Time to think again about Polyurea

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Abstract
Polyurea technology is a type of elastomer that is being used worldwide as a superior coating system for waterproofing and corrosion protection. Applications transcend industries and include tank coatings and linings, waste water treatment and sewer linings and marine applications. Polyureas were first developed in the early 1980’s for automotive fascia applications due to their high strength and impact resistance. The first sprayable polyureas hit the market in the late 1980’s as a plural component system. Some of the very first product formulations of polyurea were associated with high profile coating failures, which has resulted in some scepticism. One famous failure, the San Mateo Bridge in the San Francisco Bay Area, has been the subject of many articles. Key problems in this famous failure included improperly specified surface preparation, lack of product knowledge and inadequate application equipment. The Polyurea Development Association (PDA) was set up in 1999 followed by the PDA Europe to further the sustainable growth of the polyurea industry and establish standards for polyurea applications. With improvements in the application technology, acknowledgement of the product chemistry and an appreciation of the importance of correct application by trained specialists, is it now time to think again about polyurea technology?

Definition and chemistry
The Polyurea Development Association (PDA) Europe define polyurea as an elastomer obtained chemically by the polyaddition reaction of aliphatic or aromatic isocyanate or of an isocyanate preplomer with a polyfunctional amine mixture of amines, generally in a mixing ratio by volume 1:1.

The technology of polyurea is based on the chemical reaction of the two-component systems applied by spraying, through the use of two-component pumps.

In aromatic systems, the isocyanate (NCO) component is made from prepolymers based on methylene diphenyl diisocyanate (MDI); in aliphatic systems, it is made from hexamethylene diisocyanate, isophorone diisocyanate or H12MDI methylene dicyclohexyl diisocyanate and it constitutes the hard segment of the chain. The selection of the isocyanate prepolymer influences most of the properties of the polymer.

MDI-based prepolymers, with a NCO content between 15 and 16% are typically used in the formulation of standard polyurea.

In this range of NCO, you get a good compromise between the viscosity of the material and the reactivity of the system. With lower values of NCO, prepolymers have a higher viscosity but give the system a greater elasticity and a lower reactivity.

The amine component of the polyurea is generally much more complex than the isocyanate component, and consists of:

- High molecular polyetheramine, due to its flexible nature, constitutes the soft segment of the chain;
- Low molecular weight polyetheramine used as chain extenders;
- Pigments and additives.

The choice of the amines is crucial for the processing and subsequent performance of the polyurea.

The polyether amines are propylene oxide/ethylene oxide-based polyethers that are amine terminated, generally with a molecular weight between 200 and 5000 g/mole. The primary amino group of these molecules reacts rapidly with the isocyanate, which does away with the need for a catalyst.

The polyether amines can be bi/trifunctional, aromatic or aliphatic; the latter are used in applications where the stability of colour exposed to light is obviously a priority, since they are very expensive.
The chain extenders are key for the reactivity and the properties of polyurea. The diethyltoluenediamine, mostly used in the formulation of aromatic polyureas contributes to the hard segment and improves the heat resistance. In recent years, there have been specifically designed chain extenders such as secondary and/or sterically hindered amines in order to slow down the reactivity of the polyurea for the particular types of application.

Pigments and additives must be used in limited quantities since the viscosity of the two components must be kept under control during the application. Any substantial amounts of fillers or reinforcing additives can be added to the system as a third component.

There is still no uniformity with regard to the denomination of components A and B of the polyurea. In Europe, the isocyanate component is commonly component B (resulting from polyurethane chemistry), while in other countries there is an inversion of the denomination.

The term ‘polyurea’ is the description of the technology. There are a variety of possible formulations which can be used to achieve the desired properties and therefore the selection of the appropriate raw materials is of fundamental importance.

**Pure polyurea**

The polyurea term has been used in the past in an improper manner, creating confusion between pure polyurea and hybrid polyurea. Pure polyurea should not contain hydroxyl groups in its formula, unlike hybrid systems which are characterised by the presence of OH groups and catalysts (Table 1).

A hybrid system has a composition that is a combination of the aforementioned systems (polyurethane and polyurea). The isocyanate component may be the same one used for pure polyurea. The mixture of resins is instead a combination of terminated amine and terminated polymeric hydroxyl resins and/or chain extenders.

The addition of one or more catalysts is required to obtain the same reactivity. For this reason, hybrid systems, despite having a wide scope of applications, are more sensitive to moisture than pure polyurea.

Furthermore, since the catalysed reaction between the polyol and isocyanate is affected by changes in temperature at the application phase, unlike the reaction of amine and isocyanate, the system performs more poorly.

Polyurea is formed when the amine reacts with the isocyanate. The reaction is fast and autocatalytic (therefore it does not require a catalyst even at low temperatures, unlike the polyurethane and hybrid systems) and it acquires many specific properties that distinguish it from other types of polymers.

**Preparation of substrate**

The preparation of the surfaces to which the system will be applied is of fundamental importance for its final success. Preparation will depend on several factors that can be summarised as follows:

- Type of substrate.
- State of substrate.
- Coating cycle.
- Total loads.

