Low Hydroxyl Number Polyester Polyols for Lamination

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ABSTRACT

In 2005, the polyiso lamination industry experienced a shortage of polymeric isocyanate. This shortage also brought rising costs of isocyanate. To counteract the situation, the polyiso laminators looked to reducing isocyanate consumption. The polyester polyol producers were asked to develop polyester polyols in the 200 OH NO range as this would save about 7 to 10% of the isocyanate usage.

Reducing the OH NO of a polyester polyol alone will cause the 2.5 index foam to be softer and depending on the polyester polyols could reduce the dimensional stability of the foams. Additionally, the lower OH NO can also cause deterioration in the thermal stability of the foam if the polyol is not designed properly. Oxid will show through laboratory work that the minimum OH NO should be 200; that as the OH NO is reduced, the functionality of the polyol should be increased to minimize a reduction in dimensional stability; and that the aromatic content should be increased to improve thermal stability.

INTRODUCTION

Throughout 2005, the rigid foam lamination industry was concerned with the rising cost and diminished supply of isocyanate. With the threat of isocyanate shortages, the lamination industry needed to find ways to meet production demands in the market place. The obvious solution was to reduce isocyanate consumption.

There are a number of options to consider when evaluating isocyanate consumption. Final foam physical properties and processing capabilities need to be taken into careful consideration before implementing any of these options. In the rigid foam lamination industry, the consumption of isocyanate can be reduced by focusing on the following items:

- Reducing the index
- Reducing the water level in the formulation
- Introducing surfactants with lower hydroxyl value
- Introducing catalysts with lower hydroxyl value
- Lowering the finished product density
- Reducing the hydroxyl value of the polyol

As a polyol manufacturer, Oxid focused on producing a polyol with lower hydroxyl value without jeopardizing finished foam physical and fire properties.

Polyol processing technology holds that a higher functional mixture does not flow well and since trimer rings provide all the functionality needed for physical properties, there was little or no need for high functional polyols. In fact, current technology utilizes polyester polyols that are at most a diol. When we apply that rationale to a system with a lower hydroxyl polyol, we find that foam physical properties are diminished. Since the consumption of isocyanate is reduced in a lower hydroxyl system, the end effect of the trimer is diluted. We propose to solve this problem by increasing the functionality of the polyester polyol.

In this paper, we will show that when we modify the chemistry of the polyester polyol it is possible to make a successful Polyiso board with reduced isocyanate consumption. This next generation polyester polyol has the potential to reduce costs and mitigate swings in isocyanate availability.

LABORATORY WORK

One way to reduce the hydroxyl of a polyester polyol is by diluting the polyol with non-reactive additives. The non-reactive additives serve to weaken the foam and thus have detrimental effects on final physical properties. At Oxid, we do not use non-reactive additives to reduce hydroxyl value. We use reactive materials that serve to strengthen the foam while reducing overall hydroxyl value. Furthermore, we use blowing agent compatibilizers and functionality modifiers to get lower hydroxyl values while maintaining necessary physical properties.

The first step to produce a lower hydroxyl value polyester polyol was to make model compounds to determine the minimum hydroxyl value for Polyiso board stock. During this stage numerous experimental polyols were generated and tested to see the effect of the reduced hydroxyl value. These polyols vary in pentane solubility and functionality. All polyols were tested in a pentane blown Polyiso formulation using the hand-mix method. The polyols are summarized in Table 1:

Table 1. Experimental Polyols

Component	Hydroxyl Number	Functionality	Pentane Solubility
DS 1069	185	1.9	Yes
DS 1122	200	2.05	Yes
DS 1154	200	2.25	Yes
Terol 567	200	1.9	Yes
Terol 565	245	1.9	Yes
Terol 563	245	1.9	No

The hydroxyl value varied from 185 to 245 mg KOH / g; the functionality ranged from 1.9 to 2.2 while the viscosity ranged from 3500-5000 cps @ 25ºC. These polyols were tested in a generic lamination formulation (see Table 2) that Oxid would provide to customers.

Table 2. A generic lamination formulation

Component	phpp
Polyester Polyol (240 OH)	100.00
TCPP	15.00
Potassium Octoate	5.00
Potassium Acetate	1.00
PMDETA	0.30
Surfactant	2.00
Water	0.50
Pentane	20.00
Polymeric MDI (index 250)	180.00

Foam physical property data is shown in Table 3.

