

Pour-in-place Discontinuous Panels Using Pentanes

AL DELEON

*Oxid L.P.
101 Concrete Street
Houston, TX 77012*

DAVID SHIEH

*Oxid L.P.
101 Concrete Street
Houston, TX 77012*

E. F. FESKE

*Albemarle Corporation
P. O. Box 14799
Baton Rouge, LA 70898*

ABSTRACT

The conversion from R-141B to suitable alternate blowing agents in the rigid foam markets has accelerated as the deadline for its disappearance nears. Pentanes have been selected by the flexible faced laminate industry to replace R-141B. Plant conversions are underway. Other foam applications are considering pentanes. One such large application is the metal faced panels using pour-in-place systems.

The work reported here will show that if properly formulated, systems containing pentanes can be used in this application. The paper will show several fire retardant combinations needed to reach the desired results in the E-84 Tunnel Test.

INTRODUCTION

As the end of the year 2002 nears, the urethane foam industry is yet faced with another challenge. What would be the replacement for R-141B as the blowing agent?

The answer is becoming clearer as this day approaches. In the US, the flexible faced laminators are converting to pentane. It appears that a blend of cyclopentane and isopentane is favored at this time. However, n-pentane is being evaluated because it offers the best economics of all the pentanes.

The majority of the US appliance manufacturers will switch to 245FA, while R-134a will be used by one producer.

The US System Houses are faced with a more complicated conversion. The choices are R-245fa, R-134a, water, hydrocarbons and a combination of these. Work with R-245fa has progressed well with Honeywell. Pour-in-place systems with this blowing agent have been developed. The challenge with R-245fa in these systems is balancing the ratio of water/R-245fa to get optimum properties.

The use of R-134a in pour-in-place systems have been demonstrated and several commercial pour-in-place, class I rated and non-rated systems are available commercially. Usually this blowing agent is used in conjunction with water.

The use of hydrocarbons by system houses to replace R-141B has been lagging because of flammability concerns. Because of this, the use of hydrocarbons by system houses could be limited. This paper will discuss using pentane as a blowing agent in class I rated pour-in-place systems. We will show foam formulations and E-84 tunnel test. We will also discuss new polyester polyols developed and their application.

BACKGROUND

Unmodified aromatic polyester polyols whether based on PET, DMT bottoms, pure terephthalic acid or phthalic anhydride have poor pentane solubility. Cyclopentane is only slightly soluble in these polyols while isopentane or n-pentane have little or none. [Table I](#) shows the pentane solubility of commonly found aromatic polyester polyols. Pentane solubility is expressed as parts per hundred parts of polyol (PPHP). In order to use these materials one must depend on the addition of emulsifiers or solubilizers.

The selection of an emulsifier can be difficult, as they are system specific. Emulsion stability is dictated by the application. In the production of flexible faced laminate board where pentane is introduced via in-line blending, emulsion stability needs to be only a few minutes. If a polyol/pentane blend is to be stored or shipped, the emulsion stability needs to be several weeks. The use of emulsifiers limits the use of pentane in pour-in-place systems because of the high probability of losing pentane. This can be significant as the polyol/pentane blend is exposed to elevated temperatures.

[Table 2](#) shows new polyester polyols with pentane solubility. This was accomplished by modifying the polyester polyol backbone with pentane soluble materials.

Table 1. Pentane Solubility of Standard Polyols

Polyol	Pentane Solubility, pphp		
	n-Pentane	Isopentane	Cyclopentane
Terol 256	2	4	2
Terol 352	2	4	2
Terol 198	3	4	5
Terate 203	0	1	2
S-3152	0	1	2

Table 2. Pentane Solubility in New Polyols

Polyol	Pentane Solubility, pphp		
	n-Pentane	Isopentane	Cyclopentane
Terol 595	10	12	15
Terol 588	15	14	15
Terol 681	13	13	15

These polyols still maintain high aromatic content and yield good foam physical properties.

