Production of PIR Laminate Boardstock Insulation with Ecomate® Blowing Agent.

GEORGE COMBS
WILLIAM NICOLA
SUSAN PIGOTT
Bayer MaterialScience
100 Bayer Road
Pittsburgh, PA 15205

JOHN A MURPHY
DAVID L MODRAY
RAUL A DACOMBA
Foam Supplies, Inc.
4387N Rider Trail
Earth City, MO 63045

ABSTRACT

Changes in the regulatory environment over the last 25 years have challenged manufacturers of polyisocyanurate laminate boardstock insulation to adapt to the use of alternative blowing agents for production of rigid foam. The transition from CFC's to HCFC's to hydrocarbons and HFC's has prompted various formulation and processing modifications to address unique issues for each system.

One alternative [non halogenated] blowing agent that has received little attention in this application in the United States is methyl formate, a major component of Ecomate® blowing agent sold under license by Foam Supplies, Inc. It has a lower thermal conductivity and higher LEL than n-pentane and should provide boards with better R-values that require less flame retardant to pass E-84 tunnel and FM 4450 calorimeter tests for use in roofing and wall insulation. However, Ecomate® blowing agent has a reported tendency to plasticize the foam resulting in potential shrinkage when not properly optimized. This paper describes work done in collaboration with Foam Supplies, Inc. on the Bayer pilot scale laminator in Pittsburgh to define formulation and processing conditions needed to make acceptable PIR laminate boardstock insulation based on US production standards with Ecomate® blowing agent and the physical properties and flammability performance of these materials.

INTRODUCTION

There had been a lot of concern in the polyiso insulation industry about finding suitable replacements for the CFC's and HCFC's that were being phased out in accordance with federal regulations enacted in 1990 in response to the Montreal Protocol of September 1987. This treaty provides a timetable for global reduction in production of ozone-depleting chemicals and their eventual elimination. Thanks to a very aggressive R&D program by the industry and its suppliers, acceptable formulations based on hydrocarbon blowing agents were developed in time to meet the January 2003 deadline for removing HCFC's in these products. Interestingly, another legislative initiative, the Energy Policy Act of 1992, has provided the industry with an opportunity to leverage the superior performance of polyiso insulation to reduce energy consumption in the U.S. and lower greenhouse gas emissions. This law was passed in the wake of the Gulf War and contained a broad range of provisions designed to promote energy efficiency, energy conservation, competition in the electric power generation industry, the use of renewable energy, and to assess the financial impact of addressing greenhouse gas emissions. This was the first instance where the Federal government directed the use of voluntary building standards developed by ASHRAE and IECC as reference standards for state building energy codes to improve the energy efficiency of commercial and residential buildings. This Act also required the DOE to determine if subsequent changes in ASHRAE and IECC standards resulted in sufficient energy efficiency improvements to require states to upgrade their building codes. Although polyisocyanurate rigid foam has been a material of choice for roofing insulation above deck for years, new opportunities have developed for use of this product as continuous insulation in walls of commercial buildings. However, fire code test requirements unique to wall applications pose new challenges for manufacturers seeking product approvals. We decided to evaluate Ecomate® as a blowing agent in PIR foam formulations to determine if the differences in thermal conductivity and flammability between Ecomate® and other hydrocarbons translate into foam products with better k-factors that require less flame retardant to pass ASTM E-84 tunnel and FM 4450 roof calorimeter tests. Since there have been

Table 1. Comparative Properties of PIR Blowing Agents				
	n-Penane	Isopentane	Cyclopentane	Ecomate®
MW	72	72	70	60
LEL (vol%)	1.5	1.4	1.1	5.0
Boiling Point (°C)	36	28	49	32
Lambda (mW/mK)	14	14	11	10.7
Flash Point (°C)	-40	-51	-37	-19
ODP	0	0	0	0
GWP	<25	<25	<25	<25
VOC	Yes	Yes	Yes	Exempt

disruptions in phosphorus supplies over the years that have historically led to changes in use cost-effectiveness of flame retardants, the higher Lower Explosive Limit (LEL) of Ecomate® as shown in Table 1 may be utilized to mitigate this problem. Another reason for doing this work is to determine if Ecomate®/n-pentane blends can be used to replace pentane in the event of reduced availability of this blowing agent for rigid foam applications. Pentane is used as a diluent for the bitumen and heavy crude oils derived from the tar sands of Canada and there was some concern in early 2012 that this new outlet for pentane might create a shortage for the chemical [1]. Fortunately, hydraulic fracturing (fracking) of shale deposits for natural gas has resulted in more pentane and light condensates, but drillers could focus on "dry" wells which are nearly free of pentanes and light condensates in the future and thus change the supply situation.

The objective of this paper is to provide formulations and processing details for the production of polyisocyanurate boardstock with Ecomate® on a pilot-scale laminator that has been proven to scale well with commercial units. In particular, the effect of Ecomate® level, isocyanate content, index, foam density, and polyol functionality on eliminating foam shrinkage was studied. The authors did not evaluate different types of polyester polyols in this study. Standard foam physical properties were measured in accordance with ASTM C 1289 and Long Term Thermal Resistance (LTTR) values are reported for the samples as determined using CAN/ULC S770-09. Samples were submitted to Underwriters Laboratories for ASTM E-84 (UL 723) testing and to FM Approvals for testing on the Roof Calorimeter in accordance with FM4450.

LAMINATOR OPERATION

Safety Considerations

The laminator at the Bayer Pittsburgh site employs n-pentane, isopentane, and cyclopentane in the production of rigid foam boards and Draeger Polytron IR 7000 detectors monitor the work area for actionable levels of any of these chemicals. A single Draeger unit is positioned at each of five different points around the machine. Even though Ecomate® is less flammable than our normal blowing agents, the detectors had to be properly calibrated such that an appropriate response to each gas would occur to ensure that alarms would be activated well before explosive limits were reached. Figure 1 illustrates the relative sensitivity of the Draeger devices as configured for the Pittsburgh laminator with cyclopentane as the target gas represented by the 45° line. Note that methyl formate and pentane read "high" as compared to the actual value, providing an extra margin of safety. Foam Supplies recommends using seals made from polytetrafluoroethylene (PTFE) or Kalrez with neat Ecomate® to avoid leaks and Bayer has found that gasket fittings comprised of Viton or EPDM can suffer slight to moderate degradation with hydrocarbon blends containing more than about 40% Ecomate®.

