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DEVELOPMENT OF POLYISOCYANURATE POUR FOAM
FORMULATION FOR SPACE SHUTTLE EXTERNAL
TANK THERMAL PROTECTION SYSTEM

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ABSTRACT

Currently four commercially available polyisocyanurate/polyurethane spray-foam insulation formulations are being used to coat the external tank of the space shuttle. There have been several problems associated with these formulations. For example, some of the formulations do not perform well as pourable closeout/repair systems. Some do not perform well at cryogenic temperatures (poor adhesion to aluminum at liquid nitrogen temperatures). Their thermal stability at elevated temperatures is not adequate. A major defect in all of the systems according to NASA is the lack of detailed chemical information. The formulations are simply supplied to NASA and Martin Marietta, the primary contractor, as components; Part A (isocyanate) and Part B (polyol(s) and additives).

Because of the lack of chemical information and performance behavior data for the current system, NASA sought the development of a non-proprietary room temperature curable foam insulation. Requirements for the developed system were that it should exhibit equal or better thermal stability both at elevated and cryogenic temperatures with better adhesion to aluminum in comparison to the current systems.

As a result of this study several formulations were developed that met the material requirements of NASA. This study describes the various ingredients from commercial sources used and their performance behaviors. The formulations cited exceed the thermal stability of NCFI in the range of 300°C to 600°C, exhibit good pourability, good appearance of the cured foam, and bond well to aluminum at cryogenic temperatures.

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I. INTRODUCTION

While several space shuttle flights have been completed, there have been certain problems associated with the sprayed-on foam insulation (SOFI) on the external fuel tank (ET). Closeout/repair operations are required for replacing quality control samples, for filling cracks which occur during filling or detanking of the liquid hydrogen and liquid oxygen fuel tanks, and filling in irregular surfaces and repairing damaged surfaces.

Martin Marietta Corporation, the prime contractor for the external tank currently uses four commercially available foam formulations. These systems are CPR-488, NCFI 22-65, BX 250, and PDL-4034.

Each one of these formulations has certain advantages and disadvantages associated with it. For example, the most widely used systems, CPR-488 and NCFI 22-65, cannot be used for closeout/repair applications. These systems require highly controlled temperature and humidity conditions during processing and have a very short pot life. The present closeout/repair system, BX 250, does not have high thermal stability and requires the use of a heavy ablative material as an undercoat in the repair section. The system PDL-4034 is relatively new and its performance has not been fully assessed.

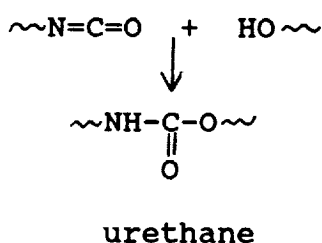
One disadvantage associated with all four commercially available systems pertains to their proprietary nature. Chemical information on the make up of each foam system has not been given to either the National Aeronautics and Space Administration (NASA) or to Martin Marietta.

In order to eliminate the processing and performance problems associated with the current systems and to make available to NASA a nonproprietary chemical system, the University of Dayton Research Institute was requested to develop an improved pourable thermal protection foam system for closeout/repair applications.

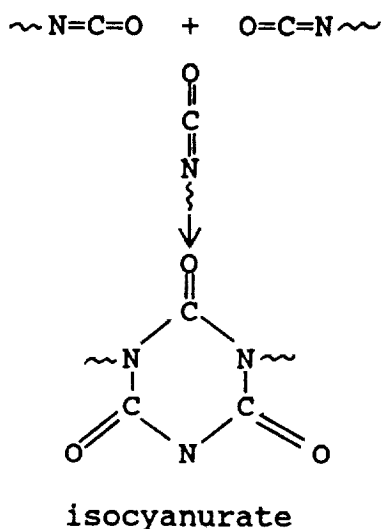
II. CHEMISTRIES OF THE CURRENT SYSTEMS

The current formulations are based upon a two component reaction system. One component (A) contains isocyanate functionalities. While the second component (B) contains polyol(s) and various additives. In most cases the overall chemical system is so designed that the functionality ratio of isocyanate to hydroxyl favors the isocyanate. Thus upon reacting the final chemical structure of reacted (cured) material will contain some segments based on the reaction of the isocyanate with the hydroxyl group and also segments based on the homopolymerization of the isocyanate groups.

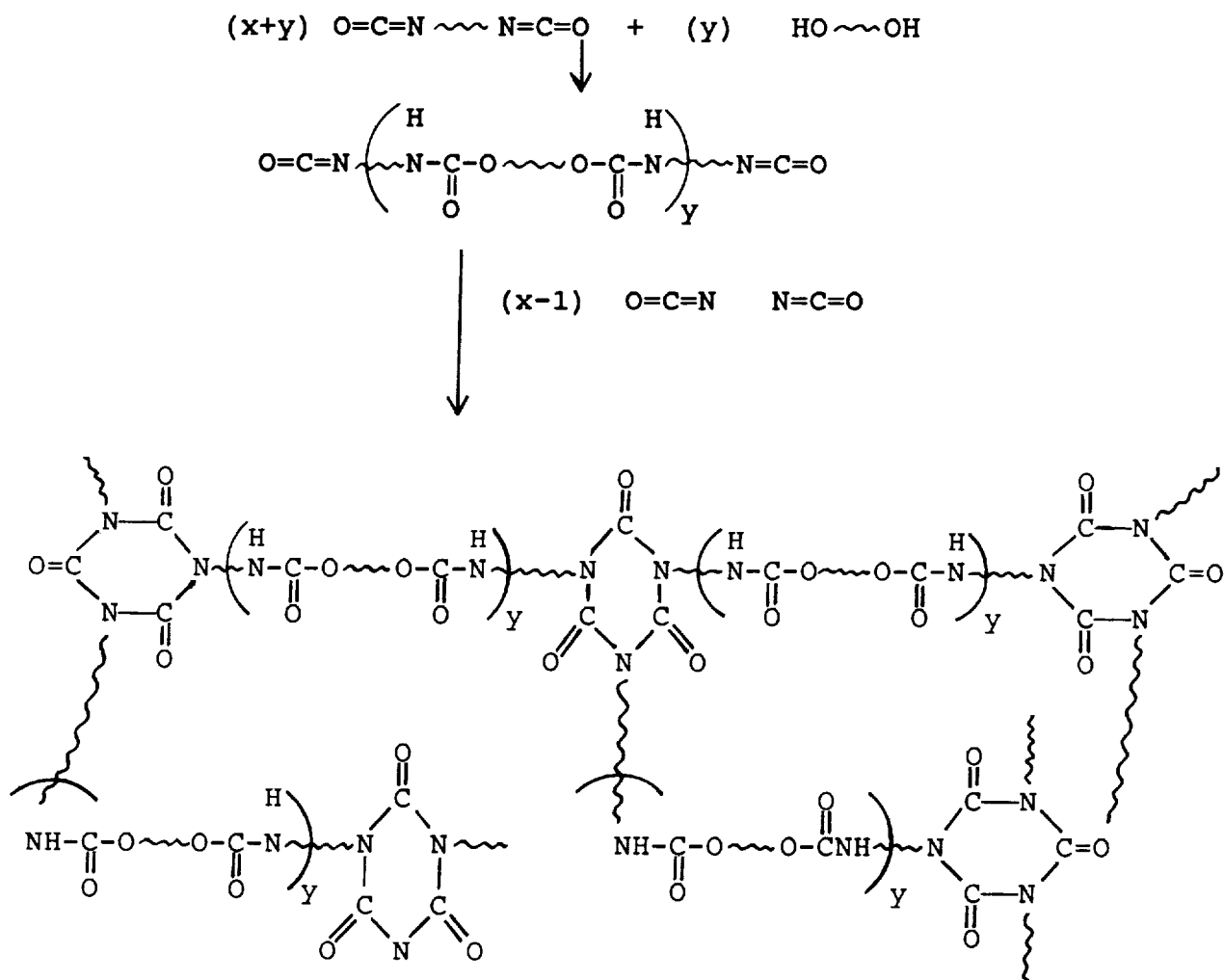
The reaction between the isocyanate and hydroxyl functionalities lead to the formation of a urethane linkage.



The homopolymerization of the isocyanate functionalities consists of a trimerization of the group to give a substituted triazine ring (isocyanurate linkage).



Since the starting reactants of the commercially available foam formulations were believed to contain multifunctional isocyanate and hydroxyl reactive sites and the systems were rich in isocyanate the overall curing scheme can be described in terms of the following events. First a long chain isocyanate terminated oligomer is formed from the reaction of the isocyanate reactive oligomer with the hydroxyl reactive oligomer (polyol). Next the final reaction takes place. This is between the newly formed long chain isocyanate-terminated oligomer and the residual isocyanate functionalities. Pictorially the sequence of events can be illustrated as follows.

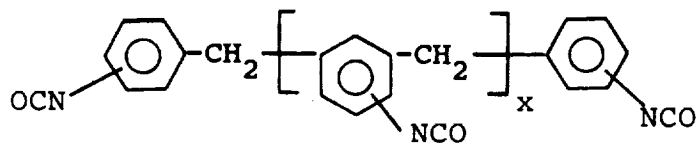


The final cured structure now contains isocyanurate crosslink sites with long chain urethane linkages between the crosslinking sites.

