Low Cost Polyols from Natural Oils

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SUMMARY

The chemistry of natural oils is reviewed with particular reference to reactions which facilitate their use as polyurethane components. Several types of commercially-available polyols are described together with formulation know-how sufficient to utilise the properties of these novel polyols to their optimum performance. A comparison is made between the properties of polyurethanes obtained using natural, renewable vegetable oils and their traditional, polyether-based counterparts.

Details are given of the successful application of CFC-free polyurethane foams and elastomers using natural oils as the starting component. Of particular interest are those applications in the insulation industry where the production of low density polyurethane foams have been commercialised for discontinuous panels, blockfoam and spray foam applications. The flame retardant qualities of these polyols allows the formulator to incorporate lower levels of traditional chlorophosphorus additives than with polyether polyols.

The use of these polyols in the automotive industry is also described. In particular, the very successful use of natural products to obtain high performance GMFU (Glass Mat Filled Urethane) structural items is described in detail.

The commercial implications of using natural, renewable oils as initiators for polyol production are reviewed with particular reference to the resultant environmental and financial advantages gained, particularly in areas where low cost oils are found in abundance.

INTRODUCTION

With a global market of approximately six million tonnes per annum, the polyurethane industry is a large and diverse business area covering a multitude of applications. Some polyurethane markets are relatively mature whilst others are in their infancy. The versatility of polyurethane has led to the development of countless applications from low density packaging material to high performance medical items and from thermally stable insulation for space exploration vehicles to highly flame-retarded flexible cushioning.

The production of polyurethanes involves the reaction between a polyisocyanate and a hydroxylated species. In many cases the isocyanate has a functionality of two or more and the polyhydroxy material has a functionality between 2 and 6. By altering the equivalent weight of each component, the polymer structure can be significantly modified in order to achieve a product with specific properties. This paper describes one of the approaches to the manufacture of polyhydroxy compounds (polyols) and the application of such products in the marketplace.

Conventional Polyols

Polyols are generally manufactured by one of two possible chemical routes, namely alkoxylation and esterification. Alkoxylation, by far the most common route, involves the reaction between a hydroxyl or amine-containing initiator (such as sucrose, glycerol, ethylene diamine etc.) and either propylene- or ethylene-oxide. This reaction, which is carried out at elevated temperatures and pressures, can be tailored to add varying amounts of the alkoxylating species in order to modify the polyol chain length, or molecular weight. In this manner, low molecular weight polyols can be produced for rigid foams, having molecular weights from about 200 to 450. By extending the polymer chain with the addition of a higher level of alkylene oxide, a molecular weight of up to 6000 can be obtained. This latter product is suitable for more flexible polyurethanes in cushioning and elastomeric applications.

The alkylene oxides used in this process are derived from mineral oil via the petroleum industry. Propylene is derived from the petroleum cracking process and is then converted to propylene oxide before being further converted to a polyol by reaction with an amine or hydroxyl-containing initiator, such as glycerol, sucrose or ethylene diamine.

Polyester polyols are manufactured by the reaction between an acid (or anhydride) and a polyhydroxy compound. For example, a successful rigid foam polyol has been obtained by reacting phthalic anhydride with diethylene glycol to yield an aromatic diol suitable for further reaction with a polymeric isocyanate to give a good quality rigid foam for roof-board applications. Similarly, higher molecular weight polyesters can be produced for flexible foam and low modulus elastomer applications. As in the case of alkoxylation, the major raw materials used in the polyester process are derived from mineral oil.

Table 1. Manufacturing Routes for Conventional Polyol Production

Polyol type	Route to Manufacture
Polyether	(OH)/(NH) group initiator + alkylene oxide
Polyester	(OH) group + carboxylic acid

Natural Oils and Fats

Naturally occurring oils and fats are water-insoluble, hydrophobic substances of vegetable, land animal or marine animal origin which consist predominantly of glyceryl esters of fatty acids, often referred to as triglycerides.

Structurally, a triglyceride is the reaction product of one molecule of glycerol with three molecules of fatty acids to yield three molecules of water and one molecule of a triglyceride. Natural oils and fats vary widely in their physical properties, even though they are made up of the same or similar fatty acids. This is because individual oils and fats vary over relatively large ranges in the proportions of the component fatty acids and there is some variation in the structures of the individual component triglycerides.

