CertiPUR-US® Compliant MDI Flexible Polyurethane Foams

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ABSTRACT

Flexible polyurethane foams, particularly visco-elastic foams, have seen increased applications in the bedding market in recent years. In particular, the application of visco-elastic polyurethane foams has not only enjoyed tremendous growth, but also seen positive recognition and acceptance from consumers. On the other hand, consumers are becoming better informed and would like to understand the materials inside the mattresses that they buy and use. The voluntary CertiPUR-US® program was developed to address consumer concerns, such as durability, content and indoor emissions. Huntsman has developed a unique MDI-based flexible polyurethane foam technology, which offers premium-grade polyurethane foams that meet or exceed CertiPUR-US requirements. These innovative approaches will enable slabstock foam producers to more fully meet the needs of the market and regulatory requirements. In addition, our new MDI-based technology also offers advantages over traditional TDI-based technology. These advantages include simple and robust processing, fast curing, and easily tunable densities and reduced catalyst requirements. This paper demonstrates that high-quality MDI visco-elastic can be readily produced with outstanding properties. These improved properties include superior compression set, compliance with California Technical Bulletin 117 Vertical Fire Tests and low emissions as required by the CertiPUR-US program.

INTRODUCTION

Visco-elastic polyurethane foams are commonly known as memory foams. The main characteristic of this type of foams is slow recovery after compression. The technology to produce this type of flexible polyurethane foams has been available for more than 30 years. The first commercial memory foam was developed during the mid 1960s as a result of NASA's AMES Research technology transfer program. However, only in recent years have commercial products been made widely available to consumers, thanks to the research and development efforts by a number of companies. Nowadays, typical visco-elastic foams are almost all based on open-cell technology, which would allow better airflow. Due to their pressure-relieving property, visco-elastic polyurethane foams have found increasing applications in beddings, such as mattresses and pillows, upholstered furniture, etc. Even during the economic downturn, memory foams continue to enjoy increasing acceptance by customers. It is estimated that mattresses made with memory foams will grow significantly in the United States in the coming years. Currently, memory foam-based mattresses only represent a small fraction of the market for the United States in particular and for the rest of the world in general. Over 600,000,000 lbs. of flexible polyurethane foam (FPF) were sold into bedding applications during 2008 in the NAFTA region. Visco-elastic grades of FPF accounted for approximately 250,000,000 lbs. of this total [1]. It is estimated that the total wholesale mattress market in the United States is about $4.6 billion. Among them, visco-elastic memory foam based mattresses are far and away the fastest-growing segment. Sales of memory-foam mattresses have grown impressively from 14% to almost 20% of the mattress market in just the past eight years. [2]

On the other hand, consumers are becoming better informed and would like to understand the materials inside the mattresses that they buy and use. Hence, the non-profit organization, the Alliance for Flexible Polyurethane Foam, Inc., developed a voluntary CertiPUR-US® program which addresses consumer concerns, such as durability, content and indoor emissions. According to the requirements of CertiPUR-US, "*Certified flexible polyurethane foams have been independently laboratory tested and certified to be:*

- *Low Emission (VOCs) for indoor air quality*
- *Made without ozone depleters*
- *Made without PBDE flame retardants*
- *Made without mercury, lead and heavy metals*
- *Made without formaldehyde*
- *Made without prohibited pthalates*[3]

In fact, CertiPUR-US is mainly adapted from European CertiPUR program, which was developed in 2002 by EUROPUR, the association of European flexible polyurethane foam block manufacturers. The recognition of CertiPUR-US is increasing phenomenally. As of April 2012, there are 21 companies offering CertiPUR-US flexible polyurethane foam products.

