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# Assessment of Technologies for the Space Shuttle External Tank Thermal Protection System and Recommendations for Technology Improvement

## *Part 1: Materials Characterization and Analysis*

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July 2004

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# ASSESSMENT OF TECHNOLOGIES FOR THE SPACE SHUTTLE EXTERNAL TANK THERMAL PROTECTION SYSTEM AND RECOMMENDATIONS FOR TECHNOLOGY IMPROVEMENT

## PART I: MATERIALS CHARACTERIZATION AND ANALYSIS

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## INTRODUCTION

The use of foam insulation on the External Tank (ET) was necessitated by the potentially hazardous build up of ice on the vehicle prior to and during launch. This use of foam was initiated on the Saturn V rocket which, like the Space Shuttle, used cryogenic fuel. Two major types of foam have been used on the ET. The first type is an 'acreage' material that is automatically sprayed on in a controlled environment. This material is designated as NCFI 24-124. It replaced CPR 488 in 1998 and has been used since that time. The other major foam is a 'hand-sprayed' foam that is used to 'close out' regions where the various sections of the ET are attached. Two types of close-out foams have been used on the ET, known as BX-250 or BX-265, depending on when the ET was built. The external tank designated as ET-116 was the first tank to use BX-265 in place of BX-250, however, ET-93 did have some rework done with BX 265 on the fairing over the aft ET/Solid Rocket Booster (SRB) fitting. The bipod-ramp foam that was lost during the ascent of Columbia was made of the BX 250 material.

The NCFI 24-124 foam is primarily a polyisocyanurate. The CPR 488 was also a polyisocyanurate, but its exact chemistry has not been disclosed to the authors at this time. The BX 250 and BX 265 foams are primarily polyurethane. Chemically, all of these foams are quite different although they are made from the same basic starting chemical compounds. The difference is in the ratio of reactive compounds. In both foams, there are many 'side products' that can possibly form if the humidity or the reaction temperature varies. This report concentrates on BX 250 and BX 265 polyurethane foams that are used for the manual close-out sprays because these materials have been identified as the source of most of the observed 'foam shedding.' Comparisons of the CPR 488 to the NCFI 24-124 are not addressed in this document because of 1) the lack of chemical information about the CPR 488, and 2) the lack of major problems with this foam

The objectives of the present report are to study the chemistries of the various foam materials and to determine how physical and mechanical anomalies might occur during the spray and curing process. To accomplish these objectives, the report is organized as follows. First, the chemistries of the raw materials will be discussed. This will be followed by a discussion of how chemistry relates to void formation. Finally, a TGA-MS will be used to help understand the various foams and how they degrade with the evolution of chemical by-products. Future plans will also be discussed with an emphasis on developing a more comprehensive understanding of foam chemistry.

## Comparison of the BX-250 and BX-265 foams

The BX 265 foam evolved from BX 250 polyurethane foam, which was originally developed for the Saturn V Program. From the excellent laboratory analyses that have been performed at the Michoud Assembly Facility (MAF) (as reported in MMC-ET-SEO5-650), the major differences in the starting materials used for the two foams are as follows: (1) BX-250 foam used the blowing agent CFC-11, while BX-265 uses the more environmentally-friendly HCFC 141b, (2) BX-250 foam used a form of Methylene Di-Isocyanate (MDI) that was sold commercially but is no longer available, while BX-265 uses a newer commercial form of MDI, and (3) BX-265 foam has an additional catalyst that appears to allow spraying at lower than expected temperatures. Details of each of these differences are discussed subsequently.

**Blowing Agent Difference.** The blowing agent difference is an extremely important factor affecting foam performance because the two blowing agents have different boiling points, which greatly affects their ability to expand the cells during formation of the foams. CFC-11 has a boiling point of 75°F, as compared to 90°F for HCFC-141b. This difference in boiling points necessitates that BX 265 should be sprayed at a temperature 15°F higher than BX-250 in order to create the same amount of gas available for cell expansion. According to the specifications that are in place at MAF, this step in the spray process is not always done. The lower temperature limit for spraying BX-250 is 65°F, while the lower temperature for spraying BX-265 is only 70°F. This relatively low spray temperature is possibly a source of major processing problems for BX-265. Even though one would expect that the spray temperature should always be at, or above, the boiling point of the blowing agent, it is possible to have a marginally successful spray at 5°F lower. In the case of BX-250, there is a 'heat of reaction' that drives the reaction components to a temperature above the ambient temperature (probably above the 75°F boiling temperature of the CFC-11). In the case of BX-265, this elevation in temperature would have to be 15°F higher to generate the same amount of gas for blowing that foam. There is the possibility that the 'heat of reaction' in BX-265 could be higher because when it was formulated, an additional catalyst was added that should accelerate the chemical reaction. However, the Arrhenius relationship dictates that a 15°F increase in reaction temperature will result in a doubling of the reaction rate. This holds true whether the added heat comes from the environment or from the heats of the chemical reactions. Thus the reaction for BX-265 should proceed at a much faster rate than BX-250 due to the increase in foaming temperature that results from the exothermic reaction. Finally, incomplete foaming could cause either of the foams to have additional unreacted components within the system which act as a decomposition by-product and an unwanted increase in foam density. Likewise, a large exothermic reaction could cause unwanted voids to form due to an acceleration of gas by-products that can become entrapped within the system.

The other major factor involved in changing the blowing agent is that HCFC-141b is more likely (because of its more dipolar molecular structure) to act as a solvent as well as a blowing agent. Because of the molecular structure of CFC-11, it probably acts only as a blowing agent. If HCFC-141b does act as a solvent, it probably speeds up the reaction rate between the Part A and Part B components of the foam. Likewise, it will probably remain physically attached (or dissolved) in the final foam. This attribute can cause the final foam to be plasticized and it will certainly result in a slower loss of the blowing agent during subsequent storage. Additionally, because of the higher polarity of HCFC-141b, there should be a greater affinity for BX-265 foam to absorb moisture.

**MDI Difference.** The MDI component is a chemical mixture of the 'pure' compound methylene di-isocyanate and its higher molecular weight oligomers. The ratio of the 'pure' compound to each of its higher molecular weight oligomers is an extremely important variable that must be closely monitored and controlled to assure reproducible foam properties from spray to spray. There is a ratio that the manufacturer of this material tries to maintain and this ratio is monitored at MAF on all incoming batches of this material.

