High Functional Aromatic Polyester Polyols for PUR Systems

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ABSTRACT

The transition to the next generation blowing agents has caused the Polyurethane industry to re-evaluate the necessity of polyester polyols in PU systems. The change to these novel blowing agents has caused diminished fire properties. This problem can be overcome by increasing polyester polyol levels. When attempting to introduce higher levels of polyester polyol, with current technology, the resulting system is inferior in terms of physical properties. In this paper the authors would like to introduce the next generation Terol polyols that will allow for greater loading of polyester in a system without sacrificing physical properties.

INTRODUCTION

With all blowing agent transitions there has followed a period of adjustment to the new features and drawbacks. The options for system houses replacing HCFC 141b are HFC 245fa, HFC 134a and cyclo/iso pentane blends. All of these blowing agents yield foam that is inferior to HCFC 141b in terms of fire properties. To compensate for this, higher level of fire retardants or polyester polyols are needed.

Unfortunately, most commercially available polyester polyols lack sufficient functionality to overcome problems caused by high loadings.

Table.1 Common System House Polyols

Polyol	OHV, mgKOH/g	Viscosity, cPs	Nom. Func.
Terol 250	250	5000	2.00
Terol 305	300	5500	2.15
Terol 256	265	12000	2.30

It is well known that using high loadings of these polyols will cause problems with dimensional stability, compressive strength, and demold time. It is also known using high loadings of fire retardants causes similar problems.

In our 2005 API paper we concluded that the polyester level was critical to obtaining the desired fire properties and that one must compensate for diminished physical properties by increasing the nominal functionality of the system (1). Last year we augmented functionality by introducing and/or elevating levels of sucrose/glycerin polyols. This year we will show that by changing to higher functional polyester polyols it is possible to increase polyester loading while maintaining physical properties. In this paper the authors would like to introduce the next generation polyester polyols.

GREEN STRENGTH MEASUREMENTS

While there are many ways to measure the contribution of crosslinking in a system there is one experimental method that is done quickly and reproducibly. This test measures firmness of a bun and correlates well with demold time. This test involves using a standard weight on top of a moveable shaft. After a specified amount of time the weight is placed on a bun of foam and a micrometer measures the penetration into the bun (2). The firmness of the bun or "green strength" is determined by the amount of penetration. Obviously, a quicker "greening" system will have less penetration.

Figure.1 Green Strength Apparatus

For pour in place systems a quicker demold time is related to foam strength at the given time. This test measures the strength of the foam at a specified time after mixing. So it follows that the green strength test will help predict demold times.

While there are many factors that regulate the resulting measurement, it is possible to set the main parameters so that one can compare different systems. The main physical factors that affect green strength measurement are: density, gel time, age of bun, cell orientation, and sample size. There are many chemical variables that affect green strength such as: system functionality, crosslink character, index, and degree of plasticization. By keeping physical factors constant we are able to compare different systems. It is also possible to set up experiments whereby you evaluate different components of a given formulation.

TEROL POLYOLS

As a result of the industry transition from CFC 11 to HCFC 141b, Oxid introduced Terol 256 for the pour in place market. HCFC 141b was softening the foam and higher functional polyols were required to provide strength. Although HFC 245fa does not weaken foam as much as HCFC 141b, it does provide diminished fire properties, and thus the need for more polyester polyol in the formulation. In 2005 Oxid introduced Terol 925 into the panels market. Terol 925 has even greater functionality than Terol 256 while maintaining similar aromatic content and viscosity.

Table.2 Oxid Polyols

Polyol	**OHV, mgKOH/g**	**Viscosity, cPs**	**Nom. Func.**
Terol 250	250	5000	2.00
Terol 305	300	5500	2.15
Terol 256	265	12000	2.30
Terol 925	300	11000	2.45

To prove the effect of functionality of the polyester polyol in a panel formulation we designed an experiment with the green strength apparatus. The four polyols listed above were treated so that all variables were eliminated, including hydroxyl number, and tested accordingly.

