

Thermal Protection System for the Space Shuttle External Tank: Applications of Instrumental Methods of Analysis

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ABSTRACT

External Tanks (ET's) for Space Shuttle missions are coated with isocyanurate foams. These materials must perform as an insulator for cryogenic propellants and as an ablator during ascent conditions. Because of the limited high-temperature stability of conventional urethane foams, qualification of Spray-On Foam Insulation (SOFI) systems was undertaken early in the Shuttle program. The criteria used to chemically evaluate the individual components of the insulation and the flame retardancy tests correlating composition, radiant recession rate and bond tension of the finished product are described in this paper. Laboratory methods to measure and control predefined component ratios for production units are also discussed.

KEY WORDS

Isocyanurate foam insulation, Space Shuttle External Tank, HPLC, TG, dTG, flame retardants.

INTRODUCTION

The Space Shuttle flight vehicle is composed of three major sections: a reusable manned orbiter, an expendable external tank (ET), and two reusable solid rocket boosters (SRB's). The ET, the largest component of this system, has a dual mission since it serves as the attachment point of the orbiter and the SRB's and must also contain and deliver propellants for the three orbiter main engines. Figure 1 gives a schematic representation of the main ET characteristics.

In early NASA programs, launch vehicles fueled with liquid oxygen (LO_2) and liquid hydrogen (LH_2) were insulated with BX-250, a urethane spray-on foam insulation (SOFI) manufactured by Stephan Chemical Co. The foam was applied to the cryogenic fuel tanks and served only as an insulation system to maintain propellant quality and minimize boiloff. However, the requirements for the thermal protection system (TPS) for the Space Shuttle External Tank are quite different, since the SOFI must function both as an insulator and as an ablator during ascent conditions.

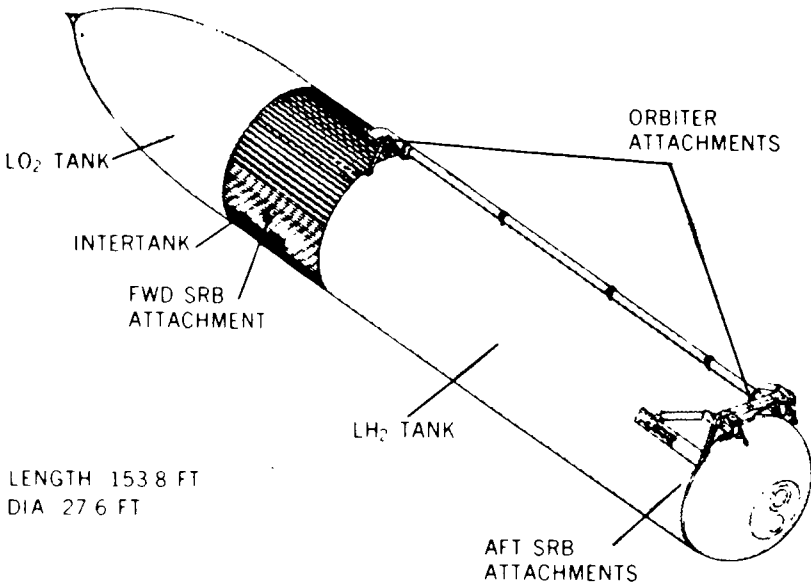


Figure 1. Space Shuttle external tank.

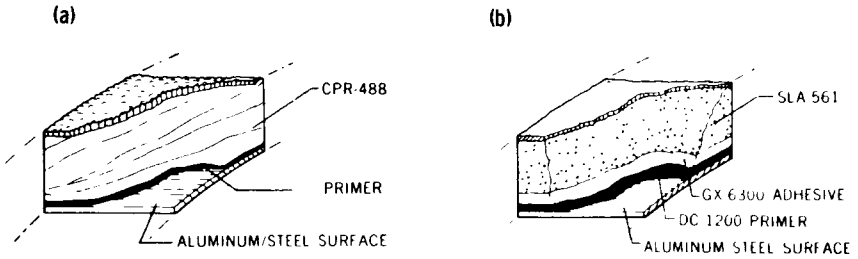


Figure 2. Insulated surface cross sections: a) CPR-488 and b) SLA-561.