Ecomate® has an NFPA health rating of 2, flammability rating of 4, and a reactivity rating of 0 while the respective ratings for the hydrocarbon blowing agents are 1, 4, and 0. OSHA has established permissible exposure limits for methyl formate at 100 ppm (TWA) with a STEL at 150 ppm and at 1000 ppm (TWA) for pentane.

Machine Configuration

The laminator is approximately 26 feet long and equipped with a single mix-head which makes boards that are 30 inches wide. The mix-head is outfitted with a two-stream “T” made with CPVC piping. The B side resin was premixed with the third-streamed blowing agent or blowing agent blend inline via a special Triple Action Dispersion Device (TADD) from

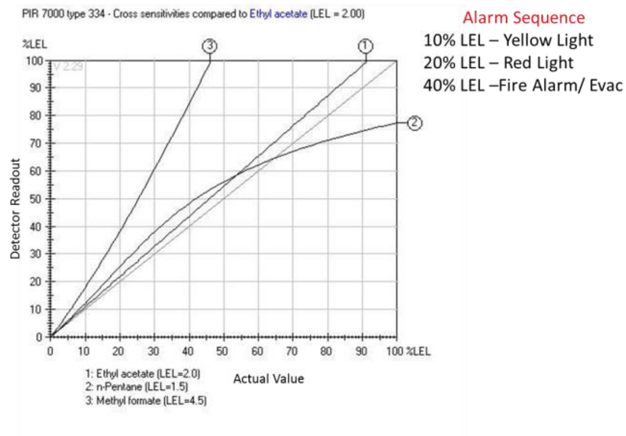

Figure 1. *Draeger Gas Detector Cross Sensitivities for Pentane, Cyclopentane, and Methyl Formate*

Komax, Inc. The mixture enters the static mixer and exits the mix-head after being subjected to impingement mixing at 2000 psi. The conditions used for foams made in this study were as follows:

Total Feed Rate	22 to 58 lbs./min
Resin Temperature	82°F
Isocyanate Temperature	82°F
Platen Temperature	145°F
Line Speed	35 to 39 ft./min

The nominal thickness for boards tested in accordance with E-84 (UL 723) was 3 inches and 1.5 inches for foam samples tested in accordance with the Roof Calorimeter requirement of FM4450. Conventional black facer was used in all experiments and each board was perforated on the top surface using an adjustable weighted spiked roller and on the bottom surface with a fixed spiked roller as it exited the unit. The laminated rigid foam samples were cut manually to slightly more than eight feet in length using a handsaw.

Sample Collection

Normally, boards are stacked in bundles approximately 35 inches high to cool overnight. However, since we wanted to evaluate edge shrinkage that might be observed in a commercial laminator equipped with side saws, two boards from the middle of the run were cut to 24 inch widths by cutting 3 inches from each edge with a bandsaw as soon as they were taken from the laminator. The freshly cut boards were placed back in the middle of the stack so that they would experience the same heat history as the other material. The next day, the edge cut samples were examined to determine the extent of any shrinkage and boards without edge cuts were used to obtain samples for initial k-factor measurements, samples (49" x 24") for standard physical property testing, and sample retains (24" x 24"). Samples are aged at least seven days before any physical property testing is performed.

TESTING PROTOCOLS

Bayer Alpha Mini Tunnel Test

Performance in this small scale tunnel test roughly correlates to results obtained in the Steiner Tunnel used to conduct ASTM E-84 testing. Facer material is shaved from the bottom of foam samples that are cut to dimensions of 6 7/8" x 48" x 1". Multiple foam samples of equal length can be used for a total length of 48 inches. Typically, three sample sections 16 inches long are used to simulate the three 8' long samples commonly used in the full scale test. The sample sections are placed in the tunnel and ignited by the burner that is positioned such that the flame tip is 14" from the start end of the tunnel. Progression of the flame from the burning foam along the tunnel is recorded at timed intervals for 60 seconds by an operator observing through windows installed in the tunnel "floor". The operator actually monitors the flame by looking at the flame reflection in an angled mirror positioned underneath clear window "floor" of the raised tunnel apparatus. An optical sensor in the tunnel ventilation system gathers data for three minutes that is used to calculate the smoke index. The Flame Spread Constant of a 48 inch sample (FSC_{48}) is calculated using the following equation:

$$\frac{\text{Average Distance} - 14}{FSC_{48}} = \frac{29.9-14}{22} \qquad (1)$$

Based on historical comparisons of results obtained for samples tested in both the Steiner Tunnel at Underwriters Laboratories and the Bayer Alpha Mini Tunnel, a FSC_{48} of 28 or less and a smoke index of 200 or less is expected to correspond to an E-84 flame spread index of 25 or less with a smoke index of 450 or less. The alpha tunnel test does not correlate as well with foam samples having a flame spread index (FSI) greater than 35 in the large scale ASTM E-84 tunnel test since the flame spread of such foams usually exceeds 48 inches in the lab tunnel.

Bayer Muffle Furnace Test

This test was designed to compare behavior of test materials to that of controls that are known to pass requirements of the Factory Mutual Roof Calorimeter test (FM 4450). A laminated foam sample with dimensions of 4" x 4" x up to 2.5" is completely wrapped in aluminum foil. The mass of the foil and foam are recorded separately along with the foam height. A small muffle furnace containing a removable open top metal compartment sized to hold the foam sample is preheated to 450°C. The oven is opened briefly to insert the foil-wrapped foam sample into the metal holder and the foam is heated for 20 minutes at 450°C. The metal holder is removed from the oven and allowed to cool. The weight of foil-wrapped foam sample is recorded before gently un-wrapping the foam to measure and record its residual height at the sample's thinnest section of remaining foam. Also, the height of any foam area free of char is recorded. Test results are reported as % weight lost, % height retained, and the amount of "no char" in inches. The results are compared to those of a control sample that is known to pass the Roof Calorimeter test with the expectation that the experimental sample will pass also if its results are equal to or better than those of the control. For new formulations without controls, a minimum height retention of 40% to 50% is targeted to ensure good performance in the full-scale test.