The molecular weight of the glyceryl portion (C_3H_5) of a triglyceride molecule is 41. The combined molecular weight of the fatty acid radicals (RCOO-) comprising the remainder of the molecule will vary with different fats from about 650 to 970. Thus the fatty acids contribute 94-96% of the total weight of the molecule. Because of their preponderant weight in the glyceride molecules, and also because they contribute to both the chemical and physical properties of the glycerides, the fatty acids greatly influence both the physical (hydrophobic character) and chemical character of the glycerides.

With some exceptions, most fatty acids that occur in nature are straight-chain acids, which contain an even number of carbon atoms. Those fatty acids in which all carbon atoms in the chain contain two hydrogen atoms and thus no double bonds are termed saturated. The fatty acids that contain double bonds are termed unsaturated. The degree of unsaturation of an oil depends on the average number of double bonds in its fatty acids. The more common fatty acids are usually referred to by a trivial name, such as lauric, palmitic oroleic acids. The Geneva system of nomenclature provides a systematic name for each acid. Under this system, the number of carbon atoms is indicated by a Greek prefix. Thus, for example, acids of 12, 14, 16 and 18 carbon atoms take the respective prefixes dodec-, tetradec-, hexadec-, and octadec-. Saturated acids are distinguished by the suffix - anoic. Palmitic acid, for example, is hexadecanoic acid. The number of double bonds in the fatty acids is indicated by modifying the prefix. Thus oleic acid, with one double bond, is an octadecenoic acid; linoleic acid, with two double bonds, is an octadecadienoic acid; and linolenic acid, with three double bonds, is an octadecatrienoic acid.

Unsaturated Fatty Acids

A large number of unsaturated fatty acids occur naturally, some having up to seven double bonds. As the number of double bonds exceeds three, the source of the oil is most likely to be marine rather than land animal based. Those containing one, two and three double bonds and 18 carbon atoms are the important unsaturated fatty acids of vegetable and land animal origin.

Linoleic acid is undoubtedly the most important polyunsaturated fatty acid in abundance and in distribution. It is present in high proportions in safflower oil (75%), sunflower oil (60%), cottonseed oil (45%), soyabean oil (50%) and corn oil (50%). Linolenic acid is also widely distributed in nature as a major component of many of the more highly unsaturated vegetable oils. It is the principal fatty acid in hempseed (35%) and linseed (45-50%).

Table 2. Chemical Structure of Saturated and Unsaturated Fatty Acids
-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-COOH Stearic Acid (18 carbon atoms) saturated fatty acid
-C-C-C-C-C-C=C-C-C=C-C-C-C-C-C-C-C-COOH Linoleic Acid (18 carbon atoms) unsaturated acid

Chemical Reactions of Natural Oils

Natural oils, being complex mixtures of triglycerides, can undergo a number of standard chemical reactions, some of which are relevant to their use as a component for polyurethanes.

1. Hydrolysis

Triglycerides of oils and fats can be hydrolysed to free fatty acids and glycerol. The reaction is not a simple one and it is reversible. The reaction is catalysed by acids, certain emulsifiers and other substances, including lipolytic enzymes.

2. Esterification

Esterification of fatty acids occurs with alcohols, glycols, triols (e.g. glycerol) and many polyfunctional materials, including sugars and starches.

3. *Interesterification*

Methyl esters of fatty acids are conveniently prepared by displacing the glycerol from fats, usually with an alkaline catalyst.

4. Saponification

The oil or fat is reacted with an alkali, such as sodium hydroxide, to give glycerol and a salt (or soap) of the alkali metal. The reaction is a fundamental one in soap making.

5. *Hydrogenation*

When treated with hydrogen under high pressure and with suitable metal catalysts, fatty alcohols are produced by reaction with the carboxyl group. Using suitable catalysts, hydrogen can also be added to the double bonds of unsaturated fatty acids.

6. Nitrogen derivatives

Fatty acids react with ammonia at elevated temperatures to form amides which can be dehydrated at slightly higher temperatures to yield nitriles.

7. Alkoxylation

Ethoxylation and propoxylation reactions of common fatty acids such as stearic and oleic acids are important reactions used industrially for the production of valuable polyoxyethylene ester emulsifiers and surfactants.

