

Optimizing Polyiso Blowing Agents

SACHCHIDA N. SINGH,
MONICA NTIRU-KARAMAGI,
AND MICHAEL RITCHIE

*Huntsman Advanced Technology Center
8600 Gosling Road
The Woodlands, TX 77381*

ABSTRACT

The polyisocyanurate (polyiso) boards used in commercial roofing applications in North America and Europe are currently blown with pentane. The zero ozone depletion potential (ODP), negligible global warming potential (GWP), and low atmospheric lifetime of pentanes has meant that producers of polyiso boards no longer need to be concerned about future regulations on ozone depletion or global warming. Thanks to the tailoring of formulations and processing parameters, the performance of polyiso has improved in many respects when it pertains to meeting the stringent building code requirements related to fire safety, structural integrity and thermal insulation.

Though these are lofty and laudable achievements, the need for better and more cost-effective insulation remains in this ever-increasing energy and environmentally conscious society. Also, the requirements of insulation foam continue to evolve. A recent development has been the use of the long-term thermal resistance (LTTR) method as a measure of thermal insulation. In North America, LTTR is defined as the time-weighted average of thermal resistance over a 15-year period. Another development is increased physical property requirements for polyiso demanded by the market. For instance, the minimum compressive strength in the thickness direction and the dimensional stability of the polyiso board, as defined in the 2001 edition of ASTM C1289, are more stringent than those in the 1998 edition. Such changes in the end-use requirements and the need to maintain the competitive edge of polyiso compared to other types of foam insulation have prompted us to re-examine the optimization of formulation and processing variables.

Learning from the ongoing commercial production with pentanes in North America and Europe, as well as from published work, this study looked at the effect of changes in physical blowing agent composition on the key polyiso performance characteristics, as defined by the new requirements contained in ASTM C1289. Based on these evaluations, this study suggests that there is indeed

potential to further reduce cost while maintaining performance. The potential cost savings would come from lower blowing agent costs and, more importantly, reducing the density of the foam required to make boards meeting all the structural, insulation and fire property requirements.

INTRODUCTION

With over 350 million lbs in use, rigid polyisocyanurate foam was one of the largest segments of the total US polyurethane market in 2002 [1]. Polyiso has enjoyed a growth rate of over 10% since then and is likely to remain a crucial segment for the continued success of the Polyurethane industry. Polyiso boards are used primarily in commercial roofing applications, where it competes with other types of insulation materials such as polystyrene foam, perlite, and wood fiberboard. In 2002, polyiso boards represented nearly 55.6% of the low slope (commercial) roofing insulation (see Figure 1). Low slope roofing represents about 64% of all roofing applications, with the remainder being steep slope (residential) applications [2]. Though impressive, the market share for polyiso board has stayed within this 50-60% range of the commercial roofing market in North America for number of years.

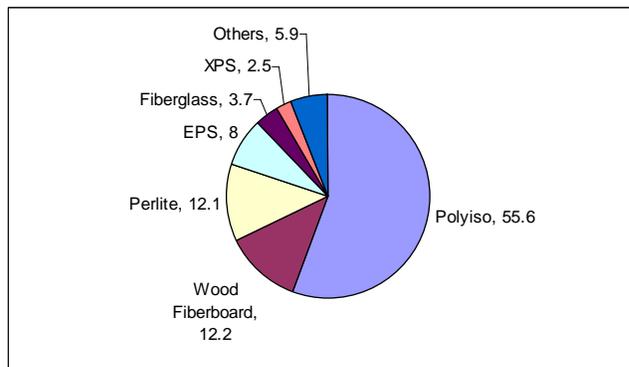


Figure 1. Commercial Roofing Market Share

With high energy prices and near universal affirmation of global warming phenomena, the impetus for growth of insulation materials in general and highly insulating polyiso boards in particular has never been greater. To seize this moment, we need to promote the many attributes of polyiso even more vigorously. This includes not just its excellent performance attributes but also the fact that it is the only foam insulation currently blown with a zero ODP, extremely low GWP blowing agent. Additionally, we need to develop technology that enhances the cost-performance benefit of polyiso board relative to other insulation. After all, the continued success of polyiso boards can be attributed to many factors such as the superior thermal resistance, good structural properties, and excellent fire performance, but above all to cost-effectiveness. Polyiso boards have always strived to be the lowest installed cost insulation per unit of R-value while meeting the structural and fire requirements of the building codes and blowing agent mandates of EPA.