Huntsman has developed a unique MDI-based flexible polyurethane foam technology[1b, 4], which offers premium-grade polyurethane foams that meet or exceed CertiPUR-US requirements. These innovative approaches will enable slabstock foam producers to more fully meet the needs of the market and regulatory requirements. In addition, our new MDI-based technology also offers advantages over traditional TDI-based technology. These advantages include simple and robust processing, fast curing, and easily tunable densities and reduced catalyst requirements. This paper demonstrates that high-quality visco-elastic foams can be readily produced with outstanding properties by the use of SUPRASEC® MDI and carefully chosen polyols and additives. These improved properties include superior compression set, compliance with California Technical Bulletin 117 Vertical Fire Tests and low emissions as required by the CertiPUR-US program. As the market share of visco products has increased, differentiation of such products is naturally happening. Therefore, there is an increasing need to introduce innovative memory foam products to the market. In any case, high quality and durability with low emissions of VOCs will be desirable. Traditionally visco-elastic foams have been made with TDI-based formulations, but these technologies have some limitations, such as hardness and density range. As one of the pioneers of MDI visco technology, Huntsman has been providing technology and polyurethane systems to customers globally for a number of years. We believe that our current innovative technology will provide our customers an additional option to meet the ever-changing market needs while meeting the new CertiPUR-US standards. The extreme flexibility for processing and outstanding physical properties of this new technology will enable slabstock foam producers to provide luxury grade memory foams.

RESULTS AND DISCUSSION

Formulations for visco foams made with all SUPRASEC MDI and carefully chosen polyols are given in Table 1. These formulations typically have MDI isocyanate index in the range of 75 to 90. The physical and chemical properties, exothermic maximum temperature and block heights of these foams are shown in Table 2. It is worthy to point out that CertiPUR-US guidelines are strictly followed in preparing the samples for all physical, chemical and emissions chamber tests. These foams were produced on a continuous line using a pilot Cannon machine. Details of these experimental runs can be seen in the Experimental section. The processing for these formulations is very robust and simple. Typically, only a small amount of nitrogen is needed to help nucleation. The cell structures are generally fine. These specially designed SUPRASEC MDI-based visco foams are fast curing with open cell structures that need no crushing.

As seen in Table 2, a nice feature of these foams is that they all have fantastic compression set properties. We use ASTM D-3574 method to conduct 50%, 75% and 90% dry compression and 70% wet compression, and all of the foams have less than 3% set under above conditions. This outstanding compression set means that these foams

are of exceptional durability. Another feature is that without any additional fire retardants, all of these visco foams passed California T.B. 117 vertical burn test for both aged and unaged samples.

Table 1. Formulations using SUPRASEC® MDI

	A	B	C	D	E	F
SUPRASEC® MDI	66.8	70.7	46.5	52.7	50.6	57.4
Polyol 1	40	40	40	40	40	40
Polyol 2	40	40	40	40	40	40
Polyol 3	20	20	20	20	20	20
Polyol 4	10	10			10	10
Water	2.4	2.4	1.7	1.7	1.7	1.7
JEFFCAT® ZF-22	0.1		0.1	0.1	0.1	0.1
JEFFCAT® LE-210	0.1	0.08	0.1	0.1	0.1	0.1
JEFFCAT® ZF-10		0.25				
DABCO® T-9	0.025	0.025	0.025	0.025	0.025	0.025
Silicone Surfactant	0.3	0.3	0.3	0.3	0.3	0.3
Additive	0.5	0.5	0.5	0.5	0.5	0.5
Iso index	85	90	75	85	75	85