8. Halogenation

Chlorine, bromine, iodine monochloride and iodine monobromide add to double bonds of unsaturated acids and their derivatives. This reaction is used as a method for determining the degree of unsaturation in oils and fats.

9. Hydroxylation

Although a large number of oxidising agents are available which could be used to hydroxylate the double bonds of oils and fats, only two routes are currently of importance - peroxyacetic acid addition and oxidation with dilute aqueous alkaline potassium permanganate.

A great deal of work has been accomplished in recent years by Carlo Venturello of the Instituto Guido Donegani in Novara, Italy. He has succeeded in producing high yields using hydrogen peroxide in combination with tungstate-phosphate catalysts. Further recent research with rape seed oil has shown that the unsaturated links can be partly or wholly hydroxylated at 100°C using dilute aqueous hydrogen peroxide in the presence of a cost-effective peroxophophomolybdate catalyst. The reaction is smooth and high yielding and the extent of hydroxylation can be varied controllably to provide a range of hydroxyl values.

10. Diels-Alder reaction

A variety of dienophiles have been used to add to the conjugated double bonds of fatty acids to yield compounds capable of hydrolysis to tricarboxylic acid functionality. The Diels-Alder addition of maleic anhydride with conjugated and elaidinised safflower oil is typical of the preparation of this kind of condensation reaction.

11. Reaction with formaldehyde

Formaldehyde adds to the double bond of unsaturated fatty acids under the conditions of the Prins reaction to give a variety of products, several of which have pendant hydroxyl groups suitable for reaction with isocyanate groups to yield polyurethanes.

Polyol Production

The above reactions of natural oils can be used to great advantage in generating a wide variety of products suitable for use in polyurethane foams and elastomers. High yields can be produced at a very moderate cost and products can be tailor--made for specific end uses. The concept is designed to take full advantage of the natural chemistry of oils and fats so that countries which have native supplies of these materials can take full advantage of them in the commercialisation of polyurethane chemicals. The polyol manufacturing process involves no alkoxylation and is inherently safe. The plant is relatively inexpensive, easy to operate and has very high yields at short reaction times.

Table 3. The Envirofoam Process for Polyol Manufacture
The Envirofoam Process
Natural Oil + Polyform Catalyst Package = Enviropol

Rigid Foam Polyols

The Envirofoam polyol process involves the one stage reaction of a suitable natural oil with a catalyst system at elevated temperature to give a reaction product which is composed of various chemical species depending upon the nature of the oil and the catalyst system used. The latter is chosen to give rise to the most appropriate polyol for the intended application. A typical process would involve the reaction of approximately 80% oil (e.g. castor, sunflower, palm) with 20% catalyst package. This is carried out using a proprietary plant design which is capable of being set up in a relatively small factory unit. A plant capable of manufacturing 4000 tonnes per annum can be accommodated in a 150m^2 area.

Advantages of the Envirofoam Process

1.Safety

Compared with the manufacture of polyether-based polyols, the process is extremely safe, since it involves the use of chemicals having a low order of hazard. Generally, they are non-flammable, non-toxic and of low volatility. The process itself requires no elevated pressures and moderate temperatures.

2. Attractive economics

Conventional polyols are derived from petrochemical based products which have often undergone a series of reactions to convert simple molecules of low molecular weight to macromolecules having a more complex structure. Each stage of the reaction sequence requires a considerable energy input, which clearly involves a cost element. As a result, even a relatively low crude oil cost is converted to a substantially high polyol cost due to the energy, manpower and hardware costs involved in this conversion to a more added-value product.

Non-mineral oil-based products, on the other hand, are naturally formed macromolecules which nature creates at a very low cost. They are extremely plentiful, easy to process and refine, capable of being cultivated with minimum capital investment and suitable for conversion to quality polyols using an inexpensive reaction process. Refined natural oils can be purchased for DM 0.7-1.2 per kg. Since the proportion of such oil in the final polyol product is approximately 80%, it is clear that an economic advantage is to be gained by replacing or part-replacing conventional polyols by those manufactured from natural oils. Polyols can be manufactured for DM 1.2 per kg when using inexpensive products such as rape seed, palm kernel and cottonseed oils. As in the case of polyether or polyester polyols, no product is ideally suited to all applications and in many cases natural oil-derived polyols are mixed with mineral based products in order to fully optimise the system formulation.

