

## New patented technology for greener urethanes

During 2009, the team at Green Urethanes in the UK, started to discuss how to preserve the essential physical properties of urethane foams which contain small volumes of polyols derived from so called green feedstock – specifically palm oil, soy bean oil, rapeseed and castor oil as well as oils from animal sources. The result was that a total of six patents were applied for during 2009, and in March 2010 these were consolidated into a single application, now published as WO 2010/100421 A2 and WO 2010/100421 A4 (US 2010/0227151 A1). The Green Urethanes patent application has recently been registered in Canada, China, Japan, Malaysia, Mexico, and Brazil. An application has already been lodged in the USA. Further examinations are planned for Russia, India, Indonesia, and Europe. By the end of 2011, Green Urethanes technology will be registered for patent examination in 23 countries worldwide. The patent application shows that the technology developed by Green Urethanes could remove the troublesome low molecular species normally present in natural oil polyols (NOPs) by reacting the NOP with isocyanates using specific catalysts. This results in a molecular weight distribution more similar to that of a conventional petrochemical based polyol. Foams produced using these polyols have processing and physical properties characteristics similar to traditional “non green” foams.

### 1. Current NOP usage

It is becoming increasingly desirable to make polyurethane foams from lipid-based polyols such as natural oil polyols. Currently, there are limits to the maximum incorporation of NOPs into urethane formulations. For example, one of the largest uses for NOPs is in the production of flexible slabstock foam in which typically only a maximum of 22 php (parts per hundred polyol) of conventional polyol can be replaced by NOP. Higher levels of up to 30 php incorporation are possible but the resulting foam has poor compression set, foam settle after rising, poor stability, as well as other reduced physical properties, tensile tear and elongation, making it unsuitable for use by most customers particularly in the furniture and bedding industries. In HR (high resilience) foams the maximum toler-

ated NOP level may be only 5–10 php. Above this level the HR foam exhibits unacceptable faults, such as splits and internal pockets of collapsed foam.

The incorporation of unmodified NOPs into polyurethane formulations is complex for two main reasons:

- NOPs are hydrophobic because the chains do not contain oxygen linkages compared to conventional petroleum-based polyols. As such they do not readily mix and react with other components in the formulation.
- In NOPs the OH groups are formed through the use of double bonds, transesterification with multifunctional alcohols or cleavage/oxidation. This tends to give sterically hindered hydroxyl groups distributed along the carbon chain rather than at the end of the chain as in conventional polyols. This leads to the characteristically lower reactivity of NOPs.

#### 1.1 Introduction to the Green Urethanes technology

Green Urethane technology allows the use of very high levels of NOPs in all types of

urethane foams, including flexible, rigid, semi-rigid and microcellular types. There are examples in the application of flexible foams made containing for example, 75 php of palm oil and soy oil based polyols. The resulting foams have all their essential physical properties preserved by this innovative technology. In simple terms this means that (at for example the 75 php inclusion level) 50 % of the flexible foam mass has been grown on top of a farm field and not drilled from under an oil field. Also, the processability of these foams is excellent, and has been commented on as being superior to that of so called conventional foams, particularly in terms of tin processing range and the tendency to form undesirable splits. In addition to this greatly increased renewable content, the use of Green Urethanes' polyols will increase the hardness of a flexible foam by up to 25 % and also increase its flame retardancy by up to 25 % compared to standard polyether flexible foam slabstock. Flame retardant levels can therefore be reduced compared to their normal use levels.

Another frequent problem associated with NOPs is the characteristic odour of residual aldehydes and other odour generating species that can be present in the finished foam. Whilst not a problem in rigid foams, consumers of flexible foams in furniture and in particular mattresses do not always like these odours. The odour of foams made with NOPs tend to smell of popcorn or french fries due to the presence of hexanal, nonanal, decanal and other aldehydes, ketones and carboxylic acid derivatives. Through the selection of the correct isocyanate and catalyst in the Green Urethanes technology, these very odourous species can be wrapped up and eliminated from the NOP and therefore eliminated or substantially reduced in the finished foam.

