National Aeronautics and
Space Administration
Headquarters
Washington, DC 20546-0001

II-D-1

Reply to Attn of: JE

OCT 11 2001

The Air and Radiation Docket (6102)
Air Docket No. A-98-33
U.S. Environmental Protection Agency
401 M Street, SW
Washington, DC 20460

Subject: EPA Proposed Rule: Protection of Stratospheric Ozone; Allowance System for Controlling HCFC Production, Import and Export; 66FR 38064, July 20, 2001

The National Aeronautics and Space Administration (NASA) appreciates the opportunity to review and comment to the Environmental Protection Agency on the referenced proposed rule. Currently we anticipate a need for continual availability of HCFC 141b and HCFC 225 for use on critical space vehicle applications under our Space Shuttle Program (SSP). Our comments on the proposed rule are provided in the enclosure.

The comments reiterate the need for NASA to obtain an adequate supply and continue use of HCFC 141b and HCFC 225 for critical space vehicle applications under the SSP. The SSP cannot function without the availability of these substances. We concur with the proposed space vehicle/defense exemption process for continued production and import of HCFC 141b and recommend that the modifications discussed in the enclosed comments be fully incorporated into the final rule. The comments also provide an overview of our extensive and continuous efforts and progress in the search and evaluation of alternatives for an HCFC 141b substitute that will satisfy our very unique and stringent requirements. We feel the proposed exemption process will support the U.S. obligations under the Montreal Protocol while still allowing NASA to continue seeking HCFC replacements without compromising the safety and mission success of our Programs.

If we can be of further assistance, or if further discussions are needed on the comments provided, please contact Ms. Maria Bayon at 202-358-1092.

Richard A. Wickman for

Olga M. Dominguez
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Enclosure

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DFRC/D-4-4850B/D. Morgan
DFRC/D-4-4850B/D. Mullen
GRC/6-4/M. Blotzer
GRC/3065/C. Myers
GSFC/205.2/K. Moxley
GSFC/205.2/T. Spagnuolo
JPL/301-420/C. Buril
JPL/301-420/J. Pham
JPL-NMO/180-808B/P. Robles
JSC/JA131/D. Hickens
JSC/JA131/K. Hummel
KSC/TA-C/B. Summerfield
KSC/TA-C3/D. Callier
KSC/TA-C3/D. DeLaPascua
LaRC/418/R. Brown
LaRC/418/M. Morris
MAF/SA-39/F. Celino
MAF/SA-39/M. Jennings
MSFC/AD01/S. Cloud (Acting)
MSFC/AD10/F. Davis
MSFC/AD10/S. Scroggins
SSC/RA00/R. Magee
SSC/RA00/C. Kennedy
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NASA Comments on EPA's Proposed
Allowance System for Controlling HCFC Production, Import and Export [66 FR 38064]

INTRODUCTION

The Space Shuttle Program (SSP) provides the only capability in the United States for human access to space and is the pathfinder for reusable space hardware. The Space Shuttle uses a solid propellant, together with cryogenic fuels, to achieve the thrust required to lift it and its payload from the launch pad into orbit. The cryogenic fuels used are liquid oxygen (LO_2) and liquid hydrogen (LH_2). Use of these cryogenic fuels imposes certain requirements. LO_2 systems must be precision cleaned and their cleanliness verified using oxygen-compatible materials. HCFC 225 is the only approved material available for this purpose in certain critical SSP applications.

Because LO_2 and LH_2 boil at -300°F and -423°F respectively, cryogenic insulation is required to maintain propellant quality and reduce heat input into the propellants. The primary structures and their subsystem components must remain within design temperature limits during prelaunch and ascent phases. A thermal protection system (TPS) provides these capabilities for the major Shuttle elements illustrated in Figure 1. The TPS for SSP cryogenic systems incorporates foam insulation using HCFC 141b as the blowing agent. HCFC 141b has a low heat of evaporation and an ideal boiling point to deliver foam with small, uniform and stable cells. This results in a foam insulation with appropriate thermal conductivity and sufficient dimensional stability to withstand the hostile environments encountered by space launch vehicles.

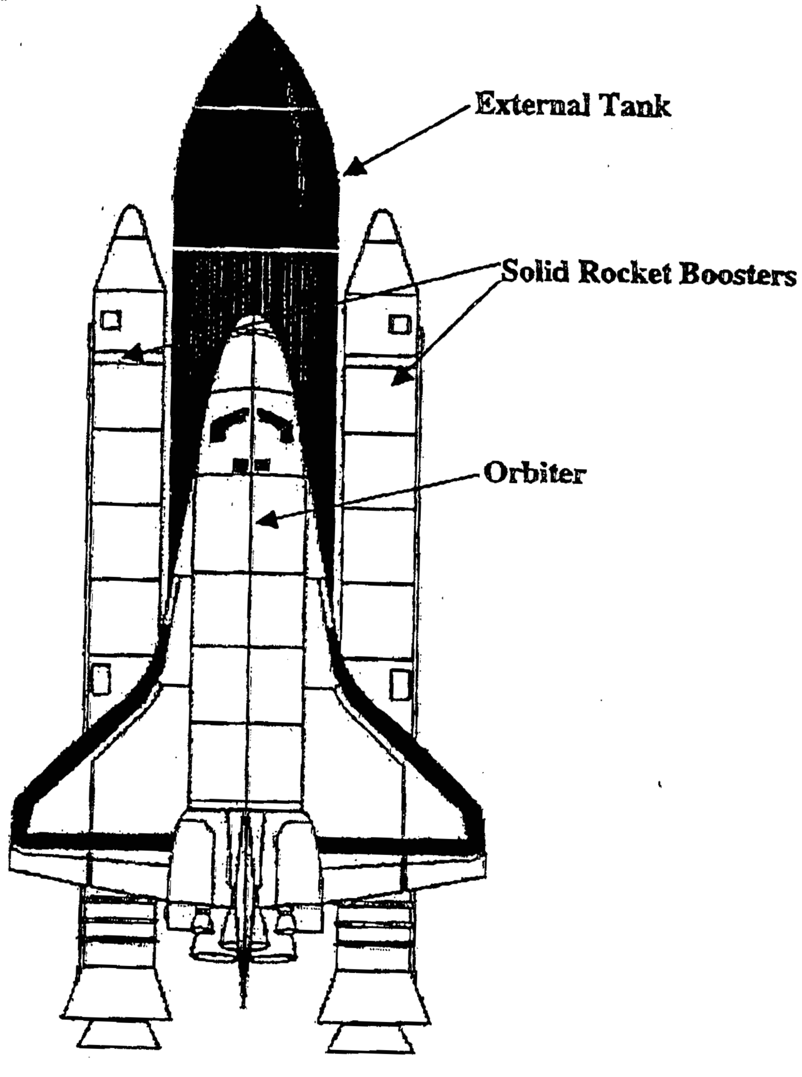

Figure 1: Major Elements of the Space Shuttle

These HCFCs will be regulated by EPA's proposed Allowance System for Controlling HCFC production. NASA would like to take this opportunity to provide the following comments regarding this proposed regulation.