3. *Small plant dimensions*

The low cost and small scale of the polyol plant for converting natural oils is a particular advantage in countries where transportation routes are poor. Instead of importing polyols or transporting them over large distances, small polyol plants can be erected in a number of areas close to the polyurethane industries that they are designed to serve. Locally-derived natural oils are converted to polyols, formulated and processed to manufactured goods which are required by the local market.

Figure 1
Envirofoam polyol plant

4. Versatility

The standard polyol manufacturing facility can accommodate a variety of oils and fats. By altering the catalyst package, the molecular weight, functionality and reactivity can be varied. In this way, the polyol structure can be significantly varied, rendering it suitable for rigid, semi-rigid and elastomeric applications. In addition, the same apparatus can be used to manufacture a Mannich base, which also has significant attributes in many rigid foams. These products, which are formed by the reaction between a substituted phenol, formaldehyde and an alklanolamine, have been used to produce mixed polyols having both a phenolic and a natural oil base. In this way, a relatively low cost polyol is produced with the reactivity and fine cell structure that derives from an amine-containing aromatic species.

5. Simplicity

The natural oil polyol process has been designed to ensure that very little expertise is required to produce consistently good quality polyols. Two semi-skilled men can run a small plant capable of producing up to 3,000 tonnes per annum. A batch process is used with a reaction time of between 40 and 70 minutes.

6. Environmental Aspects

Two major environmental advantages can be realised when using polyols derived from natural oils. Firstly, the oil source is truly renewable, that is, it does not lead to a permanent depletion of a resource which has a limited global availability. Secondly, the amount of energy required to convert natural oils into polyols is considerably less than that required using more conventional routes.

Suitable Natural Oils for Polyol Production

Most naturally-occurring oils can be used for polyol production but the type of product obtained and the suitability of the polyol for it's intended application is determined by the fatty acid composition.

Cottonseed oil is one of the most important edible oils throughout the world. Four million tonnes per annum are consumed, with most being derived from the seeds of *Gossypium barbadense,* usually by a solvent extraction method. About 70% of the fatty acid content is made up of oleic and linoleic acids, with palmitic acid being the principal saturated fatty acid.

Palm oil has been used for polyol manufacture but, in general, suffers from a relatively high free acid content. This gives rise to a product which is waxy or semi-solid in form, although more refined grades with lower levels of free acids have been successfully used. Palm oil polyols usually have an orange colour which derives from the high level of carotene which is found in this natural oil.

Sunflower oil is obtained from the seed of the plant *Helianthus annus* which has an oil content of between 22 and 36%. It is grown in large quantities in Russia and has the technical advantage of a high unsaturation level, with oleic and linoleic acids accounting for about 92% of the total fatty acid content.

Other oils which have been converted to polyols and in turn used for the production of polyurethanes are rape seed, olive, peanut, sesame, corn, poppyseed and linseed. Higher degrees of unsaturation are obtained from marine oils which often contain appreciable quantities of C_{14} to C_{24} fatty acids, with between 3 and 6 double bonds.

Polyol Properties

Most of the work carried out by Envirofoam Chemicals Ltd has been in the area of rigid products for insulation, buoyancy and moulding applications. In this respect, hydroxyl values have been between 380 and 500 mg KOH/g. Typical values of three commercial products are given in **Table 4.**

Table 4. Typical Properties of Rigid Foam Polyols

	Enviropol 1324	**Enviropol 1356**	**Enviropol 433**
Hydroxyl value, mg KOH/g	380-400	420-450	485-500
Acid value (max.), mg KOH/g	2.0	2.0	2.0
Water content (max.), %	0.2	0.2	0.2
Specific gravity	1.04	1.05	1.05
Viscosity @ 25°C, kPa	3200	4300	5100

Rigid foam polyols derived from natural oils have excellent compatibility with most modern blowing agents including HFA141b, HFA134a and both n- and iso-pentane. In most systems, Enviropols are used in combination with conventional polyethers. In medium/high density foams they are used as the sole polyol component, but in these cases a non-standard catalyst package is used. Much of the development of the Enviropol series of polyurethanes has involved the optimisation of unorthodox catalyst systems which are not normally applied to conventional polyether systems.

Rigid Foam Applications.

Experimental Procedures.