Huntsman has a history of taking a lead role in growing the polyiso industry. As an example, anticipating phase-out of 1,1-dichloro-1-fluoroethane (HCFC-141b) in the USA at the end of 2002, we presented a paper at the Polyurethanes Expo'98 in Dallas with the recommendation that a blend of cyclo and iso-pentane would be the optimum zero ODP physical blowing agent [3]. This recommendation was followed by many boardstock producers. At present all boardstock manufacturers are using pentane as the physical blowing agents though the exact isomer composition varies widely. With the conversion to pentane behind them, the boardstock manufacturers are looking at ways to further improve their cost-effectiveness while meeting the performance requirements. The performance requirements have actually evolved since the paper in 1998. R-value is no longer measured just by PIMA-101, which entailed measuring k-factor of boards aged for six months at room temperature. Now, it is also measured using what is referred to as the long-term thermal resistance (LTTR) method and is defined as the time-weighted average of thermal resistance over a 15-year period. The exact methodology used to measure LTTR is outlined in ASTM C1289-02 in the USA and CAN/ULC S770 in Canada and is discussed in a paper presented by Huntsman at the 2002 API [4]. Another development is more stringent physical property requirements for polyiso boards demanded by the market. For instance, the minimum compressive strength in the thickness direction and the dimensional stability of the polyiso board, as defined in the 2001 edition of ASTM C1289, are more stringent than those in the 1998 edition. Such changes in the end-use requirements and the need to maintain the competitive edge of polyiso compared to other types of foam insulation have prompted us to re-examine the optimum physical blowing agent for use in boardstock.

BLOWING AGENTS

Both liquid and low boiling blowing agents were considered in this study. The liquid blowing agents contemplated included all isomers of pentane, 1,1,1,3,3-pentafluoropropane (HFC-245fa), 1,1,1,3,3-pentafluorobutane (HFC-365mfc), 2-chloropropane and trans-1,2-dichloroethylene. After laboratory scale

evaluations and consideration of blowing agent cost, compatibility with the Regenerative Thermal Oxidizers, and availability for use in the North American market, we chose cyclo-, n- and iso-pentane for in-depth evaluations.

The polyiso industry has used low boiling blowing agents (LBBAs) as co-blowing agents in the past, namely dichlorodifluoromethane (CFC-12) with trichlorofluoromethane (CFC-11) and chlorodifluoromethane (HCFC-22) with HCFC-141b, to improve flow and reduce the minimum stable density. We contemplated many different LBBAs, namely n-butane, isobutane, 1,1-difluoroethane (HFC-152a) and 1,1,1,2-tetrafluoroethane (HFC-134a). After considerations similar to those described in the previous paragraph, we chose iso-butane for in-depth evaluation.

The following seven physical blowing agent packages were chosen for evaluation in this study:

- (a) 80 : 20 cyclopentane : isopentane by weight
- (b) 100% isopentane
- (c) 70 : 30 isopentane : n-pentane
- (d) 30 : 70 isopentane : n-pentane
- (e) 100% n-pentane
- (f) 64 : 28 : 8 isopentane : n-pentane : isobutane
- (g) 73 : 19 : 8 cyclopentane : isopentane : isobutane

Blowing agent (a) is the reference from our 1998 API paper on this subject [2]. As seen in Table 1, the boiling point and cost for cyclopentane (cyclo-P) is higher as compared to isopentane (iso-P) and n-pentane (n-P) and thus for this study, we decided not to use cyclo-P in any of the non-LBBA blends. Blowing agents (b)-(e) represent mixtures of iso-P and n-P with the goal to find an optimum blend of the two. In blowing agent (f) and (g), we took two of the blowing agents from above and added 10 molar % (8 weight %) of isobutane. Similar level of CFC-12 or HCFC-22 were used historically by the industry.

