

# STATE-OF-THE-ART REPORT



## Polyurea in the Construction Industry and the Environment

1<sup>st</sup> Edition, June 2009

A cooperation between



Polyurea Development  
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and





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## PREFACE

The 1<sup>st</sup> edition of this State-of-the-Art Report, „Polyurea in the Construction Industry and the Environment“, was prepared by Deutsche Bauchemie's Working Group „Polyurea in the Construction Industry“ in cooperation with experts from PDA Europe. Its purpose is to provide information for all members and professional users.

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Deutsche Bauchemie e.V. would appreciate your opinion and any comments you would like to make on this State-of-the-Art Report.

### Deutsche Bauchemie e.V.

More than 110 companies are organized in Deutsche Bauchemie, the German industrial association for the manufacturers of chemical products for the construction industry. With annual sales of 4 billion Euros, these companies cover half of the volume of the European market and approximately one-third of the world market. The spectrum of Deutsche Bauchemie's members ranges from small and medium-sized special suppliers to internationally operating global players. The work of the association is carried out in approximately 40 internal bodies as well as special committees, work groups and project groups by approximately 300 experts from the member companies and by the team at the association's main office in Frankfurt am Main. In its special committee „Plastics in Concrete Construction“ and „Polyurea in the Construction Industry“, experts from Deutsche Bauchemie deal in particular with the subjects of application safety, occupational safety, environmental protection and the durability of protection systems for buildings, some of which are highly specialized, including polyurea coating products. Deutsche Bauchemie is also active in creating technical rules at national and European level.

### Polyurea Development Association Europe (PDA Europe)

Polyurea Development Association Europe (PDA Europe) is the official industrial association of the European polyurea industry and comprises the entire value chain from raw material manufacturers, formulators, manufacturers of machines and equipment all the way to users in the various industry segments. Registered as an international Non Profit Organization under Belgian law in June 2007, PDA Europe helps to create uniform standards for polyurea coatings. Members of PDA Europe include leading experts from the European chemical industry as well as professional users of polyurea and can therefore provide comprehensive support for the selection of products, product quality and application possibilities. The organisation also provides information on best practices in the area of environmental protection and safety and offers a forum for its members to have a say in the future development of the polyurea market. PDA Europe maintains close relations with the American PDA that was founded in 1999.

For further information on PDA Europe, go to [www.pda-europe.org](http://www.pda-europe.org)



## 1 INTRODUCTION

Polyurea technology is based on a recently developed two-component (2C) chemistry for fast curing spray applied coatings.

The first polyurea products were developed in the US during the 1980's. The products were introduced to the market in 1987 and the market has grown rapidly ever since. In 1990 less than 5t were produced worldwide. By 2006 the quantity (polyurea and polyurethane-polyurea hybrids) had already reached to 35,000 t (PDA market study 2007).

Polyurea technology is also used in Europe, but mostly under the umbrella term polyurethane coatings. The continuous further development in the application field of spray coatings clearly shows the diverse potential of polyurea technology.

Due to the fact that polyurea has not yet been listed as an independent product group and technology, there are only a few direct references to this product group in relevant regulations. There are, nevertheless, numerous reference objects on which polyurea products have proved to be outstanding from a technical standpoint. Polyurea has been successfully used for many years, for example, in the areas of industrial buildings, construction and civil engineering, secondary containment and surface protection.

In this State-of-the-Art Report, not only the typical application areas but also the raw materials of polyurea, handling polyurea and its behavior in the environment will be described.

## 2 DEFINITION OF POLYUREA

The following definitions are used among the member companies of Deutsche Bauchemie and PDA Europe:

### ■ Polyurea (PUA)

The cross-linking reaction takes place solely between the isocyanate and the amine-terminated compounds. Hydroxyl groups added through additives or pigment pastes should not have a significant influence on the cross-linking reaction. Humidity cross-linking and humidity-activated polyurea-based reactive polymers are not dealt with in this report.

### ■ Polyurethane (PU)

The cross-linking reaction takes place solely through the isocyanate and hydroxyl-terminated compounds.

### ■ Polyurethane-polyurea hybrids (PU-PUA hybrids)

The cross-linking reaction takes place through isocyanate and both amine and hydroxyl-terminated compounds.

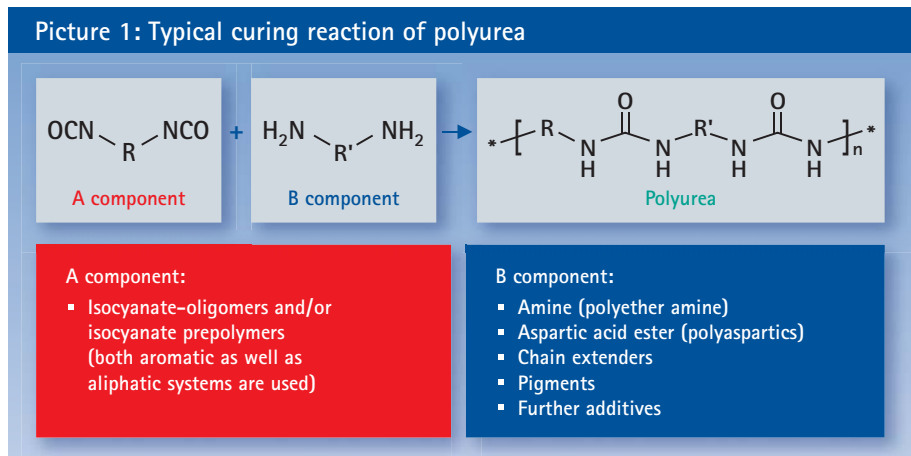


### 3 PRODUCTION AND FORMULATION

Polyurea systems are reactive systems. They cure through cross-linking of the reactive groups contained in the components.

Polyurea polymers are produced through a 2-component system. The A component, an isocyanate or isocyanate prepolymer, reacts with the B component, multifunctional amines or mixtures of amines, to become polyurea. Pigments, fillers and other additives may be added to the base components.

The typical curing reaction is shown in picture 1.



In practice there is often confusion concerning the A and B components. While the isocyanate component is designated the B component in the European coatings industry (derived from polyurethane chemistry), the amine mixture is designated the B component in North America and Asia (from epoxy resin chemistry).

This State-of-the-Art Report is aligned with the A and B designations that have become established in North America and the Asian countries.

The A component is the part that contains the isocyanate and the B component is the amine-based part (see picture 1).



## 4 PROPERTIES AND RANGE OF USE

### 4.1 General information

Polyurea-based products are characterized by their high performance and are therefore used in various application areas worldwide.