All rigid polyurethane foams were developed using a standard procedure, which can be described in the following manner. Initial formulation development was carried out by means of laboratory hand-mix methods. The effect of formulation variables on foam properties was determined in the following manner:

In the case of polyurethane (i.e. not polyisocyanurate) foams, an isocyanate index of 110 was used throughout. A total of 100g of resin (polyols, water, catalysts, silicones etc.) and isocyanate was mixed with a 50mm diameter propeller stirrer at a speed of 3000rpm for 10 seconds. The cream, gel, rise and tack-free times were measured from the onset of stirring and core samples were taken after two hours for free rise density measurements.

In cases where good flowability was required (e.g. commercial refrigerators, panels etc.) hand-mixed foams were evaluated in a`°Triangle Mould". This apparatus consists of a thermostatically controlled aluminium mould as shown in Figure 2. The mould is 750mm long, 170mm wide and 45mm deep. It consists of a 120mm diameter circular reservoir into which the mixed chemicals are poured. Within the circle is a flush-mounted pressure transducer (Model LH44/5) with a range from zero to 35psi (24OkPa). This is fed simultaneously to a digital display and to a continuous chart recorder. Extending vertically upwards from the circular reservoir is a 600mm long flow arm containing 15 triangular shaped restrictions. The foam is able to flow around and behind these restrictions as it rises vertically towards the top of the flow arm, at which point there is a small vent to allow air to escape during the foaming operation. The mould is covered with a 1Omm thick polymethacrylate cover, held firmly in place with aluminium sections as shown.

Figure 2
Triangle mould used to assess flowability)

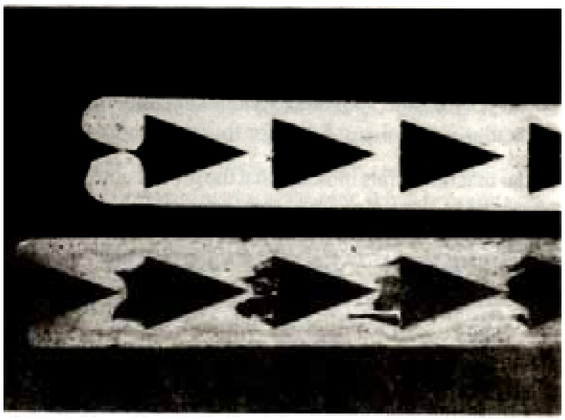

Figure 3
Foam "knit-lines" for good and poor flowing foams)

During these evaluations, the mould was maintained at 25°C and a constant weight of 120g of mixed foam chemicals was poured into the mould when at 20 degrees to the horizontal. The mould was positioned vertically and the foam allowed to expand in an upward direction. The flow characteristics were evaluated using the following criteria:

(a) Flow Index: the distance travelled by the foam along the vertical arm divided by the total weight of foam.
(b) Pressure history during the expansion time interval (i.e. up to 200 seconds).
(c) Visual assessment of the foam's ability to create an effective knit-line around the triangular restrictions. This was regarded as the most important measure of flowability as assessed by later line trials at customer's premises.

Blowing Agent Compatibility

It is well known that certain blowing agents are relatively unstable in polyether polyols. This is particularly the case with hydrocarbons and certain heavily fluorinated species. The Enviropols described here were found to have excellent compatibility with blowing agents, especially isopentane, cyclopentane, HFA134a, HFA141b and an azeotropic mixture based upon methyl formate/diethyl ether/n-pentane (5:1:6).

Fire Retardant Qualities

The burning behaviour of Enviropol-based rigid foams was evaluated in comparison with foams prepared from polyether polyols. At a similar polyol hydroxyl value, a small benefit was observed with natural oil-based products as determined by the foam performance on the standard fire test BS 4735/ASTM D1492.

Production Trials

1. Laminated Boardstock

Enviropo1433 can be used to produce flexible-faced laminates capable of meeting a B2 classification on the DIN 4102 fire test apparatus. Excellent adhesion to paper and foil substrates is obtained and processing characteristics are similar to those obtained using conventional polyether polyols. Recent trials with hybrid polyol systems containing a mixture of rape seed oil based polyols and substituted phenolic condensates has led to particularly promising foam for this application.

Initial machine trials indicate that the processing characteristics of this type of system are suitable for relatively slow running laminating machines and more development work is required to ensure that satisfactory dwell times are achieved. Recent work with delayed-action catalysts indicates that this aspect of processing can be improved without the risk of premature gelation. Adhesion to paper and foil faces is excellent.

