

traditional instrumentation methods, along with substantial benefits in the handling of the sensor wiring.

Acknowledgments

U.S. Air Force (USAF) Contract F33615-98-C-2895, with Technical Monitor Charles Cross, and the Dayton Area Graduate Studies Institute Project PR-AFIT-99-07 sponsored this research. Their support is most gratefully acknowledged. In addition, the support of the Compressor Aero Research Laboratory staff and use of the U.S. Air Force facility is acknowledged.

References

- ¹Probasco, D. P., Leger, T. J., Wolff, J. M., Copenhaver, W. W., and Chriss, R., "Variations in Upstream Vane Loading with Changes in Back Pressure in a Transonic Compressor," 2000, *Journal of Turbomachinery*, Vol. 122, No. 3, pp. 433–441.
- ²Sanders, A., and Fleeter, S., "Forcing Function Variability and Its Effect on Airfoil Response," AIAA Paper 98-3898, July 1998.
- ³Manwaring, S. R., and Wisler, D. C., "Unsteady Aerodynamics and Gust Response in Compressors and Turbines," *Journal of Turbomachinery*, Vol. 115, No. 4, pp. 724–740.
- ⁴Rao, K. V., Delaney, R. A., and Dunn, M. G., "Vane-Blade Interaction in a Transonic Turbine, Part I: Aerodynamics," *Journal of Propulsion and Power*, Vol. 10, No. 3, 1994, pp. 305–311.
- ⁵Dring, R. P., Joslyn, H. D., Hardin, L. W., and Wagner, J. H., "Turbine Rotor-Stator Interaction," *Journal of Engineering for Power*, Vol. 104, Oct. 1982, pp. 729–742.
- ⁶Koch, P. J., Moran, J., and Wolff, J. M., "3-D Inlet Guide Vane Generated Vortical Forcing Functions," *International Journal of Turbo and Jet Engines*, Vol. 17, No. 4, 2000, pp. 289–302.
- ⁷Karolys, A., and Swanson, B., "The Pressure Belt: A Smart Sensor Network System," *NASA Tech. Briefs*, Vol. 23, No. 10, Oct. 1999, pp. 72, 73.
- ⁸Swanson, B., "Smart Pressure Belt," *Design News*, Vol. 54, No. 17, Sept. 1999, pp. 71, 72.
- ⁹Kobayashi, H., "Unsteady Pressure Measurement Issues for High Speed Turbomachinery Applications," M.S. Thesis, Dept. of Mechanical Engineering, Wright State Univ., Dayton OH, Sept. 1999.

Studies on Ferrocene Polyglycol Oligomer—Burning-Rate Modifier for Composite Propellants

G. M. Gore,* R. G. Bhatewara,† K. R. Tipare,‡
A. N. Nazare,§ and S. N. Asthana¶
High Energy Materials Research Laboratory,
Pune 411021, India

Introduction

LIQUID-FERROCENE derivatives have evinced great interest as burning-rate catalyst for ammonium-perchlorate (AP)-containing composite propellants. A major advantage of these speciality materials over conventionally used solid catalysts (Fe_2O_3 or copper chromite) is that they do not impose penalty on loading of the energy-producing solid oxidants and fuels.¹ However, a widely used ferrocene derivative, namely, n-butyl ferrocene (nBF),

tends to migrate during storage, resulting in changes in programmed burning rates leading to reduction in useful life of the propellant. Moreover, air oxidation of nBF migrated to the surface converts it to products rendering propellants susceptible to impact and friction stimuli. One of the approaches to mitigate migration problem is to select ferrocene derivatives carrying large and bulky substituents. This led to the emergence of 2,2' bis(ethyl ferrocenyl propane) [catocene] and 1,3 di ferrocenyl-1-butene (DFB)^{1,2} as an alternate choice. However, the problem of migration exists for them through to a lesser extent. A major technological breakthrough was achieved at SNPE, France, with the development of technology of BUTACENE obtained by grafting ferrocene moiety on pendant $-\text{CH}=\text{CH}_2$ of hydroxyl-terminated-polybutadiene (HTPB) prepolymer.³ Another innovative approach involves modification of ferrocene molecule by introducing reactive isocyanate or hydroxyl groups,⁴ which can get bonded to the end groups of the polymeric binders through curative during the course of curing of polymer/propellant. Nilesen⁵ has reported use of functional di ferrocenyl compounds.

