Silicone Surfactants for Pentane Blown Rigid Foam

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1. Abstract

Auxiliary blowing agents are utilized in most polyurethane applications, however the impact of these blowing agents on final foam properties is most critical in the rigid foam area. In most rigid applications the blowing agent serves a dual role in both generating the foam volume, and in addition the residual gas remaining within the cells functions to reduce the rate of heat transfer and improve the insulation properties of the foam.

Traditionally CFC's have been used as the preferred blowing agent within the polyurethane industry due to their excellent volatility, flammability, and thermal characteristics. Within the last few years the use of many grades of CFC's have come under restriction due to their implication in depleting atmospheric ozone levels, and these products will ultimately be banned according to the Montreal Protocol. Other types halogen containing replacements such as HCFC's and HFA's are being examined as potential replacement for the CFC's, however the future viability of these types of materials is in question as their toxicological, environmental and economic impact are still under examination.

One of the most viable alternatives to replace CFC's as a blowing agent in rigid foam formulations is n-pentane or one of the isomers of pentane. These materials are considered to be excellent replacement candidates due to their availability, low pricing, and most importantly, zero ozone depleting potential (ODP). The use of pentane in rigid continuos laminate boardstock foam has already been initiated, with commercial utilization anticipated in other rigid applications within the next 12 to 18 month.

Pentane is the most non polar of the auxiliary blowing agents used in urethane foam applications. As a result of the chemical and physical characteristics of pentane, the solubility and compatibility with the polyurethane raw materials, and developing foam mixture are completely different compared to all other blowing technologies. This low solubility of pentane in the final polyurethane foam matrix results in very low diffusion rates of pentane, therefore initially obtained thermal insulation values are maintained with minimal drift.

Due to the inflammable nature of pentane, new processing and handling procedures are required in addition to modifications to the foam formulations. Considering the potential flammability and explosion hazards, minimizing pentane emissions during production is an absolute requirement to safely utilize this new technology. The current and proposed environmental legislations on organic

emissions is another reason to ensure minimal levels of VOC's when using pentane as a blowing agent in the production of rigid foams.

One of the primary applications for panels produced by the continuos lamination process is in the construction industry, where the flammability rating is one of the most important properties of these materials. The use of an inflammable liquid as a blowing agent where most of the residual material is retained within the foam cells, requires further formulation modifications to maintain the flame retardancy characteristic of the foams. System modifications, such as incorporating flame retardant additives and water as a co-blowing agent, further increases the polarity of the resultant polyol preblend. The increased polarity of this preblend accompanied by the very low polarity of the pentane puts further limitations on the total system solubility. To improve the solubilization/compatilization of pentane into these systems new surfactant technology is required.

The primary role of a silicone surfactant in a rigid polyurethane system is to emulsify the incompatible reactants of the preblend and phases that occur during the reaction. In order to achieve similar processing performance and final foam physical properties with these modified formulations containing pentane, new specially designed silicone surfactant molecules are required.

In order to investigate the silicone surfactant structure / foam performance relationship, a design study was initiated in a variety of formulations. In addition to the standard performance evaluations, special techniques were developed and effected to understand the solubility, emulsification and compatibility characteristics of pentane during the production and aging of the foam.

This paper will discuss the influence of different silicone surfactants on the emulsification and stabilization of pentane in polyol premixes, reaction mixtures and during foam formation. The influence of the silicone surfactants on the physical properties of the final foam will also be discussed.

2. Introduction

Rigid polyurethane foams are widely used because of the high insulation values that these materials provide per unit area compared to other materials, and also the dimensional stability of the products which makes them effective structural components. The excellent insulation capabilities of these foams are well known in both the appliance and construction industries. The unique processing of rigid polyurethane foam allows for the production of parts having difficult geometries. The molded parts have excellent surface appearance, good physical properties and most important minimal weight. The following is a list of typical applications for rigid polyurethane foam.

- Rigid bunstock or block production (insulating, construction industry)

- Continuous lamination of insulating panels with rigid or flexible surfaces

- Appliance industry (freezers, refrigerators cooling/freezing cabinets)

- Pour in place technology (gap filling at construction sites, pipe insulation)

- Structural foams (computer housings, wood imitation)

- Packaging foams

As described previously, the main advantage of rigid polyurethane foam versus other insulation materials is the very low thermal conductivity per unit area. An overview of commonly used insulating materials is given in Table 1.

Table 1: Thermal conductivity of commonly used insulating materials

Material	Density [Kg/m³]	λ value [W/m*K]	Thickness required for same insulation [mm]
PUR Foam (CFC)	32	0,017	20
Polystyrene Foam	16	0,035	44
Rockwool	100	0,037	46
Cork board	220	0,049	61
Timber: white pine	350-500	0,112	140+

Historically the most commonly used blowing agents for rigid polyurethane foams have been CFC 11 and CFC 12. With the ratification of the Montreal Protocol and other legislations to reduce or eliminate the use of these materials, there is the urgent need to identify and qualify replacement products to serve as auxiliary blowing agents in polyurethane formulations. An overview of some of the alternative blowing agents that are being used or are under investigation is shown in Table 2.

