poorer in increasing the energy than aluminum powder.

4. Curing agent and crosslinker

Curing agent and crosslinker are the components of thermosetting adhesive system. Their function is to change the big molecule of linear liquid prepolymer into net-structured polymer of suitable crosslink so as to increase the mechanical properties of solid propellant for fear of plastic flowing at high temperature and embrittlement at low temperature.

The linear polymer is a two-dimension structure and there is no chemical bond between molecules. Under the condition of heating and force, molecules can slide against each other without mechanical property. There is three-dimension space structure for polymer of net-