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Optimized Silicone Surfactant for the Manufacture of Flame Retarded Foams

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For many applications flexible polyurethane foam has to meet certain flammability requirements. Therefore special formulations are required which include the use of flame retardants, modified polyols and also the proper choice of silicone surfactants.
In the past, Evonik has put a lot of resources into the development of tailor-made highly sophisticated FR silicone surfactants which are optimized regarding their impact on flammability as well as their processing in combination with different types of flame retardants and different types of polyols (hydrophilic, natural oil-based polyols or standard polyols).
A new FR surfactant is presented which meets the requirements of a broad range of FR foam grades, including different polyols, FR additives, conventional blown foams and CO_2-blown foams.

INTRODUCTION

Since flexible polyurethane foams are organic in nature, they are flammable and the flammability of polyurethane foams is an important industry issue. To reduce this flammability, flame retardants are often added to the formulation. The choice of flame retardant for any specific foam grade depends on the intended foam application and the corresponding flammability test. Aspects of flammability that may be influenced by additives include the ease of ignition, burning rate and smoke evolution.

Flame retardants (FR) decrease the combustibility due to physical and chemical mechanisms. The FR acts in the gaseous phase as a radical scavenger. In the solid phase some FRs increase flowability of the molten polymer, which separates the polymer from the flame. Other FRs can initiate a catalytic splitting of the polyurethane matrix and lead, through dehydrogenation and dehydration reactions, to a carbonized protective char hindering the escape of pyrolysis gas [1].

In well balanced, optimized flame retarded flexible polyurethane foams the amount and structure of the chosen silicone surfactant has a detectable influence on the burning behavior. The impact of silicone surfactants on flammability has been published in the past by Weier et al. [2], Burkhart et al. [3], Boinowitz et al. [4], Hubel et al. [5], Landers et al. [6] and Terheiden et al. [7].

Evonik differentiates three types of surfactants for flexible foam:

- Conventional Surfactants: Not recommended for FR grades.
- Universal surfactants: Suitable for non FR grades and FR grades with the exception of BS5852.
- FR Surfactants: Optimized for application in FR grades. Suitable also for BS5852, in other FR tests significant reduction of FR dosage is possible.

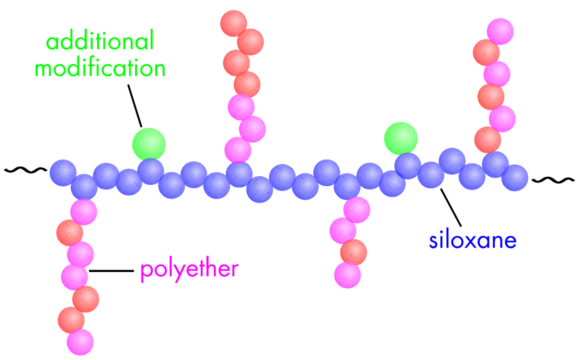

Figure 1. *General structure of a silicone surfactant, optimized for FR applications.*

Chemically, most of the silicone surfactants for flexible foam consist of a silicone backbone (blue) with pendent polyethers (red/pink). As shown in Figure 1, FR surfactants can contain additional modifications (green).
It is well known that the higher the modification density of the siloxane, the lower the negative contribution to flammability. When PU foam burns, the polyether-modified siloxane in the foam decomposes as well. In the first step, the polyether portion is oxidized and silicon oil is formed. The unmodified siloxane oil is not compatible with the polymer melt and migrates to the surface where it further promotes the combustion of organic material [6]. In addition, the unmodified siloxane fragments reduce the viscosity of the fused material. Consequently, the carbonized charred surface, which has been formed through dehydrogenation and dehydration reactions, is circulating on the molten polymer matrix and flows off. Without this charred surface, there is nothing to prevent the stream of pyrolysis gas from escaping.

The challenge in optimizing FR silicone surfactants is to achieve a high number of modifications while still maintaining the required nucleation and stabilization potency. By increasing the degree of modification of the polyether modified siloxane, the overall molecular characteristics change as well. The surfactant becomes more compatible with the polyol and therefore less surface active. By being less surface active, the silicone surfactant has a negative impact on foam stability and requires a higher use level.

When introducing TEGOSTAB® B 8239 to the marketplace, Evonik was able to offer a highly sophisticated FR surfactant which provides excellent FR properties with high stabilization potency. TEGOSTAB® B 8239 achieves similar stabilization potency in comparison to a universal surfactant while allowing for a significant 25% reduction in flame retardant use levels to achieve equivalent FR performance. Being able to reduce the use level of the flame retardant can be beneficial for several reasons. The resulting foams are less sensitive to scorch, the hydrolytic aging behavior can be improved and the emanation at higher temperatures can be reduced when reducing the FR additive load.

