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Thermal Assault and Polyurethane Foam-Evaluating Protective Mechanisms.

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Rigid polyurethane foam utilizes a variety of mechanisms to mitigate the thermal assault of a "regulatory burn". Polymer specific heat and foam k-factor are of limited usefulness in predicting payload protection. Properly formulated rigid polyurethane foam provides additional safeguards by employing ablative mechanisms which are effective even when the foam has been crushed or fractured as a result of trauma. The dissociative transitions from polymer to gas and char, and the gas transport of heat from inside the package out into the environment are also thermal mitigators. Additionally, the in-situ production of an intumescent, insulative, carbonaceous char, confers thermal protection even when a package's outer steel skin has been breached.

In this test program, 19 liter, "Five gallon" steel pails are exposed on one end to the flame of an "Oil Burner" as described in the US Federal Aviation Administration (FAA) "Aircraft Materials Fire Test Handbook". When burning #2 diesel at a nominal rate of 8.39 kg (18.5 pounds)/hr, the burner generates a high emissivity flame that impinges on the pail face with the thermal intensity of a full scale pool-fire environment. Results of these tests, TGA and MDSC analysis on the subject foams are reported, and their relevance to full size packages and pool fires are discussed.

I. INTRODUCTION

Packaging design for the safe transport of nuclear materials would be far simpler if thermal protection was the only requirement. There are many insulative inorganic materials adequate for this purpose. But of course, transportation packages are also called upon to protect their "payloads" from kinetic accidents[1] (and in today's world even explosive blasts[2]) before thermal exposure. Hence the package must first preclude inadvertent release resulting from loss of containment and preserve package insulative integrity for subsequent fire blocking.

General Plastics has installed rigid polyurethane foam in transportation overpacks and impact limiters for this dual purpose since 1971. Foam Impact energy absorption is reasonably well understood, but deep insight into its thermal protective mechanisms has remained elusive. Whether or not a package survives an IAEA fire[3] depends upon many variables, including those of both package design and materials. Our research objective was to isolate and quantify foam properties in order to provide enhanced protective characteristics.

II. POSSIBLE FOAM THERMAL PROTECTIVE MECHANISMS

To begin, we hypothesize likely mechanisms for the thermal protection imparted by LAST-A-FOAM® FR-3700 series rigid polyurethane foams[4]. These mechanisms are both physical and chemical and result from foam characteristics like specific heat, thermal conductivity (k-factor) and ablative characteristics such as pyrolysis gas heat transfer, evolved combustion products, enthalpy of anoxic pyrolysis, conditions for char formation and char quality.

III. METHODOLOGY

Though fires are notoriously difficult to scale, we sought to design a medium-scale test that would yield engineering data relevant to full size fires and packages. Regulatory fires impinge on all sides of a package, and of course the area/volume ratios and payload thermal mass of designs vary greatly.

First: to better understand foam decomposition, we reviewed Thermogravimetric Analysis (TGA) on the foam both in air and N_2, and Differential Scanning Calorimetry (DSC) in N_2.

Second: for our medium scale testing, we elected to reduce the dimensions our test methodology from three to two by subjecting only one surface of our test article to thermal assault. For pool fire representation, we chose the "Oil Burner", as called out in commercial aircraft "Joint Airworthiness Regulations" FAR/JAR 25.853, which is used for testing the flammability of seating and the fire hardening of cargo wall liners. This burner is completely described in the US FAA's "Fire Test Handbook"[5]. The 280 mm wide x 152 mm high burner exit cone, when adjusted to produce a ~1050°C temperature at a distance of 100 mm from the burner exit cone, results in a radiant heat flux of 19.6 W/cm^2 on our calorimeter[6]. This is somewhat higher than that for pool fire heat flux referenced[7] for Diesel, JP4 or Gasoline (Petrol) at 13.0 W/cm^2, though less than that for Butane at 22.5, Propane at 25.0 or LNG at 26.5 W/cm^2.