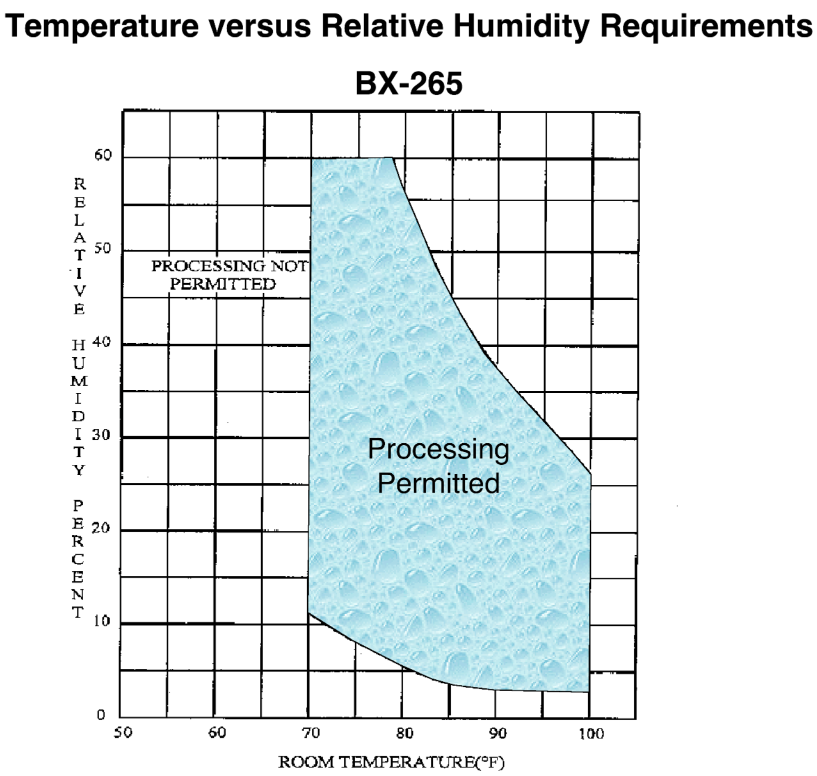
Unfortunate circumstances in the chemical industry have resulted in the discontinuation of the original MDI mixture that had been used for years in BX-250 foam. A source for a nearly identical replacement resulted in the acceptance of another lighter colored MDI mixture for use in BX-265 foam. Although the two MDIs are probably very similar, chemically, they certainly have some differences. This is evidenced by the difference in color. The MAF laboratory has done an excellent job in monitoring the quality of the old and new MDI mixtures. This monitoring will certainly need to continue due to the probability that another change in vendors for this MDI component will occur because of the hazards associated with its production. Most chemical compounds of this type are being manufactured outside the USA because of more lenient restrictions regarding safety in manufacturing issues. Thus, it is all the more important for the Analytical Lab at MAF to develop as much comprehensive chemical data as possible on this material.

**Other Raw Material Differences.** A third situation with the 'other raw materials' is the same as for the MDI; that is, there will be a continual environment of change in sources for these materials. As an example, the Analytical Lab at MAF noted a change in a catalyst within the last two years. When this change was reported to Mr. John Bzik (MAF), he found out that the supplier had stopped making the catalyst and had replaced it with a product that had a very similar numerical designation. The Analytical Lab noted a color change and a significant drop in the overall available catalyst level in the new material. Scotty Sparks of MSFC alerted the authors to this change in a technical interchange meeting at MAF in September 2003. The authors found that many such compounds are being made in other countries and are being shipped to the USA for use. It was determined that most of these compounds have been 'stabilized' with a 'radical trapping' chemical called butylated hydroxy toluene (BHT). When the authors met with the Analytical Lab personnel (Rando, Spiers and Smith), they found that they had detected this chemical in the newer form of the catalyst. The function of this BHT is to stabilize chemicals during shipping and storage. This function is also likely to cause this compound to behave differently in the mixture that is used to create the foam. In particular, the BHT may inhibit the catalytic effect of the catalyst compound or it may affect some other reaction that occurs in the complex chemistry associated with foam formation.

This example is not meant to convey that significant changes occurred in the final foam properties, it is simply being used to show that the Analytical Lab personnel will need to continue to update their analytical capabilities to maintain a careful watch over all incoming starting/raw materials. Failure to do so may result in deleterious effects on the foams.

At this time it is not possible to comment on the effect of the additional catalyst in BX-265 because the exact composition of BX-250 and BX-265 have not been disclosed. This situation is in the process of being corrected and this matter will be addressed in a subsequent document by the authors.

**Manual-Spray Process for BX-250 and BX-265.** Both BX-250 and BX-265 foams are manual-spray, closeout foams, in contrast to NCFI 24-124 foam, which is automatically sprayed. Manual spraying of the close out foams can lead to problems that are hard to isolate to one specific cause. Manual spraying requires a trained operator who sprays the foam at the exact same distance each time and allows each foam layer to rise the same amount of time between passes to insure adequate rise and cure before the next pass. Each pass needs to have the same gun angle and sweeping motion to ensure that the foam in one section of the ET is the same as in another. Consistent and repeatable spraying is very hard to achieve, even for the highly skilled of operators at MAF. In addition to the immense amount of skill required by the operator, these foams require a specific temperature and humidity to insure a quality product. In order to insure that the BX 265 foam is sprayed at an adequate temperature, a spray-parameter chart has been developed (see MAF document number RTF-T0X-001) that is shown in figure 1. However, as reported earlier, the minimum temperature allowed for spraying BX-265 foam is 70°F and this temperature is well below the boiling point of HCFC-141B Freon blowing agent in the foam. Spraying at this minimum temperature could present many problems, as stated earlier, and could result in some of the defects associated with these foams that will be discussed in a later section of the present report. The best solution to insure that quality foam is produced is to develop a method by which the entire closeout foam is automatically sprayed onto the ET. While this procedure is a very difficult proposition, it would produce a quality foam with more uniformity on a repeatable basis. In the meantime, improvements to the guns that are used to spray the foam, as well as increasing the temperature in the chamber, will help to produce foams that are similar from lot to lot.



**Temperature versus Relative Humidity Requirements**

**BX-265**

Figure 1. Processing parameters for manually sprayed BX 265 TPS foam.