S770-09 Comments

Method CAN/ULC S770-09 for determination of long term thermal resistance for closed cell foams has been described elsewhere [2]. For this study, two boards were taken from the center of the foam bundle within 48 hours of production after cooling and three 2' x 2' samples were cut from each board and sealed. A total of six 12" x 12" samples were cut from the 2' x 2' foot sections within 10 to 14 days of manufacture and thermal conductivity was measured on five of them to obtain an average R-value for the boards. Then, the 12" x 12" pieces were cut to obtain four core and four surface slices with a minimum foam thickness of at least 10 mm for LTTR measurements. It should be noted that this test method requires that two homogeneity checks be performed to eliminate sample collection or slicing protocols where differences greater than 12% are observed between the R-value for either surface or core slices and the average initial R-value for the board or where values greater than 12% are observed between the difference in aging factors for the surface and core slices and their mean. In our tests, two of the samples failed both homogeneity checks, one sample failed the R-value check, and one sample passed both checks. Nevertheless, all values are reported for analysis and comparison since the collection protocols were identical and no particular protocol has been adopted by the Polyisocyanurate Insulation Manufacturers Association (PIMA) as standard. However, PIMA has announced that LTTR values reported in 2014 under the QualityMark^CM Certification program are to be measured in accordance with either CAN/ULC S770-09 or ASTM C-1303-11 as required by revised ASTM C-1289 (C-1289-11) Standard Specification for Faced Rigid Cellular Polyisocyanurate Thermal Insulation Board. Polyiso insulation certified under this program in 2014 will have a design R-value of 5.7.

FORMULATION PARAMETERS

Initial Studies

Foam Supplies, Inc (FSI) has published a number of articles that provide some guidance on optimizing processing and formulation parameters for use of Ecomate® in boardstock applications [3.4]. These suggested formulation modifications essentially strengthen the cell wall to minimize or eliminate the risk of dimensional instability and include increasing foam density, adding a at least 0.6% water based on total weight of reactants, and/or adding higher functionality polyols to increase crosslink density. Also, more information was disclosed at the 2012 CPI Polyurethanes Technical Conference [5] regarding previously reported data in reference [4] revealing that Ecomate® blends with hydrocarbons were used in some of those trials along with polyol and surfactant changes to obtain about a 9% reduction in k-factor. However, many commercial U.S. laminate boardstock producers would be reluctant to accept the 12% increase in density and 36% decrease in compressive strength that accompanied this impressive improvement in thermal conductivity. So Bayer and FSI worked on a project to further optimize formulations and process conditions such that the finished boards would meet ASTM C-1289 specifications at densities acceptable to the industry. Results of some preliminary screening experiments are shown in Table 2. All formulations are based on commercially available polyester polyol, surfactants, or flame retardant. We found that 100% Ecomate® can only be used as the sole physical blowing agent with foam densities greater than about 1.95 pcf where the Ecomate® level is less than about 4% on total formulation weight. However, compressive strength is about 25%

Table 2. Preliminary Experiments with Ecomate®											
Sample ID	% Ecomate	% Pentane	Foam Density	% water	% isocyanate	Index	Shrinkage	FSC_{48}	Smoke	1 month k	6 month k
1*	3.54	0.00	2.08	0.43	67.2	300	none	24	160	0.166	0.192
2*	4.33	0.00	1.88	0.51	65.1	300	severe				
3	2.79	1.20	1.81	0.47	64.6	300	very slight	26	76	0.165	0.183
4*	3.43	1.47	1.77	0.50	64.7	300	severe				
5*	2.44	2.44	1.71	0.45	68.0	350	none	29	112	0.175	0.195
6	2.54	1.09	1.71	0.59	69.2	300	none	31	367	0.170	0.191
7	3.51	0.00	1.81	0.59	69.3	300	moderate				
8	2.56	3.19	1.71	0.13	62.9	350	none	29	97	0.171	0.180
9	**0**	**5.87**	**1.68**	**0.14**	**59.7**	**300**	**none**	**34**	**89**	**0.166**	**0.171**
* - 20% of polyol component has fn = 6			**9 - Pentane Control**								

to 50% lower than values for comparable pentane systems and very severe edge shrinkage was observed at lower density. Exceptional flame spread values are obtained as shown in Example 1, but six month k-factors are quite high. Increasing water levels to about 0.6% as in Example 7 significantly reduces shrinkage at lower foam density, but we found that blends with pentane where the Ecomate® level is kept below about 3% on total and using more isocyanante and/or higher index produces the most stable boards in the 1.70 to 1.90 pcf range. We also noted that offline facer adhesion is notably worse when more than about 67% isocyanate is present in the formulation. Example 9 is the control where 100% pentane was used as the sole blowing agent in a higher index roofing type formulation. The roofing polyiso board in Example 8 that was blown with a 55/45 blend of n-pentane and Ecomate® also exhibits a 15% improvement in Bayer Mini Tunnel flammability test performance and only a 5% reduction in k-factor.

