New Silicone Surfactants for Rigid Polyurethane Foam

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ABSTRACT

Rapid changes in blowing agent technology are forcing the development of new rigid foam systems. Particular attention must be focused on the role of the surfactant and other additives to obtain desired physical, processing, and performance properties as non-CFC blowing agents are employed. Two new surfactants have been developed to meet the diverse requirements of these systems based on an optimization of surfactant structure versus performance. DABCO® DC5604 surfactant has been designed for HCFC-141b / water co-blown and all-water blown rigid polyurethane systems to provide an optimal balance of both thermal and mechanical properties. XF-J2557 experimental surfactant was developed for finer cell structure, improved flame retardancy and emulsification in n-pentane rigid lamination formulations. A new technique will also be described for evaluating the polarity of a silicone surfactant, enabling better characterization, development and selection of surfactants for specific applications.

INTRODUCTION

Changes in polyurethane foam formulations have been dramatic in the past decade as CFC blowing agents have been eliminated in most countries throughout the world. No application area has been more affected than rigid polyurethane foam because CFCs acted not only as a physical blowing agent but also as a thermal insulating medium within the foam cells. Further changes in blowing agent technology for rigid polyurethane foam are likely since HCFCs will be eliminated at the beginning of the next century and since further optimization of pentane technology is underway. In addition to the physical blowing agent changes, the level of the chemical blowing agent, water, has generally increased. These dramatic changes in both chemical and physical blowing agents have significantly impacted the polarity, reactivity, flowability, thermal and mechanical properties of the polyurethane rigid foam.

Blowing agent technology continues to evolve and therefore our work has focused on developing surfactants and catalysts to meet the objectives of foam processors who are investigating or utilizing new blowing agents. Regional attention is important since the evolution of blowing agents has varied with geographical location. In Europe and Asia, development has focused on cyclopentane for appliance applications and n-pentane for lamination and pour-in-place applications, although recent work [1] also considers iso/n-pentane mixtures for appliances. Isomers of pentane have zero ozone depletion potential and low global warming potential. Progress has been made so that the energy efficiency of pentane systems is becoming competitive with reduced CFC11/ water co-blown technology. In North America, HCFC-141b is the dominant blowing agent because a large emphasis is placed on energy efficiency in addition to global warming and ozone depletion potential; insulation inefficiency leads to environmental penalties because of increased electrical demands. When North America converted from CFC-11, HCFC-141b

systems provided better energy efficiency than pentanes with low capital investment for conversion. However, HCFC-141b is expected to be eliminated after the turn of the century and foam processors who use HCFC-141b are searching for alternatives. In all regions, blowing partially or solely with water has become another important formulating tool.

The need to meet tough environmental, processing and property requirements makes the search for and implementation of new blowing agents difficult, however, creative additives development can aid in the transition. For example, we developed DABCO DC5555 for pentane blown rigid lamination to minimize pentane emissions during foaming and aging while also improving emulsification of the reactive components. As another example, in the conversion from CFC-11 to water co-blown systems, catalyst changes were required, such as the addition of POLYCAT 5, to better utilize the higher levels of water found in these new formulations. In HCFC-141b formulations, foam plastisizing can occur resulting in dimensional stability deficiencies, and so trimerization catalysts such as the DABCO TMR series of catalysts were utilized to provide better mechanical properties. New surfactants such as DABCO DC5357 have been developed to provide finer cells and improved k-factor in new appliance formulations blown with HCFC-141b.

Air Products and Chemicals continues to develop new catalysts and surfactants to meet regional needs as blowing agent technology in rigid foam evolves. To assist in this goal, a new technique that we developed to characterize the performance of silicone surfactants based on polarity will be described. Also in this paper, two surfactants are introduced for the new blowing agent technologies: DABCO DC5604 for improved thermal and mechanical properties in HCFC-141b / water co-blown and all-water blown rigid systems

and XF-J2557 surfactant for finer cell structure, improved flame retardancy and emulsification in n-pentane rigid lamination formulations.