It is also recommended that the human environment for manually spraying the foam should be made reasonably comfortable for the operators. As previously stated, the temperature for manually spraying that has been used is too low. Increasing this temperature by 10-15°F will make that environment more uncomfortable, which could lead to operator error. For this reason, the authors strongly recommend that the personnel who perform this process be outfitted with “Cool Suits” that are similar to those worn by race-car drivers. The need to place high value on the comfort of these valuable people is critical to quality manually sprayed foam.

## NCFI 24-124 Acreage Foam

The NCFI 24-124 foam covers most of the ET and is automatically sprayed in a cell where the temperature and humidity are very tightly controlled. This is opposed to BX-265 that is manually sprayed in an environment that is not as rigidly controlled. It is very important to note that the allowed low-end spray temperature for NCFI 24-124 is 85°F. The BX-265 uses the exact same blowing agent, HCFC-141b, and has an allowed low-end spray temperature of 70°F. It was pointed out earlier in this report that HCFC-141b has a boiling point of 90°F. In order for the blowing agent to generate the proper amount of gas required to expand the foam cells, it must be used at or near its boiling point. Since there are fewer problems with the NCFI 24-124, the importance of the lower temperature limit for spraying needs to be thoroughly investigated.

The NCFI 24-124 has a tightly controlled environmental chamber in which the foam is sprayed. In addition, NCFI 24-124 foam is automatically sprayed and other than small-scale cohesive failures, known as 'popcorning,' in the intertank region, this foam does not pose a significant threat to the Space Shuttle in the form of large debris. The 'popcorning' issue was identified after post-flight analysis of STS-87, which showed higher than normal tile damage on the Orbiter. It was determined that temperature (slow heating) and the differential between the foam internal pressure and the external vacuum was the cause of 'popcorning.' To fix this problem, small holes of 0.1 inch diameter were placed in the foam every 0.3 inches to serve as a venting mechanism for alleviating 'popcorning.' This simple fix has significantly reduced the 'popcorning' in the intertank region and, for the most part, has eliminated the debris threat of NCFI 24-124. However, the punching of holes raises other issues such as allowing water to penetrate the foam in this area. This penetration could lead to water freezing and thawing in these holes which would cause further damage to the foam. Such damage could create loci for foam failure and 'popcorning' in cases where the Space Shuttle is left on the launch pad for long periods of time.

The NCFI 24-124 has the same problems as all of the other foams previously discussed with regard to having continuity and consistency of raw materials. In fact, the catalyst that was found to contain a radical-trapping agent is a component in NCFI 24-124 foam. Also, since this foam is primarily composed of the lighter colored MDI, the constant constituency of this raw material is extremely important.

## Void Formation Issues

A possible reason for formation of large voids in the bipod-ramp area of the ET may be related to the fact that the reaction of the raw materials can be greatly affected by the temperature at the time of spraying. As previously stated herein, the Arrhenius equation indicates that a doubling of reaction rates occurs with a 15°F increase in temperature. Therefore, the reactivity can be greatly diminished when a manual-spray operation occurs at lower temperatures.

In foam formation, there are two critical factors that can often be problematic in creating a high quality cellular structure. The first factor is cell growth, which is a direct effect of how the blowing agent creates 'bubbles' in the liquid mixture of reactants. If the reaction occurs too slowly, these 'bubbles' will form and collapse prematurely because the molecular weight buildup (polymerization) has not reached a critical level when the reaction mixture has reached a gel point. Secondly, if the reaction proceeds too rapidly, the 'bubbles' do not grow to their optimum size or shape prior to gellation. Both factors degrade the performance of the foam significantly.

A large void such as the one that was discovered in the bipod ramp of a test panel sprayed at MAF may have resulted from spraying the foam at too low a temperature. In such a case, the various layers of spray may have created foam structures that collapsed prematurely. This weak structure was most likely over sprayed in subsequent spray passes with foam that formed better cell structures because the heat of reaction of the underlying layers raised the temperature of the part. Since the bipod region requires numerous overpasses of material to build-up the thickness desired for that region, the exothermic reaction would be significantly higher in this area than in sections of the vehicle where less foam is required. The result would be a significant amount of heat being generated through the thickness of the foam before the material has become fully cured. This heat could then result in large amounts of volatiles being produced that cannot escape due to the outer rind layer. The result would be formation of a void similar to the void found on the test panel sprayed at MAF (figure 2 left). In addition, any material that failed to attain proper molecular weight could continue to react with ambient moisture at a later time and enlarge the void because such a chemical reaction evolves carbon-dioxide gas, with accompanying build up of internal pressure.

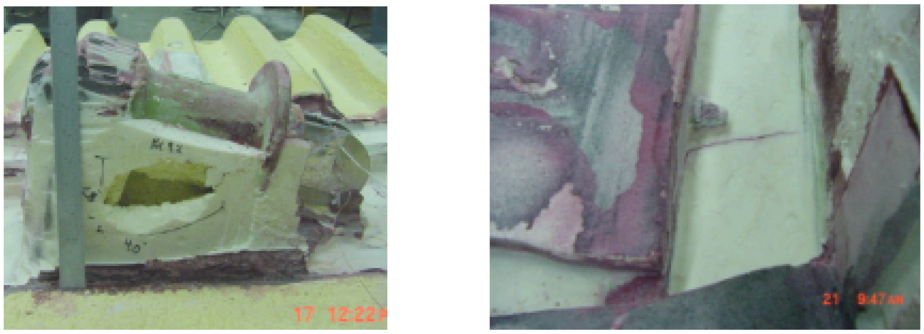


Figure 2. Cross section of test-panel bipod ramp.

**Assessment of Foam Defects**

In a memo from A. Clouatre and L. Shows of MAF, dated 31 January 2004, definitions and causes were listed for a variety of defects that have been found in foam sprayed on flight hardware surfaces at MAF. In particular, this memorandum outlines twelve TPS defect categories that appear to have been discovered during the Dissection Test Plan (809-9341) activities, and it includes a short description of their formation. These defects and descriptions are itemized subsequently, along with comments of the authors of the present report that are given parenthetically in italic type.