FR performance and stabilizing potency are not the only important features of a FR surfactant; its contribution to processing and matrix compatibility are important as well. In recent years, FR foam grades have become more and more specific due to the use of different types of flame retardants (halogenated and halogen-free) and polyols (hydrophilic polyols or natural oil-based polyols). Changing the type of flame retardants and/or polyols is often accompanied with changes in the processing latitude. For specific foam grades, especially non-halogenated FR additives, using TEGOSTAB® B 8239 can result in a narrow processing latitude accompanied by limited formulation adjustments. The narrowed processing is most likely related to changes concerning the compatibility properties of the raw materials. Because of these restrictions for TEGOSTAB® B 8239 there was a need for a new FR surfactant which combines the key characteristics of TEGOSTAB® B 8239 such as excellent FR performance and good nucleation support for CO_2-applications, with universal processing characteristics for the whole range of different FR foam types.

This paper presents a new FR surfactant which meets these desired properties for a multitude of FR foams, including different polyols, FR additives, conventional blown foams and CO_2-blown foams.

EXPERIMENTAL

Formulations for the Evaluation of Stabilization Potency and Processing Latitude

Evonik has developed a critical formulation for the evaluation of the stabilization potency of surfactants (Formulation 1). The final foam density is 18 kg/m³ (1.1 pcf). For this study the surfactant concentration was varied from 0.5 to 0.6 pphp (Table 1). To evaluate the influence of the surfactant on nucleation and cell structure, a formulation based on propylene oxide polyether polyol (Formulation 2) was used resulting in a density of 25 kg/m^3 (1.6 pcf). The FR surfactants were evaluated regarding their processing latitude using a formulation containing 4.05 parts of water resulting in a density of 23 kg/m^3 (1.4 pcf). The surfactant concentration was varied from 0.6 to 1.5 pphp. The corresponding formulations are given in Table 1.

Conventional flexible slabstock foams were made using 300 g of polyol with the other constituents of the formulation scaled accordingly. Here, for example, 1.0 part of a component means 1 g of this substance per 100 g of polyol. Water, catalysts and silicone surfactants were added to the polyol and mixed together by stirring at 1000 rpm for 55 s. After addition of the isocyanate, the mixture was stirred at 2500 rpm for 7 seconds. The liquid material was then poured into a paper-lined wooden box (base area: 27 cm x 27 cm). The following measurements were taken and recorded: rise time, settling after 3 min, foam density, air permeability of the foam (determined by measuring the back pressure on a constant airflow through the foam) and cell size.

Table 1. Formulations for conventional flexible slabstock polyether foams. The amounts of raw materials and additives are given in parts per hundred parts (pphp).			
Formulations	Formulation 1	Formulation 2	Formulation 3
	Critical for Potency	Critical for Nucleation and Cell Size Distribution	Processing Latitude
Polyol OHN 48	100	-	100
Polyol OHN 56	-	100	-
Total Water	5.0	4.05	4.05
Surfactants	0.5/0.6	0.6	varied
TEGOAMIN® 33	0.15	-	-
TEGOAMIN® DMEA	-	0.20	0.20
KOSMOS® 29	0.23	0.20	0.20
Methylene Chloride	5	-	2.5
TDI 80	63.04	52.5	52.5
TDI Index	113	110	113

Flammability of Flexible Slabstock Foams

FLAMMABILITY TESTS

For all flammability tests the samples have been conditioned for a minimum of 48 hours at 20°C and less than 55% relative humidity. For the flammability test CAL117 five unaged specimens have been tested.

California Technical Bulletin 117 (March 2000)

California Technical Bulletin 117 (March 2000) [8] has become an industry standard for upholstered furniture in the US. It consists of a vertical burn test (shown in Figure 2.a) and a cigarette smoldering test. For this paper only the CAL117 vertical burning has been applied. Here the specimen (7.5 cm x 0.5 cm x 1.3 cm) is placed vertical in the cabinet in such a manner that the lower end of the specimen is 0.75 inches above the top of the burner. The burner flame is applied vertically at the middle of the lower edge of the specimens for 12 seconds. One requirement of this test is that the average char length of all specimens shall not exceed 6 inches and that the maximum char length of any individual specimen shall not exceed 8 inches.

(a) CAL TB 117 (March 2000). Vertical burning.

(b) BS5852, Crib 5. Fire in case of a failed test

Figure 2. *Photos of different flammability tests.*

British Standard 5852

The British Standard 5852, which is also known as Crib 5 [9], is a critical flammability test for residential furniture and is a requirement for furniture foams in the UK. It consists of a horizontal and vertical foam requirement. The foam is covered with specified textile and the flame source is a wooden crib soaked with propan-2-ol. The sample passes if the weight loss is less than 60g. Figure 2b shows the fire in case of a failed test.