These conditions demand good adhesion to the substrate at -257°C (-430°F), and minimum recession at the surface where temperatures ranging from 260°C (500°F) to greater than 538°C (1000°F) are encountered. Because of the limited high-temperature stability of urethane foams, achieving SOFI systems with high-temperature resistance was considered an immediate priority early in the Shuttle program [1].

The currently used SOFI is Upjohn's CPR-488, a urethane-modified isocyanurate foam that is applied to the entire tank and functions as a TPS. In some areas, however, the ablative properties of CPR-488 are insufficient, the Tank's aft dome, protuberances, and structural members requiring, for example, an additional underlayer of super-light ablator (SLA), in this case SLA-561.

SLA-561 is a composite of silicone resins, cork particles, silica glass and phenolic microballoons, and silica fibers that is sprayed as a heptane slurry onto the prepared surface. Cross-sectional views of surfaces containing SOFI insulation (CPR-488) for conventional use, and the type of TPS used on aft domes and other areas which are subjected to extensive friction, are seen in Figures 2a and 2b, respectively.

Greater emphasis on reduced weight and manufacturing time has resulted in design changes that reduce the SLA requirements on some areas of the tank to light weight (LW). The largest area affected is the aft dome because its proximity to the SRB's plumes generates maximum heat and friction during ascent. Failure of the TPS in this most critical area could abort the mission.

A subsequent development program was initiated to identify a SOFI system with improved high-temperature stability that could function in the absence of the SLA layer. NCFI 25-13 (North Carolina Foam Industries), was selected for further evaluation. An isocyanurate foam, although exhibiting excellent ablative and recession properties, its adhesion to the substrate was poor. Reformulation of the package to alter its

flame-retardant composition and to include additional reactivity was found to enhance its adhesion. The new product, NCFI 22-65, is a reactive isocyanurate package that meets these requirements. This reactive system has already replaced CPR-488 and SLA on the aft dome of the LH₂ tank on lightweight tank 7 (LW-7) and has performed very well. In addition, the change on this section of the tank has reduced the weight by about 114 kg (250 lb). Future improvements are expected to lead to considerable weight savings. The development of the ET insulation system from the first NASA flights to the present is shown in Figure 3.

The instrumental methods used to evaluate the individual components of the new type of SOFI insulation and the flame retardancy tests correlating composition, radiant recession rates and bond tension are described in this paper as are the laboratory methods adapted to measure and control the predefined component ratios for production units.

EXPERIMENTAL METHODS

The starting materials for isocyanurate foams produced using NCFI 22-65 were characterized and quantified by techniques such as high performance liquid chromatography (HPLC), Fourier transform infrared spectroscopy (FTIR), and Fourier transform ¹³C nuclear magnetic resonance (FT-NMR). The finished products were also characterized by FTIR, thermogravimetric analysis (TG), and differential thermogravimetric analysis (dTG). The foams were tested according to NASA's flammability tests (NHB 8060.1A) and the following physical and mechanical tests: a)

Evolution of NASA's Thermal Protection System (TPS)

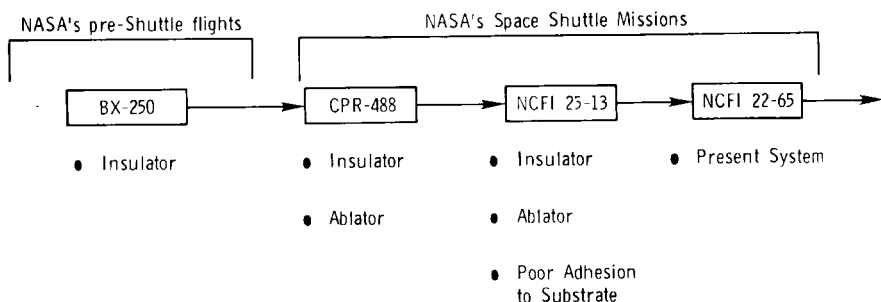


Figure 3. Development of thermal protection system for the external tank.

tensile strength for rigid cellular plastics (ASTM D-1623), b) compressive strength for rigid cellular plastics (ASTM D-1621), c) density (ASTM D-1622), and d) thermal conductivity (ASTM C-177).

Several lots of starting materials and products already applied as SOFI layers on ET sections were analyzed. Foams with varying ratios of components A to B (isocyanate precursor to crosslinkers, respectively) were sprayed and used as needed for calibration.