Table 5. Small Scale Fire Test Results

	1	2	3	4
Enviropol 324 (OHV 390)	100	100		
Glycerol/PO (OHV 400)			100	100
Tegostab B8404	12	12	12	12
Water	1.5	1.5	1.5	1.5
DMCHA	22	22	22	2.2
HFA141b	25	25	25	25
TCPP	10		10	
Amgard V490		10		10
Suprasec 5005 (115 index)	136	136	136	136
Extent of burn (mm)*	105	68	135	96
Rate of burn (mm/sec)*	1.8	0.8	21	13

*Ref * The numerical results obtained on this test do not reflect the performance of the foam in an actual fire situation*

Table 6. Formulation of Foam for Laminated Boardstock

	Envirofoam 722
Enviropol 433	65
Puranol SR1291	35
Tegostab B 8404	2
Fyro16	15
Water	2.5
HCFC 141b	15
Polycat 8	2.6
Envirocat SP44E	0.8
Suprasec 5005	160

Table 7. Properties of Foam: Laminated Boardstock

Cream time (secs) - machine dispensed	15
Rise time (secs)	75
Tack-free time (secs)	95
Foam density (kg/m^3)	34.0
Compressive strength (parallel) kPa	220
Compressive strength (perpendicular)	180
Dimensional stability (-30°C)	<0.1% vol.
Thermal conductivity (W/mK) initial	0.024
Closed cell content (%)	92.4
Fire retardancy (DIN 4102)*	B2

*Ref. * The numerical results obtained on this test do not reflect the performance of the foam in an actual fire situation*

2. Discontinuous insulated panels

General building and cold-room panels can be manufactured using vegetable-based polyols combined with conventional polyether or polyester polyols. Suitable commercial products are being made with both Enviropols 324 and 356. A typical formulation is given below:

Table 8. Formulation for Discontinuous Panel

	Envirofoam 566P
Enviropol 324	45
Enviropol 356	33
Ixol B251	22
Water	3.2
Tegostab B8404	2.2
Klea 134a	2.8
HFA 141b	14.5
Polycat 5	0.5
Polycat 77	1.8
Envirocat SP26R	1.3
Suprasec 5005	185

Table 9. Typical Properties of Panel Foam

Cream time (secs): low pressure m/c	20
Rise time (secs)	145
Tack-free time (secs)	210
Foam density (kg/m^3)	36.2
Compressive strength (parallel), kPa	265
Compressive strength (perp.), kPa	225
Dimensional stability (-30°C)	<0.1 % vol.
Thermal conductivity (initial), W/mK	0.022
Fire retardancy (DIN 4102)*	B3

*Ref. *The numerical results obtained on this test do not reflect the performance of the foam in an actual fire situation*

The Envirofoam 566P was dispensed from a low-pressure Cannon C60 unit into a horizontal panel press with substrate temperatures maintained at 35°C. The panel was filled with foam at an overall foam density of 39.6 kg/m^3. The foam exhibited excellent flowability and adhesion. The demould time for a 50mm thick panel section was 25 minutes.

Figure 4
Insulated panels produced from rape seed oil based polyurethane

A variation of this type of foam system, albeit with CFC11 as the blowing agent, was used to insulate a pipeline at Tuticorin in India. This project involved the in-situ application of a corn-oil based polyol system using a ProblerT3A dispensing machine. The pipeline was 1lkm in length, the insulation thickness was 50mm, giving a U-value of 0.4W/m^{2}K.

Figure 5
Pipeline being insulated with corn-oil based polyurethane foam

3. Spray-applied polyurethane insulation

Externally applied low density foam for building insulation has been successfully accomplished with polyols systems based on Enviropol products. In-place densities of 48 to 60 kg/m' have been obtained, giving compressive strengths of between 350 and 480 kPa. This renders the foam insulation strong enough to allow foot traffic whilst attaining a low thermal conductivity of 0.025 W/mK. Adhesion to most dry substrates is good.