1. Delamination from the primer (figure 3-1) – The foam pulls away from primer. The causes include inadequate surface preparation, improper substrate temperature (too cold), overly thick foam application, or an inadequate overlap time. (*The given causes appear to cover the primary scenarios.*)

2. Delamination from the adhesive (figure 3-2) – Formation of an inadequate bond between the foam and adhesive. The causes include stress build-up in foam that results from thick passes or an excessive total foam thickness. (*Other causes could be a cold surface or contaminants on the adhesive*.)

3. Delamination from the super light ablator (SLA, see figure 3-3) – The foam pulls away from SLA. The causes are similar to the causes of the previous defect and also result from inadequate cleaning of SLA prior to foam application. (*Since all the SLA is coated with the adhesive, Conithane, prior to spraying, the delaminations may be associated with poor adhesion of the adhesive to the SLA or to a cold surface. Another factor may be excessive moisture pickup on the SLA or adhesive*.)

4. Delamination along a knit line (figure 3-4) – Separation along foam-to-foam interface. The causes include inadequate overlap time, excessive thickness per foam pass, or contamination. (*The given causes appear to cover the primary scenarios*.)

5. Delamination from the substrate (figure 3-5) – Separation between foam and the substrate that results in a layer of broken cells remaining on the primed aluminum surface (appears as a thin fuzzy film). The causes are normally related to thick spray passes, a substrate temperature that is too cold, or to surface contamination. (*Another cause may be excessive moisture on the substrate, which leads to the MDI component reacting with the moisture to form carbon dioxide that could lead to weak cell walls in the layer adjacent to the substrate*.)

6. Delamination between the PDL repair material and the adhesive (figure 3-6) – A condition where the PDL foam that is used in a repair area tears away from the adhesive tie coat. The causes include excessive charge size of the foam being applied to the repair and premature release of pressure in the mold during the first five minutes of foam rise and cure. (*Other possibilities include excessive moisture being present and contamination of the adhesive surface*.)

7. Presence of concentrated material ejected by a gun spit (figure 3-7) – This effect occurs when gun closes or opens in an irregular manner, ejecting material that rich in either the A or B component. (*The explanations given are the most likely problems*.)

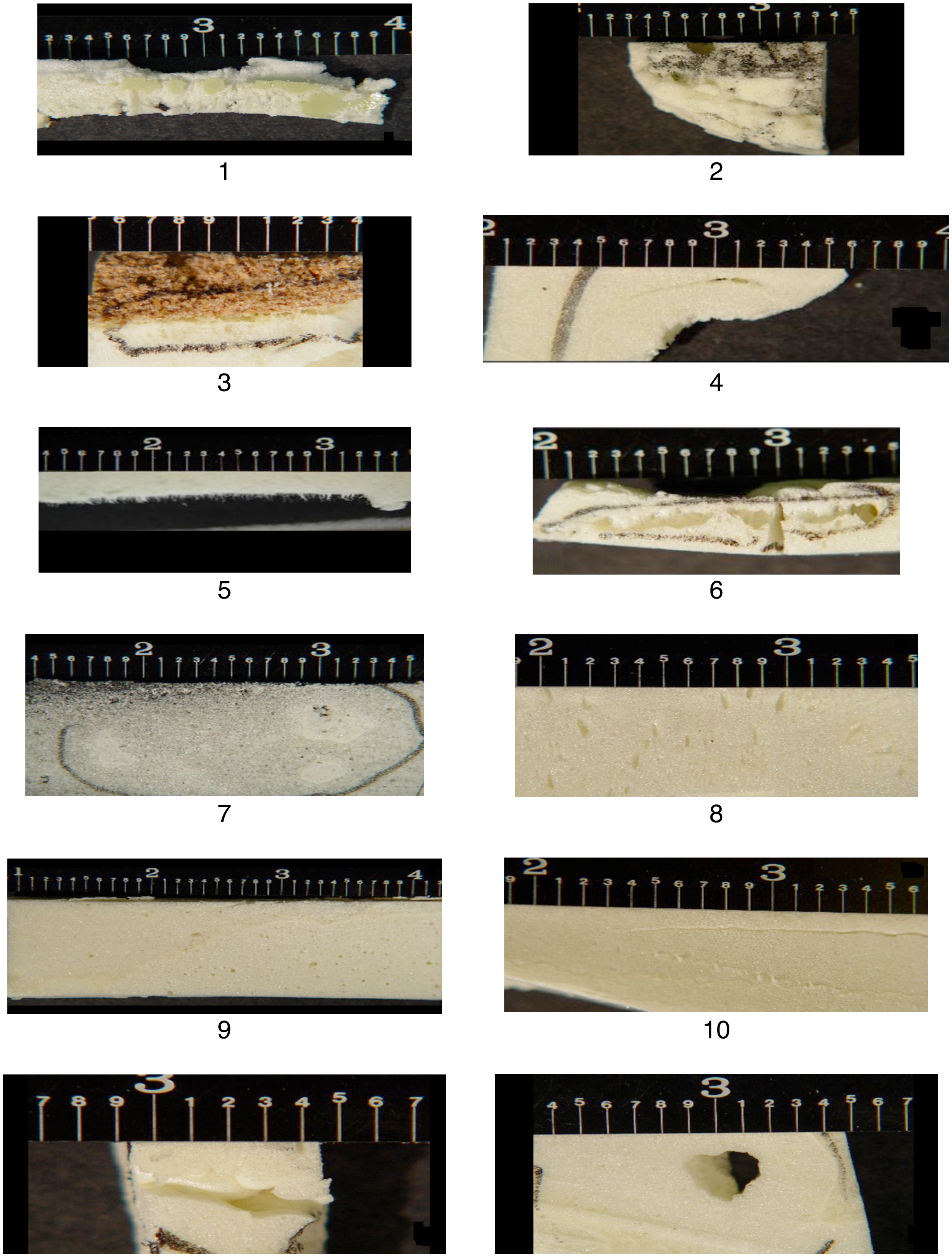
8. Formation of elongated cells (figure 3-8) – This defect is characterized by the presence of cells with excessive expansion and is typically found in thick foam applications where blowing agent escapes during foam rise. (*This situation could occur when the spray temperature is on the high side, causing excessive gas formation by the blowing agent. Excessive temperature could also be an artifact of the 'heat of reaction' of the reactants. This situation should result in a lower viscosity in the 'forming' foam that could result in overly large cell formation*.)