Manke et al.⁶ demonstrated that ferrocene compounds containing a single hydroxyl end group are as effective (or even more) as catocene in enhancing the burning rates of composite propellants.

This Note reports synthesis and characterization of ferrocene polyglycol oligomer (FPGO) having reactive hydroxyl ($-\text{OH}$) end groups capable of chemically bonding to HTPB by the agency of isocyanate curatives through urethane bridge. Potential of FPGO vis-à-vis nBF and DFB was evaluated as burning-rate enhancer for AP-HTPB composite propellants during this work. Fe_2O_3 was also evaluated to generate the reference data. Thermal studies were undertaken to get information on decomposition pattern of ferrocenes and the propellants.

Experimental

Synthesis and Characterization of FPGO

FPGO was synthesized on the lines of the method reported in patent.⁷ The synthesis involved condensation of ferrocene with acetyl chloride in the presence of AlCl_3 leading to the formation of diacetyl ferrocene (DAF). DAF was converted to bis (hydroxy ethyl) ferrocene (BHEF) on reduction by sodium borohydride (NaBH_4) in isopropanol. Condensation of BHEF with 1,4 butane diol in the presence of BF_3 etherate yielded FPGO. Synthesized material was characterized by ultra violet-near infrared (UV-NIR) (Hitachi model 340-C) in acetonitrile, Fourier transformed infrared (FTIR) (Perkin Elmer Model 1605) in KBr pellet, and ^1H Nuclear Magnetic Resonance ($^1\text{H-NMR}$) (Bruker 300 MHz) in CDCl_3 . Iron content was determined by colorimetric estimation. Number average molecular weight (M_n) was obtained on a vapour-pressure osmometer (KANUER make), and viscosity was measured on Brookfield viscometer (model DV-3). DFB was synthesized and characterized as per the methods reported earlier,⁸ whereas nBF and Fe_2O_3 (mean average particle size 5μ) were obtained from commercial source and used as such to generate comparative data.

Processing of Propellant

Composite propellant selected for the present study comprised 85% AP and 15% binder {prepolymer-HTPB 7.5%, plasticizer-diethyl adipate-DOA 4.5%, antioxidant cum cross linker-pyrogallol 0.5%, process aid-lecithin 0.3% and curative-toluene di isocyanate-TDI 2.2% [isocyanate (NCO):Hydroxyl (OH) 1:1]}. HTPB, DOA, and pyrogallol were mixed under vacuum (10 torr) for 2 (h). Bi-modal (60:40 blend of 250μ and 9μ size) or monomodal fine (9μ) AP was added to the binder, and mixing was continued for 30 min. Burning-rate catalysts (Fe_2O_3 /nBF/DFB/FPGO) were incorporated into one to two parts by weight over 100 parts of the composition and mixed for 10 min. Subsequently, curative (TDI) was added, and final mixing of the contents was carried out for 45 min (including 15 min under vacuum). The slurry was cast in a mould evacuated to <10 torr and cured at $60 \pm 2^\circ\text{C}$ for 10 days. All of the solid ingredients were dried to the moisture level of $<0.5\%$ before processing. Particle size of AP was determined on Malvern particle size analyser (Model Series 2600 C). The 80% particles fall at mean average value.

Received 3 December 2002; revision received 29 October 2003; accepted for publication 5 December 2003. Copyright © 2004 by the American Institute of Aeronautics and Astronautics, Inc. All rights reserved. Copies of this paper may be made for personal or internal use, on condition that the copier pay the \$10.00 per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923; include the code 0748-4658/04 \$10.00 in correspondence with the CCC.

*Scientist 'D.'

†Technical Officer 'A.'

‡Technical Officer 'A.'

§Technical Officer 'C.'

¶Scientist 'F,' Group Director.