BASELINE ALLOWANCES

EPA has listed baseline allowances to industry for HCFCs on a chemical-by-chemical basis [66 FR 38065, et. seq.]. NASA offers comments on the baseline allowances listed for two HCFCs: HCFC 141b and HCFC 225.

HCFC 141b

EPA has proposed to limit the total quantity of HCFC 141b produced or imported for space vehicle or narrow defense needs to one percent of the aggregate of HCFC 141b baselines for one year [66 FR 38095, proposed §82.18(j)(4)]. NASA not opposed to this limit, provided that this amount of material is sufficient to meet US space vehicle/defense requirements. The SSP expects to use approximately 40,000 lbs (18,000) kg of HCFC 141b annually throughout the waiver timeframe.

HCFC 225

The SSP is among the many industry sectors that selected HCFC 225 to replace class I ODCs such as CFC 113 and methyl chloroform in critical precision cleaning and verification applications. HCFC 225 is the only SNAP-approved material that met SSP criteria, particularly those involving oxygen systems. Considerable resources have been spent in qualification testing and implementation of this material.

NASA is concerned that the proposed HCFC 225 allowance is insufficient for the requirements of the SSP and other end users who have made good-faith efforts to replace higher-ODP chlorinated solvents. The SSP expects to require 20,000 lbs (9,000 kg) HCFC 225ca and 40,000 lbs (18,000 kg) HCFC 225cb annually through 2015. Demand is expected to grow for HCFC 225 as stockpiles of CFCs are depleted for use in critical precision cleaning applications. EPA must consider this increased demand when determining allowances.

SPACE VEHICLE/DEFENSE EXEMPTION FOR CONTINUED USE OF HCFC 141B

NASA supports the establishment of a mechanism by which space vehicles may be allowed continued use of HCFC 141b [66 FR 38094, proposed §82.18(j)]. Comments on certain aspects of the proposed exemption are followed by our justification for such an exemption mechanism.

Specific Provisions of Space Vehicle/Defense Exemption

NASA offers the following comments on certain aspects of the space vehicle/defense exemption.

Definitions

In the interest of clarity and consistency, NASA recommends that EPA define the term "space vehicle" in §82.3 as it is defined in the Aerospace NESHAP [40 CFR 63.742].

Petition Timeframe

EPA proposes that space vehicle/defense entities must submit petitions for exemption prior to July 1, 2002 [66 FR 38094, proposed §82.18(j)(1)]. We are not opposed to limiting the timeframe, but recommend that EPA allow at least 6 months between publication of the final rule and the deadline for petition submittal.

Exemption Timeframe

EPA proposes that the exemption will initially be available in 3-year increments through 2009 [66 FR 38094, proposed §82.18(j)(1)(ii), and others]. We support this timeframe for potential exemption availability. However, we also recommend that EPA reevaluate US consumption figures in 2008 – 2009 to determine feasibility of extending the potential timeframe for exemption continuation while maintaining compliance with the internationally-mandated production cap. The SSP will continue to work on TPS replacement materials, but if implementation has not been completed, additional time may be required.

Recordkeeping and Reporting Requirements

EPA has proposed quarterly report submittal [66 FR 38102, proposed §82.24(g)(1)] for space vehicle/defense exemption activities. Although EPA does not specify a deadline for these reports, other required reports in the proposed rule must be mailed within 15 days of the end of the applicable reporting period [66 FR 38098, proposed §82.24(a)(1)]. We understand the need to track class II controlled substances, but we propose annual reporting rather than quarterly reports, with a forty-five day turn-around consistent with that specified in the class I allowance system [40 CFR 82.13(c)]. In the class I allowance system, Essential Use Exemptions primarily involved the user company and the CFC supplier. Allowances for class II ODC products will be significantly more complex, as the supply chain for formulated products containing HCFCs will involve multiple layers. HCFC 141b is purchased by intermediaries (foam formulators) who in turn blend the resulting foam insulation products. The frequency of reporting proposed, as well as the turnaround time, would be unduly burdensome. The SSP material procurement flow may be used as an example. The responsibility for each of the major Shuttle elements lies with a prime contractor. Three contracting companies use it in five locations and ship material back and forth. Those companies buy foam from three formulators, who currently buy HCFC 141b from two manufacturers. Figure 2 depicts the various stages of the SSP TPS supply chain.

