Layman's report

LIFE ENV/D/000398

"Large scale polyurethane recycling"
### List of key words and abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>APP’s</td>
<td>Aromatic polyester polyols (often used in the manufacture of insulation materials)</td>
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<tr>
<td>DKR</td>
<td>Deutsche Gesellschaft für Kunststoff-Recycling mbH (German company dealing with the recycling of plastics)</td>
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<tr>
<td>DSD</td>
<td>Duales System Deutschland (German waste disposal system)</td>
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<tr>
<td>RCA 5000</td>
<td>Recycling plant with a capacity of 5 tonnes</td>
</tr>
<tr>
<td>Recypol</td>
<td>Registered brand name of recycling-polyols produced by RAMPF</td>
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<tr>
<td>Recypur</td>
<td>Registered brand name of PUR-Systems produced by RAMPF</td>
</tr>
<tr>
<td>Petol</td>
<td>Brand name of aromatic polyester-polyols manufactured by RAMPF from post-consumer PET</td>
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<tr>
<td>PET</td>
<td>Polyethylenterephthalate; a plastic from which soft-drink bottles and packaging are mostly manufactured nowadays</td>
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Project goals

The overall goal of the LIFE Project was to demonstrate a real economically and ecologically viable recycling (cycle) of all polyurethane plastics (PUR) and then to effectively implement it.

More than 2.6 million tonnes of PUR are produced annually in the EU which are recycled either directly or only partially after having been used; otherwise they are incinerated.

It is possible to recycle all PUR waste, to save resources and also to avoid, to a large extent, both waste products and the liberation of CO$_2$ through the widespread use of large-scale demonstration plants and new processes.

A further area of application, which became apparent during the course of the project, is the recycling of post-consumer PET waste in the large-scale recycling plant which came into being during the project.

The final product of this is a high quality aromatic polyester-polyol which is exceptionally well suited to the production of insulation foams.

Polyurethane recycling

Polyurethane (PUR) is produced from a basic liquid materials, polyol (A-components) and isocyanate (B-components). After the two components have been mixed (in various proportions), hardening spontaneously begins followed by cross-linking giving rise to PUR-polymer. By adding various reagents, numerous PUR foams with various properties can be produced. The plastic, polyurethane, in the form of flexible foams (mattresses, seats), insulation foams, integral foams (car parts, shoe soles) and compact elastomeres (coatings) has become an indispensable part of our everyday lives. In fact, about 5% of the total world consumption of plastics is for polyurethane. The consumption in Western Europe was 2.6 million tonnes in 1999 and 546,000 tonnes in Germany; there is an upward trend! Now, although plastics of the thermoplastic type, such as polypropylene, polyethylene, PET or PVC can be recycled simply by melting them down, the possibilities of recycling PUR foams have up to now been limited, due to their duroplastic nature. Hence, PUR had long been thought to be non-recyclable or that it was very complex to recycle.

With greater attention being given to the environment, the ecological requirements of materials are also becoming more stringent. So, in order not to restrict the use of the plastic PUR due to inadequate recyclability, research on numerous processes was carried out, so as to also be able to recycle this duroplastic type of plastic.

In addition to the less environmentally friendly processes for the recovery of energy, several mechanical processes for the reuse of PUR have come into being. Whereas only a small portion of the energy used for manufacturing is retrieved in the form of heat during the energy-recovery process, in the case of material recycling, at least the recyclate is reintegrated into the original production. Nevertheless, even with the best process, the so-called regrind method by which extremely finely ground PUR powder is added to the polyol components, only about 10% of the recyclate can be added due to the increased viscosity.
Hence it is the only recycling process which is worthy of the name **chemical recycling**. It has no disadvantages and is the only process which offers the possibility of producing high-quality polyurethane products from 100% recycled polyols.