The Green Urethanes technology also allows the production of a wide range of stable, low odour blends of NOPs and polyether polyols which can be stored for long periods, making them highly suitable for use in the systems market. Therefore this new approach to raising the level of NOP usage in poly-

\* Jeff Rowlands  
jeff.rowlands@greenurethanes.com  
Dr Frans Paap  
Green Urethanes Ltd.,  
Walton on Trent, Derbyshire, UK  
www.greenurethanes.com

urethane foam, appears to solve three problems simultaneously.

## 2. Summary of the invention

A foam, preferably flexible, can be made from a mixture of isocyanate modified polyol (i. e. prepolymer), and foam forming ingredients, where the isocyanate modified polyol is made by reacting at least one lipid-based (NOP) polyol with at least one multifunctional isocyanate. The isocyanate modified polyol is a non-foamed polyol polymer with available OH groups. The isocyanate normally reacts with between 0.01–70 % of the OH groups present but most preferably less than 30 %

of the OH groups present. The reaction is generally powered by a polyurethane gelation catalyst.

No additional external heat is required for this process and the resulting prepolymer is storage stable for use in the production of polyurethane foam of all types.

The suggested mechanism of the invention is that the process makes the reaction characteristics and dynamics of NOPs more similar to those of conventional polyols through a reduction in the hydrophobic behaviour of the NOP and an increase in the NOP's reactivity. This results in a more even distribution of NOP and conventional polyol

throughout the reaction mix; instead of the NOP reacting relatively late in the foam forming process. The more even distribution and behaviour of the NOP also avoids adverse plasticising effects which NOP can have, which can affect the stability and physical properties of the foam. These adverse effects may occur when the macro polymer created by the relatively early reaction of the conventional (synthetic) polyols and isocyanate, is then coated on its outer surface by the polymer strands formed by the polyurethane reaction with the NOP, because of the delay caused by the NOP reacting late, onto the already partially formed macro synthetic polymer chain. This especially is thought to be the characteristic effect of

▼ **Tab. 1:** Data for high index NOPs prepolymers

Isocyanate modification of the NOPs									
(pbw)									
Green E		99	99		97.5			75	
Green C	97,3			99		96.5	97.5		75
P1388/P4156								25	25
DBTL			0.002	0.002					
Sn Oct 33 %	0.03	0.03							
Kosmos EF					0.03	0.03	0.03	0.03	0.03
TDI 80/20	2.7	0.4	1	1	2.6	3.6	2.4	1	1
Percentage of total OH groups being reacted	11	4	11	4	28	15	10	9	9
Foams using isocyanate modified NOPs from above									
Iso modified Green E from above	0	50	50	0	50	0	0	100	0
P1388	50	50	50	50	50	50	50	0	0
Dabco 33LV	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Amine A1	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Sn Oct 33 %	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70
Silicone B2370	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80
Iso modified Green C from above	50			50		50	50		100
Water	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
TDI (index)	105	105	105	105	105	105	105	105	105
TDI php	58.7	51.2	51.2	58.7	50.1	58.7	58.7	50.9	66.0
Density kg/m <sup>3</sup>	21.8	22.7	22.8	22.3	22.1	22.3	22.6	21.7	24.1
Density PCF	1.36	1.42	1.425	1.39	1.38	1.39	1.41	1.36	1.51
Hardness IFD ASTM 25 % lbs	57	38	35	57	38	55	56	39	74
Hardness 40 % CLD kPa	5.74	3.78	3.56	5.73	3.77	5.5	5.6	3.91	7.42
Hardness after humid age HALL	4.61	2.79	2.65	4.41	2.87	4.5	4.52	3.02	6
Hardness loss %	19.7	26.2	25.6	23	23.9	18.2	19.3	22.8	19.1
Hysteresis %	19	25	25	19	24	21	20	25	20
Tensile kPa	93	90	88	94	88	105	92	70	89
Elongation %	83	122	125	80	110	85	78	71	38
Processing comments	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
Php green content approximately %	50	50	50	50	50	50	50	75	75

Source: Green Urethanes application

NOPs with their relatively low hydroxyl or sterically hindered functionalities.