Formulation and the resulting performance characteristics of polyurea products are adjusted for the respective application areas. They typically have the following advantages in spray applications:

- PUA reacts, sets and cures quickly – coated surfaces can return to service fast or be further processed in just a few hours
- PUA can be used in a wide temperature and humidity range (larger application window)
- PUA has a high thermal resistance and a good low temperature flexibility
- PUA has outstanding mechanical and chemical resistance
- PUA is hydrolysis stable and insensitive to water
- Color stability is possible (aliphatic systems)
- PUA does not contain solvents (100% solids)
- PUA forms flexible, seamless and elastic films
- Because of the fast reaction speed, even vertical surfaces can be coated in any desired layer thickness in one pass (seamless, three-dimensional waterproofing)
- PUA adheres well to all substrates
- PUA does not need catalysts which results in a further improvement of the hydrolysis stability

Hand-applied polyurea systems (mostly polyaspartics) have most of the properties listed above and are complementary to spray systems. They are used as top coats and/or repair coats. Essential differences are their slower reaction time, the possibility to be applied by hand, and the occasional use of solvents.

The hand-applied PUA systems are very similar to polyurethane products in regard to their applications and properties. This State-of-the-Art-Report deals with products that can be applied by spraying.







## 4.2 Application Areas

### 4.2.1 Waterproofing

#### ■ Roofing

Roofs, particularly flat roofs, place high requirements on any waterproofing system, especially if the roof structure has many complicated openings (e.g. for air conditioning, light domes, chimneys). In these cases, the use of a liquid waterproofing material that easily adapts to the profile of the roof has great advantages and is a reliable solution. A seamless membrane results after curing. Due to the fast reaction, even thicker layers can be applied to vertical surfaces.



Based on this technology, polyurea roofing membranes are extremely durable. The outstanding properties of polyurea coatings are their high resistance (even if yellowing caused by UV is observed) and their flexibility, even at low temperatures which ensure that movements in the roof structure are compensated by the coating.

In the present ETAG 005, a „Guideline for European Technical Approval of Liquid Applied Roof Waterproofing Kits“, the polyurea products can be described for a transitional period among the polyurethanes (Part 6 „Specific Stipulations for Kits Based on Polyurethane“). In the several European countries different national standards may apply. In Germany, roofing with liquid plastics is subject to the requirements of DIN 18531 as well as DIN 4102 Parts 1 and 7.

#### ■ Concrete bridge decks

Waterproofing of concrete bridge decks and carriage way perimeter strips is one of the classic application areas for sprayed, liquid films. The use of de-icing salt in the winter months increases the risk of chlorides penetrating into the concrete. The usual build-up is:

- Concrete substrate: cleaned by blasting
- Epoxy primer, broadcasted with quartz sand
- Waterproofing layer, crack-bridging (= sprayed liquid membrane)
- Adhesion layer
- Poured asphalt

There are only a few systems certified according to ZTV-BEL-B 3 for use in Germany. Currently, these are polyurethane or polyurethane hybrid materials. Asphalt with a temperature of approx. 230 – 250 °C is usually poured onto the deck over the polymer liquid film. Polyurea has the necessary thermal stability and can thus be used as a waterproofing layer.



Examples in other countries prove that polyurea has been successfully used for repairing other concrete elements on large bridge structures such as decking, piles and roadway girders (a prominent example is the San Mateo Bridge in San Francisco, California, USA).

In Western Europe polyurea systems have not yet gained wide acceptance in this application area because of the high cost of the material.





#### ■ Railway lining

In railway line construction, a distinction is typically made between the track way and the substructure. Intermediate layers/intermediate blankets (also elastomers) are a part of the track way and there is also a special construction called a slab track. With the slab track, which has continuously gained ground since the 1990's, especially for high-speed stretches, the tracks are fastened on asphalt or concrete. In Germany, elastic waterproofing of track concrete with liquid films is not common practice. However, in damp/warm and/or maritime climates, the action of salts and moisture on track concrete is significant and in these areas robust, elastic waterproofing is needed to prevent long-term damage to the construction. As a waterproofing material, polyurea can be a reliable solution since a polyurea membrane not only elastically waterproofs the track concrete but also has superior properties when it comes to resistance to salts and moisture. Liquid plastics are of no significance for the substructure (earthworks).

#### ■ Track bed waterproofing

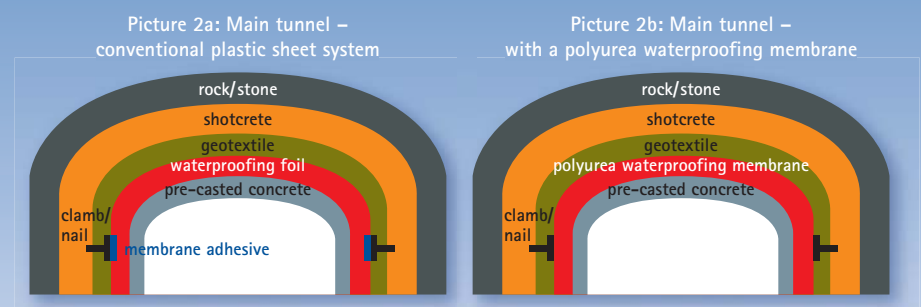
If vibration damping of the railway tracks takes place through a bed of stone ballast, the ballast beds on bridges and concrete lines need to be protected from abrasion caused by the ballast and against the ingress of water.

On concrete bridges, after grinding of the concrete surface, an epoxy primer is applied before spray applying the polyurea waterproofing membrane in an average thickness of 5 mm. The waterproofing membrane needs to withstand up to 100 kPa of water pressure, have an adhesive strength of at least 1 MPa and be resistant to salt, oil and UV radiation. At low temperatures, the elongation of the membrane must be above 100% to withstand static and dynamic crack development in the concrete. Temperature resistance ranges from  $-40^{\circ}\text{C}$  up to short term temperature loads of  $250^{\circ}\text{C}$ . Abrasion resistance towards the placed ballast bed is tested according to actual regulations in the field of railway construction. An example for the use of PUA on railway bridges is the new Bothnia Line in the Northern part of Sweden.

#### ■ Tunnel waterproofing

Illustrations 2a and 2b show a typical build up of a tunnel construction, one with conventional waterproofing membrane foil and the other with a PUA waterproofing membrane. In the main tunnel, the waterproofing membrane is placed behind the internal concrete casting. In the service tunnel and in the emergency evacuation area, the waterproofing membrane is the visible layer (no concrete casting is used). There are different requirements for the different constructions in regard to reaction to fire performance: For the sandwich construction with the membrane behind the concrete elements, the requested reaction-to-fire performance class is lower (e.g. D or E according to EN 13501-1) than for the waterproofing surfaces in the visible layer (e.g. A1 or A2 according to EN 13501-1). Smoke and droplet subclasses may be required in addition. The national implementation of the European reaction-to-fire-classes is different in the several EU member states.