9. Porosity (figure 3-9) – This defect is characterized by concentrations of elongated cells. (*A high spray temperature or excessive 'heat of reaction' may cause this phenomenon. If one performs the spraying near the upper temperature limit, the additional heat from the reacting raw materials can cause an 'out-of-limit' temperature condition within the foam itself.*)

10. Crack (figure 3-10) – A break in the TPS that does not exhibit material loss. The causes are stress build up or physical inducement. The cracks can be perpendicular or parallel to the substrate. Cracks in foams at cryogenic temperatures normally run perpendicular to the substrate and are caused by differences in thermal contraction between the TPS and substrate, or by substrate bending. (*In the absence of weak cellular structure, this explanation covers the most likely scenario.*)

11. Rollover (figure 3-11) – During foam application, air pockets can be covered by foam that rebounds off of adjacent surfaces. Rollovers are normally associated with gun over spray, regions with closely packed geometric features, and 90° corners. (*This cause is the best explanation. There is no chemistry problem to consider in this case.*)

12. Voids (figure 3-12) – These defects are characterized by an absence of foam. Voids can be caused by air pockets in bolt heads when applying foam or any condition where air can become trapped during the foam application process. (*Another explanation is that moisture could be present that could cause the MDI component to react with it to form carbon dioxide which is an excess volatile. An elevated temperature in the forming foam could exacerbate this problem by causing a lower viscosity. This condition makes the foam more susceptible to creating large voids. Problems with the surfactant could also cause this problem.*)



1 2 3 4 5 6 7 8 9 10 11 12

Figure 3. The twelve known TPS-foam defects.

## Results from TGA-Mass Spectrometry

Use of a Thermogravimetric Analyzer, coupled with a Mass Spectrometer (TGA-MS), was instituted by the authors to measure the total weight loss and weight loss of individual chemical by-products for the BX-265, NCFI-24-124, and NCFI-27-68 foams. A TGA-MS allows the chemical identification of component materials that come from a system during heating from room temperature to the decomposition temperature of the material. This analytical tool is critical to understanding what additional material is being released from the foams during prelaunch and ascent, and more importantly what chemical reactions, if any, are taking place during ascent. All three foams were heated from room temperature to 1000°C (capacity of instrument) at 10°C/min, but the major weight losses were in the range of 200 to 400°C.

The results of the testing are significant to understanding the potential cause for the ET foam shedding. The data shown in figure 4 indicates that BX-265 has the lowest thermal stability of the three materials. It began showing appreciable weight loss below 200°C and 50% weight loss at approximately 365°C. The fact that BX-265 has the lowest use temperature of the three materials was expected because BX-265 is a polyurethane foam and, in general, this type of polymer has a lower thermal stability compared to polyisocyanurate foams, like the NCFI foams. This point is significant because some of the data generated have shown that the ET foams see temperatures well in excess of 200°C at around 80 seconds into flight, which is approximately the time of foam loss on STS-107.

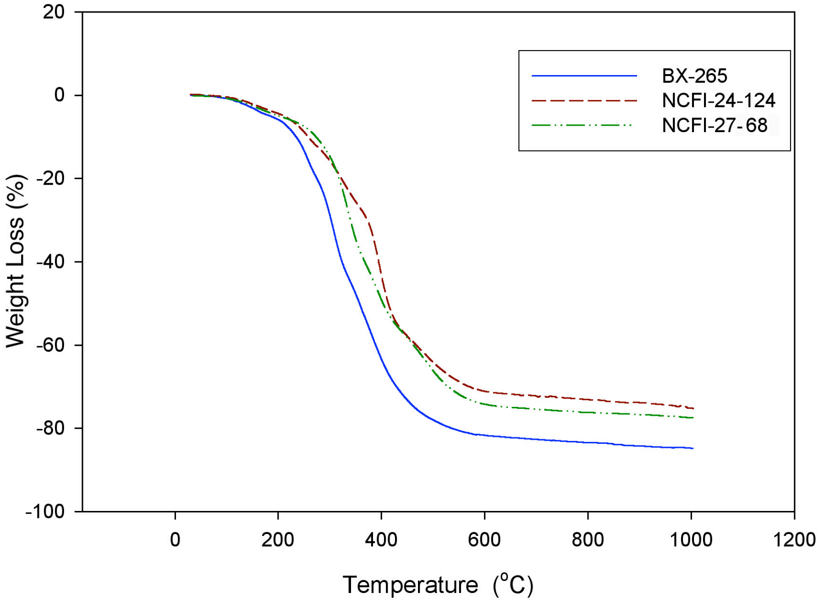


Figure 4. TGA weight loss for ET foams at 10°C/min in helium.

The mass spectrometer portion of the TGA-MS identified 12 different component materials released from the three foams tested during the heating from room temperature to 1000°C. Figures 5-10 show the rate at which each component gas was evolved from the system, with the area under the curve being proportional to the total approximate weight loss for each material identified. The data show that the most significant weight loss is attributed to two components. The first component is Freon, which begins coming out of the foam at 100°C and continues until a maximum loss has been achieved at just below 200°C (figure 5). The Freon loss can be attributed to two causes. The first cause is due to entrapped Freon in the foam cells and the second is due to Freon that was physically attached to the polymer itself.

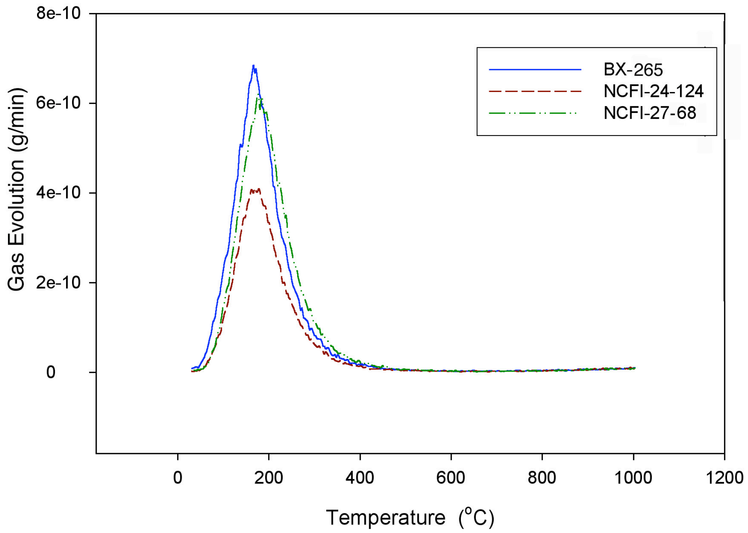


Figure 5. Freon evolution from ET foams at 10°C/min in helium.