## 2.1 Changes to molecular weight distribution

NOPs typically contain a large, wide distribution of different weight oligomers which react at different rates as the main polyurethane polymerisation reaction proceeds. The molecular weight bell curve distribution for NOPs is therefore far flatter and lower than the tight, high bell curve of conventional (synthetic) polyols which have been perfected and engineered over the years. Earlier research by Abraham et al. (WO 2006/116456 A1) shows that low level inclusion of NOP may be successful if 35 % of oligomers are tetramers or higher, 5–10 % are trimers and dimers are limited to 8–12 %. This scatter of polymers with different molecular weights leads to different NOP oligomers with different molecular weights reacting at different stages and times of the production reaction. This can create difficulties in processing and a profusion of short chain polymers being produced

which can lead to inferior physical properties in the finished polyurethane.

The technology invented by Green Urethanes, preferentially reacts the short chain triglycerides of the NOP, especially monomers and dimer oligomers, into higher molecular weight polymers. Therefore, the most undesirable oligomers will be preferentially reacted because they are naturally more reactive to the isocyanate and are preferentially “cleaned up”. Additional chain extension reactions will take place between other classes of oligomers leading to tri- and tetra-species which will also then react with either lower or higher molecular weight oligomers and species. These reactions lead to a steeper and tighter bell curve distribution of oligomer species in the NOP. The formation of macro molecules prior to foam production also gives a higher hardness to the foam, better processing and better physical properties compared to foams made with the inclusion of NOPs without the “pre-reaction” or “pre-treatment” as described here.

The use of gelation catalysts which happen to be ricinoleic acid salts can also create special complexes that can trap low molecular weight odour compounds or react with them. The amount of catalyst required is at least 0.001–0.1 mMoles/100 g polyol, although higher levels can be used.

## 2.2 Scope of the Green Urethanes technology

The scope of the technology allows the manufacture of an isocyanate modified, hydroxyl ended polyol (prepolymer) for use in the manufacture of urethane foams, which has been made from any combination of NOPs with any synthetic polyols (ether or ester) reacted with any isocyanate(s) with any gelation catalyst. Combinations of NOPs, synthetic polyols, isocyanates and gelation catalysts work too. The result is the production of a “new” polyol which has the hybrid characteristics of the NOP(s) and synthetic polyol(s) from which it was originally made. This is why the Green Urethanes prepolymer now acts and reacts as a single reactant in the foam forming process, and not as a jum-

bled mixture of molecular weights reacting at different times.

A demonstration of the width and extent of the technology is shown in **table 1**. Look at **table 1** to see how two NOPs, produced from two different natural oils (soy beans and palm mesocarp) can give flexible foams with a wide range of physical properties by varying the levels of isocyanate (in this case TDI) and also varying the type and level of gelation catalyst in the Green Urethanes technology. The last two columns, you will note, have foams with natural contents of 50 % of the total foam weight, being made with 75 php of the NOP.

So, in **table 1** (line 10) shows the preparation of various isocyanate modified NOP with between 4 % and 28 % of the available hydroxyl groups being reacted with the diisocyanate according to the invention. Also, various metal catalysts at various levels are shown being used to catalyse the hydroxyl-isocyanate interactions of the invention.

## 2.3 100 % NOP content possible

If the whole polyol element (NOP plus synthetic polyol) is subjected to this technology then the plasticising effect of the NOP during the foam production is minimised to the fullest possible level, the miscibility of the NOP element, the size of the macromolecule and optimisation of the physical properties, including the compression sets, of the material produced are further improved to the maximum extent **table 2**.