Picture 2: Typical construction of a tunnel





The advantage of using sprayed polyurea coatings in a sandwich construction in the main tunnel is the good adhesion to damp textiles or shotcrete. Conventional waterproofing foils however must always be mechanically fastened or bonded with adhesives.

Polyurea coatings release only relatively low quantities of reactive monomers during application. This needs to be verified by further investigations since isocyanate monomers in aerosols are not permitted during application in large tunnel systems (length approx. > 500 m, depending on ability to ventilate). The greatest challenge in such long tunnel systems is to ensure the necessary air exchange rate.

#### ■ Waterproofing in contact with the soil and ground water

Except in specific and expensive applications, sprayed polyurea waterproofing in areas with ground contact (subterranean waterproofing) has not gained much ground in Europe. But in Switzerland in particular, galleries with dynamic loads have been waterproofed, although predominately with PU-PUA hybrid systems.

Outside of Europe, for example, two islands were connected for the construction of an airport in Incheon, Korea. In this case, the concrete structure of the subway and railway were waterproofed against sea water pressure from the exterior with a PU primer and polyurea coating.

Occasionally concrete bridge structures have been protected with PUA coatings in the tide zone. In these cases fast application in the intervals between tides was a definite advantage (e.g. the San Mateo Bridge in California, USA).

In hydraulic engineering and in lock structures, polyurea or hybrid systems are only used as industrial coatings on pre-fab steelworks. The use of PUA for the protection of concrete in this area today is not known.

#### 4.2.2 Corrosion Protection on Steel Bridges

Polyurea is very effective at protecting steel from corrosion over the long term. Numerous examples prove this, such as coatings in steel containers and tanks, troughs, iron girders, etc. In these cases for exterior use on bridges the short reaction times, the fast application and the relative insensitivity to external parameters are important advantages. There are meanwhile a good number of test objects or repaired surfaces that show the advantages of using polyurea for protecting steel on bridges.

Case examples in the USA also demonstrate that polyurea can be successfully used for repair and for corrosion protection on steel structures, including bridges. Such surfaces have been coated on the Golden Gate Bridge.

In spite of the positive experience that has been gained worldwide, polyurea technology is only slowly gaining acceptance in Europe in this application area.





### 4.2.3 Concrete Protection

#### ■ Industrial flooring and sealers

Floors in production halls, workshops, warehouses, etc. are subjected to heavy loads. Forklifts that can weigh tons and contamination with oils, fuels and chemicals take an extremely heavy toll on floors. Cleaning procedures with hot steam and aggressive industrial cleaners also abuse floors.

Because of their specific property profile – high elasticity combined with abrasion resistance and very good thermal stability – polyurea coatings provide a reliable protection against these loads. Through the selective use of suitable raw materials, the properties of the coatings can be specifically formulated for typical loads.

In the industrial flooring/sealer sector, polyurea coatings have two important advantages:

#### 1. Their greater climatic tolerance when applied and cured

This greatly extends the period of the year – from early spring to late autumn – in which they can be applied and reduces interruptions caused by the weather (e.g. rain).

#### 2. Quick application/rapid curing

Especially in refurbishment cases, idle time (e.g. of production) contributes a considerable part of the total costs. Because they can be quickly applied (e.g. 2-component spraying equipment) and cure rapidly (spray application, polyaspartic coatings), down times are considerably reduced compared to conventional systems.

The percentage of polyurea coatings in the thick-film industrial floor sector in Europe is still relatively small compared to the well-known polyurethane or polyurethane-polyurea hybrid coatings. However, the use of polyurea coatings has clearly increased in the last years. Specific examples for this application area in which the time factor is of utmost importance are supermarkets.

#### ■ Flooring for sports facilities and playgrounds

Because of the multiple loads concerning elasticity as well as mechanical loads, running tracks in sport stadiums or floors in gymnastic or sport halls must be coated with especially high-quality coatings.

In this special application area, a 2-component polyurea coating material based on UV stable polyaspartic technology is used to make colorfast coatings, abrasion resistant topcoats and colored line coatings.

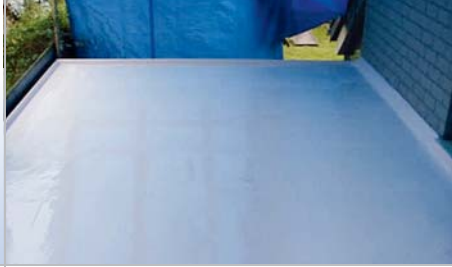
#### ■ Coatings for parking garages and ramps

Polyurea membranes alone or in a bond with a wear protective layer can withstand the typical mechanical and chemical loads found on surfaces with vehicle traffic. The coatings are distinguished by high elasticity and a long service life. The required abrasion resistance can be obtained by formulating towards the specific requirements. These coatings can also be permanently tinted by adding inorganic pigments.

Starting in Germany, polyurea membranes were already described and specified in Europe for liquid membranes in waterproofing systems for surfaces with vehicle traffic (OS 11, see [45]) in the early 1990's. While in Europe the membrane is protected against mechanical loads by a wear layer filled and broadcasted with sand, in the western part of the USA in particular, the wear layer, e.g. sand, is now being integrated into the polyurea waterproofing system. However, from a mechanical point of view, the formulations based on aromatic but also aliphatic prepolymers are formulated to be clearly harder than the membranes described in OS 11.







#### ■ Coatings for balconies and terraces

In the area of UV resistant topcoats, one component polyurethanes are common, but recently polyaspartic-polyureas are also being used. Along with good mechanical properties and UV resistance they also have the advantage of rapid curing. Most recently, hand and machine applied PUA coatings based on aromatic and aliphatic isocyanates have been tested as coatings for terraces and balconies (for example in Belgium).

#### ■ Interior coatings for cooling towers

Because they are permanently subjected to condensation moisture and fumes, interior coatings in cooling towers must withstand very heavy loads. To provide long-term protection for the concrete structure, highly chemical resistant coatings must be used. At least in the US and Asia, PUA has shown great technical advantages when used in the construction of power stations.

### 4.2.4 Water Protection

In Europe the directive 2000/60/EC [34] is the base in the field of water policy. The implementation in the EU member states differ from country to country.

