Low VOC Cal TB 117 Using Bio-Renewable Technologies.

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Abstract

The well-respected Cal 117 flammability standard is on the block because of its environmental impact through the historic use of flame-retardants, which have now been found to leave the foam and impact people. The paper will disclose an alternative route to passing this internationally accepted flammability standard which ensures that the flame retardant remains within the foam. The route involves heavy use of recently developed novel "Green Chemistry" .

Background

California TB 117 (Cal 117, Cal TB 117)* foams have traditionally been made flame resistant by having large amounts of liquid non-reactive flame-retardants added to the other chemicals routinely used to make flexible foams. It has now been determined that these non-reactive flame retardant materials will gradually migrate out of the foam and impact people and the environment. The response of the legislators in California is to propose to cancel the requirement for foams to resist open flame ignition. The thinking being that the foam manufacturer will henceforth no longer need to add these non-reactive flame retardant materials to the foam, thus eliminating future leakage of these materials into the environment.

Green Urethanes disagrees with this direction of travel proposed by the media and the legislators.

It seems desirable for the Polyurethane industry both for customer safety and strategic reasons to hang on to a means of making foam materials resistant to smolder *and* open flame ignition sources.

It is not an option to completely eliminate a simple inexpensive and well known test because there is no apparent solution. The goals of this paper are to demonstrate that a satisfactory solution to the problem exists which satisfies the new environmental concerns and is price competitive to the present routes being used to satisfy Cal TB 117. It also provides a route to reducing the environmental impact across standard foams made outside the Cal TB 117 test criteria.

***Cal 117 is a small scale flammability test & any flammability rating from the test is not intended to reflect hazards by foam or any other material under actual fire conditions.**

Green Technology

The key solution to this problem is to try to use reactive instead of non-reactive flame-retardants.

Green Urethanes' Technology (1) already makes it routinely possible to produce a new range of bio-renewable foams with the normal range of physical properties and hardnesses across the popular density range between 1.25 to over 2.0 pounds per cubic foot. These Green foams allow up to 65% of the petrochemical polyol to be replaced by a Natural Oil Polyol. We have an active program to get to 82% substitution of the petrochemical polyol with an NOP. This 82% replacement of the polyol will allow us to claim that 50% w/w of the total weight of the foam is bio-renewable under the BioPreferred® program run by the USDA.

We decided to base this new Cal TB 117 development work, on Green Urethanes technology which is already in use in the US market and which uses 55 php of a Natural Oil Polyol (NOP) to produce a range of standard foams for use in the North American bedding and furniture industries. Fifty-five parts per hundred of an NOP, based for example on readily available Palm Oil, will give a finished foam with a bio-renewable content of about 33 to 35 % by weight.

This very high level of NOP helps impart extra flame retardant properties to the foam, and we know that the addition levels of non-reactive flame retardant chemicals are routinely lower compared to other conventional, standard Cal 117 foams, at an equivalent density.

This technology produces a new classification of polyols for use in making rigid and flexible foams. These new polyols, whether based on palm, soy, rapeseed or animal oils, for example; are more hydrophobic than standard petrochemical polyols and as a result they have different solubility and reactivity characteristics compared to these standard polyols. It is well known that these particular bio-renewable foams have better humid-age properties & SAG Factors, in addition to the flammability aspects mentioned above.

Reactive flame retardant materials have been available on the market for many years, but have been found to be difficult to use because their very reactivity tightens the foam, making it unfit for use. Lowering the amount of tin or gelation, catalyst in the foam would seem to be the next idea to relieve these symptoms, but foamers find that, even removing all the gelation catalyst in the formulation, is still not enough to deliver a decent quality, open celled foam. Using a speciality isocyanate like Toluene Diisocyanate (TDI) 65/35 may be an alternative, but the cost and availability of this material are difficult, also foams made by high water formulations will still shrink even with TDI 65/35.

An interesting additional effect of being able to use high levels of NOP is that, the tin gelation catalyst use range, or processing width, is far wider and more forgiving compared to standard foam formulations (2). Manufacturing a bio renewable foam range is therefore far easier than when using normal petrochemical polyols, alone. Therefore foam formulations with these very high levels of NOP can more easily cope with the presence of a reactive flame retardant polyol than would be the case with a foam formulation based on petrochemical derived polyols.

We had the option of incorporating the reactive flame retardant as an integral part of the Green Urethanes prepolymer GU 5566 formation process. This pre-reaction of the flame retardant into the GU 5566 polyol material proved to work well for delivering flame retardancy; but it was decided that it would give more formulation freedom to the foamer if the reactive flame retardant was merely metered into the foam machine mixing head along with the other normal side streams of catalysts, water, silicone and dye paste.

Because the problem we were facing, from the media and elsewhere, involved the amount of volatiles which these flame retardant foams have been found to emit; it was decided to take an additional further step to minimize or eliminate as far as possible, any other material normally used in the formulation which could put Volatile Organic Compounds (VOCs), as well as odour, into the finished foam.