FOAMING PROCEDURE - CONVENTIONAL FLEXIBLE SLABSTOCK FOAM

Different silicone surfactants were evaluated in the flammability tests CAL117 and BS5852 (Crib 5). For CAL117 a formulation based on 4.4 parts of water resulting in a density of 24 kg/m^3 (1.54 pcf) was used. The FR characteristics in BS5852 were evaluated in a formulation based on 4.7 parts of water. The corresponding formulations are given in Table 2.

The following silicone surfactants have been evaluated: TEGOSTAB® BF 2370, TEGOSTAB® B 8244, TEGOSTAB® B 8239, TEGOSTAB® B 8245 and the new surfactant TEGOSTAB® B 8155. TEGOSTAB® BF 2370 is classified as a conventional surfactant and TEGOSTAB® B 8244 belongs to the group of universal surfactants whereas TEGOSTAB® B 8239, TEGOSTAB® B 8245 and TEGOSTAB® B 8155 are FR surfactants.

Table 2. Formulations for conventional flexible slabstock polyether foams for the flammability tests. The amounts of raw materials and additives are given in parts per hundred parts (pphp).

Formulations	Formulation 4 24 kg/m^3 (1.54 pcf)	Formulation 5 24 kg/m^3 (1.54 pcf)	Formulation 6
	CAL117	CAL117 NOP	Crib V
Polyol OHN 48	100	85	-
Polyol OHN 56	-	-	100
Natural Oil-Based Polyol*)	-	15	-
Total Water	4.4	4.4	4.7
Surfactant	1.0/1.5	1.5	1.2
TEGOAMIN® B 75	0.15	0.15	-
TEGOAMIN® 33	-	-	0.2
KOSMOS® 29	0.20	0.22	0.27
FR Additive	Varied	Varied	20 pphp Fyrol® A300TB 30 pphp Melamine
Diethanolamine	-	-	0.8
Methylene Chloride	-	-	11
TDI 80	55.0	55.2	58.5
TDI Index	110	110	105

*) Natural Oil-based Polyol based on soy bean oil

Preparation of the foams for CAL117

The foams for CAL117 were produced according to a standardized hand-mix procedure using 300 g of polyol. The other constituents of the formulation were scaled accordingly. Water, catalysts, flame retardants and silicone surfactant were added to the polyol and mixed together by stirring at 1000 rpm for 55 s. After addition of the isocyanate, the mixture was stirred at 2500 rpm for 7 seconds. The liquid material was then poured into a paper-lined box (16 cm x 40 cm x 26 cm).

Preparation of the foams for British Standard 5852

The foams were produced according to a standardized hand-mix procedure using 50 cm x 50 cm x 50 cm boxes. All ingredients, with the exception of TDI and methylene chloride, were stirred with a propeller mixer driven by a drilling machine for 45 s at 3600 rpm. Methylene chloride was added and stirring was continued for an additional 15 s at 3600 rpm to minimize evaporation. After completing this 60 s mixing time, TDI was added and stirred for further seven seconds. The liquid material was then poured into the box and rise time and settling were measured. On the next day, the foam was trimmed to five 45 cm x 45 cm x 7.5 cm horizontal slices.
Porosity and density measurements were determined for all foams since they have a major impact on flammability. Porosity was measured according to the backpressure method as well as to SCFM method. The formulation is given in Table 2.

Performance in CO_2-blown foams

To evaluate the nucleation ability and general performance in CO_2-systems TEGOSTAB® B 8155 was compared to TEGOSTAB® B 8239 on our Novaflex machine in accordance to the critical formulation of Table 3.

Table 3. Novaflex Pilot Line - Critical CO_2-formulation and processing conditions (Formulation 7)

Polyol (OH# 56)	100.0
H_2O	6.0
Tegoamin® B 75	0.11
Silicone Surfactant	0.6
Liquid CO2	3.1
Kosmos® 29	0.18
Methylene chloride	5.00
TDI <106>	68.6
Creamer diameter	40 mm / 1,58 inch
Sieve Set	16/85, 1/100, 23/100
Head Pressure	8 bar / 109 psi
Nitrogen	10 N-litres
Mixer speed	2500
Polyol throughput	4.5 kg/min / 9,9 lbs/min

Humid Aging tests

For the humid aging test, the foams were conditioned according to DIN 53578 [10], in which the samples were placed in an autoclave for 5 hours at 120°C and 100% relative humidity for three consecutive cycles [11]. This procedure follows the same severe test conditions that are established by the automotive industry.
The following measurements were taken and recorded before and after the aging test: foam density, air permeability of the foam (determined by measuring the back pressure on a constant airflow through the foam), compression load deflection (CLD at 40% compression), compression set values, tensile strength and elongation at break.

Scorching Test

For the scorching test the foams were made according to Formulation 4 and have been stressed thermally in a microwave in order to simulate the thermal stress of the production blocks. The foam samples have been placed into a microwave for 4 min and 30 s with microwaves at 400 W directly after the blow off.