SSP Flow of HCFC 141b and Formulated Foams

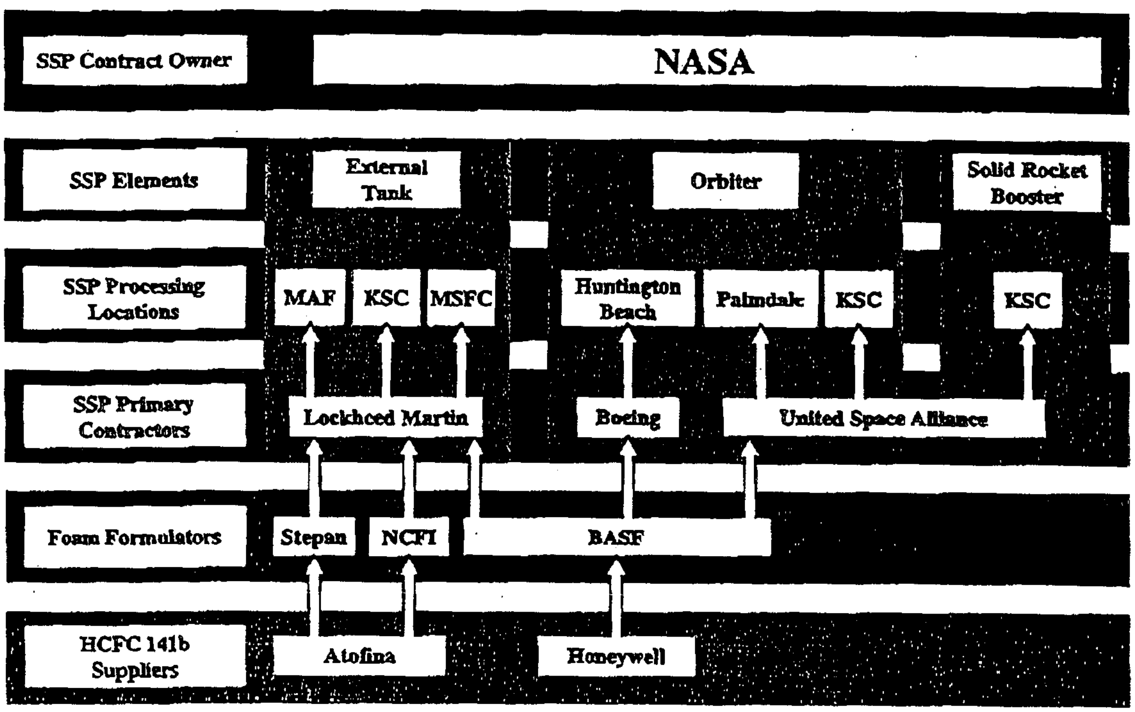

Figure 2: Shuttle TPS Supply Chain

The External Tank (ET) is manufactured at NASA's Michoud Assembly Facility (MAF) in New Orleans, Louisiana by Lockheed Martin Space Systems Company. The majority of the TPS is applied at MAF before shipping the ET to KSC. A small amount of TPS material is also applied at KSC. Foam testing is performed at MAF, the Marshall

Space Flight Center (MSFC), and vendor locations. Foam is procured by Lockheed Martin from BASF, NCFI and Stepan, who obtain HCFC 141b from Honeywell and Atofina.

Orbiter sustaining engineering, upgrades, testing and refurbishment are performed by the Boeing Company at their facilities Palmdale and Huntington Beach, California. The Orbiter contract is administered by United Space Alliance (USA). All foam to be used on Orbiter flight hardware is procured from BASF by USA at KSC. Material is both used at KSC and shipped to Palmdale, California for use in Orbiter refurbishment activity. Foam used for testing at Huntington Beach, California is procured from BASF by the Boeing Company.

USA also holds the Solid Rocket Booster (SRB) refurbishment and assembly contract. These activities are carried out at KSC. Sustaining engineering, upgrades and testing are done at KSC and MSFC. All SRB HCFC 141b blown foam is procured from BASF by USA.

The SSP is in the process of developing a mechanism to track and report required information to EPA. Quarterly reporting is unnecessary and burdensome, and the proposed 15-day window is far too short to allow the SSP to collect required data from multiple contractors and locations.

Update/Renewal of Exemption

NASA concurs with EPA's proposed space vehicle/defense exemption triennial updates. In the preamble [66 FR 38081], EPA states that such updates should submit information including efforts undertaken to find alternatives, whether an alternative has been found, and whether there is a need to extend the exemption further. However, this language is not consistent with that in the proposed regulation itself [66 FR 38095, proposed §82.18(j)(5)] that mirrors the submittal requirements for the original petition. We believe that an update, rather than a petition resubmittal, should be sufficient and requests that EPA require only the information listed in the preamble relative to the triennial reports. The information submitted in the original petition should not change, and it is not necessary to prepare a repeat submittal when an update should suffice.

NASA has made a good faith effort to identify all our critical needs, and at this time we do not foresee any additional critical requirements for HCFC 141b or HCFC 225. However, in consideration of any unforeseen requirements of future NASA programs or other activities, either developed by NASA or approved for NASA's implementation, we recommend that EPA add a provision under the space vehicle/defense exemption allowing an entity to request additional allowances for HCFCs. EPA could consider such requests on a case-by-case basis, evaluating the entity's justification of need and assertions that no viable substitutes exist for the specific application in question. NASA's intent is to reduce the use of HCFCs and to find adequate HCFC substitutes for use in our programs. However, this recommended provision would provide a process to address any unforeseen critical requirement.

Justification of Requirement for Exemption Mechanism

The SSP requires a TPS to maintain the quality of the cryogenic propellants, provide protection from aerothermal and vehicle plume heating environments, prevent formation of ice on exterior surfaces, and maintain structural integrity. These foam materials use HCFC 141b as the chemical blowing agent to provide the critical insulation and cell structure properties of the foam. It is important to note that a foam meeting Shuttle system requirements is not typical of the foam industry, which mainly provides foam materials for furniture or insulation uses not subjected to the extreme environments encountered during the launch and recovery of space launch vehicles. The three major SSP elements (see Figure 1) requiring foam insulation are the Orbiter, the ET, and the SRBs. The TPS is applied at various NASA and contractor sites using spray and mold techniques developed specifically for the space program's unique requirements. The SSP uses approximately 40,000 lbs (18,000 kg) of HCFC 141b annually. NASA intends to fly the Space Shuttle through at least 2020.

Development and implementation of an HCFC 141b replacement cannot meet the 2003 deadline. The SSP began HCFC 141b replacement efforts in 1993, far in advance of the phaseout, but no replacement has been found that meets performance requirements. Stockpiling or use of recycled or recovered HCFC 141b is not yet a viable long-term solution due to shelf life and environmental concerns. Continued production of HCFC 141b for use as a Space Shuttle foam blowing agent past January 1, 2003 is critical to the NASA Space Shuttle Program.

Role of the Foam

The TPS design is driven by a number of design requirements including staging in natural environments, pre-launch, ascent, and ET reentry environments. The role of the TPS in each environment is described below.

Natural Environments

After manufacture, SSP elements are transported to and within Kennedy Space Center (KSC) where they are stored, some for up to 6 years, until mated with the other Shuttle components. Once elements are mated and the vehicle is transported to the launch pad, Shuttle TPS foams must be able to endure a 180-day stay without performance degradation. The unsheltered environment to which these components may be exposed includes temperatures up to 115°F, humidity from 8-100%, sand, dust, salt fog, rain, ozone, solar radiation and fungus.

Induced Environments

SSP foam is designed to withstand the induced environments imposed during transportation, ground operations, handling, storage, and flight operations. The environments, illustrated in Figure 3, include both thermal and mechanical loads from prelaunch, ascent, and reentry.