**Large-scale polyurethane recycling**

Glycolosis has long been known as a process for the chemical recovery of rigid and integral foams. RAMPF Ecosystems has, in cooperation with FH Aalen and with the support of the EU LIFE-Programme, developed three new types of processes (partial glycolosis, polyolysis, acidolysis) and has also used them for the first time technically on a large scale for the recovery of raw materials, including semi-rigid and flexible PUR foams. The processes were previously only used in small laboratory and technical applications. RAMPF Ecosystems GmbH & Co. KG has now managed to incorporate all the above-mentioned recycling processes in a recycling plant **specially created by RAMPF Ecosystems** which has made industrial applications possible.
Description of the process

PUR waste is broken down into small pieces of about 5 cm in a slicer for the production of recycling polyols. These are continuously introduced into a depressurised reaction container, in which there are already process reagents as basic substances depending on the type of residual substances, namely polyol, glycol or carboxylic acid, as well as catalysts and deaminating agents. At temperatures of about 200 degrees centigrade and with constant stirring, the PUR molecular chains are split. After the completion of the reaction process (lasting about 7 hours), the resultant liquid, which is a mixture of polyols and low-molecule urethane, is filtered. Filtration residues consist exclusively of incidental foreign matter. These can easily be removed through incineration with no after-effects and resultant energy may be reused. Finally the recycling polyol which has been produced is either put into storage tanks, IBC-containers or barrels, as requested by the customer. The final product, which is a high-quality recycling polyol (RECYPOL®), may be used either alone or mixed with new polyol for the production of PUR-foams.

As polyurethanes are only partially decomposed by using basic components of polyols, the former product properties are preserved by cross-linking with isocyanate.

In future, about 97 - 99% of various types of resultant PUR can be recycled through the efficient use of these innovative methods. This is particularly significant in the field of flexible foams which are by far the most important with regard to the quantities manufactured and the waste load for which there has been no recycling up to now.
Description of the plant

The industrial plant developed by RAMPF Ecosystems essentially consists of three components:
- The temperature equalisation unit
- The materials-handling technology unit
- The reactor unit

Maximum attention was given to flexibility and automation at the stage when the size and conception of the plant parts were being decided.

The result is a recycling plant which is able to recycle residual PUR substances regardless of their shape at the time of delivery.

It is the first reprocessing plant of its kind in the world for PUR recycling, which can be implemented on an industrial scale in all the previously known chemical recycling processes for PUR.

Details of the plant

The temperature equalisation unit:

The temperature equalisation unit consists of a gas burner utilising thermal oil as a heat transfer medium.
At every possible site, there are interfaces to ensure the future expansion possibilities of the plant and the inclusion of energy-saving measures. A heat accumulator has already been installed. It serves as a buffer which can store the hot thermal oil during the cooling process and in this way can again serve as a heating medium during the next production application, without necessitating a further large expenditure of energy. A burner has been housed in a container on its own, close to the production halls as protection against fire.

The materials-handling technology unit:

Stringent requirements were placed on the materials-handling technology in order to give the maximum number of PUR producers the possibility of recycling their residual substances. The materials-handling technology unit enables RAMPF Ecosystems to handle residual substances having different powder densities at the rate of about 1.5 tonnes/hour. Rampf Ecosystems developed a concept consisting of two materials-handling units, so as to be able to satisfy such extremes of transportation within the system.
The reactor unit:

The reactor is a impellent-type mixer measuring 6m$^3$ in volume surrounded by half-pipe coil jackets filled with thermal oil for temperature equalisation. The stirring device – specially developed to match the specifications of RAMPF Ecosystems – is used to homogeneously set the temperature as well as to mix the sample with the residual substances. The plant is endowed with various pumps which introduce reagents by fully automatic means in various quantities into the reactor.

Exhaust air which does not contain pollutants from this recycling method is separated from the condensate by passing over a glass cooler. This re-enters the reactor and is then allowed to enter the atmosphere after passing over an additional active carbon filter.

After completely converting the residual PUR substances into a recycling-polyol, they are then put into various packing drums. To this end, the recycling-polyol, which has now cooled to about 80°C, passes through a filtration path with two self-cleaning lateral disk filters of different nominal widths at its core. By using the feed duct designed by RAMPF Ecosystems, it is possible to put recycling polyol into either 200 l barrels, IBC container or storage tanks, as desired.

The entire recycling plant is controlled and monitored by a Siemens SPS control system which was specifically programmed for that purpose by RAMPF Ecosystems specifications. Furthermore, all necessary data concerning the process can be documented by this control system. The usefulness of this auxiliary function is not to be underestimated with regard to quality control.
Products

Recypol

The Recycling-polyol (Recypol®) which has been produced during the recycling process is to be considered to be a basic polyol. Almost all forms of polyurethane can be industrially recycled in the plant which has been created for this, due to the processes which have been specially developed during the project. All recycling processes have been tailor-made for the customers and hence the resultant Recypol is created to satisfy the exact requirements of a particular customer. Recypols are particularly well suited for selling to customers who create their own formulae or for that matter to system-vendors that are in a position to raise these recycling-polyols to the level at which these become systems.