RESULTS AND DISCUSSION

Stabilizing Potency and Processing Latitude

The new FR surfactant TEGOSTAB® B 8155 was evaluated regarding its stabilizing potency and processing latitude with the formulations given in Table 1. The processing latitude defines the sensitivity of the foam properties to varying amounts of surfactant. Broad processing latitude means little impact on tightness of the foam with increasing surfactant levels. The results were compared to TEGOSTAB® B 8239, a commercial FR surfactant and TEGOSTAB® B 8244 which is a universal surfactant with high stabilizing potency and a broad processing latitude. The results for the stabilizing potency are shown in Figure 3. To evaluate the processing latitude for the new FR surfactants settling and air permeability were measured for varying surfactant use levels by keeping the KOSMOS® 29 level constant. The results are shown in Figure 4.

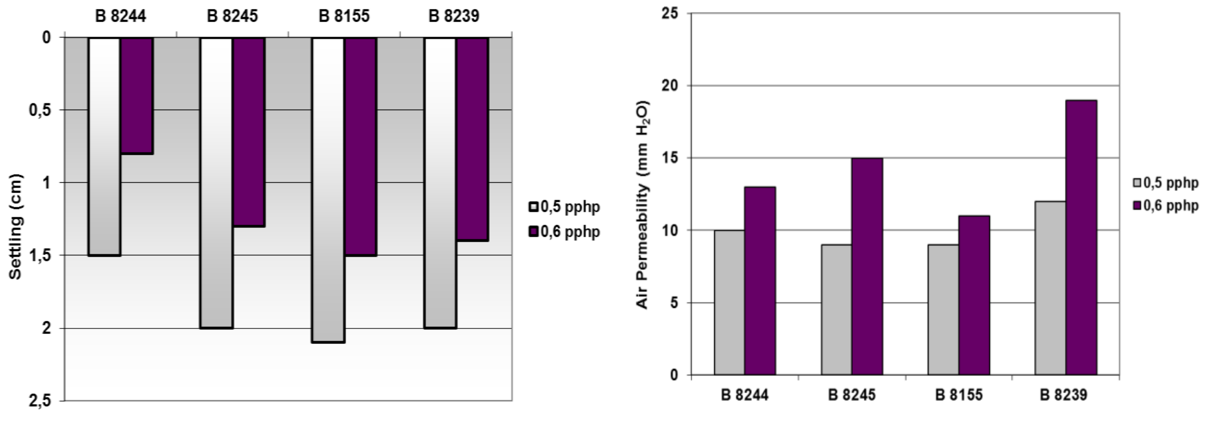

***Figure 3**. Comparison of silicone surfactants regarding their stabilizing potency. The formulation is shown in Table 1. Air permeability has been measured as back pressure (mm water column) which is obtained by an air stream passing the foam with constant speed. The lower the value, the more open celled is the foam structure.*

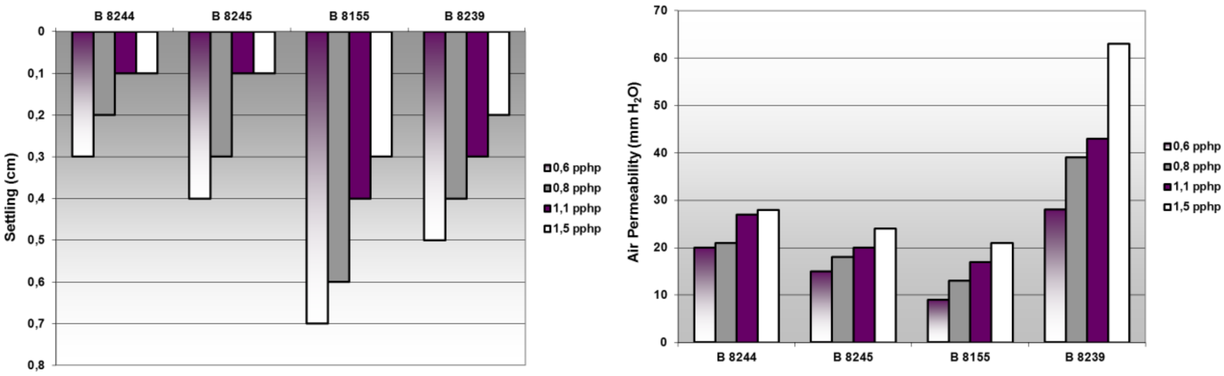

Figure 4. *Comparison of silicone surfactants regarding their processing latitude with respect to varying amounts of surfactant. The formulation being used is given in Table 1. Air permeability has been measured as back pressure (mm water column) which is obtained by an air stream passing the foam with constant speed. The lower the value, the more open celled is the foam structure.*

In comparison to TEGOSTAB® B 8239, the new FR surfactant TEGOSTAB® B 8155 is slightly weaker in potency but this potency is combined with excellent processing characteristics. At higher use levels of silicone surfactant or tin catalyst, we found that the foam maintains its openness which allows for formulation adjustments without any significant impact on the final foam properties.