EXPERIMENTAL

In order to evaluate the above listed blowing agents, it was necessary to choose a formulation that will make good quality foam with each of the blowing agents. A series of screening type evaluations were done to ascertain such a formulation. First, a series of polyols and surfactants were screened for blend stability. Then selected formulations were hand-mixed to make foam in a cup to ascertain the quality of foam as judged by cell size, cell uniformity, blow holes, etc. Laminate boards from selected formulations were then made using a high pressure foam machine and a 14" wide, 2" deep and 42" long mold. The mold sat on a conveyor which moved when the foam was poured on it. The conveyor speed was adjusted so that a "just fill" foam board with cell orientation typical of commercial lamination line was obtained. Unless stated otherwise, the following conditions were used to make all laminates:

Chemical throughput	= 25 lb/min.
Mix pressure	= 2000 psi
Isocyanate temperature	= 80°F
Polyol temperature	= 80°F
Mold temperature	= 130 - 140°F
Demold time	= 2 minutes

Table 1. Properties of Selected Zero ODP Blowing Agents

	Cyclo-Pentane	N-pentane	Iso-pentane	N-butane	Iso-butane	HFC-134a
Molecular Weight	70.1	72.0	72.0	58.1	58.1	102
Boiling Point, °F	120.7	97.2	82	31	10.4	-15.7
Vapor Pressure, psia						
@10°C	3.5	5.8	7.8	-	31.9	61.6
@25°C	6.2	10.0	13.2	35.2	55.4	94.2
Thermal Conductivity, Btu-in/hr-ft ² -°F at 25°C	0.089	0.104	0.099	0.112	0.112	0.096
Flammability Limit in Air, Vol %	1.4 – 8.0	1.3 – 8.0	1.4 – 7.8	1.8 - 8.4	1.8 – 8.4	None
TLV or OEL, ppm	600	600	600	600	NA	1000
GWP (CO ₂ = 1)	11	11	11	<10	11	1600
Relative Cost	\$\$	\$	\$	\$	\$	\$\$\$

The laminates were visually inspected for foam quality and facer adhesion. A decision was then made on the formulation to be used for the main part of this study, i.e., evaluation of the different blowing agents. As shown in Table 2, polyol blend consisted of 100 parts of the chosen aromatic polyester polyol, 10 parts tri(beta-chloroisopropyl) phosphate, 4.2 parts of potassium octoate in diethylene glycol, 0.3 parts of a tertiary amine catalyst, 2.0 parts of silicone surfactant, and 0.5 parts water. Blowing agents (a) – (g) were evaluated by making laminate boards with the conveyor mold and high pressure machine using the procedure given above.

All laminate boards were tested for density (ASTM D1622), thermal conductivity (ASTM C518), LTTR (ASTM C1289, Annex A), compressive strength (ASTM D1621, Procedure A), dimensional stability (ASTM D2126, 7 days at -40°C/amb%RH and 70°C/97%RH), peel adhesion [4], friability (ASTM C421), PIR/PUR ratio [5], Butler Chimney (ASTM D3014), and smoke density (ASTM E662). Cell gas composition was measured in selected boards [6].

RESULTS AND DISCUSSIONS

Analysis of variance was performed on the data using statistical data analysis software. Table 2 shows all of the formulations and results. A critical p-value of 0.05 was chosen to determine whether a property was significantly affected by the variables or not. With the exception of maximum smoke density with a value of 0.241, and friability with a value of 0.065, p-value for all other properties listed in Table 2 were less than 0.05, suggesting that blowing agent choice indeed has a statistically significant impact on the remaining properties.