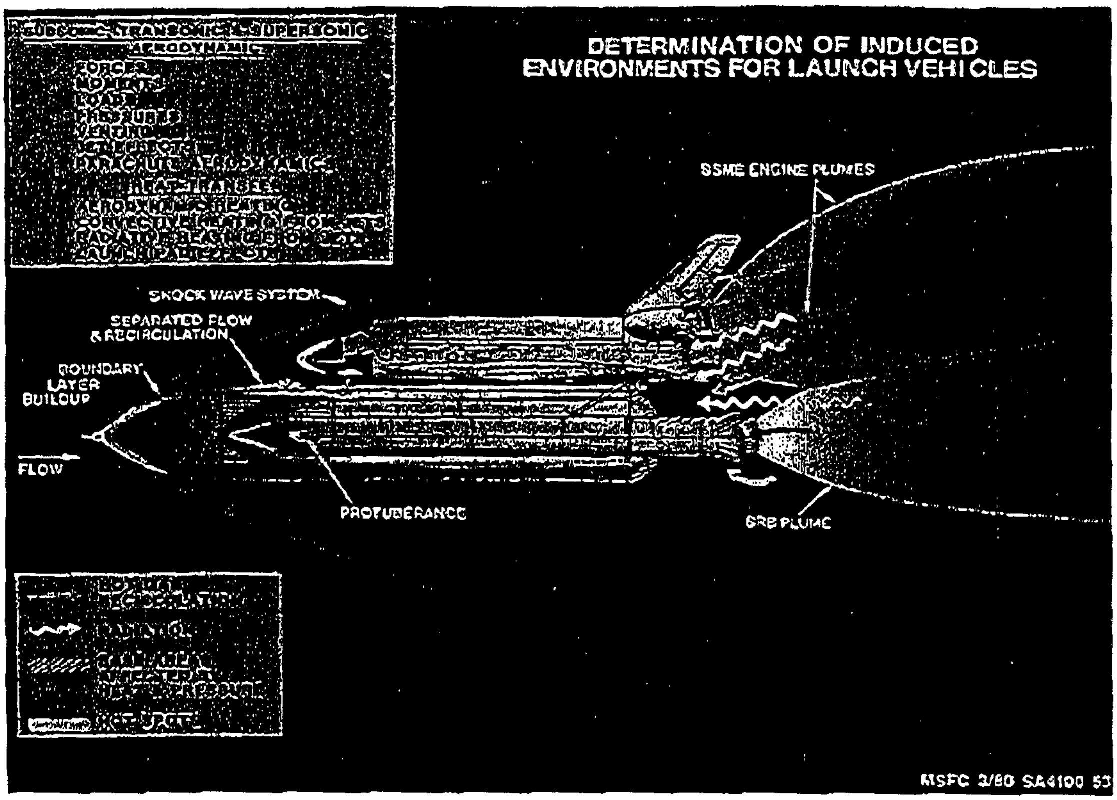

Figure 3: Shuttle Launch Environments

Prelaunch

The foam insulation thickness is primarily defined by the prelaunch requirements. Maintaining good quality/stable propellants and minimizing ice formation on the vehicle exterior are the primary considerations. In summary, prior to launch the TPS serves the following critical functions:

- Maintains LO_2 and LH_2 boil-off rates below the ET vent valve capabilities
- Contributes to propellant loading accuracy and increased propellant densities
- Maintains LO_2 and LH_2 at specified temperatures at the Orbiter/ET interface to ensure flow of propellant to shuttle main engines
- Eliminates air liquefaction on the LH_2 tank

- Minimizes ice formation on the ET exterior surfaces
- Maintains environmental integrity of various assemblies and sensitive components

Ascent

In the ascent phase, the TPS must maintain the primary structures and subsystem components within design temperature limits. For example, the Orbiter/ET umbilical 17" disconnect must be protected from the intense heat of ascent. The SRB strut assembly TPS must maintain a uniform crush condition to capture the ET/SRB connecting bolts as they are hurled by an explosive charge during the SRB separation maneuver. In the ET Attach rings, the foam must endure the heat load of flight and remain in place to mitigate descent environments. The insulation must adhere firmly to the cryogenic tank surfaces under the simultaneous loads induced during ascent to orbit. All SSP insulative foams must withstand the following loads:

- Static, dynamic and ambient pressures
- Acoustic and vibrational loads
- Cryoshrinkage,
- Ascent aerodynamic heating
- SRB and main engine plume radiant and recirculation heatings
- SRB separation motor plume heat impingement
- Autogenous tank pressurization gas heating

Reentry

Following ET separation from the Orbiter, the TPS is required to protect the ET structure from aerodynamic heating to prevent premature fragmentation at high altitudes. Another function of the TPS occurs during ET reentry when external temperatures and tank pressurization contribute to the ET fragmentation process. The residual TPS material must be adequate to provide the entry function to maintain the desired break-up footprint over a remote ocean location, protecting the population and avoiding established shipping lanes.

In the event of an emergency mission abort, the ET foam must ensure that structural temperatures are maintained to prevent ET break-up during emergency landing. Current flight rules require an intact ET and Orbiter to descend to 50,000 ft. Separation of the ET occurs at 50,000 ft or above to prevent crew endangerment.

SPACE SHUTTLE TPS REQUIREMENTS

In order to survive hostile Shuttle service environments, insulating foams must meet stringent requirements. Certain properties have been identified as being most significant as critical to making good foam. These properties are interdependent and are all related to the ability to perform under simultaneous Shuttle loads during ascent. The following properties are considered the most important for Shuttle TPS foams.

Thermal Conductivity and Density

The most important material property that SSP insulating foams must meet is low thermal conductivity at a given density. This is achieved by increasing the percentage of blowing agent trapped in the foam cells, resulting in lower foam density. The density and the required foam thickness determine the weight of the foam on the ET, which also must be limited. The amount of space that foam on the Shuttle Orbiter can occupy is limited and hence, the foam must provide adequate thermal insulation while minimizing foam thickness.

Changes in these properties could have unacceptable consequences in the flight environments. An increase in density would increase the impact energy of ET foam debris; increased thermal conductivity would increase ice formation on the tank. Foam or ice debris emanating from critical areas of the ET would compromise Orbiter tile and windshield integrity and flight crew safety on ascent and reentry. Increased weight of the ET would compromise Shuttle performance reserves required to achieve high inclination trajectories for docking with the International Space Station. It is, therefore, necessary for material properties to be optimized within the constraints imposed by mission requirements. The required properties necessitate a foam formulation that can be consistently applied within critical application processes and stringent tolerances.

Recession Rate

Recession rate is the rate at which foam material decomposes and ablates from the foam surface at elevated temperatures. Foam recession rates must be controlled to protect the Shuttle vehicle during ascent. SSP TPS must withstand extreme heating environments such as SRB plume convective temperatures of several thousand degrees Fahrenheit. It must also provide radiant heating protection from the approximately 3000°F SRB plumes and 6000°F Space Shuttle Main Engine (SSME) plumes and ascent aerodynamic heating temperatures of up to 2000°F during peak heating.