Table 2: Physical blowing agents for rigid polyurethane foams

Product	Formula	BP [° C]	MW [g/mol]	λ [W/m*K]	ODP
CFC's / H-CFC's					
R 11	CCl_3F	23,8	137,4	0,0078	1,000
R 12	CCl_2F_2	-29,8	120,9	0,0096	1,000
R 123	$C_2H_4Cl_2$	27,9	152,9	0,0096	0,020
R 134a	C_2H_5F	-26,5	102,0	0,0145	0,000
R 141b	$C_2H_3Cl_2F$	32,0	117,0	0,0087	0,150
R 142b	$C_2H_3ClF_2$	-9,2	100,5	0,0129	0,060
R 152a	$C_2H_4F_2$	-24,7	66,0	0,0147	0,000
R 22	$CHClF_2$	-40,8	86,5	0,0109	0,050
R 356	$C_4H_4F_6$	24,6	166,0	0,0095	0,000
R 22/142b (40/60)		-28,0	(94,9)	(0,0121)	(0,056)
Pentanes					
n-Pentane	C_5H_{12}	36,0	72,0	0,0150	0,000
c-Pentane	C_5H_{10}	49,0	70,0	0,0125	0,000
i-Pentane	C_5H_{12}	28,0	72,0	0,0135	0,000
Others					
PF5050*	C_5F_{12}	30,0	288,0	0,0124	0,000
PF5060*	C_6F_{14}	56,0	338,0	0,0124	0,000
PF5052*	$C_5F_{11}NO$	49,0	299,0	0,0101	0,000
LBL 2	C_3H_7Cl	35,7	78,5	0,0122	0,003
CO2	CO_2	-78,5	44,0	0,0170	0,000

[(): calculated values,*: performance fluids ex 3M]
The different pentane isomers and HCFC 141b are considered to be the most promising candidates to replace CFC's as blowing agents / insulatants in rigid polyurethane applications.

2.1 Pentane Technology

Pentane blown formulations are typically based upon water co-blown technology, which was the first development implemented to reduce the use of CFC's in rigid foams. As a result of the different chemical and physical nature of pentane compared to CFC's and H-CFC's, the use of pentane as an auxiliary blowing agent requires different approaches to the formulation technology. From a chemical stand point, the most important difference is the significantly lower polarity of pentane compared to other conventional blowing agents. This lower polarity results in a reduced solubility of pentane in the polyols and other polyurethane raw materials. The solubility values of pentane in some typical rigid polyurethane raw materials is given in Table 3.

Table 3: Solubility of n-pentane in different rigid polyurethane raw materials.

Type	vol. % n-Pentane soluble
Aromatic Polyether 1	6,0
Aromatic Polyether 2	14,0
Halogenated Polyether	12,0
Aliphatic Polyether	13,0
Crude MDI	11,0

As a result of the differences in pentane solubility in the various components of the rigid polyurethane system, there are two possible types of formulations that can occur. The first system is one in which the pentane is soluble within the polyol and a clear homogenous preblend solution is formed. The other type of system, that results when the pentane is either partially or totally insoluble in the polyol, is one in which the pentane must be emulsified into the premix formulations.

It is possible to increase the solubility of pentane in the system through the use of some commercially available polyester polyols. The solubility characteristics of n-pentane in formulations based on either pure polyether or polyester polyols and mixtures of these formulations is presented in Figure 1. The formulation in Table 4 was used to determine the influence of the polyester polyol concentration on pentane solubility:

Table 4:   Formulations to determine n-pentane solubility.

| Product	Polyether formulation	Polyester formulation
Polyester Polyol		71,7
Polyether Polyol	71,7	
DMMP	12,0	12,0
Water	2,0	2,0
DABCO® TMR	1,7	1,7
POLYCAT® 8	1,3	1,3
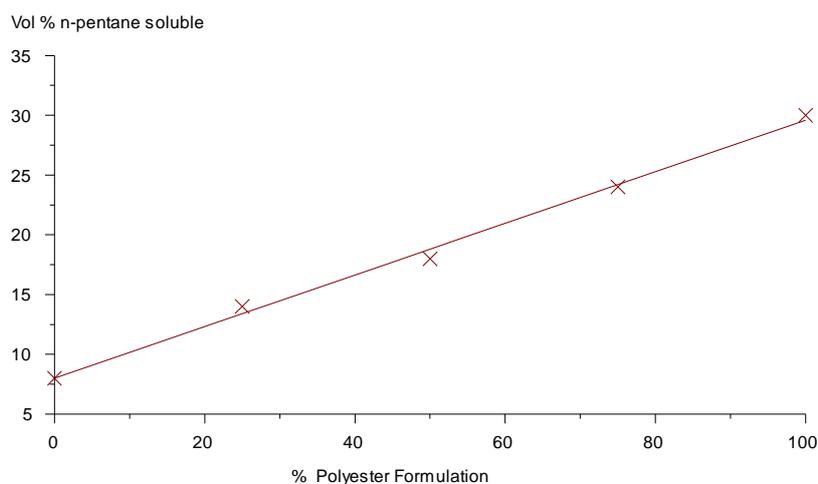
Figure 1: Solubility of n-pentane vs. polyol preblend composition.

The rigid polyurethane industry uses two different types of technologies to produce pentane blown foam. The type of process employed, is dependent upon the solubility or stability characteristics of the system. For pentane soluble formulations or stable emulsions, process 1 shown in Figure 2 is used. For unstable emulsions an alternative procedure outlined by process 2 is used (Figure 3). Process 1 requires an explosion protected area where the polyol preblend working vessel is located. This vessel is also used for dissolving pentane into the polyol preblend. The polyol stream between the vessel and the mixing head can be setup with a recirculation loop to allow for discontinuous production, such as molding and pour in place applications. Continuous production of rigid foams (panels and buns) does not require polyol recirculation.