In Germany the German Federal Water Resources Act (WHG) stipulates that when leaks occur in tanks for chemicals, the environment and ground water must be protected through suitable collection reservoirs or drip pans (bund areas). Since concrete is not permanently resistant to many liquid chemicals when used for collection reservoirs and since concrete tanks must be especially dimensioned and executed to be crack-free and liquid tight, collection reservoirs as well as the floor surfaces in facilities for storing, filling and handling hazardous liquids must be effectively and permanently protected against penetration by these liquids. Chemical resistant and crack-bridging PUA coatings meet the requirements for these applications and can ensure the desired protective function for many years. They can also be used in outdoor applications and under heavy mechanical loads, e.g. with direct vehicle traffic.

### 4.2.5 Repair of Sewer Manholes, Sewer Ducts and Sewage Treatment Plants

One of the first applications for polyurea goes back to its use as a repair material for sewage manholes in the USA. Application conditions at building sites such as sedimentation tanks, manhole systems, grease traps, etc. which characteristically have high degrees of moisture often pose problems that are difficult to overcome. Through attack by biogenous sulphuric acid, the concrete of these structures is often much more severely damaged or corroded than the concrete of other structures.

The main advantages by using polyurea when repairing shaft structures are not only its resistance to sulphuric acid but its relative insensitivity towards high ambient moisture and its ability to be reliably applied at low temperatures. As a rule, polyurea adheres sufficiently, even on concrete that is not completely dry. However, and particularly when using polyurea, the applicator must take great care during processing. The surface must always be properly prepared (concrete surfaces must be prepared by hydro-jetting, steel shot or sand blasted, the temperature at the time of application must be at least 3°C above the dew point temperature and, if this is not the case, heating equipment must be used). When preparing the substrate properly, polyurea has also proved to be reliable even on glass fiber fabric or glass fiber reinforced polyester (GRP). A number of innovative techniques have been developed and successfully implemented in this area.





#### 4.2.6 Drinking Water Reservoirs and Swimming Pools

Drinking water is the most important nutrient in the world and must be protected from unnecessary consumption and contamination. This is also reflected in legal provisions.

Polyurea coatings are increasingly being used for lining water pipes and reservoirs. Their advantageous combination of abrasion resistance and good hardness along with insensitivity to moisture when applied make them suitable especially for the repair of pipelines.

Polyurea products that come in contact with drinking water must meet special requirements concerning the release behavior of dangerous (toxic) substances. In Europe the directive 98/83/EC – „quality of water intended for human consumption“ is the basis for regulation in the field of drinking water policy. The implementation in the EU member states differ from country to country.

Since there are presently no uniform rules for construction products that come in contact with water in Europe, the products must fulfill national requirements. In Germany, this includes, among other requirements, the German Federal Environment Agency's (UBA) Coating Guideline (available in English on the UBA website at [www.uba.de](http://www.uba.de)).

Because of these regulations, in Germany the use of aromatic amines and isocyanates is strongly restricted (migration test for aromatic amines are required). For this reason, mainly aliphatic amines and isocyanates are used as raw materials for the polyurea products used in drinking water areas.

##### ■ Coatings for swimming pools

Waterproofing that is applied as a liquid material and that adapts to the geometry of a swimming pool is particularly economical and reliable. After curing, a seamless membrane is produced.

Protecting the pool structure from water and disinfectants is not the only requirement for swimming pool coatings. In addition they should not have a negative effect on the quality of the bathing water.

Because of the large number of chemicals that end up in swimming pool water, (e.g. disinfectants, sun cream and oils) as well as irradiation from UV light, topcoats intended for this purpose must meet very stringent requirements.



#### 4.2.7 Decorative Applications

##### ■ Facades

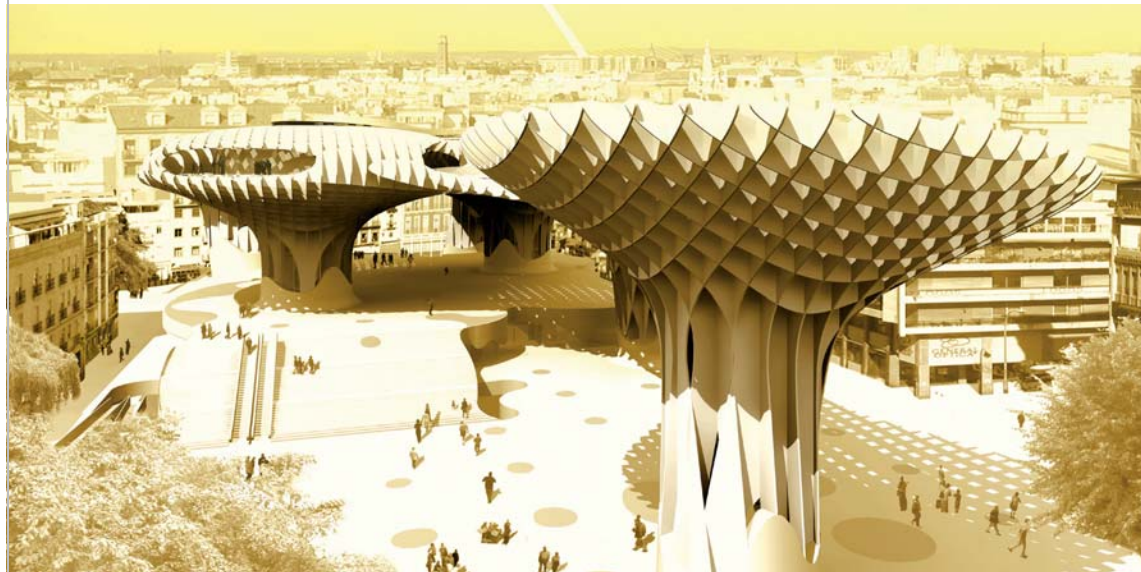
Aliphatic polyureas are easy to apply as an airless spray coating and are not prone to running because they react quickly, which results in fewer moisture bubbles and a uniform surface. Therefore aliphatic polyureas in particular have proved to be suitable for coating of three-dimensional surfaces made of foamed materials, wood, concrete or plaster. Particularly the wide range of variable layer thicknesses and the resulting mechanically strong surfaces make PUAs the material of choice. There is no limit to the realization of an architect's or a designer's artistic ideas.

The fire resistance properties of PUA products must be proven according to valid regulations.

#### ■ Designing theme parks

For the creation of landscapes and sculptures in theme parks or for exhibition purposes, construction materials made of polystyrene or PU foam are often used. Since they cure quickly and have good mechanical properties, highly reactive aromatic polyurea spray systems are used to protect the basic structures and strengthen the surface. Color stable coatings are used to decorate and seal the surface.

One example of this type of application is the 10-metre tall „Ambiorix“ created for the Land Van Ooit theme park in Tongeren, Belgium.