IV. THERMAL ANALYSIS

TGA's, figures- 1 and 2, were conducted on FR-3706 foam in both air and Nitrogen, disclosing the first (main) decomposition temperatures of 338 and 354 °C respectively. Most interesting is that through the broad temperature range of about 340 through 650 °C, the weight remaining in air is greater than in N_2- an indication that that O_2 enhances char formation!

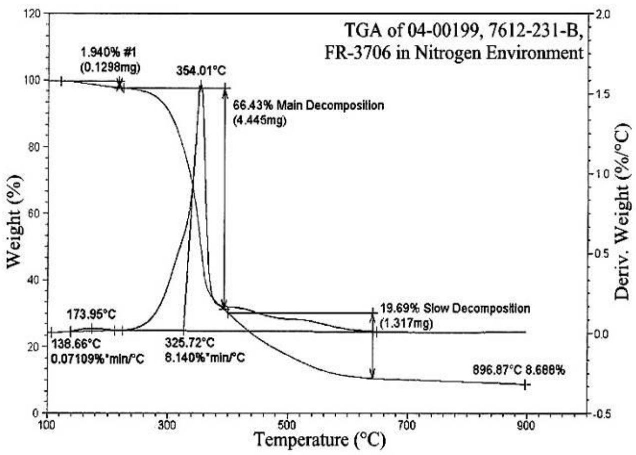

Figure-2 Thermogravimetric Analysis in Nitrogen. TA Instruments 2950, flow rate 31 cc/min
Note the dramatic weight loss centered at 354 °C.

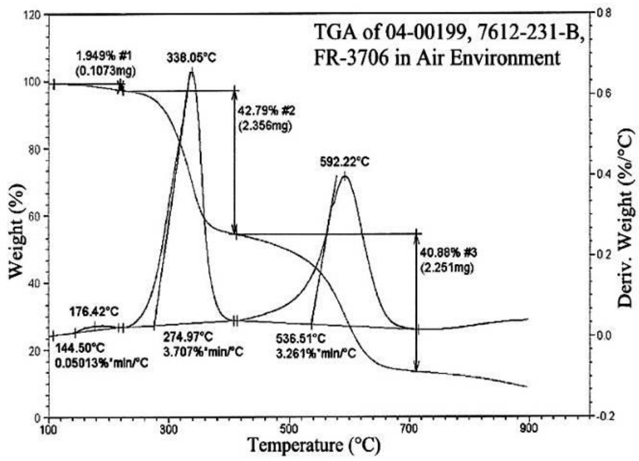

Figure-1 Thermogravimetric Analysis in air. TA Instruments 2950, flow rate 33 cc/min. Note large weight loss at 338 °C and the positive effect of Oxygen on char retention compared to an anoxic environment.

Differential Scanning Calorimetry (DSC) was performed on FR-3710 foam (10 lbs/ft^3 density before crushing) in an open pan, using a 50 cc/min N_2 purge. The high purge rate helped separate initial endotherm from the anoxic exotherm resulting from the later recombination of molecular fragments into lower energy oligomers. These oligomers "are transported into the gas phase, and sometimes referred to as tar."[8] If vented (not condensing in cooler parts of an overpack) these gases may subsequently combust with little effect outside the walls of the container (in the pool fire). In practice, the anoxic exotherm *is not* self sustaining, and the FR-3710 foam self-extinguishes when the external heat flux ceases, and the unit cools.

