PROGRESS TOWARD REPLACING HALON 2402 FOR THRUST VECTOR CONTROL

Jonathan S. Nimitz
Environmental Technology & Education Consultants (ETEC)
3300 Mountain Road NE
Albuquerque, NM 87106-1920
Voice and fax phone: (505) 256-1463

Vaughn Shell
GenCorp Aerojet Solid Propulsion
Bldg 2019,
P. O. Box 13222
Sacramento, CA 95852-6000
(916) 355-4015

Stephanie R. Skaggs and Edward A. Walters
Center for Global Environmental Technologies (CGET)
New Mexico Engineering Research Institute (NMERI)
University of New Mexico
Albuquerque, NM 87131-1376
(505) 272-7262

ABSTRACT

This report summarizes progress to date on the effort to replace Halon 2402 as a liquid injectant thrust vector control (LITVC) fluid for steering missiles. A parallel-path strategy was used of examining both potential drop-in and redesign candidates. Drop-in candidates must have similar performance to Halon 2402 and be compatible with the existing system (including hot-gas pressurization and burst disks). Minor changes in materials of construction may be required for a drop-in agent, such as a reformulated bladder material. Redesign candidates can have improved performance and can require a cold-gas pressurization system, a different enclosure, and/or different burst disks. For each path, the requirements were defined and initial lists of candidate agents were developed. The selection criteria were in four categories: environmental, system, performance, and cost/availability. Properties of interest for the candidate chemicals were collected from the literature and, when necessary, estimated. For those candidates predicted to have acceptable performance, the weighted rating of attributes process (WRAP) was applied. For the WRAP analysis, each property value was converted to a qualitative score of 0 to 10 points, depending on the attractiveness of the value. A score of 10 was optimal, while a score of zero (assigned manually, with caution) disqualified a candidate from further consideration. The qualitative score was multiplied by the weighting factor (1 to 5) for the property, and these scores were used to rank the candidates in each of the four categories (environmental, system,

performance, and cost/availability). Candidates were eliminated for any of the following reasons: ODP above 0.2, poor stability, unavailability from U.S. suppliers, not being among the top candidates in their chemical family, extremely high cost, or insufficient availability of the information necessary for evaluation. Downselection occurred in several stages from the initial long drop-in and redesign lists of approximately 125 candidates each down to current lists of three candidates each. Testing of compatibility of the top candidates with materials of consauction is in preparation at Aerojet. Full-scale performance tests using static motor firings are scheduled; these tests will determine the best agent and strategy (drop-in or redesign) to be followed.

INTRODUCTION

Halon 2402 ($CBrF_2CBrF_2$, also known as Freon 114B2, CFC-114B2, and 1,2-dibromo-1,1,2,2-tetrafluoroethane) has been used since the 1960s to steer missiles. In the Minuteman Stage 11, for example, it is stored in a toroidal bladder, pressurized with hot gas in flight, and injected through any of four nozzles into the exhaust stream. Diagrams of the Minuteman Stage II and the toroidal LITVC storage tank with associated hot gas generator are shown in Figures 1 and 2. The formation of a vapor body and the resultant shock wave deflect the thrust vector of the exhaust, changing the trajectory of the missile.

Halon 2402 is a fully halogenated bromofluorocarbon with an atmospheric lifetime of about 22 years and an ODP of about 6.4 (Ref 1). Under the provisions of the Montreal Protocol (Ref 2) and the U. S. Clean Air Act Amendments of 1990 (Ref 3), consumption of Halon 2402 will be eliminated by the year 2000 except for "essential uses"; President Bush's announcement on February 11,1992 has accelerated the U.S. phaseout date to December 31,1995. DoD directive 6050.9 has also mandated the phaseout of ozone-layer depleting substances (OLDS). Therefore an effort was undertaken to develop an alternative LITVC fluid to replace Halon 2402.

In general, to find an alternative chemical two lists of candidate agents must be developed: one for "drop-in" and one for "redesign" candidates. Drop-in candidates are those with properties as close as possible to the chemical currently in use, that might be used in existing equipment with only minor modifications. Redesign candidates would require extensive equipment changes, but could provide superior performance.