I. SURFACTANT STRUCTURE

DABCO® surfactants for polyurethane foams are members of the general class of nonhydrolyzable coupled polydimethylsiloxane/polyalkyleneoxide graft copolymers as illustrated in Figure 1. A silicone surfactant structure is actually a complex distribution since it is the reaction product of two polymeric raw materials each having an average molecular weight and a molecular weight distribution. For clarity, all surfactants will be described in terms of an "average" structure represented by Figure 1 where x is the average number of dimethylsiloxy groups, y is the average number of methylpolyethersiloxy groups, m is the average number of polyethyleneoxide groups (EO), n is the average number of polypropyleneoxide units (PO), and R is the polyether capping group. In designing silicone surfactants, structural parameters are used to denote characteristics of the surfactant. For example, the degree of polymerization of the siloxane backbone (DP) is stated in terms of x and y yielding $DP = x + y + 2$. Also, the ratio of hydrophobic siloxane backbone to hydrophilic polyether is defined by the x/y ratio (also known as the D/D' ratio). Similar parameters are used to represent the chain length and polarity of the polyalkyleneoxide.

Me   Me
| |
$Me_3SiO(SiO)_x(SiO)_ySiMe_3$
| |
Me $(CH_2)_3$
|
O
|
$(CH_2CH_2O)_m$
|
$(CHCH_3CH_2O)_n$
|
R
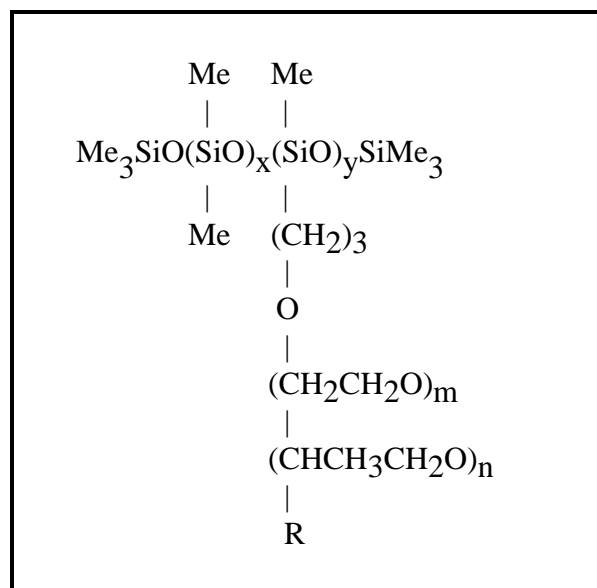
Figure 1. Generalized structure of a polydimethylsiloxane/polyalkyleneoxide copolymer (silicone surfactant) used for emulsification and stabilization in polyurethane foam production.

II. NEW METHOD FOR DETERMINING SURFACTANT POLARITY

The structure of the surfactant in Figure 1 varies widely depending on the application. In producing rigid polyurethane foam, initial viscosities are high because of highly functional polyols and isocyanates, and stabilization demands on the surfactant are therefore low. Instead, the primary role of a silicone surfactant in a rigid polyurethane system is to emulsify incompatible reactants in the preblend and the various phases that are formed during the reaction by reducing interfacial tension between incompatible phases.   In addition, the surfactant must regulate cell structure during foam formation to improve thermal insulation and dimensional stability properties. As a result, the siloxane DP and the polyether length for a rigid surfactant needs to be relatively low compared with surfactants for other polyurethane applications.

The optimum choice of surfactant for rigid foams depends on the polarity of the system and of the surfactant. For example, DABCO DC193 is a more polar surfactant than DABCO DC5357. Low polarity surfactants are less compatible with polyurethane systems which tend to be more polar, and therefore have a stronger driving force to migrate to the cell interface. In other words, they are more surface active. During mixing, the work required for creation of new surface area is proportional to the interfacial tension. Use of surfactants which provide lower interfacial tension, therefore, will lead to the formation of larger surface area or more bubbles. Since it has been shown that no new bubbles are created during the polymerization reaction [2], more and therefore smaller bubbles during mixing will lead to finer celled foam with improved k-factor due to reduced radiative heat transfer. Alternatively, high polarity surfactants are more compatible with most polyurethane preblends and therefore provide better system clarity. This type of surfactant generally provides coarser cells which can improve physical properties such as dimensional stability and isotropy. System and surfactant polarity also determine how well the surfactant will emulsify the incompatible reactants of the preblend and phases that are formed during the reaction.

The polarity of a foam formulation depends on a number of factors including the nature of the polyol, the water level, and the type and quantity of blowing agent. For example, we have found that as the water level in a polyurethane system increases, and the system becomes more polar, a lower polarity surfactant is required for increased surface activity. It would thus be useful to have a scale quantifying the polarity of silicone surfactants.