ISOCYANURATE CHEMISTRY

Isocyanurate systems generally consist of two component packages which yield the desired products as they are mixed. The commercially available packages contain a combination of additives needed to provide the main reaction leading to trimerization. They also contain catalysts, structure modifiers, flame retardants, blowing agents, and surfactants to control cell size. These have been reviewed by Reymore, et al. [2], and the reader is referred to this work for additional information.

Figure 4 shows the general mechanism of trimerization. In this particular case, the catalyst, represented by X-Y, adds to the carbon-nitrogen double bond. The generated intermediate (A) can 1) immediately react with more isocyanate, rearrange, and produce a stable dimer (B); or 2)

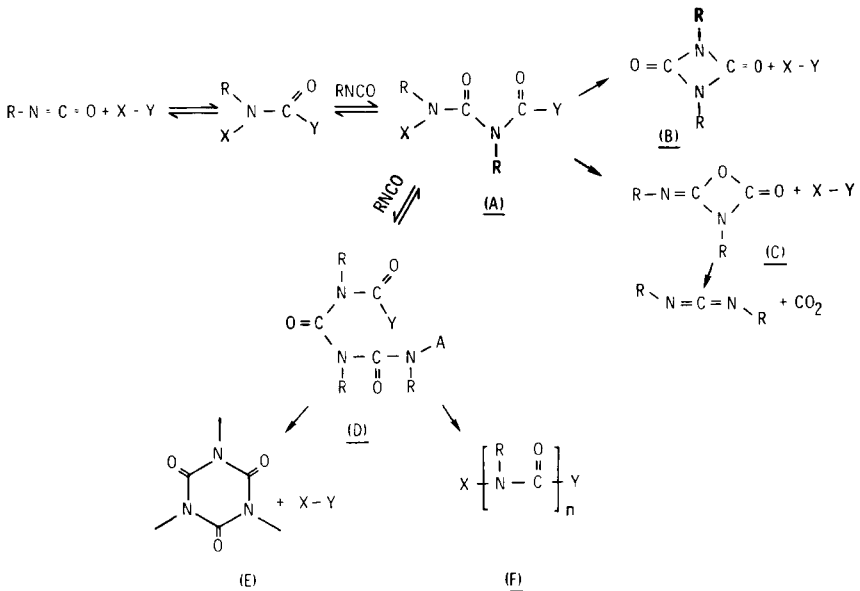


Figure 4. Scheme for catalyzed isocyanate reactions.

form another intermediate (C) via this reaction. However, compound C is unstable and degrades into carbodiimide and CO_2 . Trimerization based foams contain excess isocyanate and show evidence of reaction with A, producing the intermediate (D), which in turn can readily react to yield the trimer (E) or a polyamide (F).

The thermal stability of isocyanurates arises from the absence of labile hydrogen atoms in the isocyanurate ring. However, these products have a disadvantage since they are very friable and brittle. The introduction of other polymeric linkages along the network, via epoxides [3], polyimides [4], or urethane segments [4], has actually improved the physical characteristics of these foams. The urethane segments are introduced by adding polyhydroxylated compounds to the non-isocyanurate part of the formulation (Figure 5). The flame retardancy of the foams is further improved by using phosphorus compounds, which can also crosslink with the network since they may contain some available hydroxyl groups.

OPTIMIZATION OF FLAME RETARDANCY

The initial NCFI 25-13 isocyanurate system contained Fyrol PCF (tri- β -chloroisopropylphosphate) as a flame retardant at a total phosphorus level of 1.65%. Additional tests with reactive flame retardants demonstrated that using DOW XNS 50054.20 (this commercial product is a mixture of dibromoneopentylglycol, dimethyl methylphosphonate and

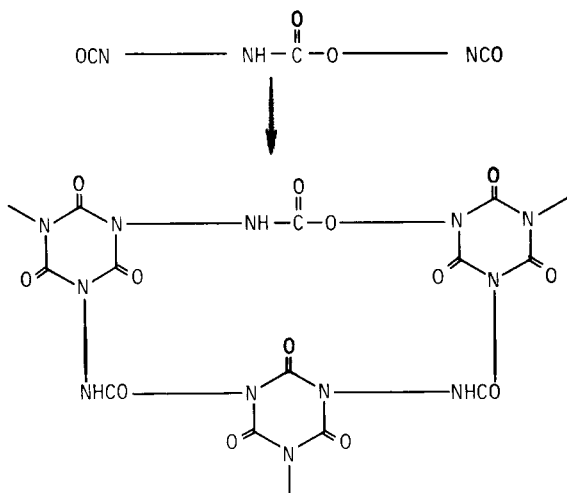


Figure 5. Final structures of urethane-modified isocyanate polymer network.