#### 4.2.8 Elastic Wood Coatings

Against all expectations, polyurea is suitable for coating wooden materials because of its good water vapor permeability and high flexibility.

The architectural trend of designing seamless and joint free facades with freedom in designs and colors requires reinforcement and joint-free materials which can only be realized with elastic spray coatings and, in most cases, because of the required high elongation, only with PU-PUA hybrid systems.

Experience with these systems is limited to just a few buildings (Parasol in Sevilla, Spain, is under construction with a PU/PUA hybrid system) and so far there is not enough long-term experience for these applications.

#### 4.3 Reaction to Fire

Polyurea formulations without additional flame retardants are generally assigned to the European fire class E or, when used as a floor coating, E<sub>fl</sub> according to EN 13501-1.

Higher fire classes can be achieved if flame retardants are added.

Since PUA binder systems can be quickly applied, cure rapidly, develop block resistance fast and can be applied in very thick layers, they are increasingly being used for intumescent systems.







## 5 EVALUATION OF THE INGREDIENTS

### 5.1 Polyurea – Raw Materials

#### ■ Polyisocyanates

Polyisocyanates, polymeric or oligomeric isocyanates and their pre-polymers are used in the construction industry today.

Polyurea systems based on a diphenylmethane diisocyanate (MDI pre-polymers or homologues) predominate. The MDI pre-polymers that are used contain isocyanate groups in a range of 10 to 18% as a rule.

For production of the preparations used in the construction industry, the raw material manufacturers utilize in their industrial plants monomers that are classified as harmful to highly toxic. In chemical plants that are designed and equipped for high process safety these raw materials are converted into intermediate products that have considerably less hazard potential. These intermediate products are supplied to formulators for the production of final products for the construction industry.

Although MDI is classified as harmful, there is no risk when properly used because of its very low volatility (the TLV value is practically never reached at room temperature). Since most of the polyurea applications are spray applications, the resulting aerosol that contains isocyanate must be taken into account when measuring TLV.

Isocyanate pre-polymers based on hexamethylene diisocyanate (HDI) as the main ingredient, which are labeled as non-toxic and used, for example, in lightfast and weather resistant coatings for balconies or facades, contain less than 0.5% of this monomer.

Isocyanate pre-polymers based on toluene diisocyanate (TDI) as the main ingredient, which are also labeled non-toxic and used in elastic coatings for parking garages, contain less than 0.1% of this monomer, for example.

As a result users of the final products receive synthetic products that are practically free of critical substances and can also be hand applied.

Since polyurea systems are normally applied by spraying, systematically selective safety measures should be enforced, such as protective clothing and respiratory protection, extraction or the use of spraying booths.

In isolated accidental cases, with intensive or repeated skin contact, aromatic isocyanates can cause allergic asthma.

Persons with sensitive reactions to isocyanates should not work with construction products that contain these substances.





### ■ Amines

The amines used in the construction industry can be assigned to one of the three following product groups: polyether amines, cycloaliphatic amines and sterically hindered aromatic amines.

Mixtures of different amines are normally used in the B component, depending on the desired properties of the product, and polyether amines predominate. The polyether amines used have molecular weights between 400 and 5000; they react extremely fast with the isocyanate groups. This reactivity remains practically unchanged even at very low ambient temperatures, therefore requiring no catalysts.

Along with the polyether amines, so-called chain extenders are used as modifiers. These are sterically hindered, aromatic diamines or secondary cycloaliphatic diamines that intervene in the cross-linking process.

Another group of predominately cycloaliphatic secondary diamines are the aspartic acid esters (polyaspartics) which are mainly used in systems that are hand applied.

If the correct safety measures are taken and the material is properly used, these substances do not present a health risk.

### Polyether amines

Polyether amines are highly alkaline and can cause irritation of the mucous membranes or even burning of the skin. Depending on the length of the chain and degree of branching, acute toxicity ranges from practically non-toxic (linear, long chain) to toxic (highly branched) when swallowed. Polyether amines do not have mutagenic properties and are not considered skin sensitizing.

Environmental hazard classification is not uniform and includes several substances labeled environmentally hazardous but also substances that do not need to be labeled environmentally hazardous because of their insignificant effects.

### Cycloaliphatic amines

Depending on the respective structure, the properties of the amine may vary. They are generally classified as toxic or harmful and some cause burns if swallowed. As a rule they do not irritate skin but may have a skin sensitizing effect. As far as their behavior in the environment is concerned, they are toxic for aquatic organisms and may have a long-term harmful effect in aquatic systems.

### Sterically hindered aromatic amines

The potential for irritation of this class of substances is not pronounced. The compounds do not normally irritate the skin but some do irritate the eyes. Certain representatives of this group of products are harmful after a single exposure and others are practically non-toxic. However, aromatic amines may disturb the transport of oxygen in the blood and it has been proven that they have skin sensitizing properties. Most of the sterically hindered amines are classified hazardous to the environment and labeled accordingly. Deutsche Bauchemie's member companies only use those aromatic amines in polyurea coatings that are not classified carcinogenic.

### ■ Reactive thinners

Reactive thinners are occasionally used in polyurea systems to reduce the viscosity of the isocyanate component and to improve the flow properties of the sprayed layer. Since they are bound into the polymer matrix, they do not contribute to VOC emissions.



## 5.2 Fillers, Pigments and Flame Retardants

### ■ Fillers and pigments

Fillers and pigments are usually added to coatings but since the viscosity of the system must be kept low there is a limit to the quantities that can be used.

Fillers are normally used to modify mechanical properties and to reduce the cost of the coating. Chemically inert fillers such as barytes, quartz powder but also silica reinforcing fillers, including short glass fibers, are used.

Pigments are added in powder form, as prepared pastes or dispersed in polyether amines, either to add color in general or to check the correct mixing ratio. Inorganic and/or organic pigments are used for this purpose. The suitability of pigments as well as pigment pastes should be checked before use since they may cause flocculation or influence the chemistry of the system.

Nearly pH neutral fillers and pigments are a prerequisite for a sufficiently long pot-life of such coating systems. Alkalinity as well as acidity of the fillers and pigments used influence working time.

### ■ Flame retardants

Flame retarding products are usually the result of specially developed formulations that are adjusted to meet the respective requirements. This makes a direct comparison of the different classes of flame retardants nearly impossible although a rough assessment can be made.

The halogenated flame retardants are highly effective in their gas phase ensuring a retarding effect on practically any type of substrate. Halogen compounds also have disadvantages because they release corrosive hydrogen halides, usually increase smoke density and also form toxic combustion products.