Foam Quality

The quality of the foam was judged visually. Except for the foams made using isobutane, all the foams looked well, i.e., fine and uniform cell size, very few voids, no un-mixed area, and typical PIR foam glassiness. The foams blown with blowing agent containing isobutane looked the same except that they contained excessive voids. This suggests that isobutane is volatilizing prematurely. This is typical of observations made in the first attempt with use of other LBBAs and it is likely that optimization of the surfactant can overcome this.

Density

Table 2 lists three sets of average densities, that of the core foam taken from the top portion of free-rise cup, core foam taken from molded foam and laminate (with facer) used for k-factor measurement. In general, the density of foams blown with iso-P and n-P and mixtures thereof gave a lower density than cyclo-P/iso-P blends. Among the iso-P, n-P and mixtures thereof, the densities are somewhat overlapping but all iso-P and iso-P rich blend gave a bit lower density than n-P. Addition of iso-butane raised the density, which is likely at least in part a reflection of skinning associated with excessive voids in the foam.

Measurement of blowing agents in cell gas and polymer matrix shed some light on the density attributes discussed above. As seen in Figure 2, the relative amounts of blowing agent found in cell gas, as compared to that in the polymer varies. This study and many others done at Huntsman have shown that the amount of pentane lost to atmosphere during foaming is low and nearly

Table 2. Formulations and Properties

	80: 20 cyclo: iso-P	iso-P	70: 30 iso: n-P	30: 70 iso: n-P	n-P	64: 28: 8 cyclo: iso-P: iso-B	73: 19: 8 iso: n-P: iso-B
Polyol Blend	117	117	117	117	117	117	117
Cyclo-pentane	19.5	25	17.5	7.5	25	17.5	15.7
Iso-pentane	5	-	7.5	17.5	-	4.5	6.7
N-Pentane	-	-	-	-	-	-	-
Iso-butane	-	-	-	-	-	2.0	2.0
RUBINATE® 1850 MDI	211.6	211.6	211.6	211.6	211.6	211.6	211.6
Index	300	300	300	300	300	300	300
Foam Quality	Good	Good	Good	Good	Good	VOIDS	VOIDS
Free Rise Density, pcf	1.67	1.63	1.63	1.62	1.64	1.68	1.71
Core Foam Density, pcf	1.99	1.87	1.87	1.88	1.90	2.03	2.05
Laminate Density, pcf	2.69	2.52	2.56	2.59	2.58	2.80	2.69
R-value, Hr-ft ² -°F/Btu-in,							
Initial	6.8	6.5	6.5	6.5	6.6	6.7	6.4
3" LTTR	6.2	6.1	6.0	5.9	5.9	6.1	6.0
2"LTTR	6.0	6.0	5.8	5.7	5.8	5.7	5.9
Dim. Stab., % Vol. Change							
1 week @ -40°F	-1.8	-0.2	0.1	-3.3	-3.7	-0.2	0.6
1 week @168°F/97%RH	7.2	5.2	4.2	5.3	6.8	9.0	5.3
Compressive Strength, psi							
Rise	22	28	30	28	24	26	30
Machine	22	25	19	21	17	17	25
Cross-machine	14	24	19	19	17	16	25
NMCS @1.9 pcf	17	26	23	23	19	17	24
Friability, %	2.0	1.8	1.5	1.6	1.6	2.4	2.1
Peel Adhesion, psi	7.5	4.1	3.4	4.5	6.9	9.1	7.6
Butler Chimney							
Weight Retention, %	81	81	78	81	80	85	88
Extinguish Time, sec	11	12	12	11	11	14	11
Maximum Smoke Density	69	80	65	66	55	60	69
PIR/PUR ratio	2.7	2.7	2.7	2.8	2.7	2.9	2.7