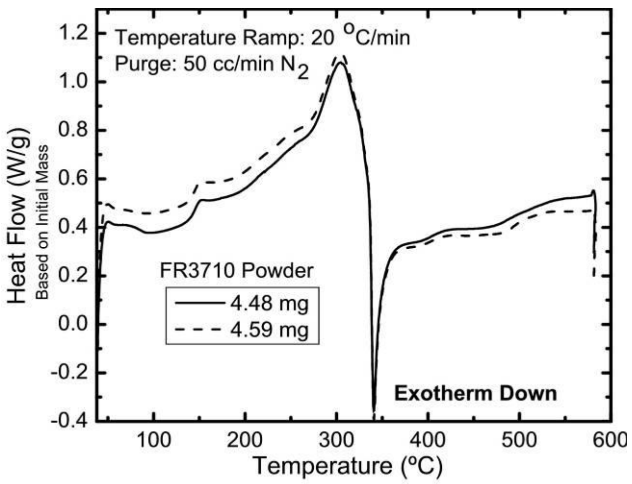

Figure-3 Differential Scanning Calorimetry, performed on powdered FR-3710 foam in a nitrogen environment
TA Instruments Thermal Analysis – DSC standard cell
(K.L. Erickson, Sandia National Laboratories)

V. EFFECT OF DENSITY AND EXPOSURE TIME ON FOAM EFFECTIVNESS

Four, 19 liter (5 gal.) steel pails, ~30 cm in diameter (tapering to 28 cm diameter at the rear) x ~33 cm deep, were filled with different densities of FR-3700 rigid urethane foam. Nominal foam densities were 0.108, 0.174, 0.305 and 0.413 g/cm3 (6.74, 10.86, 19.03, and 25.77 lbs/ft^3). 3.18 mm thick, stainless steel lids were then welded onto the pails. Each lid was vented with a 23.8 mm hole in its center. Test pails were then positioned as shown in figure-4, with the burner cone 100 mm from the lid.

When testing, the burner is turned on and the test pail lid exposed to the ~1080 °C burner flame. Tests begin when the pail lid, "hotface" temperature reaches 801°C and ends 30 minutes later (though temperature recording continues until all thermocouples pass their peak temperatures). Hotface temperatures during tests average around 950 °C as determined using 1.57mm, ungrounded, stainless-steel sheathed, type-k thermocouples in metal-to-metal contact with the rear of the hotface.

After the burner is turned off, the test pail is allowed to continue burning and then cool, while still positioned on the stand. We sometimes thermocouple the foam at various distances from the hotface, but for this test series we were interested in the foam "burn distance" from the hotface. This distance is a readily discernable, sharp transition between foam and char, as might be expected from the TGA curves (figures 1 and 2). We know from the TGA that this transition is centered at 354 °C (in N_2). At the end of the test, and when everything has cooled, the pails are weighed, lids removed, char weighed and examined. The *recession distance* (burn distance) from the hot-face (lid) to the undegraded foam is measured and recorded.

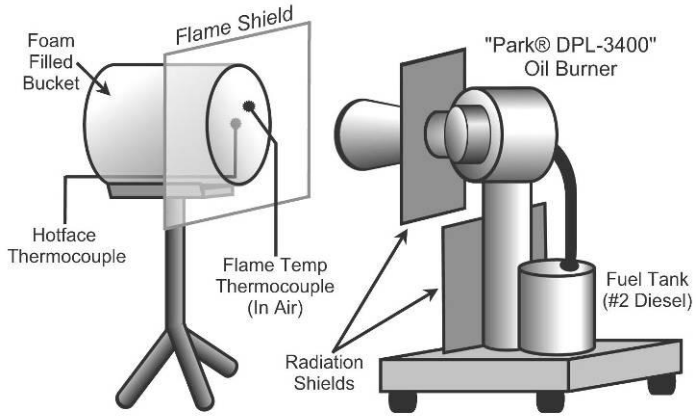

Figure-4 "Oil Burner" and test pail set-up. Note how the flame shield restricts heat and flame to the front face of the pail. Burner exit cone is 100mm from pail face when testing. (not to scale)