The HLB concept was introduced by Griffin[3] as an arbitrary scale by which emulsifying agents could be classified. HLB, or hydrophile-lipophile balance, is a measure of the polarity of a surfactant in which the least polar materials have low HLB

numbers and highly polar materials have high HLB numbers. The numbers originally referred to the weight ratio of polyoxyethylene condensed with sorbitan esters, but the concept has been expanded to cover many types of organic surfactants. Davies [4] developed a list of HLB functional group numbers which allows an HLB to be calculated directly from the molecular formula of a material. There are numerous methods for the determination of the HLB of a given material. Several excellent reviews of the HLB system and emulsions have appeared [5-7].

Unfortunately, very little literature has appeared on the determination and use of HLB numbers for silicone surfactants. Dubyaga, et. al. [8], determined the HLB numbers of a series of silicone surfactants both experimentally and by calculation. They showed that the turbidity temperatures of aqueous solutions of the silicones were directly proportional to their HLB numbers. The HLB numbers were determined from the distribution of a given surfactant between heptane and water. The HLB was then calculated using the formula [4]:

$$HLB = 7 + 0.36(C_w/C_h)$$

where C_w and C_h are the surfactant concentration in the water and heptane phases respectively. HLB numbers for the surfactants have also been calculated using the equation:

$$HLB = wt\% \ EO/5$$

This equation is a general rule of thumb that has been developed for ethoxylated surfactants [5]. Interestingly, Dubyaga found good agreement between the measured and calculated HLB numbers in this study. The HLB numbers ranged from 5 to 15. Schmidt, et. al. [9], measured the HLB numbers of a number of commercial silicone surfactants and related the HLB to surfactant performance in a polyisocyanurate foam system. The HLB numbers in this study were determined using Griffin's method [3] with a 30/70 water/mineral oil system. The HLB numbers ranged from -5 to 19.

Racz and Orban [10] demonstrated a relationship between the heat of hydration of a surfactant and its HLB number. The heat of hydration of a surfactant can be easily determined with a calorimeter. We have explored the use of calorimetry as a general method to determine the polarity of silicone surfactants. We have found this approach to provide a more useful scale than calculated HLB values based solely on the ethylene oxide content of the surfactant.

III. EXPERIMENTAL

Experimental Procedure for Heat of Hydration Technique

The heat of hydration, Q, of a surfactant was determined using a SETARAM C-80 Calorimeter. The surfactant (60 mg) was loaded into the bottom of the calorimeter. Water (2.000 g) was loaded into the top of the calorimeter. The top and bottom chambers were separated by a thin non-permeable membrane. The calorimeter was equilibrated at 30.0 °C. The membrane was then punctured, and the heat flow measured as the two components mixed.

Experimental Procedure for Handmix Foam Data

Polyurethane rigid foams were prepared with a laboratory handmix procedure. Resin side components were combined in a 5 liter plastic container and stirred for 60 seconds using an electric mixer with a 7.6 cm diameter stirring blade. The amount of preblend required to make one foam was then weighed from the masterblend into a 1 liter cup, the surfactant was added, and the mixture was stirred for 20 seconds. Compensation was made for loss of blowing agent during mixing by monitoring the weight of the preblend before and after mixing and adding more HCFC-141b as necessary. Isocyanate was weighed into a second ''wet-tared'' one liter beaker and the temperature of the resin

mixture and isocyanate were adjusted to $22 \pm 1^{\circ}C$ in an incubator. The pre-weighed isocyanate was added to the resin blend; the mixture was stirred for 6 seconds with the electric mixer; and was then either poured into a physical property plaque mold (30.5 cm x 30.5 cm x 5.1 cm) or the cup containing the mixture was dropped into a hole cut into the horizontal portion of an aluminum L-panel mold. A detailed diagram of the L-panel mold may be found in reference 11. The height to which the foam had flowed up the vertical portion of the L-panel was used as a measure of flowability. K-factor was measured on a Lasercomp Fox 200 instrument. Dimensional stability and compression strength were measured according to ASTM standards.