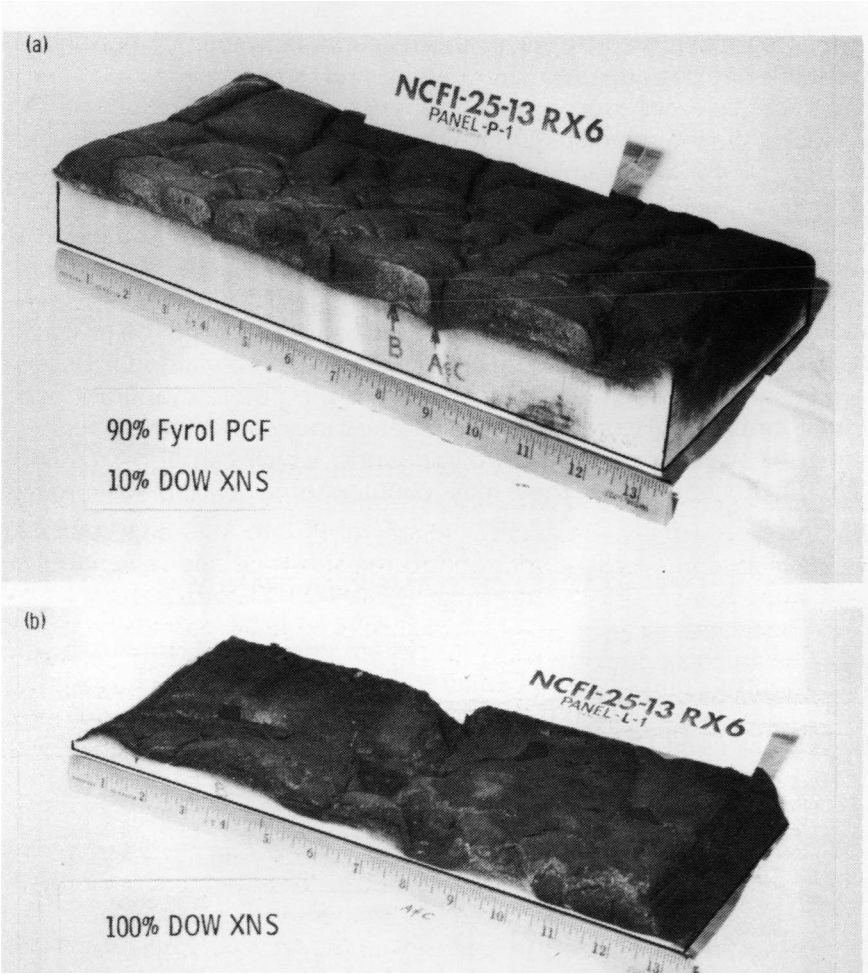


Figure 6. Panels after flame retardancy tests: a) 90% Fyrol PCF/10% DOW XNS and b) 100% DOW XNS.

a glycol known as voranol) also improved the adhesion of the insulation to the substrate.

Consequently, blends of the Dow XNS 50054.20 materials and Fyrol PCF (Stauffer Chemicals) were added to the B component to a concentration of 1.65%. Figures 6a and 6b shows photographs of two actual panels from this test (NASA method NHB 8060.1A); the superior performance of the 90/10 blend is clear.

Table 1. Effects of flame retardant composition on recession rates.

Flame Retardant	% Phosphorus "B" Side	Groove Recession* (in./sec.)	Virgin Foam Left
Fyrol PCF	1.45	0.0075	Yes
Fyrol PCF	1.65	0.0064	Yes
Fyrol PCF	2.5	0.0065	Yes
30/70 DOW/PCF	1.65	>0.0098	No
20/80 DOW/PCF	1.65	0.0133	Yes
10/90 DOW/PCF	1.65	0.0084	Yes

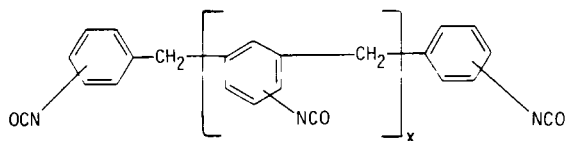
*Desired rate = 0.015 (max)
Rate for CPR-488 = 0.24