Final Formulations

Based on these preliminary experiments, formulations were developed for commercial wall and roofing applications to obtain the required flammability ratings in ASTM E-84 tunnel tests. Under ASTM E-84, a test material must have a flame spread index (FSI) of 25 or less and a smoke-developed index (SDI) of 450 or less to attain a NFPA 101 Life Safety Code Class A designation. To attain a NFPA 101 Life Safety Code Class B designation under ASTM E-84, the test material must have a FSI less than or equal to 75 and an SDI of 450 or less. However, insulation that is part of an approved roofing assembly does not have to meet the smoke requirement. In this paper, we will use the terms Class A and Class B rather than Class I and Class II to avoid confusion with the Class 1 designation for steel decks. Any insulation used in exterior walls of most commercial buildings must pass the NFPA 285 – "Standard Test Method for Evaluation of Fire Propagation Characteristics of Exterior Non-Load Bearing Wall Assemblies Containing Combustible Components" per section 2603.5.5 of the IBC. Since these assemblies are full scale two story exterior walls, the combustibility of the external wall covering may demand more or less flammability resistance from the underlying insulation to pass this test. The roofing formulations were designed to produce polyiso boards that would pass the Roof Calorimeter test requirement for FM 4450 Class 1 Insulated Steel Deck Roof assemblies using a 3-ply built up roof type of configuration without a cover board. Since we had not conducted this test with boards made on the pilot laminator unit in the last 17 years, somewhat conservative levels of flame retardant were used. The wall formulations are shown in Table 3 and the roofing formulation are in Table 4. Foam boards made with Formulation A contain 100% Ecomate® as the physical blowing agent, controls made with Formulations B and H contain 100% n-pentane, and those made with Formulations C-G contain 55% n-pentane and 45% Ecomate®.

As illustrated in Table 3, laminate boards can be made that don't shrink during production over a range of foam core densities from 2.2 to 1.7 pcf using Ecomate® or Ecomate® / hydrocarbon blends and they meet dimensional stability requirements of ASTM C 1289-11 for Type II products where the maximum linear change allowed for length and width is 2% and the maximum change allowed for thickness is 4%. In order to meet IBC requirement for continuous exterior wall insulation with a FSI of 25 or less and a SDI of 450 or less, Bayer has found that hydrocarbon blowing agents with LEL values below about 2% must be limited to less than about 4% by weight in the foam as exemplified by control Formulation B in Table 3. Since Ecomate® has a LEL of 5%, it can be used alone as in Formulation A to obtain a flame spread index of 20 or in combination with pentane to extend the density range for producing Class A polyiso boards. Furthermore, we found less than 4% of the flame retardant TCPP is needed to achieve a Class A rating. The acronym CFS in the tables

Table 3. Formulations for Exterior Wall Applications				
Formulation % on total	A	**B***	C	D
PS 2352	22.90	**23.26**	22.17	22.50
TCPP	7.68	**5.81**	4.95	3.81
Tegostab® B-8465	0.56	**0.58**		
Tegostab® B-8513			0.55	0.56
Potassium Octoate	1.18	**1.15**	1.66	1.66
Potassium Acetate	0.23	**0.18**	0.26	0.26
PMDETA	0.20	**0.09**	0.13	0.13
Water	0.46	**0.47**	0.44	0.45
n-Pentane		**3.42**	2.24	2.22
Ecomate®	2.31		1.84	1.81
Total Polyol Side	35.52	**34.97**	34.24	33.40
Mondur® 489	64.48	**65.03**	65.76	66.60
Index	3.00	**3.00**	3.10	3.10
PHYSICAL PROPERTIES				
Board Thickness (inches)	3	**2**	3	3
Density (pcf)				
Core foam	2.21	**2.07**	1.70	1.72
Overall foam	2.34	**2.20**	1.82	1.81
Compressive Strength @ 10% (psi)	17	**20**	16	18
Dimensional Stability Laminate 12"x12"				
70ºC / 100% RH 7 day (% change)				
Length	-0.40	**-0.40**	-0.45	-0.40
Width	-0.35	**-0.25**	-0.45	-0.40
Thickness	-0.75	**-0.10**	-0.60	-0.75
Volume	-1.50	**-0.75**	-1.40	-1.55
93ºC / Ambient RH 7 day (% change)				
Length	-0.15	**0.10**	-0.20	-0.20
Width	-0.20	**0.20**	-0.10	-0.20
Thickness	0.40	**0.55**	0.45	0.70
Volume	0.15	**0.90**	0.15	0.30
-40ºC / Ambient RH 7 day (% change)				
Length	-0.10	**0**	-0.10	-0.10
Width	-0.05	**0**	-0.05	-0.10
Thickness	0.10	**-0.35**	0	0
Volume	0	**-0.40**	-0.20	-0.15
FLAMMABILITY TESTING				
Bayer Alpha Tunnel				
FSC_{48}	21	**28**	25	25
Smoke	143	**40**	69	69
UL 723 (2.5" thick)				
CFS	19.4	**22.9**	20.3	22.8
FSI	20	**25**	20	25
SDI	160	**139**	115	90
*** - Pentane Control**				

Table 4. Formulations for Roofing Applications				
Formulation % on total	E	F	G	**H***
PS 2352	24.93	24.85	28.16	**31.79**
TCPP	3.99	3.98	4.00	**4.01**
Tegostab® B-8513	0.62	0.62	0.70	**0.79**
Potassium Octoate	1.41	1.41	1.41	**1.42**
Potassium Acetate	0.22	0.22	0.22	**0.23**
PMDETA	0.11	0.11	0.12	**0.11**
Water	0.12	0.12	0.14	**0.16**
n-Pentane	3.19	3.35	3.07	**5.80**
Ecomate®	2.61	2.74	2.51	
Total Polyol Side	37.21	37.41	40.33	**44.31**
Mondur® 489	62.79	62.59	59.67	**55.69**
Index	3.53	3.53	3.00	**2.50**
PHYSICAL PROPERTIES				
Board Thickness (inches)	1.5	1.5	1.5	**1.5**
Density (pcf)				
Core foam	1.76	1.68	1.76	**1.73**
Overall foam	1.92	1.87	1.94	**1.94**
Compressive Strength @ 10% (psi)	16	16	14	**14**
Dimensional Stability Laminate 12"x12"				
70ºC / 100% RH 7 day (% change)				
Length	-0.25	-0.40	-0.50	**0.40**
Width	-0.20	-0.10	-0.20	**0.00**
Thickness	-0.35	0.05	0.15	**0.85**
Volume	-0.80	-0.45	-0.55	**1.30**
93ºC / Ambient RH 7 day (% change)				
Length	-0.25	-0.20	-0.35	**-0.20**
Width	-0.30	-0.30	-0.30	**-0.25**
Thickness	-1.10	-1.05	-1.30	**0.05**
Volume	-1.60	-1.50	-2.00	**-0.35**
-40ºC / Ambient RH 7 day (% change)				
Length	0	-0.20	-0.20	**-0.15**
Width	0.10	0.05	-0.05	**-0.10**
Thickness	0.10	0.05	0.60	**0**
Volume	0.15	-0.10	0.35	**0.10**
FLAMMABILITY TESTING				
Bayer Alpha Tunnel				
FSC_{48}	29	28	27	**34**
Smoke	91	121	102	**81**
UL 723 (2.5" thick)		Not Tested	Not Tested	
CFS	24.2			**33.0**
FSI	25			**35**
SDI	120			**120**
*** - Pentane Control**				