Recypur

An additional aim of the project, "industrial polyurethane recycling", foresaw the possibility for PUR producers, who only deal with ready-to-use systems, thus being able to recycle their residual material and thereby reintegrate them as polyols in the current production. Hence, only as a result of specific formulation involving the addition of cross-linking agents, extenders, catalysts, stabilisers and propellants is it possible for specifications to be achieved. Within the scope of our own foam-production, new PUR systems have been and are also currently being manufactured on the basis of recycling polyols and sold under the brand name of Recypur.
Recycling polyols, are based on PUR residual materials and hence already contain stabilisers and catalysts. The following formulation is hence less complex and also less expensive. Since recycling polyols are in fact high-grade, liquid polyols, not only can these be added in small quantities to the system-polyol, but they can in fact be used 100% as the main polyol. When using recycling polyols, no additional investments are required, nor is a refitting of machines required by someone using PUR.

**PUR-Systems**

Some PUR systems which were produced within the framework of the EU LIFE project on the basis of Recypol, have been presented in excerpts. RAMPF Ecosystems carried out the recycling of integral rigid foam residual products on demand most successfully. In this way, raw materials from the production of casings and window-frames can be successfully reintegrated into the original manufacturing process in the form of recycling polyol. Advantages in using the product become apparent, the surface properties of moulds are better. Numerous new processes were developed in the area of semi-rigid PUR foams. In this context, residual substances from production were used, including the manufacture of shoe soles, arm rests and barrel casings.

It was also possible to manufacture PUR systems with up to 60% of recycling-polyol.

![Fig. 7: Integralskin parts with up to 62% Recypol](image)

<table>
<thead>
<tr>
<th>Foaming Parameters</th>
<th>Polyol Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing Ratio</td>
<td>Recypol® 62,0 %</td>
</tr>
<tr>
<td>Gel Time</td>
<td>Virgin Polyol 34,5 %</td>
</tr>
<tr>
<td>Rising Time</td>
<td>Additives 2,5 %</td>
</tr>
<tr>
<td>Free Rise Density</td>
<td>Water 1,0 %</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>700 g/l</td>
</tr>
<tr>
<td>Hardness (Shore D)</td>
<td>64</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>20 N/mm</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>13 %</td>
</tr>
<tr>
<td>Tensile modulus</td>
<td>163 N/mm²</td>
</tr>
<tr>
<td>Head – SAG – Test</td>
<td>4 mm</td>
</tr>
</tbody>
</table>

Tab.1: rigid integral system mit 62% Recypol (Source: Rühl-Puromer)
In the field of semi rigid foams a lot of new processes were developped by RAMPF Ecosystems during the project. The waste was taken out of shoe sole, arm rests, automotive spoilers and beer keg productions. It was possible to create PUR-blendings with 60 % of such a Recypol in it. They have shown no quality loses against the original systems.

![Fig. 8: semi rigid integral Recypol](image)

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Recypol® (60% Recypol®)</th>
<th>R6600</th>
<th>Test – Results Original - System</th>
<th>Test - Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength [N/mm²]</td>
<td>5,2</td>
<td>3,8</td>
<td>DIN 53504</td>
<td></td>
</tr>
<tr>
<td>Elongation at break [%]</td>
<td>464</td>
<td>473</td>
<td>DIN 53504</td>
<td></td>
</tr>
<tr>
<td>Tearing strength [N/mm]</td>
<td>10,1</td>
<td>8,7</td>
<td>DIN 53507</td>
<td></td>
</tr>
<tr>
<td>Hardness [Shore A]</td>
<td>57</td>
<td>57</td>
<td>DIN 53505</td>
<td></td>
</tr>
<tr>
<td>Flexibility</td>
<td>100.000</td>
<td>100.000</td>
<td>DIN 53543</td>
<td></td>
</tr>
</tbody>
</table>