In addition to ascent requirements, resistance to reentry heating is necessary to maintain a limited ET debris footprint over an isolated ocean area.

Material Properties

SSP TPS possesses material properties that are unique to space launch vehicle requirements. The foam must not delaminate internally nor debond from the substrate when the substrate is stressed to its yield point under Shuttle flight loads at -423°F and the external surface is exposed to temperatures in excess of 3000°F. This requirement is necessary to prevent debris that could impact the Orbiter, creating a Safety of Flight issue or cause structural failure of the launch vehicle components. Foam insulation on all cryogenic surfaces must withstand expansion and contraction stresses associated with prelaunch and flight.

Structural material properties such as tensile strength and bond strength must be maintained over a substrate temperature range of -423°F to +300°F to meet flight requirements. TPS must meet flammability and outgassing requirements for SSP materials specified in NASA Handbook 8060.1. Cured foams must be stable for 6 years under natural conditions.

Additionally, all TPS foams must be compatible with surrounding materials under all natural and induced environments. For example, SRB pour foams must have comparable density and thermal ablative properties as the surrounding spray foam. It must also adhere to substrates such as sealed cork, rubber, painted steel, painted aluminum and silicone sealants.

The performance of Space Shuttle foam insulation in environments experienced during ascent and descent is of primary importance. The imposition of simultaneous loads such as static pressure, dynamic pressure, ambient pressure, vibration loads, acoustic loads, cryoshrinkage, aeroheating, plume convective heating, and plume radiant heating on the foam prove to be the most critical aspect of determining whether a material is acceptable for Space Shuttle use. These loads, shown in Figure 4, are interrelated. No test facility can recreate and accurately synchronize this loading profile completely. Out of necessity, simpler methods of testing have been developed. However, they do not test all simultaneous loads completely, resulting in program risk.

An example of this issue occurred during the implementation of HCFC 141b blown foams. The new materials successfully met all test requirements and were implemented on the ET. One of the new foams failed during flight, producing debris that damaged the Orbiter. Modifying SSP TPS results in risk to the Shuttle that cannot be fully anticipated by the qualification testing program. The complete suite of simultaneous loads, and the materials' response to those loads, can only be experienced during actual Shuttle flights.

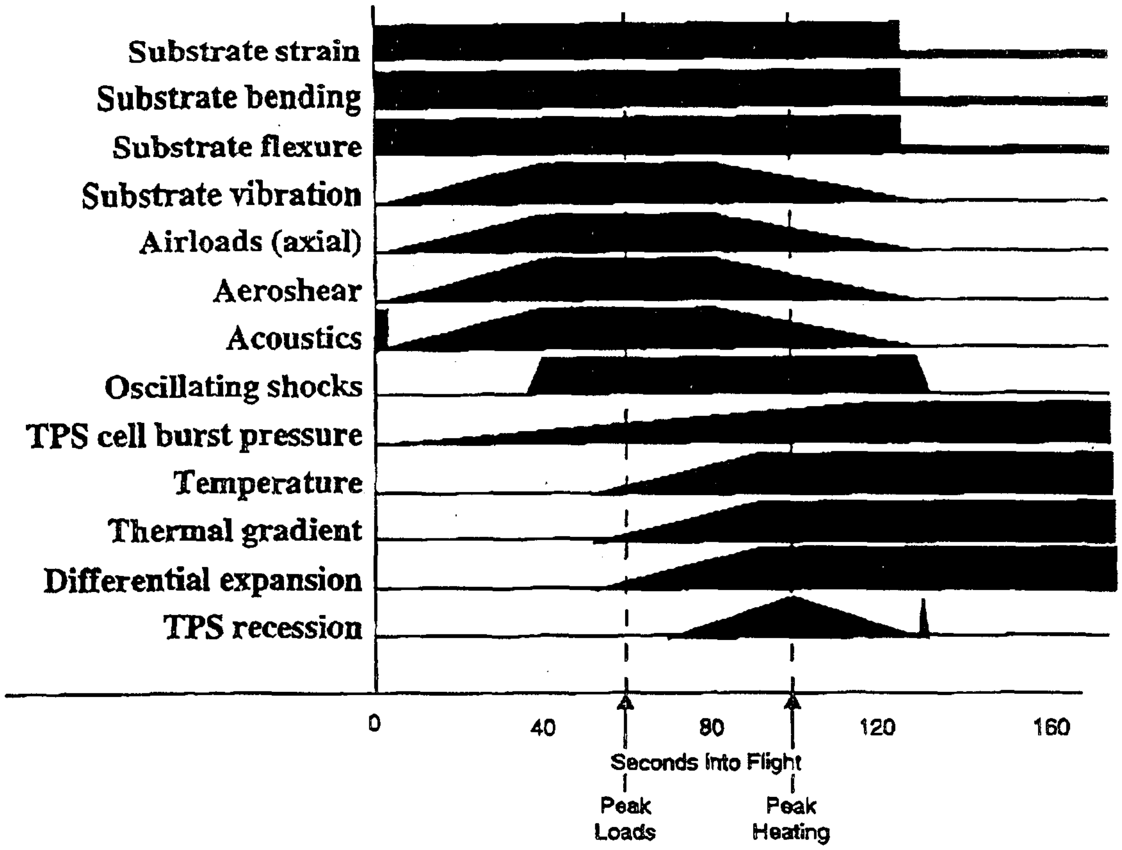

Figure 4: SSP Simultaneous Loads

EVALUATION OF HCFC 141b ALTERNATIVES

Human space flight safety is of paramount importance to NASA. It is critical to recognize the importance of demonstrated reliability in the SSP. The Space Shuttle is a human-rated flight vehicle and introduction of new materials jeopardizes proven reliability. Prior to implementation on the Shuttle system, a new material must undergo a rigorous development and qualification program. This section discusses the steps that must be taken to implement a new material on the Space Shuttle, and specifically those that have been taken to find next generation alternatives to HCFC 141b as the blowing agent for the Space Shuttle foam thermal protection systems. The SSP is constrained by flight safety and performance requirements.

Requirements and Implementation Issues for Foam Systems

Foam Development and Qualification Process

Prior to implementation on the Space Shuttle, a new material must undergo a rigorous development and qualification program. The SSP approach to evaluating blowing agents is comprised of steps illustrated in Figure 5.