stands for Calculated Flame Spread, which is the value reported for the test result before it is indexed to the tunnel red oak calibration standard. The Bayer FSC_{48} number historically is most closely correlated with the UL CFS value, but foams made with Ecomate® appear to perform somewhat better than expected. There is a 15% reduction in compressive strength for Formulation A relative to the control at 7% higher density, but values for Formulations C and D made with the blowing agent blend are normal for a1.8 pcf foam made at about 300 index on the Bayer laminator. Compressive strengths for foams made on this laminator are typically 15% to 25% lower than those obtained on a commercial unit. But all foams in Table 3 meet the minimum requirement of 16 psi for PIR laminate foam based on the pilot machine trial data alone.

Use of the roofing formulations in Table 4 also resulted in rigid foam boards that did not shrink during production and they also meet the dimensional stability requirements of the standard. Attempts to make stable foams in this density range at 255 index were unsuccessful since slight edge shrinkage occurred even though the Ecomate® content in the foam was less than 2%. As expected, the compressive strengths for Formulations E and F are higher than control H since they contain more isocyanate at a much higher index. All Formulations in Table 3 would be expected to meet ASTM C 1289 compressive strength requirements in commercial production. The most surprising observation about the data is that Formulation E boards were rated Class A even though we expected them to have a flame spread index greater than 25 based on the Bayer FSC_{48} number of 29. Formulations F and G should yield product that is comparable to or better than Formulation E in Steiner tunnel performance. Obviously, significant reductions in flame retardant levels would be possible since only a Class B rating as observed for control H is necessary. However, polyiso boards for roofing applications must also pass the FM4450 Roof Calorimeter test in an appropriate assembly.

FACTORY MUTUAL FM4450 ROOF CALORIMETER TEST

Roofing Formulations E-H were tested in assemblies that were built by personnel at Factory Mutual's test laboratory in West Glocester, RI comprised of the following layered sequence:

1. Approved 18 gauge steel deck.
2. Rigid foam roof insulation samples with standard black facer, mechanically attached to the deck.
3. 3 ply organic felt Built-Up roof with hot asphalt applied at 25 lbs. per 100 square feet.
4. 60 lb. flood coat of asphalt.

The layout for installation of these roof insulation boards was slightly different from the conventional diagram based on 48-inch wide commercial product and is shown in Figure 2. In the conventional assembly, a 36-inch wide panel and 24-inch wide panel form a single vertical seam in the assembly, but the installation used for testing of roofing assemblies made with foams from the pilot laminator require that two vertical seams using two 24-inch wide boards and a single 12-inch wide panel be used because the machine made boards with a maximum width of 30 inches. No thermal barrier was used between the deck and foam insulation and no cover board was used on top of the foam insulation. It is very difficult to pass with this configuration assembly and its severity is only surpassed by one in which fiberglass felts are used rather than organic felts since the glass fibers are porous and therefore more likely to allow melting asphalt to seep through the covering to the

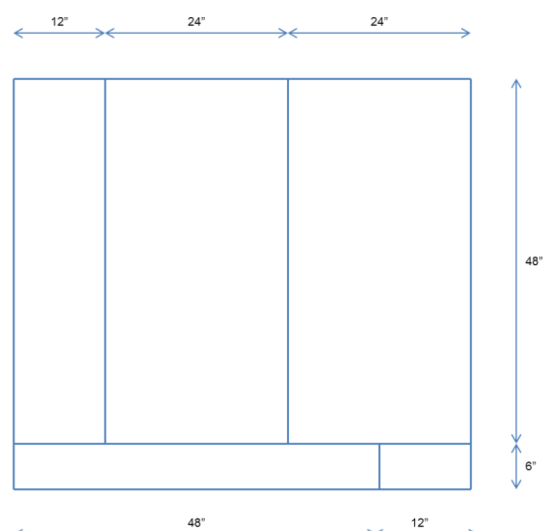

Figure 2. *Layout Diagram for Bayer Foam Insulation Panels Over Steel Deck (FM4450)*

insulation and seams. As previously mentioned, the Bayer Muffle Furnace test is used as a very rough predictive guide to performance in the Roof Calorimeter test and results for the Bayer test and the FM Calorimeter are found in Table 5. Flame retardant level was set at 4% in order to achieve 40% to 50% height retention for the 100% pentane control Formulation H as is customary in our labs for new systems. Based on the muffle furnace values, all samples would be expected to pass the Roof Calorimeter test and the predicted ranking would be for the higher index Formulations E and F to be more thermally stable and perform better than Formulations G and H. In the Roof Calorimeter test, limit values are set for heat contribution from the roof assembly to the fire in the pit below it at three minute (410 Btu/ft^2/min), five minute (390 Btu/ft^2/min), and ten minute (360 Btu/ft^2/min) intervals. The average heat contribution over the entire thirty minute duration of the test cannot exceed 285 Btu/ft^2/min. All of our samples passed this test with heat contribution values that were 36% to 58% below the limit values and this observation means that further reductions in the flame retardant levels are possible. However, unlike the Steiner tunnel test, Ecomate®/n-pentane blends don't improve performance in the Roof Calorimeter evaluation and there is a slightly negative but negligible effect on the thermal stability of the higher index Formulations E and F that contain more Ecomate® in the foam.