In process 2, pentane is injected into the polyol preblend stream just before the mixing head. A static mixer is used for the homogenization of the polyol preblend and pentane streams. This process can only be utilized in continuous production, as it does not allow for polyol preblend/pentane recirculation. The major advantage of this second process, versus the process described earlier, is a minimization of pentane amounts in the foam production area. There is an economic advantage to this process as only the pentane vessel has to be located in an explosion protected area. This process allows for the production of pentane blown rigid foam from either soluble or emulsion type formulations, regardless whether the emulsion is stable or not.
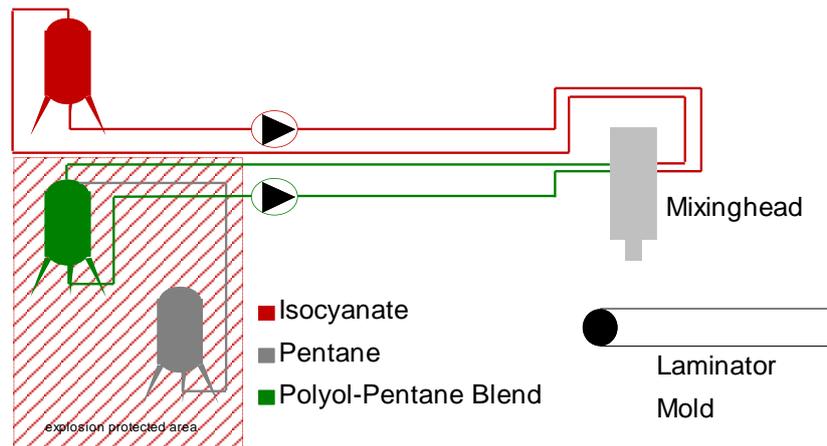
Figure 2: Continuous or discontinuous process for producing pentane blown rigid foam
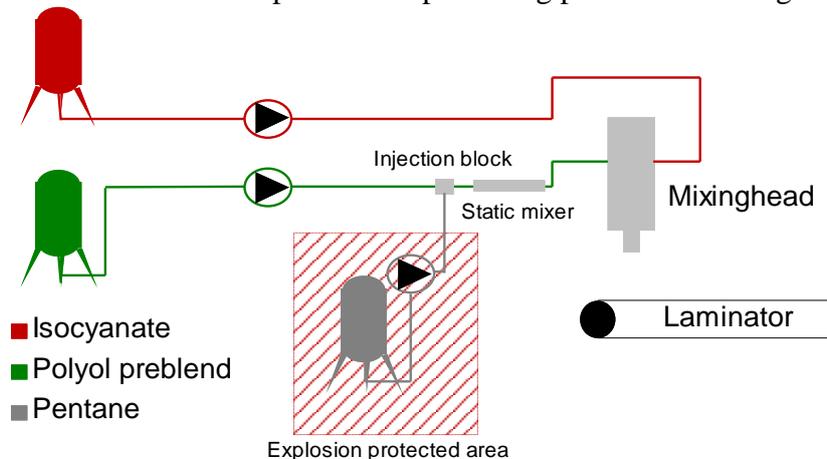

Figure 3: Continuous production of rigid foam panels using pentane as blowing agent

2.2 Silicone Surfactants

The ability of a silicone surfactant to function as both, an emulsifier of urethane components and as a foam cell stabilizer, is dependent upon the composition and molecular structure of the surfactant. A silicone surfactant is comprised of two dissimilar components, a non polar-lipophilic (hydrophobic) silicone portion, and a polar-hydrophilic polyether portion. This difference in polarity between functional groups present within the same molecule results in organo siloxane copolymers exhibiting extremely high surface activity. The low surface tension exhibited by polymethylsiloxanes, coupled with its high surface activity results in low surface energies in aqueous and organic phases. This lowering of surface tension results from the low cohesive force of the molecules, which allows favorable orientation and packing of siloxane methyl groups at an interface.

Two basic types of silicone polyether surfactants can be prepared dependent upon the type of bond between the siloxane and polyether. When the bond is between the silicone atom on the backbone and the carbon atom of the polyether (Si-C), the copolymer is considered non hydrolyzable. When the bond is between the silicone atom and an oxygen atom on the polyether (Si-O-C), the molecule is considered hydrolyzable and susceptible to cleavage in acid or basic medium. Many of the surfactants produced commercially are of the non hydrolyzable form. The general molecular structure for a non hydrolyzable silicone surfactants can be represented by the structure in Figure 4.
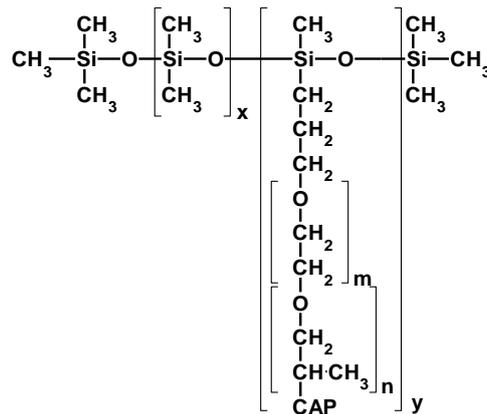
Figure 4: General structure for a silicone surfactant.

The silicone surfactant due to its unique structure performs a variety of functions during the foaming process including emulsification of reactants, nucleation and stabilization of the developing foam. The silicone-polyether surfactant is solubilized in the polyurethane intermediates in a manner that it functions as an emulsifier promoting efficient mixing. The degree to which the surfactant compatilizes these different reactants depends upon the relative quantities and ratios of silicone and polyether present in the molecule and the relative number of ethylene and propylene oxide units present in the polyether. A higher percentage of polyether in the surfactant (greater ratio of y to x), with more ethylene oxide units present in the polyether (greater ratio of m to n), results in copolymers with increased water solubility. Increased emulsification of the reaction mixture contributes to superior flowability. The surface active nature of the silicone surfactants increases both, the volume of air nuclei mixed into the reactants (nucleation) and decreases the tendency of the gas to diffuse from smaller bubbles to larger ones. This results in a foam with finer more uniform cells. Once air nuclei are formed in the initial foam system, the expanding cells must be stabilized until the catalysts have initiated polymerization of the cell walls and struts to provide the final matrix of the foam. The surfactant accomplishes this stabilization effect by increasing capillary flow which allows the liquid in the expanding cell walls to draw toward the thinner area of the cell (susceptible to rupture) and restore the thickness of the cell wall.

The properties of the silicone surfactant copolymer can be adjusted by varying the following parameters of the structure in Figure 4.