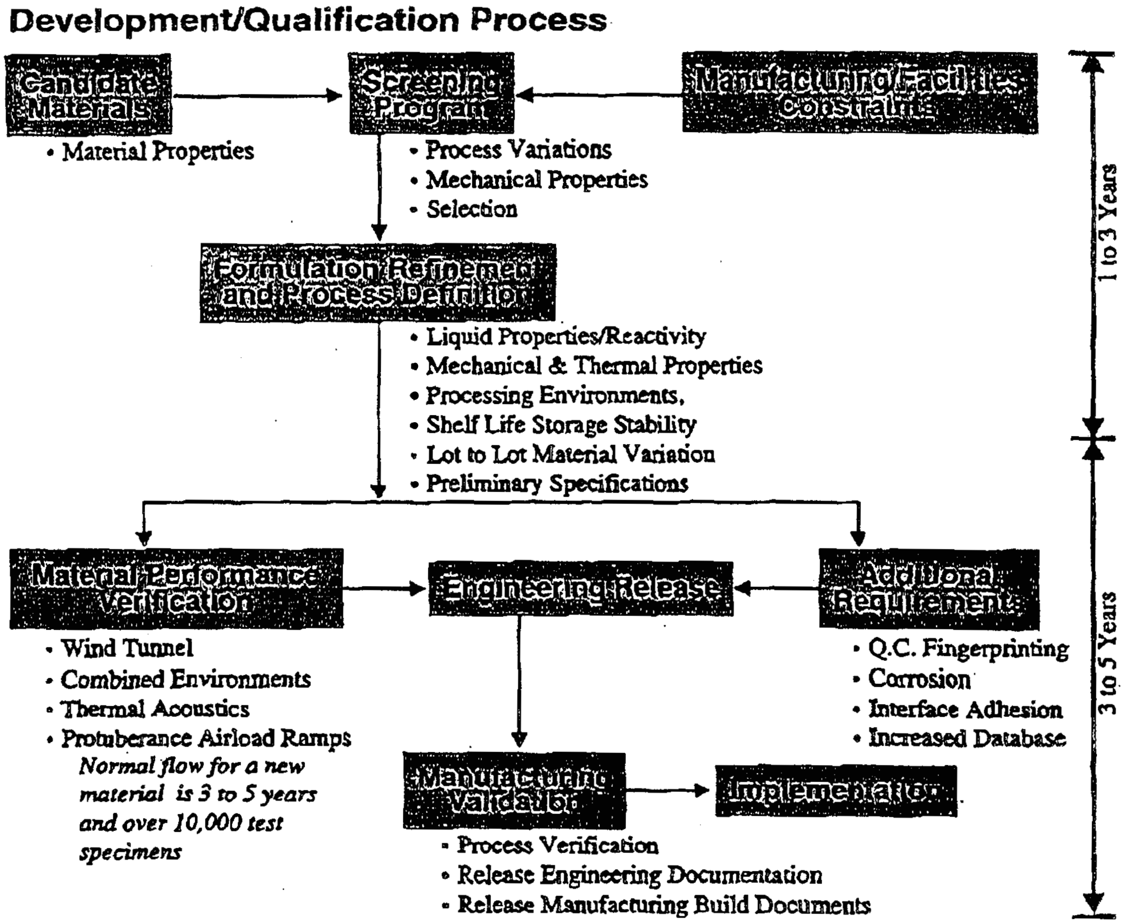

Figure 5: Foam Development and Qualification Process

The first step in this process is to screen potential materials and select likely candidates based on material properties and their compatibility with manufacturing and facilities constraints. Certain criteria are used for selection of a new blowing agent that can be used to make SSP foam insulation. Materials are sought that are soluble in isocyanate and polyol components of urethane insulators; low toxicity, with supporting data from toxicity tests; boiling point range of 77°F – 113°F; EPA-approved, preferably zero ozone depletion potential (ODP) and minimal global warming potential; and commercially available. Process variations and mechanical properties are evaluated in the selection process.

Formulation refinement and process definition include assessment of liquid properties/reactivity, mechanical and thermal properties, processing environments, shelf life storage stability, and lot-to-lot material variation. Preliminary specifications are also established at this time. SSP foams must be sufficiently robust to survive manufacturing and transportation activities. Foam components must have a shelf life stability of one year. Both foam components and formulated foams must be able to maintain lot-to-lot manufacturing consistency. Process control must be maintained within defined manufacturing constraints to assure material repeatability and meet predictable flight performance requirements. Development is an iterative process involving several blowing agent candidates and various foam formulations.

Once a candidate is selected, the qualification phase begins. This phase greatly expands testing of the new foam system to include processing variations, lot-to-lot variability, shelf life, manufacturing capability, and design verification testing using various lots of material. Wind tunnel, cryogenic strain, radiant heating, physical property, density, and thermal conductivity materials tests are performed on potential foam systems.

Development of an extensive database is required before a product is ready for implementation on manned space flight hardware. The blowing agent used in a foam material can significantly affect any or all of the foam properties. A significant amount of development and qualification testing must be performed to ensure that the material meets all of the requirements for mission success and human flight safety.

Certain tests have been identified as critical requirements for each material. These tests are for mechanical properties (tensile and compressive strength), physical properties (density, thermal conductivity, and dimensional stability), cryostrain (to -423°F), and ablative recession (aero and radiant heating). Test samples/specimens are obtained from foam-insulated panels that are processed to meet engineering or flight requirements and represent actual manufacturing conditions. Upon successful completion of the above tests, the foam material must be validated in the manufacturing process before implementation.

In summary, Shuttle material and process changes require extensive development and qualification programs prior to implementation. All of the information gained from the implementation of HCFC 141b is being utilized in the development of next-generation blowing agents. Lessons learned from implementation of HCFC 141b blown foams demonstrate that changes in materials and processes, even when thoroughly tested, present opportunities for unforeseen problems. Minimizing these issues is critical to the Shuttle program, and is part of what makes development of the next-generation TPS foams a lengthy and complex process.

HCFC 141b Replacement Efforts

The blowing agent community has been fragmented in its development of HCFC 141b replacements. Patent rights, licensing agreements, and business decisions have complicated and slowed the availability of materials for scientific research and progress toward HCFC 141b replacement. SSP personnel have been driven to research a wide variety of replacement options. This research has included coordination with industry involving direct communication with numerous companies, such as Honeywell, Solvay, Exxon, Mobil, Bayer, 3M, Atochem, Halocarbon Products, PCR, and others. Transfer of foam replacement technology and exchange of successes, challenges, and disappointments in the search for blowing agent replacements continues with these companies and with our systems suppliers.