The polyols were evaluated in a simple panel formulation. The samples were mixed for 10 seconds with a drink mixer and then poured into a 6” x 6” x 4” cake box. The cake box was inside of a plywood mold to ensure that cell orientation was consistent in all tests. The green strength test was started at 18 minutes and data was collected up to 30 minutes. These experiments were run in triplicate. Table 3 lists the formulation and resulting green strength data collected. The “GS” field refers to the amount of penetration the weight made into the bun.

Table.3 Effect of Nominal Functionality of Polyester

Formulations	**Terol 250**	**Terol 305**	**Terol 256**	**Terol 925**
Terol Polyol	35.00	35.00	35.00	35.00
Polyether Polyol	28.50	28.50	28.50	28.50
Surfactant	1.10	1.10	1.10	1.10
Fire Retardants	16.00	16.00	16.00	16.00
Catalyst Package	0.90	0.90	0.90	0.90
Water	1.50	1.50	1.50	1.50
HFC 245fa	17.00	17.00	17.00	17.00
Total	100.00	100.00	100.00	100.00
PMDI	103.00	103.00	103.00	103.00
GS 18 min (mm)	0	0	0	0
GS 20 min (mm)	15.8	13.1	9.9	6.5
GS 25 min (mm)	19.9	17.1	12.9	8.4
GS 30 min (mm)	20.8	18.4	14.0	9.2

This table clearly shows the effect of polyester nominal functionality on green strength. Obviously, higher functional polyesters will make harder foams much quicker than lower functional polyesters. For a panel manufacturer this translates into faster demold times or increasing polyester loading while maintaining current demold times.

SUCROSE POLYOLS

During our investigation into pour in place formulations one of our first goals was to define which sucrose polyol would give the best green strength value. We looked at two commercially available polyols:

Table.4 Sucrose Polyols (3,4)

Polyol	**OHV, mgKOH/g**	**Viscosity, cPs**	**Nom. Func.**
Voranol 370	370	30580	7.00
Jeffol SG-522	520	27000	5.00

An experiment similar to Table 3 was carried out to define which sucrose polyol would result in better green strength numbers. There was no attempt to adjust hydroxyl value of the polyols. Instead, the Voranol 370 polyol was foamed at the same A/B ratio and at the correct index. The blowing agent and catalyst package were adjusted accordingly. The polyester level was elevated and the sucrose level was reduced. Also, the catalyst level was reduced. By doing so, we hoped to exaggerate the effects of the sucrose polyol. Table 5 lists the formulations and results.

Table.5 Effect of Sucrose Polyol

Formulations	SG 522	V 370.1	V 370.2	V 370.3
Terol 925	40.00	40.00	40.00	40.00
SG 522	18.00			
Voranol 370		18.00	18.00	18.00
Surfactant	1.15	1.15	1.15	1.15
Fire Retardants	22.00	22.00	22.00	22.00
Catalyst Package	0.35	0.30	0.25	0.45
Water	1.50	1.50	1.40	1.40
HFC 245fa	17.00	17.00	16.00	16.00
Total	100.00	99.95	98.80	99.00
Index	1.30	1.40	1.30	1.30
PMDI	103.00	103.00	93.00	93.00
GS 20 min (mm)	0.0	0.0	0.0	0.0
GS 25 min (mm)	15.1	>33	>33	19.1

These experiments show that Jeffol SG-522 makes harder foam quicker than Voranol 370. The Voranol 370 measurements were beyond what the micrometer could read. This was an obvious indication of a weak system. All three systems had the same gel time. As an adjunct experiment we added more gellation catalyst to formulation "V370.2" to increase gel time by 30 seconds. The average response at 25 minutes was 19.1 mm. This is still worse than Jeffol SG-522.

These findings seem to indicate that the green strength test is not an absolute measure of functionality. As the published nominal functionality of Voranol 370 is 7.0 and the published nominal functionality of Jeffol SG-522 is 5.0. We would conjecture that Voranol 370 might have longer alkoxy chains that would generate flexibility where SG-522 has shorter chains that provide more rigidity and strength. That conjecture would be reflected in the hydroxyl value differences.