The second most significant component that came off the foams tested is carbon dioxide (see figure 6). $CO_2$ is the by-product of the reaction between water vapor and unreacted isocyanate. It's presence at the lower temperature regime of the experiments suggests that the foam reaction is incomplete and can be triggered by the elevated temperature experienced during launch. For all cases, the carbon dioxide begins releasing from the foams at around 200°C, with a maximum in the case of BX-265 at 365°C. In addition, the data shows that at approximately 600°C for the BX-265 and slightly higher for the NCFI foams, a second peak which can be associated with the decomposition of the foams begins to form. Figure 7 confirms that decomposition occurs above 600°C due to the evolution of hydrogen gas, which is indicative of decomposition in these polymers.

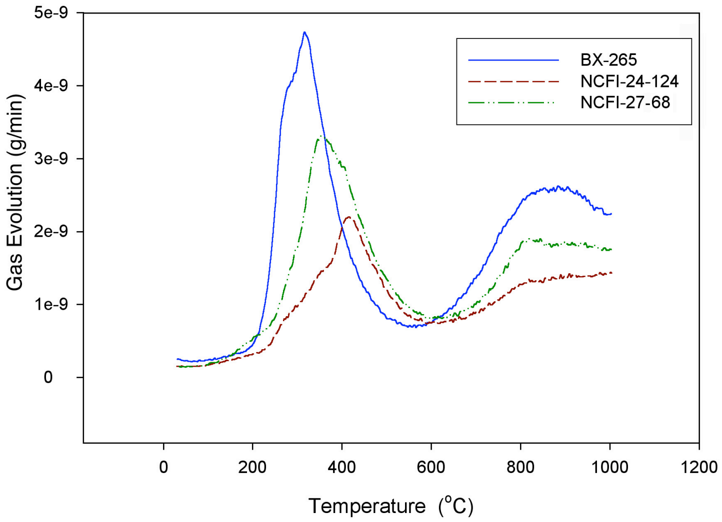


Figure 6. $CO_2$ evolution from ET foams at 10°C/min in helium.

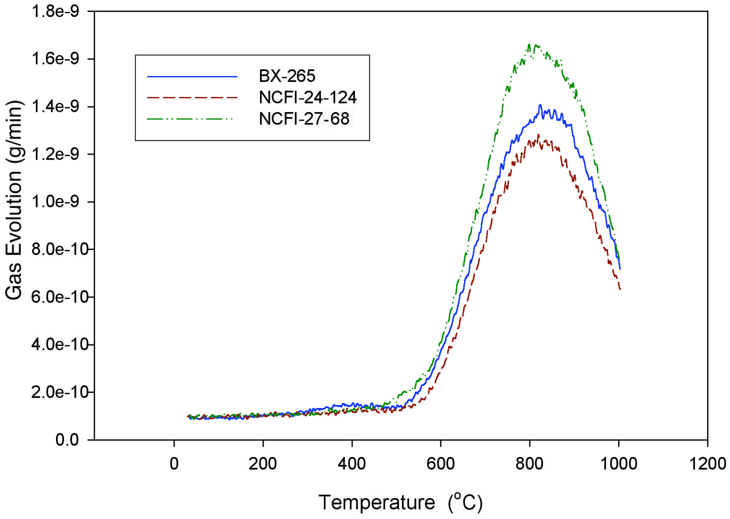


Figure 7. Hydrogen-gas evolution from ET foams at 10°C/min in helium.

In addition to the Freon, carbon dioxide and hydrogen gas, nine other components were released from the foam during heating from room temperature to 1000°C. Figures 8-10 show the most significant materials that were released by the BX-265 foam. These components are important because they all began coming out of the foam at approximately 180°C. This finding is significant because these additional losses of gases could increase the volume of entrapped gases within the foam cells or defects, and as the external pressure drops during ascent, the internal pressure of the cell or defect could exacerbate the shedding of popcorn-size foam.

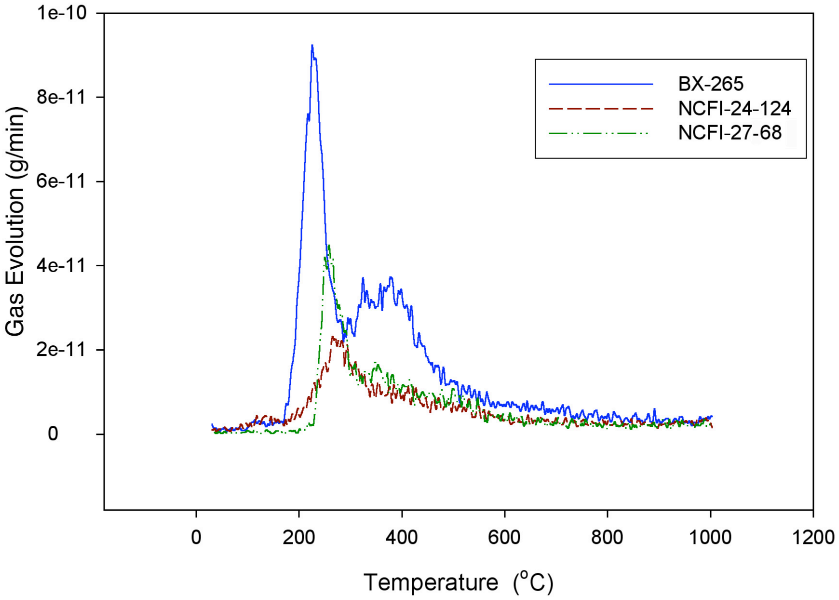


Figure 8. Phenol evolution from ET foams at 10°C/min in helium.

Figure 8, shows that phenol begins evolving from the foam at approximately 190°C and that the rate rapidly increases up to a maximum peak of 9.5 x $10^{-11}$ g/min and then drops off to essentially zero at approximately 350°C. Figures 9 and 10 show results for two components that could not be identified with complete certainty because the exact chemistry of the BX-265 foam was never divulged. For both gases, significant amounts of both components, m/z 31 and m/z 152 (unidentified mass numbers), began evolving from the foam at approximately 180°C and return to zero evolution at approximately 400°C and 250°C for the m/z 31 and m/z 152, respectively.