One halogenated flame retardant used in polyurea systems is tris(2-chloroisopropyl) phosphate (TCPP). Since it is not bound to the polymer matrix, it can contribute to VOC emissions. It is also known to have a plasticizing effect which, depending on the quantity added, can have a negative influence on mechanical properties. TCPP is also classified as harmful.

End users increasingly demand flame retardants that are migration stable and halogen-free. In case of fire, halogen-free flame retardants have the advantage that the fumes do not contain corrosive flue gasses.

Halogen-free flame retardants that intervene chemically and/or physically are also extremely efficient. These can be based on ammonium polyphosphate, for example.





## 6 BEHAVIOR IN THE ENVIRONMENT

Several of the substances utilized for the production of polyurea are classified as harmful or toxic for aquatic organisms. In Germany, these substances and their formulations are assigned to water hazard class (WGK) 1 – 3. Additional notes on this subject are found in the chapters on transport and storage.

According to the stipulations of the German Federal Water Act (WHG) and the German Federal Soil Protection Act (BBodSchG), harmful changes to ground water and/or harmful changes to soil must be prevented or reduced in such manner that there are no negative changes in the natural environment.

Cured polyurea coatings are practically resistant to external influences, e.g. biodegradation, and are practically insoluble in water. Because of polyurea's high molecular weight and poor solubility in water, it can be presumed that polyurea will not accumulate in organisms. Consequently, they do not pose a risk to the environment when used properly.

## 7 REACH

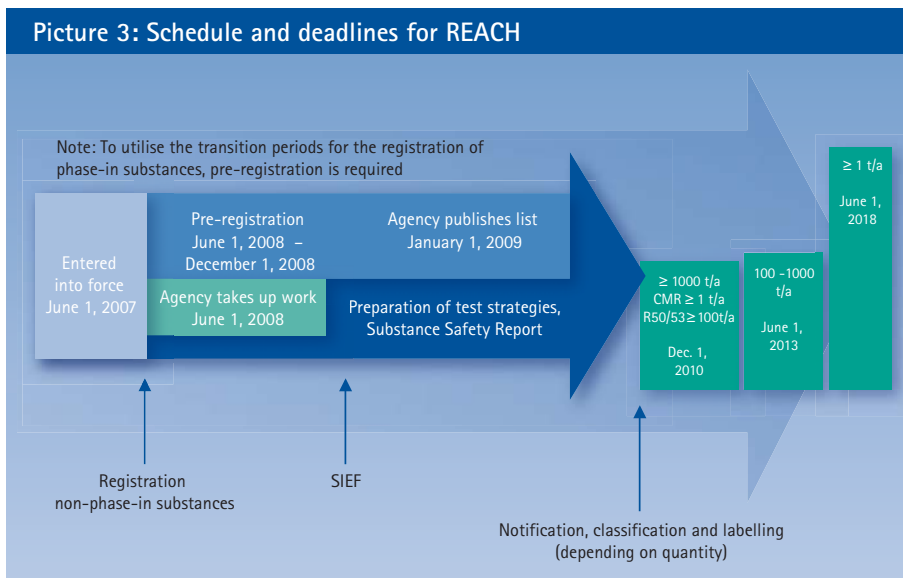
The new European Chemical Regulation came into force in all EU countries on June 1, 2007. It governs the registration, evaluation and authorization of chemical substances with the goal of safe production and use of chemicals. With this regulation, new and uniform legislation on chemicals applies in the EU which must be implemented by the companies concerned.

The REACH regulation stipulates that as of June 1, 2008, an individual substance or a substance utilized in a preparation may no longer be produced, imported or marketed by a company in quantities of more than 1 t/a if it has not been registered beforehand. However, there are also substances that are excluded from obligatory registration.

The REACH regulation allows transition periods for registration. In order to profit from these transition periods, each manufacturer/importer must pre-register his substances, in which case only so-called phase-in substances can be pre-registered. These are usually EINECS substances, i.e. all substances in the European Inventory of Existing Commercial Chemical Substances.

The transition periods until registration are presented in the following overview.

Picture 3: Schedule and deadlines for REACH





The EU has set up a special European agency for chemical substances, abbreviated ECHA, with offices in Helsinki, for the implementation of the REACH regulation.

As a rule, the manufacturers of polyurea products belong to the group of downstream users since they normally only formulate products. To ensure the production of their products in the future, the downstream user (formulator) must ensure that his suppliers have pre-registered and correspondingly registered the substances/products he obtains from them. The intended application must also be covered in the extended Safety Data Sheet. The supplier of raw materials must in turn be informed how the raw materials are used by the downstream user (formulator). This information is used to assess possible risks for humans and the environment and communicated in an extended Safety Data Sheet. In the end, all of this information benefits the final user in safely handling the final product.

With technical support from Oekopol, Deutsche Bauchemie has prepared a REACH Guideline, the first edition of which was published in March 2008 and is also available in English. The guideline, which is directly aimed at formulators of chemical products used in the construction industry, briefly explains the most important tasks and responsibilities (available from: [www.deutsche-bauchemie.de](http://www.deutsche-bauchemie.de)).

## 8 TRANSPORT

Goods which could be hazardous to humans or the environment when put on transport, e.g. solvent based products, are designated as hazardous goods and divided into nine different groups.

Depending on the type of transport, the handling of these goods is subject to the provisions of ADR/RID or GGVSE (transport by land), IMDG/GGVSee (transport by sea) and ICAO-TI/IATA-DGR (transport by air). Information is found in the extended Safety Data Sheets under section 14. The manufacturer is responsible for the classification.

The following documents must accompany the shipment:

- Declaration of responsibility (confirming that the shipment has been prepared according to regulations; applies for IMSG/GGVSee)
- Transport emergency card (since 1.1.99: directed towards drivers of hazardous goods, behavior in an emergency = written instruction; no longer required as of the 2<sup>nd</sup> half of 2009)
- Hazardous goods delivery note (stating classification, quantity, information on sender/receiver, special agreements, if applicable, etc.)

Prepolymers of diphenylmethane diisocyanate (MDI) which are commonly used in polyurea products are not hazardous goods for any mode of transportation. The amine component that contains amines or their mixtures is, as a rule, a hazardous good according to transport regulations.

Classification as a hazardous good may also apply when the product contains flammable substances (class 3) or substances that are hazardous to the environment (class 9).

The selection of adequate packaging is stipulated for the transport of hazardous goods. The packaging must be tested and approved for the respective type of transport and ensure the highest degree of safety during storing, handling and transporting. The exact packaging material specifications result from the classification of the hazardous good. For fast recognition of a substance (e.g. for the fire department), every package must bear the UN number and the hazardous goods label for the respective class.