- Polysiloxane / polyether ratio and overall copolymer molecular weight (ratio of x to y).

- Ethylene oxide to propylene oxide ratio (EO/PO) and length of these side chains (ratio of m to n, polyether molecular weight).

- The number of polyether pendants attached to the silicone backbone.

- The type of the capping group.

One of the methods utilized to quantify the relative performance attributes of a surfactant in terms of its relative solubility characteristic is HLB (**H**ydrophilic - **L**ipophilic - **B**alance). The current Air Products rigid silicone surfactant product line can be characterized by this method and is presented in Table 5.

Table 5. Air Products Rigid Silicone Surfactant Range

Product	HLB	Application
DABCO DC193	13,18	CFC or H-CFC blown formulations
DABCO DC5103	10,85	CFC or H-CFC blown formulations for high polar systems
DABCO DC5098	12,57	CFC or H-CFC blown formulations, isocyanate compatible
DABCO DC5357	9,60	Water or high water co-blown formulations
DABCO DC5367	8,41	Water or high water co-blown formulations
DABCO DC5374	10,10	Water co-blown formulations
DABCO DC5454	10,55	Water co-blown formulations

In order for the silicone surfactant to produce the desired effect during the foam formation it is necessary for the molecule to align itself at the surface of a developing cell or at the chemical interface between the dissimilar chemical reactants. Systems having a higher polarity, such as water co-blown formulations therefore require less polar surfactants (lower HLB value), conversely systems characterized by low polarity, such as all CFC blown formulations, require surfactants having higher polarity (higher HLB value). Although the different pentane isomers are soluble in many polyol preblends, the compatibility with the system decreases during the course of the reaction as a result of the changing concentration of urethane and/or urea present within the reaction mixture. This phasing of the reactants of the system is due to the incompatibility of polyurethane and/or polyurea with aliphatic hydrocarbons (pentane). In pentane blown formulations, silicone surfactants must provide for a different level and type of emulsification and stabilization throughout the entire foaming process when compared to standard co-blown formulations. These emulsification requirements are presented in the following Table:

Requirement	Soluble Process	Emulsion Process
Fine distribution of pentane in emulsion		+
Quick emulsification of pentane in polyol preblend		+
Stable emulsification of pentane in polyol preblend		+
Maintain pentane emulsified during foam formation	+	+

3. Experimental

Four formulations were selected for this laboratory program, that are typical for the systems currently being commercialized for the production of continuous rigid insulation panels. The foam formulations that were chosen varied in type of polyether polyol and content of polyester polyol. These formulations are shown in Table 6. The differences in polyols within these systems allowed for a complete understanding of the performance capabilities of the silicone surfactants. In formulations E 1 and E 2 the pentane is mainly insoluble in the polyol and must be emulsified into the preblend, while the addition of a polyester polyol to formulations S1 and S2 increased the solubility characteristic and a clear preblend resulted. All formulations in this study are water co-blown containing 2 % water, with 12 % DMMP flame retardant additive. The systems were catalyzed with DABCO TMR trimerisation catalyst (index 131 - 158) and POLYCAT 8, a balanced gel blow catalyst. Polyether 1 and 2 were selected in order to understand the silicone surfactant performance

in formulations with different capabilities for solubilizing pentane (Table 3). Although polyether polyol 2 solubilizes 14 vol. % n-pentane, a heterogeneous polyol preblend was obtained (formulation E 2), and the pentane had to be emulsified into the system. The laboratory study included the evaluation of 21 different silicone surfactant molecules from a design study, all of the Air Products standard commercial surfactants and two competitive products.

Table 6:   Formulations for foam evaluations.

Product	OH [mg KOH/g]	E 1	S 1	E 2	S 2
Polyether 1	485	71,7	46,2		
Polyether 2	560			71,7	46,2
Polyester Polyol	345		25,5		25,5
DMMP	0	12,0	12,0	12,0	12,0
n Pentane	0	10,0	10,0	10,0	10,0
Water	6232	2,0	2,0	2,0	2,0
DABCO TMR	463	1,7	1,7	1,7	1,7
POLYCAT 8	0	1,3	1,3	1,3	1,3
Silicone Surfactant	varied	1,3	1,3	1,3	1,3
Crude MDI		170	170	170	170
NCO Index		146	158	131	146

3.1 Laboratory Handmix Procedures

Handmix procedures were used for all foams prepared during this study. The following represents a typical procedure used in these evaluations.

100 g of polyol preblend, containing polyol, n-pentane, water, catalyst and silicone surfactant where pre weight in a 1 l plastic cup. The corresponding amount of isocyanate was added to the polyol preblend and mixed for 10 s at 5000 rpm using a 4 cm, mixing blade. The reaction mixture was poured immediately into a 2.9 l paper bucket to allow the rigid polyurethane foam to rise freely.

For the evaluation of foam flammability the reaction mixture was poured into a paper box to obtain larger foam samples necessary for performing foam flammability.

3.2 Determination of Foam Properties

The following foam properties were measured on all samples generated during the course of the study.

- Cup and core densities allowing for calculation of density distribution, as a measure of flow and skin formation.

  Density Distribution [%] =100 * Density Core / Density Cup

- Thermal conductivity as λ value. All measurements have been performed on the Anacon Model 88 equipment 24 hours after the foams were prepared. Aged λ values were obtained from foams stored in an oven at 70 ° C for 1 week.

- DIN 53421 standard was used for determining foam compression strengths. Both compression strengths, parallel and perpendicular to the foam rise direction, were measured. The isotropy , as a measure of cell geometry was calculated by dividing the perpendicular by the parallel compression strength.

- Closed cell content [%] measurements were conducted on a Beckmann air comparison pycnometer.

- Cell size was calculated while determining the percentage closed cells. The closed cell determination method includes a correction for the cut cells on the   surface of the foam sample.   The cell size was obtained by dividing the volume of cut cells by the surface area of the foam   samples.