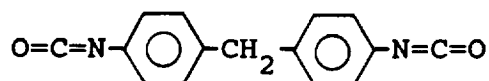
The previously mentioned chemistries formed the basis of each formulation; that is, an isocyanate "A" component and a polyol "B" component. NASA and/or Martin Marietta would receive drums from the vendors simply labeled "A" and "B". The foams were formulated from these drums. Detailed breakdowns of the chemistries in these "A" and "B" drums were not made available due to the fact that the various vendors were treating this information as proprietary.

The most chemical information pertaining to the chemistries of the various supplied "A" and "B" components was published in 1985.^[1] This report described the characterization of the "A" and "B" components of the North Carolina Foam Industries supplied NCFI 22-65 system.

High performance liquid chromatography (HPLC), Fourier Transform Infrared spectroscopy (FTIR), and Fourier ¹³C Nuclear Magnetic Resonance (FT-NMR) were used to analyze the starting "A" and "B" components. The cured material also was characterized by FTIR, Thermogravimetric Analysis (TGA), and Differential Thermogravimetric Analysis (DTGA). The results of this study indicated that the "A" contained the main isocyanate reactant. The spectral analysis of the isocyanate(s) gave the general structure:



Isocyanates used in commercial polymer synthesis are available from industrial sources as a mixture of isocyanates. The HPLC analysis of the "A" component indicated that this was true. The predominant isocyanate in this mixture was diphenylmethane-diisocyanate (MDI).



The analysis of the "B" component was very complex. The ingredients found in "B" are listed in Table 1.

TABLE 1
INGREDIENTS FOUND IN NCFI 22-65 "B" COMPONENT

<u>Types</u>	<u>Chemical Nature</u>
Catalysts	Amines Tin-based catalysts
Polyols (Co-reactant)	Polyol I Polyol II
Fire Retardant	Fyrol PCF Dow XNS 50054.020 DMMP (dimethyl methylphosphonate) FR-1137
Blowing Agent	Freon 11-B
Others	Various

The data contained in Table 1 were based upon spectral and chromatographic analyses and comparisons with known materials.

Information pertaining to the other formulations consists of the following: BX-250, a proprietary polyurethane spray-on foam insulation manufactured by Stepan Chemical Co.; CPR-488, a proprietary urethane-modified polyisocyanurate foam supplied by Upjohn; and PDL-4034, a polyurethane foam from Polymer Development Labs, Inc. Thermogravimetric analysis data for cured samples of three of the four commercially available formulations also has been reported in the literature.^[2] The results indicated that NCFI 22-65 cured foam exhibited superior thermal stability in a nitrogen atmosphere at temperatures below 700°C. The CPR-488 cured foam exhibited the next best thermal stability, followed by BX-250.

III. TECHNICAL APPROACH

The overall goals of this project were discussed at a meeting in Huntsville with representatives from NASA, Martin Marietta, and UDRI. The major goals were to obtain a room temperature curable foam formulation using known ingredients. The thermal stability of the cured new formulation should exhibit equal or better thermal stability than the current commercially available systems.

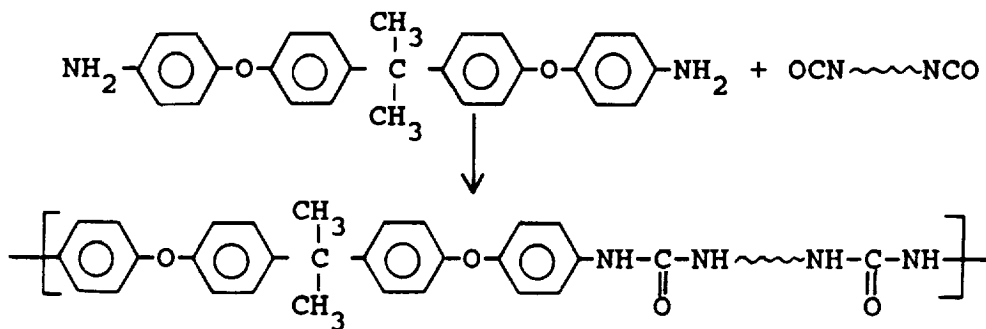
Our first efforts consisted of outlining a strategy for searching the literature for articles pertaining to polyisocyanurate and polyurethane foams and of developing a plan for contacting all the major suppliers of polyisocyanurate and polyurethane foams and raw material suppliers.

As previously mentioned only one article was found which was pertinent to our efforts.^[1] This article described the general formulation of the system from North Carolina Foam Industries. Their foam formulation was a two-part system: part "A" contained the main isocyanate reactant; while part "B" contained catalysts, the fire retardant mixture, Freon 11-B (a blowing agent), and a mixture of polyols. In this formulation only two chemical manufacturers were listed as suppliers for the NCFI foam system. These were Stauffer Chemical Company and Dow Chemical Company. Stauffer supplied Fyrol PCF, a tri- β -chloroisopropyl phosphate, a fire retardant. Dow supplied XNS 50054.020, a fire retardant system specifically formulated for NCFI to be used in the foam system for the external tank of the space shuttle. Conversations with Stauffer Chemical indicated that they did not have any new chemistries which were better than Fyrol PCF for this particular application. Dow recommended that we use XFS-43357.00 (FR-2000) in our formulation work in place of XNS 50054.020. FR-2000 is a total polyol and flame retardant system. This in essence combined part of the polyol and flame retardant II portion of the NCFI system.

In addition to NCFI, Stepan Chemical, supplier of the BX-250 foam formulation, was contacted for chemical information pertaining to their system. However, no useful chemical information was provided by them.

Based on the literature obtained, the reassessment of UDRI's three original concepts, that is formulations based on novolac-based polyols, sugar and sugar based polyols, and hydroxyl terminated chlorinated polyesters appeared still to be valid concepts to employ in this formulation effort.

Also, a new concept was proposed to NASA based in UDRI's work with 2,2-bis[4(4-aminophenoxy)phenyl] propane (BAPPP) to flexibilize bismaleimides and epoxy resins. This concept takes into account the reaction of an amine with an isocyanate to form a urea linkage.



Using this chemistry the phenoxy groups within the diamine would help flexibilize the cured structure and would also increase the overall thermal stability of the cured structure. Also, since this reaction can be performed at ambient temperatures, it will not interfere with the normal isocyanurate/urethane reaction which occurs when part "A" is mixed with part "B" in a system such as the NCFI system.

In order to improve on the current formulations used as either spray-on or pourable insulation for the external tank of the space shuttle, there are two basic approaches we could take. The first would involve the modification of the current systems; while the second would be to formulate a new system based on

existing chemistries and knowledge. Since the detailed chemical information pertaining to the commercial foam insulation formulations was not available, to improve on the performance of the current systems by modifying them with new chemical replacements would at best involve a shotgun type of approach.

The approach we took was to totally formulate a new system(s) based on the information we had. Currently the formulations were two-part systems; one part contained isocyanate, while the other part was a mixture of polyols, fire retardants, catalysts, and blowing agents. We also knew that the formulations were designed so that upon curing the resultant polymer structure was rich in isocyanurate functionalities. From their beginnings polyisocyanurates showed excellent flame resistance and low smoke generation but they suffered from brittleness and friability. Thus, the polyisocyanurates were modified by incorporation of some urethane linkages. This was accomplished by using a certain amount of polyol in the mix. Thus, upon curing, the final structure contained a combination of urethane linkages and isocyanate rings. This resulted in a final structure with a lower degree of crosslinking and more chain flexibility.

Using this as our starting point, our general methodology was as follows:

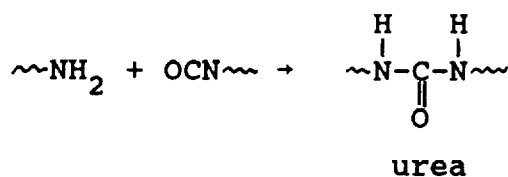
(a) Various polyols at different equivalents were mixed with isocyanates to form polyisocyanurate (PIC)/polyurethane (PU) copolymers. The polyol equivalent was equal to or less than 0.5 isocyanate equivalent. These formulations were cured at ambient temperatures and at 85°C for the purpose of observing the kinetics of curing.