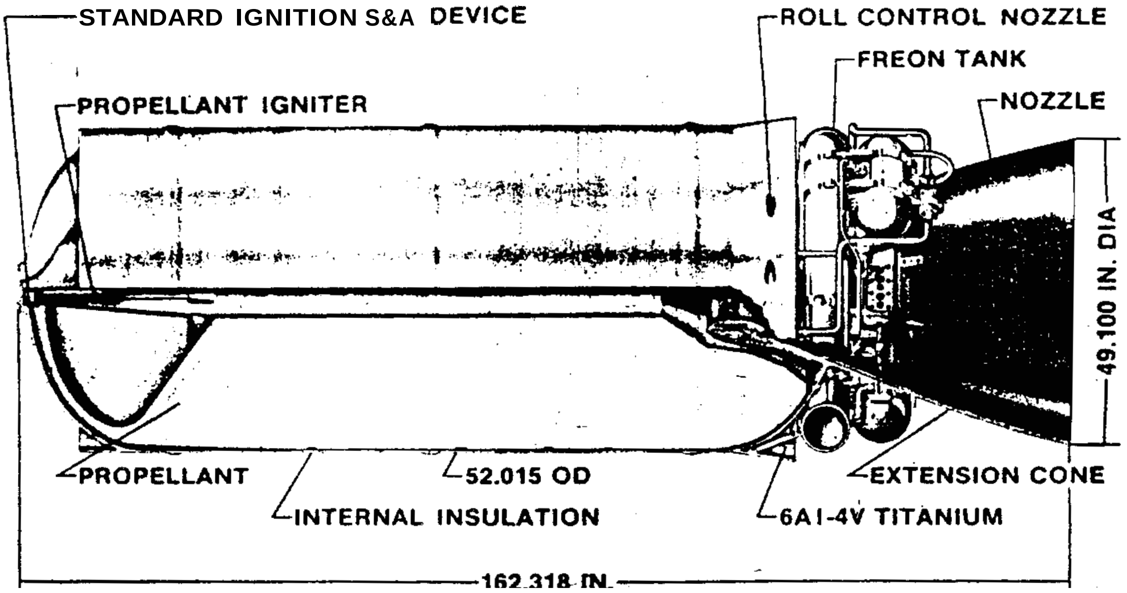

Figure 1. Diagram **of** the Minuteman Stage II

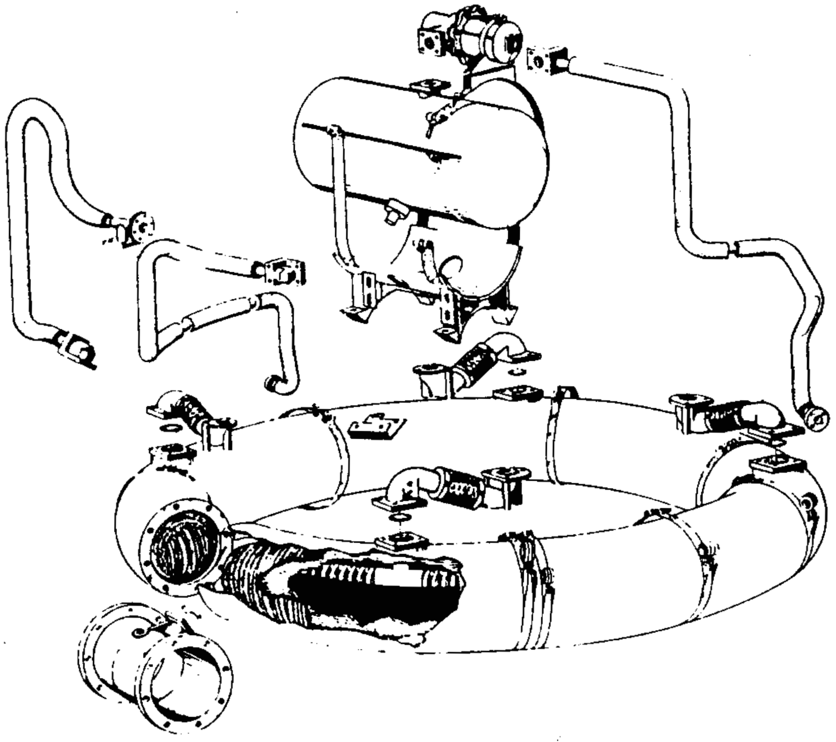

Figure 2. Diagram **of** the toroidal **LITVC tank** and associated hot gas generator

INITIAL CANDIDATE SELECTION

The selection criteria were in four categories: environmental, system, performance, and cost/availability. Environmental considerations included ozonedepletion potential (ODP), global warming potential (GW), and toxicities of neat materials and breakdown products. System criteria included vapor pressure, stability on storage, and packaging (the ability of the current system to contain an adequate amount of agent for the performance required). Performance was predicted using thermodynamic calculations of the heat released when the injectant reacts with the exhaust stream, and using these calculations in computer performance models.

The parameters and weights for candidate selection are shown in Table 1. These criteria were converted to the following computer-searchable criteria for organic compounds: molecular weight below **300,** boiling point in the range of **35-60** "C (drop-in) or **25-60 °C** (redesign), total atom count **3-20.** The compounds could contain 1-6 carbon, 0-2 oxygen, 0-2 nitrogen, 0-2 sulfur, and 0-14 fluorine atoms; the presence of other types of atoms was allowed in the initial search. The molecular weight, boiling point, and total atom count criteria were designed to yield compounds of reasonable volatility, so that a large vapor body of unreacted injectant would form quickly. For boiling point, the lower limit for redesign agents **(35** "C) corresponds to the upper limit of vapor pressure that current burst disks can withstand during storage. The upper limit **(60** "C) corresponds to a compound of lower volatility than Halon **2402** (boiling point **47** "C) but still able to vaporize rapidly to form a vapor body. For redesign candidates the lower boiling point cutoff was decreased to **25** "C because stronger burst disks could be installed on a redesigned system. Selected additional compounds were added to the list manually because, even though they did not meet the search criteria in one aspect, they possessed several highly desirable properties such as expected high performance, low toxicity, and commercial availability. The compounds added manually included inorganics such as nitrates, perchlorates, and N_2O_4 and organics with boiling points higher than the optimum range. The organic chemicals added manually included, for example, ethylene glycol, propylene glycol, and several high-molecular-weight amines. Perchlorates were considered because an aqueous solution of strontium perchlorate is used as an LITVC injectant in the Minuteman Stage III. Because it has been well studied and is known to be effective, it (and other perchlorates) was considered as a redesign candidate. However, because they contain chlorine which would be injected into the stratosphere as HCl, our calculations indicate that all perchlorates examined may have effective ODPs above **0.2** and these candidates were rejected for environmental concerns.

TABLE 1. PARAMETERS AND WEIGHTS FOR CANDIDATE SELECTION

	PARAMETER	WEIGHT	RATIONALE FOR WEIGHT ASSIGNMENT
ENVIR	1. OZONE DEPLETION POTENTIAL (ODP)	5	High weight assigned in that environmental regulations specifically restrict these materials.
	2. GLOBAL WARMING POTENTIAL (GWP)	3	An important factor to consider in that environmental regulations are now evaluating this parameter.
	3. SAFETY & HANDLING (I.E., TOXICITY)	3	An important discriminator. However, precautions can be taken for the handling of some hazardous materials.
PERF	4. DECOMPOSITION	5	The performance of the injectant is directly related to the volume of gas produced by the injectant when it vaporizes and/or reacts with the fuel-rich exhaust.
	5. ROM COMPUTED SIDE FORCE	5	A computer model is used to calculate expected side force for a given flow rate of injectant The end use of an injectant is the development of a side force. From side force data, the thrust vector angle can be calculated This parameter is influenced by several physical **properties.**
SYSTEM	6. EROSION RATE OF NOZZLE MATERIAL	4	A significant consideration for erosion of the exit cone during a flight
	7. VAPOR PRESSURE	2	Vapor pressure at normal temperatures should not exceed the capability of the valves and rupture diaphragms to contain it. However, a high vapor pressure would be desirable during motor operation.
	8. COMPATIBILITY WITH LITVC MATERIALS	4	The injectant must be compatible with the materials that it contacts over a span of approximately 35 years.
	9. STABILITY IN STORAGE	4	A significant discriminator in that the injectant must be stable (i.e., not drop out of solution nor decompose) over a span of approximately 35 years.
	10. COMPATIBILITY WITH HOT GAS	4	The LITVC system must not over-pressurize as a result of the gas generator hot gas warming the injectant.
	11. PACKAGING	1	The volume of material needed for the required total impulse of the system must be able to fit into the LITVC tank and bladder.
COSTS	12. INJECTANT COSTS - LAB	1	A consideration but not a prime one. Cost of injectant for lab samples is not recurring and quantities are minimal.
	13. INJECTANT COSTS - PRODUCTION	3	A major consideration in that production quantities may be purchased.
	14. AVAILABILITY	4	The injectant elected must be available in sufficient quantities to support production.

Four on-line databases were searched using the criteria established. These databases were the Design Institute for Physical Property Data (DIPPR), Thermodynamic Research Center Thermodynamic Data (TRCTHERMO), the NMERI Halocarbon Database, and Beilstein's Handbook of Organic Chemistry. The DIPPR database contains extensive physical property and reactivity data on approximately 1000 commercial (high-volume) chemicals. The TRCTHERMO database contains data on properties of approximately 7000 widely-used chemicals. The NMERI Halocarbon Database contains physical property data on approximately 650 one- to eight-carbon haloalkanes, most of which have very few properties reported and could only be considered far-term candidates. Beilstein's Handbook of Organic Chemistry contains data on approximately 4 million organic and organometallic compounds, the vast majority of which also have very few properties reported and could only be far-term candidates. A wide variety of organic chemical classes was covered in the searches, including alcohols, ethers, esters, ketones, sulfides, amines, hydrazines, alkanes, aromatics, heterocycles, fluorocarbons, and hydrofluorocarbons. The numbers of compounds in each database that met the initial search criteria are shown in Table 2.

Table 2. Number of Chemicals Meeting Initial Search Criteria

Database	Number of Hits
DIPPR	6
TRCTHERMO	5
NMERI	60
eilstein	2400

There was significant overlap among the "hits" from different databases. For example, the set of hits from Beilstein contained all the compounds from the other databases. The hits from DIPPR and TRCTHERMO were the most valuable because all compounds in those databases are well-studied and readily available.

SCREENING AND DOWNSELECTION

The candidates identified in the initial search were screened. A candidate was rejected if any of the following conditions held: (1) it clearly did not meet one or more of the agent requirements, even though it met the broad search criteria, (2) it contained a highly reactive (unstable) functional group, (3) it contained chlorine or bromine and therefore would have non zero ODP, (4) there was an obvious error in the tabulated data (e.g., melting point had been entered in the boiling point field), (5) it was not among the top candidates in its chemical class, or (6) almost no properties were reported. A chemical having very few properties reported could not be deployed by the 1994/1995 time frame desired because it is not available even in research quantities and it would take several years for synthesis and adequate testing of properties including toxicity and materials compatibility.

To provide a logical and traceable downselection pathway, the weighted rating of attributes process (WRAP) was developed and applied! WRAP consists of six steps: (1) identify all discriminating parameters, (2) assign weights based on relative importance, (3) establish quantitative values (e.g., actual boiling point) for each parameter, (4) transform these quantitative values to qualitative scores between 0 and 10, (5) multiply these qualitative values by the appropriate weighting factors for each parameter, and (6) sum the resultant multiplied values for each candidate. The highest scores represent the most promising candidates.

Performance is the most difficult criterion to evaluate. The current system has a maximum side force of **3800** lbf and total impulse of 40,000 lbf-sec. However, it is generally agreed that the current LITVC system is highly over designed. Based on our current models we expect the performance of most of the alternative agents to be below these levels. In anticipation of this finding, flight analysis personnel at Hill AFB initiated a study to determine more realistic system requirements. The results, based on review of data from over 100 flights, showed that the criteria could be relaxed significantly and still maintain $x + 3\sigma$ levels at 95 % confidence level. This study also showed that after 0.5 seconds or less of high flow demand to offset staging that nearly all later commands were at very low flow rates of 1 lb/sec or less. Performance predictions were made using several modeling techniques, each approach completely independent of the others for improved confidence. During the downselection using WRAP, a rough order of magnitude (ROM) model was used. This ROM model was "anchored" to existing Halon 2402, strontium perchlorate, and nitrogen tetroxide experimental data. The ROM model was supplemented by a thermochemical I_{sp} (specific impulse) model for low flow rates and a computational fluid dynamic (CFD) model developed by Aerojet for both low and high flow applications.

CURRENT CANDIDATE LIST

After applying the WRAP, the "short list" of nine drop-in candidates consisted of methanol, 2-methoxyethanol, methyl acetate, dimethoxyethane, sodium nitrate in water, ethanol, furan, perfluorohexane, and propylene glycol. The "short list" of ten redesign candidates consisted of methyl formate, perfluoropentane, aqueous barium or strontium perchlorate, and the following aqueous nitrates: ammonium, barium, hydroxylammonium, lithium, magnesium, and sodium. From among these the top three candidates for both drop-in and redesign have been selected, based on overall expected performance, environmental, system, and cost/availability criteria. The top three drop-in candidates selected for further testing are propylene glycol (1,2-propanediol), perfluorohexane, and a 40 % solution of sodium nitrate in water. For redesign, the top three candidates are perfluoropentane, a 38 % solution of magnesium nitrate in water, and an 80 % solution of hydroxylammonium nitrate in water. These candidates represent a wide variety of chemical classes. Propylene glycol has a relatively high boiling point, but is expected to be exothermic in the exhaust stream, has low toxicity, and degrades rapidly in the environment. The perfluoroalkanes are expected to have the highest stability, lowest toxicity, and best compatibility with materials. The GWP of perfluorocarbons is of some concern. All candidates have zero or negligible ODP. Although nitrogen oxides such as NO_2 deplete ozone, in the highly reducing exhaust stream all nitrates are expected to be converted to molecular nitrogen (N_2).

TESTING

Preparations are underway for compatibility testing of the six current candidates with the LITVC system materials. Testing will consist of six months immersion at 77 °F with periodic removal of samples and testing of physical and mechanical properties. An accelerated aging test will be conducted concurrently, in which the LITVC fluids and materials will be maintained at 110°-135 °F. The materials tested will include all LITVC tank components in contact with the injectant, plus materials under consideration for use in a redesigned system. Materials in the present system include the metals 17-7PH, 304 SS, 347 SS, and Ni (B162), the fabrics dacron polyester and 91-LD Glass/phenolic, the adhesive EC-1838, and the gaskets and elastomers of Flexicarb, Viton A, and Viton A/polyester composite. Over 2600 samples will be prepared and tested.

The final selection of an agent and of a strategy (drop-in or redesign) will be determined from the results of static gain curve motor firing. The gain curve indicates the efficiency of the injectant in providing side force. It is a plot of the ratio of injectant flow to motor axial flow (exhaust stream) versus the ratio of the side force to the axial force.

SUMMARY AND CONCLUSIONS

The logical process described here is a powerful tool for identifying and developing safe, effective, environmentally-sound alternative chemicals. It is equally useful for other applications including firefighting, cleaning solvents, refrigerants, foam blowing, and aerosol propulsion.

For both drop-in and redesign paths, initial long lists of candidates were developed by screening chemical databases by selected properties including boiling point, elemental composition, availability, and quantity of data available. As additional properties were collected from the literature, estimated, and measured, these values were entered in a spreadsheet. Further collection of properties and ranking enabled the downselection to "final" or "short" lists of chemicals for laboratory and full-scale testing.

Six promising alternative LITVC candidates (three drop-in and three redesign) have been identified. These candidates all have zero or negligible ODP, low toxicity, and expected satisfactory performance. Preparations are underway for material compatibility testing of these six agents and the top four candidates (two drop-in and two redesign) will undergo full-scale static firing testing in approximately March 1993.

ACKNOWLEDGMENT

The support of this work by the U.S. Air Force and TRW are gratefully acknowledged.

REFERENCES

1. Dr. Peter Connell, Lawrence Livermore National Labs, personal communication, 1992.

2. United Nations Environment Programme, Montreal Protocol on Substances that Deplete the Ozone Layer---Final Act, 1987.

3. Clean Air Act Amendments of 1990, Conference Report to accompany S.1630, 101st Congress, 2nd Session, U.S. House of Representatives, Report 101-1952, October 26, 1990.

4. Nimitz, J.S., and Shell, V., "How to Find Safe, Effective, Environmentally Sound Alternative Chemicals," Proceedings of the 3rd Annual New Mexico Air and Waste Management Technical Meeting, Albuquerque, NM, 31 October, 1991.