Table 10. Formulation for Spray-Applied Polyurethane

	Environfoam 48-3
Enviropol 433	64
Voranol RA800	36
Water	1.2
Tegostab B8408	1.2
Fyrol 6	15
TMEDA	2.5
HFA 141b	24
Suprasec 5005	145

Table 11. Properties of Spray-Applied Polyurethane Foam

Cream time (sees): hand-mix, l0°C	2.5
Rise time (secs)	22.0
Foam density (in-place)	48-52
Compressive strength (parallel), kPa	360
Compressive strength (perpendicular)	250
Dimensional stability (-30°C)	<0.I % vol.
Thermal conductivity (initial) W/mK	0.028
Fire retardancy (DIN 4102)	B2

4. Glass mat filled urethane (GMFU)

An increasingly important area of polyurethane technology, particularly in the automotive sector, is the production of moulded items which are light in weight and capable of fulfilling demanding mechanical requirements. Initially GMFU was used primarily for door panel substrates but is now commonly used for instrument panels, consoles, seat frames and parcel shelves. By preforming the glass mat, it has become possible to manufacture complex-shaped items. In addition, fast foam demould characteristics have led to a technology which is finding ever-increasing applications.

Table 12. Formulation for Urethane Component of GMFU

	Envirofoam 655
Enviropo1433	70
Voranol RA640	15
Glycerol	15
Water	1.5
Tegostab B8404	1.5
Toyocat TF	1.2
DBTL	0.02
Envirocat SP	1.4
Isopentane	2.0
Suprasec 2050	205

Table 13. Typical Properties of GMFU Composite Produced from Enviropo1433

	Units	Value
Cream time	secs	40
Rise time	secs	92
Free-rise density	kg/m^3	90
Moulding thickness	mm	4.2
Flexural modulus	MPa	760
Gardner impact (25°C)	J	1.2
Tensile strength	MPa	15.2
Dimensional stability (100°C, 24 h)	% vol. change	0.11

Figure 6
Spray-applied insulation based upon Enviropol 433

A variety of automotive mouldings were produced using the above system. Preformed glass mat was placed in an open mould maintained at a temperature of 60°C. The two-component mix was dispensed into the mould using a Cannon high-pressure machine and the mould closed hydraulically. After 4 minutes the mould was opened and the GMFU item removed. In this manner, a number of commercially acceptable items have been manufactured including television housings, automotive seats, arm-rests and crash-pad armatures.

Figure 7
GMFU moulding operation

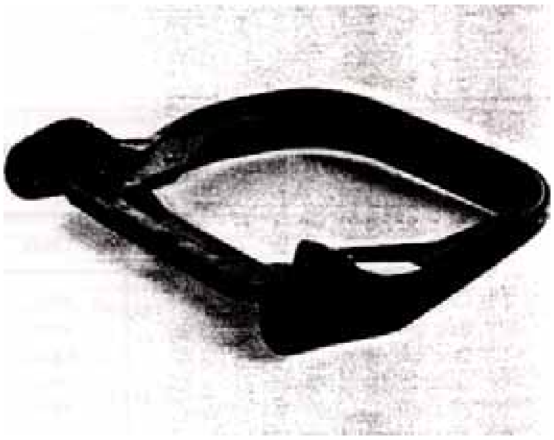

Figure 8
Rolls-Royce seat back produced from vegetable-based polyol

Figure 9
Television-back produced from Envirofoam 655

S. Commercial refrigeration

Both small and large commercial refrigerators have been produced using a formulated system containing a castor-oil based polyol. A programme was initiated to evaluate the flowability characteristics of natural polyols using the Triangle Mould described earlier.

FlowabilityResults of Selected Catalysts in Envirofoam Systems

A standard commercial polyol combination was taken as the basis of the flowability studies, using HFA 141b as the blowing agent. Six catalyst types were evaluated at a constant fibre time of 120 secs. A summary of part of the evaluation is given below.

Table 14. Flowability Rating of Foams Based on Enviropo1324

	1	2	3	4	5	6
Enviropol 324	80	80	80	80	80	80
Voranol RA640	15	*15*	*15*	*15*	15	15
MEG	5	5	5	5	5	5
Tegostab B 1048	1.5	1.5	1.5	1.5	1.5	1.5
Fyrol6	12	12	12	12	12	12
Water	2.0	2.0	2.0	2.0	2.0	2.0
HFA 141b	30	30	30	30	30	30
PV/DMCHA (1:5)	1.2					
AI/DMAE(L10)		1.9				
Texacat ZR70			1.1			
Texacat DP924				1.7		
Toyocat MRlTMF					2.1	
Toyocat B2						1.5
Suprasec 5005 index	115	115	115	115	115	115
Flow index (nun/g)	0.83	1.27	1.22	1.31	*1.15*	0 96
Knit-line rating**	3	4	3	4	5	3

*** Visual assessment: 1: Poor to 5: Very good*

The results obtained above were used as a basis for further evaluations aimed at producing a commercially acceptable foam system for the UK cold storage market.