Terol 588 was introduced early in the year 2000 for use in continuous flexible faced lamination. Table 3 and 4 show typical formulations used commercially in the US and Europe. Table 3 show typical European formulations where the pentane used is n-pentane. Table 4 shows a typical American formulation using Exxsol I200 as the blowing agent. Both formulations yield foam boards that meet or exceed all specifications.

Table 3. European Lamination Formulation

	Name	EQWT	PBW
Polyester	Terol 588	245.50	85.75
FR Additive 1	TCP		12.50
Surfactant 2	B8443		1.75
CAT 1	K Acetate	50.00	2.00
CAT 2	Koctoate	196.15	2.00
CAT 3	PMDTA		0.25
Water		9.00	0.70
N-Pentane			18.00
Total			125.95
Index	Mondur 489	134.00	3.300
Iso Total			212.00
B/A			0.580
Cream			10
Gel			31
T.F.			45
Rise			65
Core Density			1.88
Comp. St.			
perpendicular, psi			27
parallel, psi			18

Table 4. U.S. Lamination Formulation

Ingredient	Name	EQ WT	PBW
Terol	Terol 588	235	100
Fire Retardant	TCP		10
Surfactant	B-8443		2
CAT 1	Koctoate		3.6
CAT 2	Kacetate		0.85
CAT 3	PC5		0.25
Water		9	0.5
Exsol (60/40)			
Cyco/Iso			18.9
Total			136.10
Index			3.000
Iso Total	E-489	136	196.00
Core Density			1.78
Overall Density			1.9
Comp. St.			20.4
E-84 Tunnel Test			
Flame spread index			27
Smoke			64
K-factor			
Initial			0.149
1 month			0.158
2 month			0.160
3 month			0.158

Terol 588 has sufficient pentane solubility for use in PUR or PIR systems, but its functionality is too low to achieve the required foam physical properties. Terol 681 has the same pentane solubility as Terol 588, but has a much higher functionality.

The data presented in this paper was generated using Terol 681 in pour-in-place systems aimed at the discontinuous metal-faced panel application. Specifically, the applications where E-84 class I requirements are needed.

EXPERIMENTAL WORK

The initial part of this study was conducted in the laboratory using the hand-batch method. The screening test used to predict the E-84 tunnel test performance was the Cone Calorimeter test developed by Albemarle Corporation and presented at the 1994 SPI Conference¹. Large foam samples were generated and tested in the E-84 tunnel test at Omega Point Laboratories in San Antonio, Texas.

RESULTS AND DISCUSSION

Table 5 shows a formulation combining Terol 681, a sucrose based polyether polyol, and a combination of RB-79 a tetrabromo phthalic anhydride based polyether and Fyrol CEF, a tris, chloroethyl phosphate, a liquid non-reactive fire retardant. The objective was to obtain the lowest possible flame spread and smoke numbers as predicted by the Cone Calorimeter. At a fixed level of fyrol CEF, increasing the RB-79 from 25 to 35 PPHP accomplished this. This is the equivalent to increasing the Bromine content from 3.6% to 4.8% at essentially a fixed chlorine and phosphorous content

Table 5. Screening Formulation for E-84 test

Name	EQ WT	E-2	E-5	E-6
Polyester	Terol 681	233	36	36
Polyether	Sucrose/PO	151	39	39
Fire Retardant 1	RB-79	249	25	30
Fire Retardant 2	Fyrol CEF		25	25
CAT 1	PC5		0.2	0.2
CAT 2	TMR-3		2.6	2.7
CAT 3	PC-8		0.1	0.1
Water		9	0.7	0.7
Exxsol 1200***			20.77	21.6
Total			151.4	157.0
Index			1.80	1.80
Isocyanate	E-489	134.00	165	170
Core Density, LB/CUFT			1.9	1.9
Cone Calorimeter Projections				
Flame Spread			23.3	26.5
Smoke Density			854	798
%Chlorine			2.90	2.80
%Bromine			3.63	4.22
%Phosphorous			0.85	0.82