Table 1 presents the data obtained for recession rates of various formulations, including those in which the Fyrol PCF to DOW XNS 50054.20 ratio was varied. Experimentally, 90% Fyrol PCF to 10% XNS 50054.20 ratio resulted in excellent adhesion to the substrate and radiant recession rates comparable to the original NCFI 25-13 formulation. DOW XNS concentrations in excess of 20% produced unacceptable recession rates while concentrations less than 10% resulted in marked deterioration of adhesive properties (Figure 7). The modified isocyanurate formulation is identified as NCFI 22-65.

CHEMICAL CHARACTERIZATION OF NCFI 22-65

NCFI 22-65 is provided in two separate packages: one, designated as "A," contains the main isocyanate reactant; "B" contains the catalysts, the flame retardant mixture, Freon 11-B, and a mixture of polyols. The polyols provide the urethane branches in the final polymeric network.

"A" Component: The structure of the A component can be easily interpreted by means of ^{13}C FT-NMR. The spectral analysis of this material is in agreement with the general structure:



Conventional industrial synthesis of these types of materials produces a mixture of isocyanates and FT-NMR cannot distinguish whether the A side of the formulation is a single species or a mixture of similar structures. This problem can be solved easily using HPLC. Figure 8 shows a

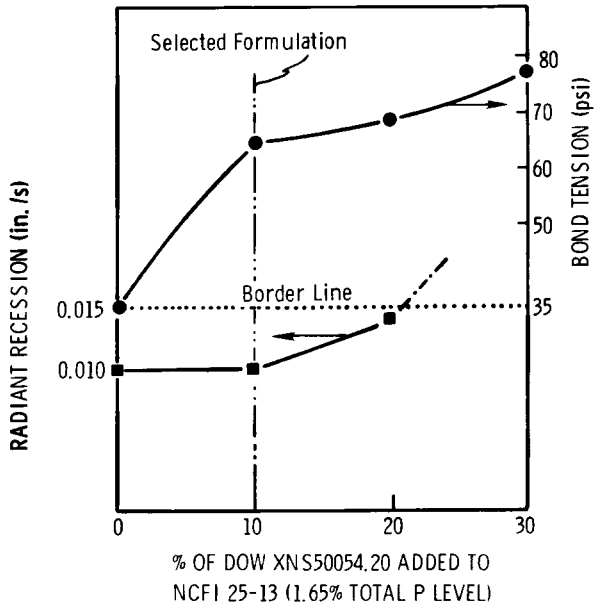


Figure 7. Radiant recession rates of SOFI vs addition of flame retardant package.

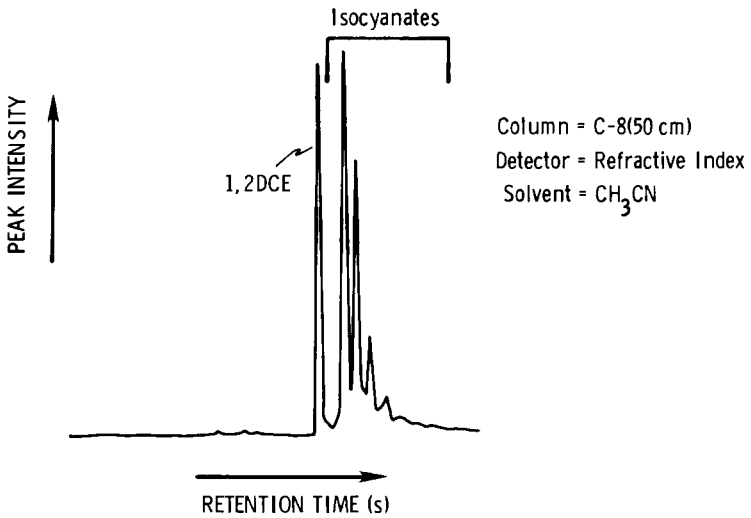


Figure 8. Separation by HPLC of "A" component (NCFI 22-65).

typical HPLC separation of A components using acetonitrile as the solvent and two Zorbax-C₈ columns with a refractive index detector. In this separation, 1,2-dichloroethane (DCE) has been added as an internal standard and can be used if quantitative determination is required.