Table 2. Properties of SUPRASEC® MDI-based Viscoelastic Foams

	A	**B**	**C**	**D**	**E**	**F**
Density, pcf (kg/m^3)	3.22 (51.5)	3.32 (53.1)	4.06 (64.9)	3.83 (61.3)	4.37 (69.6)	4.14 (66.3)
Block Height (in)	30.3	30.3	24.4	25.2	23.2	22.8
Max Temp (℃)	129.2	139.6	-	130.1	-	118.9
CLD 40% ; Peak, kPa	3.36	6.34	3.93	6.00	2.46	3.65
CLD 40% ; 3`, kPa	2.69	3.75	3.45	4.75	2.18	3.32
Relaxation, %	20.1	40.9	12.2	20.8	11.4	9.2
IFD 25% , lb	21.5	28.9	25.1	38.4	17.3	26.7
IFD 65%, lb	44.6	60.8	52.5	78.3	38.7	56.7
IFD SAG	2.1	2.1	2.1	2.0	2.2	2.1
C.S. Dry 50%, %	0.7	1.1	0.7	0.8	0.9	1.3
C.S. Dry 75%, %	3.2	0.6	1.0	0.9	1.4	0.7
C.S. Dry 90%, %	3.4	2.9	3.2	3.0	4.1	3.4
C.S. Hum. 70%, %	-1.9	-1.7	-2.1	-2.0	-2.5	-2.2
HACS 120`C 75%, %	3.2	1.4	1.7	2.4	2.5	1.8
Resilience, %	6.61	6.43	16.16	9.13	20.2	18.86
Recovery (s)	1	2	1	1	1	1
Tear, lb/in	0.900	1.500	0.600	1.000	0.400	0.600
Elongation, %	130	146	121	101	132	105
4,4-MDA , ppm	4.9	0.6	2.5	0.4	3.8	2.5

CertiPUR-US requires not only certain physical properties, but also chemical analyses. The chemical analysis includes 4,4'-MDA (4,4'-methylenedianiline, or 4,4'-diaminodiphenylmethane) and emission VOC test. To achieve

CertiPUR-US certification emissions must not exceed 5 ppm of MDA and less than 500 µg/m^3 of total VOC. We are glad to report that all of the visco foams reported in this paper meet the MDA requirement even in the case of as high as 140 ℃ exothermic temperature (Table 2, Run B).

Figure 1 shows the chromatogram of chamber emissions test of representative sample A (3.22pcf). Surprisingly, this foam has a very low level of total VOC (72 µg/m^3). Table 3 lists the details of identified VOC compounds. Among them, propylene carbonate can be traced back to the flushing solvent we added after each run. In reality, the contribution of propylene carbonate to total VOC can be eliminated. Therefore, we would expect an even lower level to total VOC. If we take a closer look at these VOC compounds, their origins can be suggested in most of cases. For example, amine-containing compounds are from the catalysts, and silicone compounds are from surfactants. Halogenated species such as chlorobenzene are probably from the MDI processes. Dioxanes, alcohols, aldehydes and ketones are possibly either from the degradation or from the processing of polyols. However, there are also some compounds that are difficult to trace down.

Table 3. Emissions Chamber Test (CertiPUR-US® Test)—Sample **A** (3.22pcf)

Retention Time, s	Area	Components	µg/m^3 tol. Eq.
13.878	1957768	dimethyl, 1,4-dioxane	11.0
15.021	1357293	dimethyl, 1,4-dioxane	7.6
15.611	119410	1-(2-propenyloxy)-2-propanol	0.7
16.038	170818	chlorobenzene	1.0
20.1	2314565	propylenecarbonate	13.0
20.74	1220398	benzaldehyde	6.8
21.434	159112	phenol	0.9
23.503	758248	octamethyl cyclotetrasiloxane	4.2
25.729	430687	acetophenone	2.4
25.883	122207	unknown	0.7
27.565	380863	JEFFCAT® ZF22	2.1
27.91	156133	p-BCB	0.9
29.613	101141	benzenecarboxylic acid	0.6
29.801	220637	PPG	1.2
29.947	245404	PPG	1.4
30.141	118898	halogenated cyclohexane	0.7
30.935	751148	siloxane	4.2
32.766	1010906	dodecane	5.7
38.343	112253	siloxane	0.6
39.073	61165	hydrocarbons	0.3
40.83	891655	tetradecane	5.0
44.201	119377	phenylmaleic anhydride?	0.7
47.996	85898	hexadecane	0.5
			72.1

Comment [H1]: Is this correct? Time,s..should it be Times

Figure 1. Chromatogram of Emissions Test—Sample A

CONCLUSION

A new visco technology that is based on SUPRASEC® MDI has been developed which offers premium grade visco foams with excellent physical properties. The processing of these foams is simple and tunable. These foams are of outstanding compression set properties and in compliance with California 117 burn tests without any additional fire retardants. More importantly, these visco foams have low levels of VOCs and MDA and meet the requirements of CertiPUR-US®.