Potential blowing agents that have been screened include the leading industry rigid foam candidates, HFC 245fa and pentanes, as well as other hydrofluorocarbons (HFCs), hydrofluorinated ethers (HFEs), hydrocarbons (HCs), and water as both a sole and co-blowing agent. The SSP has researched and tested over 200 potential blowing agent candidates.

Extensive tests, including flight performance tests, were conducted on certain TPS materials blown with HFCs, HFEs, HCs, and water. Limited test quantities and lack of availability have delayed development and qualification schedules of the HFCs and HFEs. For example, it was necessary to obtain HFC and HFE samples from specialty fluorine synthesis houses because test quantity samples of these materials were not available from the major manufacturers.

Key characteristics and SSP concerns associated with potential blowing agent categories are summarized in Table 1.

Candidate	Results	Comments
Water/Carbon Dioxide (H_2O/CO_2)	• Candidate for limited close-out applications • Requires substantial development for spray systems • Co-blowing required	• Currently used by industry in polyurethane foam systems • Unacceptable thermal conductivity for most SSP applications • Significant formulation modifications required • Reduced cryogenic strain compatibility
Hydrofluorocarbons (HFCs)	• Handling and process challenges due to low boiling point • Reduced solubility • Good mechanical properties • Thermal testing and analysis in progress	• Require special handling equipment & significant processing adjustments • Tradeoff between boiling point and solubility; those that are optimum for both are not easily manufactured, or will not be commercially available (HFC 245ca) • HFC 245fa is planned for commercial production in mid 2002, pending customer commitments • Other HFCs are not commercially available due to licensing or patent issues.
Hydrocarbons (HCs)	• Improved dimensional stability • Fine cell structure in rigid foam systems • Handling & process challenges due to flammability • Limited data due to OSHA and NFPA imposed processing restrictions	• Requires special handling equipment and significant process adjustment • May require emission controls • Evaluations are planned
Hydrofluoroethers (HFEs)	• Excellent thermodynamic properties • Compatible with existing chemical formulations • Limited data to OSHA and FDA imposed restrictions	• High cost, but comparable to some HFCs • Limited toxicity data for some materials, extensive human and laboratory testing completed on other HFEs • Promising materials include commercial anesthetics, appreciable quantities have not been readily available for analysis • SSP is researching avenues for industry wide toxicology studies necessary to understand exposure limits, and any engineering controls that might be necessary to limit exposure. • Extensive testing will be conducted pending resolution of FDA- and OSHA- related issues.

Table 1: Summary of Potential SSP Blowing Agent Replacements

NASA would like to take this opportunity to share with EPA a summary of the SSP experience with candidate blowing agents to date.

Water/Carbon Dioxide (H_2O/CO_2)

Water-blown foams tested for use on the SSP were rejected due to a number of factors. Thermal conductivity, compressive strength, adhesion and structure of CO_2 blown foam did not meet SSP requirements. These foams exhibited insufficient cryogenic strain compatibility, as well. However, such foams are potential candidates for limited close-out applications.

Using water as a blowing agent would likely require significant modification of foam formulations and development of spray systems. The SSP is continuing the evaluation of water co-blowing with HFC 245fa to reduce the vapor pressure and with pentanes to reduce flammability of blended systems, but water as a sole blowing agent is not considered an acceptable alternative for Shuttle use.

Hydrofluorocarbons (HFCs)

Limited studies have been done with HFCs obtained from specialty blend houses, including HFC 245fa, HFC 356, HFC 365, HFC 245eb, and HFC 245ca. Several appear to be promising candidates, but availability has been limited due to patents and licensing agreements. The results of SSP evaluation of HFC 245fa follow.

HFC 245fa has a significantly lower boiling point than that of HCFC 141b. This has resulted in the need for equipment modifications and presents challenges in foam formulation processing. Once blended, application of HFC 245fa blown foams requires significant process adjustments compared to current systems. The exothermic chemical reaction of urethane insulations must be adjusted and tuned to accommodate changes in heat of reaction, vapor pressure of blowing agent, and solubility of blowing agent in both the liquid materials and reacting polymer.

HFC 245fa has a significantly higher vapor pressure than HCFC 141b, which results in more overspray (material that accumulates on adjacent areas during spraying) during the warm-up and spray activities This overspray tends to char and degrade, resulting in heat buildup and potential for fire. The SSP is aware of the dangers associated with exothermic reactions and heat build-up in urethane insulations. Precautions are taken to break up the foam overspray material produced during processing to allow the heat it generates to dissipate. These precautions were not sufficient when handling experimental HFC 245fa blown foams, and fire resulted. The SSP has implemented special procedures to accommodate the safety concerns associated with fire protection, and we are again conducting evaluations with precautionary procedures.

Extensive testing within the SSP has been conducted on HFC 245fa-blown spray foams. Preliminary data from a large experiment conducted this year shows promise for spray-on foam applications, but significant processing changes are required. Analysis of the available data continues, and additional tests are scheduled. HFC 245fa is not suitable for typical hand-mix and pour procedures used in SSP operations due to its low boiling point.

Hydrocarbons (HCs)

Hydrocarbon blowing agents, most prominently pentane-based blowing agents, are volatile organic compounds (VOCs) and are significantly more flammable than HCFC 141b. This flammability has resulted in the need for modifications to handling and processing equipment, including electrical grounding systems, inert gas purges, extensive gas sensors to monitor for explosive limits, integration of the sensors with processing controls to ensure fail safe operations, and increased exhaust demands to comply with National Fire Protection Association (NFPA) standards. Class I Division 1 explosion proof equipment and facilities are the only proven method to ensure safety and continued Space Shuttle production.

The flammable nature of pentanes also presents challenges in foam formulation processes. Blending of liquid components must now be accomplished in closed systems to prevent migration of flammable vapors. The SSP has developed special procedures to accommodate the safety concerns associated with fire protection for limited research and bench scale testing of flammable materials. Proprietary formulation changes are necessary to achieve targeted densities, reaction profiles, and material properties. In order to complete this work, extensive facilities upgrades are necessary. The flammability of the pentane-based blowing agents would require extensive facilities modifications at multiple locations, both NASA and contractor facilities. VOC emission controls and permit modifications may also be necessary.

Despite the challenges posed by their flammability and volatility, these materials exhibit promising characteristics. The hydrocarbons produce a very fine cell structure in rigid foam systems. They also provide foams with greater dimensional stability than HCFC 141b. The SSP will continue to evaluate hydrocarbon-based TPS foams.