Transport regulations must also be observed when a car is used for transport. In these cases, the guideline issued by VCI [42] provides information.

Substances must be classified as of December 1, 2010 and preparations as of June 1, 2015 according to the European regulation on the implementation of the Globally Harmonized System (GHS). Other classification may then result since hazard characteristics and symbols are defined differently in GHS

## 9 STORAGE

According to the German „Hazardous Substances Ordinance (GefStoffV)“ polyisocyanates as well as amines used in polyurea products for the construction industry are substances and preparations that are subject to mandatory labeling. When storing, the following must be taken into account:

### a) Classification based on flash point according to RL 67/548/EEC

This concerns the storage of solvent based cleaners for machines and equipment. Depending on the content of solvent and flash point, the polyurea components may be assigned to a hazard class (highly flammable (F+, R12), easily flammable (F, R11) or flammable (R10)). In Germany, such products are subject to the „Ordinance on Industrial Safety and Health (BetrSichV)“ [29]; products with a flash point up to and including 55 °C fall under this category. Also substances with a flash point above 55 °C require a hazard assessment (e.g. behavior if the product runs out).

Since polyurea systems are predominately solvent-free systems with a flash point above 100 °C as a rule, they are not subject to the „Ordinance on Industrial Safety and Health (BetrSichV)“. In Germany, this ordinance distinguishes between storage that requires a permit and storage that does not require a permit. The governing factor for assignment is the above mentioned hazard class of the product, the quantity to be stored and the type of container used for storage. Requirements on facilities for storing combustible liquids in all of the above named hazard classes are found in TRbF 20 (Technical Rules for Combustible Liquids, Warehouses) which in the future will be converted into Technical Rules for Industrial Safety (TRBetrSich).

### b) Water hazard classes (WGK) according to the German „Federal Water Act (WHG)“ or the „Administrative Regulation on the Classification of Substances hazardous to Waters into Water Hazard Classes (VwVwS)“

Water hazard classes are taken as the basis for assessing any eventually existing negative effects on the environment if hazardous substances should leak out of the storage facility. According to the German „Administrative Regulation on the Classification of Substances hazardous to Waters into Water Hazard Classes (VwVwS)“, liquid polyisocyanates are typically assigned to Water Hazard Class (WGK) 1 (low hazard to water). The amines used may be assigned to Water Hazard Class 1 (low hazard to water), 2 (hazard to water) or, in individual cases, even 3 (severe hazard to water). The aromatic amines used are assigned to Water Hazard Class 2.

The requirements on the design and equipment of a storage facility such as the standard and size of retention rooms depend on the type of storage facility, the availability of storage capacity and the respective water hazard class of the stored products.







### c) Other classifications according to the German „Hazardous Substance Ordinance“ that go beyond a) (danger symbol)

Beyond the general rules of the „Hazardous Substance Ordinance“, particularly §24, there are no special rules for the storage of polyurea systems.

Isocyanate components react with water and release carbon dioxide. Normally, humidity alone suffices for this reaction. After opening containers of isocyanates, leaving containers standing open or filling isocyanates into other containers, pressure from the gas that forms may build up in the container and even cause safe, UN tested containers to expand and burst open in rare cases, releasing the contents. Once containers have been opened, they must be handled with special care.

## 10 PROCESSING OF POLYUREA



The most important aspect during application of polyurea is mixing. Thorough mixing is ensured by a suitable mixing chamber with mechanical purge. Working pressure and working temperature are decisive for optimum mixing results.

It has proved to be useful to identify the containers by marking them with different colors. The container for the isocyanate component should be marked RED and the container for the amine component BLUE. This rule for identification has meanwhile been adopted by most machine manufacturers (for marking pumps and storage containers) since mistaking the components in high pressure spraying equipment can lead to severe damage.

The high cross-linking speed of polyureas along with their short mixing time makes applying with high pressure a necessity. When worked on site, the system should preferably be formulated in a mixing ratio of 1:1 (parts by volume). Working pressure ranges between 150 and 250 bar. The viscosity of the two components should be as similar as possible at working temperature and ideally below 100 mPa\*s.

The viscosity of the B component is approx. 900 mPa\*s at 25 °C and falls at working temperature (up to max. 80 °C) below 100 mPa\*s. Lower NCO content of the A component leads to lower reactivity and higher viscosity but also higher elasticity of the coating. Higher NCO content lowers viscosity which improves miscibility with the B component (for spray application) but increases reactivity and leads to greater surface hardness of the coating. A higher content of the 2,4'-MDI isomer reduces reaction time and leads to better leveling which improves surface quality.

Investigations have shown that the properties of the polyurea film differ when worked at 65 °C, 70 °C and 80 °C and improve with increasing temperature.

The spraying machines are equipped for the following possibilities:

- Separate regulation of temperature for both components
- Simple regulation of mixing ratios
- Simple control of output
- Processing parameters are recorded in a clear manner



Polyurea systems are worked with a slightly increased NCO index in a range of 1.05 - 1.10. Since the NCO groups react with moisture, the loss of isocyanate groups during storage and/or working is compensated. The properties of the polyurea film in a mixing ratio of 1:1 parts by volume have been tested with an index ranging from 0.90 to 1.15. The values clearly show that the best properties are achieved with an index of 1.05 or higher. Below 1.05, values vary greatly and become uncontrollable even at index changes of 0.02.



### Safety measures, personal protective equipment

Inhalation or contact with skin may cause harmful and/or allergic reactions. When working, always:

- Wear suitable protective gloves, safety glasses and protective clothing
- Use respiratory protection
- Work only in well ventilated spaces

Work should only be executed by qualified personnel. Further useful information is found in the extended Safety Data Sheet for the product.

### Personal protective equipment – example: spray application

- Respiratory protection (with good ventilation): particle filter with medium retention capacity for solid and liquid particles (e.g. EN 143 or 149, type P2 or FFP2). If there is not sufficient ventilation, breathing apparatus with a fresh air supply is an absolute necessity.
- Skin protection – suitable protective gloves (EN 374); for longer exposure or direct contact, protection index class 6 which corresponds to > 480 min. permeation time according to EN 374: e.g. nitrile butadiene rubber (0.4 mm), chloroprene rubber (0.5 mm), butyl rubber (0.7 mm) or similar.
- Closed, long-arm, protective overalls and protective footwear so that no portion of the skin is exposed to the aerosol.
- Personal protective eyewear – safety glasses with side protection corresponding to EN 166.

## 11 RECOVERY AND RECYCLING

According to our knowledge base today, no effects that harm the environment are to be expected from the recovery and recycling of construction elements to which cured polyurea adheres.

