

# Novel Polyester Polyol to Enhance the Physical Properties of R245fa Foams

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## ABSTRACT

As the end of 2002 nears, the task to find a replacement for R-141b intensifies. R-245fa is an available alternative blowing agent. However, because of its high cost, the amount of this material in a typical spray or PIP foam system must be minimized. This presents the system formulator with a significant challenge to meet the physical properties of foams.

Terol 708 has been developed to enhance foam physical properties because of its high functionality and high aromatic content. The high functionality will improve compressive strength and reduce demold time. Since high functionality will allow higher loading of this polyester polyol, this will also enhance foam fire properties.

We will present actual physical properties of field produced foams in both of these applications.

## INTRODUCTION

About thirteen years ago, the polyurethane foam industry was forced to move away from R-11 due to its ozone depletion potential. The accepted replacement was R-141b. Before transitioning to R-141b, the industry switched to R-11-reduced systems by using water/R-11 combinations up to 1:1 mole ratio. This caused a significant problem with dimensional stability. The permeation rate of carbon dioxide through the cell wall was much faster than that of air infusion into the cell. This caused a pressure difference between the inside and outside of the cell wall eventually leading to foam shrinkage. Once R-141b was implemented, we learned how to overcome the challenges associated with a new blowing agent.

A decade has passed, and we are facing the challenge again: the conversion from R-141b to suitable alternative blowing agents in the rigid foam markets. This process has accelerated as the final deadline approaches. Compared to R-11 conversion, this time we have many

potential candidates to replace R-141b. The list includes pentanes, R-245fa, R-134a, R-22 and water. As we all know, the majority of appliance manufacturers will go to R-245fa or R-134 and all the laminators will use pentanes. The question is what about the system houses? Which blowing agents are they going to use in their pour-in-place, discontinuous panel, and spray foam? The answer is all of the above. Depending on the process requirements and equipment capabilities, the system houses will use 245fa, water, pentane, R-134a, R-22, and combinations of these to make foam.

Last year, Oxid presented a paper, "Pour-in-place discontinuous panel using pentanes" at the API conference in Columbus, Ohio. This year, we would like to focus on R-245fa.

R-245fa is identified as 1,1,1,3,3-pentafluoropropane. It is a non—ozone-depleting compound with an acceptable global warming potential (GWP) and it is a not considered

Table 1. Blowing agent physical properties [1].

|  | R-141b                           | R-245fa  |
|--|----------------------------------|--|
| Structure  | Cl <sub>3</sub> FCH <sub>3</sub> | CF <sub>3</sub> CH <sub>2</sub> CHF <sub>2</sub> |
| Molecular weight   | 116                              | 134  |
| Boiling point, °C  | 32.1                             | 15.3   |
| Liquid Density, g/cc@ 20°C   | 1.24                             | 1.32   |
| Vapor pressure, PSIA @ 20°C  | 10                               | 17.8   |
| Vapor thermal conductivity,<br>BTU.in/hr.ft <sup>2</sup> .°F @ 44 °C | 0.084                            | 0.097  |
| BTU.in/hr.ft <sup>2</sup> .°F @ 25 °C                                | 0.072                            |  |
| Flame limits, volume%  | 7.6-17.7 <sup>a</sup>            | none <sup>a</sup>                                |
| Flash point, °C  | none                             | none   |
| Miscibility with polyol  | good                             | OK   |

<sup>a</sup>ASTM E681, ambient conditions, match ignition, dry air

a volatile organic compound (VOC). A summary of this data is presented in Table 1. The table shows a comparison

between R-141b and R-245fa in terms of physical properties.

The good things about R-245fa are:

- that it contains no chlorine,
- it is good for the environment,
- It has good miscibility with most polyether and polyester polyols,
- it shows less solvency effects towards the foam than with R-141b,
- its insulation value is close to 141b and better than pentanes or carbon dioxide.

The bad characteristics of R-245fa are:

- it contains no chlorine, which means the foam blown by R-245fa will need more flame retardant than R-141b blown foam to meet the same fire requirements
- it costs more than R-141b and
- it has higher vapor pressure than 141b.