Table 6 shows the effect of increasing Fyrol CEF at a fixed level of RB-79. Here, there is a noticeable negative effect on smoke generation with a slight increase in flame spread. At fixed % bromine in the foam, increasing the % phosphorous from 0.8 to 1.1 increase smoke and flame spread

Table 7-1. E-84 Tunnel Test Results, PIR Foams

	Terol 588	Terol 588
Polyester Polyol	TCPP	TCPP
Fire Retardant	5	10
Fire Retardant pbw	3.0	2.5
Index		
E-84 Tunnel Test		
Flame Spread	35	40
Smoke	50	110
Board Thickness, in	4.0	4.0

Table 6. Screening Formulation for E-84 test

Name	EQ WT	E-6	E-7	E-8
Polyester	Terol 681	233	36	36
Polyether	Sucrose	151	39	39
Fire Retardant 1	RB-79	249	35	35
Fire Retardant 2	Fyrol CEF		25	30
Surfactant	B8443		2	2
CAT 1	PC5		0.2	0.2
CAT 2	TMR-3		2.76	2.8
CAT 3	PC-8		0.1	0.1
Water		9	0.7	0.7
Exxsol 1200***			22.4	22.8
Total			163.16	168.60
Index			1.80	1.80
Isocyanate	E-489	134	175	175.
Core Density, LB/CUFT			1.9	1.9
Cone Calorimeter Projections				
Flame Spread			23.3	24.2
Smoke Density			735	763
%Chlorine			2.75	3.20
%Bromine			4.83	4.69
%Phosphorous			0.81	0.94

It is well known that PIR foams are more thermally stable than PUR foams. Typically, PIR foams display low flame spread and smoke in the E-84 tunnel test with little or no fire retardants. Table 7-1 shows the E-84 tunnel test results for two levels of fire retardants. These foams were made using Terol 588.

In Table 7 we explore the effect of increasing the index. Here the comparison is between a 2.50 index foam and a 1.85 index foam. The lower index foam contains a higher level of fire retardant and yet the effect of a higher index is overwhelming in reducing flame spread and smoke.

Increasing the loading of polyester, reducing the level of polyether produced foams with the lowest smoke ratings. Table 8 shows these results. At the same index and same fire retardant loading, reducing the polyether content reduces smoke significantly with little change in flame spread.

In table 9, we combine the highest level of bromine, constant level of phosphorous from three different fire retardant sources and high index. These foams were collected from large buns and tested in the E-84 tunnel test at 4 inches in thickness. The sample with the highest index yielded the lowest smoke. All three samples fell in the 25-30 flame spread range.

CONCLUSION

We believe that it is possible to develop a system for discontinuous panels using pentane to meet Class I E-84 tunnel test rating.

Table 7. Screening Formulation for E-84 test

	Name	EQ WT	E-13	E-15
Polyester	Terol 681	233	40	40
Polyether	Sucrose/PO	151	16	16
Fire Retardant 1	RB-79	249	40	40
Fire Retardant 3	TEP		15	15
Surfactant	B8443		2.5	2.5
CAT 1	PC5		0.2	0.2
CAT 2	TMR-3		3.1	2.9
CAT 3	PC-8		0.1	0.1
Water		9.00	0.7	0.7
Exxsol 1200***			20.5	20.85
Total			138.1	138.3
Index			2.50	1.85
Isocyanate	E-489	134.00	185	151
A&B@ 28 °C				
Core Density, LB/CUFT			1.9	1.9
Cone Calorimeter Projections				
Flame Spread			25.8	22.1
Smoke Density			676	868
%Chlorine			0.00	0.00
%Bromine			5.69	6.36
%Phosphorous			0.79	0.89