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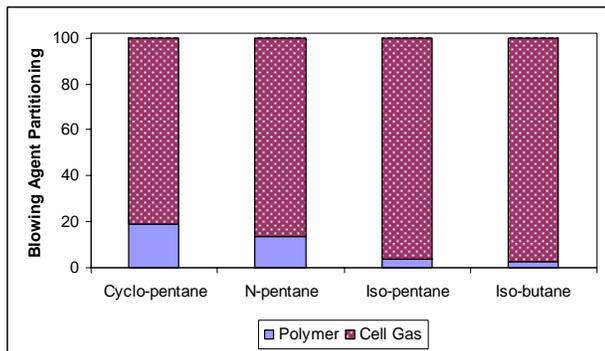


Figure 2. Relative distribution of blowing agent

independent of the isomer selection but the amount found in cell gas is highest for iso-pentane and lowest for cyclopentane. For isobutane, the amount lost to atmosphere during foaming was comparable to that for pentane in this study, but we have not repeated such studies. The higher density for isobutane containing foam in this study is likely attributable to skinning related to excessive void formation.

R-value

Three sets of R-values, initial, 3" LTTR and 2" LTTR are listed in Table 2 and shown in Figure 3. For initial R-value, cyclo-P/iso-P blends give the highest values and iso-P, n-P and mixtures of the two, give overlapping but slightly lower values. Looking at the 3" and the 2" LTTR values, we see that though cyclo-P/iso-P blends give the highest LTTR values, all iso-P gives good LTTR results and the difference between cyclo-P/iso-P and all iso-P is narrowing with more aging. Normal pentane and mixtures containing higher amounts of it seem to give poorer LTTR values as compared to all iso-P. Such R-value behaviors are likely to be explained by difference in diffusion coefficient through the foam and are consistent with previous findings [3, 7].

Iso-butane containing laminates gave good initial R-value despite the excessive voids. LTTR values for iso-butane containing blends are not as good though, especially considering the higher laminate density. Excessive voids are likely to aid in aging of the laminate and thus deteriorate LTTR values.

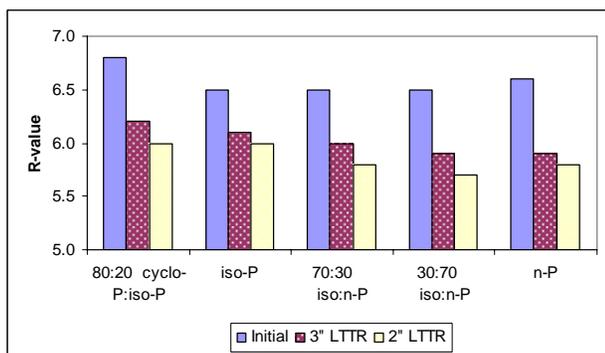


Figure 3. R-values

Dimensional Stability

Cold dimensional stability (dim. stab.) of the foam as measured by aging 4" x 4" x 1" core foam for one week at -40°F along with the foam density is shown in Figure 4. The data suggests that cold dim. stab. of all iso-P and 70:30 iso-P/n-P is good at 1.87 pcf density whereas the same for the reference 80:20 cyclo-P/iso-P is marginal at a higher, about 2.0 pcf, density. Cold dim. stab. of all n-P and 30:70 iso-P/n-P is poor at ~ 1.9 pcf density. The cold dim. stab. of foams blown with isobutane containing mixtures is good but the density of the foams is higher too.

Hot/humid dim. stab. of the foam measured by aging a 4" x 4" x 1" core foam for one week at 168°F/97% RH is shown in Figure 5. The data suggests that hot dim. stab. of all iso-P, 70:30 and 30:70 iso/n-P is better than that of the reference, 80:20 cyclo/iso-P, and all n-P. Factoring density of the foam, it is clear that iso-P and iso-P rich blend yield dimensionally stable foam at lower density as compared to cyclo-P or n-P rich blends. Not surprisingly, addition of iso-butane helps the cold dimensional stability but somewhat deteriorates the hot humid dimensional stability (see Table 2).