Table 5. FM4450 Roof Calorimeter Results

Formulation % on total	E	F	G	**H**
PS 2352	24.93	24.85	28.16	**31.79**
TCPP	3.99	3.98	4.00	**4.01**
Tegostab® B-8513	0.62	0.62	0.70	**0.79**
Potassium Octoate	1.41	1.41	1.41	**1.42**
Potassium Acetate	0.22	0.22	0.22	**0.23**
PMDETA	0.11	0.11	0.12	**0.11**
Water	0.12	0.12	0.14	**0.16**
n-Pentane	3.19	3.35	3.07	**5.80**
Ecomate®	2.61	2.74	2.51	
Total Polyol Side	37.21	37.41	40.33	**44.31**
Mondur® 489	62.79	62.59	59.67	**55.69**
Index	3.53	3.53	3.00	**2.50**
PHYSICAL PROPERTIES				
Board Thickness (inches)	1.5	1.5	1.5	**1.5**
Density (pcf)				
Core foam	1.76	1.68	1.76	**1.73**
Overall foam	1.92	1.87	1.94	**1.94**
Compressive Strength @ 10% (psi)	16	16	14	**14**
FLAMMABILITY TESTING				
Bayer Muffle Furnace				
Height retention %	61	60	64	**44**
Weight lost %	47	45	48	**50**
No Char (inches)	0.31	0.32	0.23	**0.00**
FM Calorimeter				
Fuel Contribution Rates				
Btu/ft^2/min				
3 min (**410** max)	262	229	203	**182**
5 min (**390** max)	219	226	187	**175**
10 min (**360** max)	179	198	156	**152**
30 min Avg (**285** max)	150	162	129	**137**
*** - Pentane Control**				

Table 6. Thermal Conductiviy Performance of Ecomate ® Foams									
Formulation ID	Pentane/Ecomate® Ratio	S770-09 LTTR Values					Standard Sample Aging		
		R-Value Check	Aging Factor Check	4 inch	3 inch	2 inch	Initial R-value*	1 month	3 month
A	0% / 100%	**Fail - 20%**	**Fail - 16%**	4.72	4.80	4.81	6.25	6.21	5.99
D	55% / 45%	**Fail - 16%**	**Fail - 15%**	5.18	5.11	5.12	6.27	6.10	5.85
F	55% / 45%	**Pass - 11%**	**Pass - 10%**	5.33	5.24	5.21	6.26	6.02	5.81
H	100% / 0%	**Fail - 13%**	**Pass - 6%**	5.78	5.69	5.59	6.39	6.45	6.37
* - average of five samples at 75ºF as per S770-09									

THERMAL CONDUCTIVITY PERFORMANCE

The data presented in this paper demonstrates that properly formulated Ecomate® and Ecomate®/n-pentane blends can offer significant improvements in the behavior of polyiso laminate boardstock in some flammability tests. But examples in Table 2 indicate some potential issues with thermal conductivity aging performance in rigid foam insulation produced with these blowing agents, despite Ecomate®'s better lambda value reported in Table 1. No accelerated aging studies were done in our preliminary experiments, so Formulations A, D, F, and pentane control H that are representative of wall and roofing applications were tested for LTTR in accordance with CAN/ULC S770-09 and the resultant data is shown in Table 6. All formulations were used to prepare 3 inch boards and LTTR values for 4 inch and 2 inch equivalent thickness products were calculated as well. The 2.21 pcf boards made with Formulation A contained a higher silicone strongly nucleating surfactant commonly used for rigid foam insulation in the appliance industry rather than the conventional roofing surfactant used in the other lower density (≈1.70 pcf) boards. Initial R-values for all the Ecomate® formulations were only about 2% lower than that for the pentane control and the one month R-values for the 100% Ecomate® and 100% pentane formulations were essentially unchanged. However, LTTR is the most critical parameter of insulation performance for rigid foam laminated with air-permeable facers for roofing. The number represents the predicted 5-year R-value for the insulation and this 5-year value has been determined to be equal to the time-weighted 15 year average R-value for the rigid foam insulation product. So by this measure of insulation performance, the 100% Ecomate® 3 inch board is expected to lose about 23% its thermal resistance, the Ecomate®/n-pentane blend boards are expected to lose about 16% to 19% their thermal resistance, and the pentane control boards are expected to lose about 11%. The best Ecomate foam for thermal aging using standard test methods became the worst foam using thin slices to accelerate aging. It should be noted that no design experiments to optimize k-factor performance were included in this study and it is likely that surfactant, polyol type, and hydrocarbon co-blowing agent type and level may reduce or eliminate this aging difference. In fact, FSI has conducted European laminator trials with proprietary Ecomate®/hydrocarbon blends and found that they can improve initial k-factors, compressive strengths, and dimensional stability with proper choice of surfactants and polyols (Table 7). Nevertheless, Bayer conducted more experiments to try to obtain a better understanding of the dramatic effect that accelerated aging using slicing techniques had on the relative differences in foams prepared with and without Ecomate®.

Analysis of Blowing Agent Concentration Changes in PIR Foam

Another set of three inch boards based on wall Formulation D and roofing Formulations F and H were prepared on the laminator along with modified Formulations D1 and F1 where the n-pentane/Ecomate® weight ratio was changed to 47.2/52.8 from the 55/45 ratio used in the parent systems. K. Ashida [6,7] has found that molar blends of n-pentane and methyl formate produce the lowest foam density at the azeotropic composition for the blend, i.e., 47.2/52.8 by weight, which has a boiling point of 21.7ºC (71ºF). Since foams in the paper were prepared using a free-rise lab box procedure, we wanted to find out if the binary azeotrope would show the same effect on the laminator and if the azeotropic blend might improve thermal aging of the foam. Ashida reported that box foams made with this blend had slightly lower initial thermal conductivity than with pure n-pentane but experienced more than twice as much loss in thermal resistance over a two month period. Incidentally, similar observations were made for the azeotropic blend of cyclopentane and methyl formate (34/66 weight ratio) which is claimed in U.S. Patent 5,336,696. For each board formulation, a 12" x 12" x 1" core sample was cut after the stack had cooled overnight to obtain an initial k-factor for the core. This sample was allowed to age for three weeks in our temperature and humidity controlled physical testing lab. Two 24" x 24" x 3" faced sample retains were stored as usual on edge in contact with each other in a tight arrangement on shelving in the laminator area. At the end of three weeks, a freshly cut 12" x 12" x 1" core sample was taken from one retain sample six inches from any edge for a k-factor measurement to obtain a core retain value. Although the retains were not wrapped, any core samples taken from them should have experienced only minimal aging with limited loss of blowing agent in that three week period. So the blowing