- The content of pentane in the foam was determined using a Perkin Elmer Autosystem Gas Chromatograph. The rigid foam samples were placed in a glass tube containing 20 g of concentrated sulfuric acid and 5,000 g of n-octane, the tube was immediately closed. The rigid foam decomposes in the presence of the acid, releasing the entrained pentane which is absorbed into the octane. The octane phase was analyzed, using gas chromatography.

- Foam flammability was determined using a method similar to that described in DIN 4102 (ignition of face). A gas burner, with a flame of 1 cm diameter approximately 3 cm length, was used as an ignition source. The flame was kept on the foam surface for 15 seconds, then the gas burner was removed. The time was measured from removing the flame from the foam until the flame self extinguished. The foam sample weight was determined both before ignition and after the flame was extinguished. The weight loss measurement and the time to flame extinguishment, represent the flame retardancy of the foam.

4. Results

All obtained results are summarized in four Tables attached in an appendix as follows:

- Table 7 , Silicone surfactant performances in the S 1 formulation
- Table 8 , Silicone surfactant performances in the E 1 formulation
- Table 9 , Silicone surfactant performances in the S 2 formulation
- Table 10, Silicone surfactant performances in the E 2 formulation

One Silicone surfactant from the design study provided for excellent performances specially regarding minimized pentane emissions during foam formation and minimal losses of pentane during foam aging. This product obtained the XF-H25-73 experimental silicone surfactant name.

Performances of this silicone surfactant are included in all Tables and Figures together with the standard and competitive products.

5. Discussion

In emulsion formulation, all silicone surfactants (with the exception of DABCO DC5367) yielded foams with reduced density distributions, i.e., the foams produced from these formulations had minimal differences between the cup and core densities. This result can be interpreted that in the soluble formulations, the pentane has a higher affinity to the polymer and condenses more readily in the surface of the foam layer resulting in a thicker skin. This result can be observed in Figures 5 and 6, where density distribution values vary between 80.0 and 91.5 % in the soluble formulations, and between 89.5 and 93.0% in the emulsion formulations.
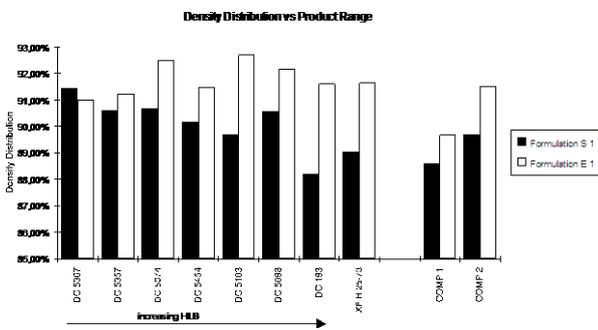
Figure 5: Density Distribution; S1-E1 Formulations
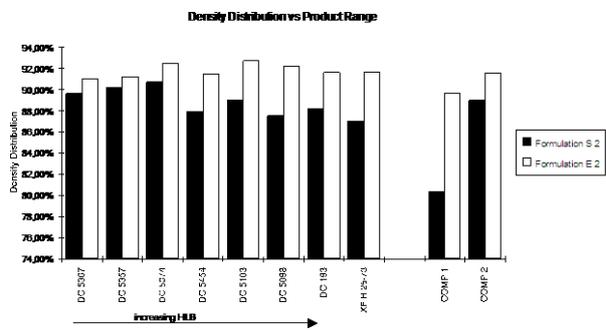
Figure 6: Density Distribution; S2-E2 Formulations

In Figures 7 and 8 the results for the cellular pentane content in non aged foams in all 4 formulations are presented. The pentane content values in foams prepared from soluble type formulations are significantly higher than for those prepared from emulsion type formulations. These results indicate that lower pentane losses occur in these systems during foam formation. It is obvious that different silicone surfactant structures have a significant impact on the level of pentane loss that occurs. The silicone surfactant is able to retain the pentane emulsified into the reacting mixture for a longer period of time, contrary to the increased concentration of urethane/urea linkages and corresponding decrease in pentane solubility. This increased emulsification effect is obvious in the results obtained with
XF-H25-73 silicone surfactant, which yielded foams with the highest pentane content in all four test formulations.
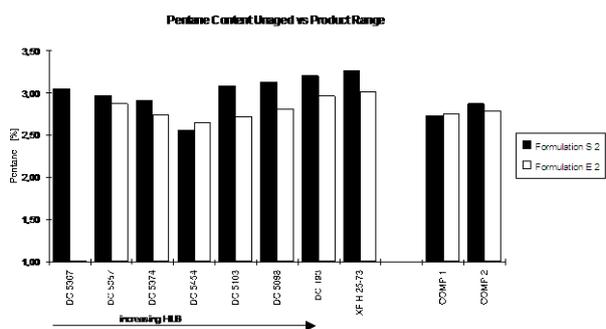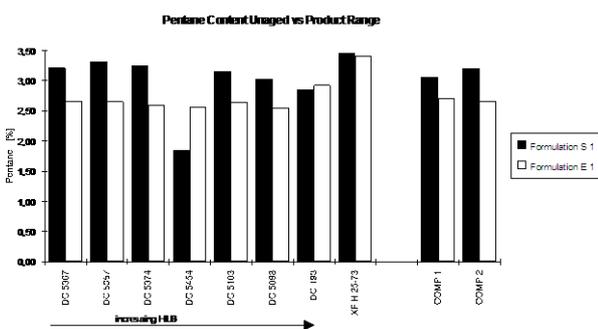
Generally foams performed with soluble formulations tend to loose significantly more pentane during the aging process as seen in Figures 9 and 10, due to higher pentane affinity to the polymer allowing for easier pentane diffusion to foam surface.