Table 3. Experimental Polyol Lab Physical Property Data

Foam Physical Properties	**DS 1069**	**DS 1122**	**DS 1154**	**Terol 567**	**Terol 565**	**Terol 563**
Core Density (pcf)	1.55	1.57	1.58	1.56	1.57	1.58
Dimensional Stability - 2 Day Age						
-40ºF % Change in Length	-15.78	-0.33	-0.74	0.37	-0.56	-0.30
-40ºF % Change in Width	-12.03	-0.53	0.06	0.39	0.36	0.09
-40ºF % Change in Thickness	-2.09	0.08	-0.23	1.26	0.11	0.64
200ºF, Dry heat % Change in Length	2.98	2.36	1.85	1.52	0.64	1.28
200ºF, Dry heat % Change in Width	2.75	2.27	2.35	2.00	1.26	0.88
200ºF, Dry heat % Change in Thickness	-0.93	-0.31	-0.68	1.37	0.03	-0.56
Compressive Strength – Parallel to rise (psi)	15.5	20.5	25.7	24.3	23.7	27.2
Compressive Strength - Perpend. to rise (psi)	6.3	9.2	14	12.7	10.6	12.1
Hot Plate Test - % Mass Retention	85.0	86.3	86.2	84.0	89.5	86.3
Hot Plate Test - % Thickness Retention	82.7	89.0	93.8	87.0	117.8	105.9

As can be seen from the physical property data in Table 3, DS 1069 shows poor dimensional stability and decreased thermal stability as shown by the hot plate data. It is interesting to note that Terol 567 and DS1069 have similar composition and functionality. The only difference is that DS1069 is below an OH NO of 200. We believe that this is the minimum OH NO for a good lamination polyol at a 2.5 index.

DS 1122 and DS 1154 show comparable dimensional stability to Terol 567, but there is a slight improvement in the hot plate results over Terol 567. This can probably be explained by the higher functionality of DS1122 and DS1154 over Terol 567. The 200 OH polyols, with functionality greater than 2, compare favorably to Terol 563 which Oxid has been successfully marketing to the lamination industry for over two years. Based on the above results, Oxid decided to focus on low OH polyols with a minimum 200 OH and functionality greater than 2, such as DS1122 and DS1154.

INITIAL LAMINATOR PLANT TRIALS

Initial plant trials were performed using Terol 567 and DS 1122 low OH polyols. Initial formulations are shown in Table 4.

Table 4. Initial Terol 567 and DS 1122 Low OH polyol formulations

Component	Terol 567	DS 1122
Polyester Polyol (200 OH)	100.00	100.00
TCPP	15.00	15.00
Potassium Octoate	varied	varied
Potassium Acetate	varied	varied
PMDETA	varied	varied
Surfactant	2.00	2.00
Water	0.50	0.50
Pentane	20.50	20.50
Polymeric MDI (index 250)	168.00	168.00

These formulations were processed using current typical processing conditions. Resulting physical property data is shown in Table 5. Fire test data is shown in Tables 6 through 8. Calorimeter test decks were constructed by mechanically attaching 1.5 inch thick insulation to a 18 gauge steel deck and hot mopping ½ inch thick wood fiber board on top of the insulation. Applied on top of the wood fiber board was 4 ply BUR using glass felts hot mopped with a 60 lb/sq flood coat. The ASTM E108 Spread of Flame test decks were constructed by attaching two layers of 1.5 inch thick insulation on top of 1/2 inch plywood. 0.060 inch standard reinforced EPDM membrane was adhered on top of the insulation with bonding adhesive.

Table 5. Initial Lamination Trial Terol 567 and DS 1122 Physical Property Data

	Terol 567	DS 1122
Thickness (inches)	1.50	1.50
Core Density (pcf)	1.72	1.68
Compressive Strength (psi)		
Parallel to Rise	23.5	24.1
Cross Machine Direction	20	19.2
Machine Direction	17.1	19.4
Dimensional Stability (7 Day Age)		
-10° F		
% Change in Length	0.14	-0.11
% Change in Width	-0.05	-0.29
% Change in Thickness	0.35	0.47
200° F, Dry Heat		
% Change in Length	3.47	1.95
% Change in Width	1.87	1.09
% Change in Thickness	2.48	0.19
158° F & 98% R.H.		
% Change in Length	2.07	1.88
% Change in Width	0.71	0.92
% Change in Thickness	1.44	1.07

Table 6. Terol 567 and DS 1122 Hot Plate Data

	Hot Plate Standard	Terol 567	DS 1122
% Mass Retention	80.1	76.7	77.9
% Thickness Retention	85.8	71.2	75.9

Table 7. Terol 567 and DS 1122 Calorimeter Data (Btu/ft²/min)

	3 min	5 min	10 min	Average
Class 1 Standard	410	390	360	285
Terol 567	259	259	252	176
DS 1122	339	328	304	202

Table 8. Terol 567 and DS 1122 ASTM E108 Results

Sample	Slope	Max Flame Spread	Class Passed
Terol 567	½ in 12	63 inches	A
DS 1122	½ in 12	50 inches	A

As can be seen in Table 5, the dimensional stability data of Terol 567 does not meet ASTM 1289-05a standard. Also, it was recognized that the processing capabilities of Terol 567 were not as good as DS 1122, primarily flow characteristics. Based on the results of the initial laminator trials, Oxid decided to focus more in the direction of the DS 1122 polyol, 200 OH NO with a functionality greater than 2. Some modifications were made to DS 1122 and DS1154 was developed. This polyol is very similar to DS 1122 but with slightly higher functionality.