Table 1 Effect of foam Density on foam thermal effectiveness

Density, g/cm^3 (lb/ft^3)	0.108 (6.74)	0.174 (10.86)	0.305 (19.03)	0.413 (25.77)
Initial Weight, g	5116	6576	9543	11228
Final Weight, g	4690	5940	8799	10563
Wt. Loss g	426	636	744	665
Extinguish Time, minutes	5:25	8:15	9:24	9:11
Recession Distance, cm	10.2	8.00	4.7	3.8

Table-1 shows the foam recession distance- the depth of foam consumed in a 30 minute regulatory exposure. In all cases, varying amounts of carbonaceous char were found in the space where foam had been consumed. The regression line in figure-5 indicates that foam effectiveness *increases with increasing foam density*- though at a decreasing rate. A 0.10 g/cm^3 density foam recesses about 10.7 cm. Doubling the foam density to 0.20 g/cm^3 does not cut the foam recession distance in half (to 5 cm). Rather, it reduces it by only 3.5 cm (a 7.2 cm recession distance). This relationship should be useful for package designers performing their initial calculations. Note: the regression coefficients are shown in figure-5.

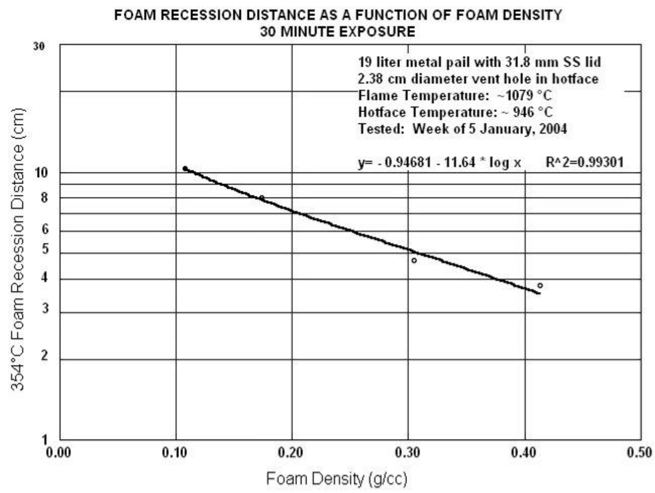

Figure-5 Foam recession distance as a function of foam density

Table 2   Recession Distance as a function of exposure time

Exposure Time, minutes	5	10	15	20	25	31
Density g/cm^3 (lb/ft^3)	0.181 (11.29)	0.181 (11.29)	0.182 (11.36)	0.182 (11.36)	0.182 (11.36)	0.182 (11.36)
Initial Weight, g	6655	6761	6778	6695	6649	6680
Final Weight, g	6380	6382	6259	6082	5952	5945
Wt. Loss, g	275	379	519	613	698	735
Extinguish Time, minutes	5:31	6:32	4:34	4:20	6:02	6:53
Recession Distance, cm	2.54	4.13	5.59	6.16	7.62	8.13

Table-2 illustrates the effect of exposure time on a single foam density. Six tests were conducted using six identical pails foamed with the same 0.181 g/cm^3 FR-3700 series foam. Exposure times were 5, 10, 15, 20, 25, and 31 minutes. Results in figure-6 show that foam recession distance *increases at a decreasing rate* with respect to time. There is likely more than one mechanism at work. Firstly, as the foam recesses away from the hotface, heat flux to the undegraded foam is reduced as the inverse-square of the recession distance, a minor effect at these distances. What we believe the regression illustrates most clearly is *the insulative effect of carbonaceous char*. As the undegraded foam retreats, an ever thicker char layer mitigates the heat flux.