Nucleation support and cell structure

To evaluate the influence of the surfactant on nucleation and cell structure, a formulation based on propylene oxide polyether polyol (Formulation 2) was used resulting in a density of 25 kg/m^3 (1.6 pcf).
The new silicone surfactant TEGOSTAB® B 8155 provides the same nucleation support as TEGOSTAB® B 8239. For both surfactants, foams with a cell structure of 13 cells per cm were obtained.

The nucleation ability and general performance in CO_2-systems of TEGOSTAB® B 8155 was compared to TEGOSTAB® B 8239 on a Novaflex machine in accordance to the critical formulation of Table 3. In addition to settling, density, porosity and cell structure, the resulting foams have been ranked according to their foam touch. Foams with a very soft and silky touch were classified with a value “5” whereas harsh and coarse foams were ranked by the number “1”. This evaluation was performed by 3 different people independently.

The CO_2-foaming results show that the new FR surfactant TEGOSTAB® B 8155 is also well suited for slabstock applications where liquid CO_2 is used as a physical blowing agent. The resulting foams are characterized by a fine cell structure combined with a soft touch of the foam surface. TEGOSTAB® B 8155 closes the gap between TEGOSTAB® B 8239 and TEGOSTAB® B 8245 in providing a FR surfactant with excellent processing and compatibility properties which is also well suited for CO_2-applications.

Table 4. CO_2-foaming results for various silicone surfactants (Formulation 7, Table 3).

FR surfactant	Risetime (s)	Settling (cm)	Density (kg/m^3/pcf)	Porosity (mm H_2O)	Cells (cm^{-1})	Ranking "Soft Touch"*			Ranking Total
B 8245	94	1.0	13.3/ 0.83	7	10	2	2	2	2
B 8239	94	1.0	13.3/ 0.83	2	12-13	5	5	5	5
B 8155	89	1.1	13.4/ 0.84	2	12	4	4	5	4
Comp.	94	1.5	13.5/ 0.84	2	12-13	4	4	3	4

The foams have been evaluated regarding their soft and silky touch. A ranking of 1 is related to very harsh and coarse foam, ranking of 5 is related to a very soft and silky touch.

Flammability Performance in different FR foam grades

IMPACT OF DIFFERENT SILICONE SURFACTANTS ON FLAMMABILITY (CRIB V)

The flammability results for BS5852 in Figure 5 show that TEGOSTAB® B 8155 with an average weight loss of <40 g is an excellent FR surfactant comparable to TEGOSTAB® B 8239. In comparison to TEGOSTAB® B 8245, the FR performance of TEGOSTAB® B 8155 could be significantly improved. As expected, the combustibility performance decreases by using the universal surfactant TEGOSTAB® B 8244 and more flame retardant is necessary to achieve equivalent FR properties.

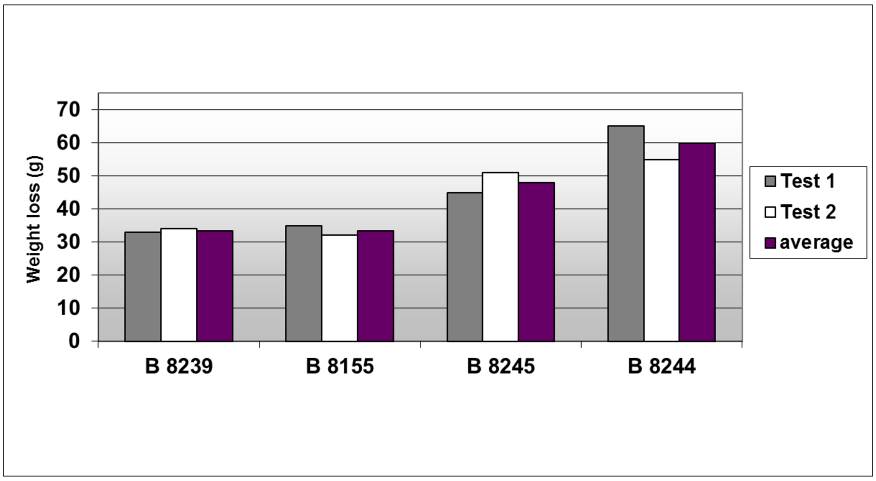

Figure 5. *Burning Results for British Standard BS5852.*

COMPARISON OF SILICONE SURFACTANTS IN CAL117 WITH DIFFERENT TYPES OF FLAME RETARDANTS

The newly developed FR silicone surfactant TEGOSTAB® B 8155 was evaluated in formulations with different types of FR additives including halogenated and non-halogenated types regarding its processing as well as its impact on flammability. For all foam grades, the air permeability was measured according to the backpressure method as well as by the scfm method. It is well known that the porosity of the foam has a significant impact on its flammability. Therefore for all foam grades the air permeability has been kept in a constant range with values below 30 mm H_20 for the backpressure method and higher than >2.5 scfm. The following types of halogenated and halogen-free FR additives have been used:

Table 5. Different types of applied flame retardants.