IV. RESULTS AND DISCUSSION

Heat of Hydration Method for Determining Surfactant Polarity

The HLB scale was introduced as an arbitrary scale by which emulsifying agents could be classified according to their polarity [3]. The experimental determination of HLB numbers, however, is relatively arduous. In some cases these determinations lead to HLB values that make little sense [9]. Many times, HLB numbers for surfactants are calculated values that may not take into account the entire structure of the surfactant [8]. Given the above, it is clear that a polarity scale for silicone surfactants, based on a straightforward measurement of a fundamental physical property would be desirable. Our preliminary results suggest that measurement of the aqueous heat of solution of silicone surfactants provides such a scale.

The heats of solution, Q, of over 30 silicone surfactants were determined. Both commercial products and experimental structures were included in the study. Structural parameters such as DP, D/D' ratio, EO/PO ratio, and EO+PO (as defined earlier) were

varied. Some surfactants contained polyethers made solely with ethylene oxide, while others contained polyethers made with both ethylene oxide and propylene oxide.

The surfactants containing EO-only polyethers provided a linear relationship between the heat of solution, Q, and the weight percent ethylene oxide (see Figure 2) . This is expected from the results reported by both Racz [10] and Becher [5]. For these surfactants the generic calculation

$$HLB = wt\% \ EO/5$$

will provide an accurate scale of polarity. Alternatively the Q values alone provide a similar ranking. The Q values of surfactants containing mixed EO/PO polyethers, however, follow no discernible trend when plotted versus weight percent ethylene oxide (Figure 2). These results indicate that calculated HLB values for these materials using the above equation do not accurately reflect the polarity of the surfactants. It is obvious that propylene oxide content is contributing to the heat of solution and, hence, the polarity of the surfactant. In fact, any functionality of the silicone surfactant other than siloxane and ethylene oxide will effect the material such that the generic HLB equation will not give an accurate reflection of polarity.

To address this issue, Davies [4] developed the structure factor method for calculating an HLB number. According to the structure factor method, an empirically derived group number is assigned to various component groups of a surfactant structure, e.g., $-CH_3$, $-CH_2CH_2O-$, $-COO-$, etc. The HLB is then calculated from the following relation:

$$HLB = 7 + \Sigma \ (\text{hydrophilic group numbers}) - \Sigma \ (\text{hydrophobic group numbers})$$

A similar approach to the heat of solution data has yielded a condensation of the data to a single linear plot. Figure 3 is the result of a linear regression in which both the ethylene oxide and propylene oxide contents of the surfactants are taken into account. This indicates that, at least for surfactants containing siloxane and polyethers comprised of

ethylene oxide or ethylene oxide and propylene oxide, the heat of solution technique provides for a simple linear scale of polarity. Work to expand the utility of this technique to include other functionality such as polyether capping groups is currently underway.

We believe the heat of hydration method to evaluate polarity of a surfactant is a more accurate reflection of polarity than traditional calculations. Polarity is one of the important parameters that must be evaluated in the development of surfactants for rigid foams especially when blowing agent technology is changing so rapidly. We are currently obtaining more data with the heat of hydration method to correlate surfactant polarity with foam performance and we will report progress in this area at a later date.