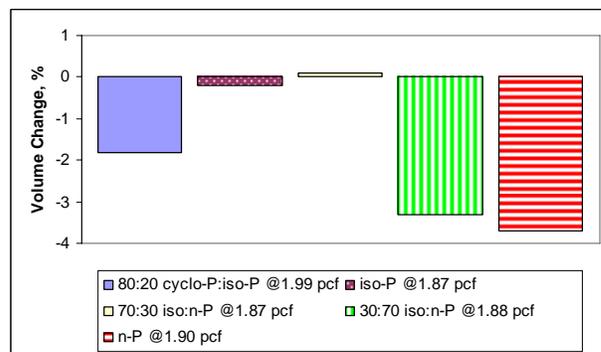


Figure 4. Cold dimensional stability of core foam

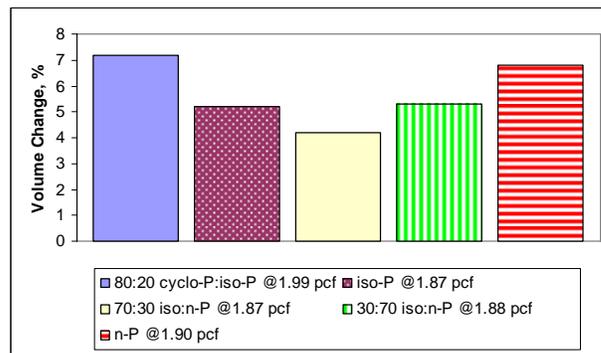


Figure 5. Hot/humid dimensional stability of core foam

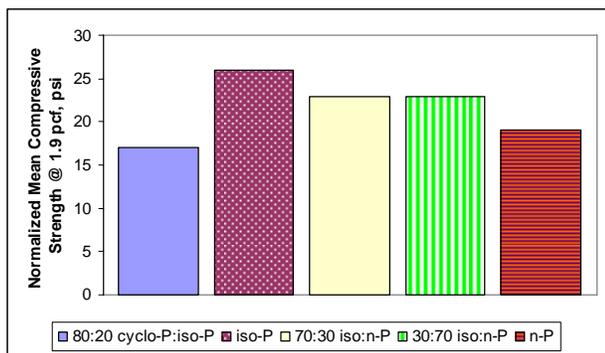


Figure 6. Normalized mean compressive strength of core foam at 1.9 pcf density

Compressive Strength

Compressive strengths (CS) in rise, machine and cross-machine directions, along with calculated normalized mean compressive strength (NMCS) at 1.9 pcf core foam density (as calculated by the formula given in Reference 5) is listed in Table 2. NMCS allows us to compare effects of BA on true strength of the foam as it removes variations due to cell orientation and density, both of which can be independently controlled at a laminator. As seen in Figure 6, iso-P/n-P blends give higher compressive strength as compared to cyclo-P/iso-P blend. Also the higher the amount of iso-P in an iso-P/n-P blend, the higher the NMCS.

Compressive strength results along with dimensional stability results suggest that iso-pentane alone or iso-P rich blend with n-pentane show potential to reduce density as compared to 80:20 cyclopentane/isopentane blown foam board.

Fire Property

Fire properties of laminates were characterized using only laboratory scale tests. The foam weight retention and time to extinguish were measured in the Butler chimney test. The maximum smoke density was measured in the NBS test, and the PIR/PUR ratio was measured using FTIR [5]. These results are shown in Table 2. Not surprisingly, the choice of blowing agent does not have any industrially meaningful impact on measured laboratory scale fire properties.