<u>Isocyanate Equivalent</u>	<u>Polyol Equivalent</u>	<u>Isocyanate/ Polyol Ratio</u>	<u>Nature of Final Cured Polymer</u>
0.50	0.50	1:1	PU
0.50	0.25	2:1	(PIC) (PU)
0.75	0.25	3:1	(PIC) ₂ , (PU)
0.90	0.10	9:1	(PIC) ₈ (PU) ₁
0.95	0.05	19:1	(PIC) ₁₈ (PU) ₁

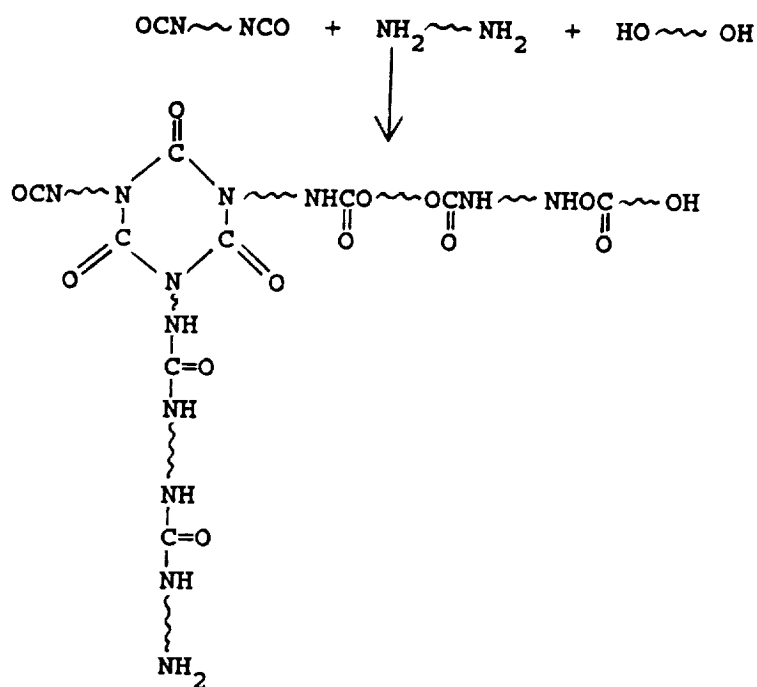
(b) The various PIC/PU copolymers were also prepared in the presence and absence of a PIC catalyst. This series of experiments was performed to insure that the formulation would be curable at ambient temperatures.

(c) Based upon our initial screening the next step involved combining various polyols at different equivalents with isocyanates in the presence and absence of a catalyst to determine synergistic efforts.

(d) Our last set of screening tests involved using the previously mentioned phenoxy diamine, BAPPP. One series of experiments consisted of its reactions with isocyanates to form polyureas.



Also reactions of this diamine in the presence of polyols and isocyanates to form tripolymers with isocyanurate, urethane, and urea linkages were planned to be evaluated. This reaction can be illustrated by the following reaction sequence.



Once the various samples were made, our testing strategy consisted of the following:

(a) test for tackiness (an indication of extent of cure) after three hours of mixing,

(b) samples which appeared to be fully cured were analyzed by thermogravimetric analysis, TGA,

(c) and based upon weight loss data, selected formulations were coated onto metal panels submitted by NASA or onto stainless steel plates and immersed in liquid nitrogen to determine the adhesion and shrinkage of these formulations at low temperatures.

Our first step was to contact all major raw material suppliers of polyisocyanurates and polyurethanes. In our discussion with these companies we sought advice on commercially available materials as possible ingredients for our formulations. Many of our contacts were uncooperative. The major reasons given were that they were already supplying the previously cited four commercial foam formulators with materials and did not want to alienate their customers; the suppliers did not want any involvement in a government project; they were not interested because of the low volume; and they had already considered this area before for others and were not interested in additional work. The companies which did supply materials are listed in Table 2.

Our first formulation step consisted of mixing various amounts of polyols with a polymeric isocyanate. The polyol as previously mentioned was mixed with the isocyanate in proportions such that the resulting cured structure would be rich in isocyanurate functionalities or contain a stoichiometric amount of polyol isocyanate to give a urethane-rich structure. Two samples were initially made for each formulation. These two samples were cured at ambient temperature for three hours. One sample for each set was used by UDRI for evaluation purposes and the other was reserved as a sample retained for possible shipment to NASA Huntsville for their visual inspection and evaluation. During the initial formulation efforts some formulations were cured at 85°C. However this practice was discontinued. Our major task was to

TABLE 2
MATERIALS RECEIVED FOR EVALUATION

<u>Trade Name</u>	<u>Functionality</u>	<u>Supplier</u>	<u>Key Feature</u>
Lupranate M200	Isocyanate	BASF Wyandotte	polymeric MDI isocyanate, NCO content 30.0%
Mondur MR	Isocyanate	Mobay	polymeric MDI isocyanate, NCO content 31.5%
Pluracol 975	Polyol	BASF Wyandotte	sucrose based polyol
NIAX HPS-480	Polyol	Union Carbide	polypropylene glycol
NIAX HPS-500	Polyol	Union Carbide	polypropylene glycol
NIAX HPP-520	Polyol	Union Carbide	polypropylene glycol
PS-2552	Polyol	Stepan Chemical Co.	aromatic polyester polyol, hydroxyl number of 245-275
PS-3152	Polyol	Stepan Chemical Co.	aromatic polyester polyol, hydroxyl number of 300-330
B251	Polyol	Solvay Technology	hydroxy terminated halogenated polyether, hydroxyl number of 330
30458 57X1A3	Polyol	Occidental Chemical	phenolic/polyester polyol, hydroxyl number of 430
Thanol R-470-X	Polyol	Texaco Chemical	
Thanol R-650-X	Polyol	Texaco Chemical	
XF 543357.00	Polyol/fire retardant	Dow	combined polyol/fire retardant system
FYrol PCF	Fire retardant	Stauffer	tris (β -chlorophyl) phosphate
Catalyst F (Code 6-4330)	Catalyst	Rohn & Haas	
DABCO TMR	Catalyst	Air Products	isocyanurate catalyst
DABCO TMR-30	Catalyst	Air Products	isocyanurate catalyst, tris (dimethyl amino-methyl phenol RQ)
DABCO K-15	Catalyst	Air Products	isocyanurate catalyst, potassium 2-ethyl-hexoate
DABCO 798	Catalyst	Air Products	isocyanurate catalyst, proprietary blend of a tertiary amine and ethylene glycol
Polycat 41	Catalyst	Air Products	isocyanurate catalyst, trade secret
Polycat 43	Catalyst	Air Products	isocyanurate catalyst, trade secret
Polycat 46	Catalyst	Air Products	isocyanurate catalyst, proprietary mixture containing glycol

develop a room temperature curable system. Also, in most cases no visual differences were observed in the curing of the formulations, at the two temperatures.

A second series of formulations also was prepared containing a catalyst. The catalyst we used throughout this study was DABCO TMR, a polyisocyanurate catalyst from Air Products. This catalyst was selected based upon recommendations of the suppliers and a screening test using 9.5g of polyisocyanate (Mondur MR) and 5.0g of a polyol (Pluracol 975) with ten weight percent of each catalyst and observing cure three hours after mixing at ambient temperature. From this screening test Air Products DABCO TMR performed the best.

Samples using other catalysts exhibited various degrees of tackiness after three hours indicating incomplete curing. The literature cited the use of tin salts as catalysts. Several different tin salts were initially used. Formulations containing a mixture of the polyisocyanurate catalyst and various tin salt catalysts showed very poor homogeneity three hours after mixing. The samples were a combination of tacky and rigid on the outside and soft on the inside. The available polymer literature also describes the use of alkali metal phenolates, alcoholates, and carboxylates as catalysts for the trimerization of isocyanate groups to yield polyisocyanurate linkages. The use of sodium phenolate and methoxide, potassium octoate, and sodium acetate as catalysts also yielded similar looking materials but with harder outer covering. Part of the problem may be attributed to the poor solubilities of these salts in the polyols used. The potassium octoate catalyst used was a commercially available solution from Mooney Chemical. The liquid observed in the samples after three hours from mixing may be due to the residual solvent.

Mobay's Mondur MR was used as the source of polyisocyanate throughout the study. Based on the initial screening formulation and the literature, the polyols we evaluated were BASF Wyandotte Pluracol 975, Solvay B251, Stepanol PS-2552 and PS-3152, Occidental 30458 57X1A3, Dow XFS 43357.00, and Texaco Chemical

Thanol R-470-X and R-650-X, and a series of NIAX polyols from Union Carbide.

A screening test of mixing the polyol with Mondur MR with an index of 2 and 10 weight percent of catalyst cured at ambient temperature was first used. Polyols which showed tackiness after three hours from mixing were eliminated from further formulation work. These were Stepanol PS-2552, the polyols from Texaco, and the NIAX polyols from Union Carbide.

Table 3 shows each component and its weight which were formulated and cured at ambient conditions.

Each formulation was prepared by mixing the ingredients together thoroughly and allowing each to stand at ambient temperature for three hours. At that time each sample was tested for tackiness. Samples which exhibited no tackiness were cut open and their interiors examined for tackiness.

Visual examinations of the formulations containing BASF Wyandotte Pluracol 975 polyol indicated that the formulations with compositions containing NCO/OH index between 1.00 and 9.00 appeared to be fully cured by three hours after mixing. This was true whether the samples contained catalyst or not. Samples with NCO/OH index of 18, with and without catalyst were not cured after three hours.

Compositions containing the Solvay hydroxyl terminated halogenated polyether with a NCO/OH index of 1 were fully cured after three hours at room temperature. This observation was made for samples with and without catalyst. Samples with NCO/OH indices either of 2 or 3 and with or without catalyst were still tacky after three hours. The samples with catalyst lost their tackiness after one day. No tackiness was observed in the other samples after five days. The same observation was also made for the composition with a NCO/OH index of 9 containing catalyst. The equivalent sample without catalyst was still a liquid after five days indicating little or no curing.

TABLE 3

POLYISOCYANURATE/POLYURETHANE FORMULATIONS, WT. OF EACH COMPONENT
IN GRAMS ROOM TEMPERATURE CURED

Part a. BASF Wyandotte Pluracol 975.