Evaluation

Strand Burner Test

Acoustic emission technique was applied to determine the burning rates in the pressure range of 1–9 MPa. The propellant samples in the form of strand ($6 \times 6 \times 100$ mm) were placed in a nitrogen-pressurized steel bomb and ignited electrically through nichrome wire. The deflagrating samples generated acoustic signals, which were sensed by piezoelectric transducer of 200-kHz resonance frequency.⁹ The accuracy of measurement of burning rate was 2–3%. Five experiments were conducted at each pressure for each sample. Standard deviation was of the order of 0.2%.

Thermal Analysis

Thermal decomposition behavior of ferrocene compounds FPGO, DFB, and nBF was studied at the heating rate of $10^\circ\text{C}/\text{min}$ on thermogravimetric (TG) analyzer (Mettler Toledo-make) under nitrogen atmosphere. To compute activation energy (E_a) of the decomposition by Coats and Redfern¹⁰ method

$$\log_{10} \left[-\log_{10}(1 - \alpha) / T^2 \right]$$

values were plotted against corresponding $1/T$. Where α = fraction of sample decomposed at time t and T is the corresponding temperature. The slope of plot gives $E_a/2.3 R$, where R is universal gas constant.

Decomposition patterns of the propellants were determined (under nitrogen) at the heating rates of 5 – $25^\circ\text{C}/\text{min}$ (at an increment of $5^\circ\text{C}/\text{min}$) using differential scanning calorimeter (DSC) of Perkin Elmer make. Activation energy (E_a) was computed by applying ASTM¹¹ method based on Kissinger relation

$$\ln(\beta/T_m^2) = \ln(ZR/E) - E/RT_m$$

where, β is the heating rate in K/min , T_m the peak temperature in K , and Z the preexponential factor. E is calculated from the slope of the curve as per the relationship

$$\text{slope} = [d - \ln(\beta/T_m^2)]/d(1/T_m)$$

Results and Discussion

Characterization

FTIR of FPGO exhibited band at 3420 cm^{-1} corresponding to -OH group. Absorptions at 3090 , 1100 , and 995 cm^{-1} are attributable to vibrational transitions associated with cyclopentadiene rings of ferrocenes. $^1\text{H-NMR}$ of FPGO exhibited signal at 4δ as a result of 8H of cyclopentadiene moiety. O-CH_2 protons resonated at 3δ . The signal at 1.9δ could be assigned to -OH proton on the basis of D_2O exchange. Signals at less than 1.9δ can be attributed to C-H and C-CH_3 protons. UV spectra of FPGO exhibited absorption at λ_{max} 325 and 445 nm because of the presence of ferrocene moiety. The iron content of oligomer was found to be $16 \pm 1\%$. Its number average molecular weight (M_n) was of the order of 700 ± 40 . The hydroxyl equivalent of FPGO ranged between 0.29 – 0.33 . These results confirm that polymer molecule comprises two units, each derived from bis hydroxy ethyl ferrocene and 1,4 butane diol with two end-OH groups. Density ($1.23 \pm 0.03\text{ g}/\text{cm}^3$) and viscosity ($4650 \pm 100\text{ cps}$ at 25°C) of FPGO were found akin to the processing of solid propellants by casting technique.

Burning Rates

In the strand burner test, the control propellant based on bimodal AP (without catalyst) gave burning rates of 2.8 – 9.1 mm/s in the pressure range of 1 – 8.8 MPa . Incorporation of one part of Fe_2O_3 over 100 parts of propellant led to an increase in low-pressure combustion limit (LPCL) to 2.9 MPa . It resulted in 25% enhancement of the burning rates of the propellant in the pressure range of 4.9 – 8.8 MPa compared to control. On the other hand, addition of nBF or DFB led to 28–80% improvement of the burning rates in the entire pressure range without affecting LPCL. FPGO exhibited catalytic effect comparable to nBF and DFB. Increase in FPGO content to two parts over 100 parts of propellant led to further improvement in the burning rates (Table 1).