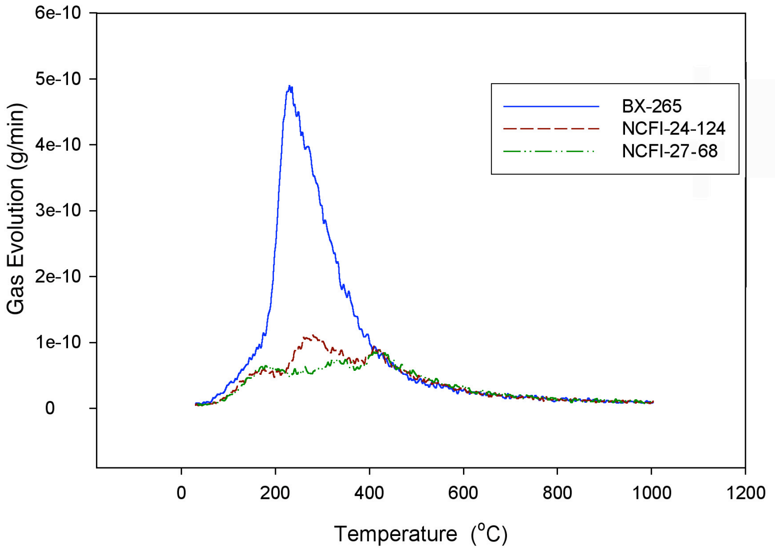


Figure 9. Evolution of m/z 31 from ET foams at 10°C/min in helium.

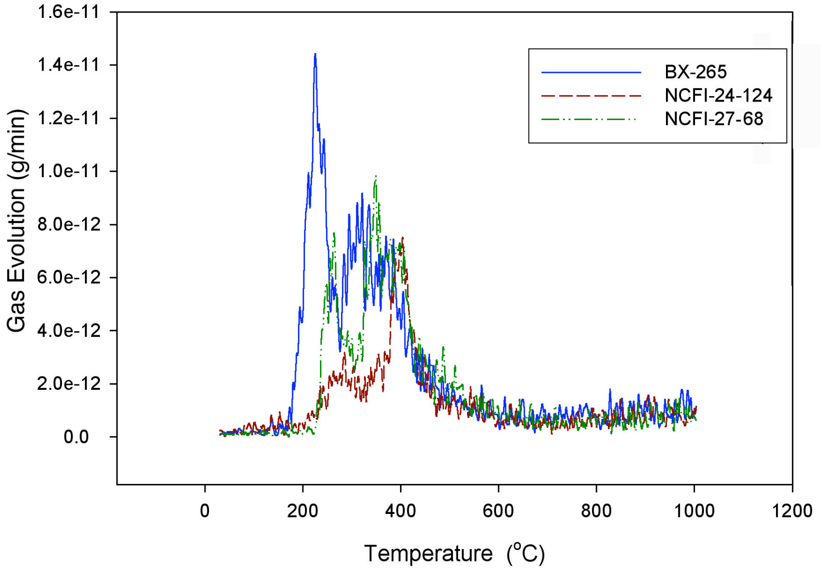


Figure 10. Evolution of m/z 152 from ET foams at 10°C/min in helium.

## Summary and Recommendations

The foams that are used on the thermal protection system (TPS) for the Space Shuttle external tank (ET) has evolved over the last 20 plus years. There have been major changes in foam formulation and foam component suppliers. Also, during the term of each of these contracts, the foam raw materials have been supplied to the contractors from different suppliers. In some cases, the supplier changed the raw materials, making it difficult to identify a change in TPS performance.

A major change that occurred in the late 1990's was the use of a new blowing agent known as HCFC 141b. The previous CFC 11 blowing agent had been a standard that dates back to the Saturn V program. CFC 11 was known to be an ozone-depleting substance and the entire foam insulation market was transitioning over to HCFC 141b. NASA was forced to follow this trend because CFC 11 was disappearing from the commercial market. This change in blowing agents was a major change since the HCFC 141b had a higher boiling point, requiring a higher application temperature for the ET foam. This higher application temperature inadvertently increased the reaction rate for the foam formation which could, in some cases, cause the foams to be sprayed with voids. Also, the chemical structure of HCFC 141b has an appreciably larger dipole that most certainly results in more solubility of the blowing agent in the foam cell walls and a greatly increased tendency to absorb water. This change in blowing agents affected both the hand sprayed material, BX 250, resulting in BX 265, and the acreage foam, CPR 488, resulting in NCFI 24-124.

The foams that were studied have been shown by some initial Thermogravimetric Analysis/Mass Spectrometry (TGA-MS) tests (performed by Phillip Morris for NASA Langley) to generate volatile materials as the temperature increases in a manner that simulates that encountered during ascent. The authors recommend that an independent, comprehensive TGA-MS study of the various ET foams be undertaken in the near future in order to verify preliminary data related to the evolution of blowing agent; to study the volatiles associated with a continuation of the chemical reactions of the residual raw materials; and to study the decomposition by-products as the foams are exposed to temperatures that approach their stability limits. It is strongly recommended that a similar program be put in place at MAF. At the present time there is no chemical quality assurance performed on the final foam materials. This activity will greatly enhance the reliability of these materials and will afford a chemical database that will be easy to use in tracking future problems with foams.

Since the acreage foam, NCFI 24-124, is automatically sprayed on in an atmospherically controlled cell, the higher temperature needed for the HCFC 141b was accommodated. A serious concern is that the lower limit for spraying the BX 265 (with the higher boiling point HCFC 141b) is 70°F; a temperature well below the boiling point of the blowing agent. The boiling point of HCFC 141b is 90°F. This lower-limit spray temperature could result in inadequate blowing of the foam and in having an excessive amount of entrapped blowing agent well below the surface of the foam. For the BX 250 foam, the boiling point of CFC 11 is 75°F and the lower spray temperature is 65°F. Thus, it is strongly suggested that this lower-limit temperature for BX 265 blowing agent be re-examined. Failure to do so could result in significant void formations, similar to those pictured in figures 2 and 3.