The optimised product, which required a blowing agent with an ozone depletion potential (ODP) of zero, was dispensed into a closed mould using an OMS low-pressure machine. A mould temperature of 40°C was maintained throughout and satisfactory products were obtained at an overall foam density of 42 kg/m^3. Knit-line ratings of 4/5 were obtainable from systems containing Toyocat MR/TMF whilst retaining excellent curing properties. Other foam properties are given below:

Table 15. Properties of Commercial Refrigerator Foam

Overall foam density (kg/m)	42.0
Compressive strength (parallel) kPa	225
Compressive strength (perpendicular)	165
Dimensional stability at-25°C	<0.15% vol.
Closed cell content (%)	95.6
Thermal conductivity (W/mK)	0.024

Figure 10
Commercial refrigerator produced using foam based on Enviropo1324

6. High modulus elastomeric polyurethane

Several polyols based on rape seed oil have been developed, using a commercially available refined grade having a high content of erucic acid (52%) and about 12% of other acids with more than 18 carbon atoms. The total level of unsaturated acids was almost 94%. One of the polyols derived from this oil had a hydroxyl value of 95mg KOH/g and was designated Enviropol F712RE. It was used as the basis of a development product for jointing pipes in Malaysia. This filled system was hand-mixed in the field to produce a hard elastomer suitable for the intended application:

FUTURE WORK

The initial success of this technology and, in particular, the commercialisation of polyurethane systems based upon natural oil polyols will be followed by a more comprehensive evaluation of both traditional and innovative catalysts suitable for this type of process. In addition, new techniques are being developed to further increase the functionality of polyols derived from natural resources, with emphasis being placed on marine oils which are abundant, very low cost and have a high level of unsaturation in the fatty acid component. Furthermore, the one-shot manufacture of hybrid natural oil and substituted phenol-derived polyols is currently being investigated. The first production trials indicate that this technology is likely to be successful and will ultimately increase the range of applications for natural oil-based products.

Table 16. Typical Formulation and Properties of High Modulus Elastomer

	Envirocast P412/3
Enviropol F712RE	55
Voranol RN41 I	30
Arcol 1342	15
Envirocat HG26	0.8
Microdol Extra	45
Enerflex 72	20
Suprasec 2010	103 index
Mixing time (sees)	30
Gel time (sees)	75
Cure time (mins)	3
Hardness (Shore D)	75
Tensile strength, MPa	32
Ultimate elongation, %	80

CONCLUSIONS

A significant number of polyols have been developed for use in rigid foam systems and high modulus elastomers. The normal foam properties have been determined and optimised allowing production trials to be carried out and, in some cases, full commercialisation to be achieved. The polyols have been included in a variety of CFC-free formulations, which have been processed at a variety of manufacturing facilities in the United Kingdom. Several products are now in full commercial production including moulded items for automotive use.

BIOGRAPHY

Barrie G. Colvin

Dr. Barrie Colvin is a polyurethane technologist with significant experience in the formulated systems market in Europe.

He attended the University of Manchester Institute of Science & Technology and obtained a B.Sc. (Honours) degree in Polymer Technology (Chemistry). Following three years of research in the area of X-ray crystallography of polymers, he was awarded a Ph.D. from the same University.

In 1973, Barrie Colvin joined Shell Research Ltd. as a polyurethane technologist, specialising in fire-retardant foams and new generation appliance insulation. In 1975, he worked on the development of base polyols for rigid foam applications followed by several years as Technical Manager for a polyurethane systems house in the UK. In 1982, Barrie Colvin founded IFS, a polyurethane formulating company, specialising in rigid and semi-rigid foams as well as speciality elastomers. The IFS Group is committed to the development of more environmentally acceptable polyurethane chemicals, having introduced a zero ODP insulation foam to the commercial refrigeration market in 1988. More recently, the company has successfully implemented the use of polyols based upon natural oils.