Table 7. FSI European Laminator Trials with Proprietary Ecomate® Blends				
Formulation % on Polyol Blend	BA Blend B	BA Blend C	Ecomate®	BA Blend A
Polyol	66.32			
TCPP	14.74			
Surfactant	1.84			
PIR catalyst 1	1.25			
PIR catalyst 2	0.29			
Tertiary amine	0.22			
Water	0.59			
Blowing agent	14.74			
Index	3.00			
PHYSICAL PROPERTIES				
Board Thickness (inches)	2	2	2	2
Density (pcf)				
Core foam	2.06	2.07	2.07	1.72
Compressive Strength @ 10% (psi) Normalized to 1.85 pcf density	23.2	21.8	20.4	24.1
K-factor @ 50ºF (10ºC)				
24 hr	0.141	0.135	0.145	0.140
168 days	0.152	0.147	0.165	0.148
Dimensional Stability 7 days (4" x 4" x 1")				
Dry (% change)				
Volume	-0.2	-1.9	-2.2	-0.7
Humid (% change)				
Volume	2.4	1.5	-10.6	-1.1
Freezer (% change)				
Volume	0.5	-0.6	3.5	-0.6
Dimensional Stability 28 days (4" x 4" x 1")				
Dry (% change)				
Volume	0.5	-0.8	No Data	-0.2
Humid (% change)				
Volume	2.1	3.1	No Data	1.2
Freezer (% change)				
Volume	0.2	-1.5	No Data	-1.4

agent concentration in the core retain should be nearly identical to that of the original initial core sample. Immediately after measuring all k-factors on the same day after three weeks, small pieces of foam were taken from the center of each core sample and treated with an extraction solvent containing an internal standard. The extracts were injected onto a GC column to determine the amount pentane and methyl formate left in the foam sample. This method has been used by Bayer to measure total blowing agent concentration in foam and does not attempt to differentiate between distributions in the gas phase or polymer matrix. Results of the experiment are shown in Table 8. There was less than 3% change in k-factor for the initial core samples and the freshly cut core retain after three weeks in all samples except D1, where the change was about 5%. However, k-factors for all the aged samples based on Ecomate® blends had increased to about 0.175 or about 14% while the k-factor for the pentane control had only increased by 9%. Although there is significant variance among values for changes in pentane concentration in the core retain after three weeks of storage based on the theoretical amount of the blowing agent used to make the foam, two to ten times more methyl formate is lost on a percentage basis from the foam sample. We measured the concentration of blowing agent in the retain sample to obtain a more reliable baseline for

Table 8. Comparative Loss of Blowing Agents from Foam					
Formulation % on total	**H***	F	F1	D	D1
PS 2352	**32.00**	24.97	25.01	22.59	22.61
TCPP	**4.03**	4.00	4.00	3.83	3.83
Tegostab® B-8513	**0.80**	0.62	0.63	0.56	0.57
Potassium Octoate	**1.43**	1.41	1.42	1.67	1.67
Potassium Acetate	**0.23**	0.22	0.23	0.26	0.26
PMDETA	**0.12**	0.11	0.12	0.13	0.13
Water	**0.16**	0.12	0.13	0.45	0.45
n-Pentane	**5.18**	3.10	2.60	1.97	1.66
Ecomate®		2.53	2.91	1.61	1.86
Total Polyol Side	**43.94**	37.10	37.01	33.08	33.04
Mondur® 489	**56.04**	62.90	62.99	66.92	66.96
Index	**2.50**	3.53	3.53	3.10	3.10
PHYSICAL PROPERTIES					
Board Thickness (inches)	**3**	3	3	3	3
Density (pcf)					
Core foam	**1.70**	1.67	1.68	1.76	1.73
Overall foam	**1.78**	1.75	1.76	1.82	1.80
Compressive Strength @ 10% (psi)	**16**	14	13	16	14
1" CORE SAMPLE ANALYSIS					
K-factor Measurement @75ºF (BTU·in/h·ft²·°F)					
Initial value	**0.148**	0.152	0.154	0.155	0.151
Retain value 3 weeks	**0.152**	0.154	0.158	0.157	0.159
Aged Core Value 3 weeks	**0.162**	0.174	0.175	0.176	0.175
Blowing Agent Concentration in Foam					
Core Retain 3 weeks					
Pentane %	**5.66**	2.81	2.56	2.18	1.78
Ecomate® %	**0**	1.78	2.49	1.14	1.58
Aged Core 3 weeks					
Pentane %	**5.58**	2.81	2.38	2.11	1.73
Ecomate® %	**0**	1.18	1.58	0.92	1.08
Change in Blowing Agent Concentration					
Core Retain 3 weeks					
Pentane on theory %	**9.3**	-9.4	-1.5	10.7	7.2
Ecomate® on theory %	**0**	-29.6	-14.4	-29.2	-15.1
Aged Core 3 weeks					
Pentane based on retain %	**-1.4**	0.0	-7.0	-3.2	-2.8
Ecomate® based on retain %	**0**	-33.7	-36.5	-19.3	-31.6
*** - Pentane Control**					