The peaks are detected in the order of increasing molecular weight beginning with diphenylmethanodiisocyanate (MDI) (where $x = 0$).

FTIR is a very sensitive technique for the analysis of organic materials and can detect minute compositional changes due to storage of A components under different conditions. This point, illustrated in Figure 9 where the spectra represent the same A component stored at low (13°C

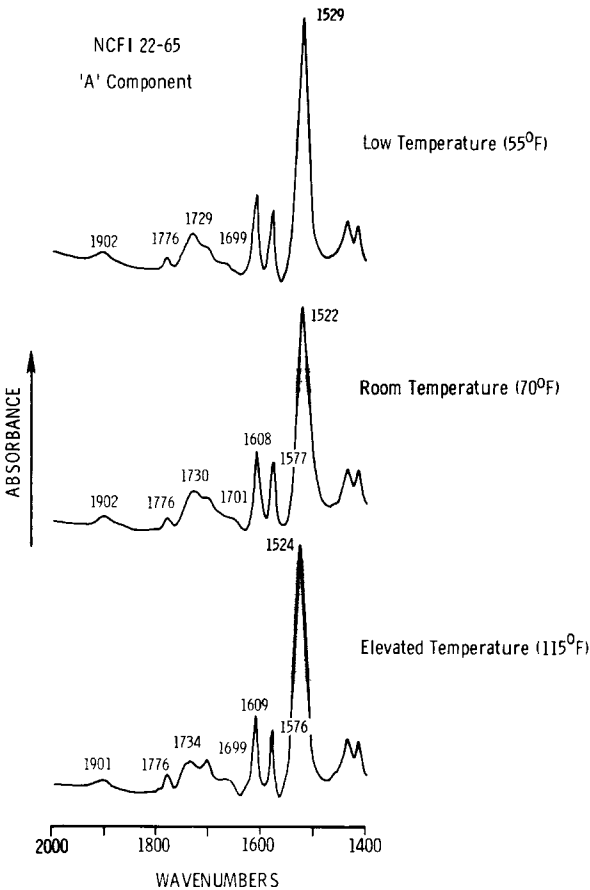


Figure 9. FTIR spectra of "A" component (NCFI 22-65) after three months at specified temperatures.

Table 2. NCFI 22-65 isocyanurate formulation typical composition of "B" package

Component	Type	Function
Catalysts	Amines, Tin-Based Catalyst	Isocyanurate formation
Polyol	Polyol I and Polyol II	Urethane segments in final lattice
Flame Retardant I	Fyrol PCF (tri- β -chloroisopropyl phosphate)	Flame retardancy
Flame Retardant II	DOW XNS 50054.020 Voranol (a glycol) DMMP (dimethyl methylphosphonate) FR-1137 (impure dibromoneopentyl glycol)	Flame retardance and adhesion promotion
Blowing Agent	Freon 11-B	Foam Expansion
Minor	Various	

or 55°F) room (21°C or 70°F), and elevated (46°C or 115°F) temperatures for three consecutive months. The change detected in these spectra occurs around 1700 cm⁻¹, a region associated with $\nu_{C=O}$ stretching frequencies. As the temperature increases, the new carbonyl band increases, indicating the appearance of a decomposition product containing an acidic group.

"B" Component: The B side of this isocyanurate system is very complex. The typical components of this mixture are given in Table 2. FTIR spectroscopy is an excellent method to identify most of the constituents. When used, it indicates the two flame retardant packages and RX-6, i.e., a mixture of polyols, catalysts, and Freon 11-B.

The burn recession rate and the bond-strength data for sprayed foam shown under the optimization of flame retardancy have indicated the importance of the ratio of the two flame retardants in the B component; therefore, it is crucial to determine their individual concentrations accurately. Since the concentration of Freon 11-B used as the blowing agent during the reaction must control the amount of cell rise, it is also analyzed by gas chromatography.