Name	Chemical Structure	Phosphorous / Chlorine / Bromine Content
Halogenated Flame Retardants		
Fyrol®A300TB	Proprietary composition	7.1 (wt%) Phosphorous Content 47.0 (wt%) Chlorine Content
TCPP	Tris (2-chloroisopropyl)phosphate	9.5 (wt%) Phosphorous Content 32.5 (wt%) Chlorine Content
Firemaster®550	Phosphorous-Bromine FR	27.1 (wt%) Bromine 4.3 (w%) Phosporous Content
Halogen-free Flame Retardants		
Non-Hal Type 1	Halogen-free Phosphorous Compound	9.6 (wt%) Phosphorous Content
Non-Hal Type 2	Halogen-free Phosphorous Compound	Not published
Non-Hal Type 3	Halogen-free Phosphorous Ester	8.1 (wt%) Phosphorous Content

The interaction of the silicone surfactants with different types of FR additives were studied at a relatively high use level of 1.5 pphp surfactant. It is well known that higher use levels of silicone surfactants result in poorer burn results due to the fact that the silicone backbone of the surfactant has a negative contribution to flammability. The high use level of 1.5 pphp was chosen to emphasize the FR performance of the new silicone surfactants since such formulations are more critical. The flammability results are summarized in Table 6.

Table 6. CAL117 vertical burning results (inches) for various silicone surfactants with different flame retardants in a foam grade based on Formulation 4, Table 2. The use level of the silicone surfactant was 1.5 pphp. All foam grades showed an air permeability values below 30 mm water column. The values given in the table are averaged burning results of 5 unaged foam samples.

FR Additive	**Use level**	**B 8239**	**B 8155**	**B 8245**	**B 8244**
Fyrol® A300 TB	12 pphp	1.3	1.4	3.1	3.2
	9 pphp	2.0	2.5	8.6	12.0
TCPP	12 pphp	1.1	1.5	5.4	6.0
	9 pphp	2.4	2.6	8.8	12.0
Firemaster® 550	12 pphp	2.3	2.3	4.3	6.9
	9 pphp	5.8	6.2	9.0	10.0
Non-Hal Type 1	10 pphp	1.3	2.4	3.6	11.7
	8 pphp	4.9	4.2	4.4	12
Non-Hal Type 2	20 pphp	Narrow processing*)	2.4	4.1	12
	18 pphp	4.1	2.9	6.4	12
Non-Hal Type 3	18 pphp	Narrow processing*)	2.2	2.9	7.5
	16 pphp	Narrow processing*)	4.5	3.8	11.0

*) *No measurement since these foams showed a tendency toward splits*

For all foam grades including halogenated flame retardants the silicone surfactant TEGOSTAB® B 8239 and TEGOSTAB® B 8155 were found to be the most efficient silicone surfactants regarding their impact on flammability, followed by TEGOSTAB® B 8245. All formulations made with the halogenated FRs showed good processing regardless of the type of silicone surfactant used. By substituting the halogenated flame retardants with halogen-free FR additives, the results are affected. Significant differences regarding processing and foam deficiencies depending on the type of surfactant could be observed, especially for the halogen-free flame retardants Type 2 and Type 3. We found that combining these FR additives with B 8239 result in an extremely narrow processing and foam splits. On the contrary, we found that TEGOSTAB® B 8155 and TEGOSTAB® B 8245 provide excellent processing and foams without any deficiencies even at the high FR use levels of 18 to 20 pphp.

The foaming results regarding processing and foam deficiencies indicate that different types of flame retardants require different compatibility characteristics of the applied silicone surfactant. These changing compatibility requirements of different FR formulations could be addressed through the use of TEGOSTAB® B 8245 and the latest development TEGOSTAB® B 8155. These FR surfactants differ in their chemical nature and therefore provide different support regarding stabilizing, processing and compatibility. In contrast to TEGOSTAB® B 8245, the new FR surfactant TEGOSTAB® B 8155 also shows excellent FR performance which is comparable to TEGOSTAB® B 8239.

FR PERFORMANCE AND PROCESSING IN CONVENTIONAL SLABSTOCK FORMULATIONS CONTAINING NATURAL OIL-BASED POLYOLS

Compared to conventional polyether polyols, most natural oil based polyols (NOPs) have different solubility characteristics due to the presence of long hydrocarbon chains. As a result of this chemical structure, these polyols are much more non-polar, hydrophobic and oleophilic. Due to the different chemical nature of NOPs, there is often a significant impact on compatibility requirements and therefore on the resulting processing of the corresponding formulations. These changes in compatibility and processing can be addressed by the choice of silicone surfactant as shown in Table 7. Different surfactants have been evaluated in a FR foam grade including NOP. In this study the natural oil-based polyol was combined with the halogenated flame retardant Firemaster® 550 as well as with the halogen-free FR Type 3. The main focus of this foaming test was on the processing of the resulting formulations rather than on the burn results.