calculating changes in pentane and methyl formate concentration in the aged core samples. Again, there was only minor change in the pentane concentration in all the samples while 19% to 36% of methyl formate has diffused out of the foam. Headspace GC was conducted on sample D1 to look for methanol, a hydrolysis product of methyl formate, but only a trace peak barely above baseline noise was found. This data indicates that methyl formate diffuses from the foam six to ten times faster than n-pentane, perhaps by way of its increased solubility in the foam matrix as an enhanced transport mechanism. The increased dimensional instability of non-optimized rigid foams made with Ecomate® blends may be accounted for by a combination of matrix plasticization and reduced cell gas pressure that would accompany rapid loss from the foam. However, the data does not necessarily support a direct relationship between diffusion of methyl formate from the foam and increase in k-factor. The components of air (nitrogen, oxygen, water) must diffuse into the foam to increase thermal conductivity and methyl formate may affect the permeability of the cell membrane and the air diffusion rate. Singh and Coleman [8] have used mathematical models to predict thermal aging of polyiso boards using cell gas partial pressures of blowing agents and their effective diffusion coefficients. They have pointed out the key role that the “skin factor” can play in affecting LTTR values and provided a rationale for negative or positive bias with different types of foam insulation. Since there are no actual five year aged samples for comparison, we don’t know how well the LTTR calculation works for Ecomate® blends as blowing agents. But the “flip-flop” in the relative ranking for Formulation A containing 100% Ecomate® could indicate a potential negative bias for LTTR values in such foams.

SUMMARY

Ecomate® and Ecomate®/hydrocarbon blends can provide laminators with another useful tool to tailor the performance of the polyiso boards they produce to the requirements of the applications for which the insulation is intended. The most important benefit of this blowing agent for PIR laminate boardstock is the improved flammability resistance that allows rigid polyisocyanurate foam free of halogenated blowing agents to readily obtain flame spread index values of 25 or less in UL723 (ASTM E-84) Steiner tunnel tests while keeping smoke developed index values below 450 across a broad range of foam densities. Although foams made with Ecomate® tend to have more dimensional stability challenges than those made with n-pentane, proper formulation of conventional systems with appropriate levels of the blowing agent, water, and isocyanate can easily resolve these issues and any compressive strength concerns. Consequently, polyiso boards made with Ecomate® or Ecomate®/hydrocarbon blends may help to meet the more stringent fire code test requirements unique to wall applications that pose new challenges for manufacturers seeking product approvals. Ecomate® blown foams may also contribute to better performance in NFPA 286 - Standard Methods of Fire Tests for Evaluating Contribution of Wall and Ceiling Interior Finish to Room Fire Growth, more commonly known as the Room Corner Test for exposed interior wall insulation. For roofing applications, this blowing agent does not improve performance in the critical FM Roof Calorimeter test that is part of the FM 4450 Class 1 Insulated Steel Deck Roof assembly requirements, but it does offer the foam manufacturer the option to provide NFPA Class A or Class B foam without increasing the flame retardant level.

Of course the most important concern raised by this paper regarding Ecomate®/n-pentane blends is the 8% to 10% reduction in aged R-value relative to pentane blown rigid foam boards using the S770-09 LTTR test protocol. This observation may not be important in applications such as exterior wall insulation where foil or other impermeable facers are used and ASTM C 518 aging test protocols apply. We plan to conduct pilot laminator trials with such facer material in the future. However, the largest market for PIR laminate boardstock is roofing insulation and additional work will have to done to determine if various combinations of polyols, surfactants, or other additives can influence thermal aging in foams blown with Ecomate® or Ecomate®/n-pentane blends so that they can meet the design R-value of 5.7. Since Bayer has no data regarding scale-up of these types of formulations to commercial units, we don’t know if the differential performance of pentane with regard to LTTR would be maintained with boards from commercial laminator trials.

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BIOGRAPHIES (required)

George Combs

George Combs received his B.S. and Ph.D. degrees from the University of Georgia in Athens, Ga. Over the last 27 years, he has worked in new product development in the areas of polyether polyols, co-polymer polyols, double metal cyanide catalysts, functional fluids, spray elastomers, flexible foam and rigid foam while working for Bayer, Lyondell, Arco Chemical, or Union Carbide. Currently, George is a Senior Principal Scientist for product development and technical support in the Rigid/Specialties and Raw Materials Group of the Polyurethanes Division of Bayer MaterialScience, LLC in Pittsburgh, Pa.

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William Nicola

Bill holds a Bachelor of Science degree in Chemistry from the University of Pittsburgh. He is a Technical Manager in Bayer's Polyurethane business unit with Applications Development and has Technical Service responsibilities for Raw Materials used in Polyiso Insulation, Composite Wood Binders, and various polyurethane products made by the Independent System Houses and the company's Diversified Raw Material customers. Bill also provides technical support to many projects sponsored by Bayer's Industrial Marketing team.

Susan Pigott

Sue Pigott has worked over 32 years for Bayer in various areas of rigid foam development and technical support. These areas include molded systems, discontinuous metal panels, spray systems, packaging systems, MDI quality assurance, and continuous metal panels. For the last 16 years, Sue has worked in the lamination area supporting new product development and providing technical support to boardstock and bunstock customers. She is currently an Associate Scientist supporting Bayer projects in continuous insulation and other energy efficiency initiatives involving rigid foam.

John Murphy

John received his BS in Chemistry in 1965. During his 40 years researching urethanes he has worked for [among others] ARCO Chemical and Elf Atochem, where he introduced HCFC-141b to the industry. Currently retired from FSI, he was responsible for New Product Development - Ecomate®.

David Modray

David received his BS in Chemical Engineering in 1995 from the University of Missouri-Columbia. For 17 years he has been employed by FSI as a research chemist. He has been formulating with Ecomate® for the last 14 years.

Raul Dacomba

Raul Dacomba is currently a Formulating Chemist at Foam Supplies, Inc. in Earth City, MO. His responsibilities include conducting research and formulation of Ecomate® polyurethane foam systems. Raul is a graduate of Michigan State University, where he earned his Bachelor of Science in Chemical Engineering. In previous roles, he worked as an undergraduate researcher in the fields of alternative energy and bio-based corrosion inhibitor technologies.