A novel approach using HPLC has been devised to simultaneously obtain these concentrations of the flame retardants and Freon [5]. An internal standard (1,2-dichloroethane) is used in this case, and accurate concentration measurements are made after separation of the various components using a mixture of tetrahydrofurane, acetonitrile, and water (30, 25, and 45%, respectively). Figure 10 is a chromatographic separa-

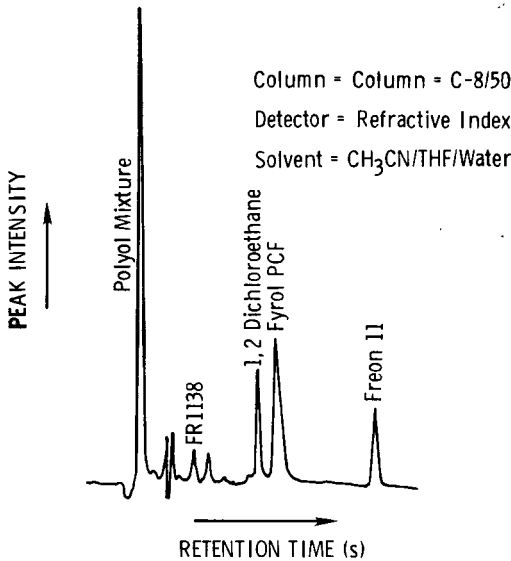


Figure 10. Separation by HPLC of "B" component (NCFI 22-65).

tion obtained for one of the B packages. The relative concentrations of FR 1138 (a component of DOW XNS 50054.20), Fyrol PCF, and Freon 11B for various lots of B component packages are listed in Table 3.

The HPLC technique can also follow the effects of accelerated aging of B components. For example, samples 83G008 and 83G008-14 in Table 3 correspond to specimens of the same material stored at low and ele-

Table 3. HPLC analysis of flame retardants and freon 11-B in "B" components of NCFI 22-65

Sample	% FR 1138 ± σ ^a	% Fyrol PCF ± σ ^a	% Freon 11-B
83G008	1.30 ± 0.07	16.6 ± 0.3	18.3
N51	0.49 ± 0.06	16.8 ± 0.2	32.5
N49	0.64 ± 0.06	16.1 ± 0.4	—
N47	0.33 ± 0.07	13.8 ± 0.05	20.9
N44	0.69 ± 0.1	16.7 ± 0.1	20.7
N28	0.45 ± 0.03	15.1 ± 0.21	25.4
N22	0.95 ± 0.05	16.7 ± 0.2	21.1
N6	0.46 ± 0.09	15.9 ± 0.1	20.5
83G008	0.45 ± 0.02	16.7 ± 0.4	6.69
RX-6	—	—	28.6

σ^a = Average of triplicate runs ± one standard deviation.

vated (108°F) temperatures for fourteen days. Accelerated aging seems to reduce the FR-1138 and Freon 11-B concentrations.

CHARACTERIZATION OF SOFI MATERIALS

The isocyanurate foam must perform up to expectations during ascent of the Space Shuttle. The physical and mechanical properties of the product depend chiefly on the reaction of the isocyanurate package, the appropriate rate of mixing of the components, and the homogeneity of the insulation layers on the surface of the ET. In order to ensure these requirements, it is necessary to establish valid criteria that can be used successfully to examine samples of SOFI.

For our evaluation, several isocyanurate foams were made by varying the ratios of components A and B in the mixtures. The resulting foams were set and then pulverized, stored in a dessicator, and analyzed by FTIR or TG.

As has already been shown, the FTIR spectra for the final foam contain various stretching frequencies assigned to bonds in various reaction products (see isocyanurate reaction scheme, Figure 5). Despite the complexity of these spectra, bands directly associated with the trimer ($\sim 1420\text{ cm}^{-1}$) and B component additives (most likely P=O and C-OH at around 1220 cm^{-1}) can be ratioed in the absorbance mode to correlate the change in relative concentration of components A and B. Figure 12 gives examples of typical spectra obtained for foams analyzed in the range of 0.73 for A, while B is kept constant at 1.00. This range allows us to study the effect of composition on mechanical properties, although in practice, the A-to-B ratio is kept at 2:1. The relationship of the absorbance bands selected and their known A-to-B ratios is linear and reproducible, as shown by the replicate analysis of these samples plotted in Figure 11.

The empirically derived correlation can be used successfully to determine foam composition of core samples from sprayed areas on a tank. The FTIR spectrum of one of these specimens is also shown for comparison. Clearly, the A-to-B ratio of this insulation meets the specifications.