The lipid-based polyol content of polyurethane foams made according to this invention can be 100 % of total polyol content by weight. The physical properties of the material may not be fantastic at this stage of the development cycle, but the 100 % NOP Green Urethanes modified material does process easily into a stable foam product. (See 5. Future work).

The foams made using the isocyanate modified polyols can be made with or without water, they can be mechanically frothed

**Tab. 2:** Comparison of flexible foam properties using various prepolymers

	Foam 1	Foam 2	Foam 3
P4156	49		
PO56 (Europe)		49	
Soy prepolymer	51	51	
(P4156/Soy) prepolymer			100
Dabco 33LV	0.2	0.2	0.2
Amine A1	0.1	0.1	0.1
Sn Oct 33 %	0.7	0.7	0.7
Silicone BF2370	0.8	0.8	0.8
Total water php	4	4	4
TDI php	52.2	52.2	52.2
Density PCF	1.4	1.46	1.5
Density kg/m <sup>3</sup>	22.4	23.36	24
CFD 40 % kPa	4	2.95	3.7
ASTM ILD25 %	40	29.5	37
Hardness after humid age	31.2	23.9	27.8
Hardness loss %	22	18.9	24.8
Hysteresis	48.8	47.1	44
Tensile kPa	87	91	103
Elongation %	126	160	182
Compression set 75 %	14.3	15	8.5

Source: Green Urethanes application

or not mechanically frothed and the foams can use auxiliary non-reactive blowing agents.

## 2.4 Odour reduction

Isocyanates can be used to reduce the odour of an isocyanate modified polyol and/or foam made from NOPs. Those based upon TDI generally show lower odour characteristics compared to MDI-based isocyanate modified polyols. Thus it is preferable to use TDI as the multifunctional isocyanate for low odour foams.

Foam odour is very important especially when the foams are used in automotive applications and used in a confined, air locked environment and subject to heat, for example via solar gain. It is also important when the foam is used for bedding. Every attempt is therefore made to reduce odours in foams for these industries. It is possible to remove or reduce the odour using part of this Green Urethanes technology. There are two routes to odour reduction described in the application. One is by using a combination of TDI as the preferred isocyanate and a metal salt of ricinoleic acid as the preferred gelation catalyst when making the isocyanate modified prepolymer.

The other techniques may be used during the NOP manufacturing process. This process

normally involves spraying the NOP as a stream into a chamber or vessel which is under some kind of vacuum. The intention is to flash off some of the lighter components. Some of these will be volatile materials which contribute to the odour of the NOP. Ricinoleic acid and/or one of its salts may be injected into the vacuum space or added as a dispersed component to the liquid NOP input stream. These salts can be incorporated at any suitable stage in the production of the NOP or the isocyanate modified polyol. Ricinoleic acid itself alone has been found to be a particularly effective deodorant.

Obviously, TDI in combination with ricinoleic acid or its metal salt may also be introduced to make an airborne isocyanate modified polyol which also removes or lessens the odour of the exiting NOP by forming an in situ weak Green Urethanes prepolymer.

The BMW smell test was conducted according to protocol VDA 270/DIN 10955. This means that each odour panellist rates the odour according to the following scale: 1 = no smell; 2 = slight smell, inoffensive; 3 = easily detectable; 4 = uncomfortable smell; 5 = very disturbing. As illustrated (tab. 3) NOP Green B has an odour of 3, when this polyol is made into a modified isocyanate polyol as used in examples 7, 8, 10 and 12 the odour level is reduced. The use

of DBTL in combination with TDI in example 13 does not reduce the odour nor does the use of stannous octoate in example 14. Example 9 does not use TDI and does not reduce the odour when compared to Green B alone (in example 11). Lupranol 4070 had an odour rating of 1–2 across all panellists.