Table 7. Foaming and burning results for various silicone surfactants in FR formulations containing 15 pphp of natural oil-based polyol (Formulation 5, Table 2).				
	B 8239	B 8155	B 8245	B 8244
Firemaster® 550 (10.5 pphp)				
Settling (cm)	0.1	0.2	0.1	0.2
Density (kg/m³/pcf)	24.0/1.50	24.0/1.50	23.9/1.49	24.0/1.50
Porosity (mm H_2O)	9	11	10	11
Porosity (scfm)	5.1	7.7	5.9	6.0
CAL117 (inch)	2.8	2.9	3.3	4.1
Non-Halogenated Flame Retardant Type 3 (21 pphp)				
Settling (cm)	-*)	0.2	0.4	-*)
Density (kg/m³/pcf)	-*)	25.7/1.60	25.7/1.60	-*)
Porosity (mm H_2O)	-*)	13	15	-*)
Porosity (scfm)	-*)	6.9	4.3	-*)
CAL117 (inch)	2.2	2.1	2.8	3.2

*) *No measurement since these foams showed severe splits. The grey areas indicate foams, which showed tendency to splits.*

When combining the natural oil-based polyol with the halogenated flame retardant Firemaster®550, all silicone surfactants allow for a good and stable processing without any foam deficiencies. However, by combining the NOP with the halogen-free flame retardant Type 3, significant differences regarding processing and foam deficiencies could be observed. Using the silicone surfactants TEGOSTAB® B 8239 and TEGOSTAB® B 8244 result in foams which tend to split whereas the silicone surfactants TEGOSTAB® B 8155 and TEGOSTAB® TEGOSTAB® B 8245 provide excellent processing and result in foams without any deficiencies. In this particular case the well balanced character of TEGOSTAB® B 8155 and TEGOSTAB® B 8245 with respect to their chemical and physical properties allow for a robust foaming process.

Scorch and hydrolytic aging behaviour of FR foam grades

In general, as a result of their chemical nature, flame retardants show a negative impact on the scorching behavior and the hydrolytic aging performance of the resulting foams. One way to reduce these negative effects is to choose the right silicone surfactant and the minimum use level of the flame retardant. In principle three different types of surfactants are available for flexible foam applications: conventional surfactants like TEGOSTAB® BF 2370, universal surfactants like TEGOSTAB® B 8244 and FR surfactants like TEGOSTAB® B 8155. These different surfactant types show significant differences in their flammability performance. Table 8 summarizes CAL117 flammability results for these different silicone surfactants in combination with the flame retardant TCPP:

Table 8. CAL117 vertical burning results (inches) for various silicone surfactants (Formulation 4, Table 2). The use level of the silicone surfactant was 1.0 pphp. All foam grades showed an air permeability with values below 30 mm water column. The values given in the table are averaged burning results of 5 unaged foam samples.

TCPP Use level	**BF 2370**	**B 8244**	**B 8155**
20 pphp	2.3	1.1	0.9
15 pphp	3.1	1.5	0.9
12 pphp	8.3	2.0	1.6
9 pphp	12	4.1	1.9

In principle, it is possible to pass CAL117 with all different surfactant types but the required FR load is significantly different depending on the surfactant used. Whereas for TEGOSTAB® BF 2370 a minimum use level of 12 parts is required to pass the test, a use level of 9 parts TCPP is already sufficient when TEGOSTAB® B 8244 is used. This results in better flammability performance compared to TEGOSTAB® BF 2370 with 12 parts TCPP. As shown in Table 8, changing to TEGOSTAB® B 8155 would allow for a further reduction of the FR additive use level below 9 parts while maintaining good FR properties of the final foam (results not shown).

The choice of silicone surfactant and required use level of the FR additive can have a significant influence on scorch sensitivity and hydrolytic aging performance as shown in Figure 6 and Table 9.

(a) ***(b)*** ***(c)***

Figure 6. *Scorching Results for different FR foam grades with comparable flammability results but different stabilizer types and different FR additive loadings. (a) BF 2370 and 20 pphp TCPP; (b) B 8244 and 12 pphp TCPP; (c) B 8155 and 9 pphp TCPP.*

Table 9. Influence of the FR additive load on the hydrolysis resistance of flexible slabstock foams, (Formulation 4, Table 2).