Since cured polyurea systems are elastomers, there is no reason to believe that dangerous substances will be released or that the recycled material will have other negative effects when crushed. In the case of polyurea products which contain critical ingredients (according to the REACH regulation regarding recovery and recycling), the measures described in the exposure scenarios in the extended Safety Data Sheet should be taken into consideration.

When sanding old coatings on a polyurea base, fine dust may be produced that can penetrate the alveoli. Inhalation of such fine dust can be prevented by wearing a respiratory protection mask with a particle filter. Safety measures specified for protection against explosion-capable dust mixtures should also be observed.

Generation of thermal energy by combustion of recycled polyurea products makes sense because of the high energy content of polyurea systems.

## 12 DISPOSAL



The disposal or recycling of packages is regulated differently in the several European member states.

In Germany for example the German „Packaging Ordinance (VerpackV)“ rules the recollection of packaging. Ever since this Packaging Ordinance came into force on June 21, 1991, manufacturers and distributors are obligated to take back packaging materials, particularly:

- Transport packaging materials
- Sales packaging materials

Since the amendment of the German „Packaging Ordinance (VerpackV)“ dated August 27, 1999, recollection of packaging for goods that contained dangerous substances is regulated.

To fulfill their obligation to take back packaging, the manufacturers and distributors of polyurea systems have established agreements with collection and recycling companies. In Germany, packaging that contained goods with harmful substances is collected through a separate disposal channel by specialist companies, for example, KBS or Interseroh. To implement this, polyurea system users must separately collect the different types of packaging (tin, plastic, paper, etc.) for disposal. Further up-to-date information on this subject, particularly for the construction industry, is found on Deutsche Bauchemie's website, (in German) [www.deutsche-bauchemie.de](http://www.deutsche-bauchemie.de) under „Subjects“ and then „Packaging and Disposal“.

The prerequisite for taking back such containers is that the containers must be completely empty. Completely empty containers are containers that have been sufficiently scraped out so that nothing drips or runs out.

Cured polyurea products are normally treated as industrial waste similar to household waste. Waste that is produced during each step of the handling must be separately collected and labeled with the corresponding waste code numbers. After coordination with the disposal company, the materials are picked up in the specified containers. The waste code numbers are described in the European Waste Catalogue (EWC).

## 13 CLOSING REMARKS



This State-of-the-Art Report builds a bridge between the well-known European and international applications and the multitude of potential applications for polyurea which lie especially in their fast and reliable curing under the most various climatic conditions and their exceptional, long-term utilization properties.

Since the technology is still young, polyurea systems are not yet directly included in the relevant regulations even though they are deemed as good as or even better than other proven liquid plastic products. Polyurea products actually are covered in the performance approaches of European regulations.

Polyurea products should find their place in national regulations for application as soon as possible. In spite of this, there are numerous applications today already (see section 4.2) in which polyurea systems are preferred by clients for technical reasons and because of the value for their money.



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## GLOSSARY

This list of term definitions makes no claim to be complete. The designations of chemicals are not explained.

**additive:** A substance that is added to other substances or products in small quantities to alter their properties in a certain way.

**aerosol:** Gas (usually air), with suspended particles, i.e. finely distributed, solid (smoke) or liquid particles (mist) in a size range of  $10^{-7}$  to  $10^{-3}$  cm.

**AGW:** [German equivalent of TLV] Work place limit value. AGW is a time-weighted, average concentration of a substance in the air at the workplace at which acute or chronic harm to the health of the persons employed is not to be expected. When determining this value, eight hours of exposure five days a week during lifetime working hours is assumed, as a rule. The work place limit value is given in  $\text{mg}/\text{m}^3$  and  $\text{ml}/\text{m}^3$  (ppm). AGW was introduced in Germany on January 1, 2005 with the new version of the German Ordinance on Hazardous Substances (GefStoffV). It replaces the Maximum Work Place Concentration (MAK) and the Technical Guideline Concentration (TRK).

**allergies:** The reaction of especially sensitive persons to certain allergens. The severity of the reaction is independent of the concentration of the allergen. Skin, eyes and the respiratory tract are mainly affected.

**aquatic:** Pertaining to water; created in water; found in water, living in water.

**aromatics:** Class of substances in organic chemistry, e.g. benzene and its derivatives as well as ring-shaped hydrocarbon compounds with an electron system typical for aromatic compounds.

**bio-degradable:** The property of substances to degrade into simple, natural compounds (e.g. water, carbon dioxide and bio-mass) through the effect of micro-organisms.

**eco-toxicology:** Study concerned with the distribution and the effect of chemical substances on animal and vegetable organisms when direct or indirect harm for the environment and humans is involved.

**inert substances:** Chemically inert substances which under normal circumstances do not take part in chemical or bio-chemical reactions.

**hydrocarbons:** Organic compounds consisting of the elements carbon and hydrogen.

**oligomers:** Compounds which, in contrast to polymers, consist of just a small number of monomer molecules.

**oral uptake:** Uptake of substances, particles, etc. through the mouth.



**pH value:** The negative decimal logarithm of the concentration of hydrogen ions in an aqueous medium. pH 7 stands for a neutral reaction, pH values < 7 are acidic and pH values > 7 are alkaline reactions.

**polymers:** Substances that result through polymerisation i.e. through a chemical process in which many small molecules of one or several substances combine into large molecules with new properties.

**self-assessment:** Derivation of water hazard classes according to a special evaluation scheme recognised by authorities (in Germany). Unless stated otherwise, the water hazard classes listed in this State-of-the-Art Report are self-assessments.

**sensitization:** Repeated action of an exogenic substance on an organism which then shows a specific, changed reaction if the substance is again brought in contact with the organism. Sensitization precedes an allergy.

**TLV value:** Toxic limit value [MAK in German]. Maximum concentration at the workplace; the highest permissible concentration of a working material as a gas, vapor or suspended particles in the air at the workplace.

**toxicology:** Study of the adverse effects of substances (poisons, toxins) on living organisms. Study of poisons and antidotes. Study of disturbances in living systems caused by these substances, i.e. poisonous effects.

**viscosity:** Physical measurement that describes the thickness or thinness of liquids.

**water hazard classes (WGK):** In Germany, substances that are able to permanently change the physical, chemical or biological state of water are assigned to water hazard classes (WGK) in compliance with § 19g of the German Water Resources Act (WHG):

On the basis of biological test methods, a characteristic value is determined for the potential of substances and preparations to adversely change the properties of water:

**WGK nwg:** not hazardous to water

**WGK 1:** low hazard to water

**WGK 2:** hazard to water

**WGK 3:** severe hazard to water





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