EXPERIMENTAL

All the foams presented in this paper were produced with a Cannon-Viking CarDio™* pilot slabstock machine. This machine is equipped with CarDio™ and traversing nozzle laydown dispensing capabilities. All the runs were carried out in "simple" conventional mode with a traversing nozzle laydown and a conveyor angle between 1.5° and 2°. We used direct-laydown setup for all the runs in this paper. The mixer speed was set to be around 2000 rpm with mixing head pressure ranging from 5 psi to about 10 psi. The traverse width is about 90 cm (35 in). The volume of the mixing head is 1.69 liters. A small amount of nitrogen is injected (typically around 1.4 liters/min) to help nucleation. Materials throughput ranges from 40 kg/min to 60 kg/min for A-side and from 70 kg/min to 90 kg/min for B-side. Bun width is typically about 40 inches with an average height of about 22 to 30 inches. Mass flow meters are used to manually control the output.

Physical property tests were done according to ASTM method (ASTM D 3574 A-F). Vertical burn flammability test were carried out according to California Technical Bulletin 117 descriptions and specifications (both fresh and aged samples). The foam recovery time was measured by an internal method, which is to compress a 4x4x2 in size sample to 10% of its original height, hold for 30 seconds and then measure the time to recover to 90% of its original height.

MDA (4,4'-methylenedianiline, 4,4'-diaminodiphenylmethane) analysis is done using an internal HPLC method developed to meet or exceed CertiPUR-US guidelines: Hewlet Packard series 1100 Liquid chromatograph with a Grace HP Altima C18 5µm, ∅=3mm, L=250mm (Grace partnr: 87603) + guard column is used. UV detector at 210nm, 235nm and 280nm is used. Preparation of sample solution: the visco samples are extracted with an acidic solution (1% acetic acid solution) multiple times (minimum 15 times) to ensure the completeness of the extraction. Standard 4,4'-MDA calibration curve is used to calculate the content of MDA.

CertiPUR-US VOC emissions chamber test: The CertiPUR-US guidelines of sample preparation are followed but this test is done using an internal method that is designed to meet or exceed CertiPUR-US guidelines. A 1 m^3 chamber with purified air supply is used. The effluent is collected over a period of three days and analyzed using a GC-MS method with an internal standard. The chamber conditions: 23 °C, 50% relative humidity. Sampling is done continuously for three days.

Trademarks

CertiPUR-US® is a registered certification mark of Alliance for Flexible Polyurethane Foam, Inc.

*CarDio™ is a trademark of Cannon-Viking.

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DABCO® T-9 is a registered certification mark of Air Products.

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BIOGRAPHIES

Yun-Shan Liu

Yun-Shan Liu received his Ph.D. in organic chemistry from Texas A&M University in 1998 and then he joined Eastman Chemical Company in early 1999 as a R&D chemist. His professional career at Eastman covered coatings, hot-melt adhesives, processing, catalysis, Oxo chemistry and hydrogenations. He joined Huntsman Polyurethanes in 2007 as a technical associate. Currently he is a technical manager providing support/service to MDI Slabstock business in both American and Asian markets. He holds six US patents and a dozen peer-reviewed research papers.

Glyn Davies

Glyn Davies graduated from Manchester Polytechnic, UK in 1985 with an honours degree in Polymer Science & Technology and joined ICI Polyurethanes in 1990. After five years in technical development and service for automotive and furniture moulding customers, he moved to Everberg, Belgium to work in the R&D Department on development and application of MDI Flexible Slabstock foam technologies. In 2003, he moved to the USA and worked with the Furniture team on furthering the introduction of Huntsman MDI technologies into the Slabstock industry in North America. Since his return to Belgium in 2008, he has been Market Development Manager for the Polyurethanes Furniture business in EAME and India.

Katherine Piasecki

Huntsman Polyurethanes is an international business unit of Huntsman International LLC. Huntsman Polyurethanes trades through Huntsman affiliated companies in different countries such as Huntsman International LLC in the USA and Huntsman Holland BV in Western Europe.