Water or R-365mfc can be introduced to the system as a co-blowing agent with R-245fa to reduce the vapor pressure. Since 365mfc will not be available in the US, water is the only choice at this point. However, when too much water is used in the formulation, it will result in high friability, poor adhesion, and dimensionally unstable foam.

With all the concerns about the physical properties of 245fa and water co-blown foam, we believe that a new polyester polyol should be created to cope with the challenge.

Terol 708 is designed for PUR or PUIR spray and pour-in-place discontinuous systems. It has a higher hydroxyl number, functionality, and aromatic content than conventional polyester polyols. It also has a manageable viscosity. These unique properties of Terol 708 will allow the system formulators to use high loadings of polyester

|                            |                      |
|----------------------------|----------------------|
| Hydroxyl number            | 365                  |
| Acid number                | 1.0                  |
| Viscosity @ 25 ° C         | 6,000                |
| % Water                    | <= 0.15              |
| Functionality              | 2.45                 |
| 245fa solubility, pphp     | 30                   |
| PH                         | 6.6                  |
| Gel Set reactivity@ 25 ° C | 9 minutes 40 seconds |

polyol to make R-245fa and water co-blown foams with low smoke, low flame spread, and good dimensional stability properties.

## SPRAY FOAM

Our objective was to spray a roof insulation foam meeting all the requirements listed in Table 3. The Spray foam

formulations are shown in Table 4. The foam was blown with 50% carbon dioxide and 50% 245fa on a molar basis.

| Criteria                   | Required performance |
|----------------------------|----------------------|
| Density, pcf               | 3.0 or below         |
| Dimensional Stability      |                      |
| 28 day aging volume change | -2.0 to +10%         |
| Interlaminar Adhesion      | good                 |
| Surface Appearance         | Smooth               |
| Compressive Strength, psi  |                      |
| Parallel to rise direction | 40                   |
| Flammability, ASTM E-84    |                      |
| Flame Spread               | less than 75         |

|                  | Formula 1<br>Wt% | Formula 2<br>Wt% |
|------------------|------------------|------------------|
| Terol 708        | 38.7             | 0                |
| Terol 256        | 0                | 38.7             |
| Polyether Polyol | 32               | 32               |
| FR Package       | 14               | 14               |
| Catalyst Package | 4.1              | 4.1              |
| Water            | 1.2              | 1.2              |
| 245fa            | 10               | 10               |
| Total            | 100              | 100              |

The amount of R-245fa was limited to 10 parts per hundred parts of total polyol for two reasons: 1) to make the cost of this formulation close to a typical R-141b formulation cost, and 2) to keep the pressure in the drum low.

When using R-245fa there is always a concern with the pressure in a drum. Figure 1 shows the vapor pressure of the B blend at different temperatures. At 95°F, a typical Houston summer temperature, the vapor pressure of the system is about 6 psi. At 122 °F, the pressure will reach about 19 psi, while at 158 °F, the pressure will reach about 45 psi, well above the rupture limit of the drums. This is a major concern when using R-245fa in spray foam systems.

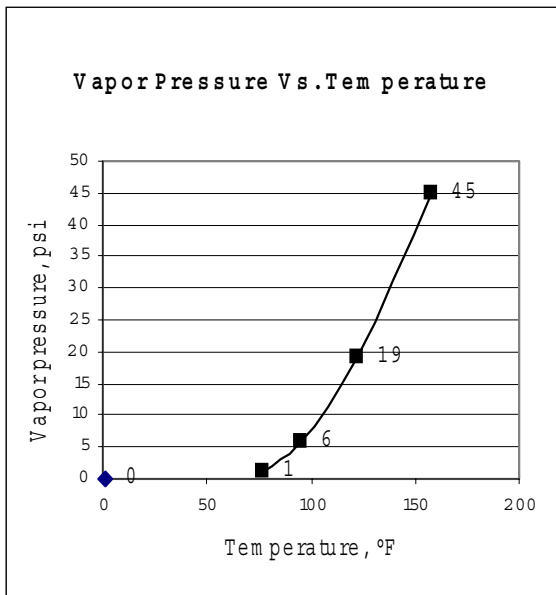


Figure 1

It is well known that a spray system containing large quantities of water and polyester polyols suffer from poor reactivity stability.