We feel that these results validate this test method as it allows for a two very similar systems to be differentiated between. And for the purposes of comparing components, like polyesters, it provides meaningful data to compare functionality, where crosslinking character is similar – as is the case in the Terol 250, 305, 256 and 925 experiments.

HIGHER FUNCTIONAL TEROL POLYOLS

At Oxid, we would like to introduce polyester polyols that will allow for maximum loading in formulations without sacrificing physical properties. In order to do so we build in the maximum functionality possible. When we increase the functionality of aromatic polyester polyols the viscosity of these materials increases. We developed an experimental polyol DS-1243 that takes advantage of higher loadings of functionality enhancers built into the backbone of the polymer. As one would expect, at a nominal functionality of 2.6, the viscosity of the material is quite high.

Table.6 Properties of DS-1243

Polyol	OHV, mgKOH/g	Viscosity, cPs	Nom. Func.
DS 1243	320	68000	2.60

However, when we compare DS-1243 to our commercial products the effect of functionality is very apparent.

Table.7 Effect of High Functional Polyesters

Formulations	**Terol 250**	**Terol 305**	**Terol 256**	**Terol 925**	**DS 1243**
Terol Polyol	35.00	35.00	35.00	35.00	35.00
Polyether Polyol	28.50	28.50	28.50	28.50	28.50
Surfactant	1.10	1.10	1.10	1.10	1.10
Fire Retardants	16.00	16.00	16.00	16.00	16.00
Catalyst Package	0.90	0.90	0.90	0.90	0.90
Water	1.50	1.50	1.50	1.50	1.50
HFC 245fa	17.00	17.00	17.00	17.00	17.00
Total	100.00	100.00	100.00	100.00	100.00
PMDI	103.00	103.00	103.00	103.00	103.00
GS 18 min (mm)	0	0	0	0	0
GS 20 min (mm)	15.8	13.1	9.9	6.5	3.0
GS 25 min (mm)	19.9	17.1	12.9	8.4	4.1
GS 30 min (mm)	20.8	18.4	14.0	9.2	4.4

Terol DS-1243 produces much harder foam than any of our commercial products. Using proprietary technology we attempted to reduce the viscosity of DS-1243. We have synthesized two polyols very similar to DS-1243 in composition but with lower viscosity and lower functionality. Their properties are listed on Table 8.

Table.8 Properties of DS-1243, 1250 and 1252

Polyol	**OHV, mgKOH/g**	**Viscosity, cPs**	**Nom. Func.**
DS 1243	320	68000	2.60
DS 1250	300	14800	2.45
DS 1252	300	6800	2.40

These polyols were tested in the same panel formulation as before. Table 9 shows the results.

Table.9 Green Strength of DS-1250 and DS-1252

Formulations	**DS 1243**	**Terol 925**	**DS 1250**	**DS 1252**
Terol Polyol	35.00	35.00	35.00	35.00
Polyether Polyol	28.50	28.50	28.50	28.50
Surfactant	1.10	1.10	1.10	1.10
Fire Retardants	16.00	16.00	16.00	16.00
Catalyst Package	0.90	0.90	0.90	0.90
Water	1.50	1.50	1.50	1.50
HFC 245fa	17.00	17.00	17.00	17.00
Total	100.00	100.00	100.00	100.00
PMDI	103.00	103.00	103.00	103.00
GS 18 min (mm)	0	0	0	0
GS 20 min (mm)	3.0	6.5	7.3	7.1
GS 25 min (mm)	4.1	8.4	9.2	9.1
GS 30 min (mm)	4.4	9.2	9.9	9.8

These results were encouraging, as DS-1250 and DS-1252 perform similar to Terol 925. However, DS-1252 has a lower viscosity than Terol 925. This type of polyol would be very useful in applications where high functionality is needed and polyester levels are elevated but viscosity is a concern.

These findings show that it is possible to produce higher functional materials with lower viscosity. Our future intentions are to elevate the functionality of these polyols even more so, while maintaining a workable viscosity. This objective will be the subject of future publications.