<u>Formulation #</u>	<u>Mondur MR, Polyisocyanate</u>	<u>Polyol</u>	<u>Isocyanate Index (NCO/OH)</u>	<u>DABCO TMR, Polyisocyanurate Catalyst</u>
1	9.56	5.00	1.91	0.1452
2	9.60	5.00	1.92	0.1456
3	9.62	5.00	1.92	---
4	10.62	5.00	2.12	---
5	4.92	5.00	0.98	0.0975
6	5.15	5.00	1.03	0.0985
7	4.90	5.00	0.98	---
8	4.86	5.00	0.97	---
9	7.41	2.50	2.96	0.0963
10	7.24	2.50	2.90	0.0977
11	7.24	2.50	2.90	---
12	7.50	2.50	3.00	---
13	8.64	1.00	8.64	0.0955
14	8.62	1.00	8.62	0.0962
15	8.72	1.00	8.72	---
16	8.73	1.00	8.73	---
17	9.19	0.50	18.38	0.0958
18	9.13	0.50	18.26	0.0962
19	9.31	0.50	18.62	---
20	9.21	0.50	18.42	---

TABLE 3 (Continued)

Part b. Solvay (B251) Halogenated Polyether Polyol.

<u>Formulation #</u>	<u>Mondur MR, Polyisocyanate</u>	<u>Polyol</u>	<u>Isocyanate Index (NCO/OH)</u>	<u>Dabco TMR Polyisocyanurate Catalyst</u>
11	8.12	5.03	2.00	0.1308
	8.12	5.02	2.00	0.1310
12	8.44	5.03	2.08	---
	8.11	5.04	1.99	---
13	4.04	5.02	1.00	0.0909
	4.05	5.02	1.00	0.0908
14	4.07	5.03	1.00	---
	4.04	5.04	0.99	---
15	6.08	2.51	3.00	0.0810
	6.04	2.50	2.99	0.0813
16	6.10	2.52	3.00	---
	6.09	2.52	2.99	---
17	7.28	1.01	8.93	0.0825
	7.33	1.01	8.99	0.0827
18	7.26	1.00	8.99	---
	7.27	1.00	9.01	---

TABLE 3 (Continued)

Part c. Stepanol PS 3152 Polyester Polyol.

<u>Formulation #</u>	<u>Mondur MR, Polyisocyanate</u>	<u>Polyol</u>	<u>Isocyanate Index (NCO/OH)</u>	<u>Dabco TMR Polyisocyanurate Catalyst</u>
19	7.69	5.00	2.05	0.1252
	7.54	5.03	2.00	0.1254
20	7.60	5.01	2.02	---
	7.50	5.00	2.00	---
21	3.87	5.03	1.03	0.0874
	3.91	5.01	1.04	0.0874
22	3.82	5.03	1.01	---
	3.81	5.02	1.01	---
23	5.90	2.53	3.11	0.0813
	5.65	2.56	2.94	0.0815
24	5.64	2.52	2.98	---
	5.80	2.50	3.09	---
25	6.77	1.03	8.76	0.0777
	6.80	1.01	8.98	0.0773
26	6.78	1.00	9.04	---
	6.87	1.00	9.16	---

TABLE 3 (Continued)

Part d. Occidental 30458 57X1A3 Polyol.

<u>Formulation #</u>	<u>Mondur MR Polyisocyanate</u>	<u>Polyol</u>	<u>Isocyanate Index (NCO/OH)</u>	<u>DABCO TMR Polyisocyanurate Catalyst</u>
27	10.29	5.03	2.00	0.1524
	10.46	5.05	2.02	0.1523
28	10.29	5.05	1.99	---
	10.49	5.05	2.03	---
29	5.23	5.02	1.02	0.1014
	5.29	5.02	1.03	0.1011
30	5.31	5.02	1.03	---
	5.37	5.02	1.04	---
31	7.67	2.52	2.97	0.1020
	7.67	2.51	2.98	0.1018
32	7.69	2.50	3.00	---
	8.30	2.52	3.22	---
33	9.23	1.05	8.59	0.1023
	9.38	1.03	8.90	0.1020
34	9.27	1.03	8.79	---
	9.23	1.01	8.93	---

TABLE 3 (Continued)

Part e. Dow XFS 43357.00 Polyol.

<u>Formulation No.</u>	<u>Mondur MR, Polyisocyanate</u>	<u>Polyol</u>	<u>Isocyanate Index (NCO/OH)</u>	<u>Dabco TMR Polyisocyanurate Catalyst</u>
35	10.34	5.03	2.01	0.1524
	10.32	5.03	2.00	0.1524
36	10.34	5.01	2.02	---
	10.43	5.02	2.03	---
37	5.35	5.02	1.04	0.1012
	5.34	5.03	1.04	0.1012
38	5.13	5.02	1.00	---
	5.17	5.02	1.01	---
39	7.69	2.51	2.99	0.1018
	7.68	2.51	2.99	0.1018
40	7.72	2.51	3.00	---
	7.78	2.52	3.01	---
41	9.28	1.01	8.97	0.1021
	9.26	1.00	9.04	0.1021
42	9.24	1.00	9.02	---
	9.22	1.01	8.91	---

Samples containing the aromatic polyester polyol, Stepanol PS-3152 from Stepan with NCO/OH indices of 1, 2, and 3 were fully cured at room temperature after three hours. Only the sample with catalyst and an index of 9 was cured. A similar formulation with a NCO/OH index of 9 without catalyst was still very tacky after five days.

The polyol, 30458 57X1A3, from Occidental Chemical, was reported to UDRI by Martin Marietta as being the polyol used in one of the formulations for insulation of the external tank. This material was supplied to UDRI with approximately 22% Freon as a blowing agent. In order to make our testing with this system compatible with our previous formulations, we removed the Freon from the polyol mixture before formulating with it. All samples formulated with this polyol cured to a very hard flaky appearance. The structural integrity of these cured materials was very poor in comparison to the other polyols used in this study. This series of evaluations was repeated using the material as received and compensating for the amount of Freon present. Again our samples were very hard friable in appearance.

The last polyol evaluated in this study was the combined polyol/fire retardant system from Dow Chemical, XFS 43357.00. Visual examination of these formulations cured at room temperature indicated that the compositions containing NCO/OH indices between 1.0 and 2.0 appeared to be fully cured after three hours from mixing. All other samples were tacky but appeared to be fully cured after one week. Samples containing the isocyanurate catalyst foamed slightly. The presence of a fire retardant in this combined system may have an adverse effect on the catalyst. We noticed this type of effect also in the polyols from Solvay and Occidental Chemical. All three of these contained organic halogens.

Overall the evaluation of first series of screening tests and formulations indicated the following:

(a) The catalyst which appeared to be the best for curing the most of the different polyol/isocyanate formulations at room temperature was DABCO TMR from Air Products.

(b) The polyols from Texaco, Union Carbide, and Stepanol PS-2552 did not pass the initial screening test. Formulations using these polyols were still tacky after 3 hours from mixing. This was true whether the formulations contained catalyst or not. Samples cured at 85°C were also tacky.

(c) All of the five polyols which passed the initial screening test were subjected to formulating work.

Samples containing Pluracol 975 appeared to perform the best in terms of reactivity and appearance. This was true for compositions contained NCO/OH indices between 1.00 and 9.00, with and without catalyst. The polyol from Stepan performed second best. Compositions containing NCO/OH indices between 1 and 3, with and without catalyst gave acceptable cured polymers. The sample of NCO/OH index of 9 with catalyst cured equally as well. Only samples of Solvay containing an index of 1 were fully cured. The combined fire retardant system from Dow, XFS 43357.00, formulated with isocyanate in a ratio of 1.0 and 2.0 gave equivalent appearance. However the two formulations with catalyst foamed. All cured formulations with the polyol from Occidental gave very friable cured structures.

The formulations which were fully cured after three hours from mixing at room temperature were subjected to thermogravimetric analysis (TGA). The conditions by which these samples were heated were in an air atmosphere and at a heating rate of 10°C. Air was selected as the test atmosphere rather than an inert atmosphere because it is more representative of what the external tank experiences during use.

Table 4 gives the results from the TGA on the formulations tested.

Table 5 represents the weight loss data obtained from cured slabs of the current foam insulation systems used by NASA.