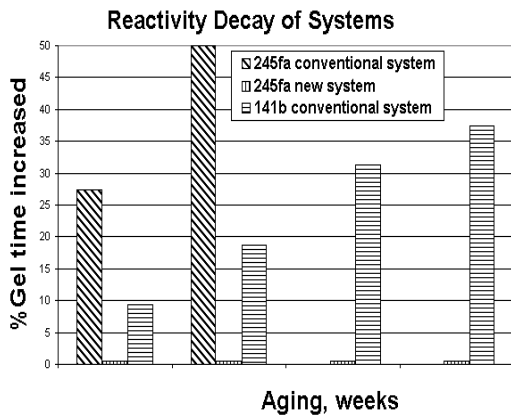


Figure 2

The acid number increases with time neutralizing the activity of the catalysts. When a conventional catalyst package containing the typical 24% lead naphthanate and DMEA was used, the reactivity decayed very rapidly as expected. However, with a properly selected catalyst package, a very stable system is obtained as Figure 2 shows. The accelerated test was conducted by placing the B blend in a pressure bottle exposed to a constant temperature oven at 50 °C. The gel time was measured initially and once a week. The aged samples were brought to 22°C before measuring gel time. The percentage increase in gel time was reported. Duplicated laboratory studies showed that properly selected catalyst packages

yield reactivity stable systems, even at high loadings of polyester polyol.

Table 5. Spray processing conditions

| Processing Conditions        |                           |
|------------------------------|---------------------------|
| Spray Unit                   | Gusmer H-2000             |
| Spray Gun                    | GX-7, no.1 module, 90 pcd |
| B Tank pressure, psi         | 80                        |
| Line Pressure                | 1500 psi                  |
| Line temperature             | 125 °F                    |
| Iso: B blend ratio           | 1:1                       |
| Cream/Gel/Tackfree in second | 1/5/6                     |



Figure 3. The appearance of 245fa/water co-blown spray roof foam

The foam system sprayed well. There was a smooth rise with no creep. The foam surface was very smooth and the interlaminar adhesion was very good. The physical properties of the foam were determined by the ASTM methods as listed in Table 7. The properties are shown in Table 6. The initial K factor is 0.15, which is much better than all water blown foam. The flame spread and smoke index predicted by the Albemarle cone calorimeter was 28.4 and 418 respectively. The E-84 tunnel test was conducted on a sample consisting of two-pass foam with two-inch total thickness. The correlation between the Albemarle cone calorimeter and the E-84 test results were excellent. All physical properties of the foam made meet the requirements stipulated in table 3.

|  |       |
|--|-------|
| Formula No                                       | 1     |
| In Place Density, pcf                            | 2.6   |
| Compressive Strength, psi                        |       |
| In parallel direction                            | 41.55 |
| In perpendicular direction                       | 24.7  |
| Initial K Factor, btu.in/hr.ft <sup>2</sup> . °F | 0.15  |
| % Close cell                                     | 94.4  |
| Dimensional Stability                            |       |
| % Volume Change after 21 day aging               |       |
| @-20 °F  | -0.95 |
| @ 200 °F   | 0.17  |
| @ 158°F/95% humidity                             | -0.44 |
| Cone Calorimeter <sup>a</sup>                    |       |
| Prediction                                       |       |
| Flame Spread                                     | 28.4  |
| Smoke Density                                    | 418   |
| E-84 tunnel test <sup>b</sup>                    |       |
| Flame Spread                                     | 30    |
| Smoke Density                                    | 500   |

<sup>a</sup> Albemarle cone calorimeter.

<sup>b</sup> Omega Point

|                       |             |
|-----------------------|-------------|
| Density               | ASTM D-1622 |
| % Close cell          | ASTM C-2856 |
| K-factor              | ASTM C-518  |
| Compressive strength  | ASTM D-1621 |
| Dimensional stability | ASTM D-2126 |

Table 8 shows a comparison between two R-245fa Spray foam systems. T708 represents the foam referred to previously in this paper. T256 is a foam system developed a few years ago using Terol 256, Oxid's highest functionality/highest aromatic content polyester polyol available at the time. T708 foam has lower flame spread and smoke index than T256. T708 foam, even with lower density, has better overall dimensional stability than T256 foam. This clearly indicates that Terol 708 is higher in functionality than Terol 256.

|                                |       |       |
|--------------------------------|-------|-------|
| Formula No                     | 1     | 2     |
| In Place Density,              | 2.6   | 2.87  |
| Dimensional Stability          |       |       |
| % Volume Change after 21 day : |       |       |
| @-20 °F                        | -0.95 | -0.70 |
| @ 200 °F                       | 0.17  | 2.04  |
| @ 158°F/95% humidity           | -0.44 | 2.26  |
| E-84 tunnel test               |       |       |
| Flame Spread                   | 30    | 35    |
| Smoke Density                  | 500   | 840   |

|                                   |       |
|-----------------------------------|-------|
|                                   | Wt%   |
| Terol 708                         | 27.24 |
| Voranol 370 <sup>a</sup>          | 27.14 |
| RB7980 <sup>b</sup>               | 16.28 |
| TEP <sup>c</sup>                  | 5.43  |
| B8433 <sup>d</sup>                | 1.63  |
| TMR2 <sup>e</sup>                 | 1.52  |
| PC5 <sup>e</sup>                  | 0.11  |
| PC46 <sup>e</sup>                 | 0.22  |
| Water                             | 1.38  |
| 245fa                             | 19    |
| Total                             | 100   |
| Index                             | 1.45  |
| Isocyanate, Rubin M. <sup>f</sup> | 110   |
| Reactivity @ 17 °C                |       |
| Cream                             | 23    |
| Gel                               | 120   |
| Tack-free                         | 195   |
| Free rise density, pcf            | 1.6   |
| B side appearance                 | clear |

<sup>a</sup> Dow Chemical Corporation.

<sup>b</sup> Albemarle Corporation.

<sup>c</sup> Triethyl phosphate, Eastman Chemical Corj

<sup>d</sup> Degussa Corporation.

<sup>e</sup> Air Product Chemical Corporation.

<sup>f</sup> Huntsman Polyurethane.

**POUR IN PLACE DISCONTINUOUS PANEL**

Our goal was to make a dimensionally stable, pour-in-place discontinuous panel with E84 class I rating. Table 10 shows the formulation as well as hand-mix laboratory results.

The B-side appearance was clear indicating that the system has enough R-245fa solubility. The processing conditions are listed in table 9.

| Processing Conditions          |            |
|--------------------------------|------------|
| Pour Unit                      | Graco      |
| Maximum Throughput, lbs/minute | 100        |
| B Tank pressure, psi           | 80         |
| Iso. B temperature             | Ambient    |
| Mold temperature               | 122 °F     |
| Machine pressure, psi          | 1000       |
| Iso: B blend, weight ratio     | 1:1.03     |
| Cream/Gel/Tackfree in second   | 2.5/80/104 |
| Free rise density, pcf         | 1.6 – 1.7  |
| Demold time, minutes           | 30         |

The pour unit was a Graco machine with a maximum output of 100 lbs/min. Again, the machine pressure was 1000 psi. The B tank was pressured by nitrogen to 80 psi. The isocyanate and B blend was at ambient temperature. A horizontal mold, measuring two feet by eight feet and four inches in thickness, was heated to 122 °F. The reaction index was 145. The gel time in the machine was 80 seconds and the tack-free was 104 seconds. The free rise density was around 1.6 – 1.7 pcf.

The system flowed well. The minimum fill density was 2.1 pcf. One panel was demolded after 10 minutes with no observed post-growth. Several 4-inch thick panels with an in-place density of 2.2 pcf were made for E-84 tunnel test. Table 11 lists all the physical properties of the foam.

|  |      |
|--|------|
| Molded Density, pcf                              | 2.2  |
| Compressive Strength, psi @ 2.01 core density    |      |
| In parallel direction                            | 28.2 |
| In perpendicular direction                       | 19.3 |
| Initial K Factor, btu.in/hr.ft <sup>2</sup> . °F | 0.15 |
| Percent closed cell                              | 94.7 |
| Dimensional Stability                            |      |
| % Volume Change after 28 day aging               |      |
| @ -20 °F   | 0.20 |
| @ 200 °F   | 1.70 |
| @ 158°F/95% humidity                             | 3.08 |
| Cone Calorimeter <sup>a</sup>                    |      |
| Prediction                                       |      |
| Flame Spread                                     | 23.1 |
| Smoke Density                                    | 693  |
| E-84 tunnel test <sup>b</sup>                    |      |
| Flame Spread                                     | 15   |
| Smoke Density                                    | 650  |

<sup>a</sup> Albemarle cone calorimeter.

<sup>b</sup> Omega Point

The correlation established in a paper published last year in Columbus, between the Albemarle Cone Calorimeter and the E-84 Tunnel test continues to be very good. The pictures, taken at Omega Point after the E-84 Tunnel Tests, showed that all three test panels were blackened during the test. As we said earlier, R-245fa has a tendency to produce more smoke than R-141b while burning. This can be seen in figures 4 and 5.



Figure 4



Figure 5

The smoke of these foams can be suppressed by increasing the reaction index from 145 to 165, increasing the loading of polyester polyol, or by selecting a different fire retardant package. Table 12 contains the final proposed formulation that should have the required E-84 Class I rating based on the prediction of the cone calorimeter.

| <i>Table 12. Formulation of Pour-in-Place panel.</i> |            |
|--|------------|
|  | <b>Wt%</b> |
| Terol 708  | 28.64      |
| Voranol 370 <sup>a</sup>                             | 20.83      |
| RB7980 <sup>b</sup>                                  | 20.83      |
| TEP <sup>c</sup>                                     | 2.6        |
| B8433 <sup>d</sup>                                   | 1.82       |
| TMR2 <sup>e</sup>                                    | 1.72       |
| PC5 <sup>e</sup>                                     | 0.11       |
| PC46 <sup>e</sup>                                    | 0.24       |
| Water  | 1.56       |
| 245fa  | 21.63      |
| Total  | 100        |
| Index  | 1.80       |
| Isocyanate, Rubinate M. <sup>f</sup>                 | 138        |

<sup>a</sup> Dow Chemical Corporation.

<sup>b</sup> Albemarle Corporation.

<sup>c</sup> Triethyl phosphate, Eastman Chemical Corp.

<sup>d</sup> Degussa Corporation.

<sup>e</sup> Air Product Chemical Corp.

<sup>f</sup> Huntsman Polyurethane.

Panels will be made and tested in the E-84 tunnel test, and the numbers will be available by the time of the Conference.

## CONCLUSIONS

With Terol 708, it is possible to develop a 245fa/water co-blown system for discontinuous panels that meets the Class I E-84 tunnel test rating and a R-245fa/water co-blown spray foam system for roofing applications.

With only ten percent of R-245fa in the roofing spray system, the vapor pressure of the system seems to be manageable. With proper selection of spray catalyst packages, the system containing 1.2% water and 38% polyester polyol can have a stable reactivity for a long time.

Because these are PUR or PUIR formulations, both systems need a fire retardant package to improve the overall fire properties of the foam. Triethyl phosphate seems to be very good to fight the flame spread.

The cone calorimeter is again proven to be a reliable tool to predict the flame spread and smoke index in the actual E-84 tunnel test.

We accomplished the spray goal that meets all the requirements of the roofing spray. However, we came a little bit short of achieving the pour-in-place goal.

We do not know at this point, the maximum amount of water that can be employed as co-blowing agent with 245fa without encountering the problem of foam shrinkage. The density and over-all functionality of the foam are also part of the equation. Nonetheless, we are able to demonstrate two good working systems blown by 245fa and water.

## ACKNOWLEDGMENTS

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## BIOGRAPHIES

### Marshall Devine

He started his career with Jefferson Chemical Co in 1963. He has extensive experience in flexible foams, rigid foams, and formulating systems for both spray and pour-in-place panels. Before joining Foam Enterprises as a System Development Specialist, he worked for Texas Urethanes, Premium Polymers, and Flexible Products.

### David Shieh

As manager of R&D for Terol polyols, David Shieh is responsible for 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 polyols for rigid foams. He holds several patents in the field of polyester polyols. His educational background includes a BS degree in Chemistry, MS degree in Chemical Engineering, and two years graduate studies in Polymer Science.