Figure 2. Heat of Solution versus Weight Percent Ethylene Oxide
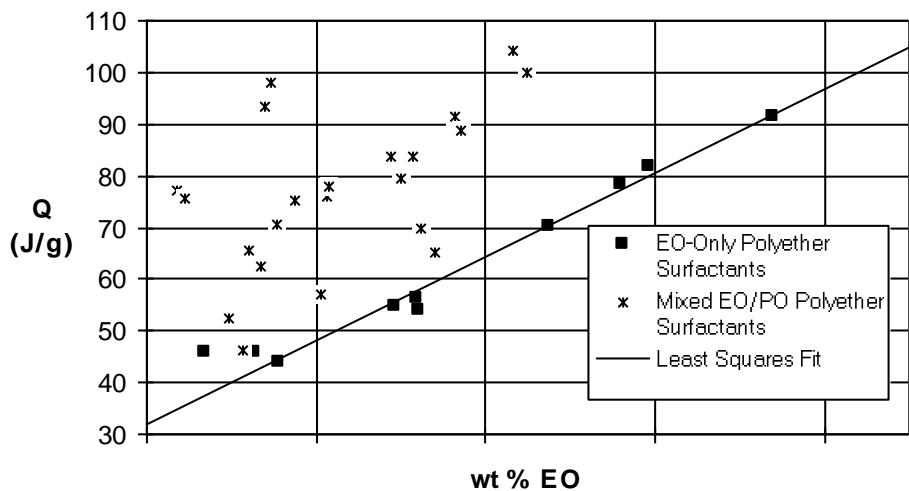
Figure 3. Heat of Solution versus Polyether Content
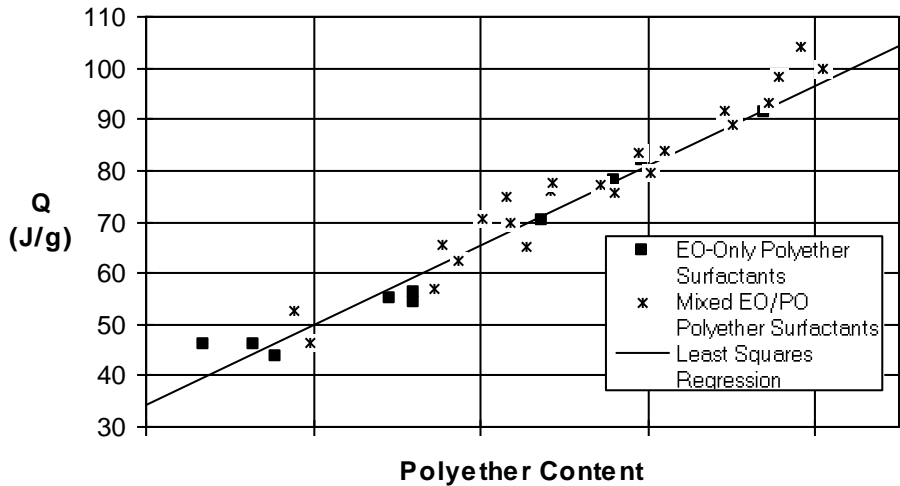
DABCO DC5604 Surfactant for 141b / Water Co-blown Pour-in-Place Systems

In addition to new analytical techniques, Air Products and Chemicals is also developing new products for the evolving blowing agent technologies. DABCO DC5604 surfactant was designed for HCFC-141b / water co-blown and all-water blown rigid pour-in-place systems to provide a good balance between mechanical and thermal properties in rigid foam. As mentioned earlier, as HCFC-141b systems were developed and water levels increased, a more hydrophobic surfactant (less polar) was required to increase surface activity in the more hydrophilic formulations. A new series of surfactant products was required to meet the demands of the new blowing agents and higher water levels and to address the specific needs of various application areas. For appliance applications, Air Products and Chemicals developed and introduced a new molecule to the polyurethane industry for high water/HCFC-141b formulations called DABCO DC5357. This product, now the leading appliance surfactant in North America, was the first in the new surfactant

series to shift our product line to more hydrophobic products. We have found, however, that for some pour-in-place applications, a surfactant affording a better balance of k-factor and mechanical properties is desired.

An experimental design was conducted to study the effect of molecular structure on the performance of a surfactant in HCFC-141b/water co-blown and all-water blown pour-in-place systems. Parameters such as DP, D/D', EO/PO and EO+PO (as defined earlier) were varied to provide response curves that depict the variation of a performance property as a function of surfactant structure. Using the response curves and response equations, an optimization was performed to identify the structure providing the best thermal, mechanical and processing properties. As expected, the D/D' variable had a strong effect on performance properties because D/D' ratio is a key variable in determining the balance of hydrophilic polyether to hydrophobic siloxane.

The result of the optimization study was the development of a new product DABCO DC5604 surfactant for rigid systems. To demonstrate the benefits of DABCO DC5604, data is presented for three formulations. The composition of each is listed in Table 1, where formulation 1 is HCFC-141b / water co-blown, formulation 2 is all-water blown, and formulation 3 is a polyisocyanurate HCFC-141b pour-in-place formulation. Table 2 provides the reactivity of each of the formulations and Table 3 lists the performance of each system with DABCO DC5604 compared with DABCO DC193 and two competitive surfactants. In general, DABCO DC5604 shows improvement in k-factor and flow while maintaining physical properties such as dimensional stability. In formulation 1, the HCFC-141b/water co-blown system, DABCO DC5604 exhibits superior flow compared to competitive products. Also in formulation 1, DABCO DC5604 demonstrates both superior flow and k-factor compared to DC193, which is a higher polarity surfactant. In the all-water system, formulation 2, DABCO DC5604 provides improved k-factor while

maintaining flow and mechanical properties compared to the competitive surfactants. In the polyisocyanurate formulation number 3, DABCO DC5604 again provides for superior flow compared with competitive surfactants and DABCO DC193 while maintaining dimensional stability.