Table 1 Burning-rate results of composite propellants based on bimodal AP

Ballistic modifier	Burning rates (mm/s) at pressure (MPa)					
	1	2.9	4.9	6.9	8.8	n
Control	2.8	4.9	6.2	7.8	9.1	0.53
Fe_2O_3 (1 part)	—	3	8.4	10.4	11.2	0.50
nBF (1 part)	5	7.0	9.7	11	12.1	0.42
DFB (1 part)	5.2	7.3	9	11.2	11.7	0.38
FPGO (1 part)	5.8	7.7	11.6	13.3	13.4	0.42
FPGO (2 parts)	6.1	9.3	14	15.4	16	0.47

Thermal Decomposition

DSC of the control propellant (bimodal AP) exhibited endotherm having T_{max} of 242°C followed by two exotherms with T_{max} of 320 and 406°C . In ballistically modified propellants, endotherm was observed at more or less same temperature while first exotherm marginally shifted to lower temperature (306 – 315°C). The effect of addition of ballistic modifier on T_{max} of second exotherm was relatively more pronounced. Propellants incorporating Fe_2O_3 , DFB, and FPGO exhibited T_{max} of second exotherm in the temperature range of 351 – 362°C while nBF gave intermediate value of T_{max} (382°C).

Mechanistic Aspects

AP is known¹² to undergo orthorhombic \rightarrow cubic transitions resulting in endotherm at 240°C followed by $\sim 30\%$ decomposition in the vicinity of 300°C . It undergoes complete decomposition at $\sim 400^\circ\text{C}$. The decomposition process is accompanied with heat release. DSC of control propellant (without ballistic modifier) exhibited basic features of AP decomposition suggesting its predominant role. The DSC pattern of the ballistically modified propellants brings out that Fe_2O_3 as well as both ferrocene derivatives; DFB and FPGO influence the second exotherm significantly, whereas nBF appears to be relatively less effective in this regard. Despite the differences in the thermal decomposition pattern as well as iron content, the extent of burning-rate enhancement by nBF, DFB, and FPGO was found to be more or less same and relatively more than that of Fe_2O_3 . It is opined that iron catalysts eject $\alpha\text{-Fe}_2\text{O}_3$ particles generated in situ into the flame, which provide a site of heterogeneous catalysis.¹³ A large number of researchers have reported that Fe_2O_3 catalyzes decomposition of AP in vapor phase rather than in subsurface/condensed phase.^{14–16} Ferrocenes tend to decompose exothermically unlike Fe_2O_3 producing ultrafine $\alpha\text{-Fe}_2\text{O}_3$ particles on oxidation of molecular Fe formed, resulting in superior burn-rate enhancement compared to latter.

To get additional information, ferrocene derivatives were subjected to TGA. It brought out that nBF gets completely volatilized below 150°C , that is, much before the attainment of the temperature required for setting in of the decomposition of AP/AP propellants. In the case of DFB, 73% weight loss was observed in the temperature region of 230 – 330°C without appreciable change in DTA followed by 20% weight loss accompanied with pronounced exothermicity in the temperature region of 330 – 440°C in which AP/AP propellants undergo major decomposition. FPGO exhibited 35% weight loss in the temperature range of 240 – 275°C , followed by 30% weight loss in temperature range of 275 – 340°C and 20% weight loss in the region of 340 – 450°C . Exothermicity was observed in the temperature region of 275 – 450°C . These patterns bring out that the appreciable proportions of DFB and FPGO, or their decomposition products remain available in condensed phase during decomposition/deflagration of AP propellants.

Activation energies of first- and second-stage decomposition of DFB and FPGO as determined by dynamic TG were $102 \pm 10\text{ kJ/mol}$ and $373 \pm 8\text{ kJ/mol}$ and $117 \pm 10\text{ kJ/mol}$ and $455 \pm 8\text{ kJ/mol}$, respectively, suggesting that their mechanism of decomposition (particularly during first stage), and thereby that of burning-rate enhancement, might be more or less same. Major exothermicity can be associated with the cleavage of ferrocene structure. FPGO being a part of polymeric chain might be having pronounced effect in near-surface region as proposed for catalytic

Table 2 Burning-rate results of propellants based on monomodal fine (9 μ) AP

Ballistic modifiers (2 parts)	Burning rates (mm/s) at pressure (MPa)						
	1	1.9	2.9	4.9	6.9	8.8	n
Control	8.1	8.5	10.2	12.3	15.5	16	0.34
nBF	12.8	14	15	17.4	20	22	0.28
DFB	12.7	14.5	16.1	18.4	20.9	22.6	0.26
FPGO	12.5	15.8	16.2	18.8	21.4	22.3	0.26

effect of butacene on burning rate of AP composite propellants by Doriath.¹⁷ The nBF being volatile must be effective in gas phase, whereas DFB is expected to occupy an intermediate position because of its higher molecular weight than that of nBF despite being nonbonded like latter.