Thermogravimetric analysis is equally useful in providing indirect information on A-to-B ratios in finished foams. However, the complexity of the finished polymer network requires the judicious applications of differential thermogravimetric analysis (dTG). Although this study has not attempted to unravel the origins of the various partial weight losses, the ratio of the signals denoted as X and Y can still be used to fingerprint A-to-B ratios and can even be correlated linearly with the expected composition of the foam (see Figure 12). Recent studies involving the

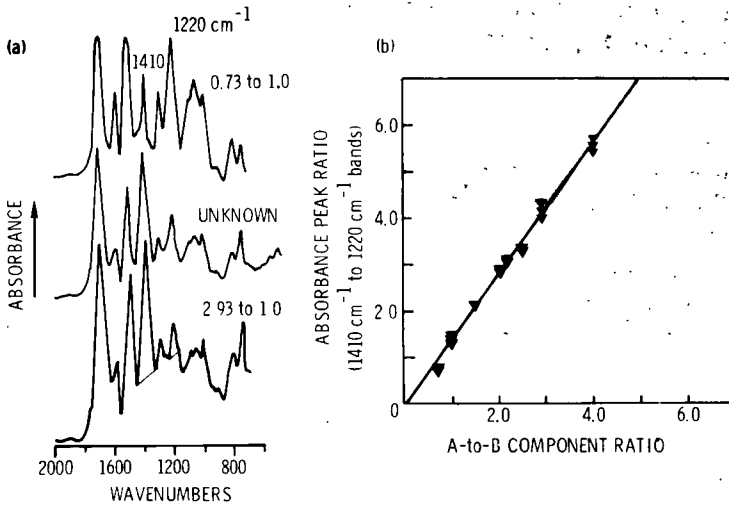


Figure 11. a) FTIR spectra of SOFI foams (NCFI 22-65) and b) calibration samples for the A-to-B component ratio and the ratio of the bands chosen for analysis.

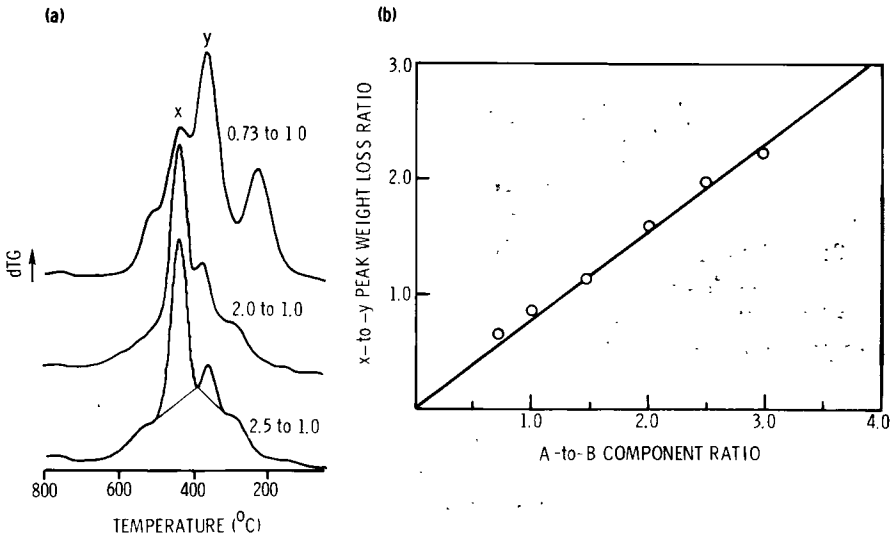


Figure 12. a) Differential thermogravimetric analysis for various SOFI foams (NCFI 22-65), and b) correlation between the ratio of weight losses X and Y vs the ratio of A-to-B components.

combination of variable temperature FTIR spectroscopy, pyrolysis GC/MS, and TG have demonstrated the power of this approach to identify polymer degradation [6]. In the future, this scheme will be applied to these isocyanurate products and a more valuable method of evaluation will be described.

CONCLUSIONS

This work has shown that in order to formulate, describe, and actually apply improved SOFI for the Space Shuttle ET, a variety of tests must be developed and used. Since the insulation's requirements arise from actual engineering calculations, the composition of the final foam must be closely controlled. Instrumental analysis can provide information on the structure, type, composition, and concentration of the ingredients of the foam as well as detect changes arising from aging, evaporation, loss of reactivity, and inadequate mixing of the starting materials.

Data derived by empirical relationships for actual SOFI samples from ET's can still be used to determine the properties of the final insulation. In all cases, these chemical changes can be correlated with changes in the mechanical properties of the insulation because component off-ratio will directly affect its thermal and cryogenic properties.

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