With this in mind, we looked at all the other components in the foam formulation and decided to exchange the normal amine catalyst for a Low VOC reactive material (3), and exchanged the familiar stannous octoate for Degussa's Kosmos EF (4).

The reactive flame retardant additive, which we used, was Exolit OP 560 from Clariant Corporation. This is a reactive polyol with an hydroxyl value of around 450. It contains a phosphorous group, and is a halogen free material. In 2009, Exolit OP 560 received a Program P2 Recognition Project Award from the United States Environmental Protection Agency. Therefore, this material has been available in the North American market for quite a while. It is understood though, that it has only found very limited use in flexible foam production.

Most of the silicone surfactants available in North America and Europe are already Low VOC, so we used in each location, standard commercially available flame retardant silicones.

Experimental

In preparation for the Machine trials we ran here at the end of March; we did some ranging work both in the laboratory, and also on a foam pilot plant; in Europe.

The laboratory foams' emissions, made using low VOC materials available in Europe were looked at under VDA 278, which is a test which originated in Europe; and the foams made on the full scale US foam machine, in March, were analyzed for emissions using the US version of the CertiPUR tests.

Results

Table 1.

Machine Formulations

Machine Foam Formulations	php Standard Cal TB 117	php Reactive Polyol OP 560 alone	php New Green Cal 117
Polyol GU5566		100	100
Conv 3000 Polyol	100	0	0
Water	~3.35	3.1	3.1
Conventional Amines	~ 0.3	0.3	**0**
Stann Octoate 50%	~0.1	0.2	**0**
Non reactive Flam Ret	**~12 to 16**	**0**	**0**
Low Emission Amine A	0	0	**0.3**
Exolit OP560	Nil	**2.8**	**2.8**
Kosmos EF	0	0	**0.2**
Flame Retardant Silicone A	0.9	0.9	0.9
TDI 80/20 (Index)		103	103
Foam Physicals			
Density PCF	1.75 to 1.85	1.71	1.68
Density kg/m3	28 to 30	27.5	26.8
ASTM IFD 25%, Lbs		17.3	17.7
CLD 40% kPa		1.7	1.77
Elongation %		162	146
SAG Factor	~1.9 to 2.1	**2.49**	**2.45**
Air Flow - scfm		3.5	2.8
Comp Set 90%, %	<10	8	8
Bio Percent. C14	~2%	**~35%**	**~35%**

Table 2.

Machine Formulations	**Specification**	**Standard**	**Standard**	**New**
CertiPUR Results	Standard Limit	**Non Cal 117**	**Cal TB 117**	**Green Cal 117**
	mg/m3			
TVOC Emissions (base rate)	0.5	0.37	0.434	0.213
Total Allowable TVOC Emission	0.8	0.474	0.456	0.255
Exolit OP 560 present	<0.001	Nil by Test	Nil by Test	Nil by Test

Polyol GU 5566 – Green technology polyol containing 55% of a well-priced NOP

Exolit OP 560 – Clariant Corp; reactive halogen free polyol

Kosmos EF – Degussa Inc; stannous salt of ricinoleic acid – Low VOC gelation catalyst

Table 3.
Laboratory Sample tested against VDA 278

Laboratory Foam Formulation	php Green Cal 117
Polyol GU5566V	100
Water	3.4

Low Emission Amine B	0.3
Exolit OP560	2.8
Kosmos EF	0.2
Flame Retardant Silicone B	0.9
TDI 80/20 (Index)	105

Bio Percent. C14	~35%

VDA 278 Daimler Chrysler - VOC Test Standard - Limit 100 ppm Maximum	ppm
100	48

Polyol GU 5566V – Green technology polyol containing 55% of a well-priced NOP(V)

Discussion

California TB 117 vertical burn response – Flame Retardant Use Levels reduced

The normal use level for non-reactive flame-retardants (**Table 1**) in flexible foam formulations needed to meet Standard Cal TB 117, is between 12 and 16 php (parts per hundred parts of polyol) for a foam density of around 1.7 to 1.9 pcf.

The second results column, **Reactive Polyol OP 560 alone**, shows the formulation and physical results of this machine produced foam; where the formulation has been rebalanced after the substitution of the normal non-reactive flame retardant by the reactive OP 560. The standard catalyst package of mixed amines and stannous octoate is unchanged.

The third column, **New Green Cal 117**, shows the full capabilities of the Green Technology, with the non-reactive flame retardant replaced by OP 560; but now with the standard amine and gelation catalysts replaced by low VOC alternatives.

Formulations in **Table 1** show that, the excellent flammability characteristics we obtain from the use of high levels of NOPs means the foams will pass the California TB 117 vertical flame test at a level of just 2.8 php.

This represents a reduction of about 80% compared to the level of non-reactive flame retardant, which would normally be required to pass Cal 117 at this density of 1.7 pounds per cubic foot (pcf).

It also shows a considerable reduction in the amount needed for a reactive flame retardant too when compared to the 6 to 12 php range normally recommended by the manufacturers of these reactive flame retardant materials; dependent on the target density.