TABLE 4
% WEIGHT LOSS AS A FUNCTION OF TEMPERATURE
(THERMOGRAVIMETRIC ANALYSIS; 10°C/MIN., AIR ATMOSPHERE)

Formulation Number	Key Chemical Features of Formulations		Isocyanate Index (NCO/OH)	Weight Loss %						
	C = catalyst	Composition		100°C	200°C	300°C	400°C	500°C	600°C	700°C
1		Pluracol 975/Mondur MR/C	1.92	0.52	1.28	7.71	41.03	52.82	93.00	
2		Pluracol 975/Mondur MR	2.12	0.59	1.55	9.26	38.36	50.18	90.67	
3		Pluracol 975/Mondur MR/C	1.03	0.71	3.63	12.20	50.69	61.69	94.14	
4		Pluracol 975/Mondur MR	0.97	0.72	1.36	15.71	51.95	61.59	87.42	
5		Pluracol 975/Mondur MR/C	2.90	0.93	4.08	13.03	48.34	58.36	93.42	
6		Pluracol 975/Mondur MR	3.00	0.86	2.34	14.34	48.76	58.94	94.91	
7		Pluracol 975/Mondur MR/C	8.62	0.11	0.59	3.30	29.81	45.12	93.20	
8		Pluracol 975/Mondur MR	8.73	0.32	0.36	4.42	30.99	46.66	81.76	
13		Solvay B251/Mondur MR/C	1.00	0.12	1.92	40.47	47.81	64.06	94.72	98.43
14		Solvay B251/Mondur MR	1.00	0.22	1.48	28.52	34.81	44.14	71.17	99.21
19		Stepanol PS 3152/Mondur MR/C	2.00	0.23	0.73	5.92	35.98	42.92	95.06	101.40
20		Stepanol PS 3152/Mondur MR	2.00	0.17	0.63	5.10	34.19	41.69	94.45	99.59
21		Stepanol PS 3152/Mondur MR/C	1.04	0.34	1.13	8.54	47.26	54.20	92.85	99.77
22		Stepanol PS 3152/Mondur MR	1.01	0.33	0.97	6.20	46.30	52.59	92.15	99.19
23		Stepanol PS 3152/Mondur MR/C	2.94	0.23	0.75	4.72	30.91	38.15	94.13	99.70
24		Stepanol PS 3152/Mondur MR	3.09	0.29	0.77	4.32	29.33	36.99	93.24	99.51
25		Stepanol PS 3152/Mondur MR/C	8.98	0.01	1.05	5.76	26.89	41.66	87.91	99.64
26		Stepanol PS 3152/Mondur MR	9.16	0.12	0.26	7.79	27.24	46.31	62.95	99.69
35		Dow XFS 43357.00/Mondur MR/C	2.00	0.38	4.36	40.10	59.48	70.06	95.74	99.81
36		Dow XFS 43357.00/Mondur MR	2.03	0.01	1.75	18.74	50.91	65.84	89.88	99.98
37		Dow XFS 43357.00/Mondur MR/C	1.04	0.45	2.88	32.18	52.47	63.72	94.25	99.31
38		Dow XFS 43357.00/Mondur MR	1.01	0.48	2.55	26.02	49.95	62.67	95.06	99.47
39		Dow XFS 43357.00/Mondur MR/C	2.99	0.08	1.17	10.58	38.15	51.32	92.00	99.76
40		Dow XFS 43357.00/Mondur MR	3.01	0.03	0.84	10.73	43.15	58.53	90.64	100.05
41		Dow XFS 43357.00/Mondur MR/C	9.04	0.15	1.72	12.69	37.69	51.55	92.37	99.70
42		Dow XFS 43357.00/Mondur MR	8.91	0.08	0.73	6.86	26.73	40.84	74.49	99.57

TABLE 5

NASA CURRENT FOAM INSULATION SYSTEMS
 % WEIGHT LOSS AS A FUNCTION OF TEMPERATURE
 (THERMOGRAVIMETRIC ANALYSIS; 10°C/MIN.)

Formulation	Weight Loss, %								Atmosphere (Testing Condition)
	100°C	200°C	300°C	400°C	500°C	600°C	700°C	700°C	
NCFI-22-65	0.66	2.73	13.85	28.28	48.02	95.50	96.71		Air
CPR-488	0.30	4.01	12.42	34.48	54.04	97.24	97.89		Air
PDL 40-34	0.68	2.64	25.35	43.27	55.58	92.15	96.80		Air
BK-250, Type 1	0.45	6.37	26.69	38.62	51.75	91.25	96.69		Air
NCFI-22-65	0.45	4.08	13.29	31.75	60.02	67.61	69.86		Nitrogen
CPR-488	0.30	2.77	14.42	41.39	60.89	67.49	70.10		Nitrogen
PDL 40-34	0.31	2.18	15.20	58.69	69.73	74.47	75.79		Nitrogen
BK-250, Type 1	0.28	5.05	21.97	58.27	72.93	76.35	78.94		Nitrogen

The current foam system NCFI 22-65 exhibited the best thermal properties in both air and inert atmospheres. Its weight losses at 300, 400, 500, and 600°C were the lowest of all four systems. Weight losses at 100, 200, 600, and 700°C were generally the same of all four systems.

Using the weight loss values at 300, 400, and 500°C for the NCFI-22-65 for comparison purposes the systems shown in Table 6 exhibited similar or better thermal behavior. These systems represent only simple formulations of an isocyanate with a polyol.

Samples of cured formulations from Table 6 were placed in a muffle furnace at 400°C (752°F) and at 500°C (932°F) for one minute each. Of all the specimens subjected to these high temperature treatments the samples containing Stepanol PS-3152 and Mondur MR with an isocyanate index of 2 (both with and without catalyst) showed the best structural integrity. Samples of the same chemistries with an index of 3 and the formulation based on the Solvay polyol showed the second best behavior at 400°C and 600°C. All other formulations showed severe flaking and cracking at 600°C.

Based on all of our previous evaluations we chose the formulation of Stepanol PS-3152/Mondur MR with catalyst and an isocyanate index of 2 (Formulation 19) as our base system. This formulation gave a room temperature curable system within three hours of mixing. Its weight loss pattern in an air atmosphere was relatively better than NCFI-22-65.

We began to formulate various systems with the Stepanol PS-3152 polyester polyol and Mondur MR isocyanate to determine if we could enhance the thermal stability of this chemistry.

The next series of formulations consisted of using other polyols in conjunction with the above chemistry. Based on the previously mentioned information and discussions with Dow we used their XFS 43357.00. Even though Dow XNS 50054.020 was cited as one of the components in NCFI foam system, they did not want to provide UDRI with a sample of this. Their XNS 50054.020 was a low

TABLE 6
% WEIGHT LOSS OF SELECTED FORMULATIONS
(THERMOGRAVIMETRIC ANALYSIS; 10°C/MIN., AIR ATMOSPHERE)

Formulation Number	Composition (C = Catalyst)	Isocyanate Index	Weight Loss, %			
			300°C	400°C	500°C	600°C
	NCFI-22-65	Unknown	13.85	28.28	48.02	95.50
7	Pluracol 975/Mondur MR/C	8.62	3.30	29.81	45.12	93.20
8	Pluracol 975/Mondur MR	8.73	4.42	30.99	46.66	81.76
14	Solvay B251/Mondur MR	1.00	28.52	34.81	44.14	71.17
19	Stepanol PS 3152/Mondur MR/C	2.00	5.92	35.98	42.92	95.06
20	Stepanol PS 3152/Mondur MR	2.00	5.10	34.19	41.69	94.45
23	Stepanol PS 3152/Mondur MR/C	2.94	4.72	30.91	38.15	94.13
24	Stepanol PS 3152/Mondur MR	3.09	4.32	29.33	36.99	93.24
25	Stepanol PS 3152/Mondur MR/C	8.98	5.76	26.89	41.66	87.91
26	Stepanol PS 3152/Mondur MR	9.16	7.79	27.24	46.31	62.95
42	Dow XFS 43357.00/Mondur MR	8.91	6.86	26.73	40.84	74.49

production volume material and they recommend XFS 43357.00 for this application. Also, XFS 43357.00 was a total polyol and fire retardant system. The polyol from Stepan and the one from Dow were mixed in a 1:1 weight basis. Since the hydroxyl number of each polyol was different the weight of the isocyanate was adjusted to give the indicated isocyanate indices. Table 7 gives the composition of these mixed polyol formulations.

The cured formulations of the mixed polyols with NCO/OH of 1 and 2 with and without catalysts appeared to be fully cured after three hours from mixing. The other two formulations with catalyst took longer to cure. The one with NCO/OH of 3 was cured after two days, while the formulation with NCO/OH of 9 took over 5 days. The formulations with indices of 3 and 9 without catalysts were still tacky after 5 days. It should be pointed out that the appearance of the cured formulations with the Stepanol/Dow mixed polyols was better than the cured formulations with Dow polyol system alone.

The thermal behavior of this series of cured formulations in an air atmosphere can be found in Table 8.

The mixed Stepanol/Dow polyol systems did not exhibit as good thermal behavior as the base Formulation 19. Formulations 43 and 44 exhibited the best thermal behavior of the mixed polyols. Subjecting samples of these two cured formulations to 400°C and 500°C indicated that they showed reasonable structural stability.