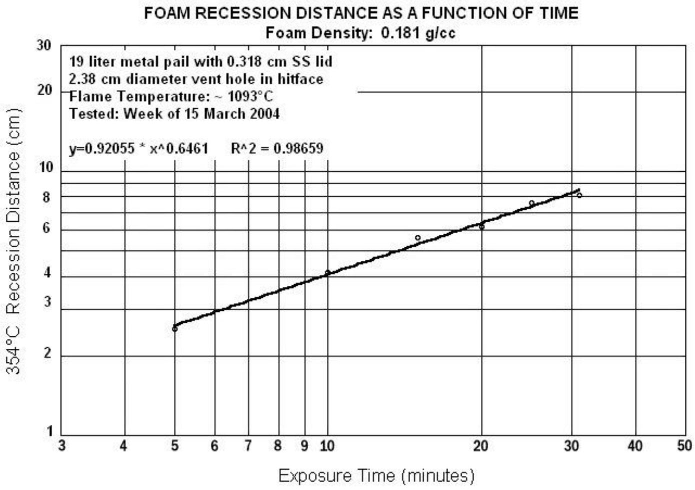

Figure -6 Foam "Recession Distance as a function of thermal exposure time (time burner is on)

VI. EFFECT OF FOAM INTUMESCENCE

A fire impinging on a damaged container is a difficult scenario to model. Drop damage can penetrate or rip the outer metal skin. Additionally, impacted foam is likely to be cracked or crushed. To reproducibly simulate severely damaged foam (or other materials) we elected to test pails filled with randomly packed, 2.54 cm test cubes. The packing fraction for randomly packed cubes with little orientational ordering, or registration between cubes, is about 0.582[9]. We discovered, that by just dropping foam cubes into an empty pail, and then spreading them out for lid installation, we achieved packing fractions in the range of 0.56 to 0.61, and with practice, the range could likely be reduced to between 0.58 and 0.60.

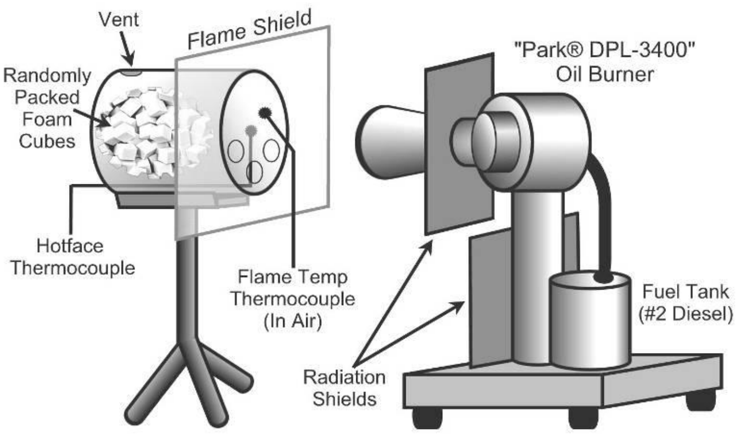

Figure-7 Pail set-up with random packed foam cubes. Note the three large holes in the lower front pail face and large vent in the upper pail rear. (not to scale)

Figure-8 Random packed foam cubes. Note: some face-to-face registration

By cutting three 46mm holes in the lower pail hot-face, and a similar vent hole at the upper rear of the pail (as oriented for testing) we create a *chimney effect* that pulls hot combustion gasses *and outside air* through the interstices between the foam cubes. These gas pathways simulate a damaged unit, where foam has been punctured and/or fractured. When tested in this manner, combustible (organic) materials lacking intumescent properties may exhibit difficulty self-extinguishing. Four test pails of randomly packed cubes were prepared:

Test-400519-1, 040521-1, and 04729-1 were conducted on standard and modified FR-3709 foams;
Test-040728-1 is FR-3718 at a density of 0.296 g/cm^3 was conducted as a direct comparison with Test 040630-1
Test 040630-1 is on GP's FR-10112, a rigid, Isocyanurate foam (possessing better high temperature performance than polyurethane, but lacking intumescent properties).
Test-040723-1 was conducted on uncoated, high density, ASTM C 208-95, Type-2 cane fiberboard.