It is well reported that propellants incorporating fine AP (particle size $\leq 10\mu$) offer greater oxidizer/fuel (O/F) contact line density implying shorter diffusion distance during combustion of propellant. Consequently, reactants can mix completely before appreciable heat is released above the contact lines leading to high combustion rate. The role of vapor-surface O/F reactions also increases in case of propellants incorporating fine oxidizer. The presence of catalyst can further enhance such reactions. In view of this, burning rates of monomodal fine AP (9 μ)-based propellant containing two parts of FPGO (over 100 parts of propellant) were also evaluated during this work. Formulation containing FPGO exhibited burning rates of the order of 12.5–22.5 mm/s (Table 2) in the pressure range of 1–8.8 MPa, which are 30–100% higher than those obtained for corresponding bimodal AP-based composition. Again, the burning-rate enhancement effect of FPGO was found to be comparable to that of other ferrocenes derivatives (DFB and nBF). The strand burning rate of FPGO modified (9 μ) AP-based propellant obtained during this work were found marginally less than that obtained at 7 MPa on static evaluation of star shaped propellant comprising of (3 μ) AP-82% and Al-4% with binder 14% containing 80:20 combination of HTPB and butacene as reported by Doriath.¹⁷

Conclusions

This study brings out that the functionalized ferrocenes like ferrocene polyglycol oligomer (FPGO) offer a viable liquid ballistic modifier, which are envisaged to be free from the migration problem of ferrocenes. FPGO offers propellants having burning rates close to those of n-butyl ferrocene- and di ferrocenyl-1-butene based systems. Thermal decomposition patterns of ferrocenes and propellants based on them bring out that physicochemical nature of ferrocenes has bearing on the site of action of catalysts during combustion process. The basic decomposition processes of DFB and FPGO appear to be same.

References

- Vuga, S. M., "Effect of Liquid Burn Rate Catalyst on Rheological Properties of High Energy Composite Propellant," *Propellants, Explosives, Pyrotechnics*, Vol. 16, No. 6, Dec. 1991, pp. 293–298.
- Ashmore, C. I., Combs, C. S., and Stephenes, W. D., "Solid Propellant Having Incorporated a Ferrocene Combustion Catalyst," U.S. Patent 4,108,696, 22 Aug. 1978.
- Raynal, S., and Doriath, G., "New Functional Prepolymers for High Burning Rates Solid Propellants," *AIAA/ASME/SAE/ASEE 22nd Joint Propulsion Conference*, AIAA, New York, 1986, pp. 1–9.
- Stephens, W. D., Flanagan, D. A., Hightower, J. O., and Mangum, G. F., "Thermally Stable Burning Rate Accelerators," Thiokol, C. C., AFRPL-TR-71-3, Quarterly Progress Report, Jan. 1971, prepared for Air Force Systems Command, Air Force Propulsion Laboratory, Edwards Air Force Base, California 93523.
- Nilesen, A. T., "Monofunctional Diferrocenyl Compounds," U.S. Patent, 3,878,233, 15 April 1975.
- Manke, K., Klaus-Brehler, P., and Bohnlein-Maub., Jutta., "New Chemically Bonded Ferrocenes for Burn Rate Modification of Composite Rocket and Gas Generating Propellants," *Proceedings of the 26th International Annual conference of ICT*, Karlsruhe, Fraunhofer Inst. Chemisch Technologie, Germany, 4–7 July 1995, pp. 53–1–53–16.
- Dewey, F. M., "Ferrocene Polyglycols," U.S. Patent, 3,598,850, 10 Aug. 1971.