The next series of formulations consisted of the addition of a fire retardant system. This was primarily based on the literature citation of the use of Fyrol PCF in the NCFI and discussions with Dr. Mullins of NASA Huntsville and Dr. Stuckey of Martin Marietta. In our discussion on the historical development of the foam systems it was mentioned that this additive was used both to enhance the fire retardant of the formulations and to promote better adhesion of the foam to an aluminum substrate. However, it should be noted that in all of our formulation efforts we mixed the ingredients in an aluminum pan. In all of the cured formulations noted, the bonding between the formulation and the aluminum

TABLE 7

POLYISOCYANURATE/POLYURETHANE FORMULATIONS--
 MIXED POLYOL SYSTEMS
 (WT. OF EACH COMPONENT IN GRAMS)
 (ROOM TEMPERATURE CURED)

Formulation Number	Mondur MR Polyisocyanate	Dow 43347.00 Polyol	Stepanol PS3152 Polyester Polyol	Isocyanate Index (NCO/OH)	DABCO TMR Polyisocyanurate Catalyst
43	8.92	2.51	2.55	2.03	0.1387
44	8.87	2.50	2.53	2.04	---
45	4.46	2.52	2.52	1.02	0.0946
46	4.45	2.50	2.50	1.03	---
47	6.65	1.25	1.26	3.06	0.0919
48	6.65	1.26	1.25	3.06	---
49	7.99	0.50	0.50	9.23	0.0898
50	8.00	0.50	0.50	9.24	---

TABLE 8

% WEIGHT LOSS OF SELECTED MIXED POLYOL FORMULATIONS
(THERMOGRAVIMETRIC ANALYSIS; 10°C/MIN., AIR ATMOSPHERE)

Formulations Number	Composition (C-catalyst)	Isocyanate Index	300°C	Weight Loss, %	
				400°C	500°C
	NCFI-22-65	Unknown	13.85	28.28	48.02
19	Stepanol PS 31521 Mondur MR/C	2.00	5.92	35.98	42.92
43	Stepanol/Dow/Mondur/C	2.03	8.53	34.81	52.42
44	Stepanol/Dow/Mondur	2.04	6.19	39.30	52.24
45	Stepanol/Dow/Mondur/C	1.02	13.74	46.48	53.89
46	Stepanol/Dow/Mondur	1.03	13.62	49.27	58.14
					600°C
					95.50
					95.06
					93.81
					93.03
					91.79
					93.09

was excellent. Most of the cured formulations could not be pulled away from the aluminum pan. Samples for thermal analysis were taken from the center of each formulation after both the aluminum pan and formulation were cut in half. Table 9 gives the composition of the combined mixed polyols plus addition fire retardant. In this series of experiments, the amounts of the 1:1 mixed polyol, isocyanate index, and amount of catalyst were held constant and the amount of Fyrol PCF fire retardant was varied.

Weight loss data of these formulations can be found in Table 10. Examination of the weight loss data from this series of experiments indicated that the weight loss at the 300, 400, and 500°C increased with increasing fire retardant concentration. The thermal stability of the formulations with catalyst appeared to be better than the formulations without catalyst. This was true for all temperatures except for 600°C; the weight loss of samples without catalyst at this temperature decreased with increasing fire retardant concentrations.

The next series of experiments consisted of adding blowing agents to the base formulation (19) to observe the foaming characteristics of this system. Table 11 gives the composition of this series. Methylene chloride and Freon 11 were used as blowing agents. The purpose of using methylene chloride as a blowing agent will be discussed later. Also, based on conversations with various foam manufacturers it was advised to compare the difference of adding the Freon to both Part A (isocyanate) and to Part B (polyol system). The formulations with both methylene chloride and Freon 11 were fully cured within three hours from mixing. The foam cell sizes of the methylene chloride formulations were larger and more irregular than the formulations using Freon 11. Table 12 shows the weight loss behavior of these formulations.

A review of the weight loss data obtained from the formulations containing blowing agents indicated that their thermal behaviors at 300°C and 500°C were equal to or better than the thermal behavior of the NCFI-22-65 foam. The weight loss of the

TABLE 9

POLYISOCYANURATE/POLYURETHANE FORMULATIONS -
 MIXED POLYOL/FIRE RETARDANT SYSTEMS
 (WT. OF EACH COMPONENT IN GRAMS)
 (ROOM TEMPERATURE CURED)

Formulation Number	Mondur MR Polyisocyanate	Dow XFS 43357.00 Polyol	Stepanol		Isocyanate Index (NCO/OH)	Stauffer's		% Fire Retardant in Formulation	DABCO TMR Polyisocyanurate Catalyst
			PS 3152 Polyester Polyol	Polyol		Fyrol PCF Fire Retardant	Retardant		
43	8.92	2.51	2.55	2.55	2.03	0.00	0.00	0.1387	
51	9.10	2.71	2.58	2.58	2.00	0.72	4.72	0.1390	
52	8.95	2.53	2.50	2.50	2.06	0.70	4.77	---	
53	8.89	2.55	2.52	2.52	2.03	1.41	9.09	0.1388	
54	8.90	2.52	2.50	2.50	2.05	1.43	9.32	---	
55	8.87	2.58	2.51	2.51	2.02	2.12	13.07	0.1388	
56	8.91	2.55	2.52	2.52	2.03	2.10	13.06	---	
57	8.89	2.52	2.53	2.53	2.03	2.81	16.64	0.1386	
58	8.91	2.55	2.54	2.54	2.02	2.80	16.67	---	
59	9.10	2.55	2.54	2.54	2.07	3.50	19.63	0.1386	
60	8.92	2.50	2.54	2.54	2.04	3.52	20.14	---	

TABLE 10

% WEIGHT LOSS OF SELECTED MIXED POLYOL/FIRE RETARDANT FORMULATIONS
(THERMOGRAVIMETRIC ANALYSIS; 10°C/MIN, AIR ATMOSPHERE)

Formulation Number	Stauffer's Fyrol PCF Fire Retardant, g	% Fire Retardant in Formulation	Weight Loss, %			
			300°C	400°C	500°C	600°C
NCFI-22-65	unknown	unknown	13.85	28.28	48.02	95.50
43 (a)	0.00	0.00	8.53	34.81	52.42	93.81
51 (a)	0.72	4.72	11.15	41.77	55.86	92.99
52 (a,b)	0.70	4.77	15.87	41.54	52.08	88.99
53 (a)	1.41	9.09	18.93	40.52	49.10	90.66
54 (a,b)	1.43	9.32	18.78	46.09	59.40	84.33
55 (a)	2.12	13.07	20.89	41.67	50.55	91.61
56 (a,b)	2.10	13.06	28.99	51.45	65.40	84.08
57 (a)	2.81	16.64	26.67	45.29	52.39	89.88
58 (a,b)	2.80	16.67	34.37	49.45	60.81	83.17
59 (a)	3.50	19.63	29.54	46.35	54.77	92.76
60 (a,b)	3.52	20.14	33.08	50.45	62.71	77.71

(a) 1:1 weight mixture of Stepanol/Dow Polyols, Isocyanate Index of 2, 1% weight catalyst.

(b) Without catalyst.

TABLE 11

POLYISOCYANURATE/POLYURETHANE FORMULATIONS -

(a) METHYLENE CHLORIDE AS A BLOWING AGENT
(WT. OF EACH COMPONENT IN GRAMS)
(ROOM TEMPERATURE CURED)

Formulation Number	Mondur MR Polyisocyanate	Stepanol PS3152 Polyester Polyol	Isocyanate Index (NCO/OH)	Methylene Chloride	% Methylene Chloride in Formulation	DABCO TMR Polyisocyanurate Catalyst
61	7.65	5.01	2.04	0.25	1.92	0.1252
62	7.56	5.00	2.02	0.25	1.95	---

(b) FREON 11 AS A BLOWING AGENT

Formulation Number	Mondur MR Polyisocyanate	Stepanol PS3152 Polyester Polyol	Isocyanate Index (NCO/OH)	Freon 11	% Freon in Formulation	DABCO TMR Polyisocyanurate Catalyst
63	7.55	5.01	2.01	1.28	9.17	0.1251
64	7.59	5.00	2.02	1.28	9.23	---
65	7.57	5.00	2.02	1.89	12.96	0.1251
66	7.55	5.00	2.01	1.89	13.09	---
67(a)	7.52	5.03	1.99	1.89	12.98	0.1249
68(a)	7.51	5.01	2.00	1.90	13.18	---

(a) Different mixing procedure, blowing agent added to isocyanate portion.

TABLE 12

% WEIGHT LOSS OF SELECTED FORMULATIONS WITH BLOWING AGENTS
(THERMOGRAVIMETRIC ANALYSIS; 10°C/MIN., AIR ATMOSPHERE)

(a) Methylene Chloride As Blowing Agent

Formulation Number	% Methylene Chloride in Formulation	Weight Loss, %			
		300°C	400°C	500°C	600°C
NCFI-22-65	---	13.85	28.28	48.02	95.50
19	0.00	5.92	35.98	42.92	95.06
61	1.92	6.63	36.71	42.98	93.38
62	1.95	6.37	40.55	47.02	86.99

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(b) Freon 11 As Blowing Agent

Formulation Number	% Freon 11 in Formulation	Weight Loss, %			
		300°C	400°C	500°C	600°C
63	9.17	10.04	37.24	43.70	92.58
64	9.23	8.46	41.37	47.04	93.37
65	12.96	12.16	43.24	49.32	94.26
66	13.09	11.15	46.62	52.03	92.91
67(a)	12.98	12.33	45.60	50.85	94.89
68(a)	13.18	13.56	40.05	45.98	95.82

(a) Different mixing procedure, blowing agent added to isocyanate portion.

NCFI-22-65 at 400°C was lower. Subjecting the cured foams to 400°C and 500°C in a muffle furnace indicated that the two foams with methylene chloride behaved similar to the standard formulations. The foams containing approximately 9% Freon 11 showed good thermal stability at 400°C and 500°C. The foams with 13% Freon 11 were friable at 500°C and showed signs of cracking.