Silicone surfactants play an even more important role regarding the control of pentane losses during foam aging. Surfactants with specific structures, like XF-H25-73 experimental silicone surfactant, allow for not only keeping most of the pentane in the foam during the foam formation, but they also prevent pentane diffusion from the foam.
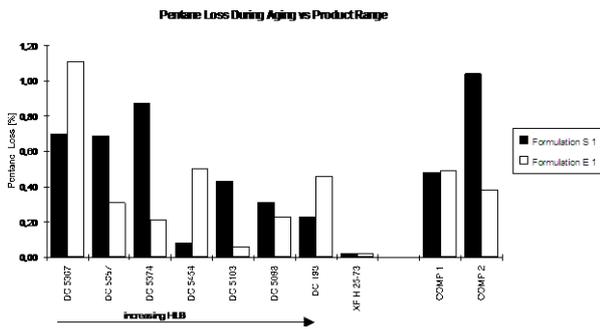
Figure 9: Pentane Losses During Aging
      S1- E1 Formulation
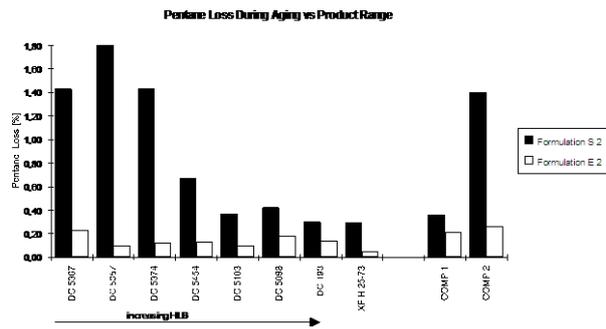
Figure 10: Pentane Losses During Aging
      S2-E2 Formulation

The surfactants ability to reduce λ value degradation over time is lower in the S1 and E1 formulations when using Polyether 1 compared to formulations employing polyether 2. In both, the soluble and emulsion formulations, the initial thermal conductivities for all surfactants were similar, regardless whether polyether 1 or polyether 2 was used. Foams prepared using emulsion formulations(E1 and E2) performed lower aged λ values in the foams, which resulted in substantially lower Δ λ values as presented in Figures 11 and 12. This is specially in polyether 2 containing formulationn (Figure 12) noticable. The lower λ values were probably a result of reduced pentane losses, that occurred in these formulations as was described previously.
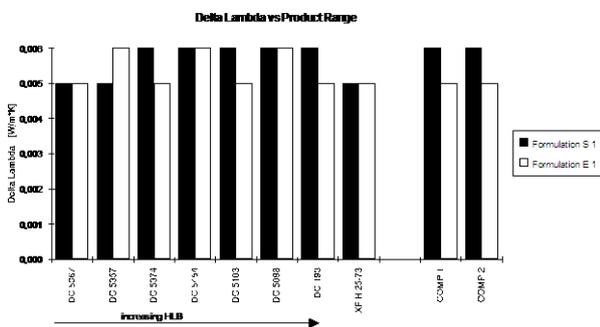
Figure 11: Δ λ of S1-E1 Formulation
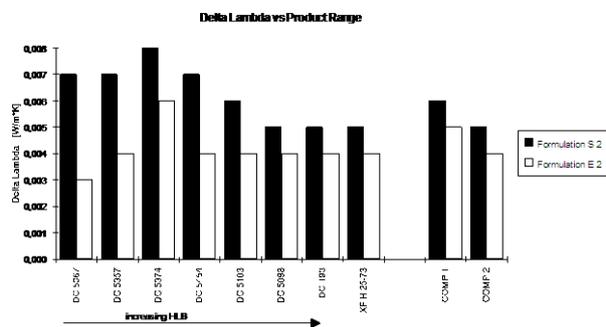
Figure 12: Δ λ of S2-E2 Formulation

It is well known that a silicone surfactant can have a significant impact on foam flammability. The flame retardancy of the foams in this study was characterized by the mass loss and time of flame extinguishment, these results are presented in Figures 13 and 14. In the emulsion formulation, the

foams prepared from surfactant DABCO DC193 demonstrated excellent results in both, time of extinguishment and mass loss. DABCO DC193 improves the mass loss values of the emulsion formulation to the same level of performance as that observed when using a higher performance FR polyester based soluble formulation. From figure 13 it is also evident that the surfactants HLB value has an influence on the extinguishing time. Less polar surfactants with higher HLB values perform better (lower extinguishing time) in the emulsion formulations, while the more polar surfactants with lower HLB values perform better in the soluble formulations. Experimental silicone surfactant XF-H25-73 demonstrated excellent performance in soluble formulations (mass loss 0.4 g., ext. time 1.0 s.), substantially better than the competitive products and similar to the best performing product; DC 5357. In the emulsion formulations experimental silicone surfactant XF-H25-73 did not perform as well as DABCO DC193, although the results were similar.
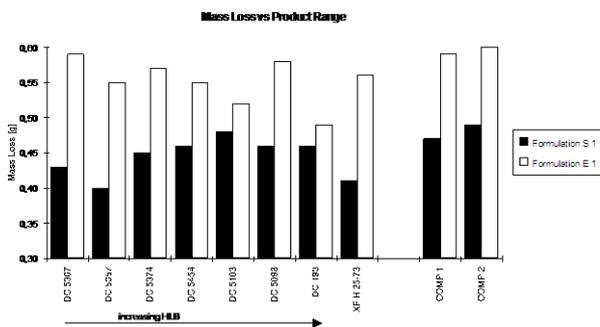
Figure 13: Mass Loss During Burn Test   Figure 14: Extinguish Time S1 E1 Formulations
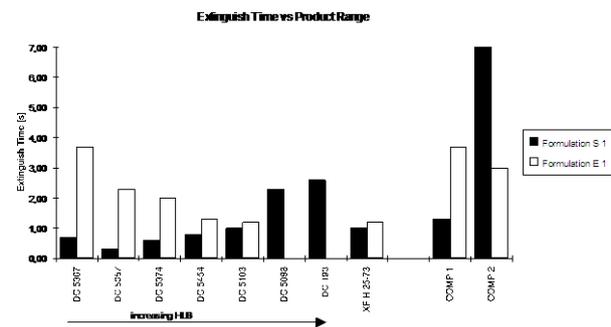
Note System

In order to find the products with the best overall performance and to make results comparable all the results were relativated employing a note system .