Friability and Peel Adhesion

Tumble friability and peel adhesion of the facer after 24 hours of cure were also measured in this study. Peel adhesion values for iso/n-pentane blown foams were lower than cyclopentane containing foams and so were the friability values. Data from this study suggests almost a linear relationship between peel adhesion and tumble friability. Even though the measured friability is for the bulk foam and not surface or skin, this trend defies conventional wisdom which is that "poor adhesion in polyiso foam is caused by high friability." We did not investigate this further but it was ascertained that choice of silicone surfactant and compatibility between the

polyol and the blowing agent play a significant role on peel adhesion.

Overall Findings

Results of this study combined with those of our previous studies [3, 8] suggest that each of the pentane isomers bring different attributes to polyiso manufacturing and performance. Cyclopentane offers the highest initial R-value, good peel adhesion and good solubility/compatibility with existing raw materials. Isopentane offers good LTTR, compressive strength and dimensional stability. Normal pentane offers a mid range performance and with its boiling point closest to HCFC-141b, brings processing familiarity.

Clearly the optimum composition would depend on the chosen criteria for polyiso board manufacturing and processing. Given the goal of reducing cost while retaining performance, all iso-pentane appears to be the liquid blowing agent of choice. It offers the highest potential to lower the density of the board. But with lower boiling point and limited solubility in existing raw materials, it presents a few challenges in manufacturing. Like CFC-11, isopentane is essentially a room temperature boiling blowing agent and thus requires cooler component and mix-head temperatures. To improve peel adhesion and to guard against an unplanned rise in component/mix-head temperature, compatibility of iso-pentane in polyol blends would need to be further improved.

If manufacturing using iso-pentane as the sole liquid blowing agent is not plausible, use of n-pentane as a minor co-blowing agent, only to the extent necessary to get good processing would be an excellent option. Cyclopentane can also be used as a minor blowing agent though it is likely to be less cost effective versus n-pentane due to its deleterious impact on compressive strength and dimensional stability.

Though this study did not demonstrate a compelling case for use of the LBBA, iso-butane, it is likely to be attributable to entrainment of excessive voids in the foam. It is likely that such voids could be eliminated with further optimization of processing parameters along with surfactant and/or other components. Keeping in mind that flammable gases like iso-butane are likely to need additional safety and handling considerations over and above those currently in place for pentanes, and given the finding that substantial cost-savings can be achieved by using isopentane as the sole liquid blowing agent, additional exploration of iso-butane seems unwarranted.

CONCLUSIONS

This study suggests that all isopentane or an isopentane rich blend of isopentane/n-pentane has the maximum potential for realizing cost savings while maintaining or enhancing performance. The potential cost savings would come from lower blowing agent cost as isopentane and n-pentane are substantially cheaper than cyclo-pentane in the present market. But the bigger savings will potentially come from the ability to make

boards at lower foam density while still meeting the structural, insulation and fire property requirements.

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BIOGRAPHIES

Sachchida N Singh



Sachchida is currently the Division Technical Expert for the Polyurethanes business at Huntsman. Since joining in 1987, he has held increasingly responsible positions in the technology development departments of the business. He has worked in many different application areas of polyurethane chemistry and technology and has lately spent significant efforts in the rigid foam sector. He has a Doctoral degree in Materials Science and Engineering from Massachusetts Institute of Technology and a Master of Science degree in Chemical Engineering from Rensselaer Polytechnic Institute.

Monica Ntiru-Karamagi



Monica is an Account Manager at Huntsman. Since joining the Polyurethanes business in 1997 as a Technical Specialist, she has provided technical service and development for various sectors of the construction industry. She is currently an Account Manager in the System House sector. She has a Master of Science degree in Chemical Engineering from Howard University, and a Bachelors degree in Chemical Engineering from Texas A & M University.

Michael J. Ritchie, Jr.



Michael joined Huntsman in 2000 after receiving his Bachelors degree in Chemical Engineering from Drexel University. He is currently a Technical Specialist for the Polyurethanes group focused on rigid foam for construction applications.