Table 8. Screening Formulation for E-84 test

	Name	EQWT	E-16	E-17
Polyester	Terol 681	233	40	60
Polyether	Sucrose/PO	151	16	0
Fire Retardant 1	RB-79	249	40	40
Fire Retardant 4	DEEP		15	15
Surfactant	B8443		2.5	2.5
CAT 1	PC5		0.2	.2
CAT 2	TMR-3		2.9	2.9
CAT 3	PC-8		0.1	0.1
Water		9.00	0.7	0.7
Exxsol 1200***			15.5	16
Total			132.9	137.4
Index			8.85	1.85
Isocyanate	E-489	134.00	158	161
Core Density, LB/CUFT			1.9	1.9
Cone Calorimeter Projections				
Flame Spread			24.0	25.6
Smoke Density			801	659
%Chlorine			0.00	0.00
% Bromine			6.33	6.17
%Phosphorous			0.96	0.94

Table 9. Screening Formulation for E-84 test

	Name	E-18	E-19	E-20
Polyester	Terol 681	60	60	60
Fire Retardant 1	RB-79	40	40	40
Fire Retardant 2	Fyrol CEF	0	26	0
Fire Retardant 3	TEP	17	0	0
Fire Retardant 4	DEEP	0	0	16
Surfactant	B8443	2.5	2.5	2.5
CAT 1	PC5	0.2	0.2	0.2
CAT 2	TMR-3	2.9	2.9	2.9
CAT 3	PC-8	0.1	0.1	0.1
Water		0.7	0.7	0.7
Exxsol 1200		16	18.3	15.9
Total		139.4	150.7	138.3
Index		2.15	2.5	2.15
Isocyanate	E-489	165	192	165
Core Density, LB/CUFT				
		1.9	1.9	1.9
Cone Calorimeter Projections				
Flame Spread		23.8	26	26.2
Smoke Density		314	182	328
E-84 Tunnel Test				
Flame Spread		25.8	28.5	27.3
Smoke		450	250	400

To accomplish this, one must use a combination of bromine from RB-79, phosphorous from three different fire retardants, the lowest possible amount of polyether, and the highest possible index.

Would this combination result in a commercially viable system? We will be addressing this in future development work. This will include pouring panels in actual molds to determine processing characteristics, optimization of foam physicals, and optimization of the fire retardant package to get the lowest possible smoke.

The Cone Calorimeter is a reasonable tool to predict flame spread in the E-84 tunnel test. However, smoke prediction from this test is less reliable. We will try to improve this in future experiments.

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REFERENCES

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BIOGRAPHIES

Al DeLeon

Al DeLeon is the VP of R & D. He began his career in 1970 working at Jim Walter Research Corp., where he was involved in the development of isocyanurate chemistry. After fourteen years there, he became Technical Director of Flexible Products Company where he stayed for four years, directing their R & D as well as TS & D efforts. In 1988, Al joined Oxid in his current position. He holds numerous patents in urethanes, and is the author of numerous publications. Al holds BS and MS degrees in Chemistry from the University of Miami (FL). He is a member of Sigma XI and ACS.

David Shieh

As Manager of R & D for Terol polyols, David Shieh is responsible for both polyester polyol development as well as PUR/PIR foam development, using these polyols. Prior to joining Oxid in 1990, David was a Research Chemist at Chardonol, where he developed numerous polyester polyols for use in foams. He holds several patents in the field of Polyester polyol, and he is recognized as an authority in this field. He holds a BS degree in Chemistry from the Catholic University of Taiwan, and graduate degrees from the University of Houston.

E. F. Feske

Elbert (Bert) Feske received a BA degree in Science from Graceland College in Lamoni, Iowa. Bert has worked in all aspects of Polyurethane product development in the last 30 years. He joined Ethyl Corp. in 1988 and is currently an R & D Specialist at Albemarle Corp. Bert has numerous technical papers in the area of Fire retardancy of rigid urethane foams.