PENTANE SOLUBLE TEROL POLYOLS

In addition to higher functional Terol polyols for hydrofluorocarbons, our aim is to introduce high functional aromatic polyester polyols into hydrocarbon based systems. Aromatic polyester polyols inherently have poor solubility with hydrocarbons. However, Oxid has the technology to develop polyols that have increased hydrocarbon solubility as well as higher functionality. Using this technology we have developed two possible candidates for use in the systems market. Their properties are listed in Table 10.

Table.10 Properties of Terol 305, 256, 1220 and 1240

Polyol	**OHV, mgKOH/g**	**Viscosity, cPs**	**CP Sol, pphp**
DS 1220	300	6440	44
Terol 305	300	5500	6
DS 1240	300	15900	40
Terol 256	300	12000	4

These polyols have much greater solubility than current technology. The possible uses for these materials include pentane blown continuous and discontinuous panels as well as spray foam. These polyols were tested against our commercial polyols. Table 11 shows the results.

Table.11 Green Strength of DS-1220 and DS-1240

Formulations	**Terol 305**	**DS 1220**	**Terol 256**	**DS 1240**	**Terol 925**
Terol Polyol	35.00	35.00	35.00	35.00	35.00
Polyether Polyol	28.50	28.50	28.50	28.50	28.50
Surfactant	1.10	1.10	1.10	1.10	1.10
Fire Retardants	16.00	16.00	16.00	16.00	16.00
Catalyst Package	0.90	0.90	0.90	0.90	0.90
Water	1.50	1.50	1.50	1.50	1.50
HFC 245fa	17.00	17.00	17.00	17.00	17.00
Total	100.00	100.00	100.00	100.00	100.00
PMDI	103.00	103.00	103.00	103.00	103.00
GS 18 min (mm)	0	0	0	0	0
GS 20 min (mm)	13.1	13.8	9.9	11.6	6.5
GS 25 min (mm)	17.1	17.1	12.9	14.7	8.4
GS 30 min (mm)	18.4	18.3	14.0	15.8	9.2

Please note that this testing was done with HFC 245fa because of the lack of pentane solubility in our existing products. Since we are only comparing polyesters, we feel that this experiment is valid.

As stated before, the green strength test allows one to compare similar components of a system. It is a useful test in finding the apparent functionality of new products. Since DS-1220 and DS-1240 are similar in composition to Terol 305 and Terol 256, we feel that we can make the statement that DS-1220 is equivalent to Terol 305 and DS-1240 is equivalent to Terol 256. This finding is encouraging for any researcher who is looking for pentane soluble analogs of these polyols. Our future area of research and publication will be in the area of creating a Terol 925 analog with high pentane solubility.

TRIALS

Using Terol 925 and DS-1240 we generated several starting formulations for spray polyurethane foam and pour in place panels. Unfortunately not all data was available by the time this paper will be published but missing data can be found during the API 2006 exposition.

HFC 245fa Spray Trials

Table.12 HFC-245fa Spray Trials

Formulations for HFC SPF	Wall	Roofing 1	Roofing 2
Terol 925	45.00	40.00	40.00
Polyethers	25.00	36.50	38.50
Surfactant	0.90	0.80	0.80
Fire Retardants	15.00	10.00	8.00
Catalyst Package	3.40	2.40	2.40
Water	1.70	1.30	1.30
HFC 245fa	9.00	9.00	9.00
Total	100.00	100.00	100.00
PMDI	103.00	103.00	103.00
Cream at 77ºF, s	3	5	5
Tackfree at 77ºF, s	10	14	14
Free rise density, pcf	1.71	2.25	2.25
B-side viscosity at 77ºF, cPs	880	1040	880
Applied Core Density, pcf	2.00	2.87	2.76
95% Rel Hum & 158ºF - 1 day, %Change Vol.	5.49	-1.38	-1.84
-10ºF - 1 day, %Change Vol.	-0.27	-0.50	-0.07
200ºF Dry Heat - 1 day, %Change Vol.	-8.52	-2.96	-3.35
Compressive Strength, psi	20.8	49.3	47.6
ASTM E84, Flame Spread	N/A	N/D	N/D
ASTM E84, Smoke Index	N/A	N/D	N/D
3 Day K-Value, 75ºF Mean Temp	0.1608	0.1627	0.1645

N/A = Not available at time of publishing, N/D = Not determined

These systems were sprayed on a Gusmer H2 machine with a Gusmer Gap gun, No.1 module. The preheater temperatures were 120 – 130ºF and dynamic pressure was 1000 psi.