Note that, because this non-reactive flame retardant material has been removed, the amount of water needed to blow the reaction is also reduced. At the same time, the foam feel is improved because the plasticizing effect of the non-reactive flame retardant oil is no longer present.

SAG Factors of the new foams are very good. Standard foams and standard Cal TB 117 foams will have SAG Factors in the region of 1.9 to 2.1. Here we see SAG Factors of 2.49. These numbers take these new foams into levels normally only associated with the higher quality High Comfort or even High Resilience, foam types.

Emission Results

CertiPUR Volatile Organic Compounds (VOCs)

Looking at **Table 2**; the Total Allowable TVOC Emissions are drastically reduced in the new foams compared to foams made with and without non –reactive flame retardant. Therefore, these new foams pass Cal TB 117 and have lower emissions than standard foams with zero non-reactive flame retardant, shown in **Table 2**, as **Standard Non Cal 117.**

Additionally, Hall Analytical based in the UK, which carried out the CertiPUR tests for us; were given a sample of Exolit OP 560 to put through the CertiPUR test rig so that its signature could be typified. We then asked them to specifically look for the presence of Exolit OP 560 in the read out of the three production foam samples, which they received, for analysis.

No trace of the reactive Flame Retardant polyol OP 560 was found in any of the foams by their test detection apparatus.

The flame suppressant was, as assumed, reacted permanently into the foam matrix and did not contribute to the VOC levels found in any of the CertiPUR tests. Testing continues and foam samples will be submitted now, probably for solvent extraction, to confirm these findings.

Volatile Organic Compounds (VOCs) tested by VDA 278

VDA 278 is a German, two part, emission test developed originally by Daimler Chrysler to look at the environment of drivers and passengers in automobiles. VDA 278 is commonly used to test emanations from all furnishings in the car’s interior; from fabrics, carpets, leathers, coatings, paints, glues, plastics and of course; foams.

The VOC part of the test is performed at 90 Celsius and looks by type and by level at all the volatile and semi-volatile organic compounds with structures up to n-C20, drawn off the foam. Maximum test limit is set at 100 ppm. The VDA 278 is severe, and like the present Cal TB 117 fire test, is well respected.

Looking at **Table 3**, you will see that the VOC level found under VDA 278 was 48 parts per million. The maximum allowable level for a pass is set at 100 ppm. With simple further work, it is anticipated that levels of less than 20 or even less 10 parts per million can be achieved in the future.

Normal VDA 278 VOC figures for a standard Cal TB 117 foam, made with non- reactive flame retardants, are expected to be in excess of 200 ppm, mainly due to the use of conventional amines and stannous octoate as the blowing and gelation catalysts, respectively.

Conclusions

This technology reduces the amount of flame retardant required to enable flexible foam to pass the smolder and open flame parts of California TB 117, by 80%. The small amount of flame retardant needed now becomes fixed into the foam matrix and will not escape and threaten people and the environment. By making small further changes to the choice of other tin and amine catalysts and silicone which can be used to make this Cal TB 117 compliant foam, it is possible to deliver a very clean environment for people. The foams demonstrated here also have a Total Bio-Renewable content of approximately 35% by weight.

It is suggested, therefore, that the open flame and smoulder parts of California TB 117 should remain unchanged and in-force. The offensive emissions, which are driving the present changes to TB 117, can be taken care of by specifically totally banning their presence in the finished foam when subjected to an approved emission test. An additional step may be to modify the CertiPUR test or; use the VDA 278 VOC regime. Each are safe and proven VOC tests for home and contract furnishing materials.

By using the new characteristics of "Green Chemistry," it is possible to ensure that the original objectives of Cal TB 117 are still met; but now with the added guarantee of long-term environmental protection from undesirable emissions, and which also to reach the necessary price point for the North American market.

These Green Cal 117 foams were launched at the recent High Point Market.

- We support California Technical Bulletin 117
- This Low Emission solution is only made possible by the unique processing characteristics of Green Chemistry
- Emissions into the environment from the use of non-reactive flame retardants are eliminated
- The route is commercially and technically viable and can be used to produce Low Emission flexible foams for the furniture and bedding markets.

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Biography

Jeff Rowlands

Jeff Rowlands is a Director of Green Urethanes Limited and also, its sister company Innochem Limited. Both companies are involved in the development, patenting and licensing of in-house, and third party-developed, technologies, for use in the Urethane foam industry, worldwide. Both Green Urethanes and Innochem are based in the United Kingdom. Prior to this, Jeff was a Director of Interchem International SA in Luxembourg, which developed and licensed the PIPA polyol process for use in the North American and European flexible slabstock and moulding, markets. He was also Technical Director of a foam production facility in the UK, which he designed and commissioned (now part of Recticel NV). He is a Fellow of the Institution of Chemical Engineers, a Chartered Engineer and a registered European Engineer at Fédération Européenne d'Associations Nationales d'Ingénieurs in Paris, France.