Another major concern is that the exact chemical structure of each of the components used in the manufacture of the various foams is not always known. This lack of information makes it difficult for the Analytical Lab at MAF to detect changes in the raw materials that are supplied. This problem was evident recently when a supplier made a change in a catalyst that is used in one of the foams. MAF was not alerted to the exact nature of the change. They were only alerted to a change in its numerical designation. In actuality, the supplier had made a major change in this product. The Analytical Lab noted a decrease in the active catalyst content and made adjustments to add more catalyst. The undocumented change that the vendor had made was to add a ‘free radical trapping agent’, designated as BHT, to the catalyst. This change allowed them to have a product with a longer shelf life, but no one can predict what effect this stabilizing agent will have on the many reactions that occur in the foaming process. Thus, there exists potential for degradation of the foam performance.

Another very important difference between CPR 488 and NCFI 24-124 and BX 250 and BX 265 is the change in the major MDI mixture component. The CPR 488 and BX 250 utilized an MDI mixture that is no longer made and the NCFI 24-124 and BX 265 utilizes a new MDI mixture source. These materials are mixtures of methylene diisocyanate (MDI) and oligomers (higher molecular weight forms) of this chemical compound. The ratio of the pure MDI to its oligomers is extremely important to the physical and mechanical properties of the foams. A thorough chemical knowledge of this component is critical since it is the major component in all of the ET foams. It is highly recommended that this issue be studied in much more detail in the very near future.

The need for more chemical-structure knowledge (with the concomitant acquisition of new analytical equipment) is important for analyzing all of the components in the foams. An expansion of this knowledge is recommended for the Analytical Lab at MAF. This task will involve learning about, documenting, analyzing and tracking all components on a routine basis. This expanded knowledge of the raw-material chemistry, along with TGA-MS data studies on the final foams, will allow the MAF Analytical Lab to operate in the same manner that their counterparts in the commercial manufacturing sector operate today. Analytical Chemistry is a rapidly changing science that is a very powerful tool in the quality manufacture of any material.

## Proposed Research Activities

As a result of the studies conducted to date, there are several areas that need more research. In particular, a planned effort to develop a full chemical database and understanding of the raw materials that are used in all of the foams is needed. It is proposed that Erik Weiser of the Langley Research Center will lead and conduct such an effort, in conjunction with contractors through the National Institute of Aerospace (Drs. St.Clair and Nelson). If empowered, this team will begin a literature search and will meet with experts in the area of polyurethane chemistry to develop an in-depth understanding of the complex chemistry of the foam systems that are used on the External Tank (ET). The expected outcome is a report that details this chemistry and discusses, in scientific terms, how the various reactive monomers and raw materials interact with the catalysts and additives to create the different foams. Also, they will chemically detail some of the possible side reactions that can occur as the environmental conditions change. Two primary foci will be on the effect of excess moisture or water and on the effect of temperature on the reactions. It is anticipated that this study will broaden the chemical understanding of the foams and will allow for better predictions of the effect of future changes in raw materials. The team will work closely with the experts in this area at MAF and at MSFC in developing this database.

At present there is no appreciable understanding of the exact state of chemistry in the as-formed foams that are used on the ET. This fact means that although the foams are seemingly in their final physical states when the ET is completed; it is quite obvious that there are still chemical reactions that can occur if the ET gets heated or is exposed to moisture. Likewise, the chemistry continues to change as the Space Shuttle is launched. Work done this past year at the Langley Research Center shows that the foam samples of BX-265, NCFI-24-124 and NCFI-27-68 contains much residual blowing agent and unreacted materials that continue to react and evolve gas as the temperature is raised. Thermogravimetric Analysis-Mass Spectrometry (TGA-MS) work conducted shows that significant amounts of the blowing agent, carbon dioxide and water are liberated as the temperature is increased. Of course, similar temperature increases occur during the ascent of the Space Shuttle. The TGA-MS data also shows that chemical reactions continue to occur as the temperature rises. Ultimately, there is an onset of decomposition that occurs and the effects of this decomposition on the foam structural and thermal performance needs to be quantified.

The proposed Langley/NIA team will form an alliance with engineers and scientists at KSC to develop a comprehensive understanding of this “Foam Chemistry.” The TGA-MS equipment that Langley has purchased will be utilized and the close alliance with Florida Institute of Technology (FIT) that KSC has developed will be employed to study this chemistry. Professor Gordon Nelson of FIT is a world-class expert in polymer degradation and has the equipment at FIT to carry out this study. His former Ph.D. student, Dr. Martha Williams of KSC, has volunteered to work closely with him on this activity. The combined studies at Langley and at FIT/KSC should provide much new information about this "Foam Chemistry."

As these activities progress, this team will try to correlate their findings with known ET-foam problems such as the formation of the twelve defect types discussed previously herein. Experiments that can be done at MAF or at MSFC to verify any postulated chemical interactions that could lead to foam defects will be identified and planned. It is envisioned that members of the Langley/NIA team will continue to offer their expertise and services to MAF and MSFC personnel in creating an in-depth understanding of TPS-foam parameters that affect thermal and structural performance of the ET.

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*Part 1: Materials Characterization and Analysis*

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**14. ABSTRACT**

The use of foam insulation on the External Tank (ET) was necessitated by the potentially hazardous build up of ice on the vehicle prior to and during launch. This use of foam was initiated on the Saturn V rocket, which, like the Space Shuttle, used cryogenic fuel. Two major types of foam have been used on the ET. The first type is NCFI 24-124, an ‘acreage’ material that is automatically sprayed on in a controlled environment. It replaced CPR 488 in 1998 and has been used since that time. The other major foams, BX-250 or BX-265, are ‘hand-sprayed’ foams that are used to ‘close out’ regions where the various sections of the ET are attached. The objectives of the present report are to study the chemistries of the various foam materials and to determine how physical and mechanical anomalies might occur during the spray and curing process. To accomplish these objectives, the report is organized as follows. First, the chemistries of the raw materials will be discussed. This will be followed by a discussion of how chemistry relates to void formation. Finally, a TGA-MS will be used to help understand the various foams and how they degrade with the evolution of chemical by-products.

**15. SUBJECT TERMS**

External tank foam; Space Shuttle; Cryogenic insulation; Chemistry; Chemical analysis

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