Identification and total removal of odour is complex. A certain odour from one species may be masked by that of another in an odour panel test. Sometimes the odour removal process may eliminate one odour but reveal another, so that the odour rating test may not change in intensity but panellists reported a change from, for example, “acid” to “sweet”. Results (tab. 4) show the effects of adding and mixing ricinoleic acid into various soy-based polyols at room temperature (18 °C) and leaving the mixture to stand for seven days. The odour panellists reported that the strength of the odour had lessened but had also changed in character.

## 3. Improved storage life

The photograph (fig. 1) shows the stability of the isocyanate modified polyol using NOPs over a period of 12 h at 18 °C. On the right 20 pbw of Green C polyol thoroughly mixed with 80 pbw Voranol RA 800, a standard rigid polyol. The mixture shows almost complete separation of the two polyols in a short time. The mixture on the left contains Green C polyol and Voranol RA 800 which has been agitated and reacted with 1 php

▼ **Tab. 3:** Changes in odour achieved with various catalysts in isocyanate modified polyols

Component	Example 1	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12	Example 13	Example 14
(pbw)									
L4070	99	0	99	0	97	0	0	0	0
Green B	0	99	0	99	0	100	99	99	99
M 220	1	0	0	1	0	0	0	0	0
Kosmos EF	0.003	0.003	0.003	0.003	0.003	0	0	0	0
Kosmos 54	0	0	0	0	0	0	0.003	0	0
DBTL	0	0	0	0	0	0	0	0.003	0
Sn Oct 33 %	0	0	0	0	0	0	0	0	0.03
TDI	0	1	1	0	3	0	1	1	0.4
<b>VDA smell test</b>									
Panellist 1	2	1	1–2	3	2	3	1–2	3	3
Panellist 2	2	1	2	3	2	3	2	3	3
Panellist 3	2	1	1	3	1	2–3	1	2–3	3
Panellist 4	2	1	1	3	1	3	1	3	3
Panellist 5	2	1	1	3	1	3	1	3	3
Source: Green Urethanes application									

▼ **Tab. 4:** Changes in polyol odour using ricinoleic acid

Component	Example 15	Example 16	Example 17	Example 18
(pbw)				
Green D	100	0	100	0
Green E	0	100	0	100
Ricinoleic acid	0	0	0.1	0.1
<b>VDA smell test</b>				
Panellist 1	3	3	2	2
Panellist 2	3	3	2	2
Panellist 3	3	3	2	2
Panellist 4	3	3	2	2
Panellist 5	3	3	2	2
Source: Green Urethanes application				

TDI and 0.004 php of Kosmos EF. There is no separation of the two polyols showing how the technology increases the compatibility of NOPs in a urethane system that has a stable shelf life and that is therefore suitable for worldwide shipment.

#### 4. Experimental laboratory test materials used

The following materials were used:

- Green B – a soy oil-based polyol BiOH 5000, Cargill Inc, USA
- Green C – a mesocarp palm oil-based polyol, PolyGreen Chemicals (Malaysia) Sdn Bhd.
- Green D – a soy oil-based polyol from USSC (Urethane Soy Systems Co.) USA
- Green E – a soy oil-based polyol from USSC, USA
- Lupranol 4070 – a trifunctional polyol with glycerol starter, PO backbone and tip, BASF AG
- Polyol Pluracol 1388 (aka Pluracol 4156) Hetro polyol – 56 OH, from BASF Inc.
- Voranol RA 800 – rigid polyol, Dow Chemical Company

- Voranate M220 – polymeric MDI, Dow Chemical Company
- Kosmos EF – catalyst of tin ricinoleate, Evonik AG
- Kosmos 54 – catalyst of zinc ricinoleate, Evonik AG
- Sn Oct 33 % - Stannous Octoate 33 % solution
- Ricinoleic acid – Sigma Aldrich Co., UK
- DBTL – Dibutyl tin dilaurate – Sigma Aldrich Co., UK
- Tegostab B2370 – flexible silicone, Evonik AG