The importance of preparation is a key area outlined in the PDAs most recent Code of Good Practice (2014). Preparation methods described include:

- **Grinding:** this is a mechanical action performed with abrasive wheels, or abrasive paper (sanding) in order to remove laitance, dirt or other material from the crust of the surface.
- **Scarification:** this is a mechanical action carried out by a rotating or non-rotating scarifier aimed at removing the surface crust from 3 to 5 m.
- **Milling:** this is the mechanical action of a rotary cutter to achieve homogeneous and total removal to a constant thickness, regardless of the resistance of the substrate.
- **Shotblasting:** this is the mechanical action of metallic granules propelled by special machines with a complete recirculation, separation and recovery of sandy and other materials, all dust free.

For successful coating it is imperative to undertake preparatory treatment. These include:

- **Polishing:** for new substrates without special hardening surface treatments.
- **Brush hammering or scarifying:** old surfaces with friable parts, not spread over the entire surface.
- **Milling:** old substrates which are particularly degraded or contaminated where it is necessary to remove a continuous and homogeneous layer.
• *Shot preening*: concrete, stone, brick, metal and tile substrates.

**Application equipment**

Polyurea is a two-component product for spray applications which requires particular mixing conditions to allow a proper chemical reaction during its application. The machine for spraying (and mixing) is the heart of the whole system. It heats the two fluids, pressurises them and keeps them at a constant during the spraying. In order to use the equipment, general understanding of how each part functions is a necessity.

The PDA sets the following minimum requirements for correct application in its most recent Code of Good Practice (2014):

- Two-component management system.
- Spray pressure between 150 and 240 bars.
- Product temperature between 50 and 80°C.
- Product flow rate between 2 and 10 l/min.
- Measuring and mixing the products in the right ration.
- Ability to produce and maintain the desired operating pressure.
- Separate adjustment of the temperatures (A heater, B heater, heated hoses) to thin application products until correct viscosity is reached.
- Deliver the desired flow rate at the desired pressure.

The application of polyurea requires a fine tuning of the complete system to meet the conditions of the specific channels:

- Supply system.
- Dosage and heating units.
- Heated hoses.
- Spray gun.
- An air compressor, essential for the supply pumps and purging of the gun.

The PDA stipulate that all components must be properly selected to meet the requirements of the desired applications regarding flow rate, temperature and pressure.

**Training**

Training is another key element for a successful application of polyurea. The PDA sets the following criteria as minimum:

- How to use the equipment for a successful application of polyurea.
- How to use the equipment provided by the manufacturer of dosage units.
- How to intervene in case of problems.
- How to perform on-site maintenance.

**Conclusion**

In summary, Hugo Herault, current PDA Europe President who has assisted in providing detail for this article states:

As these chemicals are converted into a polymer only when finally processed and applied there has been an important evolution in the market place with regard to the training of installers around substrate preparation, priming and application. Polyurea is a very interesting tool which satisfies many needs but requires respect to the key parameters (health and safety, substrate preparation, priming with the right product, spraying properly and with an adequate unit and protecting the coatings from UV or application of the right anti-skid coating). Successful installers recognise this and have a very clear idea on how to manage projects before, during and after Polyurea has been applied.

PDA Europe provides very extensive theoretical and practical training to future installers of these systems, and it will even increase its efforts in the near term as regulation on the use of chemicals at job sites will be more regulated within Europe.

In 1990, <5 t of polyurea was produced worldwide. By 2006, the quantity (polyurea and polyurethane–polyurea hybrids) had reached 35,000 t (PDA market study 2007). It is estimated that the market will continue to grow as the following benefits of pure polyurea as an optimum coating are realised worldwide:

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**Table 1** Polyurea, hybrid and polyurethane components

<table>
<thead>
<tr>
<th>Main component</th>
<th>Polyurea</th>
<th>Hybrid</th>
<th>Polyurethane</th>
</tr>
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<tbody>
<tr>
<td>Chain extender</td>
<td>Polyetheramine</td>
<td>Polyetheramine</td>
<td>Polyol</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Polyamine</td>
<td>Polyal</td>
<td>Polyetheramine</td>
</tr>
<tr>
<td></td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

| Catalysis     | No       | No     | Yes          |

| Flow rate     | 2-10 l/min | 2-10 l/min | 2-10 l/min |

| Measuring     | Yes      | Yes     | Yes          |

| Mixing        | Yes      | Yes     | Yes          |

| Spray gun     | Yes      | Yes     | Yes          |

| Air compressor| Yes      | Yes     | Yes          |

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- Rapid reactivity.
- High chemical and mechanical resistance.
- Resistance to high temperatures.
- Excellent elastic properties and crack bridging.
- Resistance to abrasions and impacts.
- High resistance to tearing.
- Water resistance.
- Absence of solvents (100% solids).

- Thick application even on vertical surfaces.
- Application able on most substrates.

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