Silicone Surfactant & TCPP use level	Rise Time [s]	Density [kg/m^3/ pcf]	Air Permea-bility[1]	CLD Hardness 40% Deflection [kPa]		Compression Set 22 h, 70°C, 90% Compression [%]		Tensile Strength [kPa]		Elongation [%]	
				Initial	After Aging	Initial	After Aging	Initial	After Aging	Initial	After Aging
20 p TCPP, BF 2370	105	26.1 1.63	10	2.9	2.2	5	11	60	66	60	100
12 p TCPP, B 8244	103	23.8 1.45	11	2.9	2.2	5	9	86	85	118	164
9 p TCPP, B 8155	93	23.8 1.45	11	3.1	2.2	4	5	80	80	116	130

1) Air permeability has been measured as back pressure (mm water column) which is obtained by an air stream passing the foam with constant speed. The lower the value, the more open celled is the foam structure.

As shown in Figure 6 and Table 9, the choice of silicone surfactant can have significant impacts on scorch and hydrolytic aging performance, especially regarding the compression set changes.

SUMMARY

In recent years FR foam grades have become more and more specific due to the different types of flame retardants (halogenated and halogen-free) and polyols (hydrophilic polyols or natural oil-based polyols) combined with different density ranges achieved with or without CO_2-technology.

Changing the type of flame retardants, polyols and physical blowing agent is accompanied with different requirements of the FR silicone surfactant with respect to its stabilizing potency, nucleation efficiency and compatibility support of the different raw materials.

We believe that the new versatile FR surfactant TEGOSTAB® B 8155 meets the requirements for a broad range of different FR foam grades, including different polyols, FR additives, conventional blown foams and CO_2-blown foams.

TEGOSTAB® B 8155 combines the excellent FR performance of TEGOSTAB® B 8239 with the superior compatibility support of TEGOSTAB® B 8245 and completes the silicone surfactant product portfolio for the multitude of actual FR foam grades.

Because of its good FR performance, TEGOSTAB® B 8155 allows for a reduction of FR additive load which has beneficial impact on scorching and hydrolytic aging behaviour.

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REFERENCES

1. J. Troitzsch. 1982. *Brandverhalten von Kunststoffen*, Hanser Verlag, p. 47.
2. A. Weier, G. Burkhart, V. Zellmer. 1994. 35th Annual Polyurethane Technical Conference, SPI 1994, p.202.
3. G. Burkhart, M. Klincke. 1996. UTECH 96 Proceedings, Paper 58.
4. T. Boinowitz, R. Borgogelli, W. Gower. 2003. "Impact of Silicone Surfactants on the Flammability of Flexible Slabstock Foam- Comparison of California TB117 draft 2002 with established Flammability Tests", presented at the Polyurethane Conference (API) Orlando, USA, October 1-3, 2003.
5. R. Hubel, H. Pelka, W. Gower. 2005. "Breaking the Rule: A new highly sophisticated Silicone Surfactant for Flame Retarded PU Foam", presented at Polyurethane Foam Asociation (PFA), Charleston, USA, October 5-6, 2005.
6. R. Landers, R. Ziegler, A. Denizhan. 2009. "Silicone FR Stabilizer for Ester Foam", presented at UTECH 2009 in Maastricht.
7. A. Terheiden, R. Hubel, J. Bullion, „Evaluation of Silicone Surfactants in Combination with various halogenated and non-halogenated Flame Retardants", presented at Polyurethane Conference (CPI) Washington, USA, 2009.
8. State of California, Department of Consumer Affairs, Bureau of Home Furnishings and Thermal Insulation, Technical Bulletin 117, March 2000, current version.
9. British Standard: Fire Test for Furniture, BS 5852, Part 2, "Crib 5", 1982.
10. DIN 53 578-88, „Testing the Aging Behaviour of Latex and Polyurethane Foam" 1988 (superceded by DIN EN ISO 2440, „Flexible and Rigid Cellular Polymeric Materials – Accelerated Aging Tests", 2000).
11. The three cycles aging is according to Daimler Benz Liefervorschrift (supplier's guideline) DBL 540, 1997.

BIOGRAPHIES

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Dr. Annegret Terheiden received her Ph.D. in Chemistry with an emphasis on interfacial and physical chemistry at the University of Duisburg-Essen, Germany. In 2006, she joined the former Goldschmidt GmbH as a Technical Manager for flexible foam. Today she is responsible for global product development and application technology for moulded foams at Evonik Industries AG.

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Dr. Roland Hubel studied Chemistry at the Ludwig-Maximilians-University of Munich, Germany. He received his Ph.D. in Coordination- and Metal organic Chemistry. After working for one year in the field of genetic engineering as civil servant, he joined the former Goldschmidt GmbH as a research scientist in 2000. He later became responsible for R&D of polyethers, and the development and application technology of additives for microcellular foams. Today he is responsible for global product development and application technology for flexible slabstock polyurethane additives at Evonik Industries AG.