From these results we can see that with a high functional polyester polyol it is possible to produce a dimensionally stable 2.0 pcf wall system with 45% polyester loading. Also it is possible to produce a 45+ psi compressive strength foam with 40% high functional polyester loading at less than 3.0 pcf. A formulation identical to “Roofing 1” was made with Terol 305 and the average compressive strength was 38 psi at 2.8 pcf - obviously nominal functionality of the polyester is an important contributor to the overall system strength.

HFC 245fa Pour in Place Panel Trials

Table.13 HFC-245fa Pour in Place Formulations

Formulations for HFC PIP	**PIP1**	**PIP2**	**PIP3**
Terol 925	40.00	50.00	42.00
JEFFOL SG-522	18.00	12.00	20.00
Surfactant	0.90	0.90	1.10
Fire Retardants	24.00	20.00	18.00
Catalyst Package	0.60	0.60	1.30
Water	1.50	1.50	1.60
HFC 245fa	15.00	15.00	16.00
Total	100.00	100.00	100.00
PMDI	105.00	103.00	143.00
Cream at 77ºF, s	25	25	25
String Gel at 77ºF, s	100	100	100
Free rise density, pcf	1.90	1.90	1.90
95% Rel Hum & 158ºF - 1 day, %Change Vol.	N/A	N/A	N/A
-10ºF - 1 day, %Change Vol.	N/A	N/A	N/A
200ºF Dry Heat - 1 day, %Change Vol.	N/A	N/A	N/A
Compressive Strength, psi	N/A	N/A	N/A
ASTM E84, Flame Spread	N/A	N/A	N/A
ASTM E84, Smoke Index	N/A	N/A	N/A

N/A = Not available at time of publishing

Oxid does not have the equipment to produce actual metal faced panels. As such, we were unable to determine demold times and measure any post growth. However, we were able to produce foam for PIP screening. The formulations were developed knowing that higher polyester loading and use of JEFFOL SG-522 will impart both better fire properties and make stronger foam. The formulations listed above were produced as free rise foam and trimmed to 4.0 inches of core foam for burning in the E84 tunnel. The panels were poured into a plywood mold and allowed to free rise. The samples were poured from a 20 lbs per minute low pressure machine. Unfortunately not all data was collected at time of publishing.

Hydrocarbon Spray Trials

Table.14 Hydrocarbon Roofing Spray Formulations

Formulations for HC Roofing SPF	HC 1	HC 2
Terol DS-1240	33.00	43.00
Polyethers	40.50	30.10
Surfactant	1.10	1.10
Fire Retardants	14.00	14.00
Catalyst Package	2.60	3.00
Water	0.80	0.80
80/20 cyclo/iso pentane	8.00	8.00
Total	100.00	100.00
PMDI	112.00	110.00
Cream at 77ºF, s	5	5
Tackfree at 77ºF, s	13	13
Free rise density, pcf	2.15	2.15
B-side viscosity at 77ºF, cPs	480	560
Applied Core Density, pcf	2.66	2.57
95% Rel Hum & 158ºF - 1 day, %Change Vol.	1.50	2.95
-10ºF - 1 day, %Change Vol.	0.34	-0.22
200ºF Dry Heat - 1 day, %Change Vol.	-0.14	-1.02
Compressive Strength, psi	46.9	42.7
ASTM E84, Flame Spread	N/A	N/A
ASTM E84, Smoke Index	N/A	N/A
3 Day K-Value, 75ºF Mean Temp	0.1591	0.1552

N/A = Not available at time of publishing

These formulations show the benefits of increased functionality of polyester polyols in pentane blown spray foams. Even with 43% loading of polyester at 2.6 pcf the compressive strength is 43 psi. This finding hints at the ability to achieve a 50 psi compressive strength at less than 3.0 pcf. That achievement would be very valuable to systems manufacturers.