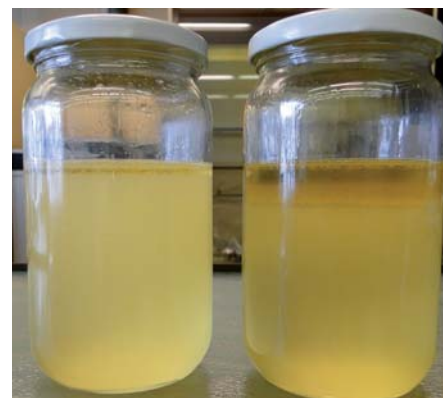
#### 5. Future work

The Green Urethanes technology is now in routine use in the USA, where our foamer licensee makes approximately 15+ different grades of foam at will. Use level of NOP in these grades is 50 php thus giving the foams a 33 % (certified) natural content. The years 2009 and 2010 have been busy years for Green Urethanes, however research is now focused upon the production of a 75–85 php NOP content foam which will have acceptable physical and compression set properties at 90 %. Initial work at this NOP level has pro-

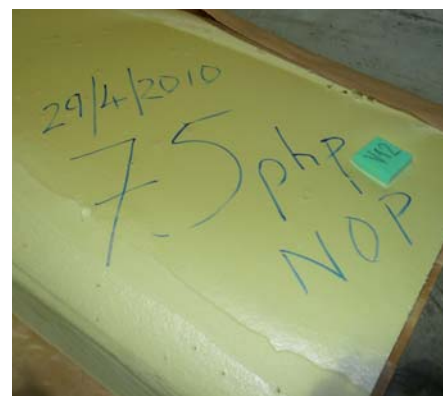
duced stable easily processable foams (**fig. 2**), but the elongation and tear results were judged to be “marginal”, with elongation results just hovering around 100 % and with less than 1.0 lbs/inch tear strength. Through changes to the Green Urethanes prepolymer architecture it should be possible to improve these results. Green Urethanes already has a live project looking at applying its technologies to HR foams. Normally the addition of even fairly low levels of NOPs to flexible foams make the foam feel dry and dead, but perhaps these properties could prove useful in viscoelastic grades of foam.

Fortunately, Green Urethanes has access to additional technology from sister company Innochem which can boost the ILD SAG factor of NOP foams to around 2.4. Conventional foams made with synthetic polyols have ILD SAG factors of around 2.0–2.2, so this 2.4 level is already a great improvement. This effort with HR should therefore, allow even higher ILD SAG ratings to be achieved. ■

▼ **Fig. 1:** Green Urethanes prepolymer stability



▼ **Fig. 2:** 75 php flexible foam sample



#### Foodnote

Just a few comments from the authors on this work with NOPs and why it was done. At Green Urethanes we are not “religious” about being green. We encountered this problem which the inclusion of NOP presented to urethane foams, and we solved it. So as far as the “Tank-und-Teller” debate, concerning the arguments about whether mankind should be converting possible foodstuffs into replacements for various crude oil derivatives; here are some figures from the United States Department of Agriculture: “There are about 6.8 billion people in the world. In 2008/2009 the wheat harvest was 682.4 million t and rice was at 444.9 million t. If the starch content is 70 % then this gives 318 g of carbohydrate each day. The worldwide harvest of sugar and potatoes gives a further 120 g per day.

The recommended daily need for the average human is 300 grammes of carbohydrate which is the 2,000 kilo calories figure which every one knows and struggles to keep down to, at least in the “Developed world”. So, we don’t need to worry about corn, meat and the other staples, because these four items, wheat, rice, sugar, and potatoes already give 50 % more calories than the world needs.” (Figures and script from USSC.)

So the problem is not the amount of food that is grown to feed the world, but where it is grown and the problems of getting the foodstuffs where it is most needed. Food for thought?