⁸Stanley, Goldberg, I., Loeble, W. D., and Tidwell, T., "Alumina-Catalysed Dehydration of 1-Ferrocenylethanol. Formation of 1,3-Diferrocenyl-1-Butene," *Journal of Organic Chemistry*, Vol. 32, Sept.–Dec. 1967, pp. 4070, 4071.

⁹Rindrof, H. J., "Acoustic Emission Source Location in Theory and in Practice," *Technical Review to Advanced Techniques in Acoustical, Electrical and Mechanical Measurement*, Bruel and Kjaer, DK-2850, Vol. 2, NAERUM, Denmark, 1981, pp. 3–32.

¹⁰Coats, A. W., and Redfern, J. P., *Nature*, Vol. 201, No. 4914, 1964, pp. 68, 69.

¹¹"Standard Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials," American Society for Testing and Materials, E 698–79(14.02), Philadelphia, reapproved 1984, pp. 520–525.

¹²Kishore, K., and Prasad, G., "Review on Decomposition/Deflagration of Oxidizer and Binder in Composite Propellants," *Defence Science Journal*, Vol. 29, No. 1, Jan. 1979, pp. 39–54.

¹³Wang, S. Y., Wang, S. S., Liu, F., and Chiu, H. S., "An Investigation of Catalysis in the Combustion of Iron Catalysed Composite Propellants," *Proceedings of the 19th International Annual Conference of ICT*, Karlsruhe, Fraunhofer, Inst. Chemisch Technologie, Germany, 29 June–1 July 1988, pp. 8–1–8–14.

¹⁴Pittman, C. U., Jr., "Location of Action of Burning-Rate Catalysts in Composite Propellant Combustion," *AIAA Journal*, Vol. 7, No. 2, 1969, pp. 328–334.

¹⁵Flanagan, D. A., Tech Rept. AFRL-TR-67-18, 1967, prepared for Air Force Systems Command, Air Force Propulsion Laboratory, Edwards Air Force Base, CA 93523.

¹⁶Pearson, G. S., "The Role of Catalysts in Ignition and Combustion of Solid Propellants," *Combustion, Science, and Technology*, Vol. 3, 1971, pp. 155–163.

¹⁷Doriath, G., "Energetic Insensitive Propellants for Solid and Ducted Rockets," *Journal of Propulsion and Power*, Vol. 1, No. 4, 1995, pp. 870–882.

Dual-Mode Operations in a Scramjet Combustor

Takeshi Kanda,* Nobuo Chinzei,† Kenji Kudo,‡
and Atsuo Murakami§

Japan Aerospace Exploration Agency,
Miyagi 981-1525, Japan

Introduction

THE application of airbreathing engines, for example, a scramjet, for use with aerospace planes, has been studied. The general operating region of the scramjet is a flight Mach number of around 6–12. The dual-mode combustion system consisting of the scramjet mode and the ramjet mode has been studied, in which the scramjet engine operates even in a lower Mach number regime.^{1–3} In the ramjet mode, supersonic air is decelerated and becomes subsonic in an isolator between the inlet and the combustor. Fuel is injected into

Presented as Paper 2001-1816 at the AIAA/NAL-NASDA-ISAS 10th International Space Planes and Hypersonic Systems and Technologies Conference, Kyoto, Japan, 24 April 2001; received 9 July 2003; revision received 2 December 2003; accepted for publication 6 December 2003. Copyright © 2003 by Japan Aerospace Exploration Agency. Published by the American Institute of Aeronautics and Astronautics, Inc., with permission. Copies of this paper may be made for personal or internal use, on condition that the copier pay the \$10.00 per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923; include the code 0748-4658/04 \$10.00 in correspondence with the CCC.

*Leader, Engine System Team, Space Propulsion Research Center, 1 Koganesawa, Kimigaya, Kakuda; kanda.takeshi@jaxa.jp. Senior Member AIAA.

†Director, Space Propulsion Research Center, 1 Koganesawa, Kimigaya, Kakuda; chinzei.nobuo@jaxa.jp. Member AIAA.

‡Senior Researcher, Engine System Team, Space Propulsion Research Center, 1 Koganesawa, Kimigaya, Kakuda.