Weight loss data of samples in which Freon was added to the polyol and samples where Freon was added to the isocyanate portion were similar. The major difference observed during this experiment dealt with the ease of mixing. It was much easier to mix the two portions together when the blowing agent was in the isocyanate.

In our discussions with NASA Huntsville and Martin Marietta concerns were raised about the moisture content of the foam systems currently being used in this application. An experiment was devised to determine the effect of moisture on our formulation efforts. Various amounts of water were added to two different formulations. The composition of these formulations are listed in Table 13. Table 14 gives the weight loss data for these formulations with water added as well as their equivalent formulations without water.

The incorporation of water into these formulations changed the chemical nature of the final cured structure of the foam. Water can react with the isocyanate functionality to form an unstable carbamic acid intermediate. This intermediate decomposes to form an amine and carbon dioxide. The amine group in turn is capable of reacting with an isocyanate functionality to form a urea linkage. This reaction sequence can be illustrated as follows.

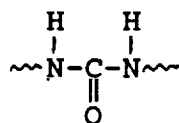
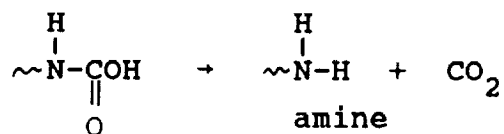
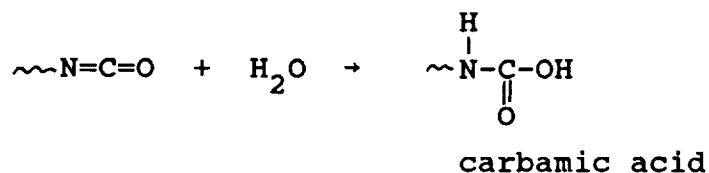
TABLE 13
 POLYISOCYANURATE/POLYURETHANE/POLYUREA FORMULATIONS
 CARBON DIOXIDE AS A BLOWING AGENT/MIXED POLYOLS/
 FIRE RETARDANT SYSTEMS
 (WT. OF EACH COMPONENT IN GRAMS)
 (ROOM TEMPERATURE CURED)

Formula- tion Number	Mondur MR Polyiso- cyanate	Stepanol PS 3152 Polyester Polyol	Dow XFS 43357.00 Polyol	Isocyanate Index (NCO/OH) ^a	Water Water	% Water in Formu- lation	Stauffer Fyrol PCF Fire Retardant	% Fire Retardant in Formu- lation	DABCO TMR Polyisocyanurate Catalyst
69	7.54	5.00		2.01	0.26	2.01			0.1251
70	7.51	5.01		2.00	0.26	2.03			---
71	7.55	5.00		2.01	0.51	3.87			0.1252
72	7.52	5.01		2.00	0.51	3.91			---
73	8.91	2.51	2.57	2.02	0.26	1.72	0.70	4.64	0.1388
74	8.89	2.54	2.55	2.02	0.25	1.67	0.71	4.75	---

^aExcluding the effect of H₂O to the NCO/OH index.

TABLE 14
 % WEIGHT LOSS OF POLYISOCYANURATE/POLYURETHANE/
 POLYUREA FORMULATIONS (THERMOGRAVIMETRIC
 ANALYSIS; 10°C/MIN, AIR ATMOSPHERE)

Formulation Number	% Water in Formulation	Weight Loss, %			
		300°C	400°C	500°C	600°C
19	0.00	5.92	35.98	42.92	95.06
69	2.01	5.91	35.98	42.56	90.20
71	3.87	7.71	36.17	42.22	93.78
20	0.00	5.10	34.19	41.69	94.45
70	2.03	4.85	36.51	43.14	89.64
72	3.91	6.22	35.94	43.83	88.00
59	0.00	29.54	46.35	54.77	92.76
73	1.72	18.70	39.91	49.53	91.69
60	0.00	33.08	50.45	62.71	77.71
74	1.67	20.64	40.59	51.35	91.56



urea

Thus, the structure of the cured formulations containing water now contains urea linkages as well as isocyanurate and urethane linkages. Also the carbon dioxide generated during this reaction serves as a blowing agent.

Based on the weight loss data of these cured formulations the incorporation of water into the formulations did not have a negative effect. In fact, for the formulations based on Stepanol polyol, Mondur MR, and water, thermal stabilities were very similar at 300, 400, and 500°C. A slight decrease in weight loss was observed at 600°C for the formulations containing water.

For the formulations containing the mixed polyol and fire retardant the addition of water showed a marked decrease in weight loss at 300, 400, and 500°C. The weight loss at 600°C for the formulation containing catalyst with and without water were essentially the same. The weight loss of the formulation without catalyst and with water showed a higher weight loss than its corresponding sample without water. Formulation 60 did show the

lowest weight loss of 77.71% at 600°C; the number was verified by a duplicate sample and thermal analysis.

The next series of formulating experiments consisted of determining the effect of the amount of catalyst on the formulations. We prepared formulation 75 containing 2 weight percent of the polyisocyanurate catalyst. This system was fully cured within three hours of mixing. Table 15 gives the weight loss behavior of this formulation as well as the corresponding formulations containing zero catalyst and 1 weight percent catalyst.

The weight loss at 300, 400, and 500°C increased as the concentration of catalyst increased. The sample with the 2 weight percent catalyst showed the lowest weight loss at 600°C.

Evaluations were performed involving the testing of the adhesion of the cured formulations to aluminum at both ambient and at liquid nitrogen temperatures. All of the formulations which were subjected to thermal analysis were tested for adhesion. Based on discussions with NASA it was suggested to test the adhesion of the formulations at ambient temperature by determining how easily the cured formulations could be removed from the aluminum weighing dishes in which the formulations were prepared. In all cases the formulations could not be easily pulled away from the aluminum. In fact, in order to evaluate the interior cured structures of these formulations, the specimen had to be cut through both the aluminum and cured foam. Based on these observations and discussions with NASA, the bonding of these formulations to aluminum was more than adequate for the specified application.

To evaluate the adhesion at liquid nitrogen temperatures, NASA and Martin Marietta recommended simply immersing the aluminum coated specimen into liquid nitrogen. One half of the cured formulation/aluminum pan specimens was submersed into a Dewar flask containing liquid nitrogen for one minute, removed, allowed to warm to ambient temperature, and examined. All formulations bonded well to the aluminum after being exposed to liquid nitrogen.

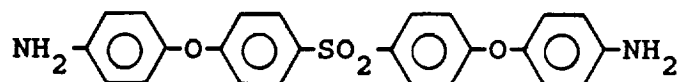
TABLE 15
 % WEIGHT LOSS OF SELECTED FORMULATIONS TO DETERMINE EFFECTS OF CATALYST;
 10°C/MIN., AIR ATMOSPHERE

Formulation Number	% Catalyst in Formulation	Weight Loss, %			
		300°C	400°C	500°C	600°C
20	0.00	5.10	34.19	41.69	94.45
19	1.00	5.92	35.98	42.92	95.06
75	2.00	6.46	38.27	45.54	90.97

The last evaluation that was performed with the previously discussed commercially available ingredients consisted of preparing large slabs of cured formulations. Using the standard formulation 19, four large slabs were prepared at two different scales. The first two were 13 times the size of the original formulation (total weight each 164 grams), while the other two were 39 times the size of the original formulation (approximately 500 grams). All slabs had good structural integrity. Thermal analysis of the larger slabs indicated that the weight loss curves of these larger samples were equivalent to the original Formulation 19. This indicated that scaling up the formulations should not pose any difficulties as far as weight loss behavior is concerned.

The last series of experiments dealt with the use of 2,2-bis[4(4-aminophenoxy)phenyl]propane (BAPPP-diamine). At UDRI a great deal of experience has been obtained in using this diamine as a starting reactant to prepare bismaleimides and epoxy resins. The incorporation of this diamine within the reactive oligomeric backbone of the bismaleimide and epoxy resins has furnished cured structures which were more flexible and exhibited better or equal thermal stabilities than state of the art materials.

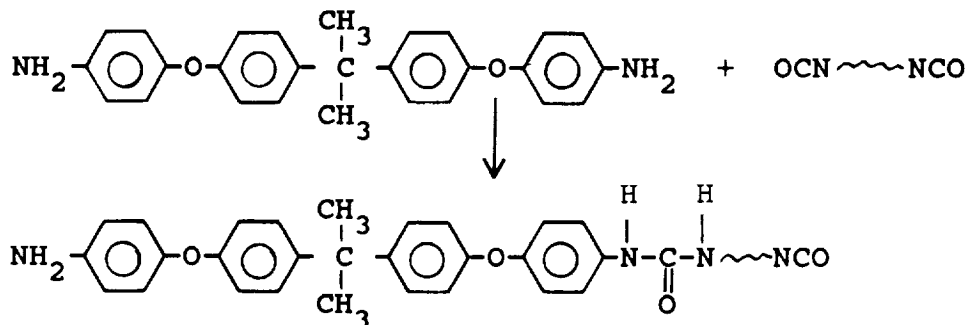
As previously mentioned one of the concepts dealt with the replacement of some of the polyol with this diamine which enhances both the flexibility and thermal stability of the formulations. In addition to experimenting with the BAPPP-diamine, UDRI also had sample of a sulfone version, bis-4(4-amino phenoxy)phenyl sulfone (BAPPS-diamine).