Hydrocarbon Pour in Place Panel Trials

Table.15 Hydrocarbon Pour in Place Formulation

Formulations for HC PIP	**PIP4**
Terol DS-1240	40.50
JEFFOL SG-522	25.00
Surfactant	0.90
Fire Retardants	24.00
Catalyst Package	0.70
Water	1.40
80/20 cyclo/iso pentane	7.50
Total	100.00
PMDI	108.00
Cream at 77ºF, s	35
String Gel at 77ºF, s	100
Free rise density, pcf	2.00
95% Rel Hum & 158ºF - 1 day, %Change Vol.	N/A
-10ºF - 1 day, %Change Vol.	N/A
200ºF Dry Heat - 1 day, %Change Vol.	N/A
Compressive Strength, psi	N/A
ASTM E84, Flame Spread	N/A
ASTM E84, Smoke Index	N/A

N/A = Not available at time of publishing

This formulation was produced in the same manor as the HFC 245fa panels. Unfortunately, most of this data was unavailable at time of publishing but will be available during the API 2006 conference.

CONCLUSIONS

With the introduction of Terol 925 into the systems market, Oxid has signaled the direction for our future polyol development. It is our goal to produce polyester polyols that are able to replace polyether polyols without dramatic loss to foam physical properties. Terol 925 is one more step in that direction and with new polyols in development we should achieve our objective. By doing this we feel that our products will bring better fire properties and economic benefit to our customers.

Also, we are introducing polyester polyols for use in hydrocarbon blown systems, both panels and spray. We have introduced two new candidates for this market and we are working to improve on these polyols. Our objective will be to produce polyols with even greater functionality while providing necessary pentane solubility.

By using these novel high functional polyester polyols it is possible to make successful systems, both hydrofluorocarbon and hydrocarbon blown. These systems will impart better fire properties and provide economic incentive without sacrificing any physical properties.

Again, we apologize that not all data was collected in time, but the missing information will be presented at the API 2006 expo.

For detailed formulations please seek out an Oxid technical or sales person. Also, these formulations will be available at the Oxid hospitality suite at the API 2006 conference.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Jeremy Leteff, Richard Donald and Sherrell Sylvester of Oxid, L.P. for assistance with sample preparation and testing. We would also like to acknowledge the following companies for their assistance with reagent procurement and testing:

- BASF-Foam Enterprises Polyurethane
- Huntsman Polyurethane
- Honeywell Corporation
- Albemarle Corporation

We would like to extend thanks to North Carolina Foam Industries for use of their pentane capable spraying apparatus.

REFERENCES AND IMPORTANT NOTES

1. Luna, J., Shieh, D., DeLeon, A. “Class I Spray Foams for Wall Insulation Application using R-245fa.” Alliance for the Polyurethane Industry, Technical Conference and Trade fair, Houston, TX, October 17 – 19, 2005.
2. Riechmann, W., Nicola, W. “Class 1 Rated Polyurethane Foam Systems for Continuous Produced Metal Panels.” Polyurethanes 1988, Proceedings of the SPI – 31st Annual Technical/Marketing Conference, Philadelphia, PA, October 18 – 21, 1988.
3. Dow Chemical. Product Information Sheet “Voranol 370.” August 2001.
4. Huntsman Polyurethane. Product Brochure “JEFFOL SG-522.” 2006.

BIOGRAPHIES

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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 from the University of Houston at Clear Lake and is currently working toward completion of his MS in Chemistry.

David Shieh

As Manger of R&D for Terol polyols. David Shieh is responsible for both polyester polyol development as well as PUR/PIR rigid foam development using these polyols. Prior to joining Oxid in 1990, he was a Research Chemist at Chardonol, where he developed numerous polyester polyol for rigid foams. He holds several patents in the field of polyester polyols. His educational backgrounds include a BS degree in Chemistry, MS degree in Chemical Engineering and two years graduate studies in Polymer Science.

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.