ADDITIONAL LAMINATOR PLANT TRIALS

The next plant trials focused on using DS 1122 and DS 1154 polyols along with Terol 563 polyol as a control. The formulations used for these trials are shown in Table 9. Typical process parameters were used with these formulations.

Table 9. Terol 563 and DS1122 / DS 1154 polyol formulations

Component	Terol 563 (245 OH)	DS 1122 / DS 1154
Polyester Polyol	100.00	100.00
TCPP	15.00	15.00
Potassium Octoate	varied	varied
Potassium Acetate	varied	varied
PMDETA	varied	varied
Surfactant	2.00	2.00
Water	0.40	0.40
Pentane	20.00	20.00
Polymeric MDI (index 250)	183.00	168.00

Both low OH polyols processed similar to the control polyol. DS 1154 seemed to have slightly better flow characteristics noticed by a slight increase in line speed. Resulting physical property data is shown in Table 10.

Table 10. Terol 563 and DS 1122 / DS 1154 Physical Property Data			
	Terol 563	**DS 1122**	**DS 1154**
Thickness (inches)	1.50	1.50	1.50
Nominal Core Density (pcf)	1.70	1.70	1.70
Compressive Strength (psi)			
Parallel to Rise	22.6	23.1	23.2
Cross Machine Direction	11.6	13.6	13.9
Machine Direction	12.5	14.6	13.9
Dimensional Stability (7 Day Age)			
-10° F			
% Change in Length	-0.21	-0.51	-0.63
% Change in Width	-0.35	-0.58	-0.58
% Change in Thickness	0.51	-1.34	-1.62
200° F, Dry Heat			
% Change in Length	1.05	2.48	2.11
% Change in Width	0.97	1.04	1.08
% Change in Thickness	0.84	0.36	-0.16
158° F & 98% R.H.			
% Change in Length	1.05	2.01	3.10
% Change in Width	-0.07	1.54	2.12
% Change in Thickness	0.64	-1.00	-0.34

The table shows dimensional stability of DS 1122 and DS 1154 being slightly higher than specified by ASTM 1289-05a standard. We attribute this to the short duration of laminator run times and non-optimized formulations.

Hot Plate data is shown in Table 11.

Table 11. Terol 563 and DS 1122 / DS 1154 Hot Plate Data

	Hot Plate Standard	**Terol 563**	**DS 1122**	**DS 1154**
% Mass Retention	78.1	85.4	81.0	78.4
% Thickness Retention	82.8	86.5	72.5	72.2

The hot plate data was encouraging enough to proceed with Factory Mutual calorimeter testing. The calorimeter test decks were constructed by mechanically attaching 1.5 inch thick insulation to an 18 gauge steel deck and hot mopping ½ inch thick cover board on top. Applied on top of the cover board was 4 ply BUR using glass felts hot mopped with a 60 lb/sq flood coat. All three of these samples passed the Factory Mutual calorimeter.

LOWER INDEX LABORATORY WORK

Some lamination manufacturers have inquired about the possibility of lowering the index using low OH polyols and further decreasing usage of isocyanate. Oxid performed some laboratory work using Terol 563, DS 1122, and DS 1154 polyols. Formulations were used at 2.5, 2.25, and no water at 2.25 indexes. Core densities, compressive strengths, dimensional stabilities, and hot plate tests were evaluated. The results are shown in Tables 12 through 14.

Table 12. 2.5 Index Data

Sample ID	**Terol 563**	**DS 1122**	**DS 1154**
Density (pcf)	1.60	1.62	1.61
Compressive Strength (psi)			
Parallel to Rise	29.1	23.8	22.7
Perpendicular to Rise	11.3	10.7	10.2
-10° F Dimensional Stability (7 Day Age)			
% Change in Length	0.59	0.93	1.04
% Change in Width	0.66	0.95	0.97
% Change in Thickness	0.82	0.35	0.47
200° F Dry Heat Dimensional Stability (7 Day Age)			
% Change in Length	3.15	2.33	2.13
% Change in Width	3.13	2.80	1.80
% Change in Thickness	-0.11	-0.49	-0.16
158° F & 98% R.H. Dimensional Stability (7 Day Age)			
% Change in Length	1.97	2.37	2.04
% Change in Width	3.00	2.35	2.71
% Change in Thickness	0.19	-0.20	0.03
Hot Plate Test			
% Mass Retention	86.6	81.3	80.9
% Thickness Retention	124.8	91.7	85.3