Table 1. Pour-in-Place Rigid Formulations

	Formulation 1	Formulation 2	Formulation 3
Voranol 490 (php)	100.00		
Voranol 370		50.00	
Voranol 360			10.00
Voranol 270			5.00
Terol 352		50.00	
Terol 235			59.2
Arconate 1000		3.00	
Antiblaze 80			3.00
Surfonic N-95			3.00
Silicone Surfactant	2.00	2.00	1.50
Polycat 5 Catalyst	0.20	0.25	0.36
Polycat 8 Catalyst	1.60	1.00	
DABCO K-15 Catalyst			1.48
HCFC-141b	25.00		17.00
Water	2.50	4.40	0.40
Polymeric MDI	177.39	181.80	116.17
index	1.15	1.20	2.10

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Table 2. Formulation Reactivity

	Units	Formulation 1	Formulation 2	Formulation 3
Initiation	[s]	17	13	15
Gel	[s]	80	31	44
Tack free	[s]	134	47	60
Rise	[s]	140	55	81

Table 3. Physical Properties of Surfactants in Representative Pour-in-Place Formulations

	Formulation 1 HCFC-141b/Water Co-Blown Pour-in-Place System				Formulation 2 All Water Blown Pour-in-Place System				Formulation 3 Polyisocyanurate Pour-in-Place System			
	DABCO DC5604	A	B	DABCO DC193	DABCO DC5604	A	B	DABCO DC193	DABCO DC5604	A	B	DABCO DC193
L-panel												
Flow, (mm)	520	480	480	470	440	440	450	440	405	360	355	375
Initial Lambda [W/m-K]	0.0196	0.0196	0.0198	0.0205	0.0219	0.0229	0.0225	0.0222	0.0177	0.0179	0.0182	0.0179
Molded Panel, 5% overpack												
Total Density, [Kg/m3]	36.0	36.8	36.3	36.2	42.7	42.6	41.6	42.6	49.3	48.6	49.9	49.9
Core Density, [Kg/m3]	32.3	33.3	33.1	33.1	38.1	38.1	37.1	38.1	43.0	43.8	42.2	43.7
Compression Strength, [KPa]												
(∥)	138	166	166	186	310	276	255	296	359	310	310	296
(⊥)	124	166	166	166	207	145	179	186	290	290	262	248
Dimensional Stability, %ΔV												
-30°C, 14 days	0.3	2.5	0.4	-3.6	-1.2	-1.1	0.7	-0.7	-0.9	-3.0	2.5	-0.5
93°C, Ambient RH, 14 days	3.4	1.4	3.5	3.1	-3.3	-3.3	-1.7	-3.0	-1.5	-1.3	0.3	1.5
21°C, 50%RH, 14days	0.2	-1.3	-3.7	-1.3	-10.2	-11.9	-9.5	-11.9	-2.7	-3.3	-1.4	-4.2

XF-J2557 Experimental Surfactant for Pentane Blown Rigid Foam

The development chemist is faced with several challenges when developing pentane systems including flammability issues, solubility kinetics, deteriorated thermal insulation properties and processability. Silicone surfactants play a vital role when n-, iso or cyclo-pentane are used as blowing agents in rigid foam applications. Although pentane is non-polar, higher water levels found in pentane formulations can add to the polarity of the system and may require a more hydrophobic surfactant. Another consideration for surfactants is that since aliphatic hydrocarbons have a very low solubility in polyurethanes, the blowing agent becomes increasingly incompatible during the reaction; even when the pentane was initially completely soluble in the polyol preblend. Silicone surfactants can not significantly increase the solubility of pentane in the raw materials or the reaction mixture; however, surfactants can improve emulsification of the pentane as it becomes increasingly less soluble during the polymerization process.