Tab.2: physical properties of a semi rigid integral system with 60% Recypol

**Results**

1. The quality of post-consumer residues of flexible foams from old automobiles and refrigeration parts is still too low. Seen from a purely technical point of view, the production of polyols using flexible foam waste from shredder residue is absolutely feasible. (so-called "Shredderleichtfraktion"). The inadequate purity of residues (at the present time) nevertheless results in an economically non-viable polyol (as there is no market for it). Post-consumer PET from the DSD-Duales System Deutschland (German waste disposal system) is available in adequate quantities and quality. The success of PET-recycling as well as the production of aromatic polyester polyols has led to the creation of a cooperation „glykolysis from PET..“ with the DKR - Deutsche Gesellschaft für Kunststoff-Recycling (German company dealing with the recycling of plastics). Approximately 50 tonnes of petol have, till now, been produced annually.
2. In the field of systems formulation, a new ready-to-use, water-propelled, fire-protected rigid foam systems were developed, containing up to 90% recycling-polyol. These types of systems are needed in the entire field of construction and insulation. A newly developed integral rigid foam system from 60% recycling polyol can be used for the manufacture of casings and window frames. In addition, our system-polyol R6300 CS1 has been improved and has already been used as a standard product by customers (20 tonnes by 01 July 2003). In 2004 several experiments on foam were successfully carried out in an EU neighbouring country, Poland, in the field of insulation foams.

3. By participating in the world-renowned polyurethane trade fair UTECH 2003 in The Hague, the results became known internationally. Drawing attention to it at the Polyurethane World Congress, participation in the Krauss Maffai Hausmesse (Krauss Maffai company fair) in Munich, our own recycling seminar at the Kunststoff-Zentrum Leipzig (KUZ), namely the German plastics centre in the City of Leipzig, as well as the technical presentation at the PUR- conference in Heidelberg for trade specialists (PUR-Fachtagung) completed the process of making the results known in 2003. Further highlights concerning various events at which the results were publicised included the participation at the plastics fair in 2004 in Düsseldorf, a presentation at the Fraunhofer Instituts in Krefeld in Krefeld in September 2004 at the 13th Plastics and Recycling Colloquium as well as participation in a panel discussion at the Niedersächsischen Kunststofftag (Plastics Convention of Lower Saxony) in Braunschweig. Hence, the results have successfully been made known in the EU and in the world at large and chemical recycling can, on the strength of these positive trends, now effectively implement the various tasks.

4. Within the framework of the project, numerous recycling formulations were produced for various polyurethane substances. The first formulation was successfully used on the new 5 tonne plant after only a few months and this involved the recycling of compact PUR. To date, some 300 tonnes of a recycling polyol have been produced from compact PUR. Integral foam from window frames and semi-rigid integral foam from shoe-sole production were also successfully converted to recycling polyols on the RCA 5000 (about 50 tonnes per annum)
Summary

Under normal conditions of production, 5 - 10% of the PUR are residual substances from within the plant.

This in turn means that for any one company, these residual materials represent an increase in costs (such as disposal fees of some 100 - 200 €/tonne) as well as valuable raw materials which are wasted. There is clearly a real necessity for raw materials to be reintegrated into the production cycle, i.e. the reutilization of raw materials.

The declared aim of RAMPF Ecosystems are therefore the saving of valuable raw materials and decreasing the burden put on waste disposal dumps whilst at the same time decreasing costs and reducing waste disposal expenses. Therefore, by reusing PUR, the ecological and economic factors are once again being brought into harmony.

With the help of the recycling plant which has been supported by the EU LIFE-Programme and developed by RAMPF Ecosystems, all PUR producers were, for the first time, given the possibility of reintegrating their residual substances into the production in the form of a recycling-polyol.

It is furthermore possible to recycle the large quantities of "post-consumer" waste, such as PET bottles, provided that the necessary purity of the post-consumer residues still permit a recypol to be marketable.

The use of recycling-polyol offers special advantages to the user:

- Preservation of former product characteristics by means of cross-linking
- Easy integration into the production cycle without the necessity of retrofitting machines
- Adding the recyclate to the new product without a loss in quality of the final product
- Obvious cost-saving with regard to the primary polyol
- 100% reintegration of the waste materials
- Saving on disposal fees by re-processing the residual PUR-substances
- Possible compliance with the legal ordinances, regulations and conditions - (TASi/German Waste Disposal Ordinance)
- Image boost through improved environmental balance sheets

The reprocessing plant developed by RAMPF Ecosystems enables the PUR processing industry the possibility of recycling PUR, something which has hardly been done till now.

This makes the recycling of PUR on a large scale possible; the immediate consequence of which is the avoidance of PUR-waste, preserving resources and the avoiding CO₂. The result is an very significant relief for the environment.

A word of thanks

A word of thanks is extended to all those who lent their support for this project within the framework of the EU LIFE-Programmes.