Table 13. 2.25 Index Data

Sample ID	**Terol 563**	**DS 1122**	**DS 1154**
Density (pcf)	1.56	1.62	1.55
Compressive Strength (psi)			
Parallel to Rise	27.5	20.6	20.2
Perpendicular to Rise	9.2	7.8	7.8
-10° F Dimensional Stability (7 Day Age)			
% Change in Length	0.51	0.80	1.21
% Change in Width	0.49	1.12	0.64
% Change in Thickness	1.20	0.58	1.72
200° F Dry Heat Dimensional Stability (7 Day Age)			
% Change in Length	5.54	3.73	2.70
% Change in Width	4.82	2.30	2.39
% Change in Thickness	-0.25	-0.88	-0.49
158° F & 98% R.H. Dimensional Stability (7 Day Age)			
% Change in Length	3.33	3.37	3.18
% Change in Width	3.31	2.45	3.09
% Change in Thickness	0.62	-0.14	-0.43
Hot Plate Test			
% Mass Retention	86.4	80.2	82.1
% Thickness Retention	120.1	88.2	83.0

As can be seen in Tables 12 and 13, reduction in index from 2.50 to 2.25 causes deterioration in dimensional stability. What is interesting is that Terol 563 suffers more in dimensional stability than DS 1122 and DS 1154. This is probably due to the higher functionality of DS 1122 and DS 1154. This deterioration is further exacerbated by eliminating the water from the formulation, as seen in Table 14.

Table 14. No Water @ 2.25 Index

Sample ID	Terol 563	DS 1122	DS 1154
Density (pcf)	1.53	1.59	1.60
Compressive Strength (psi)			
Parallel to Rise	23.4	18.0	18.8
Perpendicular to Rise	8.2	7.3	7.7
-10° F Dimensional Stability (7 Day Age)			
% Change in Length	-0.71	0.89	-0.01
% Change in Width	0.01	0.56	0.66
% Change in Thickness	-0.58	0.92	1.43
200° F Dry Heat Dimensional Stability (7 Day Age)			
% Change in Length	11.43	3.81	3.41
% Change in Width	7.86	2.13	1.72
% Change in Thickness	2.43	-0.36	0.24
158° F & 98% R.H. Dimensional Stability (7 Day Age)			
% Change in Length	6.44	3.20	4.47
% Change in Width	6.30	4.32	2.92
% Change in Thickness	-2.38	0.17	-1.41
Hot Plate Test			
% Mass Retention	83.1	76.4	77.9
% Thickness Retention	107.1	81.8	78.6

CONCLUSION

Currently, with the availability of isocyanate relatively stable, Oxid is marketing DS 1154 as a low OH polyester polyol for the lamination industry as an option. Along with giving a reduction in isocyanate usage, we feel this polyol offers equal to or better than performance characteristics when compared to our current Terol 563 (245 OH) polyol.

The higher functionality of the low OH polyols does allow for a reduction in index. Both DS 1122 and DS 1154 give better results than Terol 563. However, Oxid recommends beginning use of low OH polyols at a 2.5 index to collect sufficient data for validation of reducing index further.

FUTURE AND PENDING WORK

We plan to evaluate DS 1154 and reduction of index with laminator plant trials. Currently, we are working, both internally and with catalyst suppliers, to explore various catalyst packages necessary to process DS 1154. We are also evaluating, both internally and with surfactant suppliers, various surfactants to achieve the optimum surfactant for DS 1154. One note of interest here is that early studies reveal that usage of surfactant with DS 1154 formulations may not be necessary. This area will be evaluated further as fine cell structure and good initial k-values have been demonstrated.

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BIOGRAPHIES

Richard Donald

Richard Donald is Manager of Technical Services for Oxid L.P. He has 17 years experience in the Polyiso industry having worked for Atlas Roofing Corporation as Corporate Laboratory Technician and Process Development Manager from 1989 until 1997. He joined Johns Manville in 1997 as Process Development Specialist where he remained until joining Oxid in 2001. His responsibilities include assisting with the development of polyols for rigid foam applications, formulation development and processing support. He holds a BS degree in Medical Technology from the University of West Alabama.

Jose Luna

Jose Luna is a Project Leader at Oxid, L.P. Jose joined Oxid in 2002 as laboratory technician and upon graduation he joined Oxid as a full time Chemist. He is responsible for polyester polyol synthesis as well as development of PUR/PIR foam systems. He holds two BA degrees, one in Biology and one in Chemistry, from the University of Houston at Clear Lake and is currently working toward completion of his MS in Chemistry.

Al DeLeon

Al DeLeon is the VP of R & D for Oxid L.P. 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. He holds a BS degree in Chemistry, a MS in Chemical Engineering and has two years graduate studies in Polymer Science.