In 1993, Air Products and Chemicals introduced DABCO DC5555 [12] to meet the challenges of pentane blowing agents. DABCO DC5555 has proven to be successful in increasing the amount of emulsified pentane while reducing the pentane emissions during foam formation and aging. Flame retardancy of pentane blown rigid polyurethane foams is also a very important concern. Usually, high levels of unreactive flame retardants have to be used to meet fire standards such as the B2 test in Germany. During initial developmental work, DABCO DC193 silicone surfactant was identified as having significant benefit on the flammability of rigid polyurethane foams. DABCO DC193 can be used to reduce the amount of flame retardants required in the formulation and to provide for more consistent results when testing the foam. Typically, a two cm improvement in flame height is observed in fire performance in the German B2 flame test

according to DIN 4102-B2 when DABCO DC 193 is used compared with other silicones. (This numerical flame spread improvement and other flame ratings presented in this paper are not intended to reflect hazards presented by this or any other material under actual fire conditions).

Although DABCO DC5555 and DABCO DC193 have proven to be very successful in the marketplace, further optimization was required in some pentane systems to improve mixing of the foam components when low shear mixing equipment is used and/or viscosities vary due to inconsistent production parameters. An experimental design was conducted by varying surfactant structural parameters to improve component emulsification while also improving flame retardancy. As a result of the experimental design work, XF-J2557 experimental surfactant was developed and has demonstrated excellent performance with regard to polyol, isocyanate, and pentane emulsification in lab evaluations. Customer line trials were conducted to confirm the laboratory results and the data from the field trials is presented in Tables 4 - 6.

Production trials were conducted with XF-J2557 surfactant at two different customers. In both cases, the experimental surfactant performed well without making any processing adjustments; formulations for both trials are listed in Table 4. The panels were aluminum faced and produced on continuous laminators under standard processing conditions. The panels have been tested using standard DIN test methods and flammability testing was conducted by the customer according to DIN 4102-B2. The surfactants used in this evaluation as a comparison are DABCO DC193 (lamination surfactant for improved flame retardancy), DABCO DC5555 (lamination surfactant for improved pentane emulsification), and a competitive lamination surfactant. The physical properties of the panels are summarized in Table 5 and 6. The data show that XF-J2557 surfactant

provides a finer cell structure which is an indication of improved emulsification. Improved emulsification with XF-J2557 was also evident during the line trial by the improved process latitude and the overall appearance of the foam without mixing striations. Although not as good as DABCO DC193 for flame retardancy, XF-J2557 demonstrates an improvement in flame retardancy over DABCO DC5555 and another competitive surfactant. XF-J2557 exhibits these improvements while maintaining other physical properties such as compression strength, dimensional stability, closed cell content and thermal insulation efficiency.

Table 4. Formulations Used in Pentane Lamination Production Trials

Lamination Grade:	Formulation 4	Formulation 5
Polyol Preblend (php)	100.00	98.00
Water	1.54	2.0
n- Pentane	8.80	10.0
Catalyst Package	1.68	
DABCO TMR catalyst		0.5
Polycat 8 catalyst		1.0
Silicone Surfactant	1.10	2.00
Polymeric MDI Index 120	215.00	160.00

Table 5. Physical Property Data from Customer Trial with Pentane Blown Lamination Board (Formulation 4)

	Units	DABCO DC193	DABCO DC5555	XF-J2557 Surfactant	Competitive Surfactant
Density	[Kg/m3]	34.2	34.5	34.4	34.1
Compression Strength	[KPa]	178	177	170	171
Cell Size	[mm]	0.22	0.22	0.20	0.20
Closed Cells	[%]	98.5	98.2	99.2	98.1
Dimensional Stability at 60°C	[%ΔV]	0.75	0.98	0.31	0.87
Dimensional Stability at -25°C	[%ΔV]	-0.15	-0.22	-0.18	-0.06
Lambda	[W/m-K]	0.0211	0.0211	0.0206	0.0217
B2 Flame Test Height	[cm]	13	15	14	15

Table 6. Physical Property Data from Customer Trial with Pentane Blown Lamination Board (Formulation 5).

	Units	DABCO DC193	XF-J2557 Surfactant
Density	[Kg/m3]	32.5	31.8
Compression Strength ($\parallel$)	[KPa]	204.1	203.3
Compression Strength ($\perp$)	[KPa]	186.5	176.5
Cell Size	[mm]	0.26	0.24
Closed Cells	[%]	98.6	98.1
Dimensional Stability at 60°C	[%ΔV]	0.65	0.43
Dimensional Stability at -25°C	[%ΔV]	-0.20	-0.29
Lambda	[W/m-K]	0.021	0.021
B2 Flame Test Height	[cm]	12	13