Pound quantities of these two diamines were also furnished to Martin Marietta in New Orleans for their formulation efforts.

The first formulations using BAPPP-diamine consisted of mixing the diamine with the Mondur MR isocyanate in various portions. The reaction of an amine with an isocyanate

functionality gives an urea linkage. Thus the reaction of the isocyanate with the diamine in the amounts we used gives a structure containing both urethane and urea linkages. The equivalent weight of the Mondur MR was reported to be 130. The equivalent weight of the BAPPP-diamine is 205. (Only one hydrogen from each diamine functionality reacts with the isocyanate to form the functionality urea linkage.)



The compositions of the formulations in this series of experiments are listed in Table 16.

All the formulations containing the diamine did not cure within three hours from mixing. The samples remained liquified for over one week. The poor curing behavior of these formulations may be due to the insolubility of the BAPPP in the isocyanate. However, each formulation did form an outer skin. This may have been the result of the reaction of the isocyanate with atmospheric moisture. Similar formulations were fully cured at 100°C for 18 hours. The resultant materials were brittle.

A similar series of formulations using the BAPPS diamine in place of the BAPPP diamine was prepared. This also did not fully cure at room temperature. After two days these formulations had a hard thin outer surface with liquid on the inside. Full cure of these formulations was achieved at 130°C for 18 hours.

Discussions with NASA-Huntsville and Martin Marietta recommended the use of a solvent to first dissolve the diamine then use the solution to react with the isocyanate. A solvent such as methylene chloride was recommended because it could also serve as

TABLE 16
 POLYISOCYANURATE/POLYUREA FORMULATIONS
 (WT. OF EACH COMPONENT IN GRAMS)
 ROOM TEMPERATURE CURED

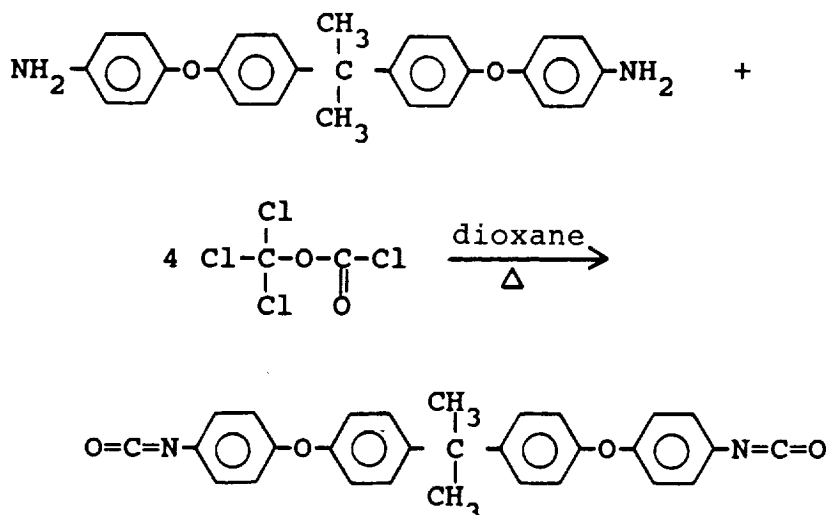
Formulation Number	Mondur MR Polyisocyanate	BAPPP-Diamine	Equivalent Ratio, NCO/NH ₂	DABCO TMR Polyisocyanurate Catalyst
76	5.00	4.00	2:1	0.09
77	5.00	4.00	2:1	--
78	5.00	2.00	4:1	0.07
79	5.00	2.00	4:1	--
80	5.00	1.00	8:1	0.06
81	5.00	1.00	8:1	--
82	5.00	0.50	16:1	0.06
83	5.00	0.50	16:1	--

a blowing agent. We had earlier reported the use of methylene chloride as a blowing agent. The loading of methylene chloride reported in Table 11 was the highest concentration of methylene chloride which still cured within three hours of mixing and did not have pockets of the methylene chloride liquid within the cured structure when it was cut open.

We prepared a saturated solution of the BAPPP diamine (1.0 grams in 546 ml) and added it to a mixture of 5.0 grams of Mondur MR and 0.05 gram of the catalyst. After less than one minute from mixture, one could see that the diamine precipitated from solution. No sign of curing was observed except for a hard skin on top of the formulation, after which the formulation was placed in an oven at 100°C. After 18 hours the material appeared to be fully cured; however, the resultant material was brittle and very friable. The experiment was repeated using a solution of 1.0 grams of the BAPPP diamine in 7 ml of methylene chloride. This time the diamine stayed into solution. However, it was only partially cured at room temperature. Subjecting this formulation to 100°C again produced a very brittle friable material.

In addition to dissolving the BAPPP diamine in methylene chloride, we also attempted to dissolve the diamine in the Freon 11 as well as in all the different polyol samples we obtained for this project. The diamine was insoluble in all three ingredients. These solubility properties make the diamine unsuitable for this application. The BAPPS diamine had a slight solubility in methylene chloride (1 gram in 41.5 ml) and was also insoluble in Freon 11 and the other polyols tried.

The last attempt to incorporate the flexible diamine into a formulation was to convert the amine functionality into isocyanate functionality and use the material as the starting isocyanate portion of the formulation. On an industrial scale the poly- and diisocyanate are prepared from the reaction of diamines with phosgene. On a laboratory scale a phosgene substitute, trichloromethyl chloroformate, can be used to convert an amine to an isocyanate functionality.



A small reaction (94.0 grams, 0.23 mole of diamine) was run using the above reaction sequence. The reaction mixture was heated to reflux for 24 hours, after which the solvent was removed by vacuum distillation. The Fourier transform infrared spectra of the oily residue indicated the absence of amine peaks and the presence of isocyanate. Due to the timing of the project, only a cursory look was taken using the new diisocyanate. The diisocyanate, BAPPPDI, was reacted with ethylene glycol (1:1) to give a rigid cured structure. The diisocyanate was mixed with the polyisocyanurate catalyst. No sign of curing was observed at room temperature. Heating the mixture to 130°C for 10 minutes yielded a rigid cured structure. Also mixing the new diisocyanate with the Stepanol polyol (2:1 isocyanate index) and catalyst gave a hard cured structure at 130°C. An equivalent formulation mixed at room temperature remained gummy after three days.

IV. CONCLUSIONS

During the initial kick-off meeting between the NASA technical monitor, representatives from Martin Marietta, and UDRI the major objectives of the project were discussed. These objectives were for a polyisocyanurate/polyurethane foam formulation(s) made up of known commercially available ingredients, room temperature curable, no tack by three hours after mixing (both on the exterior and interior portions of the cured material), equal or better

thermal stability than the current foam formulations, and better adhesion to aluminum at cryogenic temperatures.

The basic aspects of this project were achieved. Several different formulations were developed which meet the above goals. For example, the polyols, Pluracol (BASF Wyandotte), B251 (Solvay), Stepanol PS-3152 (Stepan Chemical), and Dow XFS 43357.00 (Dow Chemical) mixed with the polyisocyanate Mondur MR (Mobay) at certain isocyanate indices gave equal or better thermal stability than NCFI-22-65 as indicated in Table 6. The rate of weight loss for several of these formulations (7, 8, 19, 20, 23, 24, 25, 26, and 27) to 300°C (572°F) was less than the current formulation of NCFI-22-65. Based on discussions with NASA and Martin Marietta, this was significant. Also significant was the fact that the weight losses of the formulations 8, 14, 25, 26, and 42 were considerably less at 600°C (1112°F) than the foam from NCFI. As previously mentioned the foam formulation from NCFI exhibited the best thermal stability of the four current commercially available systems.

Any one of the formulations listed in Table 6 would be a good formulation for meeting the requirements discussed. Based on overall performance, i.e., appearance of the cured structure, thermal stability, and bonding of cured formulation to aluminum, Formulation 19 was selected as a standard formulation to determine whether thermal properties could be enhanced by the addition of other ingredients. Any of the other formulations could have served this purpose.

As expected, the ingredients added to this formulation affected its thermal behavior and performance. For example, the optimal isocyanate index for this system lies between 2 and 3. The catalyst which was found to perform the best was a commercially available proprietary material from Air Products. The optimal level of this catalyst for the systems under investigation was one weight percent based on the total weight of the formulation.

It was shown that the optimal concentration of fire retardant was in the vicinity of 9.5% (based on the one used). The formulation was shown to tolerate water. In fact, the thermal behavior at 600°C was better than expected.

Because we incurred resistance from the industry throughout the time of the project, a more logical starting point for the project would have first been the complete and total chemical analysis of each of the four commercially available foam formulation systems. Since NASA was supplied these systems as "A" and "B" from each vendor, the total analysis of each should be possible. From this a more systematic approach could be made to solving this problem. The literature only offered a partial identification of one system. We have provided useful information to NASA via this project in identifying other useful chemistries. However, our efforts were limited by the data available to us. It also would have been most helpful if samples of the currently used foam systems had been available earlier.

During the course of this project we became aware of other foam systems (for example, Flexfoam from Fiber Materials, Inc.) which might have potential for application to the external fuel tank. However, it also is referred to as a proprietary, patentable system.

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