The best performance of the foams is defined by the following criteria:

Closed cell content	maximum	Cup Density	minimum
Cell size	minimum	Core Density	minimum
λ Initial	minimum	Density Distribution	maximum
λ aged	minimum	Pentane Content Initial	maximum
Δ λ	minimum	Pentane Content Aged	maximum
Compression Strength ‖	maximum	Δ Pentane Content	minimum
Compression Strength ⊥	maximum	Mass Loss	minimum
Isotropy	maximum	Extinguish Time	minimum

(Best performance = 1   Worse performance=6)

The results of this calculations for XF-H25-73 and the commercially available silicone surfactants of the Air Products portfolio and competitive products are presented in Table 11.

Table 11: Overall performance of silicone surfactants as notes from 1-6.

Surfactant	S1	E1	S2	E2

DABCO DC 5367	2,34	4,18	3,97	4,11
DABCO DC 5357	2,17	3,46	4,11	2,36
DABCO DC 5374	2,33	3,38	4,23	3,12
DABCO DC 5454	2,76	3,76	4,04	3,27
DABCO DC 5103	2,41	2,96	2,67	2,39
DABCO DC 5098	2,42	3,35	2,27	2,13
DABCO DC 193	2,51	**2,53**	**2,22**	2,18
XF H 25-73	**1,97**	2,64	2,64	**1,82**
COMPETITIVE 1	2,73	3,54	3,12	2,90
COMPETITIVE 2	3,15	3,23	3,36	2,60

6. Conclusion

The industry trend towards total reduction of CFC's has led to reformulation in many industries. The conversion in rigid foam systems to water co-blown formulations and zero ODP auxiliary blowing agents has resulted in many processing and foam physical properties deficiencies. During this study, more than 30 silicone surfactants were evaluated in four different water co-blown formulations, using n-pentane as an auxiliary blowing agent. The silicone surfactants were evaluated in two different formulation types. In the first system the pentane was soluble within the polyol preblend, while in the second system the pentane was only partially soluble and was emulsified into the premix formulation. The results of these performance evaluations demonstrated that:

- Density distribution values are lower for the soluble formulation due to pentane condensation in the surface layer resulting in thicker foam skins.

- Soluble formulations are characterized by lower losses of pentane during the foaming process, resulting in higher initial pentane concentrations.

- Losses of pentane during the foam aging at 70 °C were higher with soluble formulations, resulting in higher degradation of foam insulating capabilities.

Experimental silicone surfactant XF-H25-73 was identified during this study as product demonstrating excellent performance while maintaining pentane levels in the foam during the foam formation process and aging. This characteristic should translate into production process to minimize emission of pentane during the foaming process. The improved pentane retention will allow for lower losses of pentane during foam aging thereby maintaining foam thermal conductivities.

In the flammability test, experimental silicone surfactant XF-H25-73 demonstrated superior performance specifically in soluble formulations. Of the two formulations evaluated during this study, the soluble ones consistently yielded better flammability results. One of the Air Products silicone surfactant types DABCO DC193 demonstrated excellent results in emulsion formulation, results that were comparable to those typically obtained in soluble systems.

Based on the results of this study, our future work will involve combining very good surfactant overall performance with its capability for producing stable pentane emulsions in polyol preblends. This work will be performed in emulsion formulations which the appliance industry is considering to use in the future.

Remark: The flammability results presented within this study are not an indication of the actual flame spread performance of the foams.

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8. Acknowledgments

9. Biographies

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Jobst Grimminger received his Dipl.Ing. (FH) Diploma in Chemistry in 1983 from Fachhochschule Aalen Germany. After 8 years of experience in development and technical service support in ZELU Chemie, a system house in Germany, Jobst joined Air Products and Chemicals PURA GmbH & Co in Norderstedt in 1991. Mr. Grimminger is a senior technical service chemist responsible for rigid polyurethane foam additives and additives for high density molding applications.

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Dr. Mark Harakal is currently Technical Director in Air Products and Chemicals PURA GmbH & Co. Other positions Mark has held while at Air Products, include Manager of the Polyurethane's Application Development and Technical Service Group, and Project manager in Commercial Development. Prior to joining Air Products in 1986, Mark worked for Union Carbide as a Senior Chemist in the Surfactant Research and Application Development Group. Dr. Harakal received a B.S degree and Ph.D. degrees in Organic Chemistry from Drexel University.

Krunoslav Muha

Krunoslav Muha is a TS&D group manager in Air Products and Chemicals PURA GmbH & Co. He is responsible for technical service and product development in flexible molded, flexible slabstock and rigid foam applications. Other positions Krunoslav has held while at Air Products, include senior chemist in flexible cold cure molded area and flexibles foam group manager. Krunoslav received his

B.S in chemical technology, from the University in Ljubljana-Slovenia in 1981. Prior to coming to Air Products he was employed by Color Medvode-Slovenia as a polyurethane R&D group leader .