V. SUMMARY AND CONCLUSIONS

Air Products and Chemicals is actively supporting the changes which are occurring in rigid polyurethane foam formulations as new blowing agent technologies emerge into the global market place. We have developed a new analytical tool, the heat of hydration technique, to better characterize surfactant polarity, which will guide us in surfactant structure selection for new formulations and help in the development of new products. In addition, we have developed products for new blowing agents. For HCFC-141b / water co-blown and all-water blown formulations, DABCO DC5604 is introduced to afford an optimal balance of flow, k-factor and mechanical properties for rigid systems. DABCO DC5604 expands upon the proven capabilities of DABCO DC5357 which has been very successful in providing excellent flow and k-factor in HCFC-141b / water co-blown appliance formulations. For n-pentane blown laminations systems, XF-J2557

experimental surfactant has been developed to provide better emulsification, finer cell structure and improved flame retardancy. XF-J2557 surfactant complements DABCO DC5555 which has found wide utility in the n-pentane lamination industry. Finally, Air Products and Chemicals will continue to develop new methods, catalysts and surfactants to meet regional needs as blowing agent technology in rigid foam evolves.

REFERENCES

1) Birch A.J., V. Parenti, K. Van Duin, G.F. Smits and P. Clavel, Proceedings of the Polyurethanes 1995 Conference SPI, p. 448-453.

2) Kanner, B., and T.G. Decker, J. Cell. Plast., 1969, 5(1), pp. 32-39.

3) Griffin, W. C. 1949. *J. Soc. Cosmetic Chemists 1*, pp. 311-326.

4) Davies, J. T., Rideal, E. K. 1963. *Interfacial Phenomena*, Academic Press, New York. pp. 371-383.

5) Becher, P., Schick, M. J. 1987. *Nonionic Surfactants Physical Chemistry* (M. J. Schick, ed.), Marcel Dekker, Inc., New York. pp. 435-492.

6) Marszall, L. 1987. *Nonionic Surfactants Physical Chemistry* (M. J. Schick, ed.), Marcel Dekker, Inc., New York. pp. 493-548.

7) Shinoda, K., Kunieda, H. 1983. *Encyclopedia of Emulsion Technology, Vol. 1, Basic Theory* (P. Becher, ed.), Marcel Dekker, Inc., New York. pp. 337-367.

8) Dubyaga, Y. G., Titarova, G. I., Tarankanov, O. G. 1984. *Polymer Science U.S.S.R. 26*, pp. 309-319.

9) Schmidt, D. L., Clarke, D. H., Urchick, D. 1984. *J. Cell. Plast.*, May-June, pp. 220-226.

10) Racz, I., Orban, E. 1965. *J. Colloid and Interface Sci. 20*, pp. 99-103.

11) Bodnar, T.W. and L.J. Petroff, Proceedings of the SPI 32nd Annual Polyurethane Technical/ Marketing Conference, 1989, p 538-546.

12) Grimminger, J. and K. Muha, Proceedings of the Polyurethanes World Congress, 1993, p 609-618.

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Biographies

Dr. John H. Frey received a bachelors degree in Chemical Engineering from Lehigh University and a Ph.D. in Chemical Engineering from the University of Delaware where he studied mixing of fast polymerizing reactions. Dr. Frey has worked for Air Products and Chemicals, Inc. since 1987 in a variety of assignments relating to polyurethanes. He started in the corporate science center working on new processes for manufacturing amines. He later transferred to the Polyurethane and Performance Chemicals Division where he worked with cast elastomers, RIM elastomers and microcellular foams. After dedicating several years to polyurethane additives technical service in Asia and Latin America, Dr. Frey is currently working on global product development of polyurethane additives for flexible and rigid foam.

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 senior technical service chemist responsible for rigid polyurethane foam additives and additives for high density molding applications.

Dr. Robert E. Stevens received a B.S. in Chemistry from the University of Wisconsin-Madison in 1980 and a Ph.D. in Inorganic Chemistry from the University of Minnesota in 1984. Bob joined Air Products and Chemicals, Inc. the same year, and has worked in a number of areas of silicon chemistry including silicon containing ligands for liquid organometallic complexes for gas separation, silicon carbide ceramic films via chemical vapor deposition, and silicone surfactants for polyurethane foam. For the last six years, Dr. Stevens has been developing new silicone surfactant products and studying the fundamentals of the use of these materials in polyurethane foam.