Table 3 Results from random packed cube experiments

Test Number	040519-1	040521-1	040729-1	040728-1	040630-1	040723-1
Material	FR-3709$_1$	FR-3709$_2$	FR-3709$_3$	FR-3718	FR-10112	Fiberboard
Density, g/cm^3 (lb/ft^3)	0.147 (9.17)	0.134 (8.36)	0.159 (9.92)	0.296 (18.47)	0.187 (11.67)	0.295 (18.41)
Packing Fraction	0.567	0.608	0.573	0.611	0.600	0.582
Void, %	43.3	39.2	42.7	38.9	40.0	41.8
Effective Density g/cm^3 (lb/ft^3)	0.083 (5.18)	0.082 (5.12)	0.091 (5.68)	0.181 (11.29)	0.112 (6.99)	0.172 (10.73)
Initial Weight, g	1808	1633	1970	3914	2421	3703
Final Weight, g	976	1077	1316	3253	1006	752
Weight Loss, g	832	556	654	661	1415	2951
Weight Loss, %	46.2	34.0	33.2	16.9	58.4	79.7
Extinguish Time, minutes	21:20	10:50	9:34	3:40	3 Hrs+ *	~5 Hrs

* test terminated by closing off all vents at 3 Hrs.

The values of merit in this test series were (1) weight loss and (2) time to extinguishment.

As expected, the modified FR-3709$_3$, formulated for increased intumescences performed best (for its density), followed by standard FR-3709$_2$. FR-3709$_1$ was formulated for reduced intumescence.

The isocyanurate foam (FR-10112) would likely have been completely consumed, except that the weather was hot on the day of the test, forcing us to turn the company office air-conditioners back on. We turn them off during tests to preclude odors… so we were unpopular that day, either way. We extinguished this test by blocking the pail vents.

Figure-9 Random packed FR-3718 foam cube test in progress

Figure-11 Pail "hotface" immediately after burner removed.

Figure-12 Pail face removed and pail cut open showing intumescent char plug and undegraded FR-3718 foam cubes

The fiberboard test ended with the cubes essentially consumed, though it took approximately five hours. Interestingly, ash cubes from the non-intumescent materials tended to remain "cubical", though they become smaller as they are consumed.

VII. SUMMARY

Thermal protection using organic materials is certainly complex- as these tests illustrate.

The "Oil Burner" methodology we describe, requires minimal instrumentation, is economical (inexpensive pails are readily available) can be used for materials characterization, package design, and for comparing production foam batches with their original qualification tests.

Foam density, thickness, and the production of an intumescent carbonaceous char are important variables. Our tests indicate that increasing foam density (increasing the mass loading) *is always protective*- even though foam thermal conductivity is greater at higher densities. Of course, impact energy absorption, cost, weight, and in to-day's world, even blast-wave mitigation[2] are major foam density drivers.

In these tests, we found the anoxic, near step-function weight loss occurring at ~354 ºC (for FR-3700 foam) to be an ideal temperature indicator, yielding a sharp, degraded/undegraded foam boundary, that preserves an accu-rate, maximum temperature record at the recession surface.

Simulating damaged foam by using randomly packed cubes, proved to be a rather severe method, *but was re-markably discriminatory,* and we believe relevant to damaged containers.

Finally, the more we learned, the more questions we asked. We did not investigate the effect of polymer heat of combustion, rate of heat release or oxygen index on foam performance. Nor did we investigate the quantity of heat transferred to the "payload"- though it should not be difficult to add a heat sink or calorimeter to the foam at any particular foam depth- we just ran out of time. Also left uninvestigated, was the use of refractory sheet mate-rials, arranged in parallel with foam, or the affect of burner (pool fire) temperature on intumescent char formation.

VIII. ACKNOWLEDGEMENTS

We wish to thank Kenneth Erickson of Sandia National Laboratories for his many helpful comments… and his DSC. To Robert Sevasin for preparing the test articles, instrumentation, conducting the tests and recording the data. And to Jamie Guenthoer, our summer-break molecular biologist (and full time post-grad student at the Uni-versity of Washington) who was a great help with graphics, style and formatting.

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