Appendix

Table 7 : Silicone Surfactant Performances in the S1 Formulation

Silicone	Closed Cells	λ initial	λ aged	Cup Density	Core Density	Comp. Strength ‖	Comp. Strength ⊥	Mass loss	Exting-ushing Time	Pentane Content initial	Pentane Content aged
	[%]	[W/m*K]	[W/m*K]	[Kg/m3]	[Kg/m3]	[KPa]	[KPa]	[g]	[s]	[%]	[%]
DC5367	95,9	0,024	0,029	30,52	27,91	184,50	57,50	0,43	0,70	3,21	2,51
DC5357	96,6	0,024	0,029	30,79	27,90	180,60	69,00	0,40	0,30	3,32	2,63
DC5374	95,6	0,024	0,030	30,89	28,01	181,10	66,20	0,45	0,60	3,25	2,38
DC5454	95,6	0,025	0,031	31,38	28,29	177,90	69,20	0,46	0,80	1,84	1,76
DC5103	95,1	0,024	0,030	30,98	27,78	178,70	71,50	0,48	1,00	3,15	2,72
DC5098	95,4	0,024	0,030	31,26	28,31	176,00	78,70	0,46	2,30	3,03	2,72
DC193	94,7	0,024	0,030	32,23	28,42	152,60	79,70	0,46	2,60	2,84	2,61
XF-H25-73	95,6	0,023	0,028	31,68	28,21	149,10	93,00	0,41	1,00	3,45	3,43
COMP. 1	92,8	0,023	0,029	32,15	28,48	177,80	66,80	0,47	1,30	3,06	2,58
COMP. 2	93,7	0,024	0,030	31,84	28,56	193,30	69,10	0,49	7,00	3,20	2,16

Table 8: Silicone Surfactant Performance in the E 1 Formulation

Silicone	Closed Cells	λ initial	λ aged	Cup Density	Core Density	Comp. Strength ‖	Comp. Strength ⊥	Mass loss	Exting-ushing Time	Pentane Content initial	Pentane Content aged
	[%]	[W/m*K]	[W/m*K]	[Kg/m3]	[Kg/m3]	[KPa]	[KPa]	[g]	[s]	[%]	[%]
DC5367	96,3	0,025	0,030	30,55	27,80	168,70	81,00	0,59	3,70	2,66	1,55
DC5357	95,5	0,023	0,029	30,42	27,75	181,40	70,90	0,55	2,30	2,65	2,34
DC5374	94,2	0,024	0,029	30,53	28,24	175,30	82,10	0,57	2,00	2,59	2,38
DC5454	94,8	0,024	0,030	31,29	28,62	182,30	77,80	0,55	1,30	2,56	2,06
DC5103	95,4	0,024	0,029	30,94	28,68	184,00	79,50	0,52	1,20	2,64	2,58
DC5098	95,6	0,024	0,030	30,86	28,44	175,90	86,20	0,58	0,00	2,54	2,31
DC193	95,4	0,024	0,029	30,62	28,05	172,40	93,20	0,49	0,00	2,92	2,46
XF-H25-73	95,1	0,024	0,029	30,74	28,17	178,00	86,50	0,56	1,20	3,40	3,38
COMP. 1	95,4	0,024	0,029	30,60	27,44	175,00	83,30	0,59	3,70	2,70	2,21
COMP. 2	96,4	0,024	0,029	30,54	27,95	175,60	85,20	0,60	3,00	2,66	2,28

Table 9: Silicone Surfactant Performances in the S 2 Formulation

SURFACTANT	Closed Cells	λ initial	λ aged	Cup Density	Core Density	Comp. Strength ∥	Comp. Strength ⊥	Pentane Content initial	Pentane Content aged
	[%]	[W/m*K]	[W/m*K]	[Kg/m3]	[Kg/m3]	[KPa]	[KPa]	[%]	[%]
DC5367	93,32	0,024	0,031	29,33	26,28	185,80	59,40	3,05	1,62
DC5357	94,86	0,024	0,031	29,46	26,57	192,20	65,30	2,97	1,17
DC5374	95,93	0,024	0,032	29,42	26,69	195,40	61,40	2,91	1,48
DC5454	95,55	0,024	0,031	30,07	26,43	206,70	77,00	2,56	1,89
DC5103	96,74	0,023	0,029	29,58	26,33	183,30	62,60	3,08	2,71
DC5098	93,16	0,023	0,028	29,97	26,23	176,40	95,20	3,13	2,71
DC193	96,90	0,023	0,028	29,86	26,34	156,70	76,20	3,20	2,90
XF-H25-73	95,23	0,023	0,028	31,00	26,97	147,50	89,00	3,26	2,97
COMP. 1	97,60	0,023	0,029	30,85	24,80	191,20	61,90	2,73	2,37
COMP. 2	96,14	0,024	0,029	29,53	26,27	190,80	67,10	2,87	1,47

Table 10: Silicone Surfactant Performances in the E 2 Formulation

SURFACTANT	Closed Cells	λ initial	λ aged	Cup Density	Core Density	Comp. Strength ∥	Comp. Strength ⊥	Pentane Content initial	Pentane Content aged
	[%]	[W/m*K]	[W/m*K]	[Kg/m3]	[Kg/m3]	[KPa]	[KPa]	[%]	[%]
DC5367	87,42	0,027	0,030	29,28	26,24	180,10	88,80	1,01	0,78
DC5357	93,89	0,023	0,027	29,29	26,68	205,20	68,50	2,87	2,77
DC5374	93,20	0,023	0,029	30,13	27,33	209,30	76,60	2,74	2,62
DC5454	92,08	0,024	0,028	30,98	27,49	213,90	79,30	2,65	2,52
DC5103	93,21	0,023	0,027	29,42	26,67	204,70	73,50	2,72	2,62
DC5098	93,92	0,024	0,028	29,24	26,92	215,10	87,70	2,81	2,63
DC193	93,40	0,023	0,027	29,28	26,72	203,20	78,00	2,96	2,82
XF-H25-73	92,72	0,023	0,027	29,06	26,61	200,60	81,80	3,01	2,96
COMP. 1	93,61	0,023	0,028	30,02	27,35	217,20	76,10	2,75	2,54
COMP. 2	93,39	0,023	0,027	29,83	26,85	209,50	81,70	2,78	2,52