Hydrofluoroethers (HFEs)

Many of the fluorinated ethers have optimal thermodynamic properties for use as a blowing agent in urethane insulations. Both HFE 245 and HFE 263 were tested for SSP use. These materials have blowing efficiencies comparable to current SSP blowing agents. They were also found to have sufficient solubility in foam components, and produce a foam with low thermal conductivity. Preliminary data also indicated acceptable mechanical/physical properties in molding and sprayed systems. Unfortunately, both HFE 245 and 263 have limited toxicity data and are not commercially available, although HFE 245 is a pharmaceutical by-product. Further research into commercially available anesthetics led the SSP to discover several materials with appropriate boiling points for potential use as foaming agents in cellular polymeric insulations. This class of materials appears extremely promising as potential blowing agents. The SSP is currently seeking the means to obtain larger test quantities of HFCs for further evaluation.

Future HCFC 141B Replacement Plans

NASA supports EPA's Significant New Alternatives Program, which strives for the substitution of chemicals that reduce overall risks to human health and the environment. However, the critical path to blowing agent selection, evaluation, qualification, and final implementation in a human-rated propulsion system is complex, lengthy, and expensive. Considerable effort and resources have been spent on replacing HCFC 141b foam systems without success. The SSP now plans to expand its list of candidates to include custom-developed materials and blowing agent blends. Candidate considerations include not only those of the SSP, but also those of potential future launch vehicles. Successful completion of TPS replacement is contingent on identification of viable alternative blowing agents.

Blowing agent replacement is technically complex, and the changes involve significant program implementation risk. The next-generation blowing agents represent a much greater technical challenge and programmatic risk than the development and implementation of HCFC 141b. Foams made with alternate blowing agents meeting Shuttle criteria are not yet available, so the transition from HCFC 141b to a zero ODP blowing agent cannot be accomplished within the existing phaseout timeline, or other recently proposed timelines, without jeopardizing the safety of NASA's human space flight program.

OTHER SOURCES OF HCFC 141b

The use of stockpiled, recycled or recovered supplies of HCFC 141b as the sole source of foam blowing agent through the time anticipated to implement next generation foams poses unacceptable risk to the Shuttle Program. The stability and purity of the blowing agent is essential to viable foam insulation meeting the stringent technical requirements of manned flight hardware.

Time for implementation, uncertainties in long-term quality of stored, recycled or recovered HCFC 141b, and logistical issues make such options appropriate only as a contingency option for continued SSP viability. Some candidate blowing agents will not be commercialized until close to the January 2003 class II phaseout date, delaying final material selection. The qualification effort to validate and implement a new blowing agent in such critical space vehicle applications has historically taken 4 – 5 years after the blowing agent has been selected. Development, qualification and implementation of next generation foams are accomplished through an iterative process during which unanticipated challenges may require changes to, modification of, or replacement of equipment, delivery methods, and other parameters. These types of changes may extend the time for full implementation of replacement insulative foams. Additional time will also be required to incorporate lessons learned from efforts associated with the implementation of HCFC 141b blown foams. Considering these additional time requirements, qualification and implementation of replacement foams is expected to be complete no earlier than 2009.

The use of recycled or recovered supplies would be counterproductive. A change in the source of any critical ingredient automatically triggers requalification requirements. The SSP has requalification requirements for flight-essential formulations that would result in years of testing and waste of resources that would be best used toward development of next generation foams. These requirements reflect the element of human risk involved in manned space flight.

The Shuttle Program does not yet have sufficient data to be assured of long-term stability of stored HCFC 141b. In November 1999, the ET project initiated a study to determine HCFC 141b shelf life. Data suggests that HCFC 141b should be stable at least 18 months in storage under ambient factory conditions. Manufacturers are unwilling to certify that the material will not chemically decompose or degrade if stored through 2009, even if a chemical stabilizer is added. HCFC 141b used in SSP insulating foams does not incorporate a stabilizer. The manufacturer's testing has demonstrated storage stability under normal conditions only for up to one year, far short of the minimum eight years required for Shuttle system support.

Long-term cyclic effects on aged blowing agent purity are unknown. The unresolved storage concerns include the effect of storage conditions such as container material, temperature, atmosphere, humidity control, and the effect of degradation products on the stability. Two potential problem schemes exist. The principal problem is that the accumulation of degradation products may have an irreversibly deleterious effect upon the foam's thermal conductivity. Second, if the deleterious effect of degradation products is not irreversible and can be remedied with chemical reprocessing, ultimate reprocessing success would still need to be established. Reductions in blowing agent purity level due to degradation by-products or the introduction of impurities from the storage vessel itself may adversely affect the performance of the TPS. Loss of the TPS would bring the SSP to a halt.

The SSP annually consumes approximately 40,000 lbs (18,000 kg). of the HCFC 141b blowing agent in foam insulation. Assuming successful implementation of replacement TPS by the earliest possible date, 2009, over 280,000 lbs (126,000 kg) must be stored to ensure adequate supply of HCFC 141b. A contingency quantity would be needed to ensure continued availability of material. Storage of such a large amount of HCFC 141b, in drums or railcars, would create the potential for material contamination, spills, emissions, and material management issues. The need to stockpile such large quantities for the length of time anticipated for next generation foam development could result in a significant disposal requirement at the time of implementation. Further, there is a risk that even this large amount of material could be insufficient for Shuttle requirements. If initial replacement blowing agent choices fail qualification testing, development work would have to be restarted with other candidate blowing agents, extending total time to implementation.

Foam insulation is critical to flight and mission success. Using recycled, recovered, or stockpiled HCFC 141b as the future blowing agent source poses unacceptable environmental and material availability risks to the Shuttle Program. Continued production and availability of HCFC 141b past 2002 is necessary to meet the stringent requirements of SSP foam insulation.

CONCLUSION

The SSP uses two HCFCs in critical space launch vehicle applications, and the program cannot function without these substances. Although availability of these materials will be affected by EPA's proposed HCFC allowance system, NASA believes that such a system will provide a reasonable and effective regulatory mechanism to control usage and emission of class II controlled substances. The establishment of such a system should also preclude the need to further control HCFC usage with changes to existing SNAP approvals of HCFC applications. SSP HCFC usage quantities are herein provided to assist EPA with establishing appropriate allowance allocations.

NASA concurs with the proposed space vehicle/defense exemption but also recommends EPA to add a provision under this exemption to allow an entity to request additional HCFC allowances for any unforeseen future requirement.

NASA recommends that the modifications discussed above be incorporated into the final rule. The proposed exemption will support US obligation under the Montreal Protocol while allowing the SSP to continue seeking HCFC replacements without